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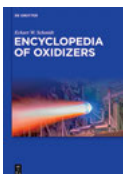


Eckart W. Schmidt

**Encyclopedia of Liquid Fuels**



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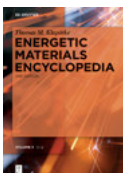


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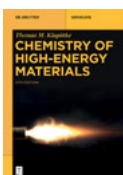


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Eckart W. Schmidt

# **Encyclopedia of Liquid Fuels**

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Volume 1: Alcohols – Amides and Imides

**DE GRUYTER**

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## Foreword

Rocket propellants are hugely important members of the larger group of energetic materials. This continuously developing field requires knowledge and understanding of a wide-range of compounds from the highly reactive fluorine and nitrogen oxides, to organic alkylboranes and alcohols. For rocket propulsion, it is essential that accurate information on the physical and chemical properties of the chemicals involved has been determined precisely and can be relied upon. This is not only the case for known rocket propellants, but is equally essential for developing new, “greener” (less toxic) propellants for the future. The demands on rocket propellants are continuously developing and changing with time, as new needs and requirements for satellites and rockets emerge. Therefore, the *Encyclopedia of Rocket Propellants* is an essential resource for understanding current and past rocket propellants, as well as for designing those for the future. A collection of the vast physical and chemical data for past, present and modern rocket propellant systems has been missing, and it is essential that a source is available in which all reliable data has been collected together and presented in a clear and informative manner.

Amongst the many ways to categorize propellants for chemical rockets, they can be separated into two groups, namely, solid propellants or liquid propellants, with the former being subdivided into double-base or composite propellants. Liquid propellants can be subdivided into monopropellants or bipropellants, the latter of which can be again subdivided into hypergolic or nonhypergolic. Therefore, the complexity of these systems is self-evident. Hydrazine and the methylated derivatives methylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) in combination with nitric acid or dinitrogen tetroxide are currently the most widely-used hypergolic propellants, however, hydrazine and its methylated derivatives are not only toxic, but also carcinogenic in test animals, and therefore it is of considerable importance to find less-toxic and non-carcinogenic alternatives which can still form hypergolic mixtures. Properties of many candidates in this context are summarized in this book. However, many more promising alternatives need to be found for the future. Despite the harmful properties of “traditional” rocket propellants such as MMH or UDMH, or the highly corrosive WFNA and RFNA, they continue to be used, while safer and more energetic alternatives are sought for the future.

Searching for new, environmentally friendly and/or increased performance rocket propellants requires knowledge of a large and diverse number of chemical compounds, many of which are not easy to handle. Despite this, since the publication of the book *Raketentreibstoffe* (Springer) in 1968 by the same author as this

encyclopedia, no other such comprehensive and detailed book has been published on rocket propellants making the *Encyclopedia of Rocket Propellants* a seminal work for past, present and future developments in this area.

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# Preface

## Encyclopedia of Liquid Fuels

This is the second set of a series of sets in the *Encyclopedia of Rocket Propellants* summarizing the existing literature on rocket propellants, both liquid and solid rocket propellants. The first set, *Encyclopedia of Oxidizers*, published a few months ago, contains information on both liquid and solid oxidizers. This second set, *Encyclopedia of Liquid Fuels*, is a summary of literature on liquid fuels. The differentiation between liquid fuels and solid fuels was necessary because solid fuels usually are the binders for solid propellants, a topic reserved for a future, planned set in this series. The third set, *Encyclopedia of Monopropellants*, planned to be published next year, will be a very comprehensive summary of the chemistry of monopropellants. The fourth and fifth sets, planned for the coming years, will describe the performance of hypergolic and nonhypergolic bipropellant combinations, usually combinations of oxidizers and fuels. If time permits, future sets will eventually deal with various aspects of solid propellants, such as “Composite Solid Propellants” and “Double-Base Solid Propellants”, and they would also include gas generants which have found numerous industrial applications such as in airbag inflators in automobile passenger passive restraint systems. “Hybrid Propellants” may find a home in a future set in the distant future.

In spite of the increased capabilities of online search engines like Google Scholar, the current sets of books will be an indispensable tool for scientists and engineers in the rocket propulsion industry and research organizations. The hazards of working with rocket propellants need to be well understood.

Our *Encyclopedia of Rocket Propellants* book series will be the preferred reference source for future generations of rocket propellant chemists. When referring to the profession of rocket propellant chemists, this should not be done without quoting, tongue-in-cheek, the preface written by I. Asimov for J. D. Clark’s landmark book *Ignition!*:

“Now it is clear that anyone working with rocket fuels is outstandingly mad. I don’t mean garden-variety crazy or a merely raving lunatic. I mean a record-shattering exponent of far-out insanity.”

The reader will notice, though, that the correct terminology should have been “rocket propellants” and not just “rocket fuels”. The author of the current book feels that this quote from the literature adequately describes the risks involved for chemists involved with developing more energetic rocket propellants and explosives. The dividing line between powerful rocket propellants and potential explosives is very narrow and rocket propellant chemists are often treading on a narrow path. Nevertheless, or just because of the inherent risk, this is one of the most exciting branches of chem-

istry to be involved with. It is the chemistry of rocket propellants that has enabled the dramatic advances in space technology, with many benefits to the common consumer.

Reviewing the recent literature on rocket propellants and other energetic materials, one will notice that the increased capabilities of modern computers have enabled chemists to predict the performance of new molecules even before these compounds were ever made and tested in the laboratory. Numerous publications referenced in our books deal just with theoretical explorations of this type, and that is a difference to previous book publications on this subject.

Rocket propellants generally consist of oxidizers and fuels. The term “rocket fuels” is often misused to describe rocket propellants in general. Correct use of the term “rocket fuel” would only apply to the combustible, fuel-rich part of a propellant combination. Oxidizers are not rocket fuels. Oxidizers for liquid rocket propellants are generally subdivided by physical properties and/or by reactivity. So we differentiate between storable and non-storable (cryogenic) oxidizers. When looking at the reactivity of hypergolic combinations, it is more often the oxidizer and not the fuel that determines if the resulting combination is self-igniting on contact or not. Hypergolic oxidizers like fluorine or chlorine trifluoride will be hypergolic with most, but not all fuels. When listing combinations of rocket propellants, we always list the oxidizer first. This is because the properties and the activity of the oxidizer determine the nature of the combination more so than properties of the fuel would. There are fewer oxidizers than fuels in our inventory, so it is easier to organize book chapters on rocket propellant combinations first by arranging them by oxidizers and later by fuels.

A less frequently used term for propellant is *propellent*. When conducting literature searches, it may be advisable to search for both variations of the spelling.

### **About the Format of the Several Sets in the Encyclopedia of Rocket Propellants**

The manuscript for the *Encyclopedia of Rocket Propellants* has evolved through several iterations and modifications, and the terminology in designating sets, volumes, chapters, and sections has changed during this period. At one time *Encyclopedia of Oxidizers* was referred to as Volume 1 and *Encyclopedia of Liquid Fuels* was referred to as Volume 2, and so on. The most recent terminology is now referring to *Encyclopedia of Oxidizers* as a set of five volumes and similarly referring to *Encyclopedia of Liquid Fuels* as a set of five volumes. The sequence of volumes in a set and the sequence of chapters in a volume is arranged in alphabetical order, similar to a dictionary.

A critical reviewer might describe the format of the books as not much more than an annotated bibliography. The author is aware of the fact that collecting and reproducing references from the literature is not a very creative job (a librarian could do it), but to arrange these thousands of references in a systematic manner requires a good understanding of the subject matter.

Fifty years ago it used to be common practice to cite literature references followed by their Chemical Abstract citation. Providing the Chemical Abstracts citation often allowed the reader to read a more detailed abstract and to decide if it is worthwhile to obtain a complete copy of the original publication. Nowadays that function has been taken over by Digital Object Identifiers (DOI) in the Internet. Nevertheless, we have continued to carry along a few Chemical Abstract citations in addition to the DOI. Some of those citations are useful because they direct users to the Chemical Abstracts Registry Number which can then be used for subsequent, more specific searches in computerized data bases. Some of the books on energetic materials even contain an index of Chemical Abstract Registry Numbers. At the beginning of some sections, at the introduction of a new chemical name, usually several alternate names are listed. In those lists, the names bracketed by semicolons ; ; are the names used by Chemical Abstracts. That information is useful for literature searches in Chemical Abstracts.

### **Selection of Liquid Fuels**

When selecting combinations of bipropellants, hypergolic or nonhypergolic, it is usually the oxidizer that determines the reactivity of the combination once oxidizer and fuel meet in the rocket engine combustion chamber. The choice of oxidizers has less of an impact on the specific impulse than the choice of fuels with their widely varying hydrogen content. The selection of fuels, similar to the criteria for selection of oxidizers, is governed by a number of considerations:

- Specific impulse
- Reactivity with the intended oxidizer partner (hypergolic or nonhypergolic?)
- Boiling point/critical point temperature (storable at room temperature or cryogenic?)
- Storage stability
- Density (important for compact, pressure-fed systems)
- Corrosivity (corrosive oxidizers require exotic metals for tankage and tubing)
- Toxicity
- Availability
- Cost

Until the beginning of the Space Age, ethanol, gasoline, and kerosene had been used most extensively as rocket fuels, primarily because of low cost, room temperature storability, and relatively easy handling characteristics.

The world of liquid rocket fuels changed dramatically with the first use of liquid hydrogen, which performance-wise is the best and irreplaceable fuel. Liquid hydrogen was first used as the fuel in the second stage CENTAUR, but eventually its use expanded to first stages (boosters) as well, such as ENERGIYA, SPACE SHUTTLE, H-II,



DELTA-IV, ARIANE-V, and now the SPACE LAUNCH SYSTEM. A future hydrogen economy where not only rockets, but also automobiles and airplanes are powered by hydrogen, will benefit from the liquid hydrogen technology which was originally developed for rocket propulsion. Emissions from hydrogen-powered vehicles are clean and do not contribute to global warming. However, the current practice of making hydrogen by steam reforming of methane and water gas shift reaction will have to be replaced by other, cleaner methods, because it generates carbon dioxide as a by-product (although carbon dioxide from this process does not have to be released into the atmosphere. It can be collected and pumped underground).

Liquid hydrogen is a cryogenic fuel and not storable for a long time. Storable hypergolic fuels are still in use in a few satellite launch vehicles such as PROTON, the early versions of LONG MARCH, and GSLV/PSLV. Besides those booster stages, storable hypergolic fuels are mostly used for the uppermost stages of satellite launch vehicles, so-called “kick stages” because they have increased maneuverability compared to cryogenic upper stages and can deliver multiple satellites to different orbits and they can compensate for eventual inaccuracies of the lower stages.

Although the primary use of jet fuels is in air-breathing engines and not in rocket engines, descriptions of jet fuels and ramjet fuels were included in this book on rocket propellants. As it happened, jet fuels were often used as rocket fuels because they were readily available.

Ionic liquids were advertised as “green”, i.e. environmentally friendly rocket fuels. While it is true that due to their low vapor pressures they are safer to handle than most currently used fuels, their multi-step organic synthesis methods leave numerous hazardous by-products that need to be disposed of.

Today we are proud to herewith present to our readers the second increment of the *Encyclopedia of Rocket Propellants*.

Eckart W. Schmidt  
Bellevue, WA, USA

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# Alcohols

## Alcohols

This chapter contains sections on alkyl alcohols (alkanols) used as rocket fuels. Looking at the structural formulas of hydrocarbons and alcohols, the simplest alcohols are derived from alkanes by replacing one hydrogen atom by a hydroxyl group (or – in theory, but not in reality – by inserting an oxygen atom between a carbon atom and its hydrogen neighbor). In the case of methane, the resulting alcohol would be methanol. A synonym for alkyl alcohols is alkanols. As most rocket propellant chemists know, inserting oxygen into a fuel molecule is not a good idea if you want to obtain a high-energy fuel. It shifts the oxygen balance of the molecule closer to that of carbon dioxide, the typical combustion product of all hydrocarbons and alcohols, and makes the molecule a less valuable fuel. The main reason that alcohols are used instead of hydrocarbons as rocket propellants is that they have higher boiling points than the hydrocarbons with the same number of carbon atoms from which they are derived, and thus they can be handled as liquids instead of cryogenics at room temperature. The lower ( $C_1$  to  $C_4$ ) alcohols are miscible with water in all proportions and, if accidentally spilt, are easier to clean up than hydrocarbons. Alcohols are widely used as cleaning solvents and disinfecting wipes in the aerospace industry. Alcohols are good solvents. Alcohols can serve as solvents for additives that make them hypergolic with hydrogen peroxide or nitric acid.

Fuels that contain some oxygen are more easily tolerated and show less of a performance loss if the oxidizer in a rocket engine is fluorine instead of oxygen. As will be shown, kerosene gives better performance with a mixture of fluorine and oxygen (FLOX) than with either oxidizer by itself. This is because, in an equilibrium mixture of combustion products, carbon goes preferentially with oxygen and hydrogen goes preferentially with fluorine to achieve the equilibrium mixture in the rocket exhaust. Thus, if one plans on using fluorine, instead of physically adding oxygen to the oxidizer ( $F_2$ ), one might as well introduce it with the fuel.

The main alkanol used as a rocket propellant is (was) ethanol. The other saturated alkyl alcohols have not achieved any significance as rocket propellants. Compilations of the physical and thermodynamic properties of alcohols are available in [1, 2].

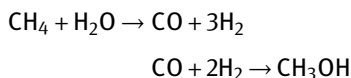
Another family of fuels that are closely related to alcohols are the ethers. Ethers are derived by combining two alkyl groups with an  $-O-$  bridge or by dehydrating two moles of an alcohol through the removal of one mole of water. The oxygen balance of ethers is more negative than that of alcohols, so they should make better fuels. Ethers are only partially miscible with water. Ethers have been tested as rocket propellants but do not offer any advantages over alcohols. Ethers will be described in a separate chapter, “Ethers,” in *Encyclopedia of Liquid Fuels*.

## 1 Methanol

Methanol (methyl alcohol,  $\text{CH}_3\text{OH}$ , CAS RN [67-56-1]) has only very rarely been used as a rocket fuel by itself. Some of the early experimenters in the founding days of JPL and Aerojet used methanol instead of ethanol because its lower combustion chamber temperature was more manageable than that of pure ethanol. Its heat of combustion and performance as a rocket fuel are inferior to those of ethanol. When, in the past, rocket engine designers chose methanol over ethanol, it was most likely because they wanted lower exhaust temperatures or they could not handle the higher rates of heat transfer from LOX/EtOH combustion at the interface between the combustion chamber and the coolant jacket. Methanol was the main constituent of a fuel blend called “C-Stoff,” which consisted of 57 mass-% methanol ( $\text{CH}_3\text{OH}$ ), 30 mass-% hydrazine hydrate ( $\text{N}_2\text{H}_5\text{OH}$ ), and 13 mass-% water with a few percent of potassium cyanoferrate(III) dissolved as a catalyst and was used with hydrogen peroxide as the oxidizer in a bipropellant rocket engine in the German interceptor rocket plane Me-163B during WWII. So, the history of the use of methanol as a rocket propellant actually started very early.

### 1.1 Production and Availability of Methanol

Methanol is made by reacting synthesis gas over a catalyst. Synthesis gas (“syngas”) is made from natural gas by steam reforming:



As long as natural gas is readily available, methanol will be readily available, too. The conversion of methane directly into methanol by partial oxidation has been attempted. This would be a useful method of capturing methane at remote petroleum well heads that would otherwise be flared off. The multi-step conversion of natural gas to methanol is already used as a means of transporting hydrocarbon fuels from one place to another. Methanol is easier to transport than liquefied natural gas (LNG). At its point of use, methanol is converted back to synthesis gas and other products – predominantly ethylene for polyethylene synthesis. Methanol can also be made from syngas by coal gasification or the conversion of cellulosic waste.

In the distant future, if the world gets serious about reducing the amount of  $\text{CO}_2$  emissions to curb global warming,  $\text{CO}_2$  captured from stationary emission sources could be converted to methanol (assuming the ready availability of hydrogen or electric power) and thus diverted, and the carbon could be recycled for a useful purpose. Methanol from  $\text{CO}_2$  would also be the fuel of choice for an in-situ resource utilization (ISRU) fuel production facility on the surface of Mars, where the atmosphere consists

mostly of carbon dioxide, and carbon dioxide forms part of the white polar caps that can be seen with even a cheap telescope. Methanol for ISRU would be easier to store than liquid methane.

## 1.2 Physical Properties of Methanol

Physical properties of methanol are summarized in Table 1.

**Table 1:** Physical properties of methanol.

| Property                                 | SI units                   | Other units        | References |
|------------------------------------------|----------------------------|--------------------|------------|
| Molecular mass                           | 32.0419 g/mol              | 31.209 mol/kg      | [3]        |
| Freezing point                           | $176 \pm 1$ K              | $-97 \pm 1$ °C     | [3]        |
| Boiling point                            | $337.8 \pm 0.3$ K          | $+64.7 \pm 0.3$ °C | [3]        |
| Density at 293 K                         | $0.7914$ g/cm <sup>3</sup> | —                  | [4]        |
| Critical temperature                     | $513 \pm 1$ K              | $240 \pm 1$ °C     | [3]        |
| Critical pressure                        | $8.1 \pm 0.1$ MPa          | 80.2 atm           | [3]        |
| Critical density                         | $8.51 \pm 0.07$ mol/L      | —                  | [3]        |
| Refractive index ( $n_D$ ) <sup>20</sup> | 1.3288                     | —                  | [4]        |

The velocity of sound in methanol was measured by a single-pulse technique for temperatures from 294 to 366 K (70–200 °F) and for pressures from 0.1 to 4 MPa (1–40 atm) [5].

### 1.2.1 Density of Methanol

The saturated liquid density of methanol for the range 175.5–512.5 K (–97.6 to +239.4 °C) can be calculated from the equation

$$\rho = A \times B^{-[1 - (T/T_c)]^{\frac{2}{7}}}$$

where  $\rho$  is the density in g/cm<sup>3</sup>, A and B are correlational constants (A = 0.2928, B = 0.2760),  $T_c$  is the critical temperature (512.5 K), and  $T$  is the temperature in kelvin [6].

The densities of methanol and ethanol are shown in Figure 2, which is in the following section on ethanol.

### 1.2.2 Vapor Pressure of Methanol

The vapor pressure of methanol can be calculated using an Antoine-type equation:

$$\log_{10} P = A - [B/(T + C)],$$



where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. The constants  $A$ ,  $B$ , and  $C$  are listed in Table 2 for three different temperature ranges, and the top two sets of data were used to create a vapor pressure curve as shown in Figure 3, together with vapor pressure data for ethanol. That figure is shown in the following section about ethanol.

**Table 2:** Vapor pressure coefficients for methanol.

| Temperature range, K | A       | B        | C       | References |
|----------------------|---------|----------|---------|------------|
| 353.5–512.63         | 5.15853 | 1569.613 | –34.846 | [7]        |
| 288.1–356.83         | 5.20409 | 1581.341 | –33.50  | [8]        |
| 353–483              | 5.31301 | 1676.569 | –21.728 | [9]        |

Note: Coefficients were calculated by NIST from the author's data

Another vapor pressure equation for the range 206–513 K (–67 to +240 °C) uses five coefficients:

$$\log p_V = A + \frac{B}{T} + C \log T + DT + ET^2$$

where  $p_V$  is the vapor pressure in mmHg and  $T$  is the temperature in kelvin. The correlation constants are  $A = -42.629$ ,  $B = -1186.2$ ,  $C = 23.279$ ,  $D = -35.082 \times 10^{-3}$ , and  $E = 17.578 \times 10^{-6}$ . For a temperature of 298 K, this equation gives a vapor pressure of 124 mmHg [10].

### 1.2.3 Viscosity of Methanol

Viscosity data for methanol and several higher alcohols were obtained in the temperature range 208–373 K (–65 to +100 °C) using an Ubbelohde viscometer [11] The results were compared with existing data, and all the data were fitted to the Fulcher (Tammann-Hesse) equation by the method of least squares. The implication of the values of  $T_0$  in this equation for these and other associated liquids was critically reviewed, and an attempt was made to interpret the significance of  $T_0$ . The quantity  $T_0$  (written as  $-C$  by some authors) was found to be largest for those liquids in which very extensive hydrogen bonding is possible. The viscosity data can be expressed by a Fulcher-type equation:

$$\log \eta = A + B/(T - T_0)$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The constants  $A$ ,  $B$ , and  $T_0$  for methanol and ethanol are summarized and compared to those of other

**Table 3:** Constants and valid ranges for the Fulcher viscosity equations.

|                    | A       | B        | $T_0$   | Viscosity at<br>298 K, cPs | % Error | Valid range, °C |
|--------------------|---------|----------|---------|----------------------------|---------|-----------------|
| Methanol           | -1.6807 | 354.876  | 48.585  | 0.55                       | 2.05    | -98.3 to +50    |
| Water              | -1.5668 | 230.298  | 146.797 | 0.90                       | 0.51    | -10 to +160     |
| Ethanol            | -2.4401 | 774.414  | -15.249 | 1.08                       | 2.66    | -98.11 to +70   |
| Glycerin           | -2.8834 | 997.586  | 128.481 | 1003                       | 4.5     | -42 to +30      |
| Ethylene glycol    | -1.5923 | 438.064  | 141.617 | 16.2                       | 0.18    | +20 to +100     |
| <i>n</i> -Propanol | -2.4907 | 725.903  | 37.474  | 1.98                       | 1.1     | 0 to +70        |
| <i>n</i> -Butanol  | -3.0037 | 1033.306 | -4.3828 | 2.59                       | 0.8     | -50.9 to +100   |

Data source: [11]

associated (hydrogen-bonded) liquids in Table 3. In the case of methanol, the equation would be

$$\log \eta = -1.6807 + 354.876/(T - 48.585)$$

At 298 K, this equation yields a viscosity of 0.55 cPs for methanol with a  $\pm 2\%$  error.

The dynamic viscosity of liquid methanol in the range 273–323 K can be calculated from the following equation:

$$\eta = 1.107 \times 10^{10} T^{-4.163}$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The viscosity at 298 K is 0.547 cPs [12].

The dynamic viscosity of liquid methanol in the range 175–512 K (-97 to +239 °C) can be calculated from the following equation:

$$\log \eta = A + \frac{B}{T} + CT + DT^2$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The coefficients for this equation are available for two different temperature ranges, as listed in Table 4.

For example, the viscosity from this equation at 298 K is 0.53 cPs.

**Table 4:** Viscosity correlation coefficients for liquid methanol.

| Temperature range, K | A      | B     | $C \times 10^2$ | $D \times 10^6$ |
|----------------------|--------|-------|-----------------|-----------------|
| 175.5–233            | -99.73 | 7.317 | 46.81           | -745.3          |
| 233–512.5            | -17.09 | 2.096 | 4.738           | -48.93          |

Data source: [10]

### 1.2.4 Surface Tension of Methanol

Once the surface tension at one temperature  $T_1$  is known, the surface tension at other temperatures can be calculated by the Othmer relation. The surface tensions of methanol and other liquids can be calculated from the following equation:

$$\sigma = \sigma_1 [(T_c - T)/(T_c - T_1)]^{\frac{11}{9}}$$

where  $\sigma$  is the surface tension in dyn/cm,  $T_c$  is the critical temperature (513 K), and  $T$  is the temperature in kelvin. A similar equation that applies to the range 175.5–512.5 K (–97.6 to +239.4 °C) uses an exponent of  $n = 0.8115$  instead of 11/9 [6]. Data for the surface tension of methanol are summarized in Table 5.

**Table 5:** Surface tension of methanol.

| Temperature |    | Surface tension |              | References |
|-------------|----|-----------------|--------------|------------|
| K           | °C | SI units        | Other units  |            |
| 293         | 20 | 22.5 mN/m       | 22.5 dyn/cm  | [13]       |
| 298         | 25 | 21.88 mN/m      | 21.88 dyn/cm |            |
| 293         | 20 | 22.6 mN/m       | 22.6 dyn/cm  | Unknown    |
| 293         | 20 | 22.56 mN/m      | 22.56 dyn/cm | [14]       |
| 313         | 40 | 20.96 mN/m      | 20.96 dyn/cm |            |
| 333         | 60 | 19.41 mN/m      | 19.41 dyn/cm |            |

### 1.2.5 Thermal Conductivity of Methanol

The thermal conductivity of methanol as a saturated liquid can be calculated from the equation

$$\lambda = A + BT + CT^2$$

where  $\lambda$  is the thermal conductivity in  $\mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin. The correlation constants for methanol in the temperature range 175–483 K (–98 to +210 °C) are  $A = 770.13$ ,  $B = -114.28 \times 10^{-2}$ , and  $C = 2.79 \times 10^{-4}$  [6]. At 293 K (+20 °C), the thermal conductivity of methanol is  $0.192 \text{ W m}^{-1} \text{K}^{-1} = 459.2 \mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1} = 0.4592 \text{ mcal s}^{-1} \text{cm}^{-1} \text{°C}^{-1} = 0.0004592 \text{ cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$ .

The thermal conductivity of methanol vapor can be calculated from the polynomial equation

$$\lambda_G = A + BT + CT^2 + DT^3$$

where  $\lambda_G$  is the thermal conductivity of methanol vapor at low pressure (approx. atmospheric pressure) in  $\mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin. The correlation constants for methanol in the temperature range 273–1273 K (0–1000 °C) are

identical to those of ethanol (namely  $A = -18.62$ ,  $B = 9.95 \times 10^{-2}$ ,  $C = 2.90 \times 10^{-4}$ , and  $D = -12.38$ ) [10]. See also [15].

### 1.2.6 Heat Transfer Coefficient of Methanol

Based on measurements in a thermosyphon heat pipe at heat flux conditions of  $7.35 \text{ kW/m}^2$ , the overall heat transfer coefficient of methanol was  $0.126 \text{ kW m}^{-2} \text{ }^\circ\text{C}^{-1}$  and the overall heat transfer coefficient of ethanol was  $0.17 \text{ kW m}^{-2} \text{ }^\circ\text{C}^{-1}$  (that of water is  $0.16 \text{ kW m}^{-2} \text{ }^\circ\text{C}^{-1}$ ) [16]. In a vertical pipe, the heat transfer coefficients were  $750$  and  $627 \text{ W m}^{-2} \text{ K}^{-1}$  for ethanol and methanol, respectively [17].

### 1.2.7 Thermodynamic and Thermal Properties of Methanol

#### 1.2.7.1 Heat Capacity of Methanol

The heat capacity of methanol vapor assuming ideal gas behavior can be calculated from the polynomial equation

$$C_p = 21.137 + 7.0843 \times 10^{-2} T + 2.5860 \times 10^{-5} T^2 - 2.8497 \times 10^{-8} T^3$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{ K}^{-1}$  and  $T$  is the temperature in kelvin. The heat capacity of methanol vapor is  $42.59 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $273.15 \text{ K}$  and  $44.06 \pm 0.03 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $298.15 \text{ K}$ .

The heat capacity of liquid methanol between  $176$  and  $368 \text{ K}$  is given by

$$C_p = 74.86 - 0.102315 T + 4.066567 \times 10^{-4} T^2$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{ K}^{-1}$  and  $T$  is the temperature in kelvin [18]. A similar polynomial gives the heat capacity of liquid methanol between  $175.5$  and  $493 \text{ K}$  ( $-97.6$  and  $+220 \text{ }^\circ\text{C}$ ) as

$$c_p = 0.8382 - 3.231 \times 10^{-3} T + 8.296 \times 10^{-6} T^2 - 0.1689 \times 10^{-9} T^3$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ }^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin [6]. The heat capacity of liquid methanol at  $298 \text{ K}$  is  $2.544 \text{ J g}^{-1} \text{ K}^{-1}$  ( $0.608 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ ). Other sources give a heat capacity of liquid methanol at  $298 \text{ K}$  of  $80.22 \text{ J mol}^{-1} \text{ K}^{-1}$ , which appears to be in error.

#### 1.2.7.2 Enthalpy of Formation and Heat of Combustion of Methanol

The average enthalpy of formation of methanol vapor from nine different sources was  $-205 \pm 10 \text{ kJ/mol}$  (NIST). For liquid methanol, one source [19] reported a value of  $\Delta H_f^{298} = -238.9 \pm 3.6 \text{ kJ/mol}$ , based on a calorimetrically measured heat of combustion of  $726.5 \pm 0.2 \text{ kJ/mol}$ . The difference between these two numbers is the heat of evaporation.

Isotope labeling is helpful when assigning bonds in vibrational spectra. Structural and spectroscopic data on  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{OD}$ , and  $\text{CD}_3\text{OD}$  were reviewed and used

in using rigid rotor and harmonic oscillator models to calculate ideal gas thermodynamic properties in the temperature range from 0 to 1500 K [20]. Experimental data for the standard enthalpy of formation at 298.15 K, the heat capacities, and the third-law entropies at elevated temperatures are available only for the CH<sub>3</sub>OH vapor phase, where intermolecular association occurs. The agreement between the observed thermal data and the calculated values is satisfactory within the experimental uncertainties.

### 1.2.7.3 Heat of Fusion of Methanol

The heat of fusion of methanol at 175.3 K is 3.18 kJ/mol. Frozen methanol exists in two crystal modifications. Thermal properties of solid methanol were studied by adiabatic calorimetry [21].

### 1.2.7.4 Heat of Vaporization of Methanol

One method to derive the heat of vaporization at other temperatures if one data point is known is to use the Watson equation:

$$\Delta H_{\text{vap}} = \Delta H_{\text{vap}1} [(T_c - T)/(T_c - T_1)]^n$$

where  $\Delta H_{\text{vap}1}$  is the heat of vaporization at a known temperature  $T_1$  (assumed to be 260.1 cal/g at  $T_1 = 337.8 \text{ K} = 64.7^\circ\text{C}$ ),  $T_c$  is the critical temperature ( $512.5 \text{ K} = 239.4^\circ\text{C}$ ), and  $n$  ( $= 0.4$ ) is an empirical coefficient. The average of 11 literature data points gave a heat of vaporization of  $37.6 \pm 0.5 \text{ kJ/mol}$  [3].

## 1.3 Chemical Properties of Methanol

The procurement of methanol for government applications may depend on Fed. Spec. O-M-332 Rev. N (Feb. 2016).

### 1.3.1 Thermal Stability of Methanol

When used as a fuel in bipropellant rocket engines, methanol has the advantage that it can be used as regenerative coolant without needing to worry about soot deposition in the cooling channels. Methanol pyrolyzes to gaseous products and does not leave any carbon residues.

## 1.4 Compatibility with and Corrosion of Materials in Methanol

Methanol contamination that was negligently left behind in tanks after center-of-gravity, spin-balance, and vibration tests caused stress corrosion of titanium

alloy tanks during the Apollo program [22]. Stress-corrosion cracking of the alloy Ti-6Al-4V in methanol was investigated using small (laboratory-scale), bent-beam, self-stressed specimens and surface-precracked tensile specimens under constant load [23]. The alloy was tested after it had been either annealed, solution-treated, or solution-treated and aged. Tests were conducted at ambient temperature and pressure in reagent methanol (99.9 mol-% pure) and in methanol containing chloride ion concentrations of 5, 10, 100, and 500 ppm added as concentrated hydrochloric acid. Self-stressed specimens were tested with outer stress levels of 25, 50, and 100 ksi (170, 340, and 690 MN/m<sup>2</sup>), and precracked specimens were tested with initial stress intensity parameters ranging from 4 ksi (in.)<sup>1/2</sup> (4.4 MN m<sup>-2</sup> m<sup>1/2</sup>) to the critical stress intensity value of the material. In the self-stressed specimen tests in reagent methanol, cracks initiated and propagated to failure in the solution-treated and aged material in as little as 15 h with initial outer fiber stresses of 100 ksi (690 MN/m<sup>2</sup>). Generally, the solution-treated and aged material had the least resistance to cracking, whereas the solution-treated material had the most resistance to cracking. In tests of self-stressed specimens, chloride ion additions of 5–500 ppm appeared to decrease the cracking time by an order of magnitude as compared with the cracking time in reagent methanol, but there seemed to be little variation in cracking time for the range of chloride contents applied in this investigation. Halide contamination from halocarbons used as degreasing cleaning fluids can have the same effect.

Even if ethanol is used instead of isopropanol as a cleaning fluid for titanium alloy tanks, the traces of methanol commonly found in poor-grade agricultural ethanol may cause the same problem. The preferred cleaning solvent for titanium alloy tanks is isopropanol and not ethanol. If ethanol of dubious quality is used instead of isopropanol, stress corrosion of titanium alloy tanks can be avoided by adding at least 5% water to the ethanol.

## 1.5 Toxicity of Methanol

Methanol is more toxic than ethanol and has been the cause of numerous tragic poisoning incidents in which it was accidentally mistaken for ethanol or deliberately or negligently mixed into the ethanol by moonshiners and bootleggers.

## 1.6 Environmental Effects of Methanol

Methanol is a more environmentally friendly automotive fuel than gasoline because it results in cleaner engine exhaust and would be easier to clean up in the case of a spill. The same advantage would apply if it was ever used as a rocket fuel. But, of course, the vehicle fuel economy would be worsened by switching from gasoline to methanol.

1.7 Explosive and Fire Hazards of Methanol

The flammable range of methanol vapor in air is 6.7–36 vol.-% (at 333 K = 60 °C), with upward propagation. The flammable range widens with temperature, as shown in Table 6.

**Table 6:** Lower limit of the flammability of methanol at different temperatures.

| Temperature |     | Lower limit, vol.-% |
|-------------|-----|---------------------|
| K           | °C  |                     |
| 373         | 100 | 6.65                |
| 423         | 150 | 6.15                |
| 473         | 200 | 5.80                |
| 523         | 250 | 5.45                |

Data source: [24]

The autoignition temperature of methanol in air is 658 K (385 °C). The open-cup flash point of methanol in air is 284 K (11 °C). The most complete summary of the flammability of methanol under a wide range of conditions (different pressures, diluents, directions of flame propagation, tube diameters, oxygen enrichments, and contaminants) is available in a NASA Handbook [25].

1.8 Applications of Methanol as Rocket Fuel

1.8.1 Applications of Methanol as Fuel in Bipropellant Rocket Engines

Specific combinations of methanol and methanol blends with hypergolic or non-hypergolic oxidizers will be described in future volumes of the *Encyclopedia of Rocket Propellants*.

Here we offer only a brief historical summary of the use of methanol as a fuel in rocket engines that serves as a justification for writing about methanol here in the fuels volume of the *Encyclopedia of Rocket Propellants*.

Methanol (“M-Stoff”) was the main fuel constituent in a fuel mixture described by the code name “C-Stoff” and used in the WALTER 109-501, 109-509, and 109-509A-2 rocket engines along with 95 mass-% hydrogen peroxide (“T-Stoff”) as the oxidizer. C-Stoff was a mixture of 57 mass-% methanol, 30 mass% hydrazine hydrate, and 13 mass-% water. These rocket engines were used in the Me-163B rocket-powered airplane and Natter manned interceptors.

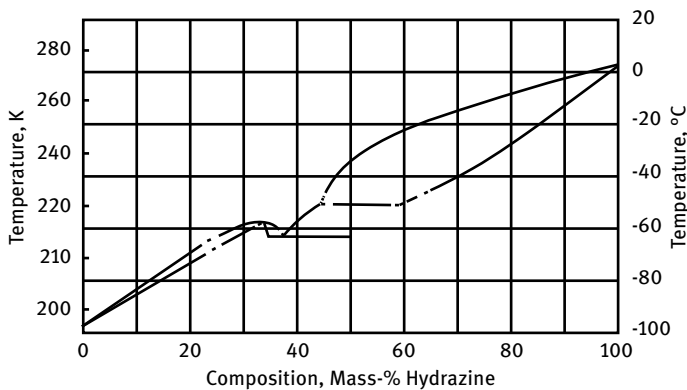
The British used a combination of LOX and 60% methanol/40% water in the test missile RTV-1 during 1948–1952. Research test vehicle-1 (RTV-1) was intended as a development tool for testing antiaircraft missile components. It was launched by

a cluster of solid boosters and sustained by a liquid-propellant engine with 3.96 kN (900 lb<sub>f</sub>) of thrust. Initially it was supposed to operate on LOX/kerosene, but the high ionization in the luminescent plume interfered with radio signal transmission and a cooler-burning propellant combination was chosen [26, p. 849].

In the UK, Armstrong-Siddeley Ltd. developed the Snarler JATO engine in 1948 using LOX and diluted methanol. The Snarler JATO unit used LOX with water-diluted methyl alcohol, had 900 kg<sub>f</sub> or 1980 lb<sub>f</sub> of thrust, and was flight tested in a Hawker P-1072 aircraft [27].

### 1.8.2 Rocket Fuel Mixtures Containing Methanol

Methanol has been tested as a freezing-point depressant for hydrazine [28]. Methanol has the ability to act as a very effective freezing-point depressant for hydrazine without detracting too much from its value as a fuel in bipropellant combinations. A hydrazine-methanol mixture containing 45 mass-% hydrazine freezes at 228 K (−45°C) (Figure 1). When 40% hydrazine is present, the freezing point is 215 K (−58°C). The freezing points of this system are lowered further when water is added.



**Figure 1:** Freezing point diagram for methanol/hydrazine mixtures. (Reproduced and modified from [28].)

### 1.8.3 Applications of Methanol as a Fuel in Monopropellant Rocket Engines

Methanol has been used as the fuel in a number of HAN-based monopropellants, for example in a balloon-dropped supersonic test missile in Japan (see the chapter “Hydroxylammonium Nitrate-Based Monopropellants” in *Encyclopedia of Monopropellants*). 30% methanol was used as a diluent for glycerin trinitrate in one of the first monopropellant experiments carried out by Crocco and Corelli in Italy in the 1930s, where several liters of the propellant mixture were carried by one of the experimenters on a passenger train from Turin to Rome for use in a monopropellant reactor [29]. For-



tunately, the train arrived without any incidents. There was concern that evaporation of the more volatile methanol might result in a more sensitive propellant, and the decomposition reactor did indeed suffer a delayed explosion during cooldown following an otherwise successful test.

Methanol has been used as a diluent for nitromethane in liquid gun propellants [30].

#### 1.8.4 Other Applications of Methanol as a Fuel

Although its energy content is not nearly as high as that of gasoline, methanol can be used as an alternative fuel in internal combustion engines, jet engines, or even fuel cells. Numerous studies evaluating the use of methanol as an automotive fuel have been published [31]. Methanol can be converted to dimethyl ether, which can be used as an alternative diesel fuel that not only results in cleaner exhaust but may also alleviate our dependence on petroleum-derived hydrocarbons as diesel fuels.

## 2 Ethanol

Ethyl alcohol (ethanol,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_6\text{O}$ , CAS RN [64-17-5]) was the first liquid rocket fuel to be used in large quantities during the 1930s and 1940s in Germany. In the US, Goddard also performed some rocket engine tests with LOX/ethanol but then reverted to LOX/gasoline for the remainder of his tests in New Mexico.

Diluted ethanol was the fuel used in the first mass-produced liquid-propellant ballistic missile (A-4, a.k.a. V-2), and it continued to be used in the US after some of the impounded V-2 missiles were reassembled and tested there. One of the first US-made V-2 derivatives, the Redstone IRBM, used 75 mass-% ethanol as fuel, and the booster for the Navaho cruise missile used 92.5% ethanol as fuel.

During the development tests in Peenemünde in the Baltic Sea in Germany, they initially used water-diluted ethanol containing only 75 mass-% ethanol because they could not manage the high chamber temperature of this rocket propellant combination with undiluted, water-free ethanol. Only later did applications of LOX/ethanol combinations in other countries make use of more concentrated and water-free ethanol. As rocket design progressed and engineering knowledge grew, the cooling problems with LOX/kerosene engines were eventually mastered and ethanol as a rocket fuel was abandoned in favor of kerosene, which gives a higher specific impulse than ethanol but burns much hotter.

Ethanol continues to receive attention as a rocket fuel because it is considered “non-toxic” (compared to hypergolic storable fuels based on hydrazines). However, it is not hypergolic with any non-fluorine oxidizers, and it requires an external source of ignition. The Dream Chaser reusable spacecraft built by Sierra Nevada Corp. uses nitrous oxide/ethanol thrusters for attitude control and deorbit propulsion.

## 2.1 Production of Ethanol

Information on the production and properties of ethanol is readily available in commonly used encyclopedias [32, 33]. Ethanol is widely used as a solvent, a germicide, a beverage, an anti-freeze, a fuel, and a chemical intermediate for other organic chemicals. Fermentation processes are the most important source of ethanol. In addition, industrial ethanol is produced from petroleum-derived ethylene by a direct hydration process. The subsidized (federal and state) use of fermentation ethanol in gasoline has fueled a rapid growth in US agricultural ethanol production. The US 1990 Clean Air Act requiring the use of oxygenates in gasoline has further driven this growth. Corn is the principal feedstock for fermentation in the United States, and sugar cane is the most important raw material outside the United States. Ethanol generation from cellulose (corn stalks, wood, saw dust) represents a valuable use of materials that would otherwise go to waste.

## 2.2 Physical Properties of Ethanol

The physical properties of ethanol are summarized in Table 7. In view of the renewed interest in ethanol as a rocket propellant, in particular as a “green,” environmentally friendly propellant, the current chapter on ethanol fills a data gap.

**Table 7:** Physical properties of ethanol.

| Property                                 | SI units                                      | Other units                                                 | References |
|------------------------------------------|-----------------------------------------------|-------------------------------------------------------------|------------|
| Molecular mass                           | 46.0684 g/mol                                 | 21.707 mol/kg                                               | [3]        |
| Freezing point                           | $158.8 \pm 0.7$ K                             | $-114.35 \pm 0.7$ °C                                        | [3]        |
| Boiling point                            | $351.5 \pm 0.2$ K                             | $78.4 \pm 0.2$ °C                                           | [3]        |
| Density at 293 K = 20 °C                 | 0.7893 g/cm <sup>3</sup>                      | —                                                           | [4]        |
| Vapor pressure at 293 K = 20 °C          | 5.862 kPa                                     | 44 mm Hg                                                    | [34]       |
| Dynamic viscosity at 288.7 K = 60 °F     | $0.012 \times 10^5$ $\mu$ N s m <sup>-2</sup> | 1.2 cPs = 0.012 Ps                                          | [4]        |
| Kinematic viscosity                      | $1.525 \times 10^{-6}$ m <sup>2</sup> /s      | 1.525 cSt                                                   |            |
| Surface tension                          | $22 \times 10^{-5}$ N/cm                      | 22.0 dyn/cm                                                 | [34]       |
|                                          | $2.2 \times 10^{-2}$ N/m                      | at 293 K = 20 °C                                            |            |
|                                          | $2.405 \times 10^{-4}$ N/cm                   | 24.05 dyn/cm at 20 °C                                       | [4]        |
| Thermal conductivity                     | 167.5 mW m <sup>-1</sup> K <sup>-1</sup>      | 0.144 kcal m <sup>-1</sup> h <sup>-1</sup> °C <sup>-1</sup> | [35]       |
| at 293 K = 20 °C                         |                                               |                                                             |            |
| Refractive index ( $n_D$ ) <sup>20</sup> | 1.3611                                        | —                                                           | [4]        |
| $t_{crit.}$                              | 516 K                                         | 243 °C                                                      | [34]       |
| $t_{crit.}$                              | 516.5 K                                       | 470 °F                                                      | [36]       |
| $P_{crit.}$                              | 6.394 MPa                                     | 63.1 atm                                                    | [34]       |
| $P_{crit.}$                              | 6.295 MPa                                     | 913 psig                                                    | [36]       |

### 2.2.1 Freezing Point and Phase Diagrams of Ethanol Mixtures

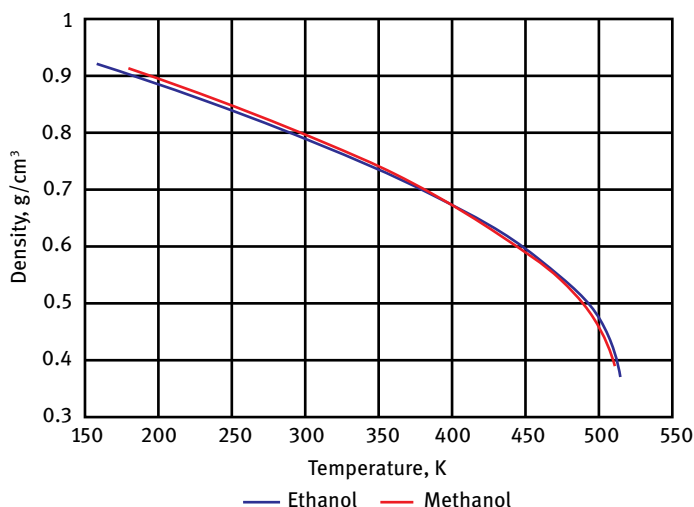
Ethanol is widely used as an anti-freeze, so its freezing point diagram in water has practical importance.

### 2.2.2 Density of Ethanol

The saturated liquid density of ethanol for the range 159–516.2 K (–114.1 to +243.1 °C) can be calculated from the equation

$$\rho = A \times B^{-[1-(T/T_c)]^{\frac{2}{7}}}$$

where  $\rho$  is the density in g/cm<sup>3</sup>, A and B are correlational constants (A = 0.2928, B = 0.2760),  $T_c$  is the critical temperature (512.5 K), and T is the temperature in kelvin [6]; see Figure 2.



**Figure 2:** Liquid density of methanol and ethanol. (Image created by Schmidt 2020 based on data from [6])

Specific gravity data for denatured ethanol-water and methanol-water mixtures were obtained by a pycnometric method at temperatures between 266 and 322 K (20–120 °F) with solutions containing between 22.5 and 100% alcohol [37]. Alcohols are added as anti-freeze to water solutions that are injected into jet engine combustors during takeoff to reduce temperatures and increase thrust.

### 2.2.3 Compressibility of and Velocity of Sound in Ethanol

The isothermal compressibility of ethanol at 293 K is  $1.098 \text{ GPa}^{-1}$ . Data on the velocity of sound in, the adiabatic compressibility of, and the density of ethanol as functions of pressure, as well as the corresponding data for methanol, are listed in Table 8.

**Table 8:** Data on the velocity of sound in, the density of, and the adiabatic compressibility of methanol, as well as the corresponding data for ethanol, as functions of pressure at 298 K (25 °C).

| Pressure, GPa   | Velocity of sound, km/s | Density, g/cm <sup>3</sup> | Compressibility, GPa <sup>-1</sup> |
|-----------------|-------------------------|----------------------------|------------------------------------|
| <b>Methanol</b> |                         |                            |                                    |
| 0.0001          | 1.10                    | 0.787                      | 0.96                               |
| 0.014           | 1.18                    | 0.797                      | 1.12                               |
| 0.028           | 1.25                    | 0.808                      | 1.27                               |
| 0.041           | 1.31                    | 0.819                      | 1.41                               |
| 0.056           | 1.37                    | 0.829                      | 1.55                               |
| 0.069           | 1.42                    | 0.836                      | 1.68                               |
| 0.083           | 1.47                    | 0.844                      | 1.82                               |
| 0.096           | 1.51                    | 0.851                      | 1.94                               |
| 1.20            | 2.72                    | 1.074                      | 7.92                               |
| 2.07            | 3.50                    | 1.153                      | 14.20                              |
| 2.92            | 3.84                    | 1.221                      | 18.03                              |
| 4.06            | 4.53                    | 1.290                      | 26.48                              |
| 4.89            | 5.10                    | 1.329                      | 34.69                              |
| 6.32            | 5.53                    | 1.383                      | 42.23                              |
| 6.82            | 5.77                    | 1.400                      | 46.57                              |
| <b>Ethanol</b>  |                         |                            |                                    |
| 0.0001          | 1.15                    | 0.785                      | 1.03                               |
| 0.58            | 2.09                    | 0.983                      | 4.29                               |
| 1.32            | 2.86                    | 1.085                      | 8.88                               |
| 1.35            | 3.08                    | 1.087                      | 10.3                               |
| 1.90            | 3.39                    | 1.138                      | 13.0                               |
| 2.12            | 3.4                     | 1.158                      | 13.7                               |
| 2.20            | 3.57                    | 1.165                      | 14.8                               |
| 3.19            | 3.97                    | 1.241                      | 19.6                               |

Data source: [38]. See also [39].

A fundamental equation of state for ethanol expressing the Helmholtz energy as a function of temperature and density has been developed [40]. Ancillary equations include equations for vapor pressure, saturated liquid density, saturated vapor density, and ideal gas heat capacity. Results from both the fundamental and ancillary equations have been compared to experimental data. It was found that the fundamental equation can compute densities to within  $\pm 0.2\%$ , heat capacities to within  $\pm 2\%$ , and the velocity of sound to within  $\pm 1\%$  of their experimentally

determined values. Values of the vapor pressure and saturated vapor density were calculated to within  $\pm 1\%$  of their experimentally determined values at temperatures of 300 K and above, while saturated liquid densities were calculated to within  $\pm 0.3\%$  of their experimentally determined values at temperatures of 200 K and above. The equation was found to be valid for pressures of up to 280 MPa and temperatures from 160 to 650 K.

The compressibility of ethanol is important for predicting water hammer effects in propellant feed systems, which are primed for the first time by dropping fuel into evacuated lines (surge flow) or by suddenly shutting off valves while the propellant is flowing, causing water hammer pressure spikes. During start-up of the propulsion system of a satellite or spacecraft, opening the tank isolation valve will cause the propellant to flow into an evacuated feedline, and the column of moving liquid to slam against a closed thruster valve. This filling process, called priming, can cause severe pressure spikes that could lead to structural failure. In the case of monopropellants such as hydrazine, the risk of adiabatic compression detonation must also be taken into account in the design of the feedline subsystem. Ethanol was used as a safe surrogate fluid to measure pressure spikes in a typical feed system, with water used as a reference fluid and ethanol used as a representative organic fuel [41]. The phenomenon of priming involves complex two-phase flow: the liquid entering the evacuated pipe undergoes flash evaporation, creating a vapor cushion in front of the liquid that mixes with the residual inert gas in the line. In addition, the dissolved pressurizing gas in the liquid will desorb, making the priming process difficult to model. Tests were performed with water and ethanol at different conditions: different tank pressures, vacuum levels, pressurizing gases (helium vs. nitrogen), geometries, etc.

#### 2.2.4 Vapor Pressure of Ethanol and Vapor-Phase Compositions of Ethanol Mixtures

The vapor pressure of ethanol can be calculated by the Antoine equation

$$\log P = A - B/(T + C)$$

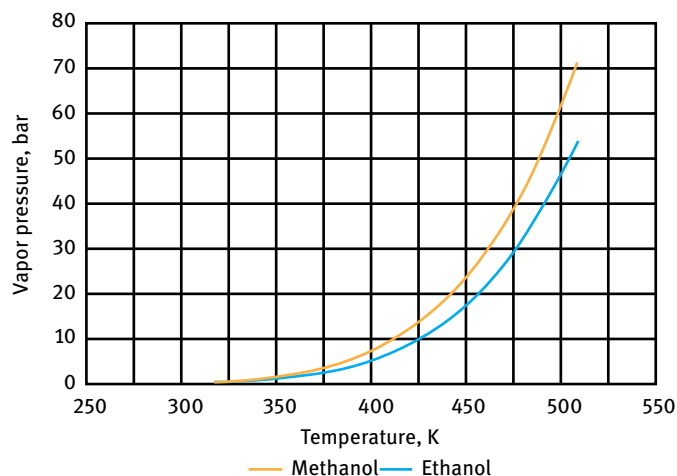
where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. NIST gives three different sets of parameters for the three constants  $A$ ,  $B$ , and  $C$ , each for a different temperature range (Table 9 and Figure 3).

**Table 9:** Coefficients for the Antoine equation for the vapor pressure of ethanol.

| Temperature range, K | A       | B        | C       | References |
|----------------------|---------|----------|---------|------------|
| 364.8–513.91         | 4.92531 | 1432.526 | −61.819 | [7]        |
| 292.77–366.63        | 5.24677 | 1598.673 | −46.424 | [8]        |
| 273–351.70           | 5.37229 | 1670.409 | −40.191 | [42]       |

Data source: [3]

Note: Coefficients were calculated by NIST from the author's data.



**Figure 3:** Vapor pressure data for methanol and ethanol. (Image created by Schmidt 2020 based on data from [3].)

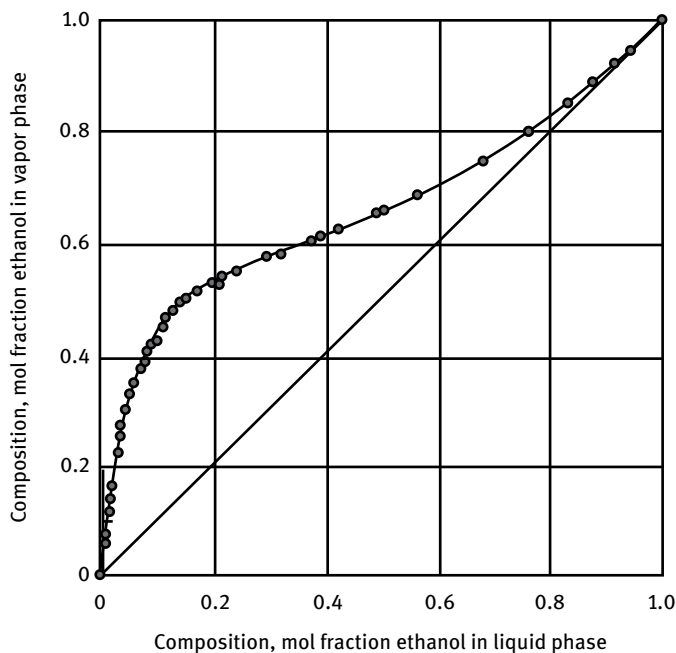
Another vapor pressure equation for the range 228–516 K uses five coefficients and the equation

$$\log p_V = A + \frac{B}{T} + C \log T + DT + ET^2$$

where  $p_V$  is the vapor pressure in mmHg and  $T$  is the temperature in kelvin. The correlation constants are  $A = -10.967$ ,  $B = -2212.6$ ,  $C = 10.298$ ,  $D = -21.061 \times 10^{-3}$ , and  $E = 10.748 \times 10^{-6}$ . For a temperature of 298 K, this equation gives a vapor pressure of 58 mmHg [6].

Accurate property data are essential for the design and evaluation of ethanol/water separation processes. Physical, chemical, and thermodynamic properties of ethanol, water and their mixtures have been compiled, including non-ideal vapor phase fugacity coefficients, liquid specific volumes, vapor pressures, reference fugacities, vapor/liquid equilibria, activity coefficients, vapor and liquid enthalpies, the effect of salt on the ethanol/water equilibrium, and multi-component equilibrium modeling [43]. The vapor phase above ethanol/water mixtures is rich in ethanol, which is of course the basis for the distillation of distilled spirits from wine. A very detailed investigation of vapor phase compositions for the ethanol/water system was conducted, based on predictions derived from a computational method. Predictions from the computational mode (Uniquac) very closely matched the measured values reported in the literature [44] (Figure 4).

Ethanol and water form an azeotrope at 96 mass-%  $C_2H_5OH$  and 101 kPa. This azeotrope is formed through hydrogen bonding between the two molecules, which



**Figure 4:** Liquid- and vapor-phase compositions of ethanol/water mixtures at 760 mm Hg, based on data from [44]. (Reproduced and modified from [43].)

is why absolute ethanol cannot be obtained by simple distillation. Heterogeneous azeotropic distillation has been studied using several entrainers: benzene, cyclohexane, trichloroethylene, or isooctane [45, 46]. Higher concentrations have been achieved by adding salts (sodium acetate) to the boiling mixture or by distillation with benzene as an auxiliary fluid. The resulting ethanol may contain some benzene as a contaminant and is thus no longer fit for human consumption.

### 2.2.5 Viscosity of Ethanol

Viscosity data for ethanol are summarized in Table 10.

**Table 10:** Viscosity of liquid ethanol.

| Temperature |    | Dynamic viscosity     |       | References |
|-------------|----|-----------------------|-------|------------|
| K           | °C | mN s m <sup>-2</sup>  | cPs   |            |
| 273         | 0  | $0.0179 \times 10^2$  | 1.790 | [34]       |
| 293         | 20 | $0.01716 \times 10^2$ | 1.716 |            |
| 343         | 70 | $0.01549 \times 10^2$ | 1.549 |            |
| 273         | 0  | $0.0177 \times 10^2$  | 1.77  | [14]       |

The viscosity of liquids can be expressed by a Fulcher-type equation

$$\log \eta = A + B/(T - T_0)$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The constants  $A$ ,  $B$ , and  $T_0$  for ethanol are summarized and compared to those for other associated (hydrogen-bonded) liquids in Table 3. In the case of ethanol, the equation would be

$$\log \eta = -2.4401 + 774.414/(T + 15.249)$$

which is applicable for temperatures between 175 and 343 K (−98.11 to +70 °C). At 298 K, this equation yields a viscosity of 1.08 cPs for ethanol with an error of  $\pm 2.6\%$ .

The dynamic viscosity of liquid ethanol in the range 273–343 K can be calculated from the following equation:

$$\eta = 5.276 \times 10^{13} T^{-5.530}$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The viscosity from this equation at 293 K is 1.2 cPs [12].

The dynamic viscosity of liquid ethanol in the range 168–516 K (−105 to +243 °C) can be calculated from the following equation:

$$\log \eta = A + \frac{B}{T} + CT + DT^2$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The coefficients for this equation are  $A = -2.697$ ,  $B = 700.9$ ,  $C = 0.2682 \times 10^{-2}$ , and  $D = -4.917 \times 10^{-6}$ . For example, the viscosity from this equation at 298 K is 1.04 cPs [10].

### 2.2.6 Surface Tension of Ethanol

The surface tension of a liquid can be predicted by a corresponding state method described by Brock and Bird, based on the boiling point temperature, critical temperature, and critical pressure. Once the surface tension at one temperature  $T_1$  is known, the surface tensions at other temperatures can be calculated by the Othmer relation. The surface tension of ethanol can be calculated from the following equation:

$$\sigma = \sigma_1 [(T_c - T)/(T_c - T_1)]^{\frac{11}{9}}$$

where  $\sigma$  is the surface tension in dyn/cm,  $T_c$  is the critical temperature (516 K), and  $T$  is the temperature in kelvin. The surface tension of ethanol is 22.39 dyn/cm at 293 K and 21.78 dyn/cm at 298 K [13]. A similar, older equation that applies in the range 159–516.2 K (−114.1 to +243.1 °C) used an exponent  $n = 0.8760$  instead of 11/9 [6]. Surface tension data for ethanol/water mixtures are listed in Table 11.



**Table 11:** Surface tension data for ethyl alcohol/water mixtures at 298 K (25 °C).

| Ethanol<br>Mass-% | Surface tension        |        |
|-------------------|------------------------|--------|
|                   | N/cm                   | dyn/cm |
| 40.0              | $2.963 \times 10^{-4}$ | 29.63  |
| 50.22             | $2.789 \times 10^{-4}$ | 27.89  |
| 59.58             | $2.671 \times 10^{-4}$ | 26.71  |
| 68.95             | $2.571 \times 10^{-4}$ | 25.71  |
| 77.98             | $2.473 \times 10^{-4}$ | 24.73  |
| 87.92             | $2.364 \times 10^{-4}$ | 23.64  |
| 92.10             | $2.318 \times 10^{-4}$ | 23.18  |
| 97.00             | $2.249 \times 10^{-4}$ | 22.49  |
| 100.00            | $2.203 \times 10^{-4}$ | 22.03  |

Data source: [47]

### 2.2.7 Thermal Conductivity of Ethanol

The thermal conductivity of ethanol as a saturated liquid can be calculated from the equation

$$\lambda = A + BT + CT^2$$

where  $\lambda$  is the thermal conductivity in  $\mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin. The correlation constants for ethanol in the temperature range 159–463 K (–114 to +190 °C) are  $A = 628.0$ ,  $B = -91.88 \times 10^{-2}$ , and  $C = 5.28 \times 10^{-4}$  [6]. At 293 K (+20 °C), the thermal conductivity of ethanol is  $404 \mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$ . The same equation in SI units is

$$\lambda = 0.2628 - 3.844 \times 10^{-4} T + 2.21 \times 10^{-7} T^2$$

where  $\lambda$  is the thermal conductivity in  $\text{W m}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin.

The thermal conductivity of ethanol vapor can be calculated from the polynomial equation

$$\lambda_G = A + BT + CT^2 + DT^3$$

where  $\lambda_G$  is the thermal conductivity of ethanol vapor at low pressure (approximately atmospheric pressure) in  $\mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin. The correlation constants for ethanol in the temperature range 273–1273 K (0 to 1000 °C) are identical to those of methanol ( $A = -18.62$ ,  $B = 9.95 \times 10^{-2}$ ,  $C = 2.90 \times 10^{-4}$ , and  $D = -12.38 \times 10^{-8}$ ) [10]. See also [48, 49].

### 2.2.8 Heat Transfer Coefficient of Ethanol

A comparison of the heat transfer coefficients of methanol and ethanol is given in a section above on methanol.

The dependence of the Nusselt number for heat transfer on laminar/turbulent flow conditions can generally be expressed in the form

$$\text{Nu} = C \text{Re}^m \text{Pr}^n$$

Rates of heat transfer to supercritical ethanol in microchannels by forced convection were measured using small-diameter circular tubes fed by a pressurized fuel supply [50]. The test sections consisted of resistively heated stainless steel hypodermic needle capillary tubes that were 4 mm in length and had an inside diameter of 95  $\mu\text{m}$ . The test conditions (temperature, pressure, film Reynolds number, bulk Nusselt number, and heat flux) were selected such that most of the physical parameters that were expected in the cooling passages of a silicon-fabricated microrocket engine were duplicated at pressures of 100 and 300 atm, corresponding to supercritical reduced pressures of 1.62 and 4.86, respectively. Heat flux values ranged from 3 to 125  $\text{W}/\text{mm}^2$ . The measured bulk Nusselt numbers ranged from 15 to nearly 400, with the corresponding film Reynolds numbers ranging from 500 to over 100000. Experimental results indicated that ethanol is a suitable fuel for regeneratively cooled microrocket engines. Post-test inspection of the inner tube wall of one of the test sections indicated that carbon deposition resulting from the pyrolysis of ethanol was not an issue.

Electrically heated tube tests were conducted to characterize the critical heat flux (for the transition from nucleate to a boiling film) of a subcritical 95 mass-% ethanol/5% isopropanol mixture flowing at conditions relevant to the design of a regeneratively cooled rocket engine thrust chamber at pressures of 1–4.8 MPa (144–703 psia), flow velocities of 9.7–77 m/s, coolant subcooling of 274–456 K (33–362 °F), and critical heat fluxes of up to 1422  $\text{W}/\text{cm}^2$  (8.7  $\text{BTU in}^{-2} \text{s}^{-1}$ ) [51]. For the data taken near to 1.38 MPa (200 psia), the critical heat flux was correlated with the product of velocity and fluid subcooling to within 20%. For data taken at higher pressures, an additional pressure term was needed to obtain a correlation with the critical heat flux. Also, at higher test pressures and/or flow rates, exceeding the critical heat flux did not result in wall burnout. This result may significantly increase the engine heat-flux design envelope for higher-pressure conditions.

In a thermosyphon heat pipe, the overall heat transfer coefficient of the thermosyphon was found to increase with increasing heat flux and coolant flow rate. At a heat flux of 7.35  $\text{kW}/\text{m}^2$ , the overall heat transfer coefficient of ethanol was 0.17  $\text{kW m}^{-2} \text{°C}^{-1}$ , as compared to 0.126  $\text{kW m}^{-2} \text{°C}^{-1}$  for methanol and 0.16  $\text{kW m}^{-2} \text{°C}^{-1}$  for water [16].

### 2.2.9 Critical Constants of Ethanol

The critical constants of ethanol are  $T_c = 516.3\text{ K}$ ,  $p_c = 6383\text{ kPa}$ , and  $\rho_c = 0.2755\text{ g/cm}^3$ .

### 2.2.10 Thermodynamic Properties of Ethanol

Thermodynamic properties of ethanol are summarized in Table 12.

**Table 12:** Thermodynamic properties of ethanol

|                                                                 | SI units                                                           | Other units                                                                                  | References           |
|-----------------------------------------------------------------|--------------------------------------------------------------------|----------------------------------------------------------------------------------------------|----------------------|
| Molar heat capacity<br>at 298 K = 25 °C                         | 111.5 J mol <sup>-1</sup> K <sup>-1</sup>                          | 26.64 cal mol <sup>-1</sup> °C <sup>-1</sup>                                                 | [3]                  |
| Standard enthalpy of<br>formation ( $\Delta H_f^{298}$ , liquid | -277.6 kJ/mol<br>-276 ± 2 kJ/mol<br>-277.6 kJ/mol<br>-277.0 kJ/mol | -66.36 kcal/mol<br>-65.96 ± 0.5 kcal/mol<br>-1440 cal/g = -66.34 kcal/mol<br>-66.20 kcal/mol | [3]<br>[52]<br>[53]  |
| Standard enthalpy of<br>formation ( $\Delta H_f^{298}$ , vapor  | -234 ± 2 kJ/mol<br>-234.8 kJ/mol                                   | -55.9 ± 0.5 kcal/mol<br>-56.12 kcal/mol                                                      | [3]<br>[53]          |
| Heat of fusion<br>at 159 K = -114 °C                            | 5.02 kJ/mol<br>4.64 kJ/mol                                         | 1.200 kcal/mol<br>1.109 kcal/mol                                                             | [54]                 |
| Heat of vaporization<br>at 351.4 K = 78.3 °C                    | 39.4 kJ/mol<br>42.3 ± 0.4 kJ/mol<br>38.56 kJ/mol                   | 9.42 kcal/mol<br>10.11 ± 0.1 kcal/mol<br>9.22 kcal/mol                                       | [3]<br>[55]          |
| Standard entropy of<br>liquid                                   | 161.21 J mol <sup>-1</sup> K <sup>-1</sup>                         | 38.53 cal mol <sup>-1</sup> °C <sup>-1</sup>                                                 | [56] as ref'd by [3] |
| Heat of combustion                                              | 1366 kJ/mol<br>1367.0 ±<br>0.42 kJ/mol                             | 326.48 kcal/mol<br>326.7 kcal/mol                                                            | [56] as ref'd by [3] |

$$M = 46.0684\text{ g/mol} = 21.707\text{ mol/kg}$$

Data on the heat capacity, free energy function, heat content function, heat content, and entropy of ethyl alcohol from 16 to 158 K (solid) and from 158 to 350 K (liquid) from calculations and measurements were tabulated and compared [56]. For the ideal gas state, these functions, together with the standard heat and free energy of formation, were tabulated from 0 to 1000 K. The best agreement between the experimental and calculated values of heat capacity and entropy was obtained with symmetrical three-fold barriers to free rotation of the CH<sub>3</sub> and OH groups of 13807 and 3347 J/mol (3300 and 800 cal/mol), respectively. See also [57–60].

### 2.2.10.1 Heat Capacity of Ethanol

The molar heat capacity of ethanol vapor assuming ideal gas behavior can be calculated from the polynomial equation [61]

$$C_p = 6.296 + 2.315 \times 10^{-1}T - 1.1856 \times 10^{-4}T^2 + 2.2218 \times 10^{-8}T^3$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. Likewise, the molar heat capacity of ethanol vapor can be calculated from the polynomial equation

$$C_p = 0.239 + 62.3 \times 10^{-3}T - 38.06 \times 10^{-6}T^2 + 9.47 \times 10^{-9}T^3$$

where  $C_p$  is the heat capacity in  $\text{cal mol}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin.

The molar heat capacity of liquid ethanol between 159 and 381 K is

$$C_p = 100.92 - 0.1118386T + 4.9854 \times 10^{-4}T^2$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin [18]. A similar polynomial gives the heat capacity of liquid ethanol between 159 and 453 K ( $-114.1$  and  $+180 \text{°C}$ ) as

$$c_p = -0.3499 + 9.559 \times 10^{-3}T - 37.86 \times 10^{-6}T^2 + 54.59 \times 10^{-9}T^3$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin [6]. The heat capacity of liquid ethanol at 298 K is  $0.58 \text{ cal g}^{-1} \text{°C}^{-1}$ .

Isochoric heat capacities of pure ethanol were measured with a high-temperature, high-pressure, adiabatic, and near-constant-volume calorimeter as a function of temperature and density [62]. Measurements were performed along 22 liquid and vapor near-critical isochores between  $193.32$  and  $365.5 \text{ kg/m}^3$  and from  $493.10$  to  $541.34 \text{ K}$ . The coverage included the one- and two-phase regions, the coexistence curve, and the near-critical and supercritical regions. The critical temperature and the critical density ( $T_c = 514.44 \pm 0.2 \text{ K}$  and  $\rho_c = 283.7 \pm 2 \text{ kg/m}^3$ ) for pure ethanol were extracted from the saturated properties near the critical point.

### 2.2.10.2 Enthalpy of Formation and Heat of Combustion of Ethanol

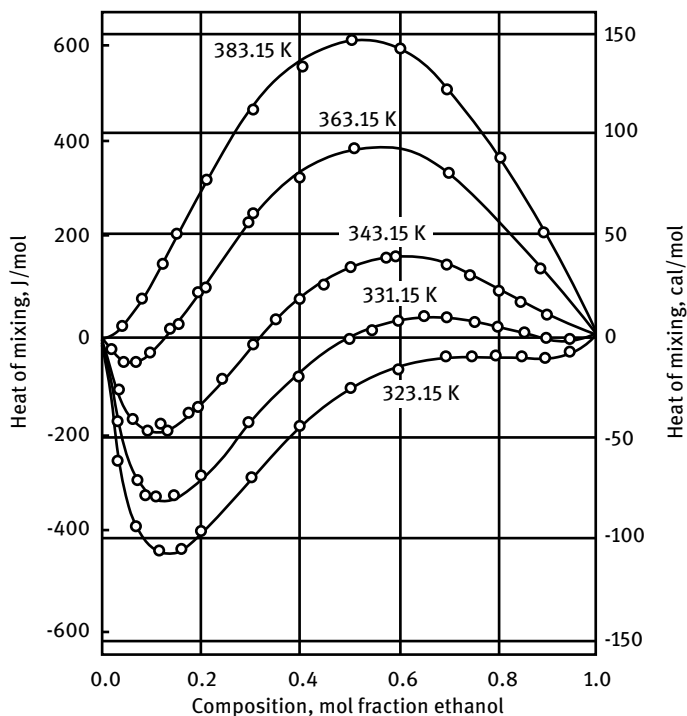
The enthalpy of formation of ethanol vapor behaving as an ideal gas can be calculated from the equation

$$\Delta H_f = -51.8 - 16.6 \times 10^{-3}T + 7.59 \times 10^{-6}T^2$$

where  $\Delta H_f$  is the heat of formation in  $\text{kcal/mol}$  and  $T$  is the temperature in kelvin.

### 2.2.10.3 Heat of Mixing of Ethanol Solutions

The ethanol/water system is extremely non-ideal, with both exothermic and endothermic heats of mixing observed, depending on the temperature and the mixture ratio [63]. At  $298.15$  and  $323.15 \text{ K}$ , mixing is exothermic, with extreme values of  $-775$  and  $-448 \text{ J/mol}$  at  $x$  values of about  $0.17$  and  $0.13$ , respectively (Figure 5).



**Figure 5:** Heat of mixing for the ethanol/water system, based on data from [63]. (Reproduced and modified from [43].)

#### 2.2.10.4 Heat of Vaporization of Ethanol

The heat of vaporization of ethanol in the temperature range 298–469 K can be calculated from the following equation [55]:

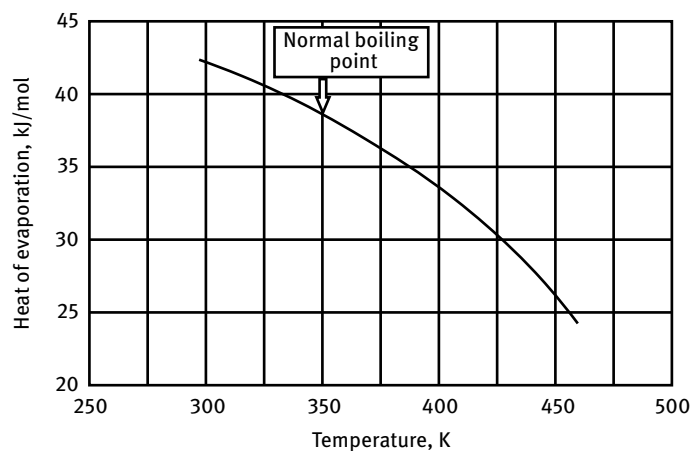
$$\Delta H_{\text{vap}} = 50.43 \exp(0.4475T/T_c) \left[ 1 - \left( \frac{T}{T_c} \right) \right]^{0.4989}$$

where  $\Delta H_{\text{vap}}$  is the heat of vaporization in kJ/mol at saturation pressure,  $T$  is the temperature in kelvin, and  $T_c$  is the critical temperature 513.9 K (Figure 6).

Another method to derive the heat of vaporization at other temperatures if one data point is known is to use the Watson equation:

$$\Delta H_{\text{vap}} = \Delta H_{\text{vap}1} [(T_c - T)/(T_c - T_1)]^n$$

where  $\Delta H_{\text{vap}1}$  is the heat of vaporization at a known temperature  $T_1$ , assumed to be 202.6 cal/g at  $T_1 = 351.4 \text{ K} = 78.3^\circ\text{C}$  (normal boiling point),  $T_c$  is the critical temperature (516.2 K = 243.1°C), and  $n$  ( $= 0.4$ ) is an empirical coefficient.



**Figure 6:** Heat of vaporization of ethanol. (Image created by Schmidt 2020 based on equation from [55].)

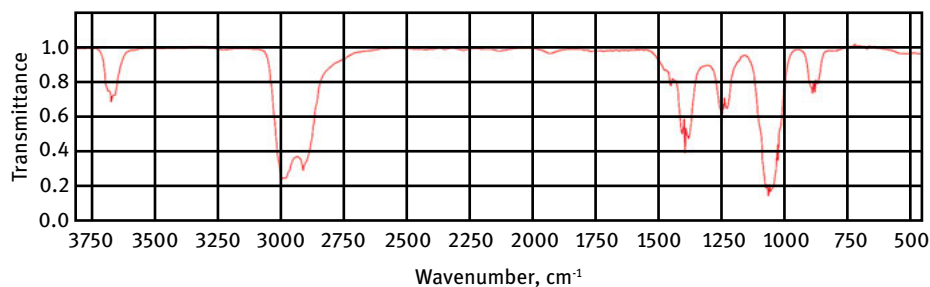
### 2.2.10.5 Heat of Fusion of Ethanol

The heat of fusion of frozen ethanol is 4.64 kJ/mol (1.109 kcal/mol) at 158.8 K [54]. Additional literature data for the enthalpy and entropy of fusion are shown in [3].

### 2.2.11 Optical Properties of Ethanol

#### 2.2.11.1 Absorption Spectrum of Ethanol

The IR spectrum of ethanol vapor is shown in Figure 7.



**Figure 7:** IR spectrum of ethanol vapor. (Reproduced and modified with permission from [64])

#### 2.2.11.2 Index of Refraction of Ethanol

Data for the index of refraction of ethanol are listed in Table 13.

**Table 13:** Index of refraction of ethanol.

| Temperature |      | Index of refraction ( $n_D$ ) |
|-------------|------|-------------------------------|
| K           | °C   |                               |
| 283.4       | 10.4 | 1.3621                        |
| 289         | 16   | 1.36048                       |
| 295         | 22   | 1.35967                       |
| 297         | 24   | 1.35885                       |
| 299         | 26   | 1.338.13                      |
| 303         | 30   | 1.35839                       |
| 307         | 34   | 1.33174                       |
| 309         | 36   | 1.3539                        |
| 311         | 38   | 1.35306                       |

Data source: [47]

**2.2.12 Electrical Conductivity of Ethanol**

The electrical conductivity of ethanol is  $1.50 \times 10^{-7}$  mho/cm at 273 K,  $6.4 \times 10^{-8}$  mho/cm at 291 K, and  $1.35 \times 10^{-9}$  mho/cm at 298 K.

**2.2.13 Dielectric Constant and Dipole Moment of Ethanol**

Data for the dielectric constant of ethanol are listed in Table 14. The dipole moment of ethanol is 1.63 Debye at 298 K. Other sources give the dipole moment of ethanol in the gas phase as 1.69 Debye.

**Table 14:** Dielectric constant of ethanol

| Temperature |        | Dielectric constant |
|-------------|--------|---------------------|
| K           | °C     |                     |
| 130.6       | -142.5 | 79.0                |
| 137.3       | -135.8 | 74.2                |
| 148.4       | -124.7 | 67.3                |
| 153.1       | -120.0 | 55.5                |
| 193.1       | -80.0  | 45.1                |
| 243.1       | -30.0  | 38.1                |
| 253.1       | -20.0  | 32.4                |
| 273.1       | 0.0    | 27.9                |
| 283.1       | 10.0   | 26.4                |
| 298.1       | 25.0   | 24.1                |
| 313.1       | 40.0   | 22.7                |
| 333.1       | 60.0   | 20.2                |

Data source: [47]

## 2.3 Chemical Properties of Ethanol

Ethanol is not very reactive and autoxidizes only very slowly in air. Bacterial fermentation converts it to vinegar. Ethanol is not very corrosive, making it easier to select suitable construction materials.

### 2.3.1 Thermal Stability of Ethanol

Ethanol is more thermally stable than hydrocarbons, but will pyrolyze at higher temperatures and may form some soot.

The rate constant for the disappearance of ethanol at temperatures between 849 and 897 K (576–624 °C) can be expressed by the equation

$$k_1 = 10^{10} \exp \left[ -46200 \pm \frac{1700}{RT} \right] \text{ s}^{-1}$$

and the principal products are acetaldehyde, hydrogen, and a polymeric product [65].

The gas mixture leaving a reactor during the thermal decomposition of ethanol at residence times of about 5 ms and temperatures from 1050 to 1275 K was analyzed by molecular beam sampling mass spectroscopy, and was found to consist of ethene, water, hydrogen, methane, and carbon monoxide, along with acetaldehyde as an intermediate [66–68]. The thermal decomposition of ethanol limits its use as a regenerative coolant in rocket engines. Adding some water to the ethanol fuel will extend its useful temperature range. This reaction can be used in the production of pyrolytic carbon and carbon nanotubes [69].

## 2.4 Handling of Ethanol

Compared to all other rocket fuels, ethanol is very safe to handle. Indeed, in the 1990s, when the call first went out to come up with environmentally friendly propellants, ethanol was one of the prime candidates for a “green” rocket fuel. At the same time, increasing quantities of ethanol were added to gasoline to reduce the exhaust toxicity and environmental impact of automobiles. Some automobiles were even modified to operate solely on ethanol as a gasoline replacement instead of using it as a gasoline additive.

### 2.4.1 Ethanol Fire Hazard

When handling ethanol in large quantities, the main hazard is the flammability of the material. The flammability safety properties of ethanol are listed in Table 15. The upper and lower flammability limits of ethanol vapor in air at 333 K (60 °C) with upward propagation are 3.28 and 19.00 vol.-%, respectively.



**Table 15:** Flammability safety properties of ethanol.

|                                                        |             |       |
|--------------------------------------------------------|-------------|-------|
| Flash point, open cup                                  | 294.3 K     | 70 °F |
| Flash point, closed cup                                | 285.9 K     | 55 °F |
| Lower limit of flammability in air, upward propagation | 3.3 vol.-%  |       |
| Upper limit of flammability in air, upward propagation | 19.0 vol.-% |       |

Data source: [36]

The flammable range widens with temperature, as shown in Table 16.

**Table 16:** Lower limit of flammability of ethanol at different temperatures.

| Temperature |     | Lower limit, vol.-% |
|-------------|-----|---------------------|
| K           | °C  |                     |
| 373         | 100 | 3.55                |
| 423         | 150 | 3.15                |
| 473         | 200 | 3.00                |
| 523         | 250 | 2.75                |

Data source: [24]

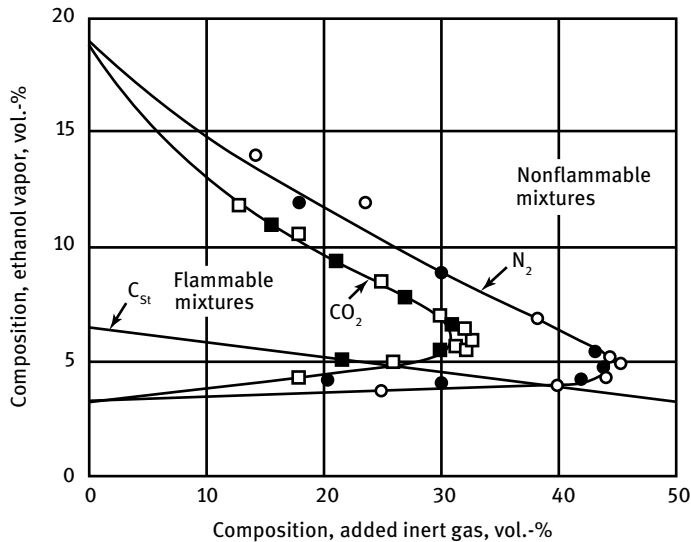
The autoignition temperatures and flammable ranges of ethanol and other combustibles must be known when investigating fire and explosion accidents [70]. The autoignition temperature of ethanol in air is 638 K (365 °C). The open-cup flash point of ethanol in air is 286 K (13 °C). The most complete summary of the flammability of ethanol under a wide range of conditions (in terms of pressure, diluents, direction of flame propagation, tube diameter, oxygen enrichment, and contaminants) is available in a NASA handbook [71].

The flammable range of ethanol vapor in air can be narrowed by adding a diluent gas. As seen in Figure 8, carbon dioxide is a more effective diluent gas than nitrogen. This is useful if there is an ethanol spill in a confined space and it is necessary to inert the atmosphere to prevent an explosion hazard. In this graph, the percentage of air in the ternary mixture was calculated from

$$\% \text{Air} = 100 - \% \text{Ethanol} - \% \text{Diluent}$$

#### 2.4.2 Spill Cleanup

If ethanol is spilled, it is easy to flush the spill away with copious amounts of water, diluting the flammable liquid to below the flash point. The open cup flash point of 100% ethanol is 288 K (15 °C), but after 1:1 dilution with water, the flash point of 50 vol.-% ethanol is above room temperature.



**Figure 8:** Flammable ranges of ethanol vapor/air/diluent gas mixtures. Note that the data obtained at higher concentrations along the dashed lines were obtained at a reduced pressure of 0.5 atm. (Reproduced and modified from [72].)

## 2.5 Toxicity of Ethanol

Besides the well-known hazard of drunkenness when ingesting ethanol in distilled spirits or other alcoholic beverages, there is the hazard of the inhalation of an excessive amount of ethanol vapor if any of the propellant is spilled during transfer and fueling operations. Working areas should be well ventilated, and the inhalation of ethanol vapors must be avoided as it can cause the same effects as imbibing the ethanol. An episode was reported where an engineer who was inspecting the inside of a warm LOX/EtOH rocket chamber to look for discoloration or burnt spots soon after a test firing, while the injector passages were still wet with liquid fuel, became intoxicated by inhaling the fumes [26].

The toxicity of ethanol is greatly increased by the addition of denaturing agents (methanol, pyridine, and benzene) to discourage consumption by humans.

### 2.5.1 Ethanol Inhalation Hazard

The NIOSH REL and OSHA PEL threshold limit value for ethanol for 8 h/d, 5 d/week exposure is 1000 ppm TWA. For vapor inhalation, the immediately dangerous to life and health (IDLH) concentration is 3300 ppm for 0.5 h (10% of the LEL flammability limit). At this concentration, the ethanol vapor in the air will irritate the eyes [73].

The original IDLH (15000 ppm) was based on human inhalation, but at 15000 ppm there is continuous lachrymation and coughing in exposed individuals. Other sources

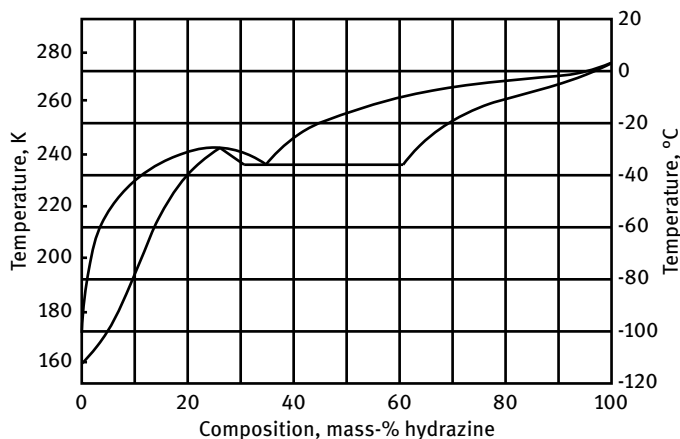
have reported that a 2 h of exposure to 19260 ppm produced only light narcosis in the rat; that 255 min of exposure to 19260 ppm produced no signs of intoxication in the guinea pig; that 75 min of exposure to 23940 ppm produced narcosis in the mouse; and that 80 min of exposure to 13300 ppm caused ataxia in the mouse. The IDLH was revised to 3300 ppm based on health considerations and acute inhalation toxicity data in humans [74, 75].

### 2.5.2 Ethanol Splash Hazard

Ethanol spilled on the skin is relative harmless. Skin exposure to ethanol may dissolve some of the skin grease if the spills are repeated, so the skin may become dry and brittle. Alcohol splashed into the eyes will cause immediate eye irritation. Alcohol splashes into eyes should be rinsed out with water. Single splash incidents will rarely leave lasting effects.

## 2.6 Rocket Fuel Mixtures Containing Ethanol

Ethanol has been tested as a freezing point depressant for hydrazine [28]. Fuel blends containing 10 mass-% hydrazine or less freeze below 233 K ( $-40^{\circ}\text{C}$ ) (Figure 9). The lowest freezing mixture containing a greater amount of hydrazine is that with a composition of about 35 mass-% hydrazine and 65% ethanol, which freezes at 237 K ( $-36^{\circ}\text{C}$ ). The freezing point of this system is lowered further when water is added as a third constituent.



**Figure 9:** Freezing point diagram for ethanol/hydrazine mixtures. (Reproduced and modified from [28].)

## 2.7 Gelled Ethanol

Two gel fuels – ethanol gel and UDMH gel using methyl cellulose as a gelling agent – were rheologically characterized using a rheometer in the low shear rate range [76, 77]. The ethanol and UDMH gels were thixotropic in nature. Their apparent viscosity values fell drastically with the shear rate, and the apparent viscosities of the gels were significantly reduced at higher temperatures. For both gels, the up and down shear rate curves formed a hysteresis loop that showed no significant variation with temperature.

A rheological study of freshly prepared gelled ethanol was carried out using a rotational rheometer (HAAKE RS600) and the gel viscosity in the shear rate range  $1\text{--}1000\text{ s}^{-1}$  was assessed. A study of the gelation of metallized and non-metallized ethanol with a methylcellulose (MC) gelling agent and the rheological properties (flow and dynamic study) of these gels showed that increasing the shear rate reduced the apparent viscosity for a given yield stress (for a shear rate range of  $1\text{--}12\text{ s}^{-1}$ ) for both shear rate ranges ( $1\text{--}12$  and  $1\text{--}1000\text{ s}^{-1}$ ) covered in this experiment [78, 79]. The gellant (MC) and metal particle concentrations significantly influenced the apparent viscosity of the gel. Distinct changes in thixotropic behavior were observed while decreasing the concentrations of the MC and the Al metal particles in the ethanol gels. The dynamic study showed that all of the linear viscoelastic (LVE) regions of the gel samples were independent of the strain percentage ( $1\text{--}10\%$ ). The  $G'$  values depended on the frequency and exceeded the  $G''$  values, which indicated the presence of a highly structured, gel-like material. The values showed that all of the ethanol gels were elastic weak physical gels with a high degree of crosslinking.

The gelation of ethanol required a gellant concentration as low as 8 mass-% for the pure ethanol case and as low as 4 and 6 mass-% for metallized ethanol, depending on the metal type used [80]. Metallized gels using 20 mass-% Al and B metal powders showed a reduction in the required gellant concentration depending on the degree of metallization. The rheological properties of metallized and non-metallized ethanol gels with MC as the gelling agent at different ambient temperatures ( $283\text{--}323\text{ K}$ ) were experimentally investigated. The gel fuels were rheologically characterized using a rheometer at shear rates ranging from  $1$  to  $12\text{ s}^{-1}$  and from  $1$  to  $1000\text{ s}^{-1}$ . In the shear rate range  $1\text{--}12\text{ s}^{-1}$ , the apparent viscosities and yield stresses of the gels were observed to significantly decrease at higher ambient temperatures and as the gellant and metal particle concentrations decreased. The thixotropic behavior was found to be a strong function of the Al and B metal particle concentration for all test temperatures in the shear rate ranges from  $1$  to  $12\text{ s}^{-1}$  and from  $1$  to  $1000\text{ s}^{-1}$ . It was also a function of the MC concentration in the shear rate range of  $1\text{--}1000\text{ s}^{-1}$ . The hypergolicity and ignition delay of pure and energized ethanol gel fuel activated with metal catalysts and squirted together with hydrogen peroxide were tested in an open spot plate apparatus [81].

If a large gelling agent (methylcellulose or hydroxypropyl methyl cellulose) concentration is used, the gelled ethanol may be stiff enough to be used as a fuel grain in a hybrid rocket [82].

### 2.7.1 Gelled Metallized Ethanol

The specific impulse of ethanol as a fuel can be improved by the addition of metal powders with high heats of combustion, such as aluminum or beryllium. In order to keep the metal particles in suspension, the fuel has to be gelled.

The gelation of liquid fuels can be achieved at gellant concentrations as low as 8 mass-% for pure ethanol and as low as 4–6 mass-% for metallized ethanol (depending on the metal type). The rheological properties of metallized and non-metallized ethanol gels with methyl cellulose as a gelling agent at different ambient temperatures (283–323 K) were characterized at shear rates ranging from 1 to 12 s<sup>-1</sup> and from 1 to 1000 s<sup>-1</sup> using a rheometer [83]. In the shear rate range 1–12 s<sup>-1</sup>, the apparent viscosities and yield stresses of the gels were observed to significantly decrease at higher ambient temperatures and as the gellant and metal particle concentrations decreased. The thixotropic behavior was found to be a strong function of the A1 and B metal particle and gellant concentrations for all test temperatures at shear rate ranges of 1–12 and 1–1000 s<sup>-1</sup>.

Impinging jets of metallized and non-metallized ethanol gels with methyl cellulose as a gelling agent have been evaluated for their atomization characteristics using an injector design that induced disturbances prior to jet impingement due to the presence of a resonant cavity [84]. The effect of metallization on the spray characteristics of the fluid was recorded using a high-speed imaging system. A reduction in the mean droplet diameter of the metallized gel was observed when compared to the pure fuel gel, which may be due to the reduced cohesive forces in the metal-containing gel structure.

## 2.8 Substituted Ethanols

Ethanol is a good rocket fuel but not quite as energetic as one might wish. Therefore, attempts have been made to boost the energy content of ethanol by attaching explosophoric groups such as azido or nitro groups to the hydrocarbon skeleton that also carries the hydroxyl group.

Ethanol derivatives that carry explosophoric groups on the C<sub>2</sub> skeleton will be discussed in the sections focusing on explosophoric groups, not in this section. One example is 2-azidoethanol, which has been tested as a monopropellant and as a fuel. 2-Azidoethanol is described in the chapter “Azides and Azido Compounds” in *Encyclopedia of Liquid Fuels*. Ethanolamine is described in the chapter “Aliphatic Amines” in *Encyclopedia of Liquid Fuels*.

### 3 Isopropyl Alcohol

Isopropyl alcohol (2-propyl alcohol, 2-propanol, isopropanol, IPA, dimethylcarbinol, secondary propyl alcohol,  $(\text{CH}_3)_2\text{CHOH}$ ,  $\text{C}_3\text{H}_7\text{OH}$ , CAS RN [67-63-0]) is used mostly as a cleaning fluid and only rarely as a rocket fuel. The name isopropanol is incorrect because there is no alkane hydrocarbon by the name of *isopropane* from which this name could be derived by adding the suffix *-ol*. Nevertheless, some of its properties are included here because residual impure IPA accidentally left in the equipment after cleaning may adversely interact with rocket propellants and cause contamination problems. The properties of IPA, such as its vapor pressure and its tendency to autoxidize and form acetone and peroxides, need to be known to ensure the complete removal of IPA by evacuation or by purging with nitrogen before the propulsion system is loaded with propellants.

Isopropyl alcohol has been evaluated as a rocket propellant with NTO, LOX, HTP, or RFNA as the oxidizer, but there has been no additional work in this field recently [85–88]. Isopropyl alcohol can be hypergolized by adding aniline as the fuel [86].

#### 3.1 Production of Isopropyl Alcohol

Isopropyl alcohol can be prepared from ethylene via oxo synthesis, from propane by partial oxidation, or from propylene. Isopropyl alcohol is produced in industrial quantities and has many applications as a solvent and as an intermediate for other organic chemicals. Isopropyl alcohol has been used in the production of hydrogen peroxide.

#### 3.2 Physical Properties of Isopropyl Alcohol

Physical properties of isopropyl alcohol are summarized in Table 17. The vapor pressure of 2-propanol can be calculated from an Antoine equation using the coefficients listed in Table 18,

$$\log P = A - B/(T + C)$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. NIST gives two different sets of parameters for the three constants  $A$ ,  $B$ , and  $C$ , each for a different temperature range (Table 18).

Isopropyl alcohol and water form an azeotrope that contains 12.6 mass-%  $\text{H}_2\text{O}$  and boils at 353.5 K (80.4 °C). The dynamic viscosity of liquid 2-propanol in the range 273–353 K can be calculated from the following equation:

$$\ln \mu = -8.0339 + 2606.8/T$$

where  $\mu$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The viscosity at 293 K is 2.3702 cPs [12].

**Table 17:** Physical properties of isopropyl alcohol.

| Property                                         | SI units                                    | Other units                                                 | References |
|--------------------------------------------------|---------------------------------------------|-------------------------------------------------------------|------------|
| Molecular mass                                   | 60.0950 g/mol                               | 16.64 mol/kg                                                | [3]        |
| Freezing point                                   | 184.65 K                                    | −88.5 °C                                                    | [3]        |
| Boiling point                                    | 355.5 ± 0.4 K                               | 82.4 ± 0.4 °C                                               | [3]        |
| Density at 293 K                                 | 0.7863 g/cm <sup>3</sup>                    | —                                                           | [89]       |
| Vapor pressure at 283 K                          | 2.26 kPa                                    | 17.0 mm Hg                                                  | [89]       |
| Viscosity at 293 K                               | 2.43 × 10 <sup>−3</sup> N s m <sup>−2</sup> | 2.43 cPs                                                    | [89]       |
| Surface tension at 293 K                         | 2.17 × 10 <sup>−4</sup> N/cm                | 21.7 dyn/cm                                                 | [89]       |
| Thermal conductivity                             | 0.1535 W m <sup>−1</sup> K <sup>−1</sup>    | 0.132 kcal m <sup>−1</sup> h <sup>−1</sup> °C <sup>−1</sup> | [47]       |
| Critical temperature                             | 509 ± 2 K                                   | 236 °C                                                      | [3]        |
| Critical pressure                                | 4.9 ± 0.5 MPa                               | 48.5 atm                                                    | [3]        |
| Heat capacity                                    | 161.2 J mol <sup>−1</sup> K <sup>−1</sup>   | 0.65 cal g <sup>−1</sup> °C <sup>−1</sup>                   | —          |
| Enthalpy of formation, liquid $\Delta H_f^{298}$ | −317.0 ± 0.3 kJ/mol                         | −75.76 kcal/mol                                             | [3]        |
| Enthalpy of formation, vapor $\Delta H_f^{298}$  | −272.8 kJ/mol                               | −62.2 kcal/mol                                              | [3]        |
| Heat of combustion                               | 2006.9 ± 0.2 kJ/mol                         | 8.03 cal/g                                                  | [3]        |
| Heat of vaporization                             | —                                           | 9.623 kcal/mol<br>= 160.13 cal/g                            | [89]       |
| Heat of vaporization                             | 39.85 kJ/mol<br>at 355.4 K                  | 9.52 kcal/mol<br>at 82.3 °C                                 | [3]        |

**Table 18:** Antoine equation coefficients for the vapor pressure of 2-propanol.

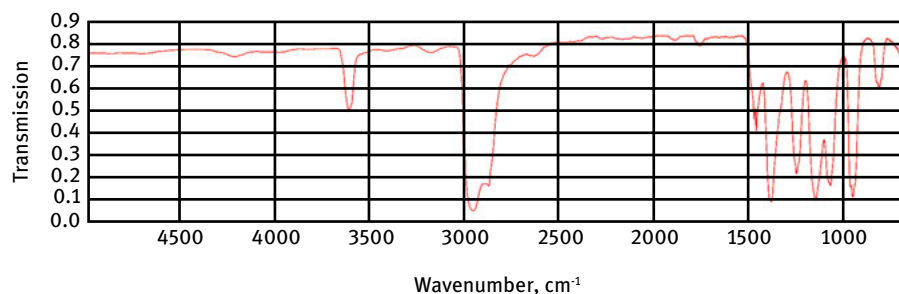
| Temperature range, K | A       | B        | C       |
|----------------------|---------|----------|---------|
| 395–508              | 4.57795 | 1221.423 | −87.474 |
| 330–362              | 4.8610  | 1357.427 | −75.814 |

Note: Coefficients were calculated by NIST from the author's data.

The velocity of sound in isopropyl alcohol was measured by a single-pulse technique for temperatures from 294 to 366 K (70–200 °F) and for pressures from 0.1 to 4 MPa (1–40 atm) [5]. The IR spectrum of IPA is shown in Figure 10. Isopropyl alcohol/hydrazine mixtures containing 20 mass-% or more hydrazine freeze above 233 K (−40 °C). Isopropyl alcohol is not a very effective freezing-point lowering additive to hydrazine.

### 3.3 Chemical Properties of Isopropyl Alcohol

Most of the isopropyl alcohol procured by the US Government is used as a cleaning solvent and not as a rocket propellant. Nevertheless, the military specification for iso-



**Figure 10:** Infrared spectrum of 2-propanol vapor. (Reproduced and modified with permission from [64])

propyl alcohol (*MIL-P-87931 – Propellant, Isopropyl Alcohol*) calls it a propellant. Other specifications have been issued by ASTM [90, 91] and the Federal Government [92].

Although isopropyl alcohol is not used as a propellant, its purity when used as a cleaning solvent in propulsion systems must be controlled, otherwise residues left behind after the cleaning solvent evaporates could gum up valve seat surfaces or clog filter screens.

There was an incident where an excessively high acetone content of aged IPA was left behind in an incompletely dried tank system. When the system was later loaded with hydrazine, a reaction between the acetone and hydrazine (hydrate) formed a brown polymer goo that clogged filters in a ground service cart for fueling a satellite at the launch site. The only solvent capable of dissolving the brown residue and cleaning the cart was hydrazine.

Acetone and isopropyl peroxide form during the storage of IPA if air is not excluded and if the IPA is exposed to sunlight in a clear glass bottle. Most space system facilities do not specify that IPA cleaning solvents should be stored under an inert atmosphere. Most IPA procurement specifications do not limit the amount of acetone allowed in IPA when it is shipped from the supplier. The specifications only limit the levels of acidity (assumed to be acetic acid), non-volatile residues, and water.

Attempts to purify IPA (i.e., to recycle used IPA) by distillation have ended in catastrophe because less volatile peroxides accumulated in the sump of the still and exploded toward the end of the distillation process [93–95]. If IPA is to be recycled and purified by distillation, the peroxides must first be destroyed by reaction with a reducing agent.

There is (was) a commercial industrial process for the production of hydrogen peroxide based on the reaction of IPA with oxygen (see the chapter “Hydrogen Peroxide” in *Encyclopedia of Oxidizers*).



### 3.4 Toxicity of Isopropyl Alcohol

The NIOSH TWA and the OSHA PEL TWA for IPA are 400 ppm (980 mg/m<sup>3</sup>). The IDLH is 2000 ppm (4920 mg/m<sup>3</sup>).

### 3.5 Safety Properties of Isopropyl Alcohol

Isopropyl alcohol is a flammable liquid. Flammability data for isopropyl alcohol are shown in Table 19.

**Table 19:** Flammability properties of isopropyl alcohol.

| Property                        | Temperature                        |        | References |
|---------------------------------|------------------------------------|--------|------------|
| Flash point (open cup)          | 294 K                              | 21 °C  | [89]       |
| Autoignition temperature in air | 746 K                              | 473 °C | [89]       |
|                                 | 713 K                              | 440 °C | [96]       |
| Limits of flammability          | Lower limit: 2.2 vol.-%            |        | [72]       |
| Limits of flammability          | 2.02–7.99 vol.-% at 333 K = 60 °C  |        | [97]       |
|                                 | 1.73–7.35 vol.-% at 403 K = 130 °C |        |            |

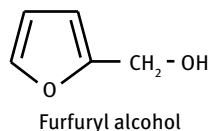
## 4 Higher Alkanols (C<sub>n</sub> > 3)

Alkanols with more than three carbon atoms in the molecule have not been used as rocket propellants.

### 4.1 Furfuryl Alcohol as Rocket Fuel

Furfuryl alcohol (2-furymethanol, 2-furanmethanol, 2-furancarbinol, furfuranol, C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>, CAS RN [98-00-0]) is an unsaturated cycloaliphatic alcohol that was, at one time, widely used as a hypergolic fuel in mixtures with aromatic or aliphatic amines in combination with nitric acid (WFNA or RFNA) as the oxidizer. It is listed here only for historical reasons. Most publications on the use of furfuryl alcohol as a rocket propellant are at least 60 years old. It is very unlikely that furfuryl alcohol will ever again be used as a rocket propellant, but if they do, they can claim to be using a sustainable biofuel, made from agricultural waste products without the use of fossil fuels, a true “green,” i.e., environmentally friendly rocket fuel. Furfuryl

alcohol is a five-membered furan ring with a hydroxymethyl group attached at the 2-position. The structural formula of furfuryl alcohol is shown here:



## 4.2 Production of Furfuryl Alcohol

Furfuryl alcohol is manufactured industrially by the catalytic reduction of furfural (its corresponding aldehyde), which is obtained from corncobs and sugar cane bagasse. Because it is made from regenerable raw products, it has been called a “biofuel.” It can be used as a solvent, but is primarily used as an ingredient in the manufacture of polymers for foundry resins, adhesives, and wetting agents. There are only a few other applications for furfuryl alcohol, so very little is produced. The use of furfuryl alcohol as a rocket propellant is now only of historical interest.

## 4.3 Physical Properties of Furfuryl Alcohol

Physical properties of furfuryl alcohol are listed in Table 20.

**Table 20:** Physical properties of furfuryl alcohol.

|                                                                    | SI units                                   | Other units                                  | References |
|--------------------------------------------------------------------|--------------------------------------------|----------------------------------------------|------------|
| Molecular mass                                                     | 98.0999 g/mol                              | 10.1934 mol/kg                               | [3]        |
| Triple point                                                       | 258.6 K                                    | −14.5 °C                                     | [3]        |
| Boiling point                                                      | 430 K                                      | 157 °C                                       | [3]        |
| Density (at 293 K)                                                 | 1.1296 g/cm <sup>3</sup>                   | —                                            | [4]        |
| Vapor pressure (at 313 K = 40 °C)                                  | 240 Pa                                     | 1.8 mm Hg                                    |            |
| Refractive index ( $n_D$ ) <sup>20</sup>                           | 1.4868                                     | —                                            | [4]        |
| Standard enthalpy of formation, liquid $\Delta H_f$ <sup>298</sup> | −276.4 kJ/mol                              | −66.06 kcal/mol                              | [3]        |
| Heat capacity at 298 K                                             | 204.01 J mol <sup>−1</sup> K <sup>−1</sup> | 48.76 cal mol <sup>−1</sup> °C <sup>−1</sup> | [3]        |
| Heat of combustion, liquid                                         | 2548.7 kJ/mol                              | 609 kcal/mol                                 | [3]        |
| Heat of vaporization                                               | 53.6 kJ/mol                                | 12.81 kcal/mol                               | [3]        |

The velocity of sound in furfuryl alcohol and aniline/furfuryl alcohol mixtures was measured by a single-pulse technique for temperatures from 294 to 366 K (70–200 °F) and for pressures from 0.1 to 4 MPa (1–40 atm) [5].

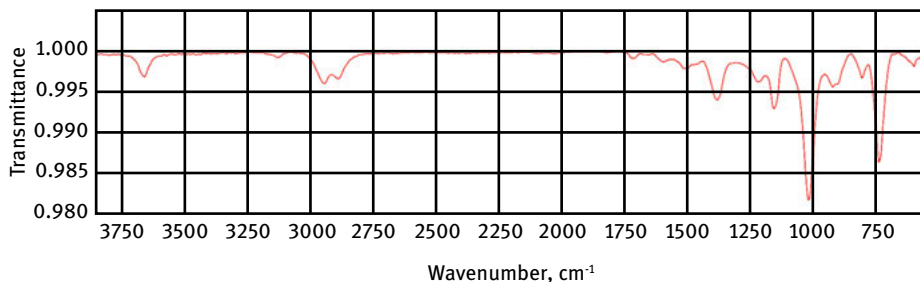
Viscosity data for furfuryl alcohol obtained with a rolling ball viscometer constructed from glass are listed in Table 21.

**Table 21:** Dynamic viscosity of furfuryl alcohol.

| Temperature |     | Viscosity              |       |
|-------------|-----|------------------------|-------|
| K           | °C  | $\text{N s m}^{-2}$    | cPs   |
| 303         | 30  | $4.402 \times 10^{-3}$ | 4.402 |
| 313         | 40  | $3.236 \times 10^{-3}$ | 3.236 |
| 323         | 50  | $2.568 \times 10^{-3}$ | 2.568 |
| 333         | 60  | $2.009 \times 10^{-3}$ | 2.009 |
| 343         | 70  | $1.631 \times 10^{-3}$ | 1.631 |
| 353         | 80  | $1.348 \times 10^{-3}$ | 1.348 |
| 363         | 90  | $1.121 \times 10^{-3}$ | 1.121 |
| 373         | 100 | $0.950 \times 10^{-3}$ | 0.950 |
| 383         | 110 | $0.813 \times 10^{-3}$ | 0.813 |
| 393         | 120 | $0.708 \times 10^{-3}$ | 0.708 |
| 403         | 130 | $0.621 \times 10^{-3}$ | 0.621 |

Data source: [98]

The IR spectrum of furfuryl alcohol is shown in Figure 11.



**Figure 11:** IR spectrum of furfuryl alcohol. (Reproduced and modified with permission from the NIST Standard Reference Data Program Collection in [3])

#### 4.4 Chemical Properties of Furfuryl Alcohol

Furfuryl alcohol in the freshly distilled state is a clear, yellowish liquid that discolors with age, turning dark red and finally dark brown due to autoxidation and polymerization.

Furfuryl alcohol is miscible with water, but solutions may autoxidize. It is soluble in most common organic solvents. When it comes into contact with acids, it will poly-

merize and form brown resins that are likely to clog valves, filters, and injector orifices. Addition of hydrazine, aniline, or alkylamines will suppress the resin formation.

The purity requirements for furfuryl alcohol, which was at one time procured by the US Government for use as rocket propellant, were spelled out in the military specification MIL-P-45702A – *Propellant, Furfuryl Alcohol* (now canceled) [99]. The requirements were max. furfural content 0.7%, max. cloud point  $295\text{ K} = 22^\circ\text{C}$ , refractive index ( $n_D$ )<sup>20</sup>  $1.486 \pm 0.003$  at  $293\text{ K} = 20^\circ\text{C}$ , and specific gravity  $1.135 \pm 0.006$  at  $293\text{ K} = 20^\circ\text{C}$ . The most likely contaminant was the aldehyde furfural, from which it was made by hydration. Furfural, a contaminant of furfuryl alcohol resulting from incomplete reduction or partial autoxidation, can be analyzed by infrared spectroscopy [100].

#### 4.4.1 Storage Stability of Furfuryl Alcohol

A significant disadvantage of furfuryl alcohol as a rocket fuel is its tendency to autoxidize and polymerize and form resins during storage. These resins may coat filters or orifices and obstruct flow. Resins plating out on the cooling channels of a regeneratively cooled rocket engine may cause burnout because heat transfer is locally impeded [101]. The resins are formed as a result of polymerization and polycondensation. Resin formation is accelerated by heat, oxygen from the air, light, and traces of acids. Basic or alkaline substances in furfuryl alcohol inhibit the reactions leading to resinification. Hydrazine or tertiary amines are the most effective inhibitors tested.

#### 4.5 Fuel Mixtures with Furfuryl Alcohol

Addition of aniline reduces the rate of resin formation by furfuryl alcohol somewhat. Furfuryl alcohol/aniline mixtures have been used in JPL-developed rockets in combination with WFNA or RFNA as the oxidizer, and there are numerous reports dating back to the 1940s on ignition delay measurements and static rocket engine tests with this propellant combination. The additive that most effectively prevents resin formation is hydrazine, since it acts as an antioxidant. Hydrazine also improves the hypergolic ignition quality of such fuel mixtures.

A 50:50 mixture of furfuryl alcohol and aniline was used in one version of the first American liquid-propellant ballistic missile, the MGM-5 CORPORAL developed by JPL, Douglas Aircraft, and Firestone Rubber for the US Army and deployed during the years 1954–1964. This missile was capable of carrying a payload of 680 kg, including nuclear warheads. An early version of the CORPORAL E used a fuel consisting of 80 mass-% aniline and 20 mass-% furfuryl alcohol. The oxidizer was RFNA with 6.5 mass-%  $\text{NO}_2$ . The later Type II CORPORAL used a mixture of 46.5 mass-% furfuryl alcohol, 46.5 mass-% aniline, and 7 mass-% hydrazine as the fuel and stabi-

lized IRFNA with 14 mass-%  $\text{NO}_2$ , 2.5%  $\text{H}_2\text{O}$ , and 0.6% HF [102, 103]. The liquid-propellant missile CORPORAL was later replaced by the solid-propellant missile SERGEANT. The 50:50 mixture of furfuryl alcohol and aniline ignites hypergolically with WFNA or RFNA, burns very smoothly without combustion instability, and can be used to cool the engine regeneratively. A bibliography of JPL publications contains more than 50 references to the CORPORAL missile, although not all of those relate to its propulsion and propellants [104]. The heat capacity of furfuryl alcohol/aniline mixtures in the range 300–422 K (80–300 °F), which was needed to calculate the regenerative cooling capability of this fuel in a rocket engine, was determined by calorimetric measurements [105].

A fuel mixture of 46.5 mass-% furfuryl alcohol and 51 mass-% aniline covered by MIL-P-45700 was also used in a US Navy surface-to-air missile called LARK. This fuel mix was similar to the fuel used by the US Army in the early version of the CORPORAL missile.

Although it is very unlikely that furfuryl alcohol/aniline mixtures will ever be used again as rocket fuels, we now review some physical properties of these mixtures. The specific heats of **(1)** a sample of aniline purified by fractional distillation, **(2)** a sample of commercial furfuryl alcohol, and **(3)** a sample of a mixture of 80 mass-% commercial aniline with 19.976 mass-% commercial furfuryl alcohol were determined by an adiabatic technique in a glass calorimeter at temperatures near to 311, 344, 378, 411, and 444 K (100, 160, 220, 280, and 340 °F, respectively) [106]. The specific heat of nitromethane was determined at temperatures near 311, 344, and 372 K (100, 160, and 210 °F, respectively) for comparison.

The specific heats of furfuryl alcohol-aniline mixtures containing mass fractions of 0.000, 0.2184, 0.4247, 0.6248, 0.8213, and 1.000 furfuryl alcohol in aniline were determined in a stainless-steel calorimeter [107]. The temperature ranges for these mixtures were approximately 322–447, 305–386, 300–378, 305–369, 305–369, and 305–339 K (120–345, 90–235, 80–220, 90–205, 90–205, and 90–150 °F), respectively. Both the aniline and the furfuryl alcohol used in these experiments were fractionally distilled for purification. About 0.1% piperidine was added to the furfuryl alcohol to retard decomposition.

The isobaric specific heats and viscosities of a mixture of aniline, furfuryl alcohol, and tetraethyl orthosilicate were determined at bubble-point pressure and various temperatures in the range from 305 to 378 K (90–220 °F) [108].

Densities and heat capacities of furfuryl alcohol/aniline mixtures were measured over the entire range of compositions and in the temperature range 283–363 K (10–90 °C) for density measurements and 313–393 K (40–120 °C) for heat capacity measurements, as listed in Tables 22 and 23 [109].

**Table 22:** Smoothed density values for furfuryl alcohol-aniline mixtures at the bubble point.

| Temperature, K<br>Temperature, °C      | 283<br>10                  | 293<br>20          | 303<br>30 | 313<br>40 | 323<br>50 | 333<br>60 | 343<br>70          | 353<br>80          | 363<br>90          |
|----------------------------------------|----------------------------|--------------------|-----------|-----------|-----------|-----------|--------------------|--------------------|--------------------|
| Weight fraction<br>of furfuryl alcohol | Density, g/cm <sup>3</sup> |                    |           |           |           |           |                    |                    |                    |
| 0                                      | 1.033                      | 1.023              | 1.014     | 1.006     | 0.996     | 0.9874    | 0.9785             | 0.9692             | 0.9602             |
| 0.1                                    | 1.043                      | 1.034              | 1.025     | 1.016     | 1.007     | 0.9976    | 0.9885             | 0.9794             | 0.9704             |
| 0.2                                    | 1.054                      | 1.045              | 1.036     | 1.027     | 1.017     | 1.007     | 0.9989             | 0.9898             | 0.9808             |
| 0.3                                    | 1.065                      | 1.056              | 1.046     | 1.038     | 1.028     | 1.019     | 1.009              | 1.000              | 0.9909             |
| 0.4                                    | 1.076                      | 1.066              | 1.057     | 1.048     | 1.038     | 1.029     | 1.020              | 1.010              | 1.001              |
| 0.5                                    | 1.086                      | 1.077              | 1.068     | 1.059     | 1.049     | 1.039     | 1.030              | 1.020              | 1.011              |
| 0.6                                    | 1.097                      | 1.088              | 1.078     | 1.069     | 1.060     | 1.050     | 1.040              | 1.031              | 1.021              |
| 0.7                                    | 1.108                      | 1.099              | 1.090     | 1.080     | 1.071     | 1.061     | 1.051              | 1.042              | 1.038              |
| 0.8                                    | 1.120                      | 1.110              | 1.101     | 1.091     | 1.052     | 1.072     | 1.062              | 1.053              | 1.044              |
| 0.9                                    | 1.131                      | 1.122              | 1.112     | 1.102     | 1.093     | 1.084     | 1.074              | 1.064              | 1.055              |
| 1                                      | 1.143 <sup>a</sup>         | 1.133 <sup>a</sup> | 1.124     | 1.114     | 1.105     | 1.095     | 1.086 <sup>a</sup> | 1.076 <sup>a</sup> | 1.067 <sup>a</sup> |

<sup>a</sup> Extrapolated values

Data source: [109]

**Table 23:** Smoothed values of the isobaric heat capacity of the furfuryl alcohol-aniline system at the bubble point.

| Temperature, K<br>Temperature, °C      | 313<br>40                                                    | 333<br>60 | 353<br>80          | 373<br>100         | 393<br>120         |
|----------------------------------------|--------------------------------------------------------------|-----------|--------------------|--------------------|--------------------|
| Weight fraction<br>of furfuryl alcohol | Isobaric heat capacity, cal g <sup>-1</sup> °C <sup>-1</sup> |           |                    |                    |                    |
| 0                                      | 0.503                                                        | 0.511     | 0.520              | 0.528              | 0.536              |
| 0.1                                    | 0.502                                                        | 0.511     | 0.520              | 0.529              | 0.537              |
| 0.2                                    | 0.501                                                        | 0.511     | 0.521              | 0.530              | 0.539              |
| 0.3                                    | 0.501                                                        | 0.512     | 0.522              | 0.531              | 0.541 <sup>a</sup> |
| 0.4                                    | 0.501                                                        | 0.512     | 0.523              | 0.533              | 0.544 <sup>a</sup> |
| 0.5                                    | 0.501                                                        | 0.512     | 0.524              | 0.536              | 0.547 <sup>a</sup> |
| 0.6                                    | 0.501                                                        | 0.513     | 0.526              | 0.538              | 0.551 <sup>a</sup> |
| 0.7                                    | 0.501                                                        | 0.514     | 0.528              | 0.542              | 0.555 <sup>a</sup> |
| 0.8                                    | 0.501                                                        | 0.516     | 0.531              | 0.547              | 0.561 <sup>a</sup> |
| 0.9                                    | 0.501                                                        | 0.517     | 0.535 <sup>a</sup> | 0.552 <sup>a</sup> | 0.568 <sup>a</sup> |
| 1                                      | 0.501                                                        | 0.519     | 0.538 <sup>a</sup> | 0.557 <sup>a</sup> | 0.576 <sup>a</sup> |

<sup>a</sup> Extrapolated values

Data source: [109]

The addition of 26 mass-% of hydrazine to furfuryl alcohol lowers the freezing point of the latter to 232.6 K (−40.5°C) [28]. The ignition properties of this mixture are slightly superior to those of furfuryl alcohol alone. Additions of as much as 5% water to this hydrazine-furfuryl alcohol solution depress the freezing point even further.

Another fuel mixture developed by JPL for a similar application had even better fuel properties. It consisted of 46 mass-% furfuryl alcohol, 47 mass-% aniline, and 7 mass-% hydrazine.

Furfuryl alcohol fuel blends were also used in other countries. Rocket engines developed at SEPR (later SEP) in France and used in the development of the two-stage solid-liquid anti-aircraft missile SE-4300 and the SEPR-48 engines used in TRI-DENT and MIRAGE rocket planes used a fuel mixture called Furaline, consisting of 41 mass-% furfuryl alcohol, 41 mass-% xylydine, and 18 mass-% methyl alcohol [110–112].

At one time, mixtures of furfuryl alcohol and triethylamine were used as hypergolic fuels. Such mixtures could be analyzed by gas chromatography [113].

Hypergolic fuels have been created by blending furfuryl alcohol (used as a solvent) with an ionic liquid, 1-ethyl-3-methyl imidazolium cyanoborohydride, in different volume proportions (80:20, 70:30, 60:40, 50:50, and 40:60) [114]. The blends exhibited good stability (chemical and thermal), low viscosity ( $\eta < 15$  mPa·s), high density ( $\rho > 1$  g/cm<sup>3</sup>), low ignition delay, and high performance in comparison to UDMH.

#### 4.5.1 Thermal Decomposition of Furfuryl Alcohol/Aniline Blends

The use of a mixture of 80% aniline and 20% furfuryl alcohol as fuel in regeneratively cooled rocket motors was hampered by the formation of gum-like deposits that gradually clogged the cooling passages. This gum formation was caused by rapid polymerization of the furfuryl alcohol while it was flowing through the cooling jacket. A program was initiated to find the threshold temperature for polymer formation so that a cooling system could be designed to operate below this temperature and thus eliminate the problem [115].

#### 4.5.2 Analytical Methods for Furfuryl Alcohol/Aniline Blends

Another fuel mixture developed by JPL for a similar application had even better fuel properties. It consisted of 46 mass-% furfuryl alcohol, 47 mass-% aniline, and 7 mass-% hydrazine. JPL also developed analytical methods for the analysis of such fuel mixtures [116, 117]. A simplified chemical method for testing the acceptability of rocket-fuel mixtures containing furfuryl alcohol, aniline, hydrazine, and water consisted of determining the amount of hydrazine and water present in the fuel, since these are the most critical constituents with regard to rocket-propulsion systems. Hydrazine was analyzed by the standard method employing chloramine-T. Water

was determined by measuring the hydrogen pressure that developed when the fuel reacted with calcium hydride.

The hydrazine contents of furfuryl alcohol/aniline/hydrazine mixtures can be determined by titrimetric methods [118]. One of the first storable hypergolic liquid fuels used in the United States was a mixture of aniline, hydrazine, and furfuryl alcohol. This mixture needed to be analyzed frequently to verify its storability [119]. The composition and purity requirements for this fuel were described in military specification *MIL-P-45700 – Propellant Mixture, Guided Missile, Aniline-Furfuryl Alcohol* (publication date: 10 March 1961), which is no longer available [99]. The requirements are listed in Table 24.

**Table 24:** Military specification *MIL-P-45700 – Propellant Mixture, Aniline-Furfuryl Alcohol*.

| Constituent      | Composition, mass-%                                         |
|------------------|-------------------------------------------------------------|
| Furfuryl alcohol | 46.3–46.7                                                   |
| Hydrazine        | 6.8–7.2                                                     |
| Water            | 1.5 max.                                                    |
| Other            | 0.7 max.                                                    |
| Aniline          | Balance, remainder to 100%                                  |
| Specific gravity | 1.070–1.085 g/cm <sup>3</sup> at 288.7 K (15.56 °C = 60 °F) |
| Melting point    | 230.35 K (–42.8 °C max.)                                    |

## 4.6 Handling of Furfuryl Alcohol

### 4.6.1 Suitability of Construction Materials for Use with Furfuryl Alcohol

Most common metals and non-metals, except rubber and neoprene, are suitable for use in equipment for handling FA. Furfuryl alcohol is a good solvent, so it will dissolve some lubricating agents. It is therefore recommended that fluorinated hydrocarbons or inorganic solid lubricants based on molybdenum sulfide or graphite should be used.

## 4.7 Safety Properties of Furfuryl Alcohol

### 4.7.1 Fire Hazard Properties of Furfuryl Alcohol

The handling of FA presents a low fire hazard because the vapor pressure of FA is low. The flammability hazard of furfuryl alcohol (Table 25) is minimal compared to that of ethyl alcohol. FA fires can be extinguished with water, in which it dissolves.



**Table 25:** Flammability properties of furfuryl alcohol.

| Property                 | Temperature                                                         |        | References |
|--------------------------|---------------------------------------------------------------------|--------|------------|
| Flash point (open cup)   | 348 K                                                               | 75 °C  |            |
| Autoignition temperature | 663 K                                                               | 390 °C | [72]       |
| Limits of flammability   | 1.8 vol.-% (at 345 K = 72 °C)<br>to 16.3 vol.-% (at 390 K = 117 °C) |        | [72]       |

#### 4.8 Toxicity of Furfuryl Alcohol

Protective clothing to be worn during the handling of FA must include goggles and gloves. FA is slowly resorbed through the skin, so splashes of FA on the skin or into the eyes must be rinsed immediately with water. Clothing or protective equipment soaked with FA must be removed immediately and washed thoroughly before reuse.

The OSHA threshold limit value TLV/TWA for 8 h/d, 5 d/week exposure is 50 ppm (200 mg/m<sup>3</sup>), but the NIOSH REL TWA is 10 ppm (40 mg/m<sup>3</sup>) with a skin notation. The NIOSH IDLH is 75 ppm.

Furfuryl alcohol vapor is a respiratory tract irritant. Extended inhalation of FA vapor causes symptoms similar to intoxication by other higher (C<sub>4</sub> to C<sub>5</sub>) alcohols [73]. The inhalation toxicity hazard of FA is relatively low due to the low vapor pressure of this compound.

Male and female rats and mice were exposed to >98% pure furfuryl alcohol by inhalation at concentrations of 0, 2, 8, or 32 ppm for 16 days, 14 weeks, or 2 years [120]. Exposure of male and female rats and male mice to furfuryl alcohol was associated with an increased incidence of non-neoplastic lesions of the nose and increased severity of nephropathy. Exposure of female mice to furfuryl alcohol was associated with increased incidences of non-neoplastic lesions of the nose and corneal degeneration.

In the very early years of liquid rocketry in the US, a mixture of furfuryl alcohol, aniline, and hydrazine was used as a hypergolic fuel in sounding rockets developed by JPL and Aerojet. The toxicity of the ternary propellant mixture was investigated in animal exposure tests [121]. Hydrazine was the most toxic constituent of this mixture.

### 5 Polyols

There are many polyfunctional alcohols, including bifunctional alcohols such as ethylene glycol and trifunctional alcohols such as glycerol. Strictly speaking, even sugar and cellulose should be listed under this heading. Polyols have not been used as fuels, but are the raw materials from which nitrate esters can be prepared by nitration with nitric acid/sulfuric acid mixtures. Properties of polyols are not included in this book because they are not useful as fuels.

## 6 Other Alcohols

Aromatic hydroxy compounds (phenols) are not discussed in the current section, which deals only with aliphatic and alicyclic hydroxy compounds.

## 7 Alcohols with Substituents in the Alkyl Group

There are many alcohols with substituents in the alkyl group, such as nitroalkanols, aminoalkanols, and azidoalkanols. In this book, these compounds are discussed in the sections relating to the groups that predominantly determine the character of these substituted alkanol compounds: nitroalkanols are considered when discussing nitro compounds, aminoalkanols when discussing amines, hydrazinoalkanols when discussing hydrazines, and azidoalkanols when discussing azides. The presence of the hydroxyl group does not substantially alter the reactivities of these substituted compounds. The hydroxyl group is the hydrophilic end of the molecule and facilitates the solubility of the molecule in water.

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# Aliphatic Amines

## Introduction

*Encyclopedia of Liquid Fuels* contains three chapters on amines, the current chapter on “Aliphatic Amines,” a chapter on “Aromatic Amines,” and a very large chapter on “Heterocyclic and Heterocycloaliphatic Amines.” Amines are used as rocket fuels and as raw materials for the synthesis of other fuels and energetic compounds. A different type of amine are the nitramines described in the chapter “Nitramines.”

## 1 Aliphatic Amines

Amines are organic fuels in which one or more hydrogen atoms of ammonia are substituted by organic groups, either alkyl or aryl or heterocyclic ring groups, shown as R in the scheme below. Depending on the number of hydrogen atoms replaced by alkyl or aryl groups, we differentiate three different types of amines: primary amines, secondary amines, and tertiary amines, where one, two, or three hydrogen atoms are replaced:

|               |                |                       |                      |
|---------------|----------------|-----------------------|----------------------|
| $\text{NH}_3$ | $\text{RNH}_2$ | $\text{R}_2\text{NH}$ | $\text{R}_3\text{N}$ |
| Ammonia       | primary amine  | secondary amine       | tertiary amine       |

In addition to primary, secondary, and tertiary amines, there are multifunctional amines that contain more than one primary, secondary, or tertiary amino group in the molecule. Most of these fuels have the advantage that they are hypergolic with nitric acid and have higher boiling points than liquid ammonia, such that they can be stored as liquids at room temperature and atmospheric pressure. They are easily accessible in industrial quantities, and they are intermediates in the synthesis of many other organic compounds. Aliphatic amines, also called alkylamines, have gained renewed attention as potential replacements for more toxic hypergolic bipropellant fuels such as monomethylhydrazine (MMH) or unsymmetrical dimethylhydrazine (UDMH), which are under close scrutiny for their toxicity. Alkylamines were tested as hypergolic fuels even before MMH and UDMH came into widespread use as rocket propellants. Alkylamines are much easier to obtain than alkylhydrazines, from which they differ by one more  $\text{—NH—}$  group. Alkylamines are the raw materials from which alkylhydrazines are made. Some amines have gross formulas that are identical or similar to alkylhydrazines, but their enthalpy of formation and performance as a rocket propellant would be less than that of the hydrazine derivatives. The advantage of the alkylamines would be that they are easier to produce and less toxic. In the wake of the growing concern about hydrazine toxicity, many of the alkylamine

fuels have been reevaluated as potential alkyldiazine replacements. We list here some alkylamines that have already been used as rocket propellants, and we are also including physical properties of other alkylamines that have not yet been used as rocket fuel but which might be used as building blocks in the synthesis of other nitrogen-containing rocket fuels.

Amines are colorless liquids at room temperature, with the exception of the three methylamines, which are gases and boil below room temperature. The lower alkylamines are readily miscible with water, but those with longer alkyl groups are only sparingly soluble in water. Higher amines with long alkyl chains are wax-like solids.

Amines, in particular aliphatic amines, are easily recognized by their characteristic fishy odor, which can even be noticed in small quantities. Amines are bases, and as such they form salts with acids. Of the many possible salts, the amine nitrates and perchlorates are those with the most interest as solid propellant or explosive ingredients, and there are several sections in this chapter that describe the properties of these energetic compounds. The salts of alkylamines are normally called alkylammonium salts rather than alkylamine salts. Despite this nomenclature rule, one will often find names like “ethylamine nitrate” instead of “ethylammonium nitrate.”

The properties of alkylammonium nitrates and perchlorates are discussed at the end of each parent amine chapter. Tertiary amines form not only simple salts with acids but may also form quaternary salts if alkylated with alkyl iodides. Quaternary alkylammonium nitrates have been tested as fuels in monopropellants. They are no longer hypergolic with nitric acid or dinitrogen tetroxide, but they are soluble in nitric acid.

Multiple substitution at the ends of the alkane chain in alkylamine molecules by amino groups, hydroxyl groups, hydrazido groups, cyano groups, or azido groups will improve the water solubility; lower the freezing point; and, in the case of hydrazido, cyano, and azido groups, improve the performance as a rocket fuel. This method of producing more energetic fuels, some considered as hydrazine(s) replacements, is mostly limited to short  $C_2$  and  $C_3$  alkane chains.

Nitro groups replacing the hydrogen on the nitrogen atom in secondary aliphatic and cycloaliphatic amines, in particular secondary amines in ring structures, result in nitramines, a group of powerful explosives and solid propellant ingredients. These are described in chapter “Nitramines” of Volume 5 of this set and they are used as energetic additives in solid propellants. Replacing two hydrogens in ammonia with nitro groups leads to dinitramide,  $(NO_2)_2NH$ , which is an acid called dinitramidic (dinitraminic) acid. It is rarely used as such, but it forms salts with ammonia, hydroxylamine, hydrazine, amines, and other nitrogen bases and metals that have found use as rocket propellant ingredients. These solid salts are thermally more stable and are safer to handle than the parent acid. Dinitramide salts are described in *Encyclopedia of Oxidizers*, chapter “Dinitramide Salts.” This is a relatively recent development that has generated a lot of new information over the past 20 years.

If only one nitrogen-bound hydrogen atom is replaced by a nitro group in an alkylamine, one obtains alkylnitramines (alkylnitroamines), and the remaining hydrogen  $\text{N-H}$  is quite acidic and forms stable salts with alkali and alkaline earth metals (see chapter “Nitramines”).

Amines are stable in air and are not easily auto-oxidized, at least not as easily auto-oxidized as the alkylhydrazines. If they are exposed to air, the main concern would be the absorption of carbon dioxide from the atmosphere. Some low-volatility amines are used in the chemical industry to wash carbon dioxide and other “sour gases” from process gas streams and from natural gas. The handling of amines is relatively simple compared to handling of alkylhydrazines. Alkylamines are not very corrosive, and they can be stored and transported in most common materials of construction.

Amines are not very toxic, and many amines are naturally occurring. They will irritate the skin if accidentally spilled on skin or clothing. The vapors irritate the mucous membranes, particularly those in the eyes. In most cases, the presence of amine vapors in the air of working areas is readily recognized by the fishy odor, and the work crew is thus alerted to avoid the area and take corrective action before dangerous concentrations are attained. All amines and their vapors are combustible and form explosive mixtures with air.

Many industrial processes for alkylamine production yield a mixture of amines with different degrees of alkyl substitution. Such mixtures need to be separated by fractionated distillation in a column. If the separation by distillation is not perfect, industrial-grade amines can be contaminated by other amines. For their use as rocket fuels, the presence of minor amounts of other amines can be tolerated. Sometimes several amines are mixed deliberately to obtain low-freezing rocket-fuel mixtures.

While the free liquid amines are used as hypergolic fuels in bipropellant combinations, the solid alkylammonium nitrate salts can be used as additives in solid propellants, or (dissolved in water) as fuels in water-based monopropellants, or (as quaternary ammonium salts) dissolved in nitric acid. The most important alkylammonium salts are the nitrates. For the organization of information in this book, it was considered to combine the properties of alkylammonium salts in one separate chapter or to move them together in *Encyclopedia of Monopropellants*, under monopropellants; however, the plan was changed, and the alkylammonium and arylammonium salts are now discussed in this chapter, immediately following their parent amine free base. The same order applies to salts of amides (urea) and imides (guanidine). Nevertheless, we assemble here several summary tables with properties of alkylammonium salts. The nitrate salts are discussed first, followed by the perchlorate salts.

The energy contained in amines can be increased by including one or more  $-\text{NH}-$  groups in place of  $-\text{CH}_2-$  groups in stressed-ring cycloalkanes, thus forming azirines (three-membered rings derived from ethyleneimine) or azetanes (four-membered rings). Nitrogen can take the place of a  $-\text{CH}-$  group in bridged and caged structures.

There is a large group of heterocyclic amines that are of interest as high-nitrogen compounds for rocket propellants and gas generants either in their unprotonated state or, more frequently, in the form of their nitrate and perchlorate salts. These compounds are listed in chapter “Heterocyclic Amines” of *Encyclopedia of Liquid Fuels*.

Amides and imides are derived from ammonia by replacing one or two hydrogens with alkylcarbonyl RCO groups. The simplest amide is formamide  $\text{H}_2\text{NCHO}$ , and its close relative is urea  $(\text{H}_2\text{N})_2\text{CO}$ . Fuel values increase if the  $\text{C=O}$  group is replaced by an imine  $\text{C=NH}$  group, leading to guanidine  $(\text{H}_2\text{N})_2\text{C=NH}$ . Fuel values increase further if the amino and imino groups are replaced with hydrazino groups, as in triaminoguanidine. All of these amide and imide compounds are discussed in *Encyclopedia of Liquid Fuels*, in chapter “Amides and Imides.”

## 1.1 Nomenclature for Amines

The International Union of Pure and Applied Chemistry (IUPAC) recommendation is to name amines ( $\text{R-NH}_2$ ) for the attached alkane chain with the suffix “-amine” (e.g.,  $\text{CH}_3\text{NH}_2$  would be methanamine written in one word), but the customary naming after the alkyl group (methanamine, ethylamine) is still widely in use. If necessary, the bonding position on longer chains is inserted as a number:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  butan-1-amine,  $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_3$  propan-2-amine. For secondary amines (of the form  $\text{R-NH-R}$ ), the longest carbon chain attached to the nitrogen atom becomes the primary name of the amine; the other chain is prefixed as an alkyl group with location prefix given as an *italic N*:  $\text{CH}_3\text{NHCH}_2\text{CH}_3$  is *N*-methylethanamine. Tertiary amines ( $\text{R-NR-R}$ ) are treated similarly:  $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$  is *N*-ethyl-*N*-methylpropanamine, with the substituent groups in alphabetical order.

Alkylamines are sometimes called azaalkanes, in which the name given to a three-membered chain of nitrogen and carbon atoms is propane, the name for a four-membered chain of nitrogen and carbon atoms is butane, and so on. The name is always derived from the longest chain of atoms in the molecule. In this nomenclature, ethylamine would be 1-azapropane, and diethylamine would be 3-azapentane. IUPAC nomenclature calls dimethylamine “*N*-methylmethanamine.”

## 1.2 Summary Literature on Amines and Amides

Chapters on amines and amides are in most books on organic chemistry. Chapters on amines and amides are in the more popular encyclopedias, such as the *Kirk-Othmer Encyclopedia of Chemical Technology* [1–3] and Ullmann’s *Encyclopedia of Industrial Chemistry* [4, 5]. Data on amines and amides are in standard reference sources such as Houben–Weyl [6] and Beilstein [7]. There are also books written specifically for properties and applications of amines [8]. For this reason, the summary of data here can be

only partially complete in comparison to the reference works that fill an entire book shelf in the library.

Lower aliphatic amines are derivatives of ammonia with one, two, or all three of the hydrogen atoms replaced by alkyl groups of five carbons or fewer. Amines are toxic, colorless gases or liquids, are highly flammable or combustible, and have strong fishy odors. Alkylamines of lower molecular mass are water soluble and are available as aqueous solutions or in pure form. Amines react with water and acids to form alkylammonium compounds, analogous to ammonia forming ammonium salts with strong acids. The lower aliphatic amines are widely used as intermediates in the manufacturing of pharmaceutical, agricultural, textile, rubber, and plastic chemicals. Because they are readily available in industrial quantities, it is easy to divert them for use as rocket propellant ingredients.

### 1.3 Physical Properties of Amines

The following section and Table 1 contain summaries and comparative tabulations of some of the physical properties of groups of amines. The data may be repeated later in sections devoted specifically to individual amines. This is a duplication, but it is very educational to see the properties listed here first in one view to identify trends of physical properties with changes in the chemical structure of the molecule.

An excellent 69-page summary of physical properties of lower alkylamines was published as part of the National Bureau of Standards National Standard Reference Data Series [9]. This summary contains data on thermodynamic and thermophysical properties of eight primary amines, including methanamine, ethanamine, 1-propanamine, and 2-propanamine, and recommended values are given for the following properties: normal boiling point, freezing point, and triple-point temperatures; critical constants; thermodynamic properties in the solid and liquid phases;

**Table 1:** Freezing point, normal boiling point, and critical point properties of primary amines.

| Compound      | Freezing point, K              | Boiling point, K   | Critical point temperature, K | Critical point pressure, MPa | Critical point volume, cm <sup>3</sup> /mol |
|---------------|--------------------------------|--------------------|-------------------------------|------------------------------|---------------------------------------------|
| Methanamine   | 179.708<br>± 0.01 <sup>a</sup> | 266.80<br>± 0.02   | 430.7 ± 0.2                   | 7.614 ± 0.015                | 120 ± 6                                     |
| Ethanamine    | 192.62<br>± 0.05               | 289.74<br>± 0.06   | 456.2 ± 1.0                   | 5.63 ± 0.11                  | 181 ± 5                                     |
| 1-propanamine | 188.389<br>± 0.01 <sup>a</sup> | 320.370<br>± 0.002 | 497 ± 1                       | 4.72 ± 0.08                  | 228 ± 11                                    |
| 2-propanamine | 178.011<br>± 0.01 <sup>a</sup> | 304.905<br>± 0.002 | 471.9 ± 0.5                   | 4.54 ± 0.06                  | 221 ± 11                                    |

<sup>a</sup> Triple-point temperature

Data source: [9]



vapor pressure; enthalpy of vaporization; density; second virial coefficients; and enthalpy of combustion. Ideal gas thermodynamic properties were calculated using statistical mechanical methods. The boiling points were taken from a least-squares fit of the Cox equation.

### 1.3.1 Enthalpy of Formation of Amines

The heats (enthalpies) of formation are needed to calculate rocket performance when these chemicals are used as fuels with red fuming nitric acid (RFNA) or dinitrogen tetroxide (NTO) as the hypergolic oxidizer. The enthalpies of formation of aliphatic amines (e.g., azetane) in the vapor state can be calculated using *ab initio* 6-31G\* energies in place of measured data or to supplement experimental data. The results were in good agreement with those obtained experimentally and suggest that this method can be used to predict heats of formation of molecules of this class with an accuracy competitive with good-quality experiments and with probable errors of less than 1 kcal/mol [10].

Table 2 is a summary of experimentally obtained enthalpies of formation of primary amines in the liquid and vapor states.

**Table 2:** Thermodynamic data of primary amines.

| Property      | Enthalpy of formation, kJ/mol |                   |                    |
|---------------|-------------------------------|-------------------|--------------------|
| Compound      | Ideal gas                     |                   | Liquid             |
| Temperature   | 0 K                           | 298.15 K          | 298.15 K           |
| Methanamine   | $-7.82 \pm 0.41$              | $-22.53 \pm 0.41$ | $-47.27 \pm 0.40$  |
| Ethanamine    | $-26.65 \pm 0.51$             | $-47.47 \pm 0.51$ | $-74.13 \pm 0.50$  |
| 1-propanamine | $-42.36 \pm 0.39$             | $-70.10 \pm 0.39$ | $-101.47 \pm 0.38$ |
| 2-propanamine | $-56.90 \pm 0.68$             | $-83.70 \pm 0.68$ | $-112.27 \pm 0.67$ |

Data source: [9]

The enthalpies of formation of 66 nitrogen compounds in the vapor state, including many amines, were calculated by seven different molecular orbital methods and were compared to experimental results [11]. The deviations rarely exceeded 1 kcal/mol. Although it would be more practical to have the data for the liquid compounds potentially used as rocket fuels, the measured results for the vapors are listed in Table 3. The heats of vaporization of these compounds are all very similar.

**Table 3:** Enthalpy of formation of aliphatic amines.

| Compound               | Enthalpy of formation, vapor state |          |
|------------------------|------------------------------------|----------|
|                        | kJ/mol                             | kcal/mol |
| Methanamine            | −23.0                              | −5.5     |
| Dimethylamine          | −18.4                              | −4.4     |
| Trimethylamine         | −23.7                              | −5.66    |
| Ethanamine             | −47.3                              | −11.3    |
| Propan-1-amine         | −69.9                              | −16.71   |
| Propan-2-amine         | −83.7                              | −20      |
| Butan-1-amine          | −95.0                              | −22.71   |
| 2-methylpropan-2-amine | −120.0                             | −28.68   |
| 2-methylpropan-1-amine | −98.6                              | −23.57   |
| Butan-2-amine          | −106.0                             | −25.33   |

Data source: [11]

### 1.3.2 Physical Properties of Amine Salts

Salts of amines can be named using the unchanged name of the parent amine followed by the name of the anion, or the name of the amine can be changed to form a name with the suffix *ammonium* in it to indicate that they have accepted a proton and have become positively charged. This is patterned after the well-characterized ammonium  $\text{NH}_4^+$  salts. *Chemical Abstracts Service* uses a different nomenclature for salts of amines in its index.

The following section is a summary of properties of amine salts as a group. There are several sections on specific amine salts immediately following the section of their parent amine. As for the anions in these salts of interest as rocket propellants, the main interest is in nitrates, perchlorates, dinitramides, and nitroformates of these amines, mostly alkylamines. There is little information on salts of aromatic amines. The salts of heterocyclic amines have moved to a special category because many of these salts exhibit properties of ionic liquids, which are compounds of high molecular mass that are liquids at room temperature with very low vapor pressures (see *Encyclopedia of Liquid Fuels*, chapter “Ionic Liquids”).

As mentioned, *Chemical Abstracts Service* used to index alkylammonium salts under the name of the acid salt, such as “Nitric acid, methylamine salt.” When looking in the substance index, one would have to look up the name of the acid first. If one has the Chemical Abstracts Service (CAS) registry number, the CAS SciFinder search can be more specific and will usually yield the desired results. We have included the CAS registry numbers when they were available, and this will help our readers obtain additional information if needed.

### 1.3.2.1 Physical Properties of Amine Nitrates

Nitrate salts of organic amines can find various applications in rocket propellants. They are rarely used as solid propellants by themselves; most of the time they are used as additives to solid propellants or as water-soluble fuels in combination with aqueous oxidizers such as hydroxylammonium nitrate (HAN; see *Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-based Monopropellants”) or ammonium dinitramide (ADN; see *Encyclopedia of Monopropellants*, chapter “Ammonium Dinitramide-Based Monopropellants”). Close to 100 different amine nitrates have been evaluated as candidate fuels for HAN for liquid gun propellants, torpedo propellants, and rocket propellants. The current chapter benefits from summaries of the properties of amine nitrates compiled by the author and other authors on various occasions when water-soluble fuels were sought as ingredients in monopropellants. Other monopropellants have been formulated by dissolving nitrates and quaternary nitrates of amines in concentrated nitric acid (see *Encyclopedia of Monopropellants*, chapter “Nitric Acid or Perchloric Acid-Based Monopropellants”). All these applications require knowledge of the physical and chemical properties of amine nitrates, in particular their water solubility, which is why we added a chapter on these compounds in this book at this location. Methods for preparation of the pure amine nitrates as precursors to rocket propellant combinations are described here. All amine nitrates (and perchlorates) in their dry state are potentially explosive, which is why their preparation and handling must be done with extreme care and with all necessary precautions. Thermal stability of amine nitrates is an important property that must be known before incorporating them in any rocket propellant. All amine nitrates are quite soluble in water, as opposed to their perchlorate counterparts, which are sometimes used to purify amines and to precipitate them as a less soluble compound. Both amine nitrates and amine perchlorates make good propellant ingredients, with the nitrates preferred if formation of hydrogen chloride in the exhaust cannot be tolerated for toxicity or environmental reasons. The nitrates are also less sensitive than the perchlorates to accidental ignition by shock or friction.

This section on amine nitrates is closely related to the section on high-nitrogen compounds. Many high-nitrogen compounds are either nitrates (listed here) or are compounds (5-aminotetrazol, aminoguanidine) that are easily converted into nitrate and perchlorate salts. Heterocyclic amines with high nitrogen content and their nitrate salts are discussed in the chapter “Heterocyclic Amines.”

The amine nitrates are discussed here in the sequence of increasing number of carbon atoms. If some of them contain the same number of carbon atoms, they are listed in the order of increasing nitrogen atoms.

To use the correct nomenclature, amine nitrates should be called alkyl- or arylammonium nitrates. Alkylammonium nitrates have also been called **aliphatic amine nitrates** and are abbreviated as AANs. If an amine contains more than one nitrogen atom that can be protonated, the number of protons added are listed in parentheses

after the name: ethylenediammonium(2+) dinitrate. *Chemical Abstracts Service* used to index them under the name of the acid salt, such as “Nitric acid, methylamine salt.” When looking in the substance index, one would have to look up the name of the acid first. If one has the CAS registry number, the CAS SciFinder search can be more specific and will usually yield the desired results. We have carried along the CAS registry numbers when they were available.

We have assembled several physical property overview tables that allow the propellant formulator to select an amine nitrate for a certain application based on its melting point, nitrogen content, or enthalpy of formation. Similar tables were assembled for amine perchlorates.

Solid amine nitrates are not typically used as rocket propellants by themselves (but they can be used as explosives without any other additives). For rocket propellant applications, they are most often dissolved in solvents, typically oxidizing solvents such as nitric acid or HAN/water or ADN/water. This chapter lists properties of dry (crystalline) organic amine (alkylammonium) nitrates only because these properties may be needed in the production and quality control of amine nitrates as propellant ingredients. The thermal decomposition and combustion of the amine nitrates by themselves (without an additional oxidizer) have been studied in an effort to explain the combustion behavior of propellants containing these chemicals. The compounds are listed in the order of increasing carbon atom content. Some alkylammonium nitrates (methylanmonium nitrate, ethylenediamine dinitrate) are used as explosive ingredients.

An important property of any alkylammonium nitrate, regardless of what application it is intended for (propellant or explosive), is its thermal stability in the solid state or in solution. Numerous studies have been conducted to derive a correlation between the chemical structure of AANs and their thermal stability. For instance, structure/decomposition relationships were developed for 26 alkylammonium nitrate salts [12]. Thermolysis studies were conducted by using rapid-scan Fourier-transform infrared spectroscopy (FTIR)/thermal profiling with heating rates of 40–250 °C/s and pressures of 6.88 kPa–6.88 MPa (1–1000 psia) of static argon. The types of products, their sequence of evolution, and the decomposition temperatures were used to develop qualitative relationships between the parent molecular structure and the thermal stability. The release of  $\text{HNO}_3$  correlates with the basicity of the parent amine [13]. A relationship between amine basicity and initial decomposition products showed a transition from acid–base chemistry at low basicity to redox chemistry at high basicity. Amines, amides, alkyl nitrates, and nitrosamines were formed as intermediates. The release of nitrosamines during use as a propellant makes these compounds a potential health risk. Similar decomposition pathways were found for all structurally related alkylammonium nitrate salts regardless of the complexity of the parent amine. However, a cycloelimination reaction was observed with the longer-chain alkyldiammonium dinitrate salts.

Tables 4 and 5 are summaries of physical and thermochemical properties of alkylammonium nitrates and similar compounds. Most of the data are for the solid salts. Because some of the nitrates, e.g., ethylammonium nitrate, melt below room temperature and are difficult to crystallize, some of the properties are given for the molten salt at 298 K. Some of the low-melting amine nitrates have found use as ionic liquids. One has to be careful to observe the physical state (solid or liquid) of the compound for which the thermodynamic data are given.

**Table 4:** Properties of open-chain alkylammonium nitrates.

| Compound                      | Heat of combustion, constant volume, liquid water, average | Heat of combustion, constant pressure | Enthalpy of formation |          | Melting point |                |
|-------------------------------|------------------------------------------------------------|---------------------------------------|-----------------------|----------|---------------|----------------|
|                               | cal/g                                                      | kcal/mol                              | kJ/mol                | kcal/mol | K             | °C             |
| Methylammonium nitrate (S)    | 2328                                                       | 218.4                                 | −337                  | −80.6    | 383.6–384.6   | 110.5–111.5    |
| Trimethylammonium nitrate (S) | 4509                                                       | 550.7                                 | −306                  | −73.1    | 428–429       | 155–156        |
| Ethylammonium nitrate (L)     | 3467                                                       | 374.5                                 | −364                  | −86.9    | 287           | 14             |
| Dimethylammonium nitrate (S)  | 3540                                                       | 382.4                                 | −331                  | −79      | 348.6–349.6   | 75.5–76.5      |
| Diethylammonium nitrate (S)   | 5047                                                       | 687.4                                 | −413                  | −98.7    | 377–378       | 104–105        |
| Triethylammonium nitrate (S)  | 6168                                                       | 1013.6                                | −407                  | −97.3    | 386–387       | 113–114        |
| Ethanolammonium nitrate (S)   | 2614                                                       | 323.8                                 | −576                  | −137.6   | 325–326       | 52–53          |
| Glycine nitrate (S)           | 1598                                                       | 219.5                                 | −726                  | −173.6   | 418–420       | 145–147 (dec.) |
| Anilinium nitrate (S)         | 5094                                                       | 795.1                                 | −178                  | −42.5    | 455–457       | 182–184 (dec.) |
| Benzylammonium nitrate (S)    | 5540                                                       | 942.7                                 | −239                  | −57.2    | 410.6–411.6   | 137.5–138.5    |

S = solid, L = liquid

Data source: [14]

Table 5: Properties of open-chain alkylammonium nitrates.

| Compound                                                          | Gross formula | CAS RN <sup>a</sup> | Enthalpy of formation |          | Melting point |     | Density           | References   |
|-------------------------------------------------------------------|---------------|---------------------|-----------------------|----------|---------------|-----|-------------------|--------------|
|                                                                   |               |                     | kJ/mol                | kcal/mol | K             | °C  | g/cm <sup>3</sup> |              |
| Mononitrates                                                      |               |                     |                       |          |               |     |                   |              |
| Methylammonium nitrate                                            | C1H6N2O3      | 22113-87-7          | -352.7                | -84.3    | 384           | 111 | 1.422             | [15], p. 225 |
| Trimethylammonium nitrate                                         | C3H10N2O3     | 25238-43-1          | -305.7 <sup>b</sup>   | -73      | —             | —   | —                 | [15], p. 380 |
|                                                                   |               |                     | -343.8 <sup>b</sup>   | -82.2    | —             | —   | —                 | [15], p. 345 |
| Tetramethylammonium nitrate                                       | C4H12N2O3     | 1941-24-8           | -331.8                | -79.3    | —             | —   | —                 | [16]         |
|                                                                   |               |                     | ± 0.1                 |          |               |     |                   |              |
| Ethylammonium nitrate                                             | C2H8N2O3      | 22113-86-6          | -363                  | -86.9    | 287           | 14  | 1.21              |              |
|                                                                   | C2H8N2O4      | 20748-72-5          | -576                  | -137.6   | 323           | 50  | 1.33              |              |
| Ethanolamine dinitrate (nitrate salt of 1-nitrato-2-amino-ethane) | C2H7N3O6      | —                   | -909                  | -217.3   | 376           | 103 | 1.53              | [15], p. 126 |
|                                                                   |               |                     |                       |          |               |     |                   |              |
| Triethylammonium nitrate                                          | C6H16N2O3     | 27096-31-7          | -407                  | -97.3    | 387           | 114 |                   | [17]         |
| Tetraethylammonium nitrate                                        | C8H20N2O3     | 1941-26-0           | -428.5 ± 4            | —        | —             | —   | —                 | [16]         |
| Isopropylammonium nitrate                                         | C3H10N2O3     | 87478-71-5          | -415.5                | -99.3    | 346           | 73  | —                 | [18]         |
| Diisopropylammonium nitrate                                       | C6H16N2O3     | —                   | —                     | —        | 461           | 188 | —                 | [18]         |
| <i>tert</i> -butylammonium nitrate                                | C4H12N2O3     | —                   | —                     | —        | 412           | 139 | —                 | [18]         |
| Triethanolammonium nitrate                                        | C6H16N2O6     | 27096-29-3          | -966.5                | -231.0   | 364           | 91  | 1.3384            | [19]         |
|                                                                   |               |                     | -776                  | -185.5   | —             | —   | at 20 °C          | [20]         |
| Cubane ammonium nitrate                                           | C8H10N2O3     | —                   | +272.0                | +65      | —             | —   | —                 |              |

Table 5: (continued)

| Compound                                                  | Gross formula                                                | CAS RN <sup>a</sup> | Enthalpy of formation |          | Melting point |            | Density           | References   |
|-----------------------------------------------------------|--------------------------------------------------------------|---------------------|-----------------------|----------|---------------|------------|-------------------|--------------|
|                                                           |                                                              |                     | kJ/mol                | kcal/mol | K             | °C         | g/cm <sup>3</sup> |              |
| <b>Dinitrates</b>                                         |                                                              |                     |                       |          |               |            |                   |              |
| Ethylenediamine dinitrate                                 | C <sub>2</sub> H <sub>10</sub> N <sub>4</sub> O <sub>6</sub> | 20829-66-7          | -651.7                | -155.7   | 461           | 188        | 1.577             | [15], p. 127 |
|                                                           |                                                              |                     |                       |          | 461           | 188.1      | 1.603             | [21]         |
|                                                           |                                                              |                     | -652                  | -155.8   | —             | —          | —                 | [17]         |
| 1,3-propane diammonium dinitrate                          | C <sub>3</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 399           | 126        | 1.595             | [21]         |
| <i>N</i> -methylethylenediammonium dinitrate              | C <sub>3</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 351           | 78         | —                 | [22]         |
| 1,4-butane diammonium dinitrate                           | C <sub>4</sub> H <sub>14</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 413.2         | 140.1      | 1.463             | [21]         |
|                                                           |                                                              |                     | —                     | —        | 412           | 139        | —                 | [22]         |
| <i>N</i> -ethylethylenediammonium dinitrate               | C <sub>4</sub> H <sub>14</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 359           | 86         | —                 | [22]         |
| <i>N,N'</i> -dimethylethylenediammonium dinitrate         | C <sub>4</sub> H <sub>14</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 403           | 130        | —                 | [22]         |
| (sym)                                                     |                                                              |                     |                       |          |               |            |                   |              |
| <i>N,N</i> -dimethylethylenediammonium dinitrate          | C <sub>4</sub> H <sub>14</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 325           | 52         | —                 | [22]         |
| (unsym)                                                   |                                                              |                     |                       |          |               |            |                   |              |
| <i>N</i> -isopropylethylenediammonium dinitrate           | C <sub>5</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 367           | 94         | —                 | [22]         |
| <i>N,N,N'</i> -trimethylethylenediammonium dinitrate      | C <sub>5</sub> H <sub>16</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 366           | 93         | —                 | [22]         |
| <i>N,N,N',N'</i> -tetramethylethylenediammonium dinitrate | C <sub>6</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 501           | 228        | —                 | [22]         |
| Piperazinium(2+) dinitrate                                | C <sub>4</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 497           | 224 (dec.) | 1.577             | [21]         |
| 1,6-hexane diammonium dinitrate                           | C <sub>6</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub> | —                   | —                     | —        | 382           | 109        | —                 | [22]         |

Table 5: (continued)

| Compound                                                                                                                                                  | Gross formula | CAS RN <sup>a</sup> | Enthalpy of formation |          | Melting point |               | Density           | References   |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|---------------------|-----------------------|----------|---------------|---------------|-------------------|--------------|
|                                                                                                                                                           |               |                     | kJ/mol                | kcal/mol | K             | °C            | g/cm <sup>3</sup> |              |
| Polynitrates                                                                                                                                              |               |                     |                       |          |               |               |                   |              |
| Diethylenetriammonium trinitrate                                                                                                                          | C4H16N6O9     | —                   | —                     | —        | 423           | 150           | —                 | [22]         |
| Trisaminoethylammonium trinitrate                                                                                                                         | C6H21N8O9     | —                   | —                     | —        | 575           | 302           | 1.50              |              |
| [(H <sub>3</sub> N <sup>+</sup> CH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N][NO <sub>3</sub> <sup>-</sup> ] <sub>3</sub> , TRN3                      |               |                     |                       |          |               |               |                   |              |
| Triethylene tetrammonium tetranitrate                                                                                                                     | C6H22N8O12    | —                   | —                     | —        | 502           | 229           | —                 | [22]         |
| Pentaerythryl tetrammonium tetranitrate,<br>[C(CH <sub>2</sub> N <sup>+</sup> H <sub>3</sub> ) <sub>4</sub> ](NO <sub>3</sub> <sup>-</sup> ) <sub>4</sub> | C5H20N8O12    | —                   | —                     | —        | 490           | 217           | 1.70<br>(calc.)   | [23]         |
| Other amine nitrates                                                                                                                                      |               |                     |                       |          |               |               |                   |              |
| Glycine nitrate                                                                                                                                           | C2H6N2O5      | —                   | −726.3                | −173.6   | —             | —             | —                 | [17], p. 644 |
| Urea nitrate                                                                                                                                              | C1H5N3O4      | 124-47-0            | −561.5                | −134.2   | 413<br>(dec.) | 140<br>(dec.) | 1.59              | [15], p. 396 |
|                                                                                                                                                           |               |                     |                       |          | 430           | 157<br>(dec.) | 1.69              | [24]         |
| Guanidinium nitrate                                                                                                                                       | C1H6N4O3      | 506-93-4            | −389.1                | −93.0    | 488           | 215           | —                 | [15], p. 163 |
| Diethylhydroxylammonium nitrate                                                                                                                           | C4H12N2O4     | —                   | −424.7                | −101.5   | —             | —             | —                 |              |

<sup>a</sup> CAS RN = Chemical Abstracts Service Registry Number<sup>b</sup> Note: The two numbers for trimethylammonium nitrate are quite different!



Table 6 is a similar summary for heterocyclic alkylammonium nitrates. Data for salts derived from other heterocyclic amines are presented in chapter “Heterocyclic and Heterocycloaliphatic Amines.”

**Table 6:** Properties of heterocyclic alkylammonium nitrates.

| Compound                   | Gross formula                                                | Enthalpy of formation |                 | Melting point   |                 | Density<br>g/cm <sup>3</sup> | References |
|----------------------------|--------------------------------------------------------------|-----------------------|-----------------|-----------------|-----------------|------------------------------|------------|
|                            |                                                              | kJ/mol                | kcal/mol        | K               | °C              |                              |            |
| 5-Aminotetrazolium nitrate | C <sub>1</sub> H <sub>4</sub> N <sub>6</sub> O <sub>3</sub>  | +80.5                 | +19.25 kcal/mol | 429.9<br>(dec.) | 156.8<br>(dec.) | 1.847                        | [25]       |
| Piperazinium dinitrate     | C <sub>4</sub> H <sub>12</sub> N <sub>4</sub> O <sub>6</sub> | —                     | —               | 497             | 224<br>(dec.)   | 1.577<br>± 0.016             | [21]       |

The most important property of alkylammonium nitrates is their enthalpy of formation. Literature data on enthalpies of formation of alkylammonium nitrates are listed in Table 7 for comparison to the enthalpies of formation of the parent amine. In a few instances, the enthalpy of formation of the nitrate salt may not be available, but the enthalpy of formation of the free amine is. In those cases, one can extrapolate from the enthalpy of formation of the free amine to that of its nitrate because the difference – the heat of protonation and the increment for the nitrate ion – is fairly constant. Some of these nitrate salts are ionic liquids.

**Table 7:** Comparison of enthalpies of formation of alkylammonium nitrates and their parent amines.

| Alkylamine          | Enthalpy of formation, kJ/mol | Alkylammonium nitrate         | Enthalpy of formation, kJ/mol |
|---------------------|-------------------------------|-------------------------------|-------------------------------|
| Methylamine (L)     | −47.27 ± 0.4                  | Methylammonium nitrate (S)    | −352.7                        |
| Ethylamine (L)      | −88.7                         | Ethylammonium nitrate (L)     | −363                          |
| Trimethylamine (L)  | −45.73 ± 0.71                 | Trimethylammonium nitrate (S) | −305.7                        |
| Isopropylamine (L)  | −103.8                        | Isopropylammonium nitrate (S) | −415.5                        |
| Ethylenediamine (L) | −63.01 ± 0.54                 | Ethylenediamine dinitrate (S) | −651.7                        |

Table 8 is a summary of molecular mass, nitrogen content, and oxygen balance of alkylammonium nitrates.

A very useful summary of the thermal decomposition and melting behavior of alkyl- and arylammonium nitrates and perchlorates is given in [22], including many references to the literature.

**Table 8:** Molecular mass, nitrogen content, and oxygen balance of alkylammonium nitrates in comparison to guanidinium nitrates.

| Compound name                         | CAS RN     | Gross formula                                                | Molecular mass, g/mol | Oxygen balance, % | Nitrogen content <sup>a</sup> , mass-% |
|---------------------------------------|------------|--------------------------------------------------------------|-----------------------|-------------------|----------------------------------------|
| Tri(2-hydroxyethyl)ammonium nitrate   | 27096-29-3 | C <sub>6</sub> H <sub>16</sub> N <sub>2</sub> O <sub>6</sub> | 212.2                 | -105.5            | 13.2                                   |
| 2-Hydroxyethylammonium nitrate        | 20748-72-5 | C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>  | 124.1                 | -51.6             | 22.57                                  |
| Trimethylammonium nitrate             | 25238-43-1 | C <sub>3</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 122.12                | -104.8            | 22.94                                  |
| Isopropylammonium nitrate             | 87478-71-5 | C <sub>3</sub> H <sub>10</sub> N <sub>2</sub> O <sub>3</sub> | 122.1231              | -104.8            | 22.94                                  |
| Ethylammonium nitrate                 | 22113-86-6 | C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>  | 108.10                | -74.0             | 25.91                                  |
| Methylammonium nitrate                | 22113-87-7 | C <sub>1</sub> H <sub>6</sub> N <sub>2</sub> O <sub>3</sub>  | 94.07                 | -34.0             | 29.78                                  |
| Tri(2-aminoxethyl)ammonium trinitrate |            | C <sub>6</sub> H <sub>21</sub> N <sub>8</sub> O <sub>9</sub> | 349.28                | -61.8             | 32.08                                  |
| Guanidinium nitrate                   | 506-93-4   | C <sub>1</sub> H <sub>6</sub> N <sub>4</sub> O <sub>3</sub>  | 122.0833              | -26.2             | 45.89                                  |
| Aminoguanidinium nitrate              | 10308-82-4 | C <sub>1</sub> H <sub>7</sub> N <sub>5</sub> O <sub>3</sub>  | 137.10                | -29.2             | 51.08                                  |
| Diaminoguanidinium nitrate            | 37160-07-9 | C <sub>1</sub> H <sub>8</sub> N <sub>6</sub> O <sub>3</sub>  | 152.11                | -31.6             | 55.25                                  |
| Triaminoguanidinium nitrate           | 4000-16-2  | C <sub>1</sub> H <sub>9</sub> N <sub>7</sub> O <sub>3</sub>  | 167.13                | -33.5             | 58.67                                  |

<sup>a</sup> Sorted by nitrogen content

Carbon-13 spin-lattice relaxation times were measured in four alkylammonium nitrates that were candidate fuels for HAN-based monopropellants: isopropyl-, triethanol-, trimethyl-, and *n*-butyl-ammonium nitrates [26]. The relaxation mechanism in these compounds was found to be predominantly by dipolar interactions with attached protons. The relaxation times increased with temperature, as expected, but were found to be essentially independent of concentrations. Attempts were made to interpret these results in terms of ion pairing, ion clustering, molecular associations, and reorientations. This method was considered for the analysis of HAN-based monopropellants.

### 1.3.2.2 Physical Properties of Amine Perchlorates

The amine perchlorates are discussed here in the sequence of increasing number of carbon atoms. If they contain the same number of carbon atoms, they are listed in the order of increasing nitrogen atoms.

To use the correct nomenclature, amine perchlorates should be called alkylammonium perchlorates. If an amine contains more than one nitrogen atom that can be protonated, the number of protons added are listed in parentheses after the name, e.g., ethylenediammonium(2+) diperchlorate. *Chemical Abstracts Service* used to index them under the name of the acid salt, such as “Perchloric acid, methylamine salt.”

When looking in the substance index, one would have to look up the name of the acid first. If one has the CAS registry number, the CAS SciFinder search can be more specific and will yield the desired results more quickly.

We have added six physical property overview tables (Table 9 through Table 14) that allow the propellant formulator to select an amine perchlorate for a certain application based on its melting point, nitrogen content, or enthalpy of formation.

**Table 9:** Nitrogen content and oxygen balance of amine perchlorates in comparison to guanidinium perchlorates.

| Name                            | CAS RN     | Gross formula                                                  | Molecular mass, g/mol | Oxygen balance to CO <sub>2</sub> and HCl | Nitrogen content <sup>a</sup> , mass-% |
|---------------------------------|------------|----------------------------------------------------------------|-----------------------|-------------------------------------------|----------------------------------------|
| Methylammonium perchlorate      | 15875-44-2 | CH <sub>6</sub> NO <sub>4</sub> Cl                             | 131.52                | -6.1                                      | 10.65                                  |
| Guanidinium perchlorate         | 10308-84-6 | C <sub>1</sub> H <sub>6</sub> N <sub>3</sub> O <sub>4</sub> Cl | 159.529               | -5.0                                      | 26.35                                  |
| Aminoguanidinium perchlorate    | 41195-24-8 | C <sub>1</sub> H <sub>7</sub> N <sub>4</sub> O <sub>4</sub> Cl | 174.544               | -9.2                                      | 32.1                                   |
| Triaminoguanidinium perchlorate | 4104-85-2  | C <sub>1</sub> H <sub>9</sub> N <sub>6</sub> O <sub>4</sub> Cl | 204.573               | -15.6                                     | 41.08                                  |

<sup>a</sup> Sorted by increasing nitrogen content

**Table 10:** Enthalpy of formation of amine perchlorates.

| Compound name                    | Molecular mass, g/mol | Formula                                                                          | Enthalpy of formation |                 |        | References |
|----------------------------------|-----------------------|----------------------------------------------------------------------------------|-----------------------|-----------------|--------|------------|
|                                  |                       |                                                                                  | kJ/mol                | kcal/mol        | cal/g  |            |
| Ethylenediammonium diperchlorate | 261.01                | (CH <sub>2</sub> NH <sub>3</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> | -479                  | -114.6          | -439   | [27]       |
| Guanidinium perchlorate          | 159.53                | C(NH <sub>2</sub> ) <sub>3</sub> ClO <sub>4</sub>                                | -310                  | -74.1<br>± 0.55 | -464   | [28]       |
| For comparison:                  |                       |                                                                                  |                       |                 |        |            |
| Ammonium perchlorate             | 117.489               | NH <sub>4</sub> ClO <sub>4</sub>                                                 | -295.77               | -70.69          | -601.7 | [29]       |

**Table 11:** Melting points and densities of amine perchlorates.

| Compound name                              | Formula                                                                          | Melting point |          | Density, g/cm <sup>3</sup>                                                  | References                                             |
|--------------------------------------------|----------------------------------------------------------------------------------|---------------|----------|-----------------------------------------------------------------------------|--------------------------------------------------------|
|                                            |                                                                                  | K             | °C       |                                                                             |                                                        |
| Methylammonium perchlorate                 | CH <sub>3</sub> NH <sub>3</sub> ClO <sub>4</sub>                                 | 528           | 255      | 1.65 monoclinic at 298 K<br>1.56 tetragonal at 321 K<br>1.52 cubic at 451 K | [30]                                                   |
|                                            |                                                                                  | 515           | 242      | 1.68                                                                        | [31], p. A227<br>Explodes when heated to 611 K = 338°C |
| Dimethylammonium perchlorate               | (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ClO <sub>4</sub>                 | 453           | 180      | 1.40 monoclinic at 298 K<br>1.4 tetragonal at 322 K                         | As referenced in [30]                                  |
| Trimethylammonium perchlorate              | (CH <sub>3</sub> ) <sub>3</sub> NHClO <sub>4</sub>                               | 548           | 275      | 1.41 at 298 K                                                               | As referenced in [30]                                  |
| Quaternary tetramethylammonium perchlorate | (CH <sub>3</sub> ) <sub>4</sub> NClO <sub>4</sub>                                | —             | —        | 1.35 at 298 K                                                               | Explodes at 690 K without melting                      |
| Ethylenediammonium diperchlorate           | (CH <sub>2</sub> NH <sub>3</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> | 573 dec.      | 300 dec. |                                                                             | Decomposes at 573 K (300°C)                            |
| Guanidinium perchlorate                    | C(NH <sub>2</sub> ) <sub>3</sub> ClO <sub>4</sub>                                | 513           | 240      | 1.772 (calc. XRD <sup>a</sup> )<br>1.743 (pycnometric)                      | [32]                                                   |
| Triaminoguanidinium perchlorate            | C(NHNH <sub>2</sub> ) <sub>3</sub> ClO <sub>4</sub>                              | 405           | 132      |                                                                             | As referenced in [30]                                  |
| Pyridinium perchlorate                     | C <sub>5</sub> H <sub>6</sub> NClO <sub>4</sub>                                  | 561           | 288      |                                                                             | As referenced in [30]                                  |
| For comparison:<br>Ammonium perchlorate    | NH <sub>4</sub> ClO <sub>4</sub>                                                 | Dec.          | Dec.     | 1.957 (orthorhombic)                                                        |                                                        |

<sup>a</sup> XRD = X-Ray Diffraction

Table 12: Melting and phase transition properties, densities, and crystal structure of amine perchlorates.

| Compound                                                                                  | Melting point, °C           | I → II<br>trans-<br>sition<br>point, °C | Phase I<br>unit cell,<br>Å | Phase I<br>temp.,<br>°C | Phase I<br>X-ray<br>density,<br>g/cm <sup>3</sup> | Phase I py-<br>cnometric<br>density,<br>g/cm <sup>3</sup> | II → III<br>trans-<br>sition<br>point, °C | Phase II<br>unit cell,<br>Å           | Phase II<br>temp.,<br>°C | Phase II<br>X-ray<br>density,<br>g/cm <sup>3</sup> | Phase II<br>pycnomet-<br>ric density,<br>g/cm <sup>3</sup> |
|-------------------------------------------------------------------------------------------|-----------------------------|-----------------------------------------|----------------------------|-------------------------|---------------------------------------------------|-----------------------------------------------------------|-------------------------------------------|---------------------------------------|--------------------------|----------------------------------------------------|------------------------------------------------------------|
| CH <sub>3</sub> NH <sub>3</sub> ClO <sub>4</sub>                                          | 255 melts and<br>decomposes | 178                                     | a = 5.18                   | 200                     | 1.58                                              | —                                                         | 48                                        | a = 3.87,<br>c = 9.28                 | 77                       | 1.58                                               | —                                                          |
| (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ClO <sub>4</sub>                          | 180                         | 180                                     | a = 5.44,<br>c = 11.22     | 45                      | 1.46                                              | —                                                         | 38                                        | —                                     | 72                       | —                                                  | 1.56                                                       |
| (CH <sub>3</sub> ) <sub>3</sub> NHClO <sub>4</sub>                                        | 275 melts and<br>decomposes | 207                                     | a = 8.20,<br>c = 6.56      | 245                     | 1.21                                              | —                                                         | 116                                       | —                                     | 25                       | —                                                  | 1.65                                                       |
| (CH <sub>3</sub> ) <sub>4</sub> NClO <sub>4</sub>                                         | 380 detonates               | 340                                     | —                          | 223                     | —                                                 | 1.27                                                      | —                                         | a = 5.95,<br>c = 9.70                 | 25                       | 1.67                                               | 1.35                                                       |
| (CH <sub>2</sub> NH <sub>3</sub> ClO <sub>4</sub> ) <sub>2</sub>                          | 290 decomposes              | 54                                      | a = 11.35,<br>c = 5.23     | 80                      | 1.94                                              | —                                                         | —                                         | —                                     | —                        | —                                                  | —                                                          |
| (CH <sub>2</sub> NH <sub>3</sub> ClO <sub>4</sub> ) <sub>2</sub><br>• 1/2H <sub>2</sub> O | 120 dehydrates              | 95                                      | —                          | 70                      | —                                                 | 1.7                                                       | —                                         | —                                     | 25                       | —                                                  | 1.80                                                       |
| (CH <sub>3</sub> ) <sub>2</sub> CHNH <sub>3</sub> ClO <sub>4</sub>                        | 150 melts                   | 25                                      | a = 7.34,<br>c = 6.98      | 30                      | 1.42                                              | —                                                         | —                                         | —                                     | —                        | —                                                  | —                                                          |
| For comparison:<br>NH <sub>4</sub> ClO <sub>4</sub>                                       | 450 decomposes              | 240                                     | a = 7.67                   | 250                     | 1.73                                              | 1.7                                                       | ~190                                      | a = 9.231,<br>b = 5.813,<br>c = 7.453 | 25                       | 1.95                                               | 1.9                                                        |

Data source: [33, 34]

**Table 13:** Ignition temperatures of amine perchlorates.

| Compound name                        | Ignition temperature <sup>a</sup> |     | Comments                |
|--------------------------------------|-----------------------------------|-----|-------------------------|
|                                      | K                                 | °C  |                         |
| Hydrazinium(2+) diperchlorate        | 488                               | 215 | —                       |
| Hydrazinium(1+) perchlorate          | 511                               | 238 | —                       |
| Anilinium perchlorate                | 523                               | 250 | —                       |
| Semicarbazide perchlorate            | 551                               | 278 | —                       |
| <i>n</i> -Propylammonium perchlorate | 563                               | 290 | —                       |
| Methylammonium perchlorate           | 611                               | 338 | —                       |
| Guanidinium perchlorate              | 640                               | 367 | Melts at 510 K (237 °C) |

<sup>a</sup> Sorted in order of increasing thermal stability

Data source: As referenced in [30]

**Table 14:** Impact sensitivity of amine perchlorates.

| Compound name                              | Formula                                                                          | 50% point, drop height, cm |
|--------------------------------------------|----------------------------------------------------------------------------------|----------------------------|
| Methylammonium perchlorate                 | CH <sub>3</sub> NH <sub>3</sub> ClO <sub>4</sub>                                 | 20                         |
| Dimethylammonium perchlorate               | (CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ClO <sub>4</sub>                 | 22                         |
| Trimethylammonium perchlorate              | (CH <sub>3</sub> ) <sub>3</sub> NHClO <sub>4</sub>                               | 25                         |
| Quaternary tetramethylammonium perchlorate | (CH <sub>3</sub> ) <sub>4</sub> NClO <sub>4</sub>                                | 35                         |
| Ethylenediammonium diperchlorate           | (CH <sub>2</sub> NH <sub>3</sub> ) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub> | 35                         |
| Guanidinium perchlorate                    | C(NH <sub>2</sub> ) <sub>3</sub> ClO <sub>4</sub>                                | 25                         |
| Triaminoguanidinium perchlorate            | C(NHNH <sub>2</sub> ) <sub>3</sub> ClO <sub>4</sub>                              | 7                          |
| For comparison:                            |                                                                                  |                            |
| RDX                                        | C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>                      | 33                         |
| Ammonium perchlorate                       | NH <sub>4</sub> ClO <sub>4</sub>                                                 | 100                        |

2-kg weight in US Bureau of Mines machine

Data source: [30]

The method used to determine the ignition temperatures in Table 13 consisted of dropping a sample into a pre-heated test tube under carbon dioxide cover gas to exclude air. Other investigators used ignition delay and isothermal rate of weight loss measurements to determine the activation energies of decomposition of several alkylammonium perchlorates [35, 36]. For instance, the ignition temperature of methylammonium perchlorate was 583 K (310 °C), and the ignition temperature of isopropylammonium perchlorate was 564 K (291 °C). The activation energy derived from isothermal rate of weight loss measurements was 167 kJ/mol (40 kcal/mol) for methylammonium perchlorate and 192 kJ/mol (46 kcal/mol) for isopropylammonium perchlorate. Proton transfer dissociation is the first step in the decomposition of these salts. The HClO<sub>4</sub> thus formed can decompose into chlorine oxides that will accelerate the decompo-

sition and lead to ignition. Alkylammonium perchlorates might have the same gross elemental composition as ammonium perchlorate (AP)/binder combinations, but the decomposition behavior is quite different from that of composite propellants.

A book on the structure and stability of salts of halogen oxyacids contains chapters on the preparation and thermal stability of organic amine perchlorates [37].

### 1.3.2.3 Quaternary Ammonium Salts

Quaternary ammonium salts were used by J. D. Clark in his (in)famous CAVEA monopropellants. A good anecdotal description of the history of the development of CAVEA monopropellants and impressive photos of the results of monopropellant explosions are contained in Clark's book *Ignition!* [38], from which the current book borrowed the preface quote by I. Asimov about the mental state of rocket propellant chemists, including the author of the book at hand.

### 1.3.2.4 Autoignition of Aliphatic Amines

It is unlikely that flammable mixtures of aliphatic amines and oxygen would form under normal conditions of use of alkylamines, but the auto-ignition temperatures of stoichiometric oxygen/amine vapor mixtures at below atmospheric pressures were measured in Pyrex vessels [39]. The amines tested included the primary, secondary, and tertiary methylamines and ethylamines. The ease of oxidation decreased in the order tertiary > secondary > primary amines. For stoichiometric mixtures, a correlation was established between the auto-ignition temperature and the pressure in the vessel. For instance, for a mixture containing 16.7% by volume triethylamine in oxygen at 26.7 kPa (200 mm Hg), the first explosion would take place at 527 K (254 °C). Leaner mixtures would only ignite at higher temperatures. Oxygen/ethylamine mixtures auto-ignited only at temperatures higher than for oxygen/triethylamine mixtures.

## 2 Aliphatic Amines with One Nitrogen Atom in the Molecule

### 2.1 Methylamines

Methylamines are the lowest members of the family of amine fuels:

|                                                                               |                            |
|-------------------------------------------------------------------------------|----------------------------|
| Methylamine (sometimes called monomethylamine or aminomethane or methanamine) | $\text{CH}_3\text{NH}_2$   |
| Dimethylamine                                                                 | $(\text{CH}_3)_2\text{NH}$ |
| Trimethylamine                                                                | $(\text{CH}_3)_3\text{N}$  |

Methylamines are derivatives of ammonia in which one, two, or all three of the hydrogen atoms have been replaced by methyl groups [2]. Methylamines are colorless gases or compressed liquids, are highly flammable, and have very strong fishy or ammonia-

like odors. They are water soluble and are available as either aqueous solutions or in pure form. Due to their high reactivity, there are numerous industrial applications for methylamines as raw materials for the synthesis of solvents, crop-protection agents, pharmaceuticals, surfactants, rubber chemicals, ion-exchange resins, explosives, animal feed, building blocks for the paper industry, and water treatment materials.

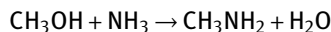
Of all the alkylamines, the methylamines are the ones most readily accessible through synthesis, starting with natural gas that is converted to ammonia and methanol. They can be obtained by reaction of ammonia with methanol on the surface of catalysts. This should make them good rocket fuels, except for the shortcoming that they are not hypergolic with nitric acid without a hypergolizing additive such as an alkyldiazine or an alkali metal.

The primary, secondary, and tertiary methylamines are all vapors at room temperature and atmospheric pressure. All three methylamines can be considered storable fuels. They can be stored indefinitely as liquids at room temperature under their own vapor pressure, a moderate vapor pressure that makes them still easy to handle. They are commonly shipped and stored in steel cylinders with pressure-relief valves or burst discs. The vapor pressures of methylamine, dimethylamine, and trimethylamine at room temperature are 2.79, 159, and 186 kPa (2100, 1200, and 1400 mm Hg), respectively.

Only a few investigations of methylamines as rocket fuels have been reported. They can be used in mixtures with hydrazine to lower the freezing point of hydrazine or to stabilize hydrazine to the point where it can be used as a regenerative coolant in bipropellant engines. The gross composition of such mixtures would be similar to that of MMH or UDMH, but the performance would not be as good. Methylamine is a precursor for the synthesis of MMH, and dimethylamine is a precursor for the synthesis of UDMH.

### 2.1.1 Preparation of Methylamines

Methylamines can be prepared by the reaction of ammonia with methanol under pressure in the presence of aluminosilicate catalysts.



In this way, an estimated 115000 tons of methylamine were produced in 2005. Dimethylamine and trimethylamine are inevitable by-products of this process, and it is difficult to stop the process at the stage of the monomethylamine. The reaction conditions and reactant ratios determine the ratio of the three products. The product most favored by the reaction kinetics is trimethylamine.

Monomethylamine, dimethylamine, and trimethylamine are major industrial chemical intermediates. Generally, these compounds are prepared by reaction of methanol and ammonia over a dehydration catalyst such as silica alumina. While thermodynamics favors trimethylamine formation, market demand is for dimethyl-



amine. This has led to the development of highly dimethylamine-selective zeolite-based catalysts [40].

### 2.1.2 Physical Properties of Methylamines

Physical properties of methylamines are listed in Table 15.

**Table 15:** Physical properties of methylamines.

|                                            |                   | Methylamine<br>$\text{CH}_3\text{NH}_2$ | Dimethylamine<br>$(\text{CH}_3)_2\text{NH}$ | Trimethylamine<br>$(\text{CH}_3)_3\text{N}$ | References |
|--------------------------------------------|-------------------|-----------------------------------------|---------------------------------------------|---------------------------------------------|------------|
| Chemical Abstracts Service registry number |                   | 74-89-5                                 | 124-40-3                                    | 75-50-3                                     |            |
| Molecular mass                             | g/mol             | 31.0571                                 | 45.0837                                     | 59.1103                                     | [29]       |
| Freezing point                             | K                 | 180.6                                   | 180.15                                      | 155.95                                      | [29]       |
|                                            | °C                | −92.5                                   | −93                                         | −117.2                                      | [29]       |
| Density, liquid at 298 K                   | g/cm <sup>3</sup> | 0.6558                                  | 0.6556                                      | —                                           | [9]        |
| Boiling point at 101 kPa                   | K                 | 266.8                                   | 281                                         | 276                                         | [29]       |
|                                            | °C                | −6.32                                   | +8                                          | +2.87                                       |            |
| Vapor pressure at 298 K                    | kPa               | 350.6                                   | —                                           | —                                           | [9]        |
|                                            | atm               | 3.47                                    | —                                           | —                                           |            |
| Critical temperature                       | K                 | 430                                     | 437.22                                      | 433.2                                       | [29]       |
|                                            | °C                | 156.9                                   | 164.07                                      | 160.1                                       |            |
| Critical pressure                          | MPa               | 7.43                                    | 5.34                                        | 4.087                                       | [29]       |
|                                            | atm               | 73.6                                    | 52.87                                       | 40.2                                        |            |
| Critical density                           | kg/m <sup>3</sup> | 216                                     | 256                                         | 233                                         | [29]       |
|                                            | g/cm <sup>3</sup> | 0.216                                   | 0.256                                       | 0.233                                       |            |

The vapor pressure of methylamine can be calculated from the Antoine equation

$$\ln p_{\text{sat}} = 6.4613 - 1010.93/(T - 39.94)$$

where  $p_{\text{sat}}$  is the saturation pressure in kPa and  $T$  is the temperature in kelvin, valid for the pressure range 20–200 kPa. A similar Antoine equation allows us to calculate the vapor pressure for the temperature range from 190 to 266.9 K from the equation

$$\log p_v = 4.520 - [1034.977/(T - 37.574)]$$

where  $p_v$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

Viscosity data for liquid methylamine have been obtained in the temperature range of 203 to 263 K (−70 to −10°C) using an Ubbelohde viscometer [41]. The results were compared with existing data, and all the data were fitted to the Fulcher (Tammann–Hesse) equation by the method of least squares. The significance of the

values of  $T_0$  in this equation for these and other associated liquids was considered. The methylamine viscosity data in Table 16 below can be expressed by a Fulcher-type equation

$$\log \eta = -1.3634 + 126.389/(T - 102.886)$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The viscosity calculated with the equation at 298 K (outside the valid range) is 0.19 cPs. The accuracy of this equation is  $\pm 0.32\%$ .

**Table 16:** Viscosity of liquid methylamine at various temperatures.

| Temperature |     | Viscosity |
|-------------|-----|-----------|
| K           | °C  | cPs       |
| 203.1       | -70 | 0.802     |
| 208.1       | -65 | 0.681     |
| 213.1       | -60 | 0.604     |
| 218.1       | -55 | 0.54      |
| 223.1       | -50 | 0.484     |
| 228.1       | -45 | 0.443     |
| 233.1       | -40 | 0.404     |
| 238.1       | -35 | 0.374     |
| 243.1       | -30 | 0.348     |
| 248.1       | -25 | 0.323     |
| 253.1       | -20 | 0.301     |
| 258.1       | -15 | 0.28      |
| 263.1       | -10 | 0.266     |

Data source: [41]

Later measurements extended the range of temperatures from  $-10$  to  $+29.3^\circ\text{C}$  [42]. The raw data are summarized in Table 17 and can be expressed by the Fulcher-type equation

$$\log \eta = 1.635 + 203.2(T - 69.87)$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin.

The viscosity of liquid dimethylamine at 298 K is  $0.000232 \text{ kg m}^{-1} \text{ s}^{-1}$ . The surface tension of dimethylamine at 298 K is  $0.02634 \text{ N/m}$ .

A fuel mixture of methylamine with hydrazine and aniline has been evaluated as a hypergolic fuel for use with white fuming nitric acid (WFNA) or RFNA. Methylamines are miscible with hydrazine and could be used as a substitute for MMH or UDMH in making hydrazine blends if there were to be a shortage of MMH or UDMH [43].

Thermodynamic properties of methylamines are summarized in Table 18. See also [44, 45].

**Table 17:** Viscosity of liquid methylamine.

| Temperature |       |       | Temperature |       |       | Temperature |       |       |
|-------------|-------|-------|-------------|-------|-------|-------------|-------|-------|
| K           | °C    | cPs   | K           | °C    | cPs   | K           | °C    | cPs   |
| 302.4       | 29.3  | 0.173 | 258.3       | −14.8 | 0.283 | 227.9       | −45.2 | 0.445 |
| 300.3       | 27.2  | 0.176 | 257.9       | −15.2 | 0.281 | 223.0       | −50.1 | 0.486 |
| 297.9       | 24.8  | 0.179 | 255.0       | −18.1 | 0.295 | 222.5       | −50.6 | 0.495 |
| 295.2       | 22.1  | 0.184 | 253.0       | −20.1 | 0.301 | 222.4       | −50.7 | 0.494 |
| 291.6       | 18.5  | 0.19  | 248.5       | −24.6 | 0.381 | 217.8       | −55.3 | 0.541 |
| 288.4       | 15.3  | 0.196 | 247.9       | −25.2 | 0.319 | 214.7       | −58.4 | 0.582 |
| 285.6       | 12.5  | 0.202 | 245.7       | −27.4 | 0.337 | 212.9       | −60.2 | 0.605 |
| 283.2       | 10.1  | 0.206 | 242.9       | −30.2 | 0.35  | 212.4       | −60.7 | 0.614 |
| 283.0       | 9.9   | 0.206 | 241.1       | −32   | 0.358 | 207.9       | −65.2 | 0.681 |
| 280.8       | 7.7   | 0.212 | 237.9       | −35.2 | 0.375 | 206.3       | −66.8 | 0.713 |
| 278.5       | 5.4   | 0.217 | 235.7       | −37.4 | 0.385 | 205.1       | −68   | 0.74  |
| 273.2       | 0.1   | 0.231 | 233.0       | −40.1 | 0.405 | 204.3       | −68.8 | 0.755 |
| 263.5       | −9.6  | 0.256 | 230.4       | −42.7 | 0.425 | 202.4       | −70.7 | 0.805 |
| 263.0       | −10.1 | 0.266 | 229.0       | −44.1 | 0.437 | —           | —     | —     |

Note: The sample pressure is 1 atm in hydrogen as a blanket gas at temperatures below 258 K (−15 °C) and the vapor pressure of methylamine at temperatures above 258 K (−15 °C).

Data source: [42]

**Table 18:** Thermodynamic properties of methylamines.

|                                                     | Unit     | Methylamine<br>CH <sub>3</sub> NH <sub>2</sub> | Dimethylamine<br>(CH <sub>3</sub> ) <sub>2</sub> NH | Trimethylamine<br>(CH <sub>3</sub> ) <sub>3</sub> N | Refer-<br>ences |
|-----------------------------------------------------|----------|------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|-----------------|
| CAS RN                                              |          | 74-89-5                                        | 124-40-3                                            | 75-50-3                                             |                 |
| Molecular mass                                      | g/mol    | 31.0571                                        | 45.0837                                             | 59.1103                                             | [29]            |
| Heat of combustion, liquid                          | kJ/mol   | 1035                                           | 1716                                                | 2398                                                |                 |
|                                                     | kcal/mol | 247.4                                          | 410.2                                               | 573.1                                               |                 |
| Standard enthalpy of<br>formation, liquid           | kJ/mol   | −47.3                                          | —                                                   | −45.73 ± 0.71                                       | [29]            |
|                                                     | kJ/mol   | −47.27 ± 0.4                                   | —                                                   | —                                                   | [9]             |
| Standard enthalpy of<br>formation, gas              | kJ/mol   | −23.5                                          | −19 ± 2                                             | −23.7 ± 0.75                                        | [29]            |
| Heat of fusion                                      | kJ/mol   | 6.13                                           | 5.94                                                | 6.54                                                | [29]            |
|                                                     | kcal/mol | 1.4658                                         | 1.4201                                              | 1.5640                                              |                 |
| Enthalpy of vaporization<br>at normal boiling point | kJ/mol   | 25.8                                           | 26.4                                                | 22.9                                                | [29]            |
|                                                     | kcal/mol | 6.169 ± 0.03                                   | 6.330 ± 0.003                                       | 5.482 ± 0.007                                       |                 |
| Enthalpy of vaporization<br>at 298 K                | kJ/mol   | 24.74 ± 0.01                                   | 27                                                  | —                                                   | [9]             |

### 2.1.3 Chemical Properties of Methylamines

Methylamines serve as intermediates in the production of methylhydrazines by the Raschig process. The assay and the analysis for contaminants in methylamines are best performed using gas chromatography.

### 2.1.4 Handling of Methylamines

The transfer of methylamines between transport and storage containers should be done under pressure. If the compounds are chilled to be transferred at atmospheric pressure, one must avoid exposure to air because moisture and carbon dioxide will condense into the cold liquids.

The transfer lines must be hermetically sealed to prevent escape of amine vapors that would endanger bystanding personnel and which may form flammable and explosive mixtures in air. All containers should be grounded to prevent buildup of electrostatic charges.

### 2.1.5 Toxicity of Methylamines

The presence of methylamine vapors in the air is easily recognized by their penetrant fishy odor. At very high concentrations above 100–500 parts per million (ppm), the odor is hard to differentiate from that of ammonia. Airborne concentrations of methylamines at the workplace should not exceed 225 ppm. At concentrations greater than 100 ppm, the strong eye and respiratory irritation will force the workers to leave the area and seek a safe place with fresh air. There are no reported poisoning incidents due to methylamine inhalation.

Methylamines and their concentrated aqueous solutions are strongly irritating to the skin and will cause chemical burns. Methylamines and their concentrated aqueous solutions spilled into eyes are dangerously corrosive and may cause blindness, similar to ammonia solutions. The eyes must be washed with large amounts of water immediately. If methylamines are spilled on clothing, the clothing must be removed and the affected skin parts rinsed with water, neutralized with 1% acetic acid (vinegar), and again rinsed with water.

The toxicology of dimethylamine animal exposure test results is summarized in Table 19.

The established legal limits for worker exposure to methylamines at the workplace are summarized in Table 20.

Additional toxicity information on dimethylamine is contained in [46–48], and similar information for trimethylamine is in [49]. The LC50 for dimethylamine is 4700 ppm. A level of distinct odor awareness (LOA) of 0.53 ppm was calculated for dimethylamine. A very detailed summary of toxicity information for dimethylamine was compiled in [50].

In a non-cancer inhalation chronic toxicity assessment of diethylamine, rats were exposed to 0, 31, 62.5, and 125 ppm diethylamine and mice to 0, 16, 31, and 62.5 ppm

**Table 19:** Toxicity of dimethylamine based on animal exposure tests.

| Compound name | Toxicity | Animal               | Mode of administration | Result     |
|---------------|----------|----------------------|------------------------|------------|
| Dimethylamine | LD50     | Mouse                | Intraperitoneal        | 736 mg/kg  |
|               | LD50     | Mouse                | Oral                   | 316 mg/kg  |
|               | LD50     | Rat                  | Oral                   | 698 mg/kg  |
|               | LD50     | Rat                  | Dermal                 | 3900 mg/kg |
|               | LD50     | Guinea pig or rabbit | Oral                   | 240 mg/kg  |
|               | LC50     | Rat, 4 h             | Inhalation             | 4700 ppm   |
|               | LC50     | Rat, 6 h             | Inhalation             | 4540 ppm   |
|               | LC50     | Mouse, 2 h           | Inhalation             | 7650 ppm   |

**Table 20:** Exposure limits for methylamines at the workplace.

| Compound name | Agency   | Exposure limit | ppm (volume) | mg/m <sup>3</sup> |
|---------------|----------|----------------|--------------|-------------------|
| Dimethylamine | NIOSH    | TWA            | 10           | 18                |
|               | NIOSH    | PEL            | 10           | 18                |
|               | NIOSH    | IDLH           | 500          | 900               |
|               | NAC/AEGL | AEGL-1, 1 h    | 10           | 18                |
|               | NAC/AEGL | AEGL-2, 1 h    | 66           | 120               |
|               | NAC/AEGL | AEGL-3, 10 min | 480          | 880               |
|               | ACGIH    | TLV, 1993–1994 | 5            | 9.2               |

NIOSH = National Institute for Occupational Safety and Health, NAC/AEGL = National Advisory Committee on Acute Exposure Guideline Levels, ACGIH = American Conference of Governmental Industrial Hygienists, TWA = time-weighted average, PEL = permissible exposure limit, IDLH = immediately dangerous to life or health, AEGL = acute exposure guideline level, TLV = threshold limit value

diethylamine for 6 h/d, 5 d/week for 105 weeks [51]. Mice were slightly more sensitive than rats. The critical effect identified in mice was hyperostosis in the turbinates, although diethylamine caused a number of other non-neoplastic lesions. The chronic reference value for diethylamine is 11 parts per billion (ppb; 33 µg/m<sup>3</sup>).

### 2.1.6 Flammability of Methylamines

Vapors of methylamines are flammable in air. Flammability and ignition characteristics are summarized in Table 21. The accidental ignition of dimethylamine vapors has been the cause of an accident in the production of UDMH [52].

**Table 21:** Flammability and ignition of methylamines.

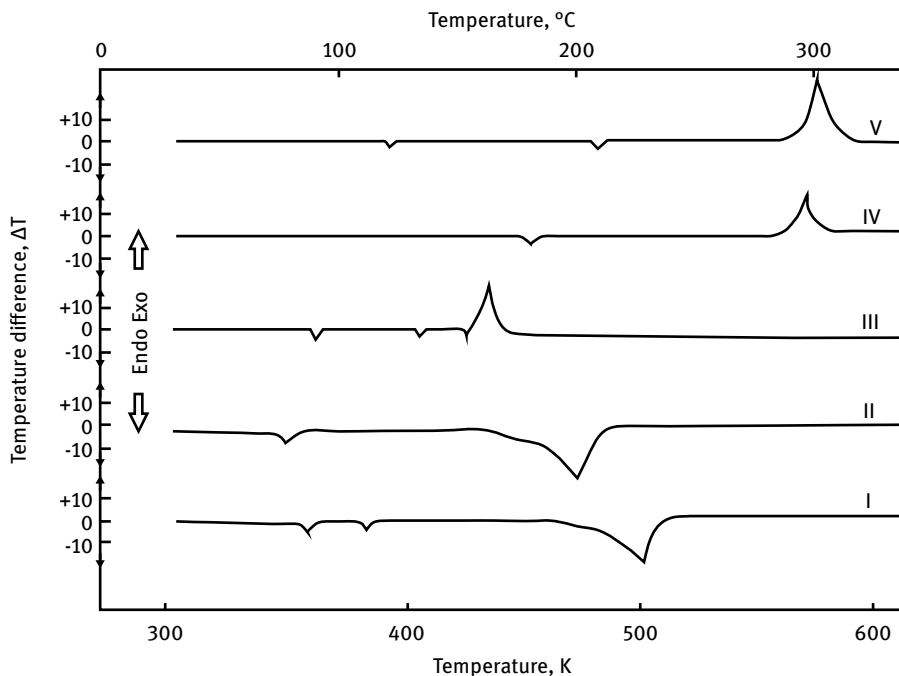
|                                                |       | Methylamine | Dimethylamine  | Trimethylamine |
|------------------------------------------------|-------|-------------|----------------|----------------|
| Flammable range in dry air, upward propagation | Vol-% | 4.95–20.75  | 2.8–14.4       | 2.0–11.6       |
| Flash point                                    | K     | 263         | 267            | —              |
|                                                | °C    | –10         | –6<br>–50 [53] | —              |
| Autoignition temperature                       | K     | 703         | 674            | —              |
|                                                | °C    | 430         | 401            | —              |

Data source: [54]

## 2.2 Methylammonium Salts

Methylammonium nitrates are useful energetic additives because with the short alkyl group they do not require as much oxygen to achieve complete combustion as the higher alkylammonium nitrates. The relative thermal stability of alkylammonium salts was studied as a function of the type and numbers of alkyl (or aryl) substituents [55]. It was attempted to explain the thermal stability of substituted ammonium cations paired with nitrate anions. The basicity of the central nitrogen atom has an effect on the thermal stability of the nitrate salts formed. Although the thermal stability of alkylammonium nitrate salts differs substantially from one salt to the next, there may be a common mechanism by which these salts decompose when they are heated. Thermographic analysis coupled with mass spectrometry of the off-gassing products showed that the thermal stability (both endotherms and exotherms) decreases with increasing number of methyl groups in the molecule, except that the quaternary tetramethylammonium nitrate was exceptionally stable due to the symmetry of the cation formed. Figure 1 shows the temperature differences recorded during differential thermal analysis (DTA) of methylammonium nitrate, dimethylammonium nitrate, trimethylammonium nitrate, dimethylammonium perchlorate, and trimethyl ammonium perchlorate. It is unusual to crowd that many thermogram traces into one image, but this display method allows easy comparison of the thermal stability of these five compounds. The terminal exotherms of methylammonium nitrate and dimethylammonium nitrate observed in air were replaced by endotherms when the test was performed under reduced pressure at 67 Pa (0.5 mm Hg) instead of air.

A common first step in the thermal decomposition of alkylammonium nitrates is proton transfer. However, in the case of alkylammonium perchlorates, the first step of thermolysis is formation of methyl carbonium  $\text{CH}_3^+$  ions.



**Figure 1:** Differential thermal analysis traces of methyl-, dimethyl-, and trimethylammonium nitrates and perchlorates at 0.5 mm Hg pressure (Reproduced and modified from [55].)

Legend: I: methylammonium nitrate; II: dimethylammonium nitrate; III: trimethylammonium nitrate; IV: dimethylammonium perchlorate; V: trimethyl ammonium perchlorate

### 2.2.1 Methylammonium Nitrates

Methylammonium nitrate, also known as monomethylammonium nitrate, methylamine nitrate, monomethylamine nitrate; methanamine, nitrate (1:1); MEAN,  $\text{H}_3\text{CN}^+\text{H}_3\text{NO}_3^-$ ,  $\text{C}_1\text{H}_6\text{N}_2\text{O}_3$ , CAS RN [22113-87-7], can be prepared by neutralization of methylamine solutions with dilute nitric acid. Methylammonium nitrate is an ingredient in commercial explosives, such as Tovex<sup>®</sup>.

#### 2.2.1.1 Physical Properties of Methylammonium Nitrate

Physical properties of MEAN are summarized in Table 22. Methylammonium nitrate forms prismatic crystals, with a melting point of 382–384 K (109–111°C), which are very hygroscopic. Methylammonium nitrate is considerably more hygroscopic than ammonium nitrate. When exposed to 50% relative humidity, it absorbs 100% by mass in 21 d.

Differential scanning calorimetry (DSC) analysis of MEAN crystals has shown an endothermic solid-phase transition at 359 K (86°C), and the onset of exothermic decomposition is at 533 K (260°C) [45, 56]. Mixtures of MEAN with ammonium nitrate

(AN), sodium nitrate, or calcium nitrate form low-melting eutectics that can be used as castable explosives.

Methylammonium nitrate with hydroxylammonium nitrate forms a low-melting ionic liquid [57].

**Table 22:** Physical properties of methylammonium nitrate.

| Property                     | Temperature in K | SI units                | Other units     | References                |
|------------------------------|------------------|-------------------------|-----------------|---------------------------|
| Molecular mass               |                  | 94.07 g/mol             | 10.6304 mol/kg  |                           |
| Melting point                |                  | 381–381.5 K             | 108–108.5 °C    | <i>Chemical Abstracts</i> |
|                              |                  | 382–394 K               | 109–111 °C      | [31]                      |
|                              |                  | 384 K                   | 111 °C = 232 °F | [15], p. 211              |
| Density                      | 298              | 1.42 g/cm <sup>3</sup>  | —               |                           |
|                              | 298              | 1.422 g/cm <sup>3</sup> | —               | [15], p. 211              |
| Enthalpy of formation, solid | 298              | –352.7 kJ/mol           | –896 cal/g      | [15], p. 211              |

### Thermodynamic Properties of Methylammonium Nitrate

The thermodynamic properties of alkylammonium nitrate are of interest to calculate theoretical performance in rocket engines and to correlate the heat of neutralization with the ignition delay in hypergolic bipropellant ignition tests. The difference between the measured heat of formation of methylamines and ethylamines and their nitrates is summarized in Table 23. This number is a composite of the heat of formation of nitric acid and the heat of neutralization.

The heat of neutralization decreases with increasing alkyl substitution in the ammonia molecule. The average difference in the heats of formation of the five salts in Table 23 is  $-122 \pm 22$  J. Methylamine seems to be “outside the family.” If methylamine were omitted, the average difference would be  $107 \pm 7$  J. Many of the alkylammonium nitrates have been evaluated as propellant or explosive ingredients, but the necessary

**Table 23:** Heat of neutralization of alkylamines plus enthalpy of formation of nitric acid.

| Amine          | Difference in enthalpy of formation, J/mol of amine |
|----------------|-----------------------------------------------------|
| Methylamine    | –132.8                                              |
| Dimethylamine  | –114.8                                              |
| Trimethylamine | –89.7                                               |
| Ethylamine     | –118.5                                              |
| Triethylamine  | –105.1                                              |

Data source: [58]



enthalpies of formation (or the heats of combustion) were not always available for performing theoretical performance calculations for specific impulse in a rocket or impetus in a cannon. In most cases, the enthalpies of the free amine were available from the literature. So if one could apply a conversion factor (addition, difference) to the enthalpy of the free (liquid) amine to obtain the enthalpy of formation of the solid amine nitrate, that would be a great help. With some precaution, a similar factor might even be applied to alkylhydrazines to obtain the heats of formation of hydrazinium salts. Table 24 is a summary of enthalpies of formation of various amine nitrates that came from literature sources or were extrapolated using application of a conversion addition. The process would be more accurate if different, separate additions were applied for primary, secondary, and tertiary amines.

**Table 24:** Enthalpies of formation of alkylammonium nitrates.

| Compound                                  | Formula                                                              | Enthalpy of formation, kJ/mol | Note <sup>a</sup> |
|-------------------------------------------|----------------------------------------------------------------------|-------------------------------|-------------------|
| Methylammonium nitrate                    | $\text{CH}_3\text{NH}_3\text{NO}_3$                                  | -354.4                        | 1                 |
| Dimethylammonium nitrate                  | $(\text{CH}_3)_2\text{NH}_2\text{NO}_3$                              | -346.9                        | 3??? 1!           |
| Trimethylammonium nitrate                 | $(\text{CH}_3)_3\text{NHNO}_3$                                       | -310.0                        | 1                 |
| Tetramethylammonium nitrate               | $(\text{CH}_3)_4\text{NNO}_3$                                        | -344.0                        | 1                 |
| Ethylammonium nitrate                     | $\text{C}_2\text{H}_5\text{NH}_3\text{NO}_3$                         | -517.1                        | 4                 |
| Ethylammonium nitrate                     | $\text{C}_2\text{H}_5\text{NH}_3\text{NO}_3$                         | -366.9                        | 1                 |
| Triethylammonium nitrate                  | $(\text{C}_2\text{H}_5)_3\text{NHNO}_3$                              | -413.8                        | 1                 |
| Triethanolammonium nitrate                | $(\text{HOCH}_2\text{CH}_2)_3\text{NHNO}_3$                          | -728                          | 4                 |
| Isopropylammonium nitrate                 | $(\text{CH}_3)_2\text{CHNH}_3\text{NO}_3$                            | -403.3                        | 3                 |
| <i>n</i> -Propylammonium nitrate          | $n\text{-C}_3\text{H}_7\text{NH}_3\text{NO}_3$                       | -404.6                        | 3                 |
| <i>n</i> -Butylammonium nitrate           | $n\text{-C}_4\text{H}_9\text{NH}_3\text{NO}_3$                       | -431                          | 1                 |
| Ethylenediammonium dinitrate              | $\text{NO}_3\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3\text{NO}_3$ | -653.5                        | 1                 |
| For comparison (data from other sources): |                                                                      |                               |                   |
| Methylammonium nitrate                    | $\text{CH}_3\text{NH}_3\text{NO}_3$                                  | -353                          | [59]              |
| Tetramethylammonium nitrate               | $(\text{CH}_3)_4\text{NNO}_3$                                        | $-331.8 \pm 0.1$              | [16]              |
| Isopropylammonium nitrate                 | $(\text{CH}_3)_2\text{CHNH}_3\text{NO}_3$                            | -414                          | [59]              |

<sup>a</sup> Source of data as referenced by [58]: 1,2 = from the literature; 3 = calculated by applying constant nitrate difference (-117 J/mol) to known heat of formation of free amine in the liquid state; 4 = both heat of free amine and nitrate calculated by Freedman

Although MEAN is (was) widely used throughout the industry, literature data for its enthalpy of formation vary widely, as shown in Table 25. An additivity density functional theory (DFT) method predicted an enthalpy of formation of -3.40 kJ/g for crystalline MEAN, and the measured value was -3.75 kJ/g [59]. The heat of combustion at constant volume of MEAN is 901 kJ/mol = 215.4 kcal/mol [60].

**Table 25:** Enthalpy of formation of methylammonium nitrate.

| Enthalpy of formation |          |       |        | References |
|-----------------------|----------|-------|--------|------------|
| cal/g                 | kcal/mol | J/g   | kJ/mol |            |
| –900                  | –84.7    | –3767 | –354.4 | [58]       |
| –896                  | –84.3    | –3750 | –352.7 | [15]       |
| –896                  | –84.3    | –3750 | –352.7 | [59]       |
| –867                  | –81.6    | –3629 | –341.4 | [60]       |
| –856                  | –80.6    | –3582 | –337   | [14]       |

Note: Molecular mass: 94.07 g/mol = 10.6304 mol/kg

### Molecular Structure of Methylammonium Nitrate

The crystal and molecular structure of MEAN is orthorhombic, space group *Pcmm*,  $a = 6.414(4)$  Å,  $b = 6.581(4)$  Å, and  $c = 10.412(3)$  Å,  $Z = 4$  [61]. Hydrogen bonds exist between the cations and anions. Differential scanning calorimetry and vibrational studies indicated phase changes occurring at 355 and 245 K.

#### 2.2.1.2 Chemical Properties of Methylammonium Nitrate

The oxygen balance of MEAN is –34%, and the nitrogen content is 29.78%. As the salt of a strong acid and a weak base, MEAN hydrolyzes to an acidic (and therefore corrosive) solution when dissolved in water.

### Thermal Stability of Methylammonium Nitrate

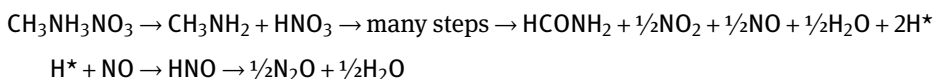
The thermal decomposition of the mono-, di-, and trimethyl-ammonium nitrates has been studied using DTA, thermogravimetric analysis (TGA), and mass spectral analysis (Figure 1) [56]. The decomposition temperature, the onset of exotherm, of these compounds at atmospheric pressure decreased in the order  $\text{CH}_3\text{NH}_3\text{NO}_3 > (\text{CH}_3)_2\text{NH}_2\text{NO}_3 > (\text{CH}_3)_3\text{NHNO}_3$ . The activation energies have been determined employing isothermal decomposition technique. Mass spectrometric investigation showed that the extent of decomposition increased with increasing substitution on the nitrogen atom, which can be explained by different C–N bond strengths.

DTA and mass spectrometry (MS) tests indicated that MEAN dissociates on heating to form methylamine and nitric acid, which then react further or decompose to form other compounds, including nitrogen oxides and nitrous acid [62]. Reaction products of nitrous acid and methylamine, such as nitromethane, are indicated in the mass spectra fragmentation profiles ( $m/e$  value of 61). A trace of hydrazoic acid was also detected. Methylamine, one of the dissociation products, is a flammable gas, and in the presence of nitrogen dioxide the auto-ignition temperature is lowered to 573 K (300 °C) or less. Rust or copper contamination will lower the auto-ignition temperature of the molten salt. Preventing acid buildup and rust formation is important for the safe handling and transport of monomethylamine nitrate.

Several types of experiments have indicated that MEAN dissociates into nitric acid and methylamine prior to decomposition. The major products at 473 K (200 °C) were H<sub>2</sub>O, NO<sub>2</sub>, NO, and N<sub>2</sub>. Other components present in smaller quantities were CH<sub>3</sub>NH<sub>2</sub>, CO, and N<sub>2</sub>O. At 573 K (300 °C) the formation of N<sub>2</sub>, NO, CO<sub>2</sub>, and N<sub>2</sub>O increased relative to NO<sub>2</sub>, CO, and H<sub>2</sub>O, and CH<sub>3</sub>NH<sub>2</sub> was no longer detectable.

The thermal reactivities of MEAN with oxidizing agents such as other nitrates, nitrites, perchlorates, and chlorates have been studied using DTA [63]. There were no oxidation–reduction reactions between MEAN and oxidizing agents, but the formation of unstable salts of methylamine was the most likely cause of the incompatibilities of the mixtures of MEAN and the other salts. Methylammonium nitrite, which is unstable even at room temperature, was formed by the reaction of MEAN and NaNO<sub>2</sub> or KNO<sub>2</sub>. Its presence as a contaminant in MEAN must be avoided. Similarly, methylammonium chlorate, formed from MEAN and NaClO<sub>3</sub> or KClO<sub>3</sub>, decomposed explosively at much lower temperature than MEAN or methylammonium perchlorate (MAP). Its presence as a contaminant in MAP must be avoided.

Another study of thermal decomposition of alkylammonium nitrates [12, 13] confirmed the dissociation of MEAN into nitric acid and methylamine, and a reaction mechanism was proposed as follows:



At higher temperatures the gaseous products detected by FTIR were CO<sub>2</sub>, N<sub>2</sub>O, HCN, NO, CO, and trace amounts of NH<sub>3</sub> and CH<sub>4</sub>. Hydrogen cyanide and methane make an abrupt appearance as soon as the temperature is increased from 513 to 553 K (240 to 280 °C).

The thermal decomposition of MEAN and the postulated intermediacy of methylnitramine, CH<sub>3</sub>NHNO<sub>2</sub>, or *aci*-methylnitramide in the decomposition of MEAN were reinvestigated [64]. If methylnitramine is an intermediate, the weakest bond (N–NO<sub>2</sub>) should break first.

The thermal decomposition of MEAN was studied because it is used in commercial water-gel explosives [65]. Because of its hygroscopic nature, MEAN crystals were placed in open pans in the differential scanning calorimeter and were first temperature-cycled to eliminate water to obtain accurate values for the solid–solid transition and the melting point. The exothermic behavior of MEAN was studied by isothermal and non-isothermal DSC in hermetic pans, by TGA, and also by accelerating rate calorimetry (ARC). The results were compared to those for AN and literature data on MEAN. Extrapolation of DSC data on the onset temperature of the exotherm yielded reasonable agreement with large-scale ARC tests, so the onset temperature can be considered a practical parameter for hazard analysis of these types of energetic materials.

Methylammonium nitrate is used for slurry explosives. It has been transported in the molten state, but several explosions of tank cars containing molten MEAN solutions have occurred in transit.

### 2.2.1.3 Safety Properties of Methylammonium Nitrate

For many decades, tank cars with molten MEAN were shipped across the United States. That changed when, on 6 August 1974, a tank car loaded with MEAN exploded while being pushed and bumped in a railroad switching yard in Wenatchee, Washington, killing two persons and injuring 66 others [66]:

Three tank-cars, owned by the Burlington Northern Railway (BNR), were en route from an E. I. du Pont de Nemours and Company chemical plant in Biwabik, Minnesota, to the company's explosives manufacturing facility in Dupont, Pierce County, Washington. The blast left a crater in the middle of the rail yard 80 feet long, 60 feet wide, and 35 feet deep, and all but leveled an area a half-mile-wide. The cars, double-walled with an inner stainless steel tank encased by a 10-inches of fiberglass insulation and an outer steel shell, each contained 10000 gallons of PR-M (monomethylamine nitrate), the company's designation for a sensitizing agent used to make Tovex, a new type of explosive gel used by the mining industry. The PR-M was shipped in an 85 percent aqueous solution, keeping the chemical stable and supposedly safe. The Department of Transportation (DOT) classified the product in solution as a 'flammable solid' whereas dry PR-M crystals were classified as a 'Class A explosive,' the same as dynamite. DuPont had been shipping the semi-solid chemical, under a special permit issued by DOT's Office of Hazardous Material, since 1968.

A few years later, on 4 July 1976, a storage tank with 60000 pounds of MEAN detonated at DuPont's Potomac River Works. Though there was no loss of life, there were many injuries and substantial loss of property. As a result, within 2 years DuPont moved out of the water-gel explosives business, but Tovex® is still used in other countries.

### 2.2.1.4 Explosive Performance of Methylammonium Nitrate

In the lead block test, MEAN gave an increase in the volume of the cavity of  $325 \text{ cm}^3/10 \text{ g}$ .

Tovex (other trade names are Trenchrite, Seismogel, and Seismopac) is a cap-sensitive water-gel explosive composed of ammonium nitrate and MEAN that has several advantages over traditional nitroglycerine/diatomaceous earth dynamite, including lower toxicity and safer manufacture, transport, and storage. Tovex is a 50/50 aqueous solution of AN and MEAN with gelling agents and stabilizers and sensitizers. It does not need a booster charge but will often be initiated by a network of strings of Detacord. It has thus almost entirely replaced dynamite. Tovex is used in quarries and by many international oil companies for seismic exploration.

### 2.2.1.5 Other Applications for Methylammonium Nitrates

An experimental liquid gun propellant, LP1776, was similar to NOS365, except IPAN had been replaced by trimethylammonium nitrate.

The U.S. Air Force Research Laboratory developed three monopropellants, RK-124A, RK-124B, and RK-916, that contained MEAN besides AN, hydrazine mononitrate (HN), and water.

Solutions of MEAN in hydrazine, for instance a 50%  $[\text{CH}_3\text{NH}_3]\text{NO}_3$  solution in hydrazine [67] or solutions of MEAN in mixtures of hydrazine and UDMH, were proposed as monopropellants or as hypergolic fuels for use with RFNA, WFNA, or fluorine as the oxidizer [68].

### 2.2.2 Alkylammonium Perchlorates

Substituted amine perchlorates have generated considerable interest since they can be used as auxiliary oxidizers and burning rate additives in composite solid propellants. However, these substituted perchlorates are quite sensitive to explosive stimuli such as impact and friction, thus restricting their use in practical propellant systems. It was shown that MAP is the most sensitive to impact and that the relative thermal stability increases with progressive substitution. The inductive effect of the methyl group is supposed to play a role in the thermal stabilization by increasing the electron density on the nitrogen, thereby making the proton transfer process more difficult. Activation energies increase with substitution up to trimethylammonium perchlorate. Tetramethylammonium perchlorate showed a different trend. This has been explained on the basis of the proton transfer dissociation mechanism, which cannot take place with four methyl substituents on nitrogen.

#### 2.2.2.1 Methylammonium Perchlorate

Methylammonium perchlorate, is also known as monomethylammonium perchlorate, methylamine perchlorate, methanamine perchlorate, aminomethane perchlorate,  $\text{H}_3\text{CN}^+\text{H}_3\text{NO}_3^-$ , MeAP, MAP, CAS RN [15875-44-2].

Many alkyl- and aryl-substituted ammonium perchlorates have been evaluated as oxidizers in solid propellants. These compounds have been reported to sublime and decompose at lower temperatures than the nitrates and were found to explode readily at higher temperatures, which is a safety hazard. These perchlorate salts are generally much more violent in their explosive behavior than nitrate salts. Some of them will explode in response to only slight shock or friction. Alkylammonium perchlorates can be prepared by reacting  $\text{HClO}_4$  with the appropriate amine in aqueous solution. Monomethylammonium perchlorate (MAP), dimethylammonium perchlorate (DMAP), and trimethylammonium perchlorate (TMAP) were prepared by titrating aqueous solutions of methyl-substituted amines with 70%  $\text{HClO}_4$  using methyl red as the indicator. The water was slowly evaporated until incipient crystallization.

MAP can be prepared by the **slow** addition of 24 mass-% aqueous methylamine solution to 71%  $\text{HClO}_4$  with stirring and cooling [69, 70]. MAP was recrystallized twice from ethanol. The low yield of 28% is due to the high solubility of MAP in water and ethanol. MAP can also be recrystallized from 2-propanol or from EtOH/chloroform 1 : 1.

MAP can also be prepared by the neutralization of an alcoholic solution of methylamine with aqueous perchloric acid, by bubbling methylamine gas into 70% perchloric acid and bubbling methylamine gas into perchloric acid in ethanol. Another way to prepare MAP is by reacting methylammonium chloride and other methylammonium salts with perchloric acid and driving off the hydrogen chloride.

But the safest and most convenient method was found to be the first one mentioned above, the **slow** addition of aqueous 24% methylamine solution to 71% perchloric acid.

### 2.2.2.2 Physical Properties of Methylammonium Perchlorate

The physical properties of MAP are summarized in Table 26.

**Table 26:** Physical properties of mono-, di-, tri-, and tetramethylammonium perchlorates.

| Compound name                          | Property                                     | SI units                       | At temperature, K | Other units | References |
|----------------------------------------|----------------------------------------------|--------------------------------|-------------------|-------------|------------|
| <b>Methylammonium perchlorate</b>      |                                              |                                |                   |             |            |
|                                        | Melting point                                | 528 K                          | —                 | 255 °C      |            |
|                                        | Density                                      | 1.65 g/cm <sup>3</sup>         | 293               | —           | [70, 71]   |
|                                        | Density, monoclinic/triclinic phase          | 1.72 ± 0.005 g/cm <sup>3</sup> | 293               | —           | [72]       |
|                                        | Density, tetragonal phase, XRD X-ray density | 1.58 g/cm <sup>3</sup>         | 350               | 77 °C       | [33]       |
|                                        | Density, tetragonal phase, pycnometric       | 1.56 g/cm <sup>3</sup>         | 345               | 72 °C       | [33]       |
| <b>Dimethylammonium perchlorate</b>    |                                              |                                |                   |             |            |
|                                        | Density                                      | 1.48 g/cm <sup>3</sup>         | 293               | 20 °C       | [70, 71]   |
| <b>Trimethylammonium perchlorate</b>   |                                              |                                |                   |             |            |
|                                        | Density                                      | 1.43 g/cm <sup>3</sup>         | 293               | 20 °C       | [70, 71]   |
|                                        | Density, monoclinic phase III                | 1.441 g/cm <sup>3</sup>        | 298               | 25 °C       | [34]       |
| <b>Tetramethylammonium perchlorate</b> |                                              |                                |                   |             |            |
|                                        | Density                                      | 1.35 g/cm <sup>3</sup>         | 298               | 25 °C       | [70, 71]   |

### 2.2.2.3 Crystal Structure and Phase Changes of Methylammonium Perchlorate

Methylammonium perchlorate undergoes several phase changes prior to melting at 528 K (255 °C). At room temperature it exists in the monoclinic/triclinic crystal form, above 321 K (48 °C) it exists in the tetragonal crystal form, and above 451 K (178 °C) it converts to a cubic crystal form. A crystallographic phase change at a little above 323 K causes a quite significant decrease in density. It decomposes slowly above the melting

point and deflagrates at 593 K (320 °C). The di- and trimethylammonium perchlorates also exist in several phases and undergo phase transitions before melting.

The thermal transformations that take place in solid methyl-substituted ammonium perchlorates were studied using high-temperature X-ray diffraction (XRD) and DTA [33, 34]. Ammonium perchlorate and tetramethylammonium perchlorate  $\text{N}(\text{CH}_3)_4\text{ClO}_4$  undergo one enantiomorphic phase transition (with decomposition), at 513 and 613 K (240 and 340 °C), respectively. This I-II transition is due to the beginning of the free rotation of the  $\text{ClO}_4^-$  ions. The free rotation of cations begins below room temperature. If the symmetry of the cation is lowered by having both methyl groups and hydrogen atoms arranged around the nitrogen, there is an additional enantiomorphic phase transition. This II-III transformation has been ascribed to the rotation of the cations, which have different moments of inertia. The properties of MAP and other amine perchlorates are summarized in Table 26.

The crystal structure of MAP is space group  $P2_1/n$ , and the cell parameters are  $a = 10.59 \text{ \AA}$ ,  $b = 7.67 \text{ \AA}$ ,  $c = 12.87 \text{ \AA}$ , and  $\beta = 101^\circ 26'$ ,  $Z = 2$  [73].

DTA of MAP revealed endothermic transitions from monoclinic to tetragonal at 322 K (49 °C), from tetragonal to cubic at 452 K (179 °C), melting at 527 K (254 °C), and ignition at 603 K (330 °C) [72].

The molecular structure of MAP can be clarified by selectively replacing hydrogen  $^1\text{H}$  in either the methyl group or the amino group with deuterium and measuring the nuclear magnetic resonance (NMR) spectra [74]. DSC data, the temperature dependence of  $^1\text{H}$  and D NMR line-shapes, and the spin-lattice relaxation times for  $\text{H}_3\text{CNH}_3\text{ClO}_4$ ,  $\text{D}_3\text{CNH}_3\text{ClO}_4$ , and  $\text{H}_3\text{CND}_3\text{ClO}_4$  confirmed the existence of three different phase modifications in  $\text{H}_3\text{CNH}_3\text{ClO}_4$  and its selectively deuterated analogs. In addition, they were used to identify the molecular motions occurring in the phases and to determine their activation parameters. In the low-temperature phase III, stable below 320 K, the  $\text{CH}_3$  and  $\text{NH}_3$  groups reorient themselves about their three-fold symmetry axes with different frequencies. In the intermediate-temperature phase II, at 320–451 K for  $\text{H}_3\text{CNH}_3\text{ClO}_4$  and  $\text{CD}_3\text{NH}_3\text{ClO}_4$  and 320 and 437 K for  $\text{H}_3\text{CND}_3\text{ClO}_4$ , the  $\text{H}_3\text{CN}^+\text{H}_3$  ions reorient themselves about an axis inclined at an angle of  $18^\circ$  to the C3 axis. In phase I, the  $\text{H}_3\text{CN}^+\text{H}_3$  ions undergo isotropic motion along with translational diffusion between different sites of the cubic unit cell.

A  $^{14}\text{N}$  and  $^{35}\text{Cl}$  double-resonance study of MAP showed that, contrary to the high-temperature phase transition being due to a change of molecular motion of the methylammonium cations, the low-temperature phase transition is triggered by a change of molecular dynamics of the perchlorate anions [75]. This could not be discovered without measuring the Cl quadrupole frequency of  $\text{ClO}_4^-$  ions in the solid state.

Static and magic-angle spinning (MAS)  $^{35}\text{Cl}$  NMR data of  $\text{ClO}_4^-$  ions in the low-, intermediate-, and high-temperature phases of  $\text{H}_3\text{CNH}_2^+\text{ClO}_4^-$  (MAP),  $(\text{H}_3\text{C})_2\text{NH}^+\text{ClO}_4^-$ , and  $(\text{H}_3\text{C})_3\text{N}^+\text{ClO}_4^-$  showed that solid–solid phase transitions are interrelated with the motional state of the  $\text{ClO}_4^-$  ions [76]. In the low-temperature phase III of  $(\text{H}_3\text{C})_3\text{N}^+\text{ClO}_4^-$  there is an anisotropic motion of the  $\text{ClO}_4^-$  ions with

a constant quadrupole frequency of 185 kHz and an increasing value of the asymmetry parameter when approaching phase transition III→II. The activation energy for this motion is 44.3 kJ/mol. At the transition III→II, the  $\text{ClO}_4^-$  ions gain orientational degrees of freedom manifested by the change of the quadrupole frequency to 159 kHz. In phase II the  $\text{ClO}_4^-$  ions start rotating, overcoming an energy barrier of 40.7 kJ/mol. In the low-temperature phase III of  $(\text{H}_3\text{C})_2\text{NH}^+\text{ClO}_4^-$  there are rigid  $\text{ClO}_4^-$  ions. At the phase transition III→II, the  $\text{ClO}_4^-$  ions gain considerable motional freedom, indicated by lowering the quadrupole frequency to 119 kHz, due to an anisotropic motion. In the high-temperature phase I, the anions undergo isotropic motion with an activation energy of 11.9 kJ/mol. The low-temperature phase III of MAP is characterized by rigid  $\text{ClO}_4^-$  ions. At the transition III→II, the  $\text{ClO}_4^-$  ions gain considerable motional freedom and undergo an axial motion in phase II. The motional behavior of the anions along with NMR data for the cations suggest that the low-temperature ordering of the ions in phase III is due to H bonds  $\text{N}-\text{H}\cdots\text{O}-\text{Cl}$ , the partial breaking of which, accompanied by the phase transition III→II, leads to an axial motion of the ions in phase II. A complete breaking of all H bonds in phase I allows the ions to reorient themselves isotropically. The quadrupole coupling constant of rigid  $\text{ClO}_4^-$  ions in this case is  $\sim 1$  MHz.

The temperature dependences of  $^1\text{H}$  NMR absorptions, the  $^1\text{H}$  spin-lattice relaxation time, and the  $^1\text{H}$  spin-spin relaxation time of MAP and its deuterated analog  $\text{CH}_3\text{ND}_3\text{ClO}_4$  were observed in the three solid phases existing over a wide range of temperatures [77]. In phase I, which is stable at temperatures greater than 451 K, the onset of the isotropic reorientation as well as the self-diffusion of the cations have an activation energy of 36 kJ/mol. In phase II, which is stable at 321–451 K, no remarkable change in the motional state of the cation was observed, but a dynamic orientational disorder of  $\text{ClO}_4^-$  anions was expected to occur. In phase III, which is stable below 321 K, the correlated reorientation (defined as the C3 reorientation of the cation having the rigid structure) was observed at lower temperatures, with very small activation energies of only 4.4 and 2.0 kJ/mol.

#### 2.2.2.4 Spectroscopic Properties of Methylammonium Perchlorate

Besides XRD, infrared (IR) spectra of MAP and other amine perchlorates were recorded to clarify structural changes during phase transitions. The IR spectra of amine perchlorates were measured in the solid state and in solution [78]. The appearance of vibrational bands in the solid-state spectra, which are absent in the spectra of the free ion in solution, was interpreted in terms of the lowering of symmetry that occurs when the ion is fixed in the crystal lattice.

The IR spectrum of MAP,  $d. 1.72 \pm 0.005 \text{ g/cm}^3$ , has absorbances at 920, 1067, 1106, 1420, 1460, 2954, 3070, 3127, 3276, and  $3349 \text{ cm}^{-1}$  [72].

A 1978 report on MAP contained details on methods for its preparation and data for solubility, hygroscopicity and IR spectra, thermal stability (DTA, TGA), and sensitivity to impact or friction [69]. This included IR spectra from  $4000$  to  $200 \text{ cm}^{-1}$  of



MAP, deuterated MAP, AP, and deuterated AP, with a list of IR absorption band assignments to fundamental vibrations in the molecule(s). The IR spectra of MAP were compared to those of AP, deuterated MAP, and methylammonium chloride. The MAP absorption band frequencies and assignments were compared to those published by other authors in the literature, and they agreed well with previously published data.

Studies of the temperature variation of the IR and Raman spectra of  $\text{H}_3\text{CNH}_3^+\text{ClO}_4^-$  at 298–460 K showed the presence of two structural phase transitions at 321 and 451 K [79]. The phase III  $\leftrightarrow$  II transition is a reaction of the first order. Phase I exhibits isotropic reorientational motion of the cations and anions.

IR and Raman spectra ( $10\text{--}5000\text{ cm}^{-1}$ ) of  $\text{CH}_3\text{NH}_3\text{ClO}_4$  and  $\text{CH}_3\text{ND}_3\text{ClO}_4$  were investigated at 90–470 K [80]. Assignments of the measured frequencies to the internal modes agreed with those of other investigators. The phase transitions at 321 and 451 K can be characterized based on the temperature dependence of widths and frequencies of prominent bands. In phase III (below 321 K), the cations and anions showed splittings due to non-equivalent sites. In phase II (between 321 and 451 K), the results showed the absence of non-equivalent sites and large motional freedom of the anion. In phase I (above 451 K), the cations and anions underwent isotropic reorientational motions.

#### 2.2.2.5 Solubility of Methylammonium Perchlorate

The solubility of MAP in water at 288 K (15 °C) is 110 g/100 mL and is six times that of AP. MAP was found to be slightly soluble in methyl acetate, 2-butanone (MEK), 1,4-epoxybutane (THF), and 1,4-dioxane. It was only very slightly soluble in ethyl acetate, butyl acetate, and acetic acid [69]. The solubility of MAP in water increased from 110 g/100 g at 263 K (–10 °C) to 250 g/100 g at 303 K (30 °C) [81].

#### 2.2.2.6 Hygroscopicity of Methylammonium Perchlorate

MAP is more hygroscopic than AP but not as hygroscopic as AN. The point of hygroscopicity of MAP varied from 84% relative humidity at 273 K (0 °C) to 59% at 313 K (40 °C) [81]. Minor amounts of  $(\text{CH}_3)_2\text{NH}\cdot\text{HClO}_4$  and  $\text{CH}_3\text{NH}_2\cdot\text{HCl}$  as contaminants in MAP adversely affected the hygroscopic properties of MAP.

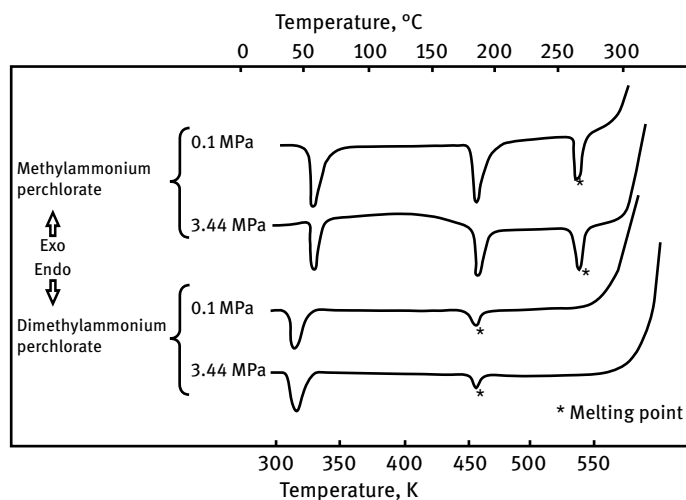
When MAP samples were placed in desiccators with constant humidity, there was no mass gain at 55, 66, or 70.4% relative humidity [69]. At 72.6% relative humidity, the sample had gained only 0.02% after 21 d. At 75% relative humidity, MAP is deliquescent. After 16 d it had increased in mass by 28%, and there was a thin layer of liquid in the dish. After 14 d the increase was 53%, and all the MAP was in solution. After 16 d the increase remained constant at 56%. At 88% relative humidity, the uptake of water became even greater: After 2 d, the increase in mass was 27%. The hygroscopic point is at 73% relative humidity.

### 2.2.2.7 Chemical Properties of Methylammonium Perchlorate

Methylammonium perchlorate has a slightly negative oxygen balance of  $-6.1\%$  and qualifies as an energetic material. However, it may be too sensitive to be used in the pure state.

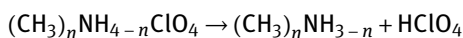
### 2.2.2.8 Thermal Stability of Methylammonium Perchlorate(s)

In DTA, the deflagration temperature of AP is lowered from 768 to  $\sim 583$  K (495 to  $\sim 310^\circ\text{C}$ ) by pressure or by metal catalysts at any pressure. In comparison, the deflagration temperature of MAP or DMAP ( $\sim 573$  K =  $\sim 300^\circ\text{C}$ ) was not significantly lowered by either pressure (Figure 2) or catalysts such as CuO-202. Although the deflagration temperatures of the methylamine perchlorates could not be lowered significantly, their decomposition could be stabilized by the same compounds that stabilize AP (e.g.,  $\text{NaH}_2\text{PO}_4$ ) [82].



**Figure 2:** Differential thermal analysis of methylammonium perchlorate and dimethylammonium perchlorate at 0.1 and 3.44 MPa (1 and 34 atm = 15 and 500 psi, respectively) at a heating rate of  $20^\circ\text{C}/\text{min}$ . (Reproduced and modified from [82].)

The thermal decompositions of the methyl-, dimethyl-, and trimethylammonium perchlorates have been studied over the temperature range 403–593 K ( $130$ – $320^\circ\text{C}$ ) by use of a time-of-flight mass spectrometer [83]. All three methyl-substituted amine salts decompose principally via



in addition to some heterogeneous decomposition. Perchloric acid, formed upon dissociation, appears to undergo limited decomposition to  $\text{ClO}_2$  and  $\text{HCl}$ .

Thermal decomposition of MAP as measured by TGA was initially noted at 533 K (260 °C), with 75% completion in 1 h at 573 K (300 °C) [72]. Holding at higher temperatures led to ignition. The activation energy for the decomposition reactions was 167 kJ/mol (40 kcal/mol). The addition of 5%  $\text{U}_2\text{O}_3$ ,  $\text{MnO}_2$ , or  $\text{Co}_2\text{O}_3$  markedly accelerated the decomposition, whereas  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$  were less effective.

The effect of particle size and loading density on the rate of decomposition of MAP was measured in comparison to that of AP for loading densities of 0.004–0.1 g/cm<sup>3</sup>, particle sizes 140 and 200 nm, and temperatures of 483–543 K (210–270 °C) [84]. At 493 K, the rate of MAP decomposition increased with decreasing particle size and decreased with increasing loading density. The initial stages of decomposition of MAP and AP were very similar. When heated rapidly, MAP exploded when the temperature reached 611 K (338 °C).

The thermal decomposition of MAP has been studied under isothermal and non-isothermal conditions using DTA [85]. The thermogram showed, in addition to the exotherm due to MAP decomposition, another exotherm at 408 °C, which was observed for the first time but was not confirmed by other investigators. The authors proved that this was due to the decomposition of AP, which had been formed as a decomposition product of MAP. It was suggested that a small fraction of the MAP decomposes via methyl group transfer to form ammonia and methyl perchlorate and that the ammonia then reacts with perchloric acid to form AP. This exotherm was not observed by other authors. Chemical analysis and the IR spectrum of the residue left behind after the decomposition proved it to contain  $\text{NH}_4\text{ClO}_4$ . The results were explained on the basis of a methyl group transfer in addition to proton transfer in the early phases of the decomposition process.

The explosive sensitivity of mono-, di-, and tri- methylammonium perchlorates has been investigated using DTA, TGA, mass spectrometry of pyrolysis products, and explosion delay measurements [86]. The thermal stability of these salts increases with the increase in the number of methyl groups. During thermal decomposition of methylammonium perchlorates, in addition to the proton transfer mechanism, occurrence of methyl group transfer has also been reported. The decomposition temperature of these compounds increased in the order  $\text{CH}_3\text{NH}_3\text{ClO}_4 > (\text{CH}_3)_2\text{NH}_2\text{ClO}_4 > (\text{CH}_3)_3\text{NHClO}_4$ . The activation energy showed the reverse trend, indicating that the stability increases with increasing substitution. Mass spectrometric analysis of decomposition products, however, suggested an increasing reactivity with increasing substitution. It was shown that explosion delay (when dropping samples onto a hot plate or into a heated glass tube) is correlated with thermal stability and impact sensitivity. The DTA trace of tetramethylammonium perchlorate did not show any endotherms or exotherms until the sample started to decompose at 623 K (350 °C).

In the DTA at three different heating rates (5, 10, and 20 °C/min), the first three endotherms showed up at 327, 456, and 534 K (54, 183, and 261 °C) [69]. The transitions are

1. monoclinic to tetragonal
2. tetragonal to cubic
3. melting at 534 K (261 °C)

When a melted sample was heated to 545 K (272 °C) and then allowed to cool, three exotherms appeared at the same temperatures as where the endotherms were observed during heat-up. The phase-change process is thus reversible. The DTA exotherm was between 609 and 612 K (336 and 339 °C), and that one is NOT reversible.

Comparing the thermal stability and strand-burning rates of the four methylammonium perchlorates with increasing numbers of methyl substituents to the properties of AP, it was concluded that a critical point was reached when the temperature of the crystal provided sufficient energy to allow free rotation of the  $\text{ClO}_4^-$  ions. For MAP, this temperature is 453 K (180 °C), compared with 513 K (240 °C) for AP. This free rotation (and phase change) leads to a reactivity that is reflected in lower DTA exotherms. Table 5, presented earlier, contains a summary of thermal stability data and other physical properties of several methyl-substituted amine nitrates.

A cold matrix isolation–IR spectroscopic technique showed that MAP vaporizes by dissociation: [87, 88]



The relative vaporization temperatures of ammonium and alkylammonium salts can be correlated with the  $\text{pK}_a$  values of the bases in aqueous solution.

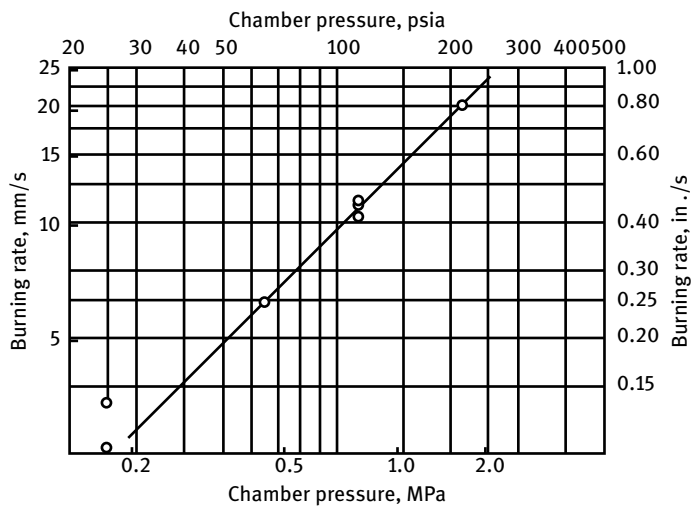
#### 2.2.2.9 Strand-Burning Rates of Methylammonium Perchlorate

Methylammonium perchlorate is a close relative of AP, differing from the latter only in the presence of a methyl group where a hydrogen atom used to be. The unusual difference between the two energetic salts is that the strand-burning rate of MAP is an order of magnitude higher than that of AP.

Pressed strands of MAP burn approximately ten times as fast as AP at 2.06 MPa (300 psi) and have a pressure exponent of approximately 1. The burning rate of MAP pellets pressed in a die at 82 MPa (12000 psi) is shown in Figure 3.

In another series of strand-burning tests with methylammonium perchlorates, where –40+50 mesh oxidizer powder was loaded into paper straws 6 mm in diameter at low bulk densities (40–50% that of the solid crystal), the burning rate of MAP was 2.5 times that of AP, while tetramethylammonium nitrate burned only half as fast as AP (Table 27) [70, 71, 89].

The strand-burning rate of MAP at 100–500 MPa was 10 times that of AP [90]. The range of pressures where stable combustion is obtained differed quite a bit, also. This phenomenon needed an explanation, and this is why burning rates of pressed MAP pellets have been extensively investigated, but the early results were sometimes quite contradictory. There was hope that MAP additions to AP might improve its burning behavior, both as a strand-burning oxidizer by itself and in propellant formulations.



**Figure 3:** Burning rate of pressed pellets of methylammonium perchlorate. (Reproduced and modified from [82].)

**Table 27:** Strand-burning rates of methylammonium perchlorates.

| Compound                      | Burning rate, cm/s | Bulk density, % of solid crystal density |
|-------------------------------|--------------------|------------------------------------------|
| Methylammonium perchlorate    | 0.103 ± 0.005      | 50                                       |
| Dimethylammonium perchlorate  | 0.132 ± 0.004      | 43                                       |
| Trimethylammonium perchlorate | 0.065 ± 0.013      | 45                                       |
| Trimethylammonium perchlorate | 0.111 ± 0.006      | 31                                       |
| Tetramethylammonium nitrate   | 0.022 ± 0.005      | 40                                       |
| For comparison:               |                    |                                          |
| Ammonium perchlorate          | 0.043 ± 0.002      | 51                                       |

Note: Burning rates at 101 kPa in paper straws 6 mm in diameter

Data source: [70,71]

MAP burning was stable starting at 2 atm, burning at a rate of 2.1 mm/s. In the intermediate range from 11 to 60 atm, the combustion was unstable and could not be sustained. At much higher pressures (up to 300 atm), the combustion stabilized again. Another study attempted to predict the burning rate based on a theory of similarity; the predicted burning rate at atmospheric pressure (if you could get it to burn at such a low pressure; the strand would probably need to be prewarmed or confined) would be 1.44 mm/s.

The burning rates of MAP were measured using strands of MAP powder pressed into Plexiglas tubes with diameters of 4, 5, 7, or 10 mm. The dependence of strand-burning rate on the initial strand temperature was tested from 293 to 443 K (20 to 170 °C) in the pressure regime from 1 to 40 atm [91]. The temperature coefficient was  $0.0044 \text{ K}^{-1}$ , and it decreased with increasing temperature. The burning rate of MAP is already higher than that of AP, and it may not be necessary to add a burning-rate catalyst. Nevertheless, a range of catalysts, typically added in the amount of 2%, was tested in the hope of allowing MAP to burn reproducibly over a wider pressure range. The effectiveness of catalysts decreased in the order  $\text{CuCr}_2\text{O}_4 > \text{V}_2\text{O}_5 > \text{Fe}_2\text{O}_3 > \text{SiO}_2$ . The addition of 3%  $\text{NH}_4\text{Cl}$  had a strong inhibiting effect.

In another effort to explain the difference in burning rates of MAP and AP, the burning surface temperature was measured using embedded capillary (10  $\mu\text{m}$ ) thermocouples (W5Re/W20Re). This allowed the measurement of the temperature profile in the combustion wave as it progressed through the strand (and eventually consumed the thermocouple) [92]. The salts were pressed into cartridges (7-mm inner-diameter [ID] Plexiglass tubes, bulk density  $d = 0.97 - 0.98 \text{ g/cm}^3$ ) and were burned in nitrogen in a constant pressure bomb at 1–54 atm. The temperature distribution in the condensed phase of the burning cartridges increased smoothly from room temperature to  $\sim 523 \text{ K}$  ( $\sim 250^\circ\text{C}$ ). The maximum combustion temperature was dependent on the pressure: At 1 atm the maximum temperature was 2253 K ( $1980^\circ\text{C}$ ), at 18 atm it was 2773 K ( $2500^\circ\text{C}$ ), and at 54 atm it was 2813 K ( $2540^\circ\text{C}$ ).

#### 2.2.2.10 Safety Properties of Methylammonium Perchlorate

The drop-weight impact sensitivity of AP, RDX, and MAP was measured on a U.S. Bureau of Mines (USBM) machine with 2-kg mass. The 50% fire point was 100, 33, and 20 cm, respectively. MAP is the most sensitive of the three explosives. For comparison, the drop-weight impact sensitivity of di-, tri-, and tetramethylammonium perchlorate is 22, 25, and 35 cm, respectively [33].

An accidental explosion occurred when MAP crystals that had settled from a saturated solution and were still covered by supernatant liquid were stirred with a rod [93].

Table 28 gives a comparison of the drop-weight sensitivities of several methylammonium perchlorates with increasing number of methyl groups in the molecule. The 50% fire point data were obtained on a USBM apparatus and were previously reported by Stammeler in an unidentified Aerojet report.

In a U-tube adiabatic compression sensitivity test apparatus with variable, pre-selected push pressure and constant bubble size, aqueous solutions containing 65% MAP or 70% ethylenediammonium(2+) diperchlorate could not be made to explode at the maximum energy input capability of the apparatus; this was much less sensitive than glycerol trinitrate or ethylene glycol dinitrate (EGDN) [94].

**Table 28:** Drop-weight impact sensitivities of methylammonium perchlorates.

| Compound name                   | Drop-weight impact sensitivities |            |                   |                         |               |                   |
|---------------------------------|----------------------------------|------------|-------------------|-------------------------|---------------|-------------------|
|                                 | in-lb                            |            |                   | m-kg                    |               |                   |
|                                 | No fire in<br>10 trials          | First fire | 50% fire<br>point | No fire in<br>10 trials | First<br>fire | 50% fire<br>point |
| Methylammonium perchlorate      | 18                               | 22         | 35                | 20.7                    | 25.3          | 40.3              |
| Dimethylammonium perchlorate    | 28                               | 32         | 38                | 32.2                    | 36.8          | 43.7              |
| Trimethylammonium perchlorate   | 32                               | 36         | 43                | 36.8                    | 41.4          | 49.5              |
| Tetramethylammonium perchlorate | —                                | —          | 61                | —                       | —             | 70.2              |
| For comparison:                 |                                  |            |                   |                         |               |                   |
| Ammonium perchlorate, ground    | —                                | 60         | —                 | —                       | 69            | —                 |
| Ammonium perchlorate, coarse    | —                                | 80         | 173               | —                       | 92            | 199               |

Data conversion: 1 in-lb = 2.54 cm-lb = 0.453 in-kg = 1.15 cm-kg

Data source: [70]

**2.2.2.11 Explosive Performance Properties of Methylammonium Perchlorate**

The Trauzl lead block indentation caused by MAP is 160% that of trinitrotoluene (TNT), or 470 cm<sup>3</sup>. The detonation velocity is 7540 m/s at 1.68 g/cm<sup>3</sup>, compared to 7665 m/s for tetryl under the same conditions. The detonation velocity is 6600 m/s at a lower packing density of 1.565 g/cm<sup>3</sup>.

The detonability of aqueous solutions of organic amine perchlorates was studied in steel and glass ampoules with an electric or intermediate hexogen detonator. The detonation temperature of aqueous solutions of MAP was 1740–1880 K, and the concentration limit of H<sub>2</sub>O below which the solutions retained their detonation capacity was 39%–42% H<sub>2</sub>O [95].

**2.2.2.12 Applications of Methylammonium Perchlorate**

There are many patents claiming the use of MAP in explosive formulations, either by itself or in combination with other explosives.

Because the material is so sensitive, it would be difficult to use it as a rocket propellant. Nevertheless, there are some patented propellant formulations in which MAP is supposed to give a performance advantage over other oxidizers [96].

### 2.2.3 Other Methylammonium Salts

Methylammonium dinitramide,  $[\text{H}_3\text{CNH}_3^+][\text{N}(\text{NO}_2)_2]^-$ , melts at 316–318 K (43–45 °C) [97]. The enthalpy of formation was measured as  $-121 \text{ kJ/mol}$  ( $-28.9 \text{ kcal/mol}$ ) [98]. The density of pressed methylammonium dinitramide pellets was  $1.53 \text{ g/cm}^3$ .

Methylammonium nitroformate, dimethylammonium nitroformate, and ethylenediammonium dinitroformate were prepared, and the crystal structures were examined by XRD, NMR, and Raman and IR spectroscopy, and the enthalpies of formation were predicted by computational chemistry [99]. All the nitroformate salts had higher predicted detonation pressures and velocities than TNT.

### 2.2.4 Dimethylammonium Salts

Dimethylamine is a stronger base than ammonia and forms salts with a wide range of acids. Salts of dimethylamine with oxidizing acids have explosive power and are potential propellant ingredients.

#### 2.2.4.1 Dimethylammonium Nitrate

Dimethylammonium nitrate,  $(\text{H}_3\text{C})_2\text{NHNO}_3$ , CAS RN [30781-73-8], is thermally more stable than the monomethylammonium nitrate. There are no known applications of this chemical as a rocket propellant.

#### 2.2.4.2 Physical Properties of Dimethylammonium Nitrate

The physical properties of dimethylammonium nitrate are summarized in Table 5. Dimethylammonium nitrate crystals are composed of discrete cations and anions that are connected by classical  $\text{N}-\text{H}\cdots\text{O}$  bonds. Geometric parameters are in the usual ranges [100].

#### 2.2.4.3 Thermal Stability of Dimethylammonium Nitrate

The thermal decomposition of mono-, di-, and trimethyl-ammonium nitrates has been examined using DTA, TGA, and MS methods [56]. The decomposition temperature of these compounds decreased in the sequence  $\text{CH}_3\text{NH}_3\text{NO}_3 > (\text{CH}_3)_2\text{NH}_2\text{NO}_3 > (\text{CH}_3)_3\text{NHNO}_3$ . The activation energies have been determined by employing an isothermal decomposition technique. Mass spectrometric investigation showed that the rate of decomposition increased with increasing substitution on the nitrogen atom.

#### 2.2.4.4 Dimethylammonium Perchlorate

Dimethylammonium perchlorate,  $(\text{H}_3\text{C})_2\text{NHClO}_4$ , CAS RN [14488-49-4], is thermally more stable than the monomethylammonium perchlorate. There are no known applications of this chemical as a rocket propellant.



### 2.2.4.5 Physical Properties of Dimethylammonium Perchlorate

Differential scanning calorimetric data revealed the existence of three different phase modifications in dimethylammonium perchlorate, analogous to those observed in mono- and trimethylammonium perchlorate. An analysis of the NMR data, the temperature dependence of proton and deuteron line shapes, and spin-lattice relaxation times reported for  $(\text{CH}_3)_2\text{NH}_2\text{ClO}_4$  and its selectively deuterated analog  $(\text{CH}_3)_2\text{ND}_2\text{ClO}_4$  enabled identification of the molecular motions occurring in the respective phases and determination of their activation parameters [101]. In the low-temperature phase III, which is stable below 309 K, there are two non-equivalent dimethylammonium cations that manifest themselves by different reorientation frequencies of methyl groups about their threefold symmetry axes  $C_3$  and by reorientation of one of the two inequivalent cations about its pseudo-threefold symmetry axis  $C'_3$  lying along one of the two N—D bonds. The intermediate phase II had not been reported previously. It was found to be stable in the temperature range 309–311 K, but it can easily be undercooled below 290 K. There is a large entropy change of  $25.5 \text{ J mol}^{-1} \text{ K}^{-1}$  associated with the III→II transition, which indicates that the  $\text{ClO}_4^-$  ions in phase II have considerable motional freedom, presumably due to breaking of N—H...O hydrogen bonds.

A temperature-dependent study of the widths and frequencies of prominent Raman and IR spectra ( $20\text{--}5000 \text{ cm}^{-1}$ ) of  $(\text{CH}_3)_2\text{NH}_2\text{ClO}_4$  and its N-deuterated analog at 90–350 K confirmed the existence of phase transitions at 309 and 311 K [102]. In the high-temperature phases II and I, the cations and anions undergo reorientational motions.

Table 11 (presented previously) contains a summary of the physical properties of dimethylammonium perchlorate.

### 2.2.5 Trimethylammonium Salts

#### 2.2.5.1 Trimethylammonium Nitrate

Trimethylammonium nitrate, CAS RN [25238-43-1], shows two solid-state phase transformations, one at 359 K (86 °C) and one at 409 K (136 °C). The liquid gun propellant LP1776 is (was) a solution of 60% HAN and 20% trimethylammonium nitrate in water.

**Table 29:** Thermodynamic properties of trimethylammonium nitrate.

| Compound name             | Gross formula                                 | Enthalpy of formation |          |       |       | References    |
|---------------------------|-----------------------------------------------|-----------------------|----------|-------|-------|---------------|
|                           |                                               | kJ/mol                | kcal/mol | J/g   | cal/g |               |
| Trimethylammonium nitrate | $\text{C}_3\text{H}_{10}\text{N}_2\text{O}_3$ | –305.7                | –73      | –2503 | –598  | [103], p. 380 |
|                           |                                               | –343.8                | –82.2    | –2815 | –673  | [15], p. 345  |
|                           |                                               | –346.4                | –82.8    | –2837 | –678  | [27]          |

$$M = 122.12 \text{ g/mol} = 8.189 \text{ mol/kg}$$

There is quite a discrepancy in the enthalpies of formation reported for trimethylammonium nitrate in the third and sixth editions of the Meyer-Koehler-Homburg text *Explosives* (Table 29). It is assumed that the more recent value is the more reliable one.

### 2.2.5.2 Trimethylammonium Perchlorate

Trimethylammonium perchlorate, CAS RN [15576-35-9], has been tested as an additive to AP, and the burning rates of compressed pellets of AP and trimethylammonium perchlorate were measured in a strand burner [104]. A mixture containing 80% trimethylammonium perchlorate had the highest burning rate. Table 11 contains a summary of the physical properties of trimethylammonium perchlorate.

### 2.2.5.3 Trimethylammonium Dinitramide

Trimethylammonium dinitramide,  $[\text{HN}^+(\text{CH}_3)_3][\text{N}^-(\text{NO}_2)_2]$ ,  $\text{C}_3\text{H}_{10}\text{N}_4\text{O}_4$ , CAS RN [165603-94-1], is an energetic salt with a low melting point.

## 2.2.6 Quaternary Tetramethylammonium Salts

There are several tetramethylammonium salts with oxidizing anions that are of interest as fuels for  $\text{HNO}_3$ -based monopropellants or as additives to trimethylamine as a fuel. This includes nitrates, perchlorates, azides, and the fluorohalogenates [105].

### 2.2.6.1 Tetramethylammonium Nitrate

Tetramethylammonium nitrate,  $\text{C}_4\text{H}_{12}\text{N}_2\text{O}_3$ , TeMAN, CAS RN [1941-24-8], is the quaternary salt of trimethylamine and can be prepared by metathetical reaction of tetramethylammonium bromide (or iodide) with silver nitrate. Quaternary alkylammonium salts are relatively stable to further oxidation. Therefore, some monopropellants have been formulated by dissolving quaternary ammonium salts in concentrated nitric acid (CAVEA; see *Encyclopedia of Monopropellants*, chapter “Nitric Acid or Perchloric Acid-Based Monopropellants”). The physical properties of tetramethylammonium nitrate are summarized in Table 30.

**Table 30:** Physical properties of tetramethylammonium nitrate.

| Property                                 | SI units               |               | Other units    |              | References   |
|------------------------------------------|------------------------|---------------|----------------|--------------|--------------|
| Molecular mass                           | 136.15 g/mol           | 7.345 mol/kg  | —              | —            |              |
| Density at 293 K                         | 1.30 g/cm <sup>3</sup> | —             | —              | —            | [106]        |
| Enthalpy of formation $\Delta H_f^{298}$ | −341.5 kJ/mol          | −2507.3 kJ/kg | −81.6 kcal/mol | −599.3 cal/g | [15], p. 305 |
|                                          | −331.8                 | −2437 kJ/kg   | −79.3 kcal/mol | −582.5 cal/g | [16]         |
|                                          | ± 0.1 kJ/mol           |               |                |              |              |
|                                          | −355.5 kJ/mol          | −2611 kJ/kg   | −85.0 kcal/mol | −624 cal/g   | [27]         |

The standard enthalpy of formation of crystalline tetramethylammonium nitrate is  $-331.8 \pm 0.1$  kJ/mol [16]. That of the corresponding crystalline tetramethylammonium azide is  $+150.1 \pm 1.0$  kJ/mol.

The mechanism of thermal decomposition of tetramethylammonium nitrate was studied using TGA and MS [107]. The first step of the decomposition is the dissociation of the salt into trimethylamine and methyl nitrate. The activation energy was 368 kJ/mol (88 kcal/mol), which is close to the dissociation energy of a N—CH<sub>3</sub> bond. The rate-determining step in the dissociation process appears to be the transfer of a methyl group. In air, at atmospheric pressure the DTA of TeMAN showed an overall exotherm at 373 °C, indicating the predominance of decomposition rather than dissociation (sublimation step). The kinetics of thermal decomposition in solid state in air was studied by several methods. The measured activation energies varied between 343 and 368 kJ/mol (82 kcal/mol and 88 kcal/mol) depending on the method used.

A high-pressure FTIR study of tetramethylammonium nitrate at up to 50 kbar using a diamond anvil cell in the frequency region 4000–400 cm<sup>-1</sup> showed that in the high-pressure phase above 30 kbar, both cation and anion bands underwent drastic changes in position, band width, and intensity [108]. Pressure-induced phase transitions were caused by the distortion of the cations and anions with increased disorder and symmetry variations.

Tetramethylammonium nitrate is not as detonable as the lower members of this series of alkylammonium salts. After three recrystallizations from water, the melting point of tetramethyl ammonium nitrate (TMA) was 683 K (410 °C), and the crystal density was 1.25 g/cm<sup>3</sup>. After the powder was compressed at 3400 kg<sub>f</sub>/cm<sup>2</sup>, the pellet density was 1.22 g/cm<sup>3</sup>. Pure TMA had essentially no explosive properties [106]. It is thermally stable and cannot be detonated by impact or by initiation with a pentaerithritol tetranitrate (PETN) booster. TMA is less hygroscopic than AN, although mixtures with AN are more hygroscopic. A eutectic consisting of 25% TMA and 75% AN melted at 411 K (138 °C). The zero-oxygen balance mixture (13.4% TMA+86.6% NH<sub>4</sub>NO<sub>3</sub>) could be detonated with 1.5 g Hg fulminate as the initiator, while the eutectic required 2.0 g. Compressing powder of the zero-balance mixture gave the following pellet properties: pressure (kg<sub>f</sub>/cm<sup>2</sup>), density (g/cm<sup>3</sup>) 170, 1.35; 340, 1.49; 680, 1.58; 3400, 1.60. The detonation velocity (m/s) as a function of density (g/cm<sup>3</sup>) was 3130, 0.90; 3020, 1.0; failure at 1.1. In the lead block test, this mixture caused an indentation 112% of the power of picric acid. It was detonated by impact with a 10-kg weight falling 3 m in 20% of the trials.

### 2.2.6.2 Tetramethylammonium Perchlorate

Tetramethylammonium perchlorate, C<sub>4</sub>H<sub>12</sub>N<sub>1</sub>ClO<sub>4</sub>, TeMAP, CAS RN [2537-36-2], is the quaternary salt of trimethylamine and can be prepared by metathetical reaction of tetramethylammonium bromide (or iodide) with silver perchlorate. Quaternary alkylammonium salts are relatively stable to further oxidation. The effect of TeMAP on the thermal decomposition and strand-burning rate of AP has been investigated and was

found to be quite different from the effect of MAP or DMAP. TeMAP deflagrates in DTA between 653 and 683 K (380 and 410 °C), and this temperature is not significantly affected by pressure, catalysts, or basic additives [82]. The data suggest the possibility of a direct exothermic oxidation of the substituted ammonium ion by the perchlorate ion.

Co-crystallizing AP with TeMAP will enhance the burning rate of composite solid propellants made with the modified AP/TeMAP oxidizer [109, 110].

The decomposition of TeMAN and TeMAP in the presence of small amounts of chromium(VI) trioxide was analyzed using DTA and TGA, and it was revealed that  $\text{CrO}_3$  does have a sensitizing effect on the thermal decomposition of these salts [111].

Table 30 (presented previously) contains a summary of physical properties of TeMAP. Crystals of TeMAP are tetragonal with  $a = 8.343 \pm 0.002 \text{ \AA}$  and  $c = 5.982 \text{ \AA}$  [112]. The space group is  $P4/nmm$  with  $Z = 2$ . The  $(\text{CH}_3)_4\text{N}^+$  ions conform very closely to the symmetry of a regular tetrahedron, with  $r \text{ C-N} = 1.470 \pm 0.014 \text{ \AA}$  and  $\angle \text{C-N-C}$  angles of 109.4 and 109.5°.

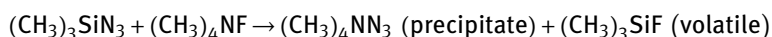
In the room-temperature phase of TeMAP, the  $\text{ClO}_4^-$  ions are disordered, with four possible equivalent orientations. There is an order-disorder transition at 170 K, revealed by heat capacity and low-temperature XRD structure determinations [113]. *Ab initio* calculations of the electrostatic intermolecular interaction suggested an almost two-dimensional (2D) system. Monte Carlo simulations for 2D and three-dimensional (3D) interaction schemes showed that the 3D scheme agreed better with the experimental data.

Single-crystal XRD structure determinations of the low-temperature crystal structures of TeMAP at 210 K gave space group  $P4/nmm$ , with  $a_1 = 8.2376(14)$ ,  $c_1 = 5.8256(12) \text{ \AA}$ , and  $Z = 2$  [114]. Below  $T_c = 170 \text{ K}$ , these groups ordered in four sublattices, with each ion gradually choosing one unique orientation. The low-temperature modification crystallized in the orthorhombic space group  $P2_12_12$ , with  $a_3 = 11.714(3) \text{ \AA}$ ,  $b_3 = 11.784(3) \text{ \AA}$ ,  $c_3 = 5.8265(9) \text{ \AA}$ , and  $Z = 4$ . The structural models and the phase transitions were explained from electrostatic octopole-octopole interactions among the  $\text{ClO}_4^-$  groups within layers perpendicular to the c-axis.

### 2.2.6.3 Tetramethylammonium Azide

Tetramethylammonium azide,  $\text{N}(\text{CH}_3)_4 \text{N}_3$ , can be dissolved in trimethylamine to improve the performance of this amine as a rocket fuel and to make it easier to handle by lowering its vapor pressure. It is also used in the synthesis of other energetic azides. It can be prepared by reaction of trimethylsilylazide with tetramethylammonium fluoride in acetonitrile [115, 116]:

$\text{CH}_3\text{CN}$  as the solvent



Earlier methods for preparation of  $\text{N}(\text{CH}_3)_4 \text{N}_3$  required the use of shock-sensitive starting materials, i.e.,  $\text{AgN}_3$  or  $\text{HN}_3$ . The new method allows preparation of azides with high purity, at room temperature, and without the use of shock-sensitive materials.

The standard enthalpy of formation of crystalline tetramethylammonium azide is  $+150.1 \pm 1.0 \text{ kJ/mol}$  [16]. The positive enthalpy of formation should make it a good propellant additive.

#### 2.2.6.4 Tetramethylammonium Dinitramide

The enthalpy of formation of tetramethylammonium dinitramide,  $[\text{N}(\text{CH}_3)_4][\text{N}(\text{NO}_2)_2]$ , CAS RN [140456-75-3], is  $-103.3 \pm 1.1 \text{ kJ/mol}$  ( $-24.7 \pm 0.26 \text{ kcal/mol}$ ) [117]. Other sources reported an enthalpy of formation for tetramethylammonium dinitramide of  $-191 \text{ kJ/mol}$  ( $-45.6 \text{ kcal/mol}$ ) [98]. Tetramethylammonium dinitramide melts at  $507\text{--}511 \text{ K}$  ( $234\text{--}238^\circ\text{C}$ ) [97]. The density of a pressed pellet of tetramethylammonium dinitramide is  $1.22 \text{ g/cm}^3$ .

#### 2.2.6.5 Tetramethylammonium Halogenides and Halogenates

The tetramethylammonium cation is stable enough to survive reaction with trifluorobromates and trifluoroiodates, forming stable salts that are nevertheless very energetic and potentially explosive [105].

### 3 Ethylamines

There are three ethylamines, and all three are potentially useful as rocket propellants, more so than the corresponding methylamines:

|                                              |                                     |                   |
|----------------------------------------------|-------------------------------------|-------------------|
| Ethylamine (sometimes called monoethylamine) | $\text{C}_2\text{H}_5\text{NH}_2$   | CAS RN [75-04-7]  |
| Diethylamine                                 | $(\text{C}_2\text{H}_5)_2\text{NH}$ | CAS RN [109-89-7] |
| Triethylamine                                | $(\text{C}_2\text{H}_5)_3\text{N}$  | CAS RN [121-44-8] |

In addition, substitution at the ends of the ethyl group in ethylamine molecules by amino groups, hydroxyl groups, hydrazido groups, cyano groups, or azido groups will improve the water solubility; lower the freezing point; and, in the case of hydrazido, cyano, and azido groups, improve the rocket performance of ethylamines as fuels. Several such substituted ethylamines are described in later sections of this book.

#### 3.1 Production of Ethylamines

The production of ethylamines by reaction of ethanol or ethylene with ammonia under pressure results in a mixture of the primary, secondary, and tertiary ethylamines, which must be separated by fractionated distillation in a distillation column. Because mono- and triethylamine do not have the same market demand as diethylamine, they

are sometimes recycled into the reaction chamber. Diethylamine can thus be obtained in 90% yield.

### 3.2 Physical Properties of Ethylamines

Ethylamine (monoethylamine) boils just below room temperature, so it can be stored as a liquid at room temperature under slight overpressure or in a refrigerator. The other two ethylamines are liquids at room temperature. The physical properties of ethylamines are summarized in Table 31.

**Table 31:** Physical properties of ethylamines.

| Property                               | Unit                   | Ethylamine<br>$\text{C}_2\text{H}_5\text{NH}_2$ | Diethylamine<br>$(\text{C}_2\text{H}_5)_2\text{NH}$ | Triethylamine<br>$(\text{C}_2\text{H}_5)_3\text{N}$ |
|----------------------------------------|------------------------|-------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|
| Freezing point                         | K                      | 192                                             | 223                                                 | 158.3                                               |
|                                        | °C                     | −81.0                                           | −50                                                 | −114.8                                              |
| Boiling point                          | K                      | 289.7                                           | 328.6                                               | 362.6                                               |
|                                        | °C                     | 16.6                                            | 55.5                                                | 89.5                                                |
| Vapor pressure at 298 K                | kPa                    | 140.9                                           | 33.3                                                | 7.6                                                 |
|                                        |                        | 1.39 atm                                        | 250 mm Hg                                           | 57 mm Hg                                            |
| Density (at °C)                        | $\text{g}/\text{cm}^3$ | 0.7059 (0 °C)                                   | 0.7094 (15 °C)                                      | 0.729 (20 °C)                                       |
| Density (at °C)                        | $\text{g}/\text{cm}^3$ | 0.6890 (15 °C)                                  | —                                                   | 0.723 (25 °C)                                       |
| Viscosity (at °C)                      | cPs                    | —                                               | 0.35 (25 °C)                                        | —                                                   |
| Viscosity (at °C)                      | cPs                    | 0.4368 (−33 °C)                                 | —                                                   | 0.347 (25 °C)                                       |
| Viscosity (at °C)                      | cPs                    | —                                               | —                                                   | 1.18 (−40 °C)                                       |
| Surface tension                        |                        | 19.2 dyn/cm                                     | 16.3 dyn/cm                                         | —                                                   |
| Standard enthalpy of formation, liquid | kJ/mol                 | −88.7                                           | −125.9                                              | −154.8                                              |
|                                        | kcal/mol               | −21.2                                           | −30.1                                               | −37                                                 |
| Heat of combustion, liquid             | kJ/mol                 | 1709                                            | 3024                                                | 4339                                                |
|                                        | kcal/mol               | 408.5                                           | 722.8                                               | 1037                                                |
| Enthalpy of vaporization               | kJ/mol                 | 28.0                                            | 27.86                                               | —                                                   |
|                                        | kcal/mol               | 6.70                                            | 6.66                                                | —                                                   |

Data source: [118]

The vapor pressure of ethylamine can be calculated from the Antoine equation

$$\ln p_{\text{sat}} = A - B/(T + C)$$

where  $p_{\text{sat}}$  is the saturation pressure in kPa,  $T$  is the temperature in kelvin,  $A = 6.1203$ ,  $B = 964.494$ , and  $C = -55.34$  for the pressure range 20–200 kPa.

Of all the amines in this chapter, triethylamine is the one most frequently used as rocket fuel. For this reason, we have assembled additional data on its physical properties in Table 32. These properties listed in Table 32 may or may not match the older data listed in Table 31.

**Table 32:** Physical properties of triethylamine.

| Property                                         | SI units                                                | Other units                                               | References |
|--------------------------------------------------|---------------------------------------------------------|-----------------------------------------------------------|------------|
| Molecular mass                                   | 101.190 g/mol                                           | 9.88 mol/kg                                               | [29]       |
| Freezing point                                   | 158.45 K                                                | −114.7 °C                                                 | [29]       |
| Boiling point                                    | 362.3 ± 0.6 K                                           | +89.2 ± 0.6 °C                                            | [29]       |
| Density at 298 K                                 | 0.723 g/cm <sup>3</sup>                                 | 45.12 lb/ft <sup>3</sup>                                  | [119]      |
| Viscosity at 298 K                               | 0.51 mPa s                                              | 0.51 cPs                                                  | [119]      |
| Thermal conductivity                             | 1209 J cm <sup>−1</sup> s <sup>−1</sup> K <sup>−1</sup> | 289 cal cm <sup>−1</sup> s <sup>−1</sup> °C <sup>−1</sup> | [120]      |
| Critical temperature                             | 535.6 ± 0.3 K                                           | 262.5 ± 0.3 °C                                            | [29]       |
| Critical pressure                                | 30 atm                                                  | 440.9 psia                                                | [119]      |
| Critical density                                 | 2.54 mol/L                                              | 0.257 g/cm <sup>3</sup>                                   | [29]       |
| Heat capacity, vapor, at 298 K                   | 161 J mol <sup>−1</sup> K <sup>−1</sup>                 | 38.46 cal mol <sup>−1</sup> °C <sup>−1</sup>              | [17]       |
| Heat capacity, liquid, at 298 K                  | 216.43 J mol <sup>−1</sup> K <sup>−1</sup>              | 51.7 cal mol <sup>−1</sup> °C <sup>−1</sup>               | [29]       |
| Enthalpy of formation, ideal gas, at 298 K       | −99.6 kJ/mol                                            | −23.8 kcal/mol                                            | [17]       |
| Enthalpy of formation, vapor, at 298 K           | −134.1 kJ/mol                                           | −32.05 kcal/mol                                           | [29, 121]  |
|                                                  | −92.9 ± 0.5 kJ/mol                                      | −22.2 ± 0.1 kcal/mol                                      | [29]       |
| Enthalpy of formation, liquid, at 298 K          | −169 kJ/mol                                             | −40.4 kcal/mol                                            | [29, 121]  |
|                                                  | −127.8 ± 0.54 kJ/mol                                    | −30.5 ± 0.1 kcal/mol                                      | [29]       |
|                                                  | −282 kJ/mol                                             | −667 cal/g                                                | [27]       |
|                                                  | −169 kJ/mol                                             | −400 cal/g                                                | [27]       |
| Enthalpy of vaporization at normal boiling point | 31.01 kJ/mol                                            | 7.41 kcal/mol                                             | [29]       |
| Index of refraction $n_D^{20}$                   | 1.40032                                                 | —                                                         | [119]      |

Both PEPCODED.DAT [27] and NIST [29] display a disparity in three sets of data from the literature for the enthalpy of formation of liquid triethylamine that has not yet been resolved.

The heat of vaporization of triethylamine in the range of 298 to 352 K can be calculated from the equation

$$\Delta H_{\text{vap}} = 50.32 \exp(0.2684 \times T_r)(1 - T_r)^{0.2684}$$

where  $\Delta H_{\text{vap}}$  is the heat of vaporization in kJ/mol and  $T_r$  is the reduced temperature, which is the quotient of the temperature (in kelvin) and the critical temperature, which is 535.6 K.

The vapor pressure of triethylamine in the range of 323 to 367 K can be calculated from the equation

$$\log 10(P) = 2.98368 - [695.814/(T - 128.271)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

### 3.3 Chemical Properties of Ethylamines

Ethylamines are thermally stable and react hypergolically with most types of nitric acid. The ethylamine most frequently used as rocket fuel is triethylamine. Ethylamines would auto-oxidize slowly. The main concern during exposure of any amine to air is the uptake of carbon dioxide. Some (less volatile) amines are used in the chemical and natural gas industry for removal of carbon dioxide and hydrogen sulfide from sour gas process streams.

For occasional instant spot checks of triethylamine vapor concentration in the air at the workplace, the easiest method is with gas-detection tubes that contain an indicator supported on a granular material that changes color when exposed to ammonia. Such tubes are available from Draeger, MSA, Kitagawa, and other suppliers. Gas-detection tubes are sensitive to as little as 5 ppm  $(\text{C}_2\text{H}_5)_3\text{N}$  and can measure up to 60 ppm  $(\text{C}_2\text{H}_5)_3\text{N}$  with ten strokes [122].

### 3.4 Handling of Ethylamines

Due to their lower vapor pressure, ethylamines are easier to handle than methylamines. Protective clothing to be worn when handling ethylamines under pressure includes gloves, goggles, and aprons. Ethylamines must be handled as flammable liquids. The lower flammable limit of ethylamine in air is 3.5 vol-%, and the auto-ignition temperature is 658 K (385 °C). The flammable range of diethylamine in air is 1.8–10 vol-%. The flammable range of triethylamine is 1.2–8 vol-%. One must avoid spills and remove any potential sources of ignition.



### 3.5 Toxic Properties of Ethylamines

The fishy odor of ethylamines is very similar to that of methylamines, and may be even a little fishier than those. The obnoxious odor is sufficient warning to stay away from ethylamine(s) vapors.

As of 2005, the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) time-weighted average (TWA) for diethylamine was 10 ppm (30 mg/m<sup>3</sup>), with a short-term excursion allowance of 25 ppm (75 mg/m<sup>3</sup>), and the U.S. Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) TWA was also 25 ppm (75 mg/m<sup>3</sup>). The original NIOSH immediately dangerous to life or health (IDLH) limit for diethylamine was 2000 ppm, but it was lowered by one order of magnitude to 200 ppm because of safety considerations a few years later. The threshold limit value (TLV) TWA for triethylamine is 1 ppm, and the short-term exposure limit (STEL; ceiling) is 3 ppm.

As of 2005, no REL had been established for triethylamine. The 1994 OSHA PEL TWA for triethylamine was 25 ppm (100 mg/m<sup>3</sup>), which was an increase from the 1989 value of 10 ppm. The 1993–1994 American Conference of Governmental Industrial Hygienists (ACGIH) TLV TWA was 5 ppm (12 mg/m<sup>3</sup>), and it was 15 ppm (36 mg/m<sup>3</sup>) for a short-term excursion STEL. The original NIOSH (Standard Completion Program) IDLH was 1000 ppm, but that was lowered to 200 ppm based on acute inhalation toxicity data in animals. The chosen IDLH was based on a report that a 4-h exposure to 1000 ppm triethylamine killed one of six rats.

### 3.6 Propellant Mixtures with Ethylamines

A hypergolic fuel mixture consisting of 50 mass-% triethylamine and 50 mass-% xylylidine with the code name of Tonka 250 was used in Germany during World War II in missiles developed by BMW; it had the code name TX-1 used by SEPR in France and was later used under the code name Samin (Samine) for several different missiles in Russia (USSR) [123]. At the end of the Cold War, large quantities of this material had to be demilitarized in compliance with the Strategic Arms Limitation Talks (SALT) disarmament agreements [124]. Unfortunately, the storage conditions were not carefully controlled, and some of the mixture had already leaked into the ground. The abandoned storage magazines constituted a hazard to the surrounding communities [125]. Various weapon systems were using the Samin fuel blend and had to be demilitarized [126].

At one time, 290 metric tons of Samin (TG-02) were stored at the Mingachevir depot in Azerbaijan, waiting for disposal. Color pictures of the unsafe conditions at the neglected storage sites are shown on page 19 of the Winkelmann thesis [127]. Where the fuel had leaked into the ground, it had formed a reddish-brown layer of xylylidine auto-

oxidation products that was sometimes revealed only if the sand drifts were scraped and moved to the side.

Several different methods were evaluated for not only disposing of but also converting the abandoned and unwanted rocket propellants, including Samin and Melanj, into commercially useful products, such as fertilizer or plastics [128–131].

The storage stability of Samin depends significantly on fuel oxidation with the air trapped in the storage tanks. Intuitively, one would guess that xylidine is more susceptible to auto-oxidation than triethylamine. Thus, it is unclear why a reduction of the triethylamine concentration (and not the xylidine concentration) from 50.2 mass-% to less than 48% was defined as the end of shelf life of the propellant. After experimental data were obtained from accelerated storage stability tests, the shelf life of Samin was estimated using the Arrhenius equation [132]. According to the kinetic studies, the oxidation reaction of the amine was a zero-order reaction, and the shelf lives of Samin in stainless-steel tanks at 293, 298, and 303 K (20, 25, and 30 °C) were 5.7, 3.7, and 2.4 years, respectively. Use of an inert gas such as nitrogen would extend the storage life. Similar results were obtained with the Berthelot equation [133].

### 3.7 Ethylammonium Salts

#### 3.7.1 Mono-, Di-, and Triethylammonium Nitrates

Ethylammonium nitrate, 1-ethylammonium nitrate; ethanamine, nitrate (1:1);  $\text{H}_3\text{C}-\text{CH}_2-\text{NH}_3^+\text{NO}_3^-$ , CAS RN [22113-86-6]; EAN, has found only a few applications in rocket propellants. At one time it was considered as a fuel in HAN-based mono-propellants. A significant property of ethylammonium nitrate is its very low melting point, at below room temperature (287 K = 14 °C). Ethylammonium nitrate is the simplest organic ionic liquid.

Eutectics of EAN with MEAN or *n*-propylammonium nitrate lower the melting point even further. Such ionic liquids have been evaluated not only as propellant ingredients but also as electrolytes in batteries, fuel cells, and other electrochemical applications.

#### 3.7.2 Physical Properties of Mono-, Di-, and Triethylammonium Nitrates

Physical properties of ethylammonium nitrate are summarized in Table 33.

Ethylammonium nitrate is not only an ionic liquid, but it is also a room-temperature ionic liquid with an unusually low melting point. It owes its unique physical properties and molecular structure to a three-dimensional hydrogen-bonded network, similar to water. EAN was the first ionic liquid recognized by a rocket propellant chemist for its potential use as a rocket propellant.

In his memoir surveying this lifetime work, John D. Clark makes mention of ionic liquids in general and EAN in particular: “*Molten salts are nothing new, but these were*

**Table 33:** Physical properties of ethylammonium nitrate.

| Property              | at ... K          | SI units                                                                               | Other units                                          | References                |
|-----------------------|-------------------|----------------------------------------------------------------------------------------|------------------------------------------------------|---------------------------|
| Molecular mass        |                   | 108.097 g/mol                                                                          | 9.2509 mol/kg                                        |                           |
| Oxygen balance        |                   | −74.0%                                                                                 | —                                                    |                           |
| Melting point         |                   | 287 K<br>281 K                                                                         | 14 °C<br>8 °C                                        | <i>Chemical Abstracts</i> |
| Density               | 298<br>298        | 1.21 g/cm <sup>3</sup> (liquid)<br>1.2104 g/cm <sup>3</sup> (liquid)                   | 75.54 lb/ft <sup>3</sup><br>75.56 lb/ft <sup>3</sup> | <i>Chemical Abstracts</i> |
| Specific volume       | 288<br>298<br>318 | 0.82263 cm <sup>3</sup> /g<br>0.82709 cm <sup>3</sup> /g<br>0.83569 cm <sup>3</sup> /g | —<br>—<br>—                                          | [134]                     |
| Heat capacity         | 298               | 1.9016 J K <sup>−1</sup> g <sup>−1</sup>                                               | 0.4545 cal °C <sup>−1</sup> g <sup>−1</sup>          | [134]                     |
| Enthalpy of formation | 298               | −363 kJ/mol                                                                            | −86.9 kcal/mol                                       | [17]                      |

*the only ones I ever heard of that were liquid at 25 °C. I've never found a use for the ethylamine compound, but something with such interesting properties ought to be good for something!"* [38], p. 140. John was correct in this prediction.

Ethylammonium nitrate has been proposed as a non-aqueous solvent for a wide variety of chemical reactions where water would interfere. Water was used as a co-solvent to study the molecular structure of EAN melts [134]. Densities, partial molar volumes, and heat capacities of EAN solutions with 0.4–99.9 mass-% EAN were measured between 288 and 318 K (15 and 45 °C). The partial molar volume of EAN increases between mole fractions of  $X_2 = 0.02$  and 0.4 and remains constant above 0.4. The partial molar heat capacity of EAN has a sharp sigmoid increase up to  $X_2 = 0.075$  and remains constant for all mole fractions above 0.1. The viscosity of EAN at 298 K is about 24 times that of water. In EAN/water mixtures, the viscosity rises sharply above EAN mole fractions of 0.8.

Multiple crystal pathways and crystal polymorphs were observed in protic ionic liquids (pILs), which are liquids at room temperature [135]. The pILs investigated were MEAN, dimethylammonium nitrate, EAN, and *n*-propylammonium nitrate. Methylammonium nitrate and dimethylammonium nitrate solidified as plastic crystals at room temperature, whereas EAN and *n*-propylammonium nitrate were liquids at room temperature. Despite its simple molecular structure, complicated phase behaviors such as multiple crystal pathways and crystal polymorphs were observed in liquid EAN at low temperature. Liquid *n*-propylammonium nitrate also exhibited low-temperature anomalies similar to those observed with liquid EAN. Rapid proton exchanges, which disturb the crystal nucleation of liquid pILs at room temperature, cause multiple crystal rearrangement pathways via non-equilibrium states.

An ionic liquid metalized fuel consisting of 61.6% EAN, 23% nano-boron, 11.55% H<sub>2</sub>O, and 3.85% AN was evaluated as a fuel with a hydrogen peroxide solution as the oxidizer, and the strand-burning rates of the fuel components by themselves were determined in a windowed constant pressure bomb [136]. The freezing point of the EAN/B/H<sub>2</sub>O/AN fuel was 269 K (−4 °C), and the density at 298 K (25 °C) was 1.34 g/mL. Strand-burning rates of the EAN/B/H<sub>2</sub>O/AN fuel were determined in both glass and combustible straws between 0.79 and 17.3 MPa (100 and 2500 psia) and ranged from 2.3 mm/s (0.09 in./s) at 0.79 MPa to 18.8 mm/s (0.74 in./s) at 17.3 MPa. Even though the pressure exponent was relatively high (0.918), this should be no problem for a liquid bipropellant engine in which the propellant is injected as an aerosol spray. Flashback characterization tests where the propellant was pumped continuously from the bottom of a 3.9-mm ID tube showed that the flame front propagated upstream at a rate of 5 mm/s. The flame front did not propagate upstream when a capillary tube 1.75 mm in diameter was inserted into the feed tube.

The thermophysical properties (densities, electric conductivities, and viscosities) of ethylammonium, propylammonium, and butylammonium nitrate ionic liquids and their binary mixtures were determined at atmospheric pressure in the range  $288 < T < 353$  K [137]. Measurements of primary amine nitrates were followed by studies of binary mixtures composed of ethylammonium nitrate (with three hydrogen-bond donor groups) and different homologous ionic liquids with differing numbers of hydrogen-bond donor groups: diethylammonium nitrate (two hydrogen-bond donors), triethylammonium nitrate (one hydrogen-bond donor), and tetraethylammonium nitrate (no hydrogen-bond donors). The results showed a quasi-ideal behavior for all monoalkylammonium nitrate mixtures. In contrast, the other mixtures showed deviations from ideality, namely when the difference in the number of carbon atoms present in the cations increased or the number of hydrogen-bond donors present in the cation decreased. Besides the length and distribution of alkyl chains present in a cation such as alkylammonium, there are other structural and interaction parameters that influence the thermophysical properties of pure compounds and their mixtures.

### 3.7.2.1 Reactions of Diethylammonium Nitrate

The most undesirable reactions of diethylammonium nitrate are those leading to nitrosamines, which are active carcinogens [138]. Such reactions could occur in the dribble volume of bipropellant engines operating on fuels containing diethylamine.

### 3.7.2.2 Physical Properties of Triethylammonium Nitrate

Based on DSC data, the heat capacity of solid triethylammonium nitrate at 348 K (75 °C) is  $1.6 \pm 0.2$  J g<sup>−1</sup> K<sup>−1</sup>. The melting point is at 387 K (114 °C), and the heat of fusion is  $61.3 \pm 1$  J/g = 10.066 kJ/mol [18]. Physical properties of triethylammonium nitrate are summarized in Table 34.

**Table 34:** Physical properties of triethylammonium nitrate.

| Property       | at ... K | SI units                                      | Other units   |                |
|----------------|----------|-----------------------------------------------|---------------|----------------|
| Molecular mass |          | 164.203 g/mol                                 | 6.090 mol/kg  | —              |
| Oxygen balance |          | −165.6%                                       | —             | —              |
| Melting point  |          | 387 K                                         | 114 °C        | —              |
| Heat capacity  | 348      | $1.6 \pm 0.2 \text{ J g}^{-1} \text{ K}^{-1}$ | —             | —              |
| Heat of fusion |          | $61.3 \pm 1 \text{ J/g}$                      | 10.066 kJ/mol | 2.405 kcal/mol |

The apparent molar volume and the partial molar volume of solvent and solute of diethylammonium nitrate and triethylammonium nitrate were derived from density measurements of aqueous solutions of these salts in the concentration range 0.01–0.5 mol/kg for the temperature range of 288 to 303 K and at 101 kPa [139]. These product ionic liquids were also characterized by  $^1\text{H}$  NMR spectra.

### 3.7.3 Thermal Stability of Mono-, Di-, and Triethylammonium Nitrates

Based on DSC data of solid triethylammonium nitrate [18], the preexponential factor of the decomposition rate equation is  $10^{13.73}$ , and the activation energy is 140.3 kJ/mol.

### 3.7.4 Physical Properties of Tetraethylammonium Nitrate

The standard enthalpy of formation of crystalline tetraethylammonium nitrate is  $-428.5 \pm 4 \text{ kJ/mol}$  [16]. That of the corresponding crystalline tetraethylammonium azide is  $+58.6 \pm 4.1 \text{ kJ/mol}$ .

### 3.7.5 Thermal Stability of Mono-, Di-, Tri-, and Tetraethylammonium Perchlorates

The thermal decomposition of ethylammonium perchlorate and isopropylammonium perchlorate has been studied using DTA, TGA, and isothermal weight-loss measurements, and the decomposition products were analyzed in a mass spectrometer [36]. The proton-transfer dissociation mechanism proposed earlier for the thermal decomposition of AP has been extended to explain the decomposition products of these two substituted ammonium perchlorates.

Triethylammonium perchlorate has a molecular mass of 201.6 g/mol, melts at  $349 \text{ K} = 76^\circ\text{C} = 169^\circ\text{F}$ , and has a heat of combustion of  $9236 \text{ BTU/lb} = 5131 \text{ cal/g} = 1034 \text{ kcal/mol} = 4328 \text{ kJ/mol}$ .

The thermal stability of tetraethylammonium perchlorate was investigated using TGA, DTA, and mass spectrometric analysis of the decomposition products [140]. It was found that tetraethylammonium perchlorate undergoes a crystallographic phase change at  $371 \text{ K} (98^\circ\text{C})$ . The heat of phase transformation was calculated to be  $10.46 \text{ kJ/mol} (2.5 \text{ kcal/mol})$ . The mass spectral data suggest that the salt undergoes thermal decomposition into neutral particles, which are then vaporized and ionized as well as oxidized. It will explode at  $571 \text{ K} (298^\circ\text{C})$ .

## 4 Propylamines

There are two known propylamines: *n*-propylamine, 1-propanamine, CAS RN [107-10-8], and isopropylamine, 2-propanamine. Their physical properties are very similar and are summarized in [9]. There are no known industrial applications of these propylamines other than the temporary use of their nitrate salts in liquid gun propellants such as NOS365.

*n*-Propylamine has been tested as an additive to furfuryl alcohol in an effort to shorten the hypergolic ignition delays of either one [141].

### 4.1 Physical Properties of Propylamines

Isopropylamine is not likely to be used as a rocket propellant; nevertheless, viscosity data at high pressure have been measured for this fuel (Table 35). This viscosity can be compared to other alkylamines that actually have been used as rocket fuels.

**Table 35:** Viscosity of isopropylamine.

| Temperature |    | Viscosity, cPs |        |        |        |        |        |
|-------------|----|----------------|--------|--------|--------|--------|--------|
| K           | °C | Pressure, atm  |        |        |        |        |        |
|             |    | Bubble point   | 50     | 100    | 150    | 200    | 250    |
| 273         | 0  | 0.4605         | 0.4794 | 0.4998 | 0.5197 | 0.5412 | 0.5610 |
| 283         | 10 | 0.3998         | 0.4120 | 0.4300 | 0.4470 | 0.4625 | 0.4758 |
| 293         | 20 | 0.3500         | 0.3620 | 0.3781 | 0.3900 | 0.4030 | 0.4140 |
| 303         | 30 | 0.3082         | 0.3179 | 0.3295 | 0.3400 | 0.3501 | 0.3610 |
| 313         | 40 | 0.2728         | 0.2802 | 0.2899 | 0.2990 | 0.3075 | 0.3176 |
| 323         | 50 | 0.2455         | 0.2528 | 0.2803 | 0.2889 | 0.2766 | 0.2849 |

Data source: [142–144]

### 4.2 Propylammonium Nitrates

*n*-Propylammonium nitrate,  $C_3H_{10}N_2O_3$ , CAS RN [22113-88-8],  $M = 122.125$  g/mol, and its isomer, isopropylammonium nitrate, have been considered as fuels for HAN-based monopropellants.

#### 4.2.1 Physical Properties of Propylammonium Nitrates

*n*-Propylammonium nitrate is a room-temperature ionic liquid that melts at 276.6 K (3.5°C) and has a density of 1.16 g/cm<sup>3</sup>.

#### 4.2.2 Thermal Stability of Propylammonium Nitrates

Based on DSC data, the heat capacity of solid isopropylammonium nitrate (IPAN) at 338 K (65 °C) is  $1.4 \pm 0.2 \text{ J g}^{-1} \text{ K}^{-1}$ . The melting point is at 346 K (73 °C), and the heat of fusion is  $16.12 \text{ kJ/mol} = 132 \pm 2 \text{ J/g}$  [18, 145]. In the range between 448 and 563 K (175 and 290 °C), several endothermic and exothermic peaks overlap. At 423 K (150 °C) it is possible to detect subliming, undecomposed IPAN in the vapor phase.

Based on DSC data, the heat capacity of solid diisopropylammonium nitrate at 403 K (130 °C) is  $2.1 \pm 0.3 \text{ J g}^{-1} \text{ K}^{-1}$ . The melting point is at 461 K (188 °C), but the heat of fusion could not be determined because the chemical began to decompose on melting [18]. There were crystalline phase transitions in the solid state, and the crystals may also have contained water as crystalline hydrates. These peaks overlapped. The IR spectra of the gas space above the melting sample revealed the presence of water,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , acetone, and propene.

#### 4.3 Propylammonium Perchlorates

The thermal decomposition of isopropylammonium perchlorate has been studied using DTA, TGA, and isothermal weight-loss measurements, and the decomposition products were analyzed in a mass spectrometer [36]. The proton-transfer dissociation mechanism proposed earlier for the thermal decomposition of AP has been extended to explain the decomposition products of isopropylammonium perchlorate.

### 5 Amines with Large Alkyl Groups

The higher alkylamines from C3 (propylamine) on up are not readily available in industrial quantities, do not offer any advantages over ethylamines, and are not considered as preferred fuels for rocket propulsion.

**Table 36:** Enthalpies of formation of butylamines.

| Compound                 | Formula                                 | Molecular mass |        | Enthalpy of formation $\Delta H_f^{298}$ |       |          | Density $\rho$    |                    | References |
|--------------------------|-----------------------------------------|----------------|--------|------------------------------------------|-------|----------|-------------------|--------------------|------------|
|                          |                                         | g/mol          | mol/kg | kJ/mol                                   | cal/g | kcal/mol | g/cm <sup>3</sup> | lb/in <sup>3</sup> |            |
| <i>n</i> -Butylamine     | $\text{C}_4\text{H}_9\text{NH}_2$       | 73.14          | 13.67  | −128                                     | −417  | −30.5    | 0.7501            | 0.0271             | [27]       |
| Di-iso-butyl-amine       | $\text{C}_8\text{H}_{17}\text{NH}_2$    | 129.25         | 7.74   | −217                                     | −402  | −51.9    | 0.7612            | 0.0275             | [27]       |
| Tri-iso-butyl-amine      | $\text{C}_{12}\text{H}_{25}\text{NH}_2$ | 185.36         | 5.39   | −316                                     | −408  | −75.6    | 0.7695            | 0.0278             | [27]       |
| <i>n</i> -Butylamine     | $\text{C}_4\text{H}_9\text{NH}_2$       | 73.14          | 13.67  | −128                                     | −417  | −30.53   | —                 | —                  | [17]       |
| <i>tert</i> -Butyl-amine | $\text{C}_4\text{H}_9\text{NH}_2$       | 73.14          | 13.67  | −150.4                                   | −492  | −35.95   | —                 | —                  | [17]       |

A series of primary, secondary, and tertiary alkylamines has been used in an academic study to clarify the relationship between ignition delay in a hypergolic propellant rocket engine and the molecular structure and heat of neutralization of alkylamines [146, 147]. It was noted that the ignition delay decreased from ethylamine to *n*-amyl amine although the viscosity increased. In spite of their shorter ignition delays, the higher alkylamines are not used as rocket propellants. The enthalpies of formation of three liquid butylamines were listed in [27] (Table 36).

### 5.1 Butylammonium Nitrates

There are at least three different butylammonium nitrates, all structural isomers. All share the same gross formula of  $C_4H_{12}N_2O_3$  and the molecular mass of 136.15 g/mol. Based on DSC data, the heat capacity of solid *tert*-butylammonium nitrate at 373 K (100 °C) is  $1.9 \pm 0.3 \text{ J g}^{-1} \text{ K}^{-1}$ . The melting point is at 412 K (139 °C), and the enthalpy of fusion is  $72 \pm 1 \text{ J/g} = 9.79 \text{ kJ/mol}$  [18]. Sublimation is dominant at 473–543 K (200–280 °C), and the enthalpy of sublimation is  $\sim 1020 \text{ J/g}$ .

*n*-Butylammonium nitrate is of interest as an ionic liquid but not necessarily as a rocket propellant [148]. The density and viscosity of the pure ionic liquid *n*-butylammonium nitrate and its binary mixtures with methanol, ethanol, 1-propanol, and 1-butanol were measured at temperatures ranging from 293.15 to 313.15 K. The thermal expansion coefficient, molecular volume, standard entropy, and lattice energy of *n*-butylammonium nitrate were deduced from experimental density results.

Tetra-*n*-butylammonium trinitromethanide is well crystallized, and its crystal structure was determined by XRD, supported by  $^{13}\text{C}$  and  $^{14}\text{N}$  NMR spectra [149].

### 5.2 C>6 Alkylammonium Salts

Most salts of lower ( $C < 3$ ) alkylamines are polar, saline compounds with poor solubility in organic binders prepolymers used in solid propellants. Alkylammonium salts with at least one longer carbon chain have improved solubility and can be added to solid propellant binders (requiring less oxidizer) or can be used as bonding agents to coat AP crystals prior to incorporating them into a composite propellant. Compounds in this category include cetyl trimethylammonium perchlorate  $\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{ClO}_4^-$ , which melts at 385 K (112 °C) and decomposes with two exothermic peaks, one at 428 K (155 °C) and another at 523 K (250 °C) [150].



## 6 Imines with One Nitrogen Atom

Imines are heterocyclic secondary amines in which two of the hydrogens of ammonia are replaced by the ends of an alkylene chain. They can be considered as ring-closed saturated secondary amines. Among the imines with the general molecular structure  $(\text{CH}_2)_n\text{NH}$ , the lowest member with a strained ring structure, ethylene imine ( $n=2$ ), and a higher member, piperidine ( $n=5$ ), have been considered as rocket propellants. Heterocyclic ring structures with one to five nitrogen atoms in the rings that also contain double bonds are discussed here in *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic and Heterocycloaliphatic Amines.” Ethylene imine would fit here under amines or under heterocyclic compounds. The discussion of ethylene imine has been moved to three-membered rings and therefore is also discussed in the chapter “Heterocyclic and Heterocycloaliphatic Amines.”

## 7 Saturated Open-Chain Aliphatic Amines with More than One Nitrogen Atom in the Molecule

Saturated open-chain aliphatic amines with more than one nitrogen atom in the molecule could be called multifunctional amines.

### 7.1 Ethylenediamine

Ethylenediamine, also known as 1,2-diaminoethane,  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ,  $\text{C}_2\text{H}_8\text{N}_2$ , CAS RN [107-15-3], often abbreviated as EDA, is a colorless, viscous, hygroscopic liquid that fumes in moist air. Like some of the other amines, it has the typical fishy odor. It is a relatively strong base, and when spilled on unprotected skin, it can be quite irritating. The gross formula of EDA is the same as that of UDMH, but its performance as a rocket fuel is not as good. Properties of EDA are summarized here because it can be used as an ingredient in hypergolic fuel mixtures, and it is the feed stock for making ethylenediamine dinitrate, an explosive and propellant ingredient. The dinitrate salt of EDA is often abbreviated as EDDN, and it has been used as an explosive. A separate section describes the properties of EDDN.

Ethylenediamine can be synthesized by reaction of 1,2-dichloroethane with ammonia. This reaction also produces diethylene triamine  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHC}_2\text{H}_4\text{NH}_2$  and piperazine  $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$  as by-products.

Ethylenediamine is the amine that is commonly used as a sensitizer for binary nitromethane explosives (PLX).

### 7.1.1 Physical Properties of Ethylenediamine

The physical properties of ethylenediamine are summarized in Table 37.

**Table 37:** Physical properties of ethylenediamine.

| Property                                                     | SI units                 | Non-SI units                        | References |
|--------------------------------------------------------------|--------------------------|-------------------------------------|------------|
| Freezing point                                               | 284.15 K                 | +11 °C                              | [29]       |
| Boiling point                                                | 391 ± 1 K                | 118 ± 1 °C                          | [29]       |
| Density                                                      | 899.4 kg/m <sup>3</sup>  | 0.8994 g/cm <sup>3</sup> (20 °C)    | [119]      |
| Viscosity                                                    | See separate table below |                                     |            |
| Critical temperature                                         | 613.1 K                  | 340 °C                              | [29]       |
| Critical pressure                                            | 67.07 bar                | 66.19 atm                           | [29]       |
| Standard enthalpy of formation<br>( $\Delta H_f^{298}$ ) (L) | −26.6 kJ/mol             | −6.36 kcal/mol <sup>a</sup>         | [17]       |
|                                                              | −63.01 ± 0.54 kJ/mol     | −15.06 ± 0.13 kcal/mol <sup>a</sup> | [29]       |
| Standard enthalpy of formation<br>( $\Delta H_f^{298}$ ) (G) | −17.0 ± 0.59 kJ/mol      | −4.06 ± 0.14 kcal/mol               | [29]       |
| Enthalpy of vaporization at NBP                              | 37.98 kJ/mol             | 9.08 kcal/mol                       | [29]       |
| Index of refraction, $n_D^{26}$                              | 1.4540                   | —                                   | [119]      |

<sup>a</sup> The data from Stull, Westrum, and Sinke [6] and NIST Chemistry WebBook [29] are quite different

Ethylenediamine could potentially be used as a rocket fuel along with other alkylamines. The viscosity of ethylenediamine and ethylenediamine hydrate in the liquid phase was measured with a steel rolling-ball viscometer over the temperature range of 303 to 488 K (30 to 210 °C) [142]. The viscosity of ethylenediamine hydrate was substantially higher than that of the anhydrous amine [143, 144]. The data are summarized in Table 38.

**Table 38:** Viscosity of ethylenediamine.

| Temperature |    | Viscosity, cPs |       |       |       |       |       |
|-------------|----|----------------|-------|-------|-------|-------|-------|
| K           | °C | Pressure, atm  |       |       |       |       |       |
|             |    | Bubble point   | 50    | 100   | 150   | 200   | 250   |
| 303         | 30 | 1.586          | 1.632 | 1.889 | 1.720 | 1.760 | 1.789 |
| 313         | 40 | 1.260          | 1.292 | 1.328 | 1.364 | 1.392 | 1.412 |
| 323         | 50 | 1.033          | 1.053 | 1.082 | 1.116 | 1.140 | 1.18  |

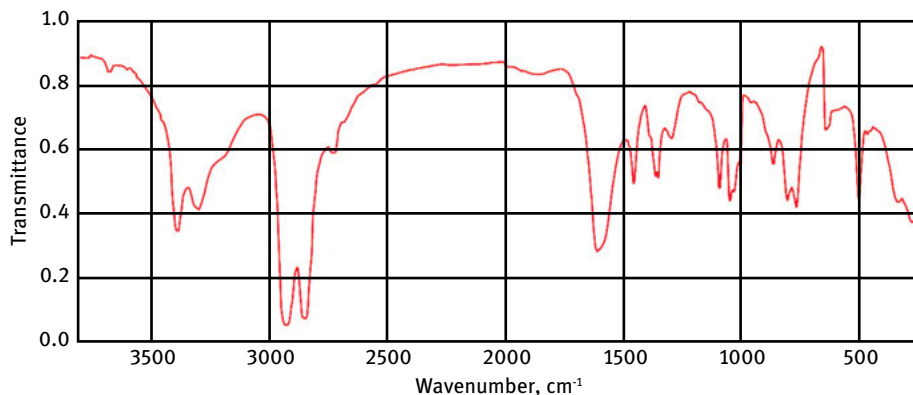
Data source: [144]

The vapor pressure of ethylenediamine in the temperature range of 299 to 391 K can be calculated from an Antoine equation:

$$\log P = A - [B/(T + C)] = 4.22368 - [1302.256/(T - 81.788)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin [29].

The IR spectrum of an ethylenediamine solution in  $\text{CCl}_4$  or  $\text{CS}_2$  is shown in Figure 4. Although EDA is not used as a rocket propellant, the IR spectrum of EDA is shown here so that it can be compared to the IR spectrum of its dinitrate salt.



**Figure 4:** IR spectrum of ethylenediamine. (Reproduced and modified with permission from [151])

### 7.1.2 Toxicity of Ethylenediamine

The conversion factor for permissible exposure limits of ethylene diamine in air is  $1\text{ ppm} = 2.46\text{ mg/m}^3$  at  $25^\circ\text{C}$  and  $1\text{ atm}$ . The NIOSH REL TWA exposure limit for ethylenediamine is  $10\text{ ppm}$  ( $25\text{ mg/m}^3$ ), the same as the OSHA PEL TWA of  $10\text{ ppm}$  ( $25\text{ mg/m}^3$ ). The ACGIH TLV is  $10\text{ ppm}$  ( $25\text{ mg/m}^3$ ). The original IDLH of EDA was  $2000\text{ ppm}$ , but it was lowered to  $1000\text{ ppm}$  a few years later. The chosen IDLH was based on a report that an 8-h exposure to  $4000\text{ ppm}$  EDA killed six of six rats, but an 8-h exposure to  $2000\text{ ppm}$  killed zero of six rats. Ethylenediamine is corrosive to the eyes, skin, and respiratory tract. Skin contact can cause blistering. Eye contact can cause pain, serious injury, and permanent damage. Prolonged inhalation can cause pulmonary edema, a medical emergency that can be delayed for several hours and can be fatal.

Ethylenediamine ended up being listed on the European Chemicals Agency (ECHA) Candidate List of Substances of Very High Concern for Authorisation on 27 June 2018 because of its respiratory sensitizing properties.

### 7.1.3 Flammability of Ethylenediamine

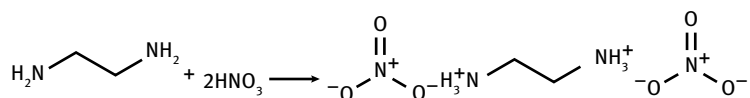
The flammable range of EDA vapors at 373 K (100 °C = 212 °F) is 2.5–12 vol-%. The flash point is 307 K (34 °C = 93 °F) [152].

### 7.1.4 Salts of Ethylenediamine

#### 7.1.4.1 Ethylenediammonium(2+) Dinitrate

The correct name for ethylenediamine dinitrate,  $[\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3][\text{NO}_3^-]_2$ , CAS RN [20829-66-7], would be 1,2-ethanediammonium dinitrate, often abbreviated as EDDN. Alternate names would be ethylenediammonium(2+) dinitrate or 1,2-ethanediamine nitrate (1:2). It may also be called ethylenediaminium dinitrate. It is prepared by neutralizing an aqueous solution of ethylenediamine with dilute nitric acid, driving off the water and crystallization from the concentrated solution. The dry salt is somewhat hygroscopic and readily soluble in water. It melts at 461 K (188 °C). Ethylenediamine dinitrate is an energetic material that is often used as an ingredient in melt-cast explosives. It can also be used in solid propellants. Its oxygen balance for combustion to carbon dioxide is -25.8%; therefore, it is a fuel but nearly stoichiometrically oxidized, and thus it does not need much additional oxidizer to achieve complete combustion to carbon monoxide or carbon dioxide.

The preparation of EDDN is a simple acid–base neutralization reaction:



Ethylenediammonium(2+) dinitrate in eutectic mixtures with ammonium nitrate and potassium nitrate can be used as a castable, intermolecular explosive [153].

#### Physical Properties of Ethylenediammonium(2+) Dinitrate

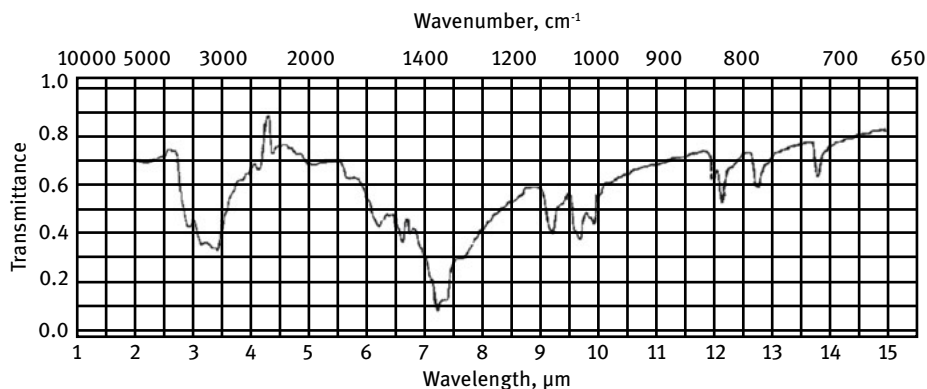
In an effort to find replacements for EDDN with improved thermal stability, a wide range of nitrate salts of other diamines and polyamines was investigated in a study called “Synthesis and Properties of Selected Energetic Organodi- and Polyammonium Nitrate Salts” [21, 154]. The objective of this program was to synthesize and characterize selected organodi- and polyammonium nitrate salts for use in a study of thermal and impact stability characteristics. A total of 22 nitrate salts were prepared and characterized, 15 of which had never been reported in the literature. The list included homologues of EDDN, as well as *N*- and *N,N'*- mono-, di-, tri-, and tetrasubstituted ethylenediamines and their nitrates. The compounds were characterized by elemental analyses and drop-weight sensitivity as well as by their NMR spectra. Other data generated were densities (calculated and measured), heats of fusion, melting points, and the temperature of the major peak associated with

exothermic decomposition as measured by DSC. Thermal stability decreased with increasing chain length, N-substitution of the amines, and molecular weight.

The physical properties of EDDN are summarized in Table 39, and an IR spectrum is shown in Figure 5.

**Table 39:** Physical properties of ethylenediammonium(2+) dinitrate

| Property              | SI units               |               | Other units             |                          | References |
|-----------------------|------------------------|---------------|-------------------------|--------------------------|------------|
| Molecular mass        | 186.124 g/mol          | 5.3735 mol/kg | —                       | —                        |            |
| Melting point         | 461 K                  | —             | 188 °C                  | 370 °F                   | [15]       |
|                       | 457 K                  | —             | 184 °C                  | —                        | [155]      |
| Density               | 1577 kg/m <sup>3</sup> |               | 1.577 g/cm <sup>3</sup> | 98.45 lb/ft <sup>3</sup> | [15]       |
| Enthalpy of formation | −653 kJ/mol            | −3511.3 kJ/kg | −156 kcal/mol           | −839.2 cal/g             | [15]       |



**Figure 5:** Infrared spectrum of ethylenediammonium(2+) dinitrate. (Reproduced and modified from [155].)

### Chemical Properties of Ethylenediammonium(2+) Dinitrate

Ethylenediamine dinitrate is somewhat hygroscopic and is readily soluble in water. See also [156].

### Thermal Stability of Ethylenediammonium(2+) Dinitrate

The species evolving during rapid thermolysis of solid EDDN were analyzed by rapid scanning FTIR spectrometry, with a complete scan performed every 100 ms [157]. This combination of DTA and product analysis is a good method to “unravel” an energetic molecule step by step and identify the weak spots in a molecule where the reaction starts first. The rapid thermolysis of 2-mg samples of solid EDDN at a heating rate of

70 K/s under 103 kPa (15 psi) argon showed a very complex behavior compared to HAN and HN, which were investigated at the same time. After melting, the temperature rises to 280 °C before decomposition products are detectable. The initial endotherm at 353 K (80 °C) leads to proton transfer and release of  $\text{HNO}_3$ . Between 548 and 603 K (275 and 330 °C) the decomposition is endothermic, and above 603 K (330 °C) it becomes exothermic and combustion products of the molecule appear: nitric acid first, followed by  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and, finally,  $\text{CO}_2$  and  $\text{HCN}$ . N—H and C—N bonds are broken before the C—C bonds. A strong exotherm follows, starting at 373 K (100 °C) [158–160]. EDDN mixtures with AN are more thermally stable than EDDN alone, and they have better explosive performance than AN alone. The eutectic mixture has a lower melting point than either component, making it suitable for melt casting. However, EDDN/AN mixtures suffer from volume changes with temperature because of the phase transitions of AN. The addition of potassium nitrate stabilizes the AN and counters the expansion of AN at 305 K (32 °C) caused by one of the solid–solid phase transitions.

Studying the fast thermal decomposition of five *N*-methyl substituted ethanediammonium dinitrate salts, it was noted that the thermal decomposition behavior of most of these compounds more closely resembles that of alkylammonium mononitrate salts than primary alkanediammonium dinitrate salts (e.g., EDDN). Only the *N,N,N',N'*-tetramethylethanediammonium dinitrate behaved similarly to EDDN [161]. The behavior of *N*-methylethylenediammonium dinitrate MEDD, *N,N,N',N'*-tetramethyl-ethylene diammonium dinitrate TMEDD, *N,N,N'*-trimethylethylenediammonium dinitrate TRMEDD, *N,N'*-dimethylethanediammonium dinitrate, *sym*-DMEDD, and *N,N'*-dimethylethanediammonium dinitrate *unsym*-DMEDD more closely resembled the behavior of alkylammonium mononitrate salts in terms of the temperature at which  $\text{HNO}_3$  was released. The first decomposition step of most primary and secondary alkylammonium nitrate salts is the production of  $\text{HNO}_3(\text{G})$ . See also [162].

### Strand-Burning Rates of Solid Ethylenediammonium(2+) Dinitrate

EDDN was compared with ethylenediamine diperchlorate and carbonylhydrazide nitrate in a study of the effect of the molecular structure of energetic materials on the burning rate [163].

### Safety Properties of Ethylenediammonium(2+) Dinitrate

The impact sensitivity of EDDN is 10 Nm when tested in the BAM apparatus. In the BAM friction test apparatus, friction sensitivity of EDDN is above 353 N pistil load, which gave no reaction at the upper load limit of the machine.

### Explosive Performance of Ethylenediammonium(2+) Dinitrate

In the lead block test, if a 10-g sample of EDDN explodes, it will enlarge the cavity so that it will hold  $350\text{ cm}^3$  of water. The detonation velocity of confined and densely pressed EDDN is 6800 m/s at a packing density of  $1.53\text{ g/cm}^3$ .

### Applications of Ethylenediammonium(2+) Dinitrate

EDDN forms a eutectic with diethylenetriammonium(3+) trinitrate (DETN), melting between 460.7 and 461.3 K (187.6 and 188.2°C) when it was being tested as a melt-cast explosive and as a replacement for Composition B in mortar rounds and bomb fills [164].

EDDN forms a eutectic mixture (melting point 373 K = 100°C = 212°F) when mixed with an equal amount of AN. This mixture is a potential melt-cast explosive.

#### 7.1.4.2 Ethylenediammonium(2+) Diperchlorate

Ethylenediamine forms a monopерchlorate from ethylene diamine and perchloric acid in 1:1 molar proportions and a dipерchlorate salt with an excess of perchloric acid [165].

Ethylenediammonium(1+) перchlorate (ethylenediamine monopерchlorate, gross formula  $C_2H_9N_2O_4Cl$ , CAS RN [25682-07-9]) is less frequently worked with.

Ethylenediammonium(2+) dipерchlorate, EDDP, ethylenediamine dipерchlorate, gross formula  $C_2H_{10}N_2O_8Cl_2$ , molecular mass 261.015 g/mol, CAS RN [15718-71-5], is an energetic material that has been considered as an ingredient in melt-cast explosives. It can also be used in solid propellants. Its oxygen balance is zero, thus it is stoichiometrically oxidized, and it does not need any additional oxidizer to achieve complete combustion to carbon dioxide and water. EDDP can be prepared by slowly neutralizing 20%  $HClO_4$  with ethylene diamine diluted with an equal amount of water and slowly concentrating the resulting solution by evaporation.

#### Physical Properties of Ethylenediammonium(2+) Diperchlorate

The IR spectrum of ethylenediammonium(2+) dipерchlorate exhibited characteristic bands due to the  $NH_3^+$  group at 3400(s), 3180(s) ( $\nu NH_3$ ), and  $1588\text{ cm}^{-1}$  ( $\delta NH_3$ ). The absorptions at 1065(s), 942(w), and 620(s) are characteristic of the  $ClO_4^-$  group.

Tables 10, 11, and 12 summarize the physical properties of ethylenediammonium dipерchlorate and its hemihydrate.

Ethylenediammonium(2+) dipерchlorate and triethylenediammonium(2+) dipерchlorate cocrystallize, and single crystals were grown from solution and characterized by  $^1H$  NMR and single-crystal XRD [166]. The results confirmed that the molar ratio of ethylenediamine to triethylenediamine is 1:1. The crystal belongs to the orthorhombic system, space group  $Cmc2_1$  with  $a = 0.8103(16)\text{ nm}$ ,  $b = 2.4725(5)\text{ nm}$ ,  $c = 1.0195(2)\text{ nm}$ ,  $V = 2.0425(7)\text{ nm}^3$ ,  $Z = 8$ , and  $\rho_{XRD} = 1.828\text{ g/cm}^3$ . The molecular structure of the co-crystals is held together by hydrogen bonding.

#### Chemical Properties of Ethylenediammonium(2+) Diperchlorate

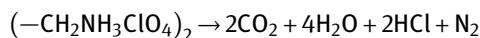
Ethylenediammonium dipерchlorate is a potential explosive and propellant ingredient. It forms a hemihydrate that, based on DTA data with a heating rate of 20 K/min, undergoes a reversible phase transition at 368 K (95°C) and loses water at 393–403 K

(120–130 °C) to form the anhydrous salt, which eventually decomposes when the temperature increases to 563 K (290 °C).

### Thermal Stability of Ethylenediammonium(2+) Diperchlorate

The TGA plot indicated that decomposition takes place in two stages in the temperature ranges of 275–310 and 320–365 °C. No residue remained at 365 °C; the whole material was oxidized to gaseous products. The weight loss observed at the end of the first stage of decomposition was 61% [167]. The DTA showed two exothermic effects peaking at 573 and 631 K (300 and 358 °C). Initially a proton transfer takes place at 548–583 K (275–310 °C), and later the entire material is oxidized to form gaseous products.

The thermal decomposition of ethylene diamine diperchlorate (EDDP) has been studied using DTA, TGA, isothermal weight-loss measurements, and mass-spectrometric analysis of the decomposition products [168]. EDDP decomposed in two temperature regions. The low-temperature decomposition stopped at about 35 to 40% weight loss below 523 K (250 °C). An overall activation energy of 54 kcal/mol was calculated for the thermal decomposition of EDDP. Mass-spectrometric analysis showed that the decomposition products were mainly CO<sub>2</sub>, H<sub>2</sub>O, HCl, and N<sub>2</sub>. The following stoichiometry has been proposed for the thermal decomposition of EDDP:



### Strand-Burning Rates of Solid Ethylenediammonium Diperchlorate

The strand-burning rate of EDDP has been compared to that of 1,4-butanediammonium diperchlorate and *p*-phenylenediammonium diperchlorate [169]. The three organic perchlorates

- ethylenediammonium diperchlorate (CH<sub>2</sub>NH<sub>2</sub>•HClO<sub>4</sub>)<sub>2</sub>,
- tetramethylenediammonium diperchlorate (CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>•HClO<sub>4</sub>)<sub>2</sub>, and
- *p*-phenylenediammonium diperchlorate O<sub>4</sub>ClH•H<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub>–NH<sub>2</sub>•HClO<sub>4</sub>

differ from one another, both with respect to the structure of the organic part of the molecule and to the heat of explosion. The substances were obtained through the reaction of amines with a 40% excess of 60% HClO<sub>4</sub> beyond that required for the stoichiometric diperchlorate salt. Of the three perchlorates under consideration, *p*-phenylenediamine diperchlorate had the most rapid rate of combustion. EDDP burned somewhat more slowly and considerably more stably than did *p*-phenylenediamine diperchlorate. The rate of combustion at atmospheric pressure was 0.1 cm/s; up to 20 atm, it increased according to the equation

$$r_b = -0.13 + 0.23p^{0.68}$$

and in the interval from 20 to 400 atm

$$r_b = 0.14p^{0.85},$$



where  $r_b$  is the burning rate in cm/s and  $p$  is the pressure in atmospheres. EDDP was compared with EDDN and carbohydrazide nitrate in a study on the effect of the molecular structure of energetic materials on the burning rate [163].

### Detonability of Ethylenediammonium Diperchlorate Solutions

The detonability of aqueous solutions/suspensions of organic amine perchlorates was studied in steel and glass ampoules with an electric detonator with or without an intermediate hexogen booster. The detonation temperature of aqueous solutions of EDDP was 2160–2220 K, and the concentration limit of H<sub>2</sub>O below which the solutions retained their detonation capacity was 21–24% H<sub>2</sub>O [95]. Similar data for ethylenediammonium monoperochlorate solutions included a detonation temperature of 1820–1960 K, and the concentration limit of H<sub>2</sub>O below which the solutions retained their detonation capacity was 39–42% H<sub>2</sub>O.

### Mixtures Containing Ethylenediammonium(2+) Diperchlorate

Ethylenediammonium(2+) diperchlorate forms a double salt with triethylenediammonium(2+) diperchlorate, which is a very energetic and very sensitive compound with a well-defined crystal structure. The molecular and crystal structures of ethylenediammonium(2+) triethylenediammonium(2+) tetraperochlorate have been determined by XRD [170]. The compound crystallized in the orthorhombic system (space group *Cmc*<sub>21</sub>) with cell dimensions  $a = 8.1030$ ,  $b = 24.725$ , and  $c = 10.195$  Å [171].

#### 7.1.4.3 Ethylenediammonium(2+) Bisdinitramide

Ethylenediamine (1,2-diaminoethane) forms a diprotonated salt with dinitramidic acid, ethylenediammonium(2+) bisdinitramide, C<sub>2</sub>H<sub>10</sub>N<sub>8</sub>O<sub>8</sub>, CAS RN [165603-96-3], which is of interest as an energetic additive to propellants and gas generants. Ethane diammonium bis(dinitramide) melts at 398 K (125 °C) [172]. The salt crystallizes in the triclinic space group *P*1 with cell dimensions  $a = 5.614(1)$ ,  $b = 6.867(2)$ ,  $c = 7.371(2)$  Å,  $\alpha = 68.89(2)$ ,  $\beta = 89.00(2)$ ,  $\gamma = 78.90(2)^\circ$ ,  $Z = 1$ , and  $\rho_c = 1.753$  g/cm<sup>3</sup> [173]. Atomic coordinates, bond lengths and angles, and equivalent isotropic displacement parameters for the salt have been calculated and tabulated. These cations provide a constrained local environment for the dinitramide anions due to extensive hydrogen bonding.

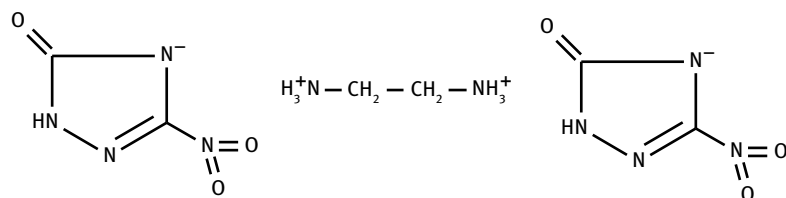
The enthalpy of formation of ethylenediammonium dinitramide (dinitramidate) is  $-194.6 \pm 1.8$  kJ/mol ( $-46.52 \pm 0.43$  kcal/mol) [117]. Other sources gave an enthalpy of formation of ethylenediamine bisdinitramide of  $-209$  kJ/mol ( $-49.9$  kcal/mol) [98].

#### 7.1.4.4 Ethylenediammonium(2+) Salts of Other Acids

Ethylene diamine forms an ethylenediammonium salt with 5-nitrotetrazole C<sub>4</sub>H<sub>10</sub>N<sub>12</sub>O<sub>4</sub> that is of interest as an energetic material. It melts at 494 K (221 °C) and has a density of 1.65 g/cm<sup>3</sup>. It is thermally stable up to 489 K (216 °C). Its enthalpy of formation is +233 kJ/mol (+55.7 kcal/mol). Its drop-weight sensitivity is 42 cm (type 12 tool). The ethylenediammonium salt of 5-nitrotetrazole forms a eutectic

with AN that is of interest as a melt-castable explosive [174, 175]. Moreover, this eutectic mixture, which contains 87.8 mol-% (66.5 mass-%) of AN, is close to the CO<sub>2</sub>-balanced composition of 90 mol-% and has a relatively low melting point of 383.6 K (110.5°C), making it readily castable. A ternary blend containing 26.33 mass-% ethylenediammonium salt of 5-nitrotetrazole, 47.54 mass-% AN, and 26.13 mass-% EDDN melts even lower, at 362.6 K (89.5°C) [176].

The ethylenediammonium(2+) salt of 3-nitro-1,2,4-triazol-5-one (NTO), C<sub>2</sub>H<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>•2C<sub>2</sub>H<sub>1</sub>N<sub>4</sub>O<sub>3</sub>, molecular mass 320.22 g/mol, crystallized in triclinic crystals, space group  $P\bar{1}$  with the cell parameters  $a = 6.528(3) \text{ \AA}$ ,  $b = 10.780(2) \text{ \AA}$ ,  $c = 14.236(3) \text{ \AA}$ ,  $\alpha = 81.11(2)^\circ$ ,  $\beta = 87.13(3)^\circ$ ,  $\gamma = 74.05(3)^\circ$ ,  $V = 951.73 \text{ \AA}^3$ ,  $Z = 3$ , and  $\rho = 1.676 \text{ g/cm}^3$  [177].



The ethylenediammonium(2+), ammonium, hydrazinium(1+), and guanidinium salts of NTO were synthesized and characterized [178]. Small-scale sensitivity tests indicated that these compounds are thermally stable and only moderately insensitive to impact.

Well-crystallized ethylenediammonium(2+) salts are formed from ethylenediamine and mono-, di-, and trinitrophenolates (picrates) [179]. Their structures were characterized and confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, IR spectroscopy, and elemental analysis.

#### 7.1.4.5 Ethylenediamine as a Ligand in Metal Complexes

Being a bidentate ligand (similar to hydrazine), ethylenediamine forms a wide array of complexes with transition metals. Such complexes with oxidizing anions (nitrate, perchlorate) have been considered as energetic additives or even as primary explosives.

Ten transition-metal nitrate and perchlorate complexes of hydrazine and ethylenediamine (EN) were synthesized, namely [Cu(EN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Co(EN)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>, [Ni(EN)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Hg(EN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Cr(N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>, [Cd(N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>, [Ni(N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, [Co(N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>, [Zn(N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub>, and [Cd(N<sub>2</sub>H<sub>4</sub>)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> [180]. All of these were tested by underwater detonation tests measuring shock-wave overpressure, shock-wave energy equivalent, and bubble energy equivalent and were further compared to typical explosives such as RDX, HMX, TNT, and PETN. Similar complex salts contain azide ion in addition to ethylenediamine as a ligand [181]. Examples are [Cu<sub>2</sub>(EN)<sub>2</sub>(N<sub>3</sub>)<sub>4</sub>] and [Co(EN)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>).

Five bis(ethylenediamine)metal perchlorate complexes such as  $[M(EN)_2](ClO_4)_2$  (where  $M = Mn, Co, Ni, Cu, Zn$ ) have been prepared and characterized by gravimetric methods, TGA, DTA, IR, and elemental analysis [182]. Thermal stability of the complexes was found to decrease in the following order:  $[Zn(EN)_2](ClO_4)_2 > [Mn(EN)_2](ClO_4)_2 > [Ni(EN)_2](ClO_4)_2 > [Cu(EN)_2](ClO_4)_2 > [Co(EN)_2](ClO_4)_2$ . Explosion-delay measurements were carried out to investigate the response of these complexes under conditions of rapid heating. If the logarithm of the explosion delay is plotted against the reciprocal absolute temperature, a straight line can be drawn through the data points.

## 8 C<sub>3</sub> and C<sub>4</sub> Di- and Triamines

### 8.1 Propylene Diamine

There exist two isomeric propylene diamines, 1,2-diaminopropane,  $H_3CCH(NH_2)CH_2NH_2$ , CAS RN [78-90-0], and 1,3-diaminopropane, bis-aminomethylmethane,  $H_2NCH_2CH_2CH_2NH_2$ , CAS RN [109-76-2], both with a gross formula of  $C_3H_{10}N_2$ . and a molar mass of 74.12 g/mol. Physical properties of diaminopropane isomers are summarized in Table 40.

**Table 40:** Physical properties of diaminopropane isomers.

|                             | 1,3-diaminopropane                | 1,2-diaminopropane            |
|-----------------------------|-----------------------------------|-------------------------------|
| Molecular mass              | 74.12 g/mol                       | 74.12 g/mol                   |
| Density                     | 0.888 g/cm <sup>3</sup>           | 0.870 g/cm <sup>3</sup>       |
| Melting point               | 261.15 K = -12 °C = 10.4 °F       | 236.0 K = -37.1 °C = -34.9 °F |
| Boiling point               | 413.2 K = 140.1 °C = 284.1 °F;    | 392.7 K = 119.6 °C = 247.2 °F |
| Vapor pressure              | <1.1 kPa or 11.5 mm Hg (at 20 °C) | 1.9 Pa (at 20 °C)             |
| Refractive index $n_D^{20}$ | 1.458                             | 1.446                         |

Viscosity data for 1,2-diaminopropane have been obtained in the temperature range of 238 to 323 K (-35 to +50 °C) using an Ubbelohde viscometer [41]. The results were compared with existing data, and all the data were fitted to the Fulcher (Tammann-Hesse) equation by the method of least squares. The significance of the values of  $T_0$  in this equation for these and other associated liquids was correlated to the molecular structure of this molecule. The viscosity data in Table 41 below can be expressed by a Fulcher-type equation

$$\log \eta = -1.0755 + 165.754/(T - 166.751)$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. This equation is valid for the range from 238 to 323 K (–35 to +50 °C). The accuracy of the results from the equation is  $\pm 1.1\%$ . The viscosity calculated for 298 K is 1.54 cPs (compared to 1.57 cPs listed in the table).

**Table 41:** Viscosity and density of 1,2-diaminopropane.

| Temperature |     | Viscosity |       | Density | Temperature |    | Viscosity |        | Density |
|-------------|-----|-----------|-------|---------|-------------|----|-----------|--------|---------|
| K           | °C  | mPa s     | cPs   | g/mL    | K           | °C | mPa s     | cPs    | g/mL    |
| 238         | –35 | 16.47     | 16.47 | 0.9140  | 283         | 10 | 2.206     | 2.206  | 0.8690  |
| 243         | –30 | 13.20     | 13.20 | 0.9087  | 288         | 15 | 1.925     | 1.925  | 0.8639  |
| 248         | –25 | 9.372     | 9.372 | 0.9030  | 293         | 20 | 1.709     | 1.709  | 0.8580  |
| 253         | –20 | 6.965     | 6.965 | 0.8987  | 298         | 25 | 1.570     | 1.570  | 0.8540  |
| 258         | –15 | 5.322     | 5.322 | 0.8935  | 303         | 30 | 1.395     | 1.395  | 0.8487  |
| 263         | –10 | 4.354     | 4.354 | 0.8880  | 308         | 35 | 1.227     | 1.227  | 0.8440  |
| 268         | –5  | 3.610     | 3.610 | 0.8834  | 313         | 40 | 1.173     | 1.173  | 0.8397  |
| 273         | 0   | 3.032     | 3.032 | 0.8787  | 318         | 45 | 1.045     | 1.045  | 0.8351  |
| 278         | +5  | 2.704     | 2.704 | 0.8737  | 323         | 50 | 0.9407    | 0.9407 | 0.8303  |

Data source: [41]

Comparing the temperature dependence of the IR spectra of the condensed phase heated slowly ( $dT/dt = 50\text{ °C/min}$ ) and the fast thermolysis ( $dT/dt > 100\text{ °C/s}$ ) of propylene-1,3-diammonium dinitrate (PDDN) and diperchlorate (PDDP), it was found that PDDP exploded on heating whereas PDDN decomposed with much less energy [183].  $\text{HNO}_3(\text{G})$  was formed by dissociation in the initial decomposition of PDDN, but no  $\text{HClO}_4(\text{G})$  was detected from PDDP. The X-ray density of PDDP is  $1.789\text{ g/cm}^3$ .

## 8.2 Diethylenetriamine

Diethylenetriamine, also known as 2,2'-iminodi(ethylamine),  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ ,  $\text{C}_4\text{H}_{13}\text{N}_3$ , CAS RN [111-40-0], sometimes abbreviated DETA, is a trifunctional, high-boiling amine. It is often used as an intermediate in the chemical industry for the production of detergents, moisturizers, solvents, dyes, and ion exchangers. DETA is a by-product of the production of ethylenediamine from ethylene dichloride. It can be produced by reaction of 1,2-dichloroethane with ammonia, but this reaction also generates ethylene diamine, piperazine, and  $\beta$ -aminoethyl-*N*-piperazine as by-products, some of which remain in DETA as contaminants. Commercial DETA may contain up to 9% of contaminants, thus affecting the properties of fuel mixtures prepared using this type of DETA. DETA was first used as a rocket fuel in the mixture with UDMH in the propellant called Hydryne (MAF-4) and in the mixed amine fuels MAF-1, MAF-3, and MAF-5.

### 8.2.1 Physical Properties of Diethylenetriamine

The physical properties of diethylenetriamine are summarized in Table 42.

**Table 42:** Physical properties of diethylenetriamine.

| Property                    | SI units                                                             | Non-SI units                                                                                             | References |
|-----------------------------|----------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|------------|
| Molecular mass              | 103.17 g/mol                                                         | 9.693 mol/kg                                                                                             |            |
| Freezing point              | 239.7 K                                                              | −33.4 °C                                                                                                 | [184]      |
| Freezing point              | 234 K                                                                | −39 °C                                                                                                   | [184]      |
| Boiling point               | 480 K                                                                | 207 °C                                                                                                   | [184]      |
| Density                     | 952.5 kg/m <sup>3</sup> at 293 K<br>909.5 kg/m <sup>3</sup> at 344 K | 0.9525 g/cm <sup>3</sup> (at 20 °C)<br>0.9095 g/cm <sup>3</sup> (at 71 °C)                               | [184]      |
| Vapor pressure              | 27 Pa at 293 K<br>683 Pa at 344 K<br>83 kPa at 393 K                 | 2.72 × 10 <sup>−4</sup> atm (at 20 °C)<br>6.74 × 10 <sup>−3</sup> atm (at 71 °C)<br>0.82 atm (at 120 °C) | [184]      |
| Viscosity                   | 4.77 mPa s at 293 K<br>0.135 mPa s at 344 K                          | 4.77 cPs (at 20 °C)<br>0.135 cPs (at 71 °C)                                                              | [184]      |
| Heat of combustion, liquid  | 51.5 kJ/mol                                                          | 12.3 kcal/mol                                                                                            | [184]      |
| Enthalpy of formation       | −64.3 kJ/mol                                                         | −149 cal/g = −15.37 kcal/mol                                                                             | [27]       |
| Refractive index $n_D^{20}$ | 1.484                                                                | 1.484                                                                                                    | [184]      |

The *USAF Propellant Handbooks, Hydrazine Fuels, Volume 1*, contains a unit with physical properties of DETA from which the following properties were copied [184]. It also has three graphs showing the density, vapor pressure, and viscosity of DETA as a function of temperature. The density of DETA as a function of temperature for the range 273–333 K (0–60 °C) can be calculated using the equation

$$\rho = 1.1955 - 8.2751 \times 10^{-4} T$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $T$  is the temperature in kelvin. The vapor pressure of DETA for the range 293 to 483 K (20 to 210 °C) can be calculated using the equation

$$\log P = 8.3982 - 2651.50/T$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The absolute viscosity of DETA as a function of temperature for the range 253 to 303 K (−20 to +30 °C) can be calculated using the equation

$$\log \mu = 18.3037 - 1.1384 \times \frac{10^4}{T} + 1.833 \times \frac{10^6}{T^2}$$

where  $\mu$  is the absolute viscosity in cPs and  $T$  is the temperature in kelvin. No reliable data on enthalpy of formation of DETA could be found, but the best available data is  $\Delta H_f^{298} = -77.4 \text{ kJ/mol} = -18.5 \text{ kcal/mol}$ .

### 8.2.2 Chemical Properties of Diethylenetriamine

When exposed to air, DETA slowly auto-oxidizes and discolors brown. Commercial DETA may contain 9–10 mass-% of other amines as contaminants. The main contaminant is 2-aminoethylpiperazine.

For U.S. government procurement, the purity requirements of DETA were at one time defined by MIL-D-50025B(MU), which was later superseded by Federal Specification O-D-1271 dated November 1967 (20 June 1985), which was canceled in 1998 and superseded by A-A-59162, which was renewed in 2015. These specifications contain descriptions of analysis methods for quality control of this fuel, which is also used as a decontaminating agent. Like ethylenediamine, DETA can also be used to sensitize nitromethane, making a liquid explosive compound similar to PLX.

### 8.2.3 Fuel Mixtures Containing Diethylenetriamine

There have been several fuel mixtures that contained diethylenetriamine, but none is still in use as a rocket fuel. The description given here is mostly a historical account. There is some duplication of the information on MAF fuel mixtures between the current section and the UDMH fuel blends section in this volume in the chapter “Dimethylhydrazines.”

### 8.2.4 Hydyne

Hydyne was a mixture of 60 mass-% UDMH and 40 mass-% DETA. It has also been designated as MAF-40 (mixed amine fuel) or MAF-4. It was first used as fuel in a Jupiter-C satellite launcher, which successfully launched the first U.S. artificial satellite, Explorer-1. Jupiter-C was originally designed for ethanol, but the substitution with the denser Hydyne in the same given tank envelope gave it a higher performance. In a Redstone ballistic missile, the substitution of ethanol with Hydyne would have increased its range by 12%. The performance of MAF-4 can be further increased by adding up to 9 mass-% acetonitrile to the fuel mix.

#### 8.2.4.1 Physical Properties of Hydyne

The physical properties of Hydyne are summarized in Table 43.

The *USAF Propellant Handbooks, Hydrazine Fuels, Volume 1* contains a unit with physical properties of MAF-4 from which the following properties were copied [184]. It also has three graphs showing the density, viscosity, and vapor pressure of MAF-4 as

**Table 43:** Physical properties of Hydyne.

| Property             | SI units                               | Other units                                |
|----------------------|----------------------------------------|--------------------------------------------|
| Freezing point       | <189 K                                 | <-84.4 °C                                  |
| Boiling point        | 343 K                                  | 69.6 °C                                    |
| Density              | 0.859 g/cm <sup>3</sup> (at 20 °C)     | 0.809 g/cm <sup>3</sup> (at 71 °C)         |
| Vapor pressure       | 0.18 atm (at 20 °C)                    | 1.23 atm (at 71 °C)                        |
| Viscosity            | 1.24 cPs (at 20 °C)                    | 0.514 cPs (at 71 °C)                       |
| Critical temperature | 559 K                                  | 286 °C                                     |
| Heat capacity cp     | 2.71 J g <sup>-1</sup> K <sup>-1</sup> | 0.648 cal g <sup>-1</sup> °C <sup>-1</sup> |

Data source: [184]

a function of temperature. The density of MAF-4 as a function of temperature for the range 223 to 343 K (-50 to +70 °C) can be calculated using the equation

$$\rho = 1.1697 - 1.086 \times 10^{-3} T$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $T$  is the temperature in kelvin. The vapor pressure of MAF-4 for the range 290 to 350 K (17 to 77 °C) can be calculated using the equation

$$\log P = 8.2762 - 1849.4/T$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The approximate absolute viscosity of MAF-4 can be calculated from the equation

$$\log \mu = -13.063 + 1.1095 \times \frac{10^4}{T} - 3.2894 \times \frac{10^6}{T^2} + 3.4457 \times \frac{10^8}{T^3}$$

where  $\mu$  is the viscosity in cPs and  $T$  is the temperature in kelvin. Assuming an average molecular mass of 72.1498 g/mol for the mixture, and assuming additive behavior and no heat of mixing of the two fluids, the average enthalpy of formation of MAF-4 would be +15.533 kJ/mol = +3.7125 kcal/mol or +51.455 cal/g.

#### 8.2.4.2 Chemical Properties of Hydyne

The chemical properties of Hydyne are determined by those of its constituents. Hydyne is hygroscopic and absorbs moisture and carbon dioxide from the air. Hydyne is miscible with water in all proportions but is immiscible with gasoline.

The analysis of Hydyne mixtures can be performed by measuring physical properties that are quite different for the two constituents, such as index of refraction or dielectric constant, and comparing the results to data from a calibration curve. This method is suitable only for binary mixtures and will fail if the propellant contains a third ingredient (e.g., acetonitrile).

Mixtures of hydrazine or UDMH with DETA can be analyzed by an acidimetric method in which a sample is taken and titrated before and after reaction with sali-

cyl aldehyde. Salicyl aldehyde ties up the hydrazine(s) as hydrazone(s), which have a different pK than the free hydrazine(s) or DETA [185].

The water content of Hydyne can be determined by gas chromatography (GC) or IR spectrophotometry [186].

The radiolysis of Hydyne, UDMH, and DETA was studied in preparation for future space use or potential radiation exposure in a nuclear war battlefield [187]. The gas evolution of UDMH, DETA, and Hydyne when exposed to  $8.5 \times 10^6$  rads was 199, 101, and 164 cm<sup>3</sup>, respectively. It was discovered that the undesirable gas evolution can be reduced by the addition of 5% of a radical scavenger, such as methyl methacrylate.

#### 8.2.4.3 Handling of Hydyne

The vapor pressure of Hydyne is governed by the vapor pressure of UDMH; consequently, the handling precautions are the same as for handling UDMH under pressure and in large quantities.

As always, good ventilation of the work area where Hydyne is transferred or stored is important. Storage tanks should have a pad of nitrogen under slightly positive pressure to prevent the intrusion of air and carbon dioxide.

Yellow discoloration may indicate that some air has intruded or was not carefully excluded when the storage tanks were filled. Hydyne can be stored for very long times. Therefore, it is also suitable for missiles with prepackaged and exchangeable propellant tanks [188]. Hydyne is non-detonable. It is insensitive to initiation by booster charges consisting of 50–100 g tetryl [189].

The flammable limits of Hydyne vapors in air are similar to those of UDMH (based on measurements by the USBM): At 788 kPa and 373 K (7.8 atm and 100 °C), the lower limit of flammability is at  $4.2 \pm 0.2$  vol-% Hydyne, and that of UDMH under identical conditions is  $2.2 \pm 0.3$  vol-%. It was difficult to determine the upper limit of flammability because at 373 K and in the presence of air, the incipient oxidation reaction and decomposition resulted in a substantial pressure increase (twice the starting pressure) before the mixture could be ignited.

This troublesome decomposition reaction had also been observed in other laboratories [190]. Hydyne vapors will auto-ignite in inert gases (helium or nitrogen) in the absence of oxygen at 671 K (398 °C). In air, the vapors will ignite at 514 K (241 °C). For pure UDMH, the corresponding values are 656 K (383 °C) and 507 K (234 °C), respectively.

Hydyne fires can be fought and extinguished with water, similar to UDMH fires. Open-pan fires of Hydyne were studied to find optimum and safe fire-extinguishing methods [191]. It was noted that fuel-rich flames emitted large quantities of hydrogen cyanide, which might be dangerous to firefighters if they inhale it. The Hydyne used in these tests consisted of 41% UDMH, 50% DETA, and 9% acetonitrile.



### 8.2.5 Mixed Amine Fuel MAF-1

Mixed amine fuel 1, MAF-1, is a mixture of a hydrazine and an amine with a nitrile compound that adds energy in the form of the  $\text{—C}\equiv\text{N}$  cyanide group. MAF-1 is a clear, yellowish liquid with a fishy odor. It is hygroscopic and will absorb carbon dioxide; therefore, air exposure must be kept at a minimum. MAF-1 was used as the fuel for inhibited red fuming nitric acid (IRFNA) in the ASM-N7A and Bullpup B (GAM-83) air-to-ground missiles, which were placed in service for the U.S. Air Force and U.S. Navy by the thousands (ASM-N-7 1959-1970s; ASM-N-7A/AGM-12B 1965-1970s). The AGM-12 Bullpup was the first mass-produced air-to-ground joystick-radio-guided missile in the U.S. military. Deployed by the U.S. Navy in 1959, it was created based on defensive needs in the Korean War. The Bullpup was used on aircraft such as the A-4 Skyhawk, A-6 Intruder, F-105 Thunderbolt, and F-4 Phantom. It was eventually replaced in the 1970s by the AGM-62 Walleye and the AGM-65 Maverick. When the Bullpup missiles were decommissioned, large amounts of MAF-1 had to be neutralized and disposed of.

#### 8.2.5.1 Physical Properties of Mixed Amine Fuel MAF-1

The *USAF Propellant Handbooks, Hydrazine Fuels, Volume 1* contains a unit with physical properties of MAF-1, from which the following properties were copied [184]. It also has two graphs showing the density and vapor pressure of MAF-1 as a function of temperature. The density of MAF-1 as a function of temperature for the range 223 to 344 K ( $-50$  to  $+71^\circ\text{C}$ ) can be calculated using the equation

$$\rho = 1.1391 - 9.0228 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. The density range at 298 K as specified by MIL-P-23741A is  $0.863\text{--}0.875 \text{ g/cm}^3$ . The vapor pressure of MAF-1 for the range 273 to 397 K ( $0$  to  $124^\circ\text{C}$ ) can be calculated using the equation

$$\log P = 12.9134 - 5008.6/T + 5.2332 \times \frac{10^5}{T^2}$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.

#### 8.2.5.2 Chemical Properties of Mixed Amine Fuel MAF-1

The composition of MAF-1 is defined by military specification MIL-P-23741A (canceled) is shown in Table 44 [192]. In addition to the composition called out in the military specification, Thiokol RMD also formulated a propellant blend that appeared to be at one boundary of the specification tolerance range.

The deviations may be partially due to the poor quality of commercial DETA, which may contain up to 10 mass-% of other amines as contaminants.

**Table 44:** Composition of mixed amine fuel MAF-1.

| Constituent        | MIL-P-23741A<br>Composition, mass-% | Thiokol RMD<br>Nominal composition, mass-% |
|--------------------|-------------------------------------|--------------------------------------------|
| DETA               | 49.7 ± 0.7                          | 50.5                                       |
| UDMH               | 39.0 ± 1.5                          | 40.5                                       |
| CH <sub>3</sub> CN | 10.0 ± 1.0                          | 9.0                                        |
| H <sub>2</sub> O   | 1.0 maximum                         | —                                          |

### Analysis of Mixed Amine Fuel MAF-1

Analytical methods for the analysis of MAF-1 are described in MIL-P-23741A. The UDMH content of MAF-1 can be determined by iodometric titration in HCl solution. The acetonitrile content of MAF-1 is determined by an IR spectrophotometric method between 4 and 5  $\mu\text{m}$  or by gas chromatography. The water content can be determined by gas chromatography.

#### 8.2.5.3 Materials Compatibility with MAF-1

Real-time storage data based on long periods of exposure of Bullpup 2014-T6 aluminum alloy tankage revealed that containment of MAF-1 fuel and IRFNA oxidizer by 2014-T6 aluminum alloy tankage for more than 3 years had not affected the mechanical, physical, or chemical properties of the materials to a degree that would impede tactical performance of the missile [193].

The compatibility of Bullpup missile tankage and components with IRFNA and MAF-1 propellants was measured for a period of 10–12 years [194]. Tankage material was the 2014-T6 aluminum alloy. Evaluation of the tank and component surfaces disclosed only minor corrosion effects of a general surface nature. The degree of material degradation that occurred was considered insignificant and would not alter the functional capability of the missile.

#### 8.2.5.4 Toxicity of MAF-1

Inhalation and cutaneous toxicity studies of MAF-1 were initiated to determine the toxicity of the fuel and compare it with those of the separate components [195]. The toxicity of MAF-1 is dominated by the vapor pressure of UDMH.

### 8.2.6 Mixed Amine Fuel MAF-3

MAF-3 was a mixture of 80% DETA and 20% UDMH and was once used in a Sparrow III missile with prepackaged propellants. Properties of MAF-3 were once specified by MIL-P-23686A, Propellant, mixed amine fuel, MAF-3. The density of MAF-3 can be calculated from the equation

$$\rho = 1.1709 - 8.5269 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. The approximate absolute viscosity of MAF-3 can be calculated from the equation

$$\log \mu = -3.3444 + 2828.6/T - 1.0403 \times \frac{10^6}{T^2} + 1.6141 \times \frac{10^8}{T^3}$$

where  $\mu$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The properties of MAF-4 are described under the previous heading "Hydyne."

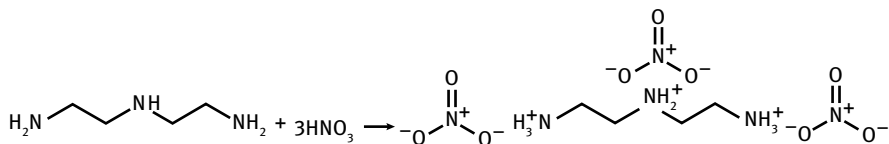
### 8.2.7 Mixed Amine Fuel MAF-5

There was never an official composition for the blend called MAF-5, but rudimentary information gathered from Thiokol RMD reports indicated that the approximate composition of this fuel mixture was 50.5% DETA, 29.5% UDMH, and 20% acetonitrile. The acetonitrile content was thus substantially higher than in MAF-1 [184].

### 8.2.8 Diethylenetriammonium Salts

Diethylenetriammonium(3+) trinitrate forms a 1 : 1 addition compound with AN, which also eliminates the III  $\leftrightarrow$  IV phase transition of AN. Diethylenetriamine nitrates form complexes with metal nitrates similar to those formed with propane-1,3-diamine and its nitrates [196].

Diethylenetriammonium(3+) trinitrate (DETN) forms a eutectic with EDDN, melting between 460.7 and 461.3 K (187.6 and 188.2°C) when it was being tested as a melt-cast explosive and as a replacement for Composition B in mortar rounds and bomb fills [164]. The preparation of DETN is a simple acid–base reaction:



### 8.3 $\text{C}_{n>2}$ Polyalkylammonium Salts

Similar to ethylenediamine, 1,3-propanediamine (bis-aminomethylmethane) forms salts with most strong acids. 1,3-propanediamine forms a diperchlorate salt with perchloric acid, with an excess of acid.

#### 8.3.1 1,3-Propanediammonium Diperchlorate

Propane-1,3-diammonium diperchlorate,  $[\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{H}_3](\text{ClO}_4^-)_2$ ,  $\text{C}_3\text{H}_{12}\text{Cl}_2\text{N}_2\text{O}_8$ , PDDP, is an energetic salt with a molecular mass of 275.04 g/mol and mon-

oclinic crystals crystallizing in space group  $P2_1/c$  with the unit cell parameters of  $a = 7.298(4) \text{ \AA}$ ,  $b = 14.388(9) \text{ \AA}$ ,  $c = 9.708(6) \text{ \AA}$ ,  $\beta = 96.79(4)^\circ$ ,  $Z = 4$ , and  $\rho_{\text{XRD}} = 1.8 \text{ g/cm}^3$  [197].

A comparison of the temperature dependence of the IR spectra of the condensed phase with slow heating ( $dT/dt = 5^\circ\text{C/min}$ ) and the fast thermolysis ( $dT/dt \geq 100^\circ\text{C/s}$ ) of propane-1,3-diammonium dinitrate (PDDN) and diperchlorate (PDDP) showed that PDDP exploded on heating, whereas PDDN decomposed with much less energy [198].  $\text{HNO}_3(\text{G})$  was formed by dissociation in the initial decomposition of PDDN, but  $\text{HClO}_4(\text{G})$  was not detected from PDDP decomposition. PDDP is unique among the compounds studied by this technique in that a solid–solid phase transition could be detected during rapid heating prior to the onset of decomposition. The initial crystal structure of PDDP was characterized by XRD: as monoclinic, space group  $P2_1/c$ , and lattice parameters of  $a = 7.316(2) \text{ \AA}$ ,  $b = 14.428(2) \text{ \AA}$ ,  $c = 9.742(2) \text{ \AA}$ ,  $\beta = 96.81^\circ$ ,  $V = 1021.1(3) \text{ \AA}^3$ ,  $Z = 4$ , and  $\rho_{\text{XRD}} = 1.789 \text{ g/cm}^3$ .

Bis(propylenediamino) metal perchlorate complexes such as  $[\text{M}(\text{PN})_2](\text{ClO}_4)_2$  (where  $\text{M} = \text{Cr, Mn, Ni, Cu, Zn}$  and  $\text{PN} = \text{propylenediamine}$ ) have been prepared and characterized by gravimetric methods, TGA, DTA, IR, and elemental analysis [199]. The thermal stability of the complexes decreased in the following order:  $[\text{Cr}(\text{PN})_2](\text{ClO}_4)_2 > [\text{Mn}(\text{PN})_2](\text{ClO}_4)_2 > [\text{Zn}(\text{PN})_2](\text{ClO}_4)_2 > [\text{Ni}(\text{PN})_2](\text{ClO}_4)_2 > [\text{Cu}(\text{PN})_2](\text{ClO}_4)_2$ . Similar complexes were formed with bis(diethylenetriamine) metal nitrates.

3-amino-1-propylammonium perchlorate,  $[\text{C}_3\text{H}_{11}\text{N}_2]\text{ClO}_4$ , forms crystals with a molecular mass of  $M = 174.58 \text{ g/mol}$ , which are held together by an extensive hydrogen-bonded system [200]. It forms orthorhombic crystals at  $T = 296 \text{ K}$  in space group  $Pbca$  and cell parameters of  $a = 12.337(4) \text{ \AA}$ ,  $b = 12.888(6) \text{ \AA}$ ,  $c = 9.677(7) \text{ \AA}$ ,  $V = 1538 \text{ \AA}^3$ ,  $Z = 8$ , and  $\rho = 1.507 \text{ g/cm}^3$ .

### 8.3.2 1,3-Propanediammonium Dinitrate and Diperchlorate

1,3-propanediammonium dinitrate  $[\text{PDDN}, \text{NO}_3\text{NH}_3(\text{CH}_2)_3\text{NH}_3\text{NO}_3]$  is a potential explosive but does not have the same thermal stability as EDDN. PDDN undergoes a solid–solid phase transition at  $335 \text{ K}$  ( $62^\circ\text{C}$ ) and melts at  $399 \text{ K}$  ( $126^\circ\text{C}$ ) without decomposition [201]. Evolution of  $\text{HNO}_3$  vapor occurs at  $553 \text{ K}$  ( $280^\circ\text{C}$ ), followed by the oxidation–reduction products of  $\text{HNO}_3$  and the alkylamine. 1,3-propanediammonium diperchlorate, PDDP,  $\text{ClO}_4\text{NH}_3(\text{CH}_2)_3\text{NH}_3\text{ClO}_4$ , is a potential explosive. PDDP undergoes a solid–solid phase transition at  $423 \text{ K}$  ( $150^\circ\text{C}$ ), which significantly changes the crystal lattice structure and the ion dynamics. The decomposition starts soon after melting at  $553 \text{ K}$  ( $280^\circ\text{C}$ ) and leads to  $\text{HCl}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  as products. 1,3-propanediammonium diperchlorate forms crystals with strong hydrogen bonding [202].

### 8.3.3 1,4-Butanediammonium Dinitrate

The effects of single or double protonation of 1, $\omega$ -alkylenediamines and of substitution along the carbon chain by methyl or fluorine groups on the molecular structure (bond lengths and bond orders) were calculated by an *ab initio* self-consistent field molecular orbital procedure using the GAUSSIAN 82 system of programs [203]. The emphasis was on 1,4-diaminobutane and its derivatives and protonated forms since these compounds have mostly been investigated using experimental methods. It was found that the protonation of a nitrogen causes its bond to the terminal carbon of the chain to become considerably weaker. The weakening is even more pronounced when the terminal carbon is methylated.

#### 8.3.3.1 Thermal Stability of 1,4-Butanediammonium Dinitrate

The kinetic deuterium isotope effect for the induction period during the decomposition of 1,4-butanediammonium dinitrate in a differential scanning calorimeter was determined at 538, 543, and 548 K (265, 270, and 275 °C) for both normal 1,4-butanediammonium dinitrate (BDD) and hexadeutero-1,4-butanediammonium dinitrate (BDD-d6) in which the hydrogen atoms on the nitrogen atoms had been replaced by deuterium atoms [204]. The  $k_H/k_D$  ratio was found to be 1.09, 1.11, and 1.33 at 538, 543, and 548 K (265, 270, and 275 °C), respectively. The faster rate for the protium compound can be interpreted as indicating C—N bond breaking in the rate-determining step. The corresponding activation energies were 288 and 241 kJ/mol (68.9 and 57.5 kcal/mol) for BDD and BDD-d6, respectively.

The thermal decomposition of 1,4-butanediammonium dinitrate (BDDN) was investigated using DSC, ARC, TGA, tandem GC/MS, and high-performance liquid chromatography (HPLC) [205, 206]. BDDN decomposes to a mixture of condensable and gaseous products. The composition of the products suggests that early in the sequence of reactions, a proton transfer takes place from a cation to an anion, followed by a C—N bond rupture. Heterocyclic decomposition products form by a cyclo-elimination process. This reminds one of the fact that 1,5-pentanediammonium dinitrate cannot be prepared at all because of its tendency to form piperidine derivatives. Nitramine and nitrosamine compounds may also play a role as intermediates in the BDDN decomposition. Isotope substitution with deuterium had a measurable effect on thermal stability and sensitivity and gave some clues about the key steps in BDDN decomposition [207].

Mass spectrometric investigation of the initial stages of the decomposition of BDDN using a molecular beam-sampling time-of-flight quadrupole mass spectrometer system showed that the initial step is the dissociation into 1,4-butanediamine and nitric acid [208]. Standard electron impact ionization and fast atom-bombardment mass spectrometric analyses of BDDN gave support to the molecular beam study. See also [21, 154].

### 8.3.4 1,4-Butanediammonium Diperchlorate

The strand-burning rate of 1,4-butanediammonium diperchlorate (also called tetramethylenediamine diperchlorate or tetramethylenediammonium diperchlorate) has been compared to that of ethylenediammonium diperchlorate and phenylenediammonium diperchlorate [169]. The burning-rate function of tetramethylenediammonium diperchlorate differs substantially from those of ethylenediammonium diperchlorate and phenylenediammonium diperchlorate. In the range of 121-atm, the rate increased according to the function

$$r_b = 0.24p^{0.7}$$

where  $r_b$  is the burning rate in cm/s and  $p$  is the pressure in atmospheres. Above 21 atm the curve slope increased somewhat, but at 37 atm the rate of combustion dropped abruptly from 4.2 to 1.0–1.3 cm/s; furthermore, it dropped so rapidly that it was impossible to obtain an intermediate rate value. In the range from 48 to 200 atm, the combustion did not propagate.

### 8.3.5 1,6-Hexanediammonium Dinitrate

Mass spectrometric investigations [205, 208], on the initial stages of thermal decomposition of 1,6-hexanediammonium dinitrate, hexamethylenediamine dinitrate, HDDN, CAS RN [6143-53-9], revealed the formation of the corresponding amine and nitric acid at 433 to 453 K (160 to 180 °C). The nitric acid partially decomposed to produce nitrogen dioxide.

The heat of combustion at constant volume of hexamethylenediamine dinitrate is 4177 kJ/mol = 998.4 kcal/mol [60].

### 8.3.6 Pentaerythritylammonium Salts

Pentaerythritol is the polyol that when nitrated forms the frequently used primary explosive PETN. Replacing all hydroxyls with amino groups leads to pentaerythritylamine, pentaerythrityltetramine,  $C(CH_2NH_2)_4$ , 2,2-bis-aminomethyl-1,3-propanediamine, a strong amine that forms energetic salts with nitric acid, perchloric acid, or trinitromethane. It can form mono-, di-, tri-, or tetranitrates or -perchlorates.

Pentaerythrityltetramine can be prepared by treating pentaerythrityl tetrachloride with excess hot, highly compressed ammonia in 57% yield at 52% conversion. The ammonolysis may be conducted either in supercritical ammonia alone or in methanol as the solvent. The product amine is isolated by precipitating it as the water-insoluble disulfate; simply washing the precipitate with water yields disulfate of high purity [209].

Pentaerythrityltetramine was prepared by starting from pentaerythritol via two steps. Pentaerythrityl tetrabromide was then treated with sodium p-toluenesulfonamide to give an intermediate, which was converted to pentaerythrityl tetramine disulfate. The overall yield was 30% [210].

### 8.3.7 Pentaerythrityl Tetraammonium Tetranitrate and Pentaerythrityl Tetraammonium Tetraperchlorate

The tetraperchlorate of pentaerythrityltetramine, a very explosive substance, was prepared for the first time in a U.S. Navy laboratory [165]. The gross formula is  $C_5H_{20}N_4O_{16}Cl_4$ , CAS RN [89416-99-9].

When the solid crystalline sulfate of 2,2-bis(aminomethyl)-1,3-diaminopropane is treated with excess dilute nitric acid, the sulfate ion is completely displaced by nitrate ion in a metathetical reaction [211]. The resulting crystalline nitrate,  $C(CH_2NH_2)_4 \cdot 4HNO_3$ , is only slightly soluble in water and therefore can be easily isolated in high purity. Its identity was established by acid–base titration, proton magnetic resonance, IR spectrophotometry, and elemental analysis. It may be stored at 423 K (150 °C) for many hours with negligible decomposition, but it decomposes within a few minutes at 473 K (200 °C). Attempts to cause it to detonate have been unsuccessful. When ignited, the nitrate burned slowly, leaving a carbonaceous residue. The low solubility, high melting point, high density, and thermal stability of this nitrate are a sharp contrast to the properties of ammonium nitrate and methyl ammonium nitrate. Density of the crystals is 1.7 g/cm<sup>3</sup>, which is well above the density of ethylene diamine dinitrate (1.58 g/cm<sup>3</sup>), MEAN (1.42 g/cm<sup>3</sup>), and hexamethylene tetramine dinitrate (1.57 g/cm<sup>3</sup>) and about the same as that of AN (1.72 g/cm<sup>3</sup>).

Pentaerythrityl tetraammonium tetranitrate decomposes by initially liberating  $HNO_3$  before an oxidation reaction consumes the organic skeleton. Ammonia, AN,  $NO_2$ , and  $N_2O$  are by-products. The pyrolysis mechanism of pentaerythrityltetraammonium tetranitrate,  $[C(CH_2NH_3)_4](NO_3)_4$ , PTTN, was determined by rapid-scan FTIR spectroscopy [23]. The initial gaseous product at about 490 K was desorbed  $HNO_3$ , resulting, most likely, from the transfer of a proton from the cation to the anion. C–N bond fission also took place and liberated  $NH_3$ , which reacted with  $HNO_3(G)$  to produce  $NH_4NO_3(G)$ .  $HNO_3(G)$  was rapidly consumed, while oxidized fragments of the hydrocarbon portion appeared. The sequence of appearance of products suggests that decomposition of the cation begins at the exterior and progresses inward, a fact that is consistent with chemical attack by an external agent, such as  $HNO_3$ . PTTN is intriguing because its melting–decomposition point is higher than that of AN (~490 vs. 440 K), and it does not undergo the solid–solid phase transitions that AN suffers from. At slow heating rates in TGA, a five-step weight loss occurred in the 493–555 K range, the first four steps of which (493–505 K) each corresponded to the loss of one  $HNO_3$ . A study of the thermal decomposition mechanism of the corresponding perchlorate salt  $[C(CH_2NH_3)_4](ClO_4)_4$  was complicated by premature deflagration or detonation as soon as the temperature reached 520 K. The salt is excessively shock sensitive. The crystal structure of PTTN at 296 K is tetragonal, space group  $P4_1$  (or  $P4_3$ ), with crystal lattice parameters  $a = 10.156(2)$  Å and  $c = 14.629(4)$  Å.

Based on a detailed study of the electron density distribution function in pentaerythrityltetraammonium tetranitrate, reconstructed from high-resolution XRD data, the effect of unusual (from the standpoint of electrostatic considerations)

anion–anion contacts on the charge distribution in the crystal was analyzed [212]. Interactions between the likely charged species can cause a significant redistribution of the charge density over the anionic (cationic) sublattice and, as a result, significantly affect the strength of conventional cation–anion bonds.

## 9 Cycloaliphatic Amines

Cycloaliphatic amines are composed of a cyclic hydrocarbon structural component and an amine functional group external to that ring. The external amino group may also carry additional linear alkyl groups [213]. The family consists of primary amines directly bonded to a cycloalkane by a single bond to a secondary carbon and includes cyclopropylamine,  $C_3H_7N$ ; cyclobutylamine,  $C_4H_9N$ ; cyclopentylamine,  $C_5H_{11}N$ ; cyclohexylamine,  $C_6H_{13}N$ ; cycloheptylamine,  $C_7H_{15}N$ ; cyclooctylamine,  $C_8H_{17}N$ ; and cyclododecylamine,  $C_{12}H_{25}N$ . Up through  $C_8$  they are colorless liquids at room temperature. There are numerous cycloaliphatic diamines. Cycloaliphatic amines are strong bases with basicities similar to those of simpler primary, secondary, or tertiary amines. Common reactions are salt formation with Brønsted and Lewis acids and exhaustive alkylation to form quaternary ammonium cations. Before a U.S. Food and Drug Administration ban on 1 January 1970, cyclamate non-caloric sweeteners were the major derivatives driving cyclohexylamine production. The melting point of cyclohexylammonium nitrate,  $C_6H_{11}NH_3NO_3$ , is 431 K = 158 °C.

### 9.1 Cyclopropylamine

Numerous hydrocarbons have been synthesized in which the strain from a three-carbon ring adds to the heat of combustion and enthalpy of formation. The same strategy has been applied to produce amines with better rocket performance. The strained bonds in the cyclopropyl ring add energy to the molecule, and that might make it a better rocket fuel than normal propylamine. The standard enthalpy of combustion of liquid cyclopropylamine,  $\Delta H_{\text{comb}}$ , was found to be  $-(2227 \pm 0.4) \text{ kJ/mol} = -(532.20 \pm 0.10) \text{ kcal/mol}$  by oxygen-bomb combustion calorimetry [214]. The standard enthalpy of formation,  $\Delta H_o^f(298.15 \text{ K})$ , of the liquid is  $+(45.8 \pm 0.5) \text{ kJ/mol} = +(10.95 \pm 0.12) \text{ kcal/mol}$ . The enthalpy of vaporization was derived from vapor pressure measurements, and the standard enthalpy of formation in the ideal gaseous state was calculated. The data are summarized and compared to those of other cycloalkylamines in Table 45.

The IR ( $4000\text{--}150 \text{ cm}^{-1}$ ) and Raman ( $4000\text{--}50 \text{ cm}^{-1}$ ) spectra of gaseous, liquid, and solid cyclopropylamine have been recorded along with the IR spectrum of matrix-isolated samples [215]. The vibrational spectra of all phases were consistent with the



predominance of a conformer having the  $\text{—NH}_2$  group in a trans position to the ring C—C bond, in agreement with microwave spectra of this molecule [216].

Salts of the charge-delocalized cations of the triaminocyclopropenium (tac) family bearing alkylamino substituents have been prepared and shown to be air-stable and water-stable ionic liquids. The reaction of tetrachlorocyclopropene with secondary amines gives triaminocyclopropenium chloride, which can be combined with various anions (azide, dicyanomethanide, or dicyanohydroborate) to yield ionic liquids that have very short ignition delays with WFNA [217]. Secondary amines used in this study were diallylamine, diethylamine, and dipropylamine.

2-Azido-*N*-cyclopropylethanamine (CPAZ) and 2-azido-*N,N*-dimethylcyclopropanamine (ADMCPA) have been evaluated as a replacement for MMH in hypergolic bipropellant combinations [218, 219]. The enthalpy of formation of liquid CPAZ was predicted to be +382 kJ/mol (+91.2 kcal/mol), with a density of 0.993 g/cm<sup>3</sup>. The enthalpy of formation of liquid ADMCPA was predicted to be +402 kJ/mol (+96.2 kcal/mol).

**Table 45:** Properties of liquid cycloalkylamines.

| Property                                                       | Cyclopropylamine                               | Cyclobutylamine                                                                      | Cyclopentylamine                                                                     |
|----------------------------------------------------------------|------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| Density                                                        | 0.808 g/cm <sup>3</sup>                        | 0.833 g/cm <sup>3</sup>                                                              | 0.860 g/cm <sup>3</sup>                                                              |
| Heat capacity<br>at 298 K                                      | —<br>2.58 J K <sup>-1</sup> g <sup>-1</sup>    | 0.586 cal °C <sup>-1</sup> g <sup>-1</sup><br>2.45 J K <sup>-1</sup> g <sup>-1</sup> | 0.556 cal °C <sup>-1</sup> g <sup>-1</sup><br>2.33 J K <sup>-1</sup> g <sup>-1</sup> |
| Heat of combustion<br>at 298 K                                 | 532.2 ± 0.1 kcal/mol<br>2227 ± 0.4 kJ/mol      | 684.96 ± 0.13 kcal/mol<br>2866 ± 0.5 kJ/mol                                          | 823.25 ± 0.19 kcal/mol<br>3444 ± 0.8 kJ/mol                                          |
| Enthalpy of formation<br>$\Delta H_0^f$ (L)                    | +10.95 ± 0.12 kcal/mol<br>+45.8 ± 0.5 kJ/mol   | +1.34 ± 0.14 kcal/mol<br>+5.61 ± 0.6 kJ/mol                                          | −22.74 ± 0.20 kcal/mol<br>−95.14 ± 0.8 kJ/mol                                        |
| Enthalpy of vaporiza-<br>tion at 298 K $\Delta H_{\text{vap}}$ | 7.47 ± 0.10 kcal/mol<br>31.2 ± 0.4 kJ/mol      | (8.5 ± 0.1 kcal/mol) <sup>a</sup><br>(35.6 ± 0.4 kJ/mol) <sup>a</sup>                | 9.606 ± 0.10 kcal/mol<br>40.2 ± 0.4 kJ/mol                                           |
| Enthalpy of formation<br>$\Delta H_0^f$ (G)                    | +18.42 ± 0.16 kcal/mol<br>+77.07 ± 0.67 kJ/mol | (+9.8 ± 0.1 kcal/mol) <sup>a</sup><br>(+41.0 ± 0.4 kJ/mol) <sup>a</sup>              | −13.13 ± 0.22 kcal/mol<br>−54.9 ± 0.9 kJ/mol                                         |

<sup>a</sup> Note: Values in parentheses were only estimated, not measured

Data source: [214,220]

## 9.2 Cyclobutylamine

The enthalpies of combustion of cyclobutylamine and cyclopentylamine were measured by precision oxygen-bomb combustion calorimetry [220]. The standard enthalpy of combustion,  $\Delta H_{\text{comb}}$  (298.15 K), of cyclobutylamine in the liquid state was 2866 ± 0.5 kJ/mol (684.96 ± 0.13 kcal/mol), and standard enthalpy of combustion of cyclopentylamine was 3444 ± 0.8 kJ/mol (823.25 ± 0.19). The enthalpies of formation

of three cycloalkylamines derived from heats of combustion are listed in Table 45 along with other physical properties.

### 9.3 Cubylamines

Cubylamines are the precursors for the synthesis of nitrocubanes. Cubylamines can be prepared from the corresponding carboxylic acids by a Curtius reaction. The CAS RN for cubylamine is [91424-46-3].

During an *ab initio* self-consistent-field molecular orbital study of the structures and relative bond strengths of some monoamine derivatives of cubane, azacubane, and 1,3-diazacubane, the focus was on the effect of the  $\text{NH}_2$  group on the strengths of the endocyclic strained bonds in these molecules and, in particular, on the conformation dependence of this effect [221]. The results showed a consistent bond weakening observed in one [and only one] C—C or C—N bond adjacent to the site of  $\text{NH}_2$  substitution. The particular bond that was weakened was in all cases essentially coplanar with the C— $\text{NH}_2$  bond and the position of the most negative electrostatic potential of the amine nitrogen. This direction-specific bond weakening was viewed as an example of an anomeric effect.

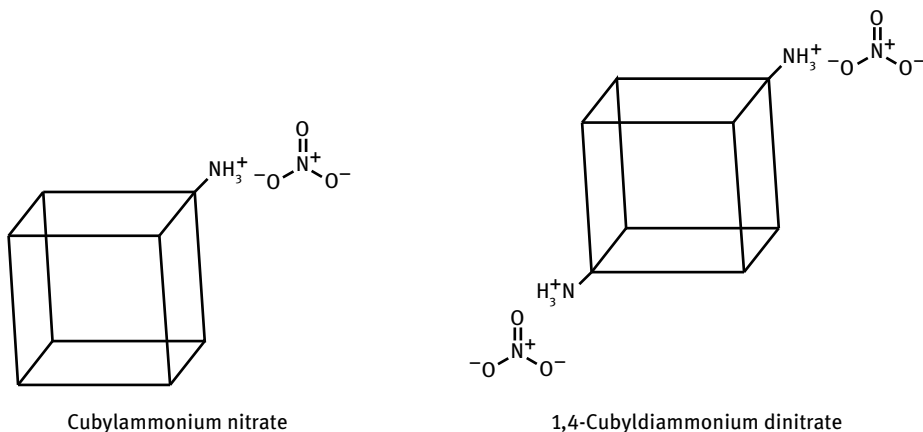
Polyamides with cubane as the backbone of a polymer chain would have high enthalpies of formation and high heats of combustion. Two monomer derivatives of cubane, cubane-1,4-dicarboxylic acid (CDA) and 1,4-diaminocubane (DAC), were used as building blocks. Polymers obtained by polymerizations of DAC, 1,6-hexamethylene diamine, and 1,4-diaminobenzene with cubane-1,4-dicarbonyl chloride, adipoyl chloride, and terephthaloyl chloride to obtain polyamides were characterized using FTIR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectroscopy [222]. Thermal decomposition of the prepared polyamides by TGA and DSC showed a highly exothermic peak above 473 K (200 °C). Hydrolysis of polyamides containing DAC and detection of the hydrolysis product by ultraviolet (UV) spectroscopy showed that DAC was again released by the hydrolysis of the amide bonds in the polymer chain.

#### 9.3.1 Cubylammonium Nitrate and 1,4-Cubyl diammonium Dinitrate

The strain energy of the cubane alkyl rest gives this alkylammonium nitrate a substantially higher enthalpy of formation than a comparable octylammonium nitrate with a straight-chain or branched alkyl rest. Cubylammonium nitrate salts have potential applications as fuels in liquid gun propellants and as explosives by themselves. Although the cubyl compounds are water soluble, their solubility in aqueous HAN solutions is not large enough to permit preparation of viable liquid gun propellant mixtures. The cubane backbone stores above 669 kJ/mol (160 kcal/mol) of strain energy, making the ammonium nitrate salt derivatives considerably more energetic than the CNO atom balance suggests. Cubylammonium nitrate and cubane-1,4-diammonium

dinitrate (CUBDAN) have been investigated for their thermal stability. See also [223, 224].

The rapid thermal decomposition of cubylammonium nitrate and 1,4-cubyl-diammonium dinitrate was studied by analyzing the decomposition products with FTIR [225, 226]. The salts were rapidly decomposed ( $dT/dt$  faster than  $70^\circ\text{C/s}$ ), and the temperature profile and gas products as a function of pressure ( $6.8\text{--}1376\text{ kPa} = 1\text{--}200\text{ psi Ar}$ ) were measured. In this environment, the full strain energy of cubane is not released simultaneously with the redox reactions that involve the ammonium nitrate site because  $\text{C}_2\text{H}_4$  and/or  $\text{C}_2\text{H}_2$  are evolved. CUBDAN is the only alkyl-diammonium dinitrate salt that sublimes undecomposed during fast thermolysis. An estimated gas-phase basicity of about  $215\text{ kcal/mol}$  for the cubylamines is obtained from the tendency to release  $\text{HNO}_3(\text{G})$ . This value is surprising in light of the basicity values for other primary amines.



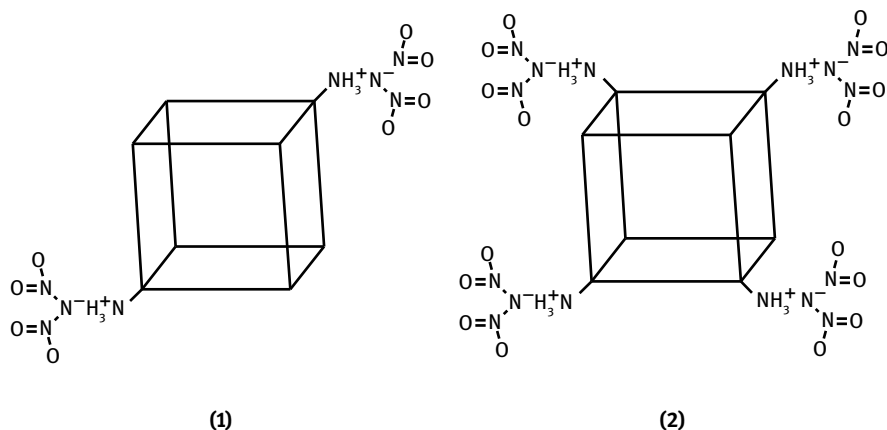
During the fast thermolysis of cubylammonium nitrate heated at a rate of  $90^\circ\text{C/s}$  under  $103\text{ kPa}$  ( $15\text{ psi}$ ) argon, no melting endotherm was detected either by DSC or in the thermal trace. During rapid heating, the decomposition exotherm appeared at  $423\text{--}448\text{ K}$  ( $150\text{--}175^\circ\text{C}$ ), depending on the pressure. By DSC, the exotherm began at about  $413\text{ K}$  ( $140^\circ\text{C}$ ). During the thermal decomposition of 1,4-cubyl-diammonium dinitrate when heated at an initial rate of about  $60^\circ\text{C/s}$  under  $7.5\text{ psi}$  argon, an exotherm occurred at about  $493\text{ K}$  ( $220^\circ\text{C}$ ) simultaneously with the appearance of gas decomposition products. In the differential scanning calorimeter, the decomposition occurred at  $448\text{--}473\text{ K}$  ( $175\text{--}200^\circ\text{C}$ ). No melting endotherm was found at low (DSC) or high heating rates. Extensive oxidation–reduction chemistry is indicated by the products, but the presence of a significant amount of  $\text{C}_2\text{H}_2$  showed that the strain energy of cubane was not released in one step under the conditions used. There were no larger hydrocarbon molecules in the gas phase. 1,4-cubyl-diammonium dinitrate was the only alkyl-diammonium dinitrate salt that was found to sublime during fast thermolysis.

*N,N*-diethanolammoniummethylcubane nitrate and 1,4-bis-(*N,N*-diethanolammoniummethyl)-cubane dinitrate have been patented as fuels in combination with HAN as liquid gun propellants [227]. The impetus of such mixtures was predicted to be higher than that of XM46.

### 9.3.2 Cubylammonium Dinitramide, 1,4-Cubyl diammonium Bis-dinitramide, and Bis-nitroformate

The crystal structure of 1,4-cubanediammonium bis(trinitromethanide)  $[\text{C}_8\text{H}_{12}\text{N}_2][\text{CN}_3\text{O}_6]_2$  was found to be monoclinic, space group  $C2/m$ , with the lattice parameters of  $a = 14.298(2) \text{ \AA}$ ,  $b = 8.408(1) \text{ \AA}$ ,  $c = 7.354(2) \text{ \AA}$ ,  $\beta = 103.42(2)^\circ$ ,  $V = 859.9(5) \text{ \AA}^3$ , and  $Z = 2$  and the X-ray density of  $\rho_{\text{XRD}} = 1.68 \text{ g/cm}^3$  [228]. The cubanediammonium cation and trinitromethanide anion have  $2/m$  and  $m$  crystallographic symmetries, respectively. The cation is linked to six trinitromethanide anions, three at each end, by a total of  $12\text{N}\cdots\text{H}\cdots\text{O}$  hydrogen bonds through the six cation H atoms. The cubane cage has a local threefold axis of symmetry along the long axis ( $\text{N1}\cdots\text{N1}$ ) of the cation and undergoes a large librational motion around this axis.

The crystal structures of cubane-1,4-diammonium dinitramide (**1**) and cubane-1,2,4,7-tetraammonium dinitramide (**2**) have been determined [229].



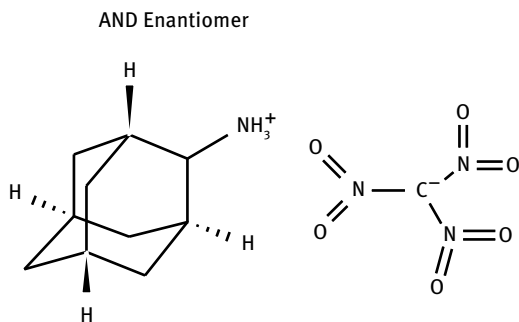
(**1**) crystallized in the space group  $P2_1/c$  with cell dimensions  $a = 6.018(2)$ ,  $b = 11.642(3)$ ,  $c = 9.754(3) \text{ \AA}$ , and  $\beta = 107.24(2)^\circ$ , while (**2**) crystallized in the space group  $P2_1/c$  with cell dimensions  $a = 9.401(4)$ ,  $b = 9.603(3)$ ,  $c = 12.603(4) \text{ \AA}$ , and  $\beta = 111.08(3)^\circ$ . In these structures, the ammonium substituents were symmetrically attached with respect to the cubane skeleton and had neither low-lying empty orbitals nor available lone pairs of electrons. Thus, they had a minimal effect on the symmetrical parameters of the cubane skeleton. All C—C bond lengths were close to the overall average C—C bond length for all reported cubanes of  $1.559 \text{ \AA}$ . The conformations

adopted by the dinitramide ions in both structures were quite different, with the bend, twist, and torsion angles for the dinitramide ion in **(1)** being significantly larger than those found for the dinitramide ions in **(2)**, due to the different types of hydrogen bonding found in the two structures. In **(2)**, the conformation adopted by the adjacent ammonium ions allowed two of the three protons from each ammonium cation to form hydrogen bonds in such a manner that they span either the *syn* or the *anti* oxygen atoms of a single dinitramide anion. The dinitramide anion is thus constrained by these interactions and is less free to twist and bend.

#### 9.4 Adamantylamine

Adamantane, tricyclo[3.3.1.1<sup>3,7</sup>]decane, C<sub>10</sub>H<sub>16</sub>, is difficult to obtain, and the expense of preparing its derivatives, such as adamantylamine and nitroadamantane, may prohibit future use of these chemicals as rocket propellants. A few adamantane derivatives have found practical applications as drugs, polymeric materials, and thermally stable lubricants. Nevertheless, these compounds have been prepared and characterized just in case they offer exceptionally high performance and just in case a more economical method of synthesis can be found.

The structure of 1-adamantanylammonium trinitromethide, was examined using XRD [230]. 1-adamantanylammonium trinitromethide, C<sub>11</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>, *M* = 302.3, crystallized in orthorhombic crystals with the space group *Pnma* and crystal lattice parameters of *a* = 23.802(9) Å, *b* = 8.431(3) Å, *c* = 7.166(2) Å, *V* = 1438.0(8) Å<sup>3</sup>, *Z* = 4, *ρ*(flotational) = 1.37 g/cm<sup>3</sup>, *ρ*<sub>XRD</sub> = 1.396 g/cm<sup>3</sup>, and melting point 464 K = 191 °C. Both the adamantanylammonium cation and trinitromethide anion have mirror symmetry.



The crystal structure of tetraammonium adamantyl tetranitrate was determined using 3D single-crystal XRD [231]. The tetragonal structure has unit cell dimensions *a* = *b* = 10.046(1) Å and *c* = 8.980(2) Å. The X-ray density is 1.643 g/cm<sup>3</sup>.

## 10 Other Open-Chain Aliphatic Amines with More than One Nitrogen Atom in the Molecule

### 10.1 Primary Aliphatic Amines with More than One Nitrogen Atom in the Molecule

Ethylene diamine was already discussed in a section dedicated to this amine because it has found more applications than any of the other amines in this group, not only as free amine, but also in the form of its dinitrate salt.

A systematic examination of the thermal stability of a series of  $\omega$ -diaminoalkanes and their dinitrate salts  $\text{NO}_3\text{NH}_3(\text{CH}_2)_n\text{NH}_3\text{NO}_3$  for  $n = 2$  through  $n = 4$  and  $n = 6$  by rapid-scan FTIR showed that all of the salts liberate  $\text{HNO}_3$  and  $\text{NH}_3$  early in the first stage [232]. When  $n = 1 - 3$ , small-molecule products from redox reactions occurred in the second stage of decomposition. When  $n = 4, 6$ , the second stage involved cycloelimination to form pyrrolidine ( $n = 4$ ) and -ethylpyrrolidine ( $n = 6$ ). The temperature of the onset of exotherm was lower when  $n = 1$  than when  $n$  was larger. Intramolecular and intermolecular hydrogen bonding may play a significant role in these decomposition patterns. The reaction of  $\text{HNO}_3$  with  $\text{NH}_3$  in the gas phase produces  $\text{NH}_4\text{NO}_3$  aerosols at about 583 K (310 °C). The reduction of  $\text{HNO}_3$  or  $\text{NO}_2$  to NO and the oxidation of hydrocarbon residues to CO or  $\text{CO}_2$  occurs only above 603 K (330 °C).

The melting points and oxygen balances of nitrates of multifunctional aliphatic amines are summarized in Table 46.

### 10.2 Secondary Aliphatic Amines with More than One Nitrogen Atom in the Molecule

This section contains information on open-chain and saturated heterocyclic amines in which at least one of the nitrogens is linked with two carbon atoms on either side. A solid, melt-castable rocket propellant containing tetraethylenepentamine pentanitrate by itself or in mixtures with AN or AP can achieve specific impulses between 215 and 246 s [233].

The polymerization of ethyleneimine or propyleneimine results in the formation of polyethyleneimines or polypropyleneimine with many secondary  $-\text{NH}-$  groups and maybe two terminal  $-\text{NH}_2$  groups. The thermal stability of the perchlorate salt of this polymeric amine was measured using DTA, TGA, and isothermal weight loss as part of an evaluation as propellant ingredients [35, 234]. The thermal sensitivity of the salts increased with molecular weight.

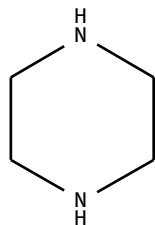
**Table 46:** Melting points and oxygen balance (OB) of nitrates of multifunctional aliphatic amines.

| Compound name                                      | Acronym  | Molecular formula | OB    | Melt-<br>ing point |     |
|----------------------------------------------------|----------|-------------------|-------|--------------------|-----|
|                                                    |          |                   | %     | K                  | °C  |
| <b>Homologues of ethylenediamine</b>               |          |                   |       |                    |     |
| Ethylenediammonium dinitrate                       | EDDN     | C2H10N4O6         | −1.07 | 461                | 188 |
| 1,3-Propanediammonium dinitrate                    | PDDN     | C3H12N4O6         | −3    | 399                | 126 |
| 1,4-Butanediammonium dinitrate                     | BDDN     | C4H14N4O6         | −4.67 | 412                | 139 |
| 1,6-Hexanediammonium dinitrate                     | HDDN     | C6H18N4O6         | −7.43 | 382                | 109 |
| <b>N -substituted ethylenediamine</b>              |          |                   |       |                    |     |
| N-methylethylenediammonium dinitrate               | MEDDN    | C3H12N4O6         | −3    | 351                | 78  |
| N-ethylethylenediammonium dinitrate                | EEDDN    | C4H14N4O6         | −4.67 | 359                | 86  |
| N-isopropylethylenediammonium dinitrate            | IPEDDN   | C5H16N4O6         | −6.25 | 367                | 94  |
| <b>N,N' -disubstituted ethylenediamine</b>         |          |                   |       |                    |     |
| N,N'-dimethylethylenediammonium dinitrate          | s-DMEDDN | C4H14N4O6         | −4.67 | 403                | 130 |
| N,N'-dimethylethylenediammonium dinitrate          | u-DMEDDN | C4H14N4O6         | −4.67 | 325                | 52  |
| N,N'-diethylethylenediammonium dinitrate           | s-DEEDDN | C6H18N4O6         | −7.43 | 466                | 193 |
| <b>N,N,N' -trisubstituted ethylenediamine</b>      |          |                   |       |                    |     |
| N,N,N'-trimethylethylenediammonium dinitrate       | TRMEDDN  | C5H16N4O6         | −6.13 | 366                | 93  |
| N,N-dimethyl-N'-ethylethylenediammonium dinitrate  | DMEEDDN  | C6H18N4O6         | −7.43 | 374                | 101 |
| N,N,N'-triethylethylenediammonium dinitrate        | TREEDDN  | C8H22N4O6         | −9.62 | 359                | 86  |
| <b>N,N,N',N' -tetrasubstituted ethylenediamine</b> |          |                   |       |                    |     |
| N,N,N',N'-tetramethylethylenediammonium dinitrate  | TMEDDN   | C6H18N4O6         | −7.43 | 501                | 228 |
| N,N,N',N'-tetraethylethylenediammonium dinitrate   | TEEDDN   | C10H26N4O6        | −11.4 | 413                | 140 |
| <b>Miscellaneous</b>                               |          |                   |       |                    |     |
| Diethylenediammonium trinitrate                    | DETn     | C4H16N6O9         | −2.05 | 423                | 150 |
| Triethylenetetraammonium tetranitrate              | TETn     | C6H22N8O12        | −2.51 | 502                | 229 |
| Piperazinium dinitrate                             | PIPZD    | C6H12N4O6         | −3.77 | 497                | 224 |

Data source: [22]

## 11 Cycloaliphatic Secondary Aliphatic Amines with More than One Nitrogen Atom in the Molecule

The most stable bifunctional cycloaliphatic amine in this category is piperazine



Piperazine

It can form mononitrate and dinitrate (PIPDN) salts. The thermal decomposition of piperazinium(2+) dinitrate was examined using DSC and rapid-scan FTIR [162]. PIPDN initially yields  $\text{HNO}_3$ , but then generates a significant amount of *N,N*-dinitrosopiperazine along with small molecule fragments. The presence of nitrosamines strongly increases the health hazard of the materials upon heating. No nitramines were detected as thermolysis products. The crystal structure of PIPDN was determined during the same effort.

## 12 Tertiary Aliphatic Amines with More than One Nitrogen Atom in the Molecule

In an effort to find a less toxic replacement for MMH, the U.S. Army started looking for saturated tertiary multiamines and ethanamine azides. Saturated tertiary multiamines are compounds whose molecules have more than one amine nitrogen; those nitrogens are bonded to methyl ( $-\text{CH}_3$ ) and methylene ( $-\text{CH}_2-$ ) or ethylene ( $-\text{CH}_2-\text{CH}_2-$ ) groups (only), and there are no multiple-order bonds in those molecules. An investigation of the linear aliphatic amines was extended to include alicyclic tertiary amines, and the theoretical heats of formation were calculated [218, 235]. Aliphatic saturated tertiary multiamines tend to have shorter ignition delays (with IRFNA) than amine azides or tertiary monoamines. The cyclic amines did not show any advantages over the linear amines when ignition delays were tested with IRFNA, and density-specific impulses were calculated. Candidate tertiary amines under consideration included very symmetrical molecules such as tetrakis(dimethylamino)methane and 1,3,5-trimethylhexahydro-1,3,5-triazine.



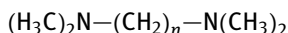
### 12.1 *N,N,N',N'*-Tetramethyl-1,2-diaminoethane

*N,N,N',N'*-tetramethyl-1,2-diaminoethane, also known as *N,N,N',N'*-tetramethylethane-1,2-diamine, *N,N,N',N'*-tetramethylethanediamine; 1,2-ethanediamine, *N,N,N',N'*-tetramethyl-; 1,2-bis(dimethylamino)ethane, TMEDA,  $(\text{H}_3\text{C})_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ ,  $\text{C}_6\text{H}_{10}\text{N}_2$ , CAS RN [110-18-9], has been evaluated as a replacement for MMH in hypergolic bipropellant combinations with WFNA or IRFNA. TMEDA is employed in various industrial applications and is therefore readily available.

TMEDA melts at 214.5 K (−58.6 °C) and boils at 394.2 K (121 °C). These data from one source differ from the data from another source in Table 47. The heat of vaporization of TMEDA is  $\Delta_{\text{vap}}H^\circ = 42.2 \text{ kJ/mol} = 10.09 \text{ kcal/mol}$  at 298 K and 39.8 kJ/mol (9.51 kcal/mol) at 295–365 K.

TMEDA has been evaluated as a constituent in fuel mixtures with 2-*N,N*-dimethylaminoethylazide (DMAZ). Fuel mixtures of TMEDA with DMAZ, tris-(2-azidoethyl)amine (TAEA), or cyclic amine azides exhibit a synergistic effect when it comes to short ignition delays with IRFNA, shorter than those of any of the ingredients by themselves, an effect that was not predictable from review of each component's composition [236–238].

A wide range of aliphatic amines have been evaluated as hypergolic fuels for WFNA or RFNA, and the most promising of the 400 chemicals investigated were the low-molecular-weight ditertiary diamines [239, 240]. They possess wide liquid ranges (low freezing points, high boiling points), short ignition delays at temperatures as low as 219 K (−65 °F), low viscosities, good long-term storage stability, thermal stability at elevated temperatures ( $\geq 533 \text{ K} = \geq 500 \text{ °F}$ ), efficient combustion with RFNA, high density-specific impulse (Isp), ease of preparation, and low cost of raw materials. A group of diamines of the general structure



where  $n = 1$  through 4 plus tetramethylhexane-1,6-diamine was synthesized. It was found that in this series of diamines, the methylenediamine was unsatisfactory at room temperature and the hexane-1,6-diamine and 2-butyne-1,4-diamine were unsatisfactory at low temperatures. The diamines were found to be miscible with JP-4 in all proportions. The diamine with the most desirable properties similar to TMEDA and the runner-up was *N,N,N',N'*-tetramethylbutane-1,3-diamine,  $(\text{H}_3\text{C})_2\text{N}(\text{CH}_2)_4\text{N}(\text{CH}_3)_2$ ,  $\text{C}_8\text{H}_{20}\text{N}_2$ , TMBDA. Other diamines for which detailed physical properties were obtained were *N,N,N',N'*-tetramethylpropane-1,2-diamine, *N,N,N',N'*-tetramethylpropane-1,3-diamine, *N,N,N',N'*-tetramethylpropene-1,3-diamine, and *N,N,N',N'*-tetramethyl-1-butenediamine. Fourteen saturated ternary multiamines were synthesized and characterized, and three were tested in rocket engine firings: 1,2-bis(dimethylamino)ethane, 1,2-bis(dimethylamino)propane, and 1,3-bis(dimethyl-amino)propane.

Table 47: Physical properties of TMEDA and TMBDA in comparison to UDMH.

|                                        | TMEDA                   |                                                    | TMBDA                   |                                                     | UDMH                     |                          |
|----------------------------------------|-------------------------|----------------------------------------------------|-------------------------|-----------------------------------------------------|--------------------------|--------------------------|
| Molecular mass                         | 116.21 g/mol            | 8.605 mol/kg                                       | 144.26 g/mol            | 6.932 mol/kg                                        | 60.102 g/mol             | 16.64 mol/kg             |
| Freezing point                         | 216 K                   | -56.7 °C                                           | 183 K                   | -91 °C                                              | 215.9 K                  | -57.2 °C                 |
| Boiling point                          | 392-395 K               | 119-122 °C                                         | 432.6-433.1 K           | 159.4-160.0 °C                                      | 335.5 K                  | 62.3 °C                  |
| Density at 293 K                       | 0.775 g/cm <sup>3</sup> | 48.38 lb/ft <sup>3</sup>                           | 0.795 g/cm <sup>3</sup> | 49.63 lb/ft <sup>3</sup>                            | 0.8006 g/cm <sup>3</sup> | 49.98 lb/ft <sup>3</sup> |
| Viscosity at 219 K (-65 °F)            | 3.0 cSt                 | 3 × 10 <sup>-6</sup> m <sup>2</sup> /s at 219 K    | 11.24 cSt               | 1.124 × 10 <sup>-5</sup> m <sup>2</sup> /s at 219 K | 4.74 cPs                 | 5.46 cSt                 |
| Viscosity at 233 K (-40 °F)            | 2.02 cSt                | 2.02 × 10 <sup>-6</sup> m <sup>2</sup> /s at 233 K | 5.68 cSt                | 5.68 × 10 <sup>-6</sup> m <sup>2</sup> /s at 219 K  | 2.55 cPs                 | 2.99 cSt                 |
| Viscosity at 297 K (75 °F)             | 0.74 cSt                | 7.4 × 10 <sup>-7</sup> m <sup>2</sup> /s at 297 K  | 1.25 cSt                | 1.25 × 10 <sup>-6</sup> m <sup>2</sup> /s at 219 K  | 0.50 cPs                 | 0.64 cSt                 |
| Enthalpy of formation at 298 K, liquid | —                       | —                                                  | —                       | —                                                   | +51.626 kJ/mol           | +12.339 kcal/mol         |
| Heat of evaporation at 298 K           | 42.2 kJ/mol             | 10.09 kcal/mol                                     | —                       | —                                                   | 32.623 kJ/mol at 335 K   | 7.797 kcal/mol at 62 °C  |
| Heat of combustion                     | 9403 cal/g              | 16926 BTU/lb                                       | 9749 cal/g              | 17548 BTU/lb                                        | 474 kcal/mol             | 14169 BTU/lb             |
| Refractive index                       | $n_D^{20}$              | 1.4170                                             | $n_D^{20}$              | 1.4300                                              | $n_D^{25}$               | 1.4053                   |

Data source: [240]

Table 47 gives the physical properties of TMEDA along with its  $C_4$  homologue TMBDA in comparison to the properties of UDMH. All of these are hypergolic fuels intended to be used with WFNA or RFNA.

The evaporation rates of TMEDA droplets suspended from a fiber in a temperature-controlled windowed oven were measured with and without addition of 10 or 20% of dissolved 1,2,4-triazole [241]. During heating, TMEDA started to evaporate at a temperature below its boiling point, and 1,2,4-triazole, a solid at room temperature, evaporated subsequently. Evaporation behaviors of TMEDA droplets with 10 and 20 mass-% of 1,2,4-triazole were studied at various temperatures. Bubbling and puffing were observed above 673 K (400 °C) in the case of the TMEDA containing 1,2,4-triazole. The rate of evaporation at the same temperature was substantially enhanced by increasing the concentration of 1,2,4-triazole.

### 12.1.1 Reactions of TMEDA

The mechanism of hypergolic ignition delays of TMEDA with WFNA or IRFNA has been studied [242, 243]. A three-stage hypergolic ignition process was revealed by both the temperature measurements in the drop tests and the pre-ignition products analysis in the confined interaction experiments. In the first stage, condensed-phase reactions take place between TMEDA and  $HNO_3$  upon their contact to form corresponding nitrate salts.

The dinitrate of  $N,N,N',N'$ -tetramethyl-1,2-diaminoethane was evaluated as a fuel for nitric acid-based monopropellants similar to CAVEA [244]. The melting point of the dinitrate salt is 493–494 K (220–221 °C).

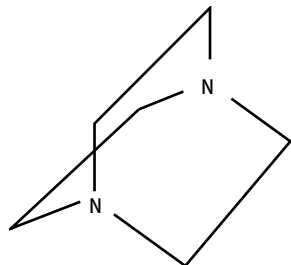
Nitrate salts of TMEDA and TMBDA have been evaluated as fuels for nitric acid-based monopropellants.  $N,N,N',N'$ -tetramethylpropane-1,3-diamine dinitrate melted at 431 K = 158 °C = 317 °F, and  $N,N,N',N'$ -tetramethylbutane-1,3-diamine dinitrate melted at 389 K = 116 °C = 240 °F. Both salts are soluble in WFNA.

### 12.1.2 Safety Properties of TMEDA

The toxicity of TMEDA is substantially less than that of MMH. TMEDA was tested for potential mutagenicity in comparison to DMAZ. TMEDA was found not to be mutagenic in any of the bacterial strains tested (*Salmonella* TA98, TA100, TA1535, and TA1537 and *Escherichia coli* WP2uvrA), with or without metabolic activation [245]. TMEDA produced a positive response in structural chromosomal aberrations in Chinese hamster ovary (CHO) cells, with or without metabolic activation, but only at the highest concentration, 5 mg/mL. DMAZ and TMEDA, when tested *in vivo* in the CD-1 mouse at doses up to 500 and 250 mg/kg, respectively, did not induce micronuclei in bone marrow erythrocytes. DMAZ and TMEDA were negative for induction of chromosomal aberrations in CHO cells *in vitro* and in the *in vivo* mouse micronucleus assay.

## 12.2 Triethylenediamine

Triethylenediamine, CAS RN [280-57-9], is a tertiary heterocyclic amine in which all three bonds between two nitrogen atoms are linked by ethylene bridges:



It really belongs in the chapter on heterocyclic amines instead of here among the open-chain linear amines. This is a nearly spherical molecule, and its symmetry also has an effect on its physical properties (it has a very narrow liquid range and sublimates like camphor). The correct nomenclature for this molecule is 1,4-diazabicyclo[2.2.2]octane. It is also known under the trade name DABCO. Triethylenediamine forms colorless, hygroscopic crystals that melt at 431 K (158 °C) and boil (sublime) at 447 K (174 °C). It is soluble in water and alcohols. DABCO is used as a catalyst in the curing and foaming of polyurethane polymers. Triethylenediamine forms mononitrate and dinitrate salts as well as monoperchlorate and diperchlorate salts.

Fast thermolysis/FTIR spectroscopy of triethylenediammonium(2+) dinitrate  $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}](\text{NO}_3)_2$  (DABCOD) and a new oxonium nitrate  $(\text{H}_3\text{O}^+\text{NO}_3^-)$  double salt of DABCOD were used to study reaction pathways during thermal decomposition of alkylammonium nitrates [162]. DABCOD produced no  $\text{HNO}_3$  vapor, but instead gave  $\text{CH}_2\text{O}$ , *N,N'*-dinitrosopiperazine and small fragments. These patterns are entirely consistent with the behavior observed for primary, secondary, and tertiary ammonium mononitrate salts in previous work. The presence of nitrosamines strongly increases the health hazard of the materials upon uncontrolled heating. No nitramines were detected as thermolysis products. Thermolysis of the oxonium nitrate double salts liberated  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  at a relatively low temperature (333 K = 60 °C). Above this temperature, the thermolysis proceeded in the same way as that of pure DABCOD.

Triethylenediammonium(2+) diperchlorate can be prepared by slowly neutralizing a solution of triethylenediamine in water with 40%  $\text{HClO}_4$  [246]. Pyrolysis of triethylenediammonium diperchlorate can lead to *N*-methyl-*N'*-ethylpiperazine and *N,N'*-diethylpiperazine as decomposition products.

Triethylenediammonium(2+) diperchlorate forms double salts with two moles of ammonium perchlorate, which can be prepared by a facile one-pot reaction of AP,  $\text{HClO}_4$ , and triethylenediamine and have perovskite crystal structure [247]. The crys-

tals were characterized by XRD, FT-IR, and TG-DSC. The ternary salt had a more stable thermal decomposition temperature (658 K = 385 °C) than AP.

## 13 C<sub>26</sub> Non-Cyclic Multifunctional Amines

### 13.1 Tris(2-aminoethyl)amine

Tris(2-aminoethyl)amine, also known as 1,2-ethanediamine, *N,N*-bis(2-aminoethyl)-; *N1,N1*-bis(2-aminoethyl)-1,2-ethanediamine, TRIS, C<sub>6</sub>H<sub>18</sub>N<sub>4</sub>, N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>, CAS RN [4097-89-6] was used as the nitrate salt in some NASA-sponsored HAN-based monopropellant studies (*Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-Based Monopropellants”). Other applications for tris(2-aminoethyl)amine are as a chelator and water conditioning agent. It can be neutralized with three equivalents of nitric acid to yield tris(2-aminoethyl)ammonium trinitrate, [(N<sup>+</sup>H<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N][NO<sub>3</sub><sup>-</sup>]<sub>3</sub>, C<sub>6</sub>H<sub>21</sub>N<sub>5</sub>O<sub>9</sub>, TRIN, TRN, TRN3, which has been tested as a substitute for triethanolammonium nitrate (TEAN) in liquid gun and rocket propellants. It is assumed that the three external amino groups in beta position from the central nitrogen atom would be protonated first. Theoretically it should be possible to form a tetranitrate in which the central nitrogen atom also becomes protonated, but it is not known whether this compound exists. Physical properties of tris(2-aminoethyl)amine are listed in Table 48.

**Table 48:** Physical properties of tris(2-aminoethyl)amine.

| Property                            | SI units                                | Other units                             |
|-------------------------------------|-----------------------------------------|-----------------------------------------|
| Molecular mass                      | 146.23 g/mol                            | 6.838 mol/kg                            |
| Density (predicted)                 | 1.002 ± 0.06 g/cm <sup>3</sup> at 293 K | 1.002 ± 0.06 g/cm <sup>3</sup> at 20 °C |
| p <i>K</i> <sub>a</sub> (predicted) | 10.00 ± 0.10 at 298 K                   | 10.00 ± 0.10 at 25 °C                   |
| Boiling point                       | 369–372 K                               | 96–99 °C                                |

### 13.2 Thermal Stability of TRN3

In DSC, TRN3 showed two weak endotherms at 372 and 435 K (99 and 162 °C) and decomposed immediately after melting at 575 K (302 °C). The exotherm peaked at 587 K (314 °C).

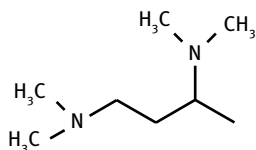
## 14 C<sub>7</sub> Multifunctional Amines

A tertiary amine fuel, *N,N,N',N'*-tetramethyl-1,2-diaminopropane (boiling point 411 to 412 K = 138 to 139 °C,  $n_D 1.4230$ ,  $\rho = 0.7900 \text{ g/cm}^3$ ) was proposed as rocket fuel [248].

The nitrate of this amine was evaluated as a fuel for nitric acid-based monopropellants (similar to CAVEA) [244]. The melting point of the dinitrate salt is 450–452 K (177–179 °C). The dinitrates of this amine and other tetramethyl C<sub>2</sub> through C<sub>8</sub> linear diamines were patented as solid propellant ingredients [249].

## 15 C<sub>8</sub> Multifunctional Amines

A theoretical rocket performance table published by Rocketdyne in the 1960s, which for many years has decorated the author's office wall, included performance data for a less frequently used amine, *N,N,N',N'*-tetramethyl-1,3-diaminobutane:



It appears to have been simply a theoretical exercise because otherwise there are no publications about this fuel. The dinitrates of this amine and other tetramethyl C<sub>2</sub> through C<sub>8</sub> linear diamines were patented as solid propellant ingredients [249, 250].

## 16 C<sub>10</sub> Multifunctional Amines

The dinitrate of *N,N,N',N'*-tetraethyl-1,2-diaminoethane was evaluated as a fuel for nitric acid-based monopropellants [244]. The melting point of the dinitrate salt is 415–416 K (142–143 °C). The same patent contains melting points of a dozen other tertiary multifunctional amine nitrates.

## 17 Other Tertiary Amines

The nitrate salts of various tertiary amines can be prepared from the corresponding chlorides by adding stoichiometric amounts of WFNA and driving off the HCl as an aqueous azeotrope until the reacting mixture is chloride-free, followed by pouring the mixture into an excess of acetone, and then filtering and drying the precipitate [251]. The nitrate salts thus prepared can be mixed with kerosene, more nitric acid, and an emulsifier to make a propellant mixture suitable for use in ramjets. The melting points of some of the tertiary alkylammonium nitrates are summarized in Table 49.

**Table 49:** Melting points of tertiary alkylammonium nitrates.

| Amine converted to nitrate salt                            | Mols of<br>HNO <sub>3</sub> | Mols of<br>amine | Yield<br>% | Melting point   |                 |
|------------------------------------------------------------|-----------------------------|------------------|------------|-----------------|-----------------|
|                                                            |                             |                  |            | K               | °C              |
| <i>N,N,N',N'</i> -tetramethylethane-1,2-diamine            | 0.608                       | 0.275            | 96.3       | 493–494         | 220–221         |
| <i>N,N,N',N'</i> -tetramethylpropane-1,2-diamine           | 0.606                       | 0.275            | 92.3       | 450–452         | 177–179         |
| <i>N,N,N',N'</i> -tetramethylbutane-1,3-diamine            | 1.19                        | 0.578            | 97.0       | 388–389         | 115–116         |
| <i>N,N,N',N'</i> -tetramethyl-2-butyne-1,4-diamine         | 0.6                         | 0.285            | 96.4       | 418–419         | 145–146         |
| <i>N,N,N',N'</i> -tetraethylethane-1,2-diamine             | 0.6                         | 0.285            | 76.5       | 415–416         | 142–143         |
| <i>N,N,N',N'</i> -tetramethylbutane-1,4-diamine            | 0.43                        | 0.208            | 98.7       | 446–447         | 173–174         |
| <i>N,N,N',N'</i> -tetramethylbutane-1,2-diamine            | 0.40                        | 0.183            | 94.3       | 446–447         | 173–174         |
| <i>N,N,N',N',N''</i> -pentamethyldiethylenetriamine        | 0.70                        | 0.23             | 80.0       | 435–436         | 162–163         |
| <i>N,N,N',N',N'',N''</i> -hexamethylpropane-1,2,3-triamine | 0.53                        | 0.173            | 65.3       | 377–379         | 104–106         |
| <i>N,N,N',N'</i> -tetraethylpropane-1,3-diamine            | 0.42                        | 0.2              | 97.0       | 430.6–<br>432.6 | 157.5–<br>159.5 |

Data source: [251]

## 18 Unsaturated Aliphatic Amines

### 18.1 Unsaturated Alkenyl Aliphatic Amines

Allyl amine and diallyl amine,  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{NH}_2$  and  $(\text{H}_2\text{C}=\text{CH}-\text{CH}_2)_2\text{NH}$ , have been proposed as hypergolic rocket fuels, but they are not readily available. Ignition delays of these fuels, alone and in mixtures with triethylamine, with RFNA as the oxidizer were measured at NASA using a modified open-cup ignition test method [252].

### 18.2 Unsaturated Alkynyl Aliphatic Amines

MAF-2 was a rarely used hypergolic fuel mixture consisting of 42.6% propargyldiglycidylamine,  $\text{HC}\equiv\text{CCH}_2\text{N}(\text{CH}_2\text{OCHCH}_2)_2$ , 48.3% dipropargylglycidylamine,  $(\text{HC}\equiv\text{C}-\text{CH}_2)_2\text{N}(\text{CH}_2\text{OCHCH}_2)$ , and 9.1% tripropargylamine  $(\text{HC}\equiv\text{CCH}_2)_3\text{N}$ . The properties of MAF-2 and its constituents are listed in Table 50. The acetylenic triple bond and the oxiridine ring tension added energy to those fuels. The disadvantages of MAF-2 were high viscosity and poor ignition with RFNA.

The *USAF Propellant Handbook, Hydrazine Fuels, Volume 1* contains a unit with physical properties of MAF-2 from which the following properties were copied [184]. It also has two graphs showing the density and absolute viscosity of MAF-2 as a function of temperature. The density of MAF-2 as a function of temperature for the range 323 to

**Table 50:** Properties of alkynylamines and MAF-2 fuel mixture.

| Property/compound                          | Propargyl-<br>diglycidylamine                                | Dipropargyl-<br>glycidylamine                                | Tripropargyl-<br>amine          | MAF-2    |
|--------------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------|---------------------------------|----------|
| Empirical formula                          | C <sub>9</sub> H <sub>13</sub> N <sub>1</sub> O <sub>2</sub> | C <sub>9</sub> H <sub>11</sub> N <sub>1</sub> O <sub>1</sub> | C <sub>9</sub> H <sub>9</sub> N |          |
| Molecular mass, g/mol                      | 167.21                                                       | 149.19                                                       | 131.18                          |          |
| Freezing point, K                          | glass point                                                  | 234                                                          | 289.6                           | 203      |
| Freezing point, °C                         | glass point                                                  | -39                                                          | +16.5                           | -70      |
| Boiling point, °C at pres-<br>sure (mm Hg) | 81 (0.5)                                                     | 61 (0.05)                                                    | 300 (760)                       | 40 (1.3) |
| Density, g/cm <sup>3</sup> , at 298 K      | 1.059                                                        | 1.054                                                        | 0.9216                          | 1.024    |
| Viscosity, cSt, at 298 K                   | 14.5                                                         | 10.7                                                         | 4.7                             | 22       |

Data source: [184]

344 K (−50 to +71 °C) can be calculated using the equation

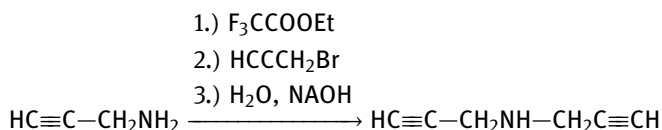
$$\rho = 1.2804 - 8.590 \times 10^{-4} T$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $T$  is the temperature in kelvin. The absolute viscosity of MAF-2 can be calculated from the equation

$$\log \mu = 8.6632 - 6714.4/T = 1.3537 \times \frac{10^6}{T^2}$$

where  $\mu$  is the viscosity in cPs and  $T$  is the temperature in kelvin.

Propargylamine can be prepared by reacting propargylphthalimide with a primary mono- or polyamine [253]. Propargylamine has a boiling point of 354–356 K (81–83 °C). Dipropargylamine has a boiling point of 326–329 K at 1.73–2.0 kPa (53–56 °C at 13–15 mm Hg). The density of dipropargylamine is 0.901 g/cm<sup>3</sup> at 293 K. Dipropargylamine can be prepared by reaction of propargylamine with propargylbromide while protecting one of the hydrogens with ethyl trifluoroacetate to prevent alkylation to the tertiary amine.



Dipropargylamine has a calculated heat of formation of 464 kJ/mol (111 kcal/mol). Tripropargylamine was prepared by addition of 2 mol propargyl bromide to propargylamine [254]. Tripropargylamine has a boiling point of 353–356 K at 1.73–2.0 kPa (80–83 °C at 13–15 mm Hg).



## 19 Azido-Substituted Amines

In many cases, hydrogen in alkyl groups of aliphatic amines has been replaced by explosophoric groups in order to improve one or several properties of the parent amine for rocket applications. The substitution is usually done with the intent to shorten ignition delays in hypergolic reactions and/or to improve specific impulse. Substituent groups that bring about the desired improvements are azido, nitro, cyano, and dinitramido groups.

Introduction of the azido group  $-N_3$  into aliphatic amines results in fuels with increased heat of combustion and improved rocket performance as fuels in bipropellant rockets. Several azido-substituted amines have been developed and tested as rocket fuels. Some of these azido molecules are so energetic that they can even decompose exothermally and can be used as monopropellants. Azidoalkanols are discussed in the chapter “Azido Compounds,” instead of in the chapter on alcohols and substituted alcohols because the properties of azidoalkanols are dominated by the azido group and not by the hydroxyl group.

In all the relatively stable azidoalkylamines, the azido group is linked to a central nitrogen atom by way of in-between carbon linkages. The most unusual azidoamines would be those in which the azido group is connected directly to an amino or amido nitrogen without intermediary carbon linkages, for instance azidoamine  $N_3NH_2$ , diazidoamine  $(N_3)_2NH$  and its anion  $(N_3)_2N^-$  (an analog to dinitramide), and eventually triazidoamine  $(N_3)_3N$ , an all-nitrogen compound. None of these azidoamines has been synthesized yet, but their molecular structures and energy levels have been calculated by computational chemistry methods [255].

### 19.1 2-Azidoethylamine

Azidoaminoethane, also known as  $\beta$ -azidoethylamine, 2-azidoethylamine, 2-azido-*N,N*-dimethylethanamine,  $N_3-CH_2-CH_2-NH_2$ ,  $C_2H_6N_4$ , is a clear liquid that boils at 320 K (47 °C) at 2.2 kPa (16.5 mm Hg) vacuum. It has a density of 1.0429 g/cm<sup>3</sup> at 298 K (25 °C) and a refractive index  $n_D^{25}$  of 1.4635. It ignites on contact with WFNA or RFNA.

### 19.2 *N,N*-Dimethyl-2-azidoethylamine (DMAZ)

2-Azido-*N,N*-dimethylethylamine, also known as dimethylaminoethyl azide, *N,N*-dimethyl-2-azidoethylamine, 2-azidoethyl-*N,N*-dimethylamine, 2-azido-*N,N*-dimethylethanamine, dimethylamine-2-ethylazide,  $(CH_3)_2NCH_2CH_2N_3$ ,  $C_4H_{10}N_4$ , DMAZ, CAS RN [86147-04-8] is a candidate to replace hydrazine fuels, especially MMH, in certain hypergolic fuel applications [256]. It can also decompose by itself in a monopropellant fashion and has been considered as a replacement for

hydrazine as a monopropellant (*Encyclopedia of Monopropellants*, chapter “Organic Monopropellants”). DMAZ has been tested with RFNA in bipropellant rocket engines.

When a fuel has a tertiary amine functionality and an azide functionality in the same molecular structure, it may have an ignition delay with WFNA or RFNA competitive with hydrazine fuels, and it has a superior density-specific impulse while probably being less toxic. The azide functionality can decompose exothermically with enough energy to sustain its decomposition in a monopropellant mode when heated. Several tertiary amine azido compounds have been synthesized, and their physical and ballistic properties were evaluated to determine their acceptability as hypergolic bipropellant fuels and liquid monopropellant gas generants. Although no hypergolic rocket engine testing was conducted, several small-scale liquid gas generator tests were performed. See also [257].

### 19.2.1 Preparation of N,N-Dimethyl-2-azidoethylamine

DMAZ can be prepared by azidation of 2-chloro-*N,N*-dimethylaminoethyl hydrochloride and neutralization of the intermediate, which is a two-step synthesis of the fuel. A kinetic study on the production reaction of DMAZ was done to optimize the yield of the process [258]. The methods of excess and equimolar concentrations were used for the measuring dependency of the reaction rate on reactants and temperature. The results showed that the reaction was first order with respect to reactants, and an integral method confirmed the reaction rate equation. The rate-determining step was extremely endothermic, with an activation energy of 90 kJ/mol. The raw product can be purified by vacuum distillation [259].

Two different synthesis routes for 2-azido-*N,N*-dimethylethanamine (DMAZ) were compared, and the product was obtained via one of the methods with a purity of better than 99% [260]. The structure and purity were confirmed by FTIR, GC-MS, and  $^1\text{H-NMR}$ .

There are at least six synthesis methods for making DMAZ [261–263].

To improve the yield of DMAZ synthesis, the kinetics of the reaction of 2-chloro-*N,N*-dimethylethylamine hydrochloride with sodium azide in aqueous solution were studied using UV absorption spectrometry [264]. The results showed that the reaction can be considered a second-order reaction. The reaction rate constants were  $1.337 \times 10^{-3}$ ,  $3.403 \times 10^{-3}$ , and  $7.082 \times 10^{-3} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ , respectively, at 337, 347, and 357 K. The apparent activation energy ( $E_a$ ) was 83.5 kJ/mol, and the pre-exponential factor was  $1.19 \times 10^{10} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ .

For most applications, DMAZ must be water-free. Water can be removed by adsorption on zeolites, calcium chloride, or nano-particles [265]. The best water adsorption from DMAZ was obtained by  $\text{CaCl}_2$  adsorbent within 10 min.

DMAZ that would otherwise be lost with wastewater dumped overboard can be recovered by adsorption on zeolites or activated carbon [266].

DMAZ can be dehydrated by water adsorption on 3A molecular sieves [267]. Experiments showed that the optimum adsorption capacity (191.3 mg/g) was obtained

with contact time = 150 min, liquid/solid ratio = 10 : 1, initial concentration of water = 3 mass-%, and agitating rate = 150 rpm. Thermal stability and regeneration behavior of the zeolite adsorbent were investigated using XRD and TGA/DSC. It was found that the best regeneration occurred in the range of 523–573 K (250–300 °C), and the zeolite structure was stable up to 673 K (400 °C). Thermal analysis verified that DMAZ molecules cannot diffuse into 3A zeolite pores.

A cobalt-doped silica (Co-SiO<sub>2</sub>) layer was synthesized in a sol-gel process as the mesoporous layer overlaid in three-step, six-step, and ten-step coating on a mullite support membrane [268]. The membranes were used in pervaporation experiments to dehydrate DMAZ containing 5 mass-% water. In dehydration tests, the membrane permeate flux decreased and its separation factor increased. During the first initial hours, it reached a steady state and subsequently remained constant.

### 19.2.2 Physical Properties of N,N-Dimethyl-2-azidoethylamine

The physical properties of DMAZ have been compared to the physical properties of MMH, which it was intended to replace in hypergolic bipropellant combinations [269] (Table 51).

A comparison shows that in all of the crucial parameters, DMAZ is generally similar to MMH. The enthalpy of formation of DMAZ is considerably higher than that of MMH and would suggest good performance as a rocket propellant.

A technique for computationally determining the thermophysical properties of high-energy-density propellants that combines quantum mechanical and molecular dynamic calculations and group additivity methods was used to determine thermophysical properties for quadricyclane and DMAZ [270, 271]. The modified force-field approach provided results that more accurately matched experimental data than the unmodified approach. In both cases, the use of high-energy-density fuels in bipropel-

**Table 51:** Comparison of physical properties of DMAZ and MMH.

| Property                                | DMAZ   | MMH    |
|-----------------------------------------|--------|--------|
| Molecular mass, g/mol                   | 114.15 | 46.07  |
| Enthalpy of formation, liquid, cal/g    | +586   | +284   |
| Enthalpy of formation, liquid, kcal/mol | +66.89 | +13.08 |
| Enthalpy of formation, liquid, kJ/mol   | +279.9 | +54.74 |
| Boiling point, °C                       | 135    | 87.65  |
| Freezing point, °C                      | −68.9  | −52.37 |
| Density, g/cm <sup>3</sup>              | 0.993  | 0.87   |
| Viscosity, centipoise                   | 2      | 0.775  |
| Surface tension, dyn/cm                 | 25     | 33.83  |
| Flash point, Tag, °C                    | 29.4   | 17     |

Note: All values measured at 298 K = 25 °C unless otherwise stated

Data source: [269]

lant combinations provides reductions in vehicle mass compared to industry-standard propellants.

Summaries of the physical and chemical properties of DMAZ are in [272–275].

### 19.2.2.1 Density of DMAZ

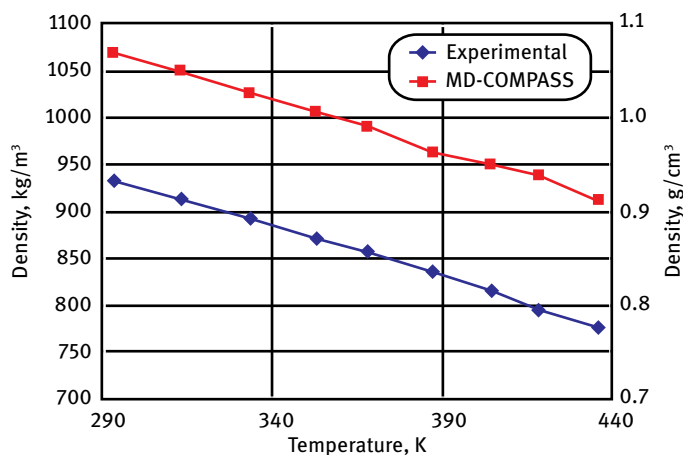
The density quoted by other sources ( $0.993 \text{ g/cm}^3$  at  $298 \text{ K} = 25^\circ\text{C}$ ) does not match that found from the curve fit ( $\rho(\text{g/cm}^3) = 0.9517 - 0.0010T$ ), which gives  $0.9267 \text{ g/cm}^3$  at  $298 \text{ K} = 25^\circ\text{C}$  [269]. Using other density/temperature data gives a density of  $0.9257 \text{ g/cm}^3$  at  $298 \text{ K} = 25^\circ\text{C}$ . The quoted curve fit

$$\rho = 0.9517 - 0.0010T$$

suffers from truncation errors in the formula, resulting in errors increasing with temperature (nearly 0.4% at  $0^\circ\text{C}$ ). The fit

$$\rho = 0.9517 - 0.00104T$$

would be better. The density predicted by molecular orbital calculations is higher than the actual measured density (Figure 6).



**Figure 6:** DMAZ experimental and predicted density vs. temperature. (Reproduced and modified from [276] with permission from Dr. Timothy Kokan on 3 July 2020.)

### 19.2.2.2 Vapor Pressure of DMAZ

The vapor pressure of DMAZ can be expressed by the equation

$$\log p_{10} = 0.4756 + 0.02434T - 0.0000629T^2 + 0.000000116T^3$$

where  $p$  is the pressure in mm Hg and  $T$  is the temperature in kelvin.

19.2.2.3 Kinematic Viscosity of DMAZ

The viscosity of DMAZ can be expressed by the equation

$$\eta = 0.998 - 0.0108T + 0.00005T^2$$

where  $\eta$  is the viscosity in cSt and  $T$  is the temperature in kelvin.

The dynamic viscosity shown in Table 2 from Reference [273] (2 cPs at 298 K = 25 °C) does not match the data in Table 4 of the same report (interpolation would give 0.7034 cPs at 298 K = 25 °C) [269].

Table 52: Measured shear viscosity of DMAZ

| Pressure<br>atm | Temperature<br>K | Viscosity $\mu$<br>cPs |
|-----------------|------------------|------------------------|
| 1.0             | 293.25           | 0.721                  |
| 1.0             | 313.00           | 0.564                  |
| 1.0             | 333.10           | 0.456                  |
| 1.0             | 353.05           | 0.379                  |
| 1.0             | 368.05           | 0.335                  |
| 1.0             | 387.35           | 0.284                  |
| 1.0             | 406.05           | 0.255                  |
| 8.0             | 406.35           | 0.249                  |
| 15.0            | 421.55           | 0.235                  |
| 19.0            | 438.95           | 0.209                  |

Data source: [276]

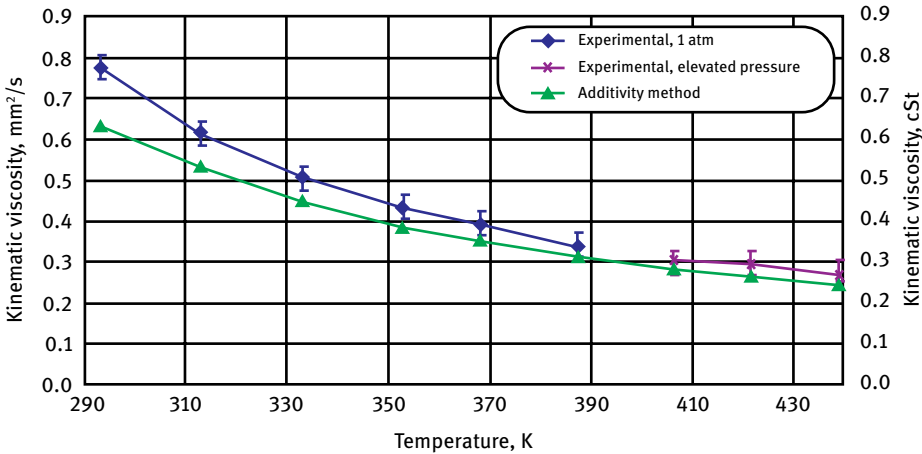


Figure 7: DMAZ kinematic viscosity vs. temperature. (Reproduced and modified from [276] with permission from Dr. Timothy Kokan on 3 July 2020.)

The shear viscosity of DMAZ was measured using a high-pressure Cannon-Fenske viscometer (Table 52) (Figure 7). The ASTM standards D445-04 and D446-04 were followed to obtain viscosity measurements.

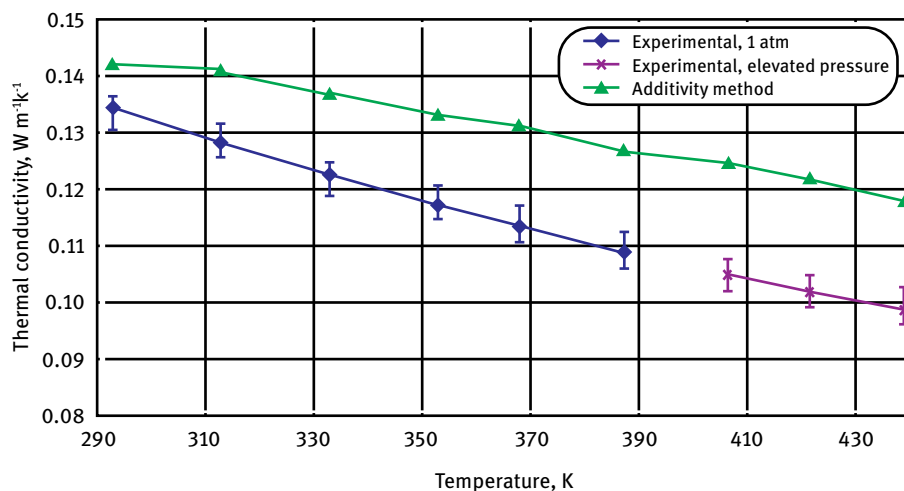
#### 19.2.2.4 Thermal Conductivity of DMAZ

The thermal conductivity was measured using a relative transient hot-wire method with a Pyrex capillary filled with mercury. Thermal conductivity predicted by an additivity method was higher than actual measured thermal conductivity (Table 53) (Figure 8).

**Table 53:** Measured thermal conductivity of DMAZ.

| Pressure<br>atm | Temperature<br>K | Thermal conductivity $\lambda$<br>$\text{W m}^{-1} \text{K}^{-1}$ |
|-----------------|------------------|-------------------------------------------------------------------|
| 1.0             | 297.40           | 0.133                                                             |
| 1.0             | 324.90           | 0.125                                                             |
| 1.0             | 349.30           | 0.118                                                             |
| 8.0             | 374.30           | 0.112                                                             |
| 11.0            | 398.50           | 0.107                                                             |
| 19.0            | 425.30           | 0.101                                                             |

Data source: [276]



**Figure 8:** DMAZ thermal conductivity vs. temperature. (Reproduced and modified from [276] with permission from Dr. Timothy Kokan on 3 July 2020.)

### 19.2.2.5 Solubility and Volatility of DMAZ

Henry's law constants at 298 K for four 2-azidoethanamine hypergols and three aliphatic amines were estimated via a density functional theory/polarizable continuum model (DFT/PCM) method as input for modeling their transport through the environment in case of accidental spills [277]. The four azidoethanamines were 2-azido-*N,N*-dimethylethanamine (DMAZ), 2-azido-*N*-methylethanamine, 1-(2-azidoethyl)pyrrolidine, and 4-(2-azidoethyl)morpholine, and the three aliphatic amines were dimethylamine, trimethylamine, and 1-methylpyrrolidine. The estimates for the three aliphatic amines were all within a factor of 5 of measured values that had been reported for them, but all were somewhat low. The estimates from both methods suggest that the volatilization of these compounds from water will be negligible.

### 19.2.2.6 Thermodynamic Properties of DMAZ

#### Specific Heat of DMAZ

The heat capacity of DMAZ as a function of temperature was measured using a DSC method (Table 54).

**Table 54:** Heat capacity of DMAZ

| Temperature |             | Heat capacity                     |                                      |
|-------------|-------------|-----------------------------------|--------------------------------------|
| K           | °C          | J g <sup>-1</sup> K <sup>-1</sup> | cal g <sup>-1</sup> °C <sup>-1</sup> |
| 223 to 273  | -50 to 0 °C | 1.22                              | 0.29                                 |
| 293         | 20          | 1.4                               | 0.33                                 |
| 303         | 30          | 1.6                               | 0.38                                 |
| 313         | 40          | 1.8                               | 0.43                                 |
| 323         | 50          | 2.2                               | 0.53                                 |
| 333         | 60          | 2.8                               | 0.67                                 |
| 343         | 70          | 3.8                               | 0.91                                 |
| 353         | 80          | 4.7                               | 1.12                                 |
| 363         | 90          | 5.6                               | 1.34                                 |

Data source: [272]

In a different set of experiments, the specific heat of DMAZ was also measured using a differential scanning calorimeter, but the data in these two tables are quite different (Table 55). It is not known which set of data is more accurate. The samples were weighed using a thermogravimetric analyzer. The ASTM standard E1269-04 was followed to obtain specific heat measurements.

**Table 55:** Measured specific heat of DMAZ.

| Pressure<br>atm | Temperature<br>K | Heat capacity $c_p$<br>$\text{J g}^{-1} \text{K}^{-1}$ |
|-----------------|------------------|--------------------------------------------------------|
| 1.0             | 320              | 1.782                                                  |
| 1.0             | 325              | 1.812                                                  |
| 1.0             | 330              | 1.817                                                  |
| 1.0             | 335              | 1.819                                                  |
| 1.0             | 340              | 1.820                                                  |
| 1.0             | 345              | 1.823                                                  |
| 1.0             | 350              | 1.823                                                  |
| 1.0             | 355              | 1.825                                                  |
| 1.0             | 360              | 1.825                                                  |
| 1.0             | 365              | 1.825                                                  |
| 1.0             | 370              | 1.830                                                  |
| 1.0             | 375              | 1.850                                                  |

Data source: [276]

### Enthalpy of Formation of DMAZ

A new technique for determining thermophysical properties of potential new rocket engine propellants used a combination of three different computational methods to predict these properties [271, 276, 278, 279]. Quantum mechanics and molecular dynamics were used to model new propellants at a molecular level in order to calculate density, enthalpy, and entropy. Additivity methods were used to calculate the kinematic viscosity and thermal conductivity of new propellants. This new technique was validated by comparing results for two fuels: quadricyclane and 2-azido-*N,N*-dimethylethanamine (DMAZ). In each case, the new technique was better than the best current computational methods at accurately matching the experimental data of the two propellants.

The enthalpy and entropy of formation of two high-energy-density matter (HEDM) fuel compounds, DMAZ and quadricyclane, are provided in Table 56.

**Table 56:** Thermodynamic properties of liquid DMAZ and liquid quadricyclane.

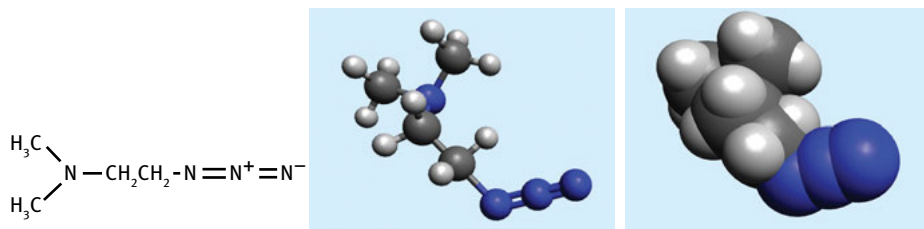
| Compound      | Enthalpy of formation $\Delta H_f$ |          | $\Delta S_f$ at 101 kPa           | $\Delta S_f$ at 1 atm                |
|---------------|------------------------------------|----------|-----------------------------------|--------------------------------------|
|               | kJ/mol                             | kcal/mol | $\text{J mol}^{-1} \text{K}^{-1}$ | $\text{cal mol}^{-1} \text{°C}^{-1}$ |
| Quadricyclane | +302                               | +72.2    | 167                               | 39.9                                 |
| DMAZ          | +280                               | +66.9    | 154                               | 36.8                                 |

Data source: [276]



### 19.2.2.7 Molecular Structure of DMAZ

The molecular structure of DMAZ is shown in Figure 9.



**Figure 9:** Molecular structure of DMAZ.

### 19.2.2.8 Computational Chemistry Studies of N,N-Dimethyl-2-azidoethylamine Molecule

Non-local density functional theory utilizing exchange-correlation functionals was used to characterize the geometric parameters and normal modes of 12 equilibrium conformations of DMAZ [280]. An experimentally acquired, mid-IR absorption spectrum of DMAZ vapor was analyzed and compared to computational results. The analysis indicated that the relative populations of DMAZ conformers in a room-temperature sample do not deviate significantly from expectations based on a Boltzmann distribution calculated from their theoretically determined zero-point corrected energies. The most abundant conformer most likely has the central nitrogen atom of the azido group aligned over the amine lone-pair electrons, a configuration likely to inhibit proton transfer to the amine site.

DMAZ had shown some promise as a less toxic replacement for MMH in hypergolic combinations, but the ignition delays observed for IRFNA/DMAZ were much longer (i.e., more hazardous) than those for IRFNA/MMH. For comparison, 2-azidocyclopropaneamine has two stereochemically distinct isomers, one of which prevents the azide group from “shielding” the amine lone-pair electrons from proton attack. The other promotes such shielding. Since shielding likely influences the manner in which nitric acid reacts with amine–azide fuels, the ignition delays for the isomers may be different, and it is possible that one of the isomers will yield shorter ignition delays than DMAZ [281, 282].

Molecular dynamics simulations to estimate the densities and heats of vaporization of aliphatic compounds with both azido and amino functional groups led to theoretical densities of these liquids that tend to be slightly overpredicted. Previously obtained DFT calculations suggested that this overprediction may be due to the attractive interaction between the amine nitrogen and the middle nitrogen of the azide group being smaller than modeled by the force field. The temperature dependence of

the density of DMAZ was well predicted, but melting point and boiling point estimates were far off the reality [283].

In an attempt to find structural features of 2-azidoethanamines that correlate with their hypergolic ignition delays, DFT-based quantum mechanics calculations were performed to characterize equilibrium configurations of two secondary 2-azidoethanamines: 2-azido-*N*-cyclopropylethanamine (CPAZ) and 2-azido-*N*-methylethanamine (MMAZ) [284]. The former is hypergolic with IRFNA, whereas the latter is not. Geometries and normal modes for MMAZ conformers and CPAZ conformers were compared to geometries and normal modes obtained previously for the hypergolic, tertiary 2-azido-*N,N*-dimethylethanamine (DMAZ).

The applicability of semi-empirical models for estimating the gas-phase enthalpies of formation, enthalpies of vaporization, and enthalpies of sublimation of azide-functionalized aliphatic compounds was evaluated [285]. Enthalpies of vaporization estimates for azide-functionalized compounds were in reasonable agreement with values derived from experiments and from molecular dynamics simulations. Best estimates were obtained for a set of compounds with multiple azide groups that was synthesized by the U.S. Army Armament Research, Development and Engineering Center (ARDEC).

The proton affinity and base strength of beta-substituted ethanamines determine the stability of salts of these bases and degradation mechanisms of spilled propellants in the soil. Aqueous-phase dissociation constants ( $K_a$ ) for the conjugate acids of such beta-substituted ethanamine bases can be measured experimentally or predicted from computations. Aqueous-phase dissociation constants ( $K_a$ ) for the conjugate acids of a group of six 2-azidoethanamine bases ( $R_1N(R_2)CH_2CH_2N_3$  [1:  $R_1 = CH_3$ ,  $R_2 = H$ ; 2:  $R_1 = CH_3$ ,  $R_2 = CH_3$ ; 3:  $R_1 = CH_2CH_3$ ,  $R_2 = CH_2CH_3$ ; 4:  $R_1/R_2 = -CH_2-CH_2CH_2CH_2-$ ; 5:  $R_1/R_2 = -CH_2CH_2OCH_2CH_2-$ ; 6:  $R_1 = CH_2CH_3$ ,  $R_2 = CH_2CH_2N_3$ ]) were measured and were found to fall between those for analogous unfunctionalized and cyano-functionalized ethanamines [286]. The Gibbs free energies of aqueous-phase (equilibrium) conformers of the bases and their conjugate acids were determined via a DFT/PCM method. See also [287].

### 19.2.3 Chemical Properties of *N,N*-Dimethyl-2-azidoethylamine

#### 19.2.3.1 Thermal Stability of *N,N*-Dimethyl-2-azidoethylamine

A laboratory-scale flow reactor was used to subject small amounts (approximately 1 mL) of deoxygenated fuels, including DMAZ, to controlled conditions of temperature and residence-time-at-temperature at constant pressure (3.44 MPa = 34 atm) in the liquid or supercritical phase [288]. The reactor was made from CRES-316 HPLC tubing. The thermal stability of the fuels as well as the thermal fragmentation products of each fuel were measured using an in-line analytical system, as well as off-line GC analysis of products. Some of the candidate materials tested (DMAZ, quadricyclane, and bicyclopropylidene) showed only marginal thermal stability, with major decom-

position occurring below 673 K (400 °C) with only ~3 s residence time. Other candidate fuels (JP-10, RP-1, RG-1, RJ-6, and RJ-7) showed excellent thermal stability and little decomposition even at 873 K (600 °C). Results showed the pyrolytic stability of candidate materials relative to each other and provided insights into the mechanisms of thermal decomposition for specific fuel candidates.

Computational quantum mechanics was used to characterize species and transition states for anticipated H-atom abstraction and scission reactions involving DMAZ and/or 1,2-bis(dimethylamino)ethane (TMEDA) and their decomposition products [289]. Two reaction types were shown to be a reasonable basis for estimating the thermochemical properties of (equilibrium) reactants and products. Based on comparisons with results obtained from other calculations, the method appeared to underpredict the energies of transition states relative to reactant asymptotes.

As part of modeling of DMAZ decomposition (as well as the decomposition of other azide-functionalized energetic materials), postulated reaction paths were characterized via *ab initio* and DFT quantum chemical calculations [290, 291]. Four types of reactions were characterized: (1) simple scission of C—H, C—N, and C—C bonds, (2) N—N<sub>2</sub> bond fission via either concerted (synchronous) [DMAZ → singlet imine(R<sub>2</sub>C=NH) + N<sub>2</sub>] or stepwise (asynchronous) [DMAZ → nitrene intermediate R—N: + N<sub>2</sub>] steps, (3) HN<sub>3</sub> molecular elimination with the formation of dimethylaminoethylene, and (4) N<sub>2</sub> elimination with the formation of molecules with three-member or four-member heterocyclic rings. N—N<sub>2</sub> bond fission reactions were found to have the lowest energy barriers.

#### 19.2.3.2 Storability of N,N-Dimethyl-2-azidoethylamine

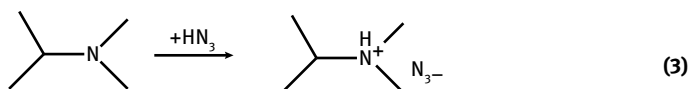
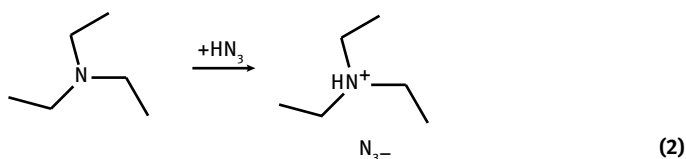
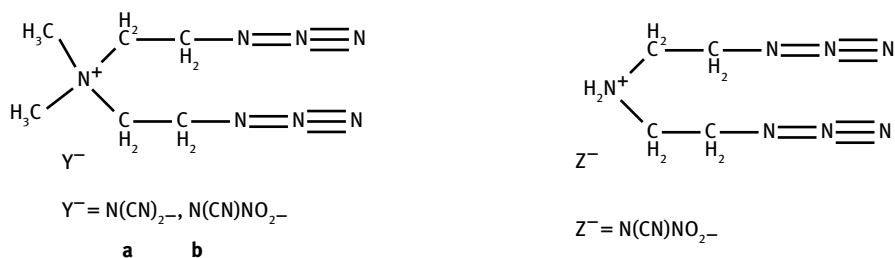
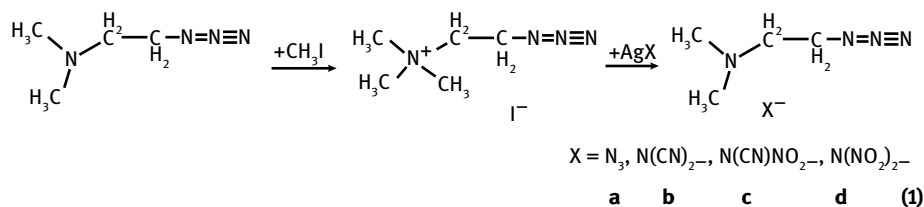
Elevated temperature *N,N*-dimethyl-2-azidoethylamine (DMAZ) storage tests under N<sub>2</sub> at a pressure of 3 bar and a moisture content of 0.05 mass-% H<sub>2</sub>O obtained a sigmoid-shaped decomposition curve and revealed that the decomposition reaction is auto-catalytic. Rate constants were measured for the first-order incipient reaction and the following auto-catalytic reaction. Modeling of the decomposition rate showed that the predicted shelf life of DMAZ was only 7.73 years at 298 K (25 °C) [292]. During the accelerated aging tests between 333 and 363 K (60 and 90 °C), the samples' color became gradually yellowish and ultimately black. Moisture contamination shortened the shelf life even further.

#### 19.2.3.3 Reactions of N,N-Dimethyl-2-azidoethylamine

*N,N*-Dimethyl-2-azidoethylamine ignites hypergolically with WFNA, RFNA, and high-test peroxide (HTP). Hypergolic ignition of DMAZ will be discussed in a future *Encyclopedia of Hypergolic Bipropellant Combinations*. The ignition of DMAZ with HTP can be improved by dissolving metal salts in the fuel [293]. As a base, DMAZ forms stable salts with many acids.

### 19.2.3.4 Salts Derived from *N,N*-Dimethyl-2-azidoethylamine

In the pursuit of higher heats of formations for low-volatility ionic liquids as replacements for MMH, energetic ionic liquids based on DMAZ as well as azide counter-anion-based ionic liquids were developed [294]. Energetic ionic liquids that contain the quaternary 2-azidoethyl-*N,N,N*-trimethylammonium cation coupled with nitrocyanamide, dicyanamide, dinitramide, or azide anions were synthesized in good yields by metathetical reactions. These ionic liquids exhibited desirable hypergolic activity with such oxidizers as 100% nitric acid and dinitrogen tetroxide.



These azide-based energetic ionic liquids were obtained either through metathetical reactions with silver azide (Reaction 1) or through direct neutralization with hydrazoic acid (Reactions 2 and 3). Of the 11 salts presented, all but one could be classified as ionic liquids with melting points below 373 K (100 °C), with several classifying as room-temperature energetic ionic liquids. Ignition-delay drop tests of several compounds with  $\text{N}_2\text{O}_4$  and WFNA exhibited hypergolicity. Among the room-temperature

energetic ionic liquids, products of Reaction 1c and Reaction 1a showed the shortest ignition-delay times for WFNA (8 and 16 ms, respectively). Despite not being room-temperature energetic ionic liquids, the products of Reaction 2 ( $T_m$  80 °C, impact sensitivity >40 J, WFNA hypergolic,  $N_2O_4$  explosion) and Reaction 3 ( $T_m$  75 °C, impact sensitivity >40 J, WFNA hypergolic) were reported as the first azide-based ionic liquids exhibiting hypergolicity. Both were hypergolic with  $N_2O_4$ , and triethylammonium azide was found to explode when exposed to WFNA. Both of these compounds are extremely hygroscopic.

Other azidoalkylamines can also be converted to energetic salts. Salts formed from 1,3-diazo-2-(azidomethyl)-2-propylammonium cations with nitroiminotetrazolate anions have been characterized by spectroscopy and single-crystal XRD [295]. The heats of formation and the detonation pressures and velocities were calculated. The silver salts were obtained by the metathesis of sodium dicyanamide and potassium dinitramide with silver nitrate in aqueous solution. Other salts based on the 1,3-diazo-2-(azidomethyl)-2-propylammonium cation and anions, such as nitrate, perchlorate, picrate, 3-nitro-5-oxo-1,2,4-triazolide, and 5-nitroiminotetrazolate, as well as dicyanamide and dinitramide, have been prepared and characterized.

Four ionic liquids were synthesized through a metathesis reaction of quaternized *N,N*-dimethyl-2-azidoethylamine with different alkyl chain lengths with silver dicyanamide [296]. The density, dynamic viscosity, and thermal properties of these ionic liquids were measured over a wide temperature range. When the effect of the alkyl chain length on the physicochemical properties was studied, it was found that density decreased while dynamic viscosity and molar heat capacity increased with increasing number of carbon atoms in the alkyl chain. The density showed a linear decrease with temperature, and the dynamic viscosity decreased with temperature. No melting points could be found for these four ionic liquids except for a glass transition temperature ( $T_g$ ). The  $T_g$  values were 184 to 171 K (−89 to −102 °C). The exothermic decomposition temperatures of these four ionic liquids ranged from 514 to 515 K (241 to 242 °C), independent of the alkyl chain length.

#### 19.2.4 Fuel Mixtures Containing *N,N*-Dimethyl-2-azidoethylamine

Various fuel mixtures of DMAZ with other amines provide short ignition delays and improve overall propellant properties. Such mixtures may contain *N,N,N',N'*-tetramethylethylenediamine (TMEDA) or tris(2-azidoethyl)amine [238, 297].

#### 19.2.5 Combustion and Flammability Properties of DMAZ

The lower flammable limit (LFL) of DMAZ has been determined to be 1.3 vol-% in air, and the upper flammable limit (UFL) is greater than 22.4 vol-% in air. Because DMAZ can decompose like a monopropellant, the UFL may even extend to 100% DMAZ vapor.

### 19.2.6 Materials Compatibility with DMAZ

DMAZ is compatible with most materials that are also compatible with organic amines, but it is more reactive with some materials.

### 19.2.7 Disposal of DMAZ

Surplus DMAZ that needs to be destroyed can be diluted with kerosene and burned in open pans.

An investigation of the chemical treatment of smaller quantities of DMAZ waste under laboratory conditions included reduction with tin (Sn) in hydrochloric acid (HCl), reduction with stannous chloride ( $\text{SnCl}_2$ ) in methanol, reduction with nickel–aluminum alloy (Raney nickel) in NaOH solution, and reduction with aluminum in NaOH solution.

Various reducing agents, Raney-nickel Al/Ni alloy in caustic 0.5-M NaOH, Al powder in 0.5-M NaOH, stannous chloride in methanol, and granular tin metal in concentrated hydrochloric acid were tested for the destruction of DMAZ and other hypergolic fuels [298]. DMAZ was reduced to *N,N*-dimethylethylenediamine in these tests.

DMAZ can be hydrolyzed in water in an autoclave at high temperatures and pressures [299, 300]. The hydrothermolysis of the water-soluble alkyl azide dimethyl-2-azidoethylamine was studied at 473–523 K (200–250 °C) and 275 bar in real time by flow-reactor FTIR spectroscopy. The kinetics of DMAZ decomposition by  $\text{N}_3^-$  formation represents only a minor reaction pathway (8% at 523 K = 250 °C). The main channel is loss of  $\text{N}_2$ , whose presence was determined by mass spectrometry. The Arrhenius parameters for decomposition by the two routes were  $E_a = 59 \text{ kJ/mol} = 14.1 \text{ kcal/mol}$  and  $\ln(A, \text{s}^{-1}) = 10.7$  for the  $\text{N}_2$  channel and  $E_a = 73 \text{ kJ/mol} = 17.4 \text{ kcal/mol}$  and  $\ln(A, \text{s}^{-1}) = 11.8$  for the  $\text{N}_3^-$  channel. Because of further reactions, the organic products could not be identified, but  $(\text{CH}_3)_3\text{N}$  appeared to be a major product. The  $\text{N}_3^-$  ion was found to be stable in water, at least to 613 K (340 °C).

DMAZ-contaminated wastewater that needs to be decontaminated before it can be released to surface waters can be purified by adsorption on zeolites or activated carbon [266]. The effects of various parameters, including the initial concentration of DMAZ, contact time, and adsorbent dosage on the DMAZ sorption efficiency, were examined, and the optimum experimental conditions were determined. DMAZ adsorption efficiencies of 60, 23, and 45% were obtained by ZSM-5, NaY zeolites, and activated carbon, respectively. It was observed that 15, 51, and 41 g of DMAZ could be removed by a unit mass of NaY zeolite, ZSM-5 zeolite, and activated carbon, respectively.

The photocatalytic activity of  $\text{TiO}_2$  deposited on expanded clay aggregate granules was determined for degradation of DMAZ in water, with mercury lamps as UV sources [301]. The results showed that the efficiency of photodegradation improved with increasing initial concentration of DMAZ and that the rate of DMAZ conversion increased with higher pH value and catalyst dosage. Under optimum conditions, a single-pass

degradation of 54.7% for DMAZ could be achieved. A first-order rate kinetic model presented good agreement with the experimental data.

### 19.2.8 Toxicity of DMAZ

It was difficult to prove that DMAZ was less toxic than MMH, which it was meant to replace.

The acute inhalation toxicity of DMAZ was determined in single-concentration studies using a minimum number of mice [274]. Initial 1-h exposures at levels of 2 mg/L (429 ppm), 9.2 mg/L (1973 ppm), and 20 mg/L (4289 ppm) showed that the low and mid-range levels could be tolerated for 1 h, but the high level was fatal in 40 min. A follow-up test was done with three exposed (1973 ppm for 1 h) and two control (unexposed) mice. The exposed mice showed signs of irritation around the eyes during exposure, but during the 14-d post-exposure observation period, the exposed mice gained weight similarly to the unexposed mice, and at necropsy no significant changes were noted by gross observations of the internal organs. It was concluded that the 1-h lethal concentration is greater than 1973 ppm but less than 4289 ppm, which rates this material as “toxic by inhalation” according to the guidelines of the U.S. Occupational Health and Safety Administration.

2-Dimethylaminoethyl azide (DMAZ, 99.3% pure) was tested for its potential to induce micronucleated polychromatic erythrocytes (MPCE) in the bone marrow cells of mice [302]. Male and female mice were dosed orally at 125, 250, and 500 mg DMAZ/kg body weight. Animals were euthanized approximately 24 or 48 h after dosing. The percentage of polychromatic erythrocytes (PCE) and the frequency of MPCE were determined at 24 and 48 h. There were no statistically significant increases in the number of MPCE in the treated groups when compared to the concurrent control group. These results indicated that DMAZ would not cause chromosome damage in the *in vivo* mouse micronucleus assay; therefore, it is not considered to be a clastogenic agent.

2-dimethylaminoethyl azide (DMAZ, 99.3% pure) was tested for mutagenic potential with *Salmonella typhimurium* strains TA 98, TA 100, TA 1535, and TA 1537 and *Escherichia coli* strain WP2uvrA by plate-incorporation method at doses up to 5000 micrograms/plate both in the presence and absence of S9 mix [303]. The results showed that DMAZ produced positive response in the TA 100 and TA 1537 strains, both with and without metabolic activation from S9 addition. No positive response was observed with any of the remaining tester strains with or without activation.

DMAZ was tested for potential mutagenicity in comparison to a tertiary amine, TMEDA. DMAZ did not produce any mutagenic effects at concentrations up to 5 mg/plate in the TA98 and TA1537 strains of *Salmonella typhimurium* or in an *E. coli* strain (WP2uvrA), with or without metabolic activation, but it did produce a positive response in the TA100 and TA1535 strains, both with and without metabolic activation [245]. DMAZ did not induce structural chromosomal aberrations at levels up to 5 mg/mL in Chinese hamster ovary (CHO) cells, with or without metabolic

activation. DMAZ, when tested *in vivo* in the CD-1 mouse at doses up to 500 and 250 mg/kg, respectively, did not induce micronuclei in bone marrow erythrocytes. These studies demonstrated that DMAZ is mutagenic in specific strains of *Salmonella*. However, it was negative for induction of chromosomal aberrations in CHO cells *in vitro* and in the *in vivo* mouse micronucleus assay.

### 19.2.9 Safety Properties of DMAZ

DMAZ has been subjected to the following safety tests [304]:

|                                |                                              |
|--------------------------------|----------------------------------------------|
| Card-gap test                  | Negative at zero cards                       |
| Drop-weight impact sensitivity | Negative at 165 kg-cm                        |
| Friction sensitivity           | Negative at 3.44 MN/m <sup>2</sup> (500 psi) |

The azido group in DMAZ may cause this compound to be sensitive to some external stimuli. Various conventional tests as well as computer codes were used to investigate the sensitivity of DMAZ to external stimuli such as impact, shock wave, Koenen test, burning, and electrostatic discharge sensitivity [305]. The results showed that DMAZ is not sensitive to impact, direct flame, or shock-wave initiation, but it has moderate and high sensitivity to heat in confined volume and electrostatic discharge, respectively.

### 19.2.10 Environmental Fate and Transport of DMAZ

Quantitative structure–property relationships (QSPRs) commonly employed as input for fate, transport, and effect modeling of hazardous materials in the environment can be predicted by computational methods. The reliability of QSPR estimates was examined for two classes of compounds considered as MMH replacements: (1) saturated tertiary multiamines and (2) ethanamine azides [306]. QSPRs contained in a program provided by the U.S. Environmental Protection Agency yielded reasonable estimates for amine normal boiling points, (ambient) vapor pressures, octanol–water partition coefficients, water solubilities, and air–water partition coefficients, but the estimates for azides were poor, or there were insufficient data with which to validate them. Alternative methods for estimating azide normal boiling points and vapor pressures were sought. Similar methods were used for predicting aquatic toxicity of these compounds to fish (LC50, 96 h), *Daphnia* (LC50, 48 h), and algae (EC50, 96 h).

### 19.2.11 Applications of DMAZ

It appears that DMAZ as a hypergolic rocket propellant fuel has been evaluated in many countries, including China [307].



### 19.2.11.1 Gelled DMAZ

Much work has been done on gelled MMH, and similar work was done on MMH replacements. In 2007, the U.S. Army awarded a Small Business Innovation Research contract to develop gelled azide amine fuels that would be less prone to leakage if the fuel tank were punctured by shrapnel [308].

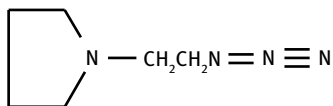
Fumed silica as a gelling agent is not readily wetted by DMAZ, and conventional kitchen-type rotary mixers do not give uniform gels. Improved dispersion of gellant and added metal powder were achieved with resonant acoustic mixing [309]. The rheology and high-gravity centrifuge stability of DMAZ gelled with EH-5 fumed silica and metallized with nano-aluminum L-Alex powder were measured with different gelling agent loadings, but with mostly the same metal loading of ~30%. A surfactant was used to help wet the nanoparticles to aid in uniform dispersion in the gelled propellant.

### 19.2.11.2 DMAZ as a Monopropellant

Many azido-substituted alkylamines have been developed and tested as rocket fuels. Some of these azido molecules are so energetic that they can even decompose exothermally and can be used as monopropellants. DMAZ can also decompose by itself in a monopropellant fashion and has been considered as a replacement for hydrazine as a monopropellant. Catalysts have been sought (without success) that might initiate the decomposition of DMAZ as a monopropellant at room temperature, not requiring any pre-heating to initiate the decomposition reaction.

## 19.3 Other Azidoalkylamines

Pyrrolidinylethylazide, 2-azidoethylpyrrolidine,  $C_6H_{12}N_4$ , PYAZ,  $M = 140.19$  g/mol, has been proposed as an MMH replacement and is also mentioned in several patents [236, 310, 311].



It has a boiling point of 428 K (310 °F) (with decomposition), a freezing point of 158 K (−176 °F), a density of 0.986 g/cm<sup>3</sup>, and an enthalpy of formation of +305 kJ/mol = +73 kcal/mol = +520 cal/g.

Another azidoalkylamine mentioned in the same patents is bis(azidoethyl)methylamine, also known as di(azidoethyl)methylamine,  $(N_3CH_2CH_2)_2NCH_3$ ,  $C_5H_{11}N_7$ , BAZ, with a molecular mass of 169.19 g/mol. It has a boiling point of 431 K (316 °F) (with decomposition), a melting point of 289 K (61 °F), a density of

1.06 g/cm<sup>3</sup>, and an enthalpy of formation of +586 kJ/mol = +140 kcal/mol = +828 cal/g. Di( $\beta$ -azidoethyl)methylamine had been previously described in the literature [312]. It boils at 371–372 K at 0.67 kPa (98–99 °C at 5 mm Hg), and the refractive index is  $n_D^{25} = 1.4824$ .

*N,N*-Diethylaminoethylazide is thermally more stable than DMAZ and can be used as a hypergolic fuel [263].

The enthalpies of formation in the gas phase, vapor pressure, and liquid densities were predicted from theoretical calculations for a group of 13 tertiary amine azides expected to be useful as hypergolic fuels for hypergolic bipropellant combinations, which can provide higher density-specific impulses than MMH but are less toxic and have lower vapor pressures than MMH. The predicted enthalpies of formation were compared to measured data for three similar compounds [313–316]. The calculated density-specific impulses for combinations with RFNA as the oxidizer predicted a 4–34% improvement over RFNA/MMH. One wonders how a bunch of theoretical calculations can lead to a patent at a time when none of the chemical compounds claimed had actually been reduced to practice or fired in a rocket engine.

Thermodynamic properties of a series of azidoamines were studied at the B3LYP/6–311 + G(2df) level of density functional theory [317]. Enthalpies of formation increased quantitatively with increasing temperature as well as the number of azido groups. The azidoamines are highly energetic, with large enthalpies of formation. The detonation performances of the azidoamines were evaluated, and their predicted performances are comparable to those of RDX and HMX. However, they are as sensitive to impact as halogen azides, according to the small potential energy barriers for initiation.

2-(dimethylamino)-1,3-diazidopropane,  $N_3CH_2CH[N(CH_3)_2]CH_2N_3$ , is a hypergolic fuel and can be prepared by methylation of 2-amino-1,3-dihydroxypropane with formaldehyde and formic acid to afford 2-(dimethylamino)-1,3-propanediol, which is then chlorinated and reacted with sodium azide to afford 2-(dimethylamino)-1,3-diazidopropane [318].

It is incomprehensible to an experimental rocket propellant chemist how a U.S. patent could have been awarded to a purely speculative idea that had never been reduced to practice [219]. Those patent examiners who allowed this patent to go through instead of rejecting it must have been either fast asleep or high on drugs. Allowing purely speculative, theoretical wild claims as patentable certainly dilutes the value of other hard-earned patents that have experimental results to prove the realization of their concept.

### 19.3.1 Tris(2-azidoethyl)amine

Tris(2-azidoethyl)amine,  $(N_3CH_2CH_2)_3N$ ,  $C_6H_{12}N_{10}$ , TAEA, is a more energetic azido compound than DMAZ. It contains 62 mass-% nitrogen. It was predicted that a gain of about 7.39% in density impulse can be achieved by the replacement of MMH with

TAEA. It has a refractive index  $n_D^{25}$  of 1.5090, an impact sensitivity of 60–65 in-lb (for comparison, TMETN = 25–30 in-lb), a density of 1.162 g/cm<sup>3</sup>, a freezing point of 254 K = –19 °C, and an enthalpy of formation  $\Delta H_f$  of +887 kJ/mol (+212 kcal/mol). TAEA can be prepared starting with readily available triethanolamine, which is first converted to the trichloride or tritosylate [319, 320]. In the next reaction step, the tris(2-haloethyl)-amine or tris(2-tosylethyl)amine is reacted with an ionic azide such as sodium azide in dipolar aprotic solvents such as dimethylformamide or dimethylsulfoxide, which are used routinely as media for azide ion substitution reactions. Another energetic azide is *n*-butyl(2-azidoethyl)nitramine, which has a refractive index of  $n_D^{24} = 1.4870$ , a freezing point below 195 K (–78 °C), and an impact sensitivity beyond the range of the instrument (> 150 in – lb).

TAEA has been patented as a hypergolic fuel ingredient in mixtures with TMEDA [236, 237]. See also [321].

### 19.3.2 Azidoalkylnitramines

There is a large group of azidoalkylnitramines that are actively evaluated as energetic plasticizers for double-base propellants.

### 19.3.3 Azidopropylamines

Propyleneimine reacts cleanly with HN<sub>3</sub> to give 1-azido-2-aminopropane. This compound can be converted directly to salts, or it can be N-nitrated to give 1-azido-2-propylnitramine, which can be used as the acidic component in energetic salt formation [322]. A similar reaction of hydrazoic acid with ethyleneimine is expected to give 2-azidoethylamine.

### 19.3.4 Azidonitroalkylamines

Azidomethyl bis(fluorodinitroethyl) amine, [FC(NO<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>NCH<sub>2</sub>N<sub>3</sub>, C<sub>5</sub>H<sub>6</sub>F<sub>2</sub>N<sub>8</sub>O<sub>8</sub>, has a density of 1.638 g/cm<sup>3</sup> at 296 K (23 °C) (for comparison, FEFO = 1.596 g/cm<sup>3</sup>) and an enthalpy of formation of  $\Delta H_f = -138$  kJ/mol = –33 kcal/mol [323, 324].

## 20 C-Nitro- and C-Nitroxy-substituted Alkylamines

The nitro groups in *C*-nitro substituted alkylamines, in particular ethylamines, are usually in  $\beta$  position. Nitro groups in  $\alpha$  position to the amino group result in unstable molecules. The *C*-nitro substituted alkyl groups can form primary, secondary, or tertiary amines. Similar amines were developed with nitroxy groups in the  $\beta$  position of ethylamines, and their nitrate salts were examined.

## 20.1 Nitroethylamines

The ethyl group that is attached to the amino nitrogen can carry one, two, or three nitro groups in the  $\beta$  position. The nitroethylamines thus formed have been evaluated as energetic plasticizers. One of the starting reactants for the synthesis of other energetic compounds is 2,2-dinitroethylamine [325, 326].

An *N*-functionalized strategy, including *N*-amination and *N*-trinitroethylation, was utilized for the synthesis of nitroimidazole-based energetic materials, opening a path to a new family of highly insensitive *N*-aminonitroimidazoles and oxygen-rich *N*-trinitroethylaminonitroimidazoles with good properties [327]. These compounds were fully characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and elemental analysis, and some high-performance compounds were further confirmed by  $^{15}\text{N}$  NMR as well as single-crystal XRD. *N*-trinitroethylaminonitroimidazoles have favorable densities (1.75–1.84 g/cm<sup>3</sup>), good detonation properties ( $P = 27.6\text{--}35.9$  GPa;  $v_D = 7815\text{--}8659$  m/s), and moderate thermal stabilities (409–445 K = 136–172 °C). These properties are better than some known energetic compounds, such as TNT ( $P = 19.5$  GPa;  $v_D = 6881$  m/s) and TATB ( $P = 31.2$  GPa;  $v_D = 8114$  m/s), and they are comparable to RDX ( $P = 35.0$  GPa;  $v_D = 8762$  m/s).

The preparation of bistrinitroethylnitramine requires bistrinitroethylamine (BTNA) as a precursor. Bistrinitroethylamine can be prepared from potassium trinitromethide and cyclohexamethylenetetramine [328]. The crystals melt at 387 K (114 °C) with decomposition.

Trinitroethanol can be reacted with different moieties through the Mannich reaction, such as ammonia or aliphatic amines as the amine component in order to synthesize the corresponding trinitroethylamine derivatives. Examples include bis(2,2,2-trinitroethyl) amine [329]. Bis(2,2,2-trinitroethyl) amine properties are as follows: DSC  $T_{\text{dec}} = 396.5$  K = 123.4 °C,  $\rho = 1.86$  g/cm<sup>3</sup>,  $\Delta H_f = -77.8$  kJ/mol (calculated),  $\Delta H_f = 0.47$  kJ/g (calculated),  $p_{\text{det}} = 34.2$  GPa (calculated),  $v_{\text{det}} = 8558$  m/s (calculated), impact sensitivity 15 cm, oxygen content 56.0%, oxygen balance +25.6%. The trinitroethanol precursor needed for such syntheses is made by reaction of nitroform with paraformaldehyde [330].

Bis(trinitroethyl)amine, also known as BTNA,  $\text{C}_4\text{H}_5\text{N}_7\text{O}_{12}$ ,  $(\text{O}_2\text{N})_3\text{CCH}_2\text{NHCH}_2\text{C}(\text{NO}_2)_3$ , has a molecular mass of 343.12 g/mol, is a liquid at room temperature, and if frozen solid forms triclinic crystals, space group *Pbca* (no. 61) with  $a = 12.8996(6)$  Å,  $b = 11.7753(5)$  Å,  $c = 16.1577(7)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 2454$  Å<sup>3</sup>,  $Z = 8$ , and  $\rho_{\text{XRD}} = 1.857$  g/cm<sup>3</sup> [331]. The measured density is 1.881 g/cm<sup>3</sup>, the calculated heat of formation is -138 kJ/kg, and the predicted detonation velocity is 8815 m/s.

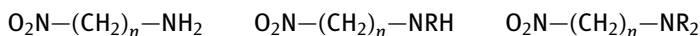
2,2-dinitroethylamine can be made by reaction of 1,1,1-trinitroethane with ammonia [326]. A similar reaction with dimethylamine instead of ammonia gives *N,N*-dimethyl-2,2-dinitroethylamine. 2,2-dinitroethylamine is a yellow solid with a melting point of 390 K (117 °C).

Desirable crystal shapes can be achieved by recrystallizing from the best solvent for this task. Bis(2,2,2-trinitroethyl) amine (BTNA) was characterized by elemental analysis, IR spectrometry, and DSC [332]. The crystal morphology and crystallization behavior of BTNA were calculated, and the relationships between the structures of important crystal faces and solvent of crystallization were analyzed. By recrystallizing BTNA from dichloromethane (weak polar solvent), it was found that the crystalloid is more uniform and the aspect ratio is smaller compared with that from water, in accordance with the behavior predicted from theory.

Instead of nitro groups, the alkyl rests in amines can carry nitroxy groups, which form alkyl nitrate esters with an amino group in the alkyl rest. These nitroxyalkylamines can form very energetic nitrate salts [333]. The raw materials for preparation of such nitroxyalkylamines would be the hydroxylalkylamines, which are readily available in industrial quantities.

## 20.2 $\omega$ -Nitroalkylamines

Nitroalkylamines are alkylamines in which the  $C_{>2}$  alkyl groups carry one or more terminal ( $\omega$  position) nitro groups



where R is another alkyl group, typically methyl. By virtue of their exceptional charge delocalization and concomitant reduction in solvation energy, 2-nitroethyl ammonium salts, especially the dinitramide salt, display remarkably low melting points while retaining acceptable stability at room temperature [322].

The nucleophilic Michael addition of nitroform to acrylamide creates 4,4,4-trinitrobutanamide in the first step that can subsequently be converted to 3,3,3-trinitropropylamine and salts containing the trinitropropylammonium cation,  $[(NO_2)_3CCH_2CH_2NH_3]^+X^-$  [334]. For  $X^- = ClO_4^-$ ,  $(NO_2)_2N^-$ ,  $IO_4^-$ , or amino-bistetrazolate, these salts are of interest as propellant ingredients [335].

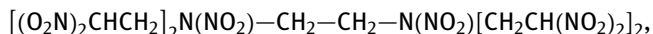
## 20.3 Fluoronitroalkylamines

Fluorodinitroalkylamines can be more energetic than nitroalkylamines. The fluoro group usually shares space with nitro groups in the  $\beta$  position of ethyl groups. They can be prepared from fluorodinitroethanol or fluorodinitromethane. The enthalpy of formation of bis(2-fluoro-2,2-dinitroethyl)amine (BFDNA) is  $-531 \text{ kJ/mol}$  ( $-126.952 \text{ kcal/mol}$ ) [121].

## 20.4 Nitroalkylnitramines

This book contains a separate section on alkylnitramines, as well as those that carry additional substituents such as nitro or nitroso groups on the alkyl rest. These compounds are mostly discussed in the section on nitramines, but they also carry some resemblance to nitroalkylamines. There may be some overlap between these sections.

Bis(2,2,2-trinitroethyl)nitroamine, CAS RN [19836-28-3], has been proposed as an ingredient in smokeless propellants [336]. Bis(2,2-dinitroethyl-*N*-nitro)ethylenediamine,



forms salts with organic bases exhibiting favorable physical properties, good detonation properties, and relatively low impact sensitivities. They can be synthesized in high yield by direct reactions of bis(2,2-dinitroethyl-*N*-nitro)ethylenediamine with organic bases [337]. The resulting salts were fully characterized by multi-nuclear NMR spectroscopy ( $^1\text{H}$  and  $^{13}\text{C}$ ), IR vibrational spectroscopy, DSC, and elemental analysis. Thermal decomposition kinetics and several thermodynamic parameters of some salts were obtained under non-isothermal conditions by DSC. The densities of the energetic salts paired with organic cations were in the range of 1.60–1.89 g/cm<sup>3</sup> as measured with a gas pycnometer. Based on the measured densities and calculated heats of formation, detonation pressures and velocities were calculated using the Explo 5.05 program and were predicted to be 23.6–44.8 GPa and 7790–9583 m/s, respectively, which makes them potentially useful as energetic materials.

## 20.5 Nitroalkylhydrazines

Due to similarity between alkylamines and alkylhydrazines, and between nitroalkylamines and nitroalkylhydrazines, a short reference to nitroalkylhydrazines is included here. It is unusual to have an oxidizing group like the nitro group and a reducing group like the hydrazino group in the same molecule. One would not expect good thermal stability from such an arrangement.

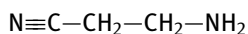
A study has been made of the IR spectra of *N*- $\alpha$ -polynitroalkylhydrazine derivatives, and band assignments were made for stretching vibrations in the NH, CO, and NO<sub>2</sub> groups [338]. Integral intensities for NO<sub>2</sub> anti-symmetrical stretching absorption bands are additive. Splitting of these bands is characteristic of nitro compounds containing a hydrazine group in the  $\alpha$ -position with respect to the nitro group. It has been shown that intermolecular hydrogen bonding exists in the *N*- $\alpha$ -polynitro-alkylhydrazines, both in the crystalline state and in concentrated solutions.

## 20.6 $\beta$ -Nitroxyethyl Amines

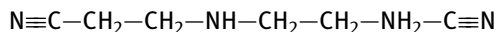
Nitroxy-functionalized cations and their nitrate salts were synthesized as potential halogen-free oxidizers for solid propellants, and their thermal stability was examined [339, 340]. It was expected that quaternized nitroxyalkylammonium nitrates would be thermally more stable than their primary ammonium salt counterparts. There was a hypothesis that the thermal stabilities of salts with nitroxy-functionalized cations might correlate with the length(s) of their O—N bond(s). Gas-phase proton affinity, heats of sublimation, and lattice enthalpies were calculated. The salts prepared and modeled by quantum mechanical computational methods included 2-nitroxy-*N,N,N*-trimethylethanammonium nitrate, 2-nitroxy-*N*-(2-nitroxyethyl)-*N,N*-dimethylethanammonium nitrate, 2-nitroxy-*N,N*-bis(2-nitroxyethyl)-*N*-methylethanammonium nitrate, and 1-(2-nitroxyethyl)-2,3-dimethyl-5-nitroimidazolium nitrate. The thermal decomposition temperatures were in the range of 403–426 K (130–153 °C), substantially lower than that of AP, which they were intended to replace. The  $\Delta G_{298}$  results indicated that it is highly unlikely that any nitrate salt with a cation having more than two  $\text{NO}_x$  groups will be thermally stable for 24 h at 348 K (75 °C).

## 21 C-Cyano-Substituted Amines

The introduction of cyano groups into alkylamines increases the enthalpy of combustion and the performance as rocket fuels. A typical example would be 2-cyanoethylamine, 3-aminopropionitrile,  $\text{C}_3\text{H}_6\text{N}_2$ , CAS RN [151-18-8]



which can be made by cyanoethylation of ammonia and has been studied for its IR spectrum [341], but it has not yet been tested as a rocket fuel. The gas-phase enthalpy of formation is 89.75 kJ/mol. It boils at 352–354 K at a reduced pressure of 0.021 bar. Bis-(2-cyanoethyl) amine



can be made by reaction of acrylonitrile with ammonia [342]. Bis-(2-cyanoethyl) amine could be used as a rocket fuel.

Continuing the reaction with an excess of acrylonitrile would eventually lead to tris(2-cyanoethyl) amine,  $\text{C}_9\text{H}_{12}\text{N}_4$ , which should also make a good rocket fuel, although it is a solid with a melting point of 326–327 K (53–54 °C) [343].

Bis-(2-cyanoethyl) amine can be reacted with oxiridines (alkoxides) to form energetic fuels to be used as building blocks in energetic binders for solid propellants [344].

## 22 Hydrazido-Substituted Amines

The introduction of a hydrazine group into an alkylamine results in fuel molecules with properties somewhere between those of alkylamines and alkylhydrazines, similar to physical mixtures of the two. Typical examples would be

|                                                  |                                                              |
|--------------------------------------------------|--------------------------------------------------------------|
| $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHNH}_2$ | $(\text{H}_3\text{C})_2\text{NCH}_2\text{CH}_2\text{NHNH}_2$ |
| 2-aminoethylhydrazine                            | <i>N</i> -dimethylaminoethylhydrazine                        |
| 2-hydrazinoethylamine                            | 2-hydrazinoethyldimethylamine                                |
| 1,2,5-triazapentane                              | 5,5-dimethyl-1,2,5-triazapentane                             |

## 23 C-Hydroxy-Substituted Amines

Hydroxy groups can be introduced into alkylamines either at the carbon atoms (discussed in this section) or at the nitrogen atom (discussed in *Encyclopedia of Oxidizers*, chapter “Hydroxylammonium Salts,” under substituted hydroxylamines). These compounds are structural isomers with identical gross formulas.

The most important *C*-hydroxyalkylamines are those derived from ethylamine, diethylamine, and triethylamine by replacing the ethyl group(s) with 2-hydroxyethyl group(s). These amines are prepared in large quantities by reaction of ammonia with ethylene oxide, and the process typically produces mixtures of the three amines that must be separated by distillation. The identifier *C*- for substitution on the alkyl group will be omitted in further discussion of these chemicals in the following sections. Because hydroxyl substitution in the alpha position of ethylamine results in unstable molecules, it is always assumed that the substitution was made in the beta position when referring to hydroxyethylamine, even if the 2- designator is missing.

Hydroxyethylamine, bis(2-hydroxyethyl)amine, and tri(2-hydroxyethyl)amine are available in large quantities and have found various industrial and cosmetic uses. They are weak bases and form salts with most acids. Because of the excellent water solubility, nitrates of any of these three amines have been considered as fuels for HAN-based monopropellants. In particular, the nitrate salt of tri(2-hydroxyethyl)amine, trihydroxyethylammonium nitrate (TEAN), has been extensively investigated and is relatively well characterized. Because these salts are readily water soluble, un-deroxidized, and compatible with HAN, the properties of their parent amines have been included in this encyclopedia.



### 23.1 Ethanolamine

Ethanolamine, also known as monoethanolamine, 2-hydroxyethylamine,  $\text{HOCH}_2\text{CH}_2\text{NH}_2$ ,  $\text{C}_2\text{H}_7\text{ON}$ , CAS RN [141-43-5], forms as one of several products in the hydroxyethylation of ammonia by reaction with ethylene oxide. Ethanolamine is a potential contaminant of diethanolamine and triethanolamine. It is more likely to be nitrosated from atmospheric  $\text{NO}_x$  than triethanolamine; therefore, its presence as a contaminant in triethanolamine is undesirable in pharmaceutical or cosmetic preparations. Ethanolamine would be a better rocket fuel than ethanol because it is more reactive, but it contains less hydrogen (11.55% H vs. 13.12% H in EtOH).

#### 23.1.1 Physical Properties of Ethanolamine

Physical properties of ethanolamine are listed in Table 57.

**Table 57:** Physical properties of ethanolamine.

| Property                        | SI units                 | Other units                   | References |
|---------------------------------|--------------------------|-------------------------------|------------|
| Molecular mass                  | 61.0831 g/mol            | 16.37 mol/kg                  | [29]       |
| Boiling point                   | 443.2 K                  | 170.1 °C                      | [29]       |
| Freezing point                  | 283.45 K                 | +10.3 °C                      | [29]       |
| Density at 298 K                | 1.0127 g/cm <sup>3</sup> | 63.22 lb/ft <sup>3</sup>      |            |
| Refractive index, $n_D^{20}$    | 1.4539                   | —                             |            |
| Enthalpy of formation, liquid   | −507.5 kJ/mol            | −121.3 kcal/mol               | [29]       |
|                                 | −507 kJ/mol              | −1986 cal/g = −121.3 kcal/mol | [27]       |
| Enthalpy of vaporization at NBP | 58 ± 3 kJ/mol            | 13.9 ± 0.7 kcal/mol           | [29]       |

The vapor pressure of ethanolamine in the range 338.6–444.1 K can be calculated from the equation

$$\log P = 4.29252 - [1408.873/(T - 116.093)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

#### 23.1.2 Chemical Properties of Ethanolamine

Ethanolamine forms salts with many strong acids.

##### 23.1.2.1 Ethanolammonium Nitrate

Physical properties of 2-hydroxyethylammonium nitrate are listed in Table 58. The thermal stability of 2-hydroxyethylammonium nitrate was measured by thermal analysis [345].

**Table 58:** Physical properties of 2-hydroxyethylammonium nitrate.

| Property              | SI units               | Other units     | References |
|-----------------------|------------------------|-----------------|------------|
| Molecular mass        | 124.096 g/mol          | 8.058 mol/kg    |            |
| Oxygen balance        | -51.5%                 |                 |            |
| Melting point         | 323 K                  | 50 °C           |            |
| Density               | 1.33 g/cm <sup>3</sup> |                 |            |
| Enthalpy of formation | -576 kJ/mol            | -137.6 kcal/mol | [17]       |

If ethanolammonium nitrate is treated in strong nitrating acid, it will form a nitrate ester with the hydroxyl group, and the resulting energetic material is called ethanolamine dinitrate:  $\text{O}_2\text{NO}-\text{CH}_2-\text{CH}_2-\text{NH}_3^+\text{NO}_3^-$ ,  $\text{C}_2\text{H}_7\text{N}_3\text{O}_6$  with a molecular mass of 169 g/mol. Its enthalpy of formation was predicted to be  $-2.27 \text{ kJ/g} = -387 \text{ kJ/mol}$ , but measurements gave an enthalpy of formation of  $-2.77 \text{ kJ/g} = -468 \text{ kJ/mol}$  [59]. There was concern that a similar nitrate ester formation reaction could take place in concentrated HAN solutions when the nitrate salts of hydroxyethylamine or trihydroxyethylamine are used as the fuels in HAN-based monopropellants. The nitrate ester nitrate salt would be more sensitive than the normal nitrate salt.

#### 23.1.2.2 Toxicity of Ethanolammonium Nitrate

The liver enzyme toxicity of a number of water-soluble oxidizer and fuel ingredients for non-toxic monopropellants intended as replacements for monopropellant hydrazine was tested *in vitro* using rat hepatocytes [346]. *In vitro* rat hepatocyte toxicity and bacteria (*Salmonella*) genotoxicity assays were performed on 13 high-energy chemicals that were candidates for potential replacement monopropellants for hydrazine. The chemicals were primarily hydrazine derivatives and amino compounds. Ethanolammonium nitrate is one of the less toxic compounds in this group. It is neither genotoxic nor mutagenic.

#### 23.1.2.3 Ethanolammonium Dinitramide

Ethanolammonium dinitramide, ethanolamine dinitramide,  $[\text{HOCH}_2\text{CH}_2\text{NH}_3^+]\text{[N(NO}_2)_2^-]$ , melts at 310–312 K (37–39 °C) [97]. The enthalpy of formation of this salt was not measured but was extrapolated from similar salts as  $-335 \text{ kJ/mol}$  (calculated) ( $-80 \text{ kcal/mol}$ ).

#### 23.1.3 Applications of Ethanolamine

Mixtures of ethanolamine and ethanol can be hypergolized with hydrogen peroxide by adding soluble catalysts. A solution of 1% copper(II) chloride in ethanolamine was found to rapidly ignite with 90% hydrogen peroxide [347, 348].

A mixture of ethanol and ethanolamine can be made hypergolic with hydrogen peroxide, featuring low toxicity and high density-specific impulse [349]. Several different catalysts were dissolved in ethanolamine. Among the catalytic materials tested, copper nitrate achieved the shortest ignition delay. The results showed that an optimized fuel composition with 61 mass-% ethanolamine, 30% ethanol, and 9% hydrated copper nitrate yielded a minimum ignition delay of 15.7 ms.

Ethanolamine with dissolved metal salt catalysts or a suspension of sodium borohydride gave a very short ignition delay in open-cup drop tests with hydrogen peroxide [350, 351].

Other laboratories started looking into how to improve the handling safety of ethanolamine as a rocket propellant by gelling it with polyvinylpyrrolidone and fumed silica [352–354]. This fuel can be hypergolic with hydrogen peroxide as the oxidizer, constituting a less toxic but also hypergolic replacement for dinitrogen tetroxide (NTO)/MMH [355].

## 23.2 Diethanolamine

Diethanolamine, also known as bis(2-hydroxyethyl)amine, 2,2'-iminodiethanol,  $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$ ,  $\text{C}_4\text{H}_{11}\text{O}_2\text{N}$ , CAS RN [111-42-2], forms as a byproduct in the hydroxyethylation of ammonia by reaction with ethylene oxide if the intended end product is triethanolamine. Diethanolamine is a potential contaminant of triethanolamine. It is more likely to be nitrosated from atmospheric  $\text{NO}_x$  than triethanolamine; therefore, its presence as a contaminant in triethanolamine is undesirable in pharmaceutical and cosmetic preparations. Both are used as moisturizers in cosmetic preparations and as sorbents to remove acidic gases from natural gas or industrial gas streams.

### 23.2.1 Physical Properties of Diethanolamine

Diethanolamine forms low-melting colorless prismatic crystals that melt at 301 K and boil at 544 K (268 °C). Physical properties of diethanolamine are listed in Table 59.

The vapor pressure of diethanolamine in the range 467–514 K can be calculated from the equation

$$\log P = 5.19445 - [2273.949 / (T - 103.362)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

### 23.2.2 Chemical Properties of Diethanolamine

Diethanolamine reacts with  $\text{NO}_x$  from the environment or from combustion products to form *N*-nitrosodiethanolamine, a proven human carcinogen. The formation of this compound must be avoided if contaminated triethanolammonium nitrate is used as a fuel in HAN-based monopropellants. There are numerous publications on the car-

**Table 59:** Physical properties of diethanolamine.

| Property                     | SI units                 | Other units              | References |
|------------------------------|--------------------------|--------------------------|------------|
| Molecular mass               | 105.1356                 | 9.511 mol/kg             | [29]       |
| Boiling point at 101 kPa     | 544.2 K                  | 268 °C                   | [29]       |
| Boiling point at 20 kPa      | 490.2 K                  | 217.1 °C                 | [29]       |
| Melting point                | 301.1 K                  | 28 °C                    | [29]       |
| Density at 298 K             | 1.0935 g/cm <sup>3</sup> | 68.26 lb/ft <sup>3</sup> |            |
| Refractive index $n_D^{20}$  | 1.4776                   | —                        |            |
| Enthalpy of formation, solid | -493.8 ± 2.6 kJ/mol      | -118 ± 0.6 kcal/mol      | [29]       |

cinogenicity of *N*-nitrosodiethanolamine (CAS RN 1116-54-7), which was also found in some aged cosmetic preparations and in tobacco smoke (one of the growth retardants applied to tobacco plants is a salt of diethanolamine). Most of these publications date to the 1980s, when this carcinogen was first discovered. It is possible that similar hazardous compounds form during partial combustion of the nitrate salts of (mono-, di-, tri-)ethanolamines in rocket engines or liquid propellant gun breeches.

Diethanolamine forms salts with strong acids. Diethanolammonium dinitramide,  $[(\text{HOCH}_2\text{CH}_2)_2\text{NH}_2^+][\text{N}(\text{NO}_2)_2^-]$ , melts at 348–351 K (75–78 °C) [97].

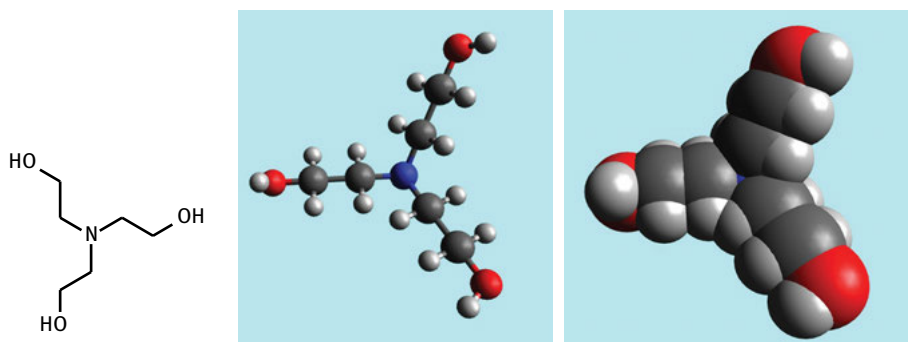
### 23.3 Triethanolamine

Triethanolamine, also known as tri(2-hydroxyethyl)amine,  $(\text{HOCH}_2\text{CH}_2)_3\text{N}$ ,  $\text{C}_6\text{H}_{15}\text{NO}_3$ , nitrilotriethanol, 2,2',2''-nitrilotri(ethan-1-ol), triethylolamine, TEA, 2-[bis-(2-hydroxyethyl)amino]ethanol, CAS RN [102-71-6], is a widely used industrial intermediate that has not been used as a rocket propellant in the form of its free base, but it once found extensive use in the form of its nitrate salt triethanolammonium nitrate (TEAN) in liquid gun propellants and a few rocket propellants. However, its use has been discontinued (see *Encyclopedia of Monopropellants*, chapter “Hydroxylammonium Nitrate-based Monopropellants”). Other names for this compound are 2,2',2''-nitrilotriethanol, tri(2-hydroxyethyl)amine, tris(2-hydroxyethyl)amine, 2,2',2''-trihydroxy-triethylamine, trihydroxyethylamine, and triethylolamine.

Triethanolamine, the free amine, is widely used as a moisturizer in cosmetic products. There is a long history of use of this chemical (the free amine), and its toxicity has been well researched. There is concern about contamination by diethanolamine in triethanolamine because the diethanolamine is likely to form nitrosamines with  $\text{NO}_x$  in the polluted atmosphere.

The structural formula of triethanolamine is illustrated in Figure 10.

It is a derivative of triethylamine (a frequently used hypergolic fuel), with hydroxyl groups attached at the ends of each of the three ethyl groups. These three hydroxyl groups raise the boiling point of the compound substantially, from 362.6 to 608 K (de-



**Figure 10:** Molecular structure of triethanolamine

composition). One might also look at it as a derivative of ethanol, another widely used rocket fuel, by combining three ethanols via a nitrogen atom. Looking at it in this way, triethanolamine has relationships to rocket fuels “in its genes” since both ammonia and ethanol have been used as rocket fuels.

We list triethanolamine here mostly because it is an intermediate in the preparation of other fuels and because its nitrate salt has been widely used in liquid gun propellants and, to a lesser extent, even in some experimental rocket propellants.

### 23.3.1 Production of Triethanolamine

Triethanolamine is produced by the reaction of ethylene oxide with ammonia. Monoethanolamine and diethanolamine are formed as undesirable byproducts.

### 23.3.2 Physical Properties of Triethanolamine

Physical properties of triethanolamine are listed in Table 60.

**Table 60:** Physical properties of triethanolamine.

| Property                      | SI units                              | Other units                               | References |
|-------------------------------|---------------------------------------|-------------------------------------------|------------|
| Molecular mass                | 149.1882 g/mol                        | 6.7029 mol/kg                             | [29]       |
| Boiling point at 101 kPa      | 608 K (dec.)                          | 335 °C (dec.)                             | [29]       |
| Boiling point at 0.7 kPa      | 464.7 K                               | 191.6 °C                                  | [29]       |
| Melting point                 | 294.72 K                              | 21.6 °C                                   | [29]       |
| Density at 298 K              | 1.1217 g/cm <sup>3</sup>              | 70.03 lb/ft <sup>3</sup>                  |            |
| Refractive index $n_D^{20}$   | 1.4850                                | —                                         |            |
| Heat capacity at 298 K        | 2.6 J g <sup>-1</sup> K <sup>-1</sup> | 0.62 cal g <sup>-1</sup> °C <sup>-1</sup> |            |
| Enthalpy of formation, liquid | -664.2 ± 1.5 kJ/mol                   | -158.7 ± 0.4 kcal/mol                     | [29]       |

The vapor pressure of triethanolamine in the range 525.9–578.8 K (252.7–305.7 °C) can be calculated from the equation

$$\log P = 7.19251 - [4543.902/(T + 24.749)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

### 23.3.3 Chemical Properties of Triethanolamine

Triethanolamine is a weak base with a  $pK_a$  of 7.74. It forms salts with strong acids. The nitrate salt of TEA, called TEAN, has been widely used as the fuel in HAN-based liquid gun propellants. There was a question of whether strongly acidic conditions in TEAN in the presence of excess nitric acid would result in partial esterification of one or more of the hydroxyl groups in TEA, resulting in a more sensitive alkyl nitrate amine nitrate. This suspicion has not been proven.

### 23.3.4 Hazard Properties of Triethanolamine

The flash point of triethanolamine in air is at 452 K (179 °C = 354 °F). The auto-ignition temperature of triethanolamine in air is at 598 K (325 °C = 617 °F).

### 23.3.5 Toxicity of Triethanolamine

Triethanolamine is not used as a rocket propellant as such, but it has been used in the form of its nitrate salt. The toxicity of the two compounds, the free base and its nitrate salt, would be very similar, except the nitrate salt is more toxic due to the toxicity of the nitrate ion.

Triethanolamine, the free base precursor to triethanolammonium nitrate, has been around for a long time. It is widely used as a moisturizer in cosmetic formulations and to wash carbon dioxide and/or hydrogen sulfide from industrial waste gases and natural gas. It is also used in cutting (cooling) fluids and oil emulsions when machining or drilling metal parts. It has a perfect use history, and no adverse effects have been reported during the many decades that it has been in use. The main toxicity concern arises from a contaminant in triethanolamine, the incompletely hydroxyethylated diethanolamine, which readily picks up  $\text{NO}_x$  from the environment to form toxic nitrosamines. The TLV-TWA for triethanolamine is 5 mg/m<sup>3</sup>.

Although TEAN is no longer anticipated to be widely used as a gun or rocket propellant ingredient, we have assembled a short list of publications on the toxicity of triethanolamine and the other ethanolamines: [356–360].

### 23.3.6 Salts of Triethanolamine

Hydroxyethylamine, di(2-hydroxyethyl)amine and tris(2-hydroxyethylamine), are available in large quantities and have found various industrial and cosmetic uses. They are weak bases and form salts with most acids. Because of the excellent water

solubility, nitrates of any of these three amines have been considered as fuels for HAN-based monopropellants. In particular, the nitrate salt of tri(2-hydroxyethyl)-amine, trihydroxyethylammonium nitrate (triethanolammonium nitrate, TEAN) has been extensively investigated and it is relatively well characterized.

#### 23.3.6.1 Triethanolammonium Nitrate

Triethanolammonium nitrate, also known as TEAN,  $[(\text{HOCH}_2\text{CH}_2)_3\text{NH}^+][\text{NO}_3^-]$ ,  $\text{C}_6\text{H}_{16}\text{N}_2\text{O}_6$ , CAS RN [27096-29-3], with a molecular mass of 212.201 g/mol, an oxygen balance of -105.6%, and a nitrogen content of 13.2%N, is the nitrate salt of triethanolamine. TEAN is one of the few amine nitrates that saw widespread application during the development of regenerative liquid propellant guns in the 1980s and 1990s. It has since fallen into oblivion. At one point, the industry was prepared to gear up for large-scale production of TEAN and other ingredients [361], but the demand never arose, and the predictions of future demand for this material were overly optimistic. TEAN manufacturing facilities have been closed and scrapped. It is unlikely that it will ever again find widespread application in HAN-based monopropellants. Nevertheless, some of its properties are summarized here.

#### 23.3.6.2 Preparation of Triethanolammonium Nitrate

TEAN slush is made by neutralizing triethanolamine with dilute nitric acid. The 80% TEAN solution must be stored warm to prevent crystallization. It is not necessary to recrystallize the salt and remove all water from the solution, but the propellant can be formulated from highly concentrated 80 mass-% TEAN solutions with accurately known water content. That is acceptable for making XM-46 as long as the water brought in with the HAN and the water brought in with the TEAN add up to 20%. The heat of solution of the two liquids is negative. This small enthalpy change is often ignored when calculating the theoretical performance of HAN-based propellants.

The most useful method in terms of both assay and organic impurity detection for quality control of the TEAN thus produced has been NMR spectroscopy [362, 363].

The heat of reaction of neutralization of TEA with  $\text{HNO}_3$  is  $-57.7 \text{ kJ/mol} = -13.8 \text{ kcal/mol}$ . If the reacting mixture gets too hot, unwanted side reactions may occur. It has been noted that the undesirable formation of *N*-nitrosodiethanolamine during the neutralization of TEA can be avoided if the temperature is kept below 277 K (4°C), the TEA concentration used is at least 97%, and the amine is added to the acid, never the other way around [364]. See also [365].

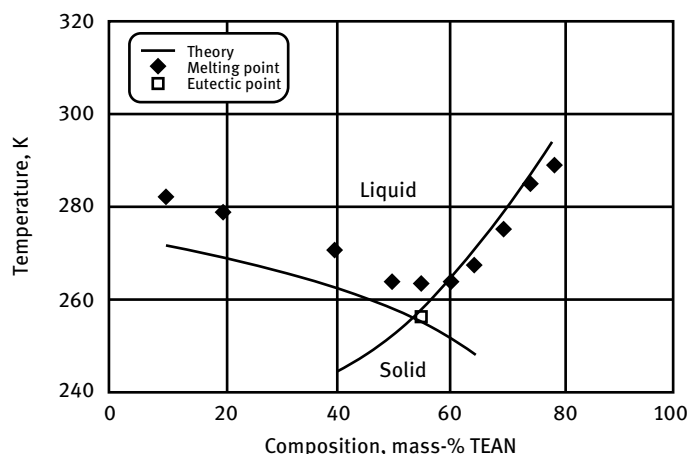
#### 23.3.6.3 Physical Properties of Triethanolammonium Nitrate

##### Melting Point of TEAN Crystals

Based on DSC data, the melting point of TEAN is 353 K (80°C). Other sources report a melting point of 357 K (84°C).

### Freezing Point of TEAN Solutions

The freezing and melting points of TEAN solutions with 10 to 79 mass-% TEAN were measured in gold DSC pans at temperatures down to 205 K [366]. All TEAN solutions showed supercooling effects, in particular a solution with 74.9% TEAN. Many heating curves showed two endothermic peaks, with the second peak being attributed to free water. It was suspected that the reason for two peaks is that some of the TEAN recrystallizes during melting or pre-melting. Figure 11 shows the phase diagram for TEAN/H<sub>2</sub>O, where the eutectic is close to 55–60% TEAN at about 260 K. The solid line is the theoretical freezing point assuming the dissociation into two ions. The diamond and square symbols are measured melting-point values where the higher melting point and the eutectic point were employed. The heat of fusion of TEAN can be calculated from the melting-point suppression and comes out to be 27.89 kJ/mol (6.665 kcal/mol) compared to that of water, 6.00 kJ/mol (1.434 kcal/mol). Similar measurements were made for HAN and LP-1845.



**Figure 11:** Melting temperature of TEAN solutions. (Republished and modified from [366], with permission of ©1991 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

The thermal behavior of the binary system of TEAN/H<sub>2</sub>O at low temperature has been investigated using DSC, and the phase diagrams of TX (a correlation of the liquidus temperature with the composition) and HX (a correlation of the apparent heat of fusion with the composition) for the system were constructed [367]. It was found that the TEAN/H<sub>2</sub>O system is a simple binary system, whose eutectic temperature is 256.9 K (−16.2°C).



### Density of TEAN Crystals

Based on XRD data, the computed density of crystalline TEAN is  $1.393 \text{ g/cm}^3$ . Other sources give a crystal density of  $1.44 \text{ g/cm}^3$ . Extrapolating from the density of TEAN solutions to 100% TEAN gives a density of  $1.328 \text{ g/cm}^3$ , which is closer to that of molten TEAN than to that of crystalline TEAN [19].

### Density of TEAN Solutions

The density of aqueous TEAN solutions as a function of TEAN concentration at 294 K (21 °C) can be calculated from

$$\rho = 0.985896 + 0.003424X$$

or

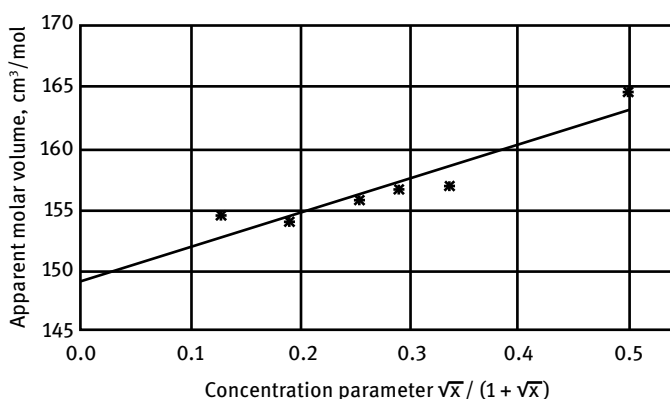
$$\rho = 1.003784 + 0.0546873M$$

where  $\rho$  is the density in  $\text{g/cm}^3$ ,  $X$  is the TEAN concentration in mass-%, and  $M$  is the TEAN concentration in mol/L [19].

The apparent molar volume of solutions is the sum of the partial molar volume of the solute and that of the solvent (water). A good correlation can be obtained by plotting the partial molar volume against a concentration parameter  $\chi$

$$\chi = \frac{\sqrt{X}}{1 + \sqrt{X}}$$

where  $X$  is the mole fraction of TEAN. This correlation was used at Olin Chemicals for calculating the densities of HAN and TEAN solutions, as well as the densities of XM46 formulations with excess nitric acid [368]. The slope of the linear function ( $X$  coefficient) shown in Figure 12 is 27.8225. The intercept at infinite dilution is at  $149.176 \text{ cm}^3/\text{mol}$ . The same method was also used for AN solutions.



**Figure 12:** Apparent molar volume of TEAN at 293 K (20 °C) as a function of concentration parameter  $\chi$ . (Reproduced and modified from [368], based on data from [19].)

### Solubility of Triethanolammonium Nitrate

The solubility of TEAN in water at 298 K is 90%.

### Velocity of Sound and Molecular Relaxation in Triethanolammonium Nitrate Solutions

Triethanolammonium and nitrate ions in concentrated TEAN solutions are surrounded by a sphere of hydration. The relaxation in the rate of exchange of water molecules in the hydration sphere in TEAN solutions was measured by Rayleigh-Brillouin spectra at atmospheric pressure over a temperature range from 205 to 298 K [369, 370]. Similar measurements were performed on HAN solutions. See also [371–373].

### Thermodynamic Properties of Triethanolammonium Nitrate

The heat of fusion of TEAN is 27.9 kJ/mol. The entropy of fusion is  $78.2 \text{ J K}^{-1} \text{ mol}^{-1}$  [374]. The enthalpy of formation of TEAN is  $-966 \text{ kJ/mol}$  ( $-231 \text{ kcal/mol} = -1089 \text{ cal/g}$ ).

### Molecular Structure of Triethanolammonium Nitrate

Triethanolammonium nitrate exhibits rather unusual liquid properties that have been attributed to its being a “molten eutectic” of fused salts rather than a normal aqueous solution. A hydrogen-bonded liquid structure for eutectic LP1846 was proposed previously, based on the known structures of neat HAN and water and a best-guess estimate of the TEAN structure. To verify this estimate, the molecular structure of neat TEAN was determined [375]. This investigation revealed that TEAN has very unusual and interesting bifurcated intermolecular and trifurcated intramolecular hydrogen bonding configurations within the crystal. If these hydrogen bonding configurations are retained in aqueous solution, they could be responsible in some part for the observed unusual liquid properties of liquid propellant XM46.

TEAN crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$ , with  $a = 6.592$ ,  $b = 16.358$ ,  $c = 9.3850 \text{ Å}$ , and  $\beta = 90.87^\circ$ . Based on four formula weights of TEAN per unit cell, the computed density is  $1.393 \text{ g/cm}^3$ . The TEAN asymmetric unit contains one TEA<sup>+</sup> cation and one nitrate anion. The TEA<sup>+</sup> cation contains six non-equivalent carbon atoms, one nitrogen atom, and 12 non-equivalent hydrogen atoms. The TEA<sup>+</sup> cation is combined with the nitrate anion which contains one nitrogen atom and three non-equivalent oxygen atoms. In this structure, each ion is surrounded by four oppositely charged ions. In addition to electrostatic forces, the structure is held together by a 3D network of hydrogen bonds between cations and between cations and anions. All of the hydroxyl hydrogen atoms of the cation and two of the nitrate oxygen atoms are involved in this interionic hydrogen-bond network. In the cation–anion linkage of this network, two of the hydroxyl groups from the TEA<sup>+</sup> cation form three hydrogen bonds with two oxygen atoms of the nitrate anion. One of the hydrogen bonds is formed between a hydroxyl hydrogen atom and an oxygen atom of the nitrate ion within the same asymmetric unit. The second hydroxyl hydrogen atom forms an asymmetrically

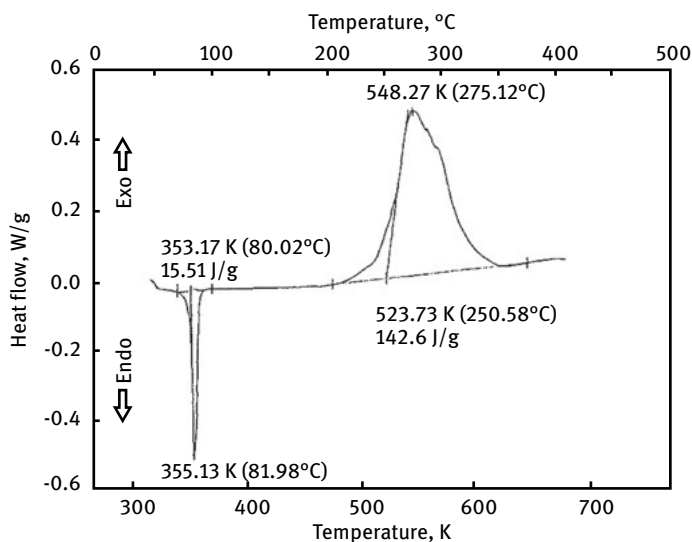
bifurcated hydrogen bond between two oxygen atoms of a nitrate. Not much is known about the structure of TEAN in solution.

#### 23.3.6.4 Thermal Stability of Triethanolammonium Nitrate

The thermal decomposition of TEAN begins below the melting point. Some decomposition products can already be detected in the gas space above the solid starting at 373 K (100 °C). Decomposition products include  $\text{N}_2\text{O}$ , acetaldehyde, and  $\text{CO}_2$ .

Measurements were made by FTIR spectroscopy to identify the thermal decomposition products of solid TEAN at atmospheric pressure in a nitrogen environment [376]. Solid TEAN produced major IR-active decomposition species such as  $\text{H}_2\text{O}$ ,  $\text{NO}$ , and  $\text{CO}_2$  over the temperature range of 533 to 613 K (260 to 340 °C).  $\text{CO}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  were also detected in small concentrations. It was also found that solid TEAN started to decompose near 533 K (260 °C), much higher than its melting temperature of 354 K (81 °C).

The TEAN DSC curve at ambient pressure (Figure 13) displays only two peaks: a sharp endotherm with an onset temperature at 353 K (80 °C) and a broad exotherm with an onset temperature at 524 K (251 °C). The sharp endotherm is caused by the melting of TEAN.



**Figure 13:** Differential scanning calorimetry analysis of TEAN. (Reproduced and modified from [375].)

#### 23.3.6.5 Combustion of TEAN

Work on the reaction kinetics of TEAN by itself (without added oxidizer) was done in support of combustion studies with XM46. It appears that TEAN is less reactive

than HAN. It lags in the sequence of combustion of constituents of the XM46 propellant mixture. Particles of molten TEAN burn in an atmosphere of HAN decomposition products, mostly nitrous oxide. A study of this process was therefore isolated from the initial HAN decomposition by burning TEAN in pure  $N_2O$ . This can be done in a shock tube where the temperature of the gas can be raised suddenly and exactly. A shock tube was used to measure the activation energy of TEAN powder ignition in oxygen/argon or nitrous oxide/argon environments [377–380]. The activation energy of solid TEAN was very close to that reported for aqueous HAN. It was suggested that the measured activation energy ( $40 \text{ kJ/mol} = 9.6 \text{ kcal/mol}$  in nitrous oxide/argon) was largely due to the melting of TEAN; that is, the melting might be the rate-limiting step, inasmuch as the heat of fusion for TEAN is  $149 \text{ J/g}$  or  $7.55 \text{ kcal/mol}$ . The activation energy for the ignition process is  $86.6 \text{ kJ/mol}$  ( $20.7 \text{ kcal/mol}$ ) in  $N_2O$  and  $71.1 \text{ kJ/mol}$  ( $17.0 \text{ kcal/mol}$ ) in oxygen.

## 24 Dimethylaminoethanol

Dimethylaminoethanol, also known as ethanoldimethylamine, dimethylethanolamine, *N,N*-dimethylaminoethanol,  $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ , DMEA, CAS RN [108-01-0], is the product of reaction of dimethylamine with ethylene oxide. Dimethylaminoethanol is hypergolic with WFNA or RFNA but not with NTO [381]. The ignition-delay times of dimethylaminoethanol with WFNA or RFNA are 26 and 42 ms, respectively.

### 24.1 Physical Properties of Dimethylaminoethanol

The density of dimethylaminoethanol is higher than that of MMH and UDMH. The viscosity of dimethylaminoethanol is relatively high, which causes more pressure drop and requires higher feed pressure or more pumping work. Since dimethylaminoethanol has a higher flash point than other fuels used as hypergolic rocket propellants, it would be safer to handle. Table 61 gives a list of physical properties of dimethylaminoethanol in comparison to other rocket fuels.

### 24.2 Diethylaminoethanol

Diethylaminoethanol, ethanoldiethylamine, diethylethanolamine, diethylaminoethanol,  $\text{HOCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$ , is the product of reaction of diethylamine with ethylene oxide. Its boiling point is higher than that of triethylamine, and it will reduce the vapor pressure of the mixture. Mixtures of diethylethanolamine with triethylamine (also filled with carbon powder and gelled with hydroxypropyl cellulose) have been patented as hypergolic fuels [382].

Table 61: Physical properties of dimethyaminoethanol in comparison to other rocket fuels.

| Property                                                                                        | Liquid fuels             |                                          |                                            |                                       |                                                      |                                                       |                                         |
|-------------------------------------------------------------------------------------------------|--------------------------|------------------------------------------|--------------------------------------------|---------------------------------------|------------------------------------------------------|-------------------------------------------------------|-----------------------------------------|
|                                                                                                 | Compound name<br>Formula | DMAE<br>C <sub>4</sub> H <sub>11</sub> O | Hydrazine<br>N <sub>2</sub> H <sub>4</sub> | MMH<br>CH <sub>6</sub> N <sub>2</sub> | UDMH<br>C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> | DMAZ<br>C <sub>4</sub> H <sub>10</sub> N <sub>4</sub> | EtOH<br>C <sub>2</sub> H <sub>6</sub> O |
| Melting point, K                                                                                |                          | 214.15                                   | 275.16                                     | 220.78                                | 215.94                                               | 204.25                                                | 159.01                                  |
| Melting point, °C                                                                               |                          | -59                                      | 2.01                                       | -52.37                                | -57.21                                               | -68.9                                                 | -114.14                                 |
| Boiling point, K                                                                                |                          | 407.2                                    | 387.4                                      | 360.8                                 | 335.47                                               | 408.15                                                | 351.44                                  |
| Boiling point, °C                                                                               |                          | 134                                      | 114.2                                      | 87.65                                 | 62.32                                                | 135                                                   | 78.29                                   |
| Liquid density at 25 °C, kg/m <sup>3</sup>                                                      |                          | 883.6                                    | 1004                                       | 870.2                                 | 786.1                                                | 933.5                                                 | 789.3                                   |
| Viscosity at 25 °C, kg m <sup>-1</sup> s <sup>-1</sup>                                          |                          | 0.003661                                 | 0.000913                                   | 0.000775                              | 0.000492                                             | 0.000703                                              | 0.001074                                |
| Surface tension at 25 °C, N/m                                                                   |                          | 0.0271                                   | 0.06645                                    | 0.03383                               | 0.02409                                              | 0.025                                                 | 0.02197                                 |
| Enthalpy of vaporization, kJ/mol, at the normal boiling temperature under a pressure of 101 kPa |                          | 35.36                                    | 41.8                                       | 36.12                                 | 32.55                                                | 43.96                                                 | 38.56                                   |
| Enthalpy of formation, kJ/mol                                                                   |                          | -253.7                                   | 50.6                                       | 54.2                                  | 48.9                                                 | 280.94                                                | -277.6                                  |
| Flash point, K                                                                                  |                          | 312                                      | 311                                        | 294                                   | 258                                                  | 303                                                   | 286                                     |
| Flash point, °C                                                                                 |                          | 38.89                                    | 38                                         | 21                                    | -15                                                  | 29.4                                                  | 13                                      |
| Lower flammability limit, vol-%                                                                 |                          | 1.6                                      | 4.7                                        | 2.5                                   | 2                                                    | 1.3                                                   | 3.5                                     |
| Upper flammability limit, vol-%                                                                 |                          | 11.9                                     | 100                                        | 98                                    | 95                                                   | 22.4                                                  | 15                                      |
| Toxicity LD50, mg/kg                                                                            |                          | 2000                                     | 60                                         | 32                                    | 122                                                  | 967                                                   | 7060                                    |
| Toxicity LC50, ppm                                                                              |                          | 1641                                     | 570                                        | 74                                    | 252                                                  | 2000                                                  | 20000                                   |

Data source: [381,152]

### 24.3 1,3-Dihydroxy-2-amino-propane (Serinol)

If the hydroxyl group on the central carbon atom in glycerol is replaced by an amino group, one obtains a low-vapor-pressure amine ( $\text{C}_3\text{H}_9\text{N}_1\text{O}_2$ , 2-aminoglycerol, serinol, naturally occurring and related to the amino acid serine) that can form salts that have ionic liquid properties and very low melting points [383]. The properties of some of these salts with oxidizing anions are summarized in Table 62. The crystal structures of these salts were identified using XRD.

There is also an isomer of serinol, 1,2-dihydroxy-3-amino-propane (3-amino-1,2-propanediol, 1-aminoglycerol, chiral) that has similar properties, but its salts have even lower melting points. Two of these salts are included in the table below.

**Table 62:** Properties of dihydroxy-amino-propane salts.

| Anion                               | Melting point |       | Onset of decomposition |     | Impact sensitivity | Friction sensitivity |       |
|-------------------------------------|---------------|-------|------------------------|-----|--------------------|----------------------|-------|
|                                     | K             | °C    | K                      | °C  | kg-cm              | N                    | kgf   |
| 1,3-dihydroxy-2-amino-propane salts |               |       |                        |     |                    |                      |       |
| Nitrate                             | 334–339       | 61–66 | 488                    | 215 | 180                | 177                  | 18    |
| Perchlorate                         | 328–333       | 55–60 | 523                    | 250 | 200                | >371                 | >37.8 |
| Dinitramide                         | 314–317       | 41–44 | 408                    | 135 | 16                 | 230                  | 23.4  |
| 1,2-dihydroxy-3-amino-propane salts |               |       |                        |     |                    |                      |       |
| Nitrate                             | 233           | –40   | 493                    | 220 | —                  | —                    | —     |
| Dinitramide                         | 268           | –5    | 408                    | 135 | —                  | —                    | —     |

Data source: [383]

## 25 Nitrate Esters of Hydroxyethylamines

It has been suspected that under strongly acidic conditions and in the presence of free nitric acid, some of the terminal hydroxyl groups of TEAN might become esterized and form nitrate esters. Such chemical changes could occur in propellant blends with TEAN and HAN, but they may occur only very slowly. The nitrate esters of mono-, di-, and trihydroxyethylamine and their nitrate salts have been prepared by other routes, not only to have them available as reference compounds but also to evaluate them as energetic additives. Some of these compounds lack thermal stability.

A group of nitroxyalkyl-functionalized ammonium salts, including *N*-(2-nitroxyethyl)-*N,N,N*-trimethylammonium nitrate, *N,N*-bis(2-nitroxyethyl)-*N,N*-dimethylammonium nitrate, *N,N,N*-tri(2-nitroxyethyl)-*N*-methylammonium nitrate, and *N*-(2,3-dinitroxypropyl)-*N*-(2-nitroxyethyl)-*N,N*-dimethylammonium nitrate, exhibited surprising thermal and hydrolytic stability [384].

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# Alkanes

## Introduction

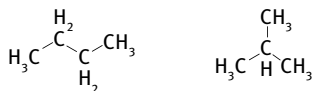
*Encyclopedia of Liquid Fuels* contains eight chapters dealing with hydrocarbon fuels. The topic of hydrocarbon fuels had to be subdivided into several smaller sections that were easier to arrange in alphabetical order in five subvolumes of equal size. The titles of the eight hydrocarbon chapters are: Alkanes, Alkenes and Alkynes, Aromatic Hydrocarbons, Cycloaliphatic Hydrocarbons, Hydrocarbons, Jet Fuels, Kerosenes, and Ramjet Fuels.

## 1 Alkanes

Alkanes, saturated hydrocarbons, have the gross formula

$$C_nH_{2n+2}.$$

For alkanes containing more than three carbon atoms, we differentiate between straight-chain hydrocarbons and branched chain hydrocarbons, e.g., *n*-butane and isobutane:



Most alkanes are obtained by fractionated distillation of petroleum and cracked oil. For the higher alkanes, this does not give pure alkanes, but a mixture of isomers with similar boiling points, often containing cycloaliphatic and aromatic hydrocarbons, along with the alkanes as the main product. The distillation fractions are characterized by their boiling range instead of distinct boiling points such as those used for identification of pure compounds. The fraction from 413 to 523 K (140 to 250 °C) is called “kerosene” and is used as diesel fuel, jet engine fuel, and rocket propellant.

Most hydrocarbon fuels that are used practically are mixtures of alkanes with characteristic boiling ranges. Occasionally, pure alkanes are used as model compounds to obtain reproducible results measuring physical and chemical properties, independent of a mixture composition. This section contains information on pure alkanes, although we realize that (with the exception of methane and propane) they are not used as rocket propellants in the pure state.

The following sections on the physical and chemical properties of kerosenes deal with more than one kerosene at a time, often comparing properties of different distillation cuts that go under different names. Following these sections on kerosenes

in general, there are sections on the physical properties of specific kerosenes, dealing only with one grade of kerosene at a time. These sections are arranged in order of significance and not in alphabetical order. Therefore, in the order of significance for rocket propulsion, RP-1 and RP-2 are discussed first, followed by JP-4 and other kerosenes for air-breathing engines.

## 1.1 Physical Properties of Alkanes

### 1.1.1 Viscosity of Alkanes

The viscosity of alkanes increases with increasing carbon chain length. An extended hard-sphere model was developed that can accurately predict the viscosity of long-chain *n*-alkanes [1]. The method is based on a hard-sphere model that makes use of an universal function relating reduced viscosity to reduced volume. The existing expression for the molar core volume was extrapolated to long-chain *n*-alkanes, whereas the roughness factor was determined from experimental data. A correlation for roughness factor was developed that allowed the extended model to reproduce the available experimental viscosity data on long chain *n*-alkanes up to tetracontane ( $n\text{-C}_{40}\text{H}_{82}$ ) within  $\pm 5\%$ , at a pressure up to 30 MPa. In the dilute gas limit a physically realistic model, based on the Lennard-Jones effective potential, was proposed and used to evaluate the zero-density viscosity of *n*-alkanes to within  $\pm 2.4\%$ .

Another model was developed to predict the viscosity of liquid, *n*-alkane mixtures [2]. It represented a mixture by a single pseudo-component characterized by an appropriate molecular weight and calculated the viscosity by means of a modified, extended hard-sphere model that made use of a universal function relating reduced viscosity to reduced volume. For mixtures that contain *n*-alkanes with a similar number of carbon atoms, the molecular weight of the pseudo-component was simply given by the molecular weight of the mixture. For more asymmetric mixtures, the choice of the molecular weight was a function of the difference in the number of carbon atoms, between the longest and the shortest chain. The developed model, named 1-component Extended Hard-Sphere, predicted the viscosity of binary and multi-component *n*-alkane mixtures with uncertainty of 5%, even when the mixtures contained very long *n*-alkanes.

*n*-Hexadecane is a constituent of RP-1 and RP-2. A correlation for the viscosity of *n*-hexadecane was based upon a set of experimental data that had been critically assessed for internal consistency and for agreement with theory [3]. It is applicable in the temperature range from the triple point to 673 K at pressures up to 425 MPa and along the saturation line.

### 1.1.2 Thermal Conductivity of Alkanes

When correlating the thermal conductivity of methane and ethane at low pressure as well as doing general correlations of the experimental data, a thermal conductivity

anomaly was noted along 295, 318, 350, and 398 K isotherms for ethane [4]. Measurements were made for ethane within a temperature range 295 to 600 K at pressures up to 70 MPa and for methane within the range 100 to 400 K at pressures from 2 to 70 MPa. A simple model was derived to estimate the anomalous conductivity. Some evidence of critical anomaly was also seen along the 200 and 240-K isotherms in the case of methane.

The thermal conductivities of five liquid *n*-alkanes: hexane, heptane, octane, decane, and dodecane were measured within the temperature range 283 to 373 K at pressures up to 250 MPa or the freezing pressures using a transient hot-wire apparatus [5]. The thermal conductivity of each alkane decreased almost linearly with rising temperature at a constant pressure and increased with increasing pressure at a constant temperature. Both the temperature coefficient of the thermal conductivity  $(\partial\lambda/\partial T)_p$  and the pressure coefficient  $(\partial\lambda/\partial P)_T$  decreased with an increasing carbon number of alkanes. The experimental results correlated with temperature and pressure by an expression similar to the Tait equation. It was found that both the dense hard-sphere model and the modified significant structure theory provided good representations of the experimental results.

The thermal conductivity of liquids may be difficult to predict with reasonable accuracy owing to the lack of accurate experimental data and reliable prediction schemes. Data of high accuracy, and covering wide density ranges, obtained using the transient hot-wire technique, can be used to revise an existing correlation scheme and to develop a universal predictive technique for the thermal conductivity of liquid normal alkanes [6]. The correlation scheme was constructed on a theoretically based treatment of the van der Waals model of a liquid, which permits the prediction of the density dependence and the thermal conductivity of liquid *n*-alkanes, methane to tridecane, for temperatures between 110 and 370 K and pressures up to 0.6 MPa, i.e., for  $0.3 \leq T/T_c \leq 0.7$  and  $2.4 \leq P/P_c \leq 3.7$ , given a known value of the thermal conductivity of the fluid at the desired temperature. It was possible to predict the thermal conductivity of pentane to tetradecane to within  $\pm 2\%$ , without the necessity of experimental measurements.

A study of the applicability of an extension of the van der Waals model to predicting the thermal conductivity of binary mixtures of pure liquid alkanes was based upon accurate data for the binary mixtures methane + ethane and *n*-heptane + 2,2,4-trimethylpentane [7]. Reduced thermal conductivity for the mixtures was defined such that its density dependence was identical to that of the pure components. A scheme was developed that enabled the prediction of the thermal conductivity of the mixtures at any temperature  $T \leq 0.7T_c$ , at any pressure, solely from data for the pure components, i.e., without resorting to any experimentally adjusted parameters for the mixtures. Such a scheme was able to reproduce the available thermal conductivity data for the above-mentioned mixed systems with an error of the order of  $\pm 2\%$ , which was commensurate with the combined uncertainty of the experimental results for the pure components and for the mixtures.

Thermal conductivity data for specific hydrocarbons are listed in the subsequent sections. Thermal conductivity data for propane, butane, isobutane, and butylene were summarized and expressed in mathematical form [8].

### 1.1.3 Critical-Point Properties of Alkanes

The critical-point properties of *n*-alkanes are listed in Table 1. Critical temperature and critical density increase with increasing chain length and critical pressure decreases with increasing chain length of the molecules.

**Table 1:** Critical-point properties of *n*-alkanes.

|                    | $M$<br>g/mol | $T_c$<br>K      | $P_c$<br>MPa  | $\rho_c$<br>g/cm <sup>3</sup> | $V_c$<br>cm <sup>3</sup> /mol | $Z_c^a$ |
|--------------------|--------------|-----------------|---------------|-------------------------------|-------------------------------|---------|
| Methane            | 16.043       | 190.564 ± 0.015 | 4.599 ± 0.003 | 0.1627 ± 0.0005               | 98.60                         | 0.286   |
| Ethane             | 30.070       | 305.32 ± 0.04   | 4.872 ± 0.01  | 0.2066 ± 0.003                | 145.5                         | 0.279   |
| Propane            | 44.097       | 369.83 ± 0.1    | 4.248 ± 0.01  | 0.220 ± 0.003                 | 200                           | 0.277   |
| <i>n</i> -Butane   | 58.123       | 425.12 ± 0.1    | 3.796 ± 0.01  | 0.228 ± 0.003                 | 255                           | 0.274   |
| <i>n</i> -Pentane  | 72.150       | 469.7 ± 0.2     | 3.370 ± 0.02  | 0.232 ± 0.003                 | 311                           | 0.268   |
| <i>n</i> -Hexane   | 86.177       | 507.6 ± 0.2     | 3.025 ± 0.02  | 0.234 ± 0.003                 | 368                           | 0.264   |
| <i>n</i> -Heptane  | 100.204      | 540.2 ± 0.3     | 2.74 ± 0.03   | 0.234 ± 0.003                 | 428                           | 0.261   |
| <i>n</i> -Octane   | 114.231      | 568.7 ± 0.3     | 2.49 ± 0.03   | 0.232 ± 0.003                 | 492                           | 0.259   |
| <i>n</i> -Nonane   | 128.258      | 594.6 ± 0.6     | 2.29 ± 0.05   | 0.231 ± 0.005                 | 555                           | 0.257   |
| <i>n</i> -Decane   | 142.285      | 617.7 ± 0.6     | 2.11 ± 0.05   | 0.228 ± 0.005                 | 624                           | 0.256   |
| <i>n</i> -Undecane | 156.312      | 639 ± 1         | 1.98 ± 0.1    | 0.227 ± 0.01                  | 689                           | 0.257   |
| <i>n</i> -Dodecane | 170.338      | 658 ± 1         | 1.82 ± 0.1    | 0.226 ± 0.01                  | 754                           | 0.251   |

<sup>a</sup>  $Z_c = p_c V_c / RT_c$ , where  $R = 8.31451 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$

Data source: [9]

### 1.1.4 Thermodynamic Properties of Alkanes

The fundamental method for calculating the enthalpies of formation of alkanes is to determine the heats of combustion experimentally in a calorimeter. The enthalpy of formation can be calculated from the heat of combustion assuming complete combustion to carbon dioxide and water. For simple alkane molecules, where experimental data were not available, it was common practice to assume additivity of bond energies and apply certain corrections for branched structures. The most simple calculational approach was to look up bond energies in a table, assume additivity, and this gave qualitatively encouraging results. It was quickly found, however, that “structural features” also had to be included in the calculation if the result was to be more than qualitative. This procedure is taught in university chemistry classes and works reasonably well for many types of compounds, alkanes, and alkane derivatives [10]. The basic method assumes the additivities of the bond energies of various structural features in molecules. The problem here is that although there are large numbers of molecules for

which these structural features do indeed have additive energies, there are also substantial numbers of molecules, in particular those with strained rings of interest as jet engine and rocket fuels, where they do not. Only after molecular mechanics computational methods became available was it possible to calculate and predict strain energies of molecules in a general way. The strain energies for a small set of hydrocarbons ranging in size from 3 to 6 carbon atoms has been calculated using homodesmotic reactions and *ab initio* methods [11]. The strain energy of two larger strained hydrocarbons, quadricyclane and cubane, were calculated and compared with the available experimental data. Unfortunately, this gives only the enthalpy of formation in the gaseous state, but most of our rocket fuels are used as liquids. The enthalpy of vaporization has to be obtained from other sources in order to calculate the enthalpy of formation of alkanes in the liquid state.

A comparison of experimental and computational enthalpies of formation of 50 alkanes showed reasonably good agreement between measured and predicted enthalpies of formation [12].

## 1.2 Chemical Properties of Alkanes

### 1.2.1 Thermal Decomposition of Alkanes

A list of several hundred free-radical reactions that occur during the low temperature (700–850 K) pyrolysis of small *n*-alkane molecules has been assembled and a set of reliable, self-consistent Arrhenius rate parameters has been assigned on the basis of experiment, theory, thermochemical estimates and structural analogy [13]. Rate parameters have been recommended for the following types of reactions, with the number of each type in parentheses: initiation (32), recombination (135), disproportionation (108), H-transfer (112), decomposition (41), addition (58), and isomerization (11), giving a total of 505 reactions. This compilation was intended for use in assembling reaction matrices in computational modeling studies of the thermal reactions of hydrocarbon molecules.

In a study of the vapor-phase thermolysis of several straight-chain alkanes and their mixtures, including C<sub>9</sub>, C<sub>12</sub>, C<sub>13</sub>, C<sub>16</sub>, and C<sub>22</sub>, in a flowing tube reactor at atmospheric pressure and temperatures from 623 to 893 K, the thermolysis of unbranched alkanes yielded a series of 1-alkenes as major products [14]. The 1-alkene selectivity strongly depended upon pressure: the lower the pressure, the higher the selectivity. Straight-chain alkane thermolysis, under any pressure, followed a free-radical mechanism that produced alkenes with double bonds in the  $\alpha$ -position via  $\beta$ -scission of bonds. Low pressure favored radical decomposition over hydrogen abstraction.

The thermal decomposition of C<sub>10</sub>–C<sub>14</sub> *n*-alkanes was studied under near-critical and supercritical conditions [15, 16]. The primary products were C<sub>1</sub>–C<sub>*m*–2</sub> *n*-alkanes and C<sub>2</sub>–C<sub>*m*–1</sub> 1-alkenes, and the secondary products were *cis*- and *trans*-2-alkenes, *n*-C<sub>*m*–1</sub>, *n*-C<sub>*m*+1</sub>, and C<sub>*m*+2</sub>–C<sub>2*m*–2</sub> normal and branched alkanes, where *m* is the num-

ber of carbon atoms in the reactant. The relative yields of the primary and secondary products were dependent on the reaction conditions. Product distributions exhibited large pressure dependence in the near-critical region. The observed product distributions and changes in product composition with reaction conditions were explained by a modified free radical mechanism.

A specific laboratory test bench has been developed that allowed the simulation of a cooling channel as part of a hypersonic scramjet combustion chamber [17]. In order to understand the cracking mechanisms and the behavior of a fuel in a supercritical environment, the thermal cracking of a model fuel (a mixture of linear hydrocarbons:  $n\text{-C}_{10}\text{H}_{22}$ ,  $n\text{-C}_{11}\text{H}_{24}$ ,  $n\text{-C}_{12}\text{H}_{26}$ ,  $n\text{-C}_{13}\text{H}_{28}$ ) was carried out at a high temperature between 873 and 1173 K (600 and 900 °C) and under a pressure of 30 bar. For the lowest temperature (600 °C), and thus at low parent hydrocarbon conversion, the entire range of  $n$ -alkanes with 1 to 9 carbon atoms and all the 1-alkenes with 2 to 10 carbon atoms were obtained. With an increase in temperature, secondary products began to appear. They were isomerized olefins and cyclic hydrocarbons.

In cooling systems where fuels undergo thermal catalytic cracking through endothermic reactions, the fuel is under high pressure and at a high temperature, corresponding to supercritical conditions. A comparison of thermal and catalytic cracking of hydrocarbons under these conditions was made [18]. To catalyze the hydrocarbon cracking reactions, two zeolites, Y and ZSM-5 zeolites, were selected and a parametric study of the thermal and catalytic cracking reactions of a model fuel ( $n$ -dodecane) under supercritical conditions was conducted. The tests were carried out in a stirred batch reactor heated to 698 K (425 °C) and under pressures up to 150 bar. After cooling down, the cracking products were characterized by several analytical techniques in order to determine the influence of the operating conditions on the cracking reaction mechanisms. The efficiency of catalytic cracking with the zeolites Y and ZSM-5 was compared with thermal cracking without catalysts. An increase in operating temperature raised the catalyst degradation rates and the number of cracking products.

Chemical kinetic models of multi-component hydrocarbon fuels decomposition can be used to predict the heat sink capacity, but require knowledge of the chemical kinetic behavior of these compounds during cracking. The heat sink capacity depends on the ratio of saturated  $n$ -hydrocarbons to olefins produced during thermolysis. A chemical kinetic model was developed for thermal and catalytic cracking of  $\text{C}_1$  to  $\text{C}_{16}$   $n$ -paraffins [19]. Predictions for decomposition of  $n$ -octane matched experimental data of  $n$ -octane decomposition over an H-ZSM-5 zeolite catalyst.

### 1.2.2 Radiolysis of Alkanes

Alkanes stored in orbital propellant depots or on board nuclear-propelled space vehicles may be subjected to cosmic radiation or unshielded radiation from the nuclear reactor. Hydrocarbons might even be used as radiation shields to protect more sensitive parts of the spacecraft (the crew cabin) from nuclear radiation. Methane and

lower alkanes present in the atmosphere of gaseous giant planets (e.g., Saturn) and their moons (e.g., Titan) are constantly subjected to cosmic radiation and photolysis, which will eventually convert them to less volatile hydrocarbons of higher molecular mass and the hydrogen will escape the atmosphere.

Methane is a potential fuel produced on the surface of Mars by conversion of indigenous carbon dioxide, a prime example of *In-situ* Resource Utilization (ISRU). If methane has to be stored on the surface of Mars for several years before it can be used, intense radiation may cause some of it to be converted to polymeric resins that might clog the orifices [20, 21]. Liquid methane at 112K has been irradiated by  $^{60}\text{Co}$  gamma rays in the pure state and with small amounts of added ethylene or propylene [22]. The effects of these olefins on products up to  $\text{C}_6$  was interpreted by a simple hydrogen atom-scavenging mechanism. The irradiations were carried to about 0.12% methane decomposition. The loss of methane per unit dose was given as  $G(-\text{CQ}) = 6$  molecules/100 eV. This is approximately 0.01% decomposition per megarad. The major products were hydrogen and ethane, which together accounted for about 95% of the products observed.

Methane, ethane, propane, or ethylene were irradiated to study radiation effects on stored liquid propellants on spacecraft with auxiliary RTG or nuclear power sources [23, 24]. There was fog formation in the gas phase above the liquid and polymer formation in irradiated ethylene.

### 1.2.3 Combustion of Alkanes

The combustion of alkanes as a source of heat is a fundamental process and has been investigated since the early days of chemistry. The chapter at hand contains only a cursory review of burning properties (flammable range, autoignition temperatures in air and in oxygen) of alkanes and specific hydrocarbon mixtures, but the velocity of burning and combustion in rocket engines will be dealt with in later volumes on non-hypergolic rocket propellant combinations. That chapter will deal with combustion of hydrocarbons with liquid oxygen at very high pressures, and not with combustion experiments that can be conducted at ambient pressure in an indoor laboratory. This division of academic papers and engineering designs, both dealing with combustion of hydrocarbons, but from different angles, is similar to that used in *Encyclopedia of Liquid Fuels*, chapter “Hydrogen.”

Combustion is a chemical reaction and therefore combustion mechanisms and burning velocities could be discussed here under chemical properties. However, the burning velocities (flame speeds) of air/alkane and oxygen/alkane flames will be discussed in later volumes on non-hypergolic combinations. The current chapter contains only the safety properties and limits of alkane combustion.



### 1.3 Safety Properties of Alkanes

#### 1.3.1 Flammability Limits of Alkanes

Table 2 gives a summary of flammability limits of alkanes for upward propagation. Additional flammability data are contained in subsequent sections on individual alkanes (See Section 2ff.)

**Table 2:** Flammability limits of alkanes.

| Compound           | Flammability limit, Vol.-% |             |
|--------------------|----------------------------|-------------|
|                    | Lower limit                | Upper limit |
| Methane            | 5.0                        | 15.0        |
| Ethane             | 3.0                        | 12.4        |
| Propane            | 2.1                        | 9.5         |
| <i>n</i> -Butane   | 1.8                        | 8.4         |
| Isobutane          | 1.8                        | 8.4         |
| <i>n</i> -Pentane  | 1.4                        | 7.8         |
| <i>n</i> -Hexane   | 1.2                        | 7.4         |
| <i>n</i> -Heptane  | 1.05                       | 6.7         |
| <i>n</i> -Octane   | 0.95                       | —           |
| <i>n</i> -Decane   | 0.75                       | 5.6         |
| <i>n</i> -Dodecane | 0.6                        | —           |

Data source: [25]

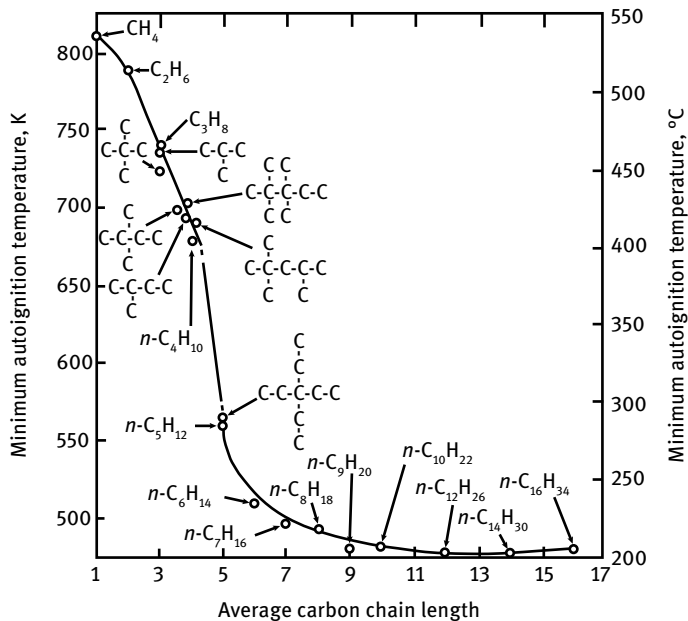
A systematic study of literature data was made to derive mathematical equations that describe the interrelationships of flammability and other properties of *n*-alkanes [26]. The properties that have been correlated are: lower and upper flammability limits, flash point, vapor pressure (at the flash point), flammability index, boiling point, stoichiometric concentration, heat of combustion, molecular weight, and carbon number. Good agreement was found between average literature data and values calculated by the derived equations. From a given flammability property, by use of the derived equations, it is possible to predict the other properties, as well as the relative magnitudes of changes in these properties as a result of a change in ambient starting conditions.

It was demonstrated by a simplified treatment that vapor pressures of individual constituents play a more important role than concentration on the overall flammability properties of hydrocarbon mixtures [27, 28]. This treatment was based on the application of Raoult's and Dalton's laws governing vapor pressure and composition above a solution of two or more liquid hydrocarbons to Le Chatelier's rule governing the flammability of vapor mixtures. The most important conclusion demonstrated by the derived equations was that a very small amount of highly volatile contaminant in a relatively non-flammable fuel may make it flammable. The amounts needed to bring

about this effect can be predicted from the equations and the properties of the components. Although precise relationships have been derived only for relatively simple solutions of pure hydrocarbons, the concepts they imply are applicable to more complex mixtures such as jet and rocket fuels. The flammability properties included in this study were lower and upper flammability limits, flash points, and flammability indices of liquid solutions. Interrelations of the flammability properties of *n*-alkanes in air have been extended to both vapor and liquid fuel mixtures [29].

### 1.3.2 Autoignition Temperature of Alkanes

The autoignition temperature of flammable liquids is determined in accordance with American Society for Testing and Materials (ASTM) D 286-30 and a revised version of the apparatus used by the US Bureau of Mines [25, 30]. The autoignition temperature of alkanes decreases with increasing chain length of *n*-alkanes (Figure 1; Table 3).



**Figure 1:** Autoignition temperature of alkane hydrocarbons. (Reproduced and modified from [25].)

Ignition temperatures of *n*-hexane, *n*-octane, *n*-decane, and JP-6 jet fuel were determined in air using heated Pyrex cylinders and Nichrome wires, rods, or tubes [31]. Ignition temperatures varied little by air : fuel ratio, but increased as the size of the heat source was decreased. In addition, the hot gas ignition temperatures of the combustible vapor-air mixtures were determined with jets of hot air. These ignition tem-

**Table 3:** Autoignition temperature of alkanes.

| Compound          | Autoignition temperature |     |
|-------------------|--------------------------|-----|
|                   | K                        | °C  |
| Methane           | 813                      | 540 |
| Ethane            | 788                      | 515 |
| Propane           | 723                      | 450 |
| <i>n</i> -Butane  | 678                      | 405 |
| Isobutane         | 733                      | 460 |
| <i>n</i> -Pentane | 533                      | 260 |
| <i>n</i> -Hexane  | 498                      | 225 |
| <i>n</i> -Heptane | 488                      | 215 |
| <i>n</i> -Octane  | 493                      | 220 |
| <i>n</i> -Decane  | 483                      | 210 |

Data source: [25,30]

peratures also varied little by air : fuel ratio and increased as the diameter of the heat sources was decreased.

### 1.3.3 Detonation of Air/Alkane Mixtures

Explosions and detonations of air/hydrocarbon mixtures have been the cause of numerous accidents [32].

#### 1.3.3.1 Critical Tube Diameter for Propagation of Air/Alkane Detonations

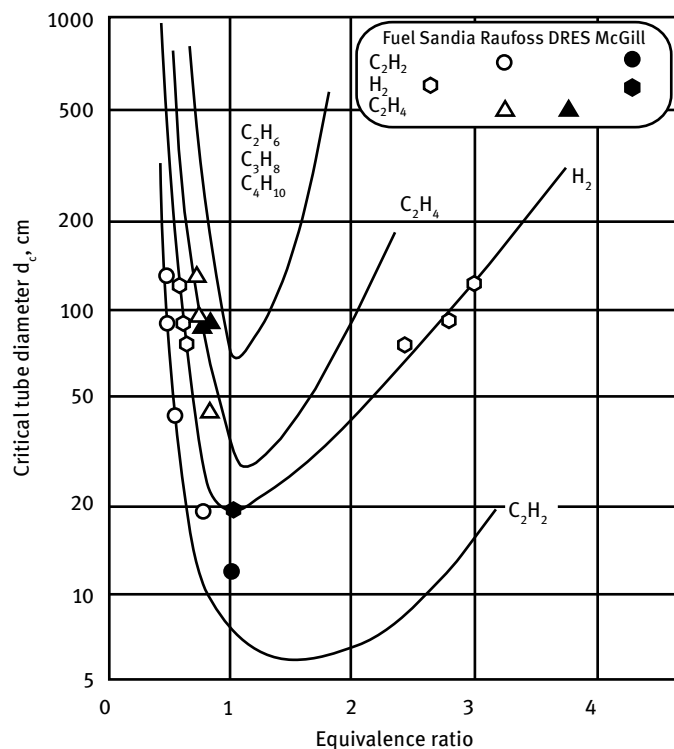
The critical diameter of tubes and orifices for propagation of air/alkane detonations has to be known for the design of flashback arrestors and micro propulsion devices. It is also useful for the design of pulsed detonation engines and rotating detonation engines.

Large-scale tests with mixtures of some common hydrocarbons ( $C_2H_2$  and  $C_2H_4$ ) and air at atmospheric pressure initially confirmed the validity of the  $d_c = 13\lambda$  correlation [33].

During experiments to obtain the critical tube diameter  $d_c$ , for air/ethylene mixtures by investigating the diffraction of detonations from tubes into large plastic bags simulating an unconfined fuel-air cloud, the critical air/ethylene compositions for successful re-establishment of detonation upon emerging from tubes 0.31, 0.45, 0.89, and 1.36 m in diameter were determined by monitoring the diffracted detonation wave in the bag [34].

Results of large-scale experiments on the transmission of air/hydrogen and air/ethylene detonations from a two-dimensional channel into a large open volume confirmed the observations by others that indicated that successful transmission of a detonation emerging from a rectangular orifice with a large aspect ratio  $L/W > 5$ ,

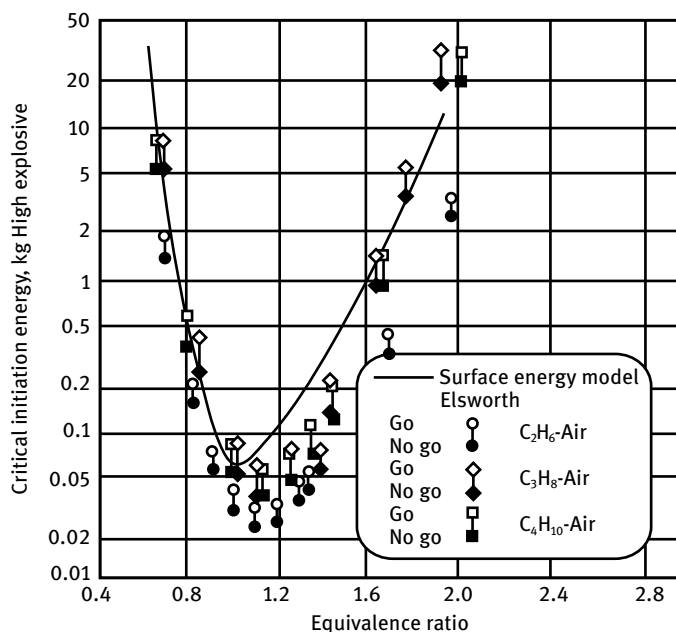
requires the minimum width of the channel to be only about three detonation cell diameters, i.e.,  $W_r \sim 3\lambda$  [35, 36]. The results of direct measurements from different sources are compared in Figure 2 with the estimated values from the  $d_c = 13\lambda$  correlation shown as solid lines for a range of equivalence ratios. From a practical point of view, the empirical law allows reliable estimates of critical tube diameters using cell size data obtained in 1/13-scale experiments. The correlation is particularly valuable for less sensitive air/fuel mixtures, which would require rather large-scale experiments.



**Figure 2:** Variation of critical tube diameter with equivalence ratio in air/ $H_2$  and air/hydrocarbon ( $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$ ) mixtures at NTP. (Reproduced and modified from [36].)

### 1.3.3.2 Minimum Energy for Initiation of Air/Alkane Detonations

The minimum energy for initiation of air/alkane detonations is illustrated in Figure 3.



**Figure 3:** Variation of critical energy for direct initiation of spherical detonation with fuel percentage in alkane ( $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$ )-air mixtures at NTP. (Reproduced and modified from [36].)

## 2 Methane

Methane,  $CH_4$ , CAS RN [74-82-8], is in the process of replacing long-established kerosenes as the hydrocarbon fuel in launch vehicles with LOX as the oxidizer. The main commercial candidate for this transition is the Vulcan launch vehicle by United Launch Alliance, propelled by BE-4 engines from Blue Origin, but newcomers such as Starship and Starhopper from Space-X and New Glenn from Blue Origin are also based on using liquid methane as the fuel.

### 2.1 Preparation, Production, and Availability of Methane

Methane is available from natural gas that is either produced from gas wells or escapes from liquid petroleum as soon as it is brought to the surface and the downhole pressure is relieved. Often the methane from remote oil field wells has to be flared off because there is no industrial use for it at those remote locations. Other than in pipelines, methane (natural gas) can be transported as a cryogenic liquid, Liquefied Natural Gas (LNG). LNG has been tested and has flown as a rocket propellant, containing a few other light hydrocarbons in addition to methane.

### 2.1.1 Liquefaction of Methane

The theoretical ideal work required for the liquefaction of methane starting at 300 K and 101.3 kPa is 1091 kJ/kg (469 BTU/lb). The optimized theoretical energy requirement of a Linde-Hampson liquefaction cycle is 3957 kJ/kg (1701 BTU/lb).

### 2.1.2 Physical Properties of Methane

Of all the hydrocarbons in this chapter of the rocket propellants book, methane is the single chemical (as opposed to fuel blends such as RP-1) that has the most literature references to digest and include in this summary. In order to keep the volume of this chapter within manageable limits, not all the data available on the physical properties of methane could be included in full. In most cases, a reference to the literature sources with additional information may suffice [37].

The mini-REFPROP computer program, which can be downloaded free from the web [38], contains methane as an example. It has the capability to create physical and thermochemical property tables and graphs for a wide range of temperatures at the click of a button. Several of the graphs in this section were created using the REFPROP demo version.

Because of the industrial importance of methane, it has become necessary to examine the newly available thermophysical property data and to re-evaluate the older data to produce more useful and accurate correlations. An empirical equation of state for methane based on extensive multi-property analysis, as well as correlations for the liquid/vapor phase boundary and for the viscosity and thermal conductivity of methane, was derived [39]. Tables of coefficients for these correlating equations and graphical representations of the functions for easy accessibility of estimated values of certain properties were included. The correlations were based on a critical evaluation of available experimental data and have been developed to represent these data over a broad range of the state variables. Estimates for the accuracy of the equations and comparisons with measured properties were given, including new and more accurate data, and improvements in the correlation functions, which allow increased accuracy of the correlations, especially in the extended critical region. The resulting equation of state is accurate from about 91 to 600 K for pressures <100 MPa and was developed by considering PVT, second virial coefficient, heat capacity, and sound speed data. For the viscosity of fluid methane, a low-density contribution based on theory was combined with an empirical representation of the excess contribution. The approximate validity range of the resulting correlation was 91 to 400 K for pressures <55 MPa.

### 2.1.3 Freezing Point of Methane

Freezing point measurements reported by various sources are summarized in Table 4. Triple-point data in Table 5 are a compilation from multiple sources, including some of those listed in Table 4.

**Table 4:** Freezing point of methane.

| SI units       | Other units |              | References |
|----------------|-------------|--------------|------------|
| 90.6 K         | −182.5 °C   | −296.5 °F    | [40]       |
| 91.2 K         | −181.9 °C   | −296.4 °F    | [41]       |
| 90.6 K         | −182.5 °C   | −296.5 °F    | [42]       |
| 90.5 K         | −182.6 °C   | −296.7 °F    | [43]       |
| 90.680 K       | −182.47 °C  | Triple point | [44]       |
| 90.67 ± 0.03 K | −182.48 °C  | Triple point | [45]       |
| 90.6856 K      | −182.47 °C  | Triple point | [46, 47]   |

**Table 5:** Triple-point properties of methane.

| References  | [25]                                | [48]               |
|-------------|-------------------------------------|--------------------|
| $T_t$       | 90.6854 ± 0.0003 K                  | 90.6941 ± 0.0025 K |
| $P_t$       | 11.696 ± 0.002 kPa                  | 11.696 ± 0.002 kPa |
| $\rho_{tL}$ | 28.145 ± 0.005 mol dm <sup>−3</sup> | —                  |
| $\rho_{tV}$ | 15.66 ± 0.05 mol m <sup>−3</sup>    | —                  |

The melting temperature of frozen methane is dependent on the pressure. Thirteen melting temperatures at pressures up to 21.28 MPa (210 atm) were represented by the Simon equation with a root mean square deviation of 5 kPa (0.05 atm) (0.08%) [44]. This representation is highly sensitive to the triple-point temperature, yielding 90.680 K (ITS-1968). See also Pavese et al. and Inaba and Mitsui [46, 49].

Solid methane exists in several modifications, of which nine are known at this time.

### 2.1.4 Boiling Point of Methane

Boiling point measurements reported by various sources are summarized in Table 6.

**Table 6:** Boiling point of methane.

| SI units           | Other units |            | References |
|--------------------|-------------|------------|------------|
| 111 ± 2 K          | −162 °C     | −260 °F    | [45]       |
| 111.420 K          | −161.73 °C  | −259.11 °F | [50]       |
| 111.668 ± 0.0025 K | −161.482 °C | −258.67 °F | [51]       |

### 2.1.5 Vapor Pressure of Methane

Three different equations were proposed for calculating the vapor pressure of methane in the range 112.45 to 190.25 K, and two of those are shown here [52]. The first one is essentially the one derived from the Clapeyron-Clausius equation.

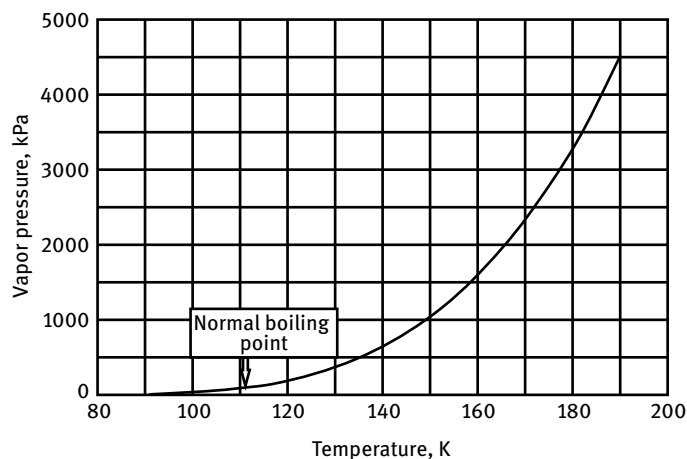
$$\log p = A \log T + \frac{B}{T} + C$$

where  $p$  is the vapor pressure in atm and  $T$  is the temperature in kelvin. The constants are  $A = 2.00224$ ,  $B = -394.275$ ,  $C = 0.761227$ . The second equation contains significantly more parameters and promised to give better accuracy data:

$$\log p = \frac{A}{T} + B + CT + DT^2 + ET^3 + FT^4 + GT^5$$

where  $p$  is the vapor pressure in atm and  $T$  is the temperature in kelvin. The constants are  $A = 22028.8$ ,  $B = -902.926$ ,  $C = 15.1525$ ,  $D = -0.134167$ ,  $E = 0.664133 \times 10^{-3}$ ,  $F = -0.174306 \times 10^{-5}$ ,  $G = 0.189568 \times 10^{-8}$ .

The vapor pressure of methane is illustrated in Figure 4.



**Figure 4:** Vapor pressure of methane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp)

The vapor pressure of liquid methane can be calculated from the Antoine equation

$$\log P = A - [B/(T + C)]$$

where  $P$  is the vapor pressure in bar,  $T$  is the temperature in kelvin, and  $A$ ,  $B$ , and  $C$  are the constants listed in Table 7 for four different temperature ranges.



**Table 7:** Coefficients for the Antoine equation for vapor pressure of methane for four different temperature ranges.

| Temperature range, K | A       | B       | C       | References |
|----------------------|---------|---------|---------|------------|
| 90.99–189.99         | 3.98950 | 443.028 | –0.49   | [44]       |
| 96.89–110.19         | 2.00253 | 125.819 | –48.823 | [53]       |
| 93.04–107.84         | 3.80235 | 403.106 | –5.479  | [54]       |
| 110.00–190.50        | 4.22061 | 516.689 | 11.223  | [50]       |

Note: Coefficients calculated by National Institute of Standards and Technology from the author's data.

The vapor pressures, heats of vaporization, and heat capacities of methane from boiling point to the critical temperature have been measured [50]. The vapor pressure data in the range 110–190 K have been represented in the form

$$\log P = 3.984667 - (444.6667/T) - \delta T$$

where  $P$  is the vapor pressure in atm,  $T$  is the temperature in kelvin, and where  $\delta T$  is in essence a deviation function. The constants of this equation were arbitrarily chosen so as to minimize the magnitude of  $\delta T$ . The function  $\delta T$  was then tabulated at equal intervals of temperature and the fourth difference smoothed. The normal boiling point of methane from this equation is 111.420 K. Critical constants have been calculated from the vapor pressure data. It was shown that the measured heats of vaporization

**Table 8:** Literature data on the vapor pressure of methane.

| References                                               | Year | Number of data points | Temperature range, K |
|----------------------------------------------------------|------|-----------------------|----------------------|
| [55] Bloomer and Parent                                  | 1953 | 20                    | 105–190.5            |
| [56] Armstrong, Brickwedde, and Scott                    | 1955 | 87                    | 90.6–112             |
| [54] Cutler and Morrison                                 | 1965 | 15                    | 93–108               |
| [57] van Dael, W., et al.                                | 1965 | 13                    | 140–188              |
| [58] Grigor                                              | 1966 | 38                    | 93–190               |
| [59] Vennix et al.                                       | 1970 | 32                    | 134–190.5            |
| [60] Jansoone et al.; [61] Gielen, Jansoone, and Verbeke | 1970 | 7                     | 189–190.5            |
| [62] Tully, deVaney, and Rhodes                          | 1971 | 9                     | 124–190              |
| [63] Liu and Miller                                      | 1972 | 9                     | 91–120               |
| [64] Pope                                                | 1972 | 13                    | 132–190.5            |
| [44] Prydz and Goodwin                                   | 1972 | 105                   | 91–190.5             |
| [65] Calado, Garcia, and Staveley                        | 1974 | 2                     | 116–135              |
| [66] Elliot et al.                                       | 1974 | 31                    | 144–190              |
| [67] Gammon and Douslin                                  | 1976 | 47                    | 113–190.5            |
| [68] Kleinrahm and Wagner                                | 1986 | 161                   | 90.7–190.5           |

Data source: [48]

were in good agreement with those calculated from the above vapor pressure equation and the known liquid and gaseous densities.

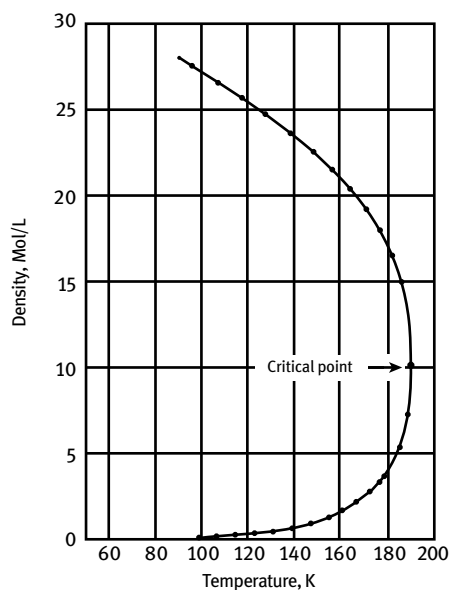
Various sources of additional literature data on the vapor pressure of methane are listed in Table 8 in chronological order. The determination of vapor pressure was sometimes only peripheral to other measurements of physical properties.

One hundred and five vapor pressure data points from the triple point to the critical point were represented by a non-analytical equation with a root mean square relative deviation of 0.01% [44]. The derived triple-point pressure was 0.1159 atm. At the assigned critical-point temperature of 190.53 K the pressure was 45.356 atm. Deviations of some of the data from those of other sources exceeded 1% only at  $T < 140$  K.

### 2.1.6 Density of Methane

Based on the results of measurements of the density behavior of liquid methane at high pressures, an equation of state and different thermodynamic properties of methane were calculated in two regions [68]. Fourteen isotherms were determined between 114 and 190 K. The maximum pressure was 31 MPa (4500 psia).

Figure 5 gives the calculated coexisting densities of vapor and liquid methane along the ordinate. The abscissa gives the saturation temperature,  $T_s(\rho)$  [69].



**Figure 5:** Coexisting vapor and liquid densities of methane down to the triple point. (Reproduced and modified from [70].)

The PVT data for liquid methane were measured at densities from 1.8 times critical density up to the density of the freezing liquid, at temperatures from 91 to 245 K and pressures up to 350 bar [71]. A non-analytic equation of state was adjusted to these and

other PVT data from ideal gas states to freezing liquid, at temperatures from the triple point to 400 K; these data cover most of the domain at  $T_t < T < 400$  K, and  $P \leq 350$  bar. The table containing the raw experimental data with temperature increments of 2 K extends over four pages. The isochoric equation of state for methane had the form

$$(Z - 1) \times \frac{\tau}{\rho} = A + B \cdot \Phi(T) + \frac{C}{\tau} + D\Psi(\rho, T).$$

where  $Z = PV/RT$  is the compressibility factor,  $\tau$  is the absolute reduced temperature reduced at the critical point  $\tau = T/T_c$ ,  $\Phi(T)$  is a function of temperature:

$$\Phi(T) = \tau \left[ 1 - \exp\left(-b - \frac{\beta}{\tau}\right) \right]$$

and  $\Psi(\rho, T)$  is a function of density and temperature:

$$\Psi(\rho, T) = \frac{1 - \omega \ln\left(1 + \frac{1}{\omega}\right)}{\tau}$$

where  $\omega$  is  $(T - \Phi)/(\delta T_c)$ .  $\beta$ ,  $\delta$ , A, B, C, and D are constants. The triple-point density of methane is  $d_t = 28.1472$  mol/L. The measured and calculated methane density data were compared with those reported by Vennix [72] and Douslin et al. [73]. The 1964 measurements by Douslin et al. covered a temperature range of 273 to 623 K (0 to 350 °C) and extended to pressures of 1.62 to 40.5 MPa (16 to 400 atm) and densities of 0.75 to 12.5 mol/L. From these data, constants were derived for the Beattie-Bridgeman and Benedict-Webb-Rubin equations of state.

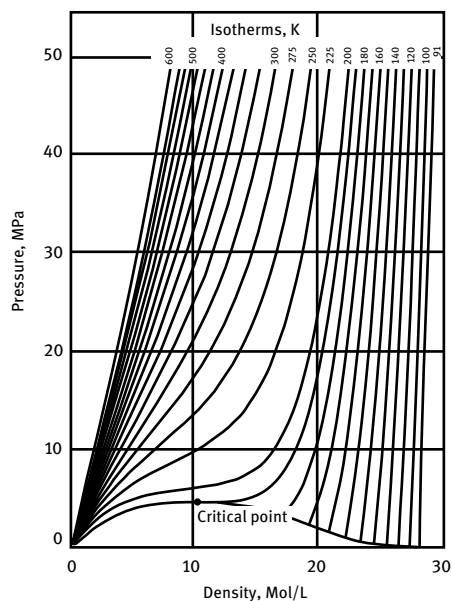
Saturated liquid and vapor densities of pure methane were measured together with the vapor pressure along the whole coexistence curve (ranges covered: 50 to 350 K, 0.01 to 8 MPa, 1 to 2000 kg/m<sup>3</sup>) [51]. Densities of the homogeneous gas could also be measured. The density measurements compensation method was based on Archimedes' buoyancy principle. Instead of the usual single sinker, two sinkers that had identical mass and surface area but that differed considerably in volume were used. A magnetic suspension coupling transmitted the suspension force without contact from the pressure cell to a microbalance (resolution: 10<sup>-5</sup> g) at ambient atmosphere. The saturated vapor densities were determined in quite a new way. As a first substance, methane (purity 99.9995 mol-%) was investigated from the triple-point temperature (90.685 K) up to 0.02 K below the critical temperature. Critical values were derived from these measurements:  $T_c = 190.551$  K,  $\rho_{n,c} = 10.139$  mol/L,  $p_c = 4.5992$  MPa.

Densities on three isotherms (189, 190, and 193 K) of the homogeneous part of the critical region were measured in the density range from 60 to 260 kg/m<sup>3</sup> ( $\rho_c = 162.660$  kg/m<sup>3</sup>) [74].

A truncated virial equation with only three adjusted parameters has been established for the range 273.15 to 323.15 K at pressures up to 8 MPa, which represented the

density of methane with an uncertainty of less than  $\pm 0.01\%$  [75]. The density under standard conditions (273.15 K, 0.101325 MPa) was calculated from this equation as  $\rho_s = (0.71746 \pm 0.00007) \text{ kg/m}^3$ . See also Kleinrahm et al. and Haendel et al. [76, 77].

In a compilation of thermophysical properties of methane, a tabulation containing 16 literature sources of PVT data of methane was used to derive a very accurate equation of state. In the phase diagram in Figure 6, the critical point is indicated by a black circle. The phase boundaries were derived from ancillary equations. A similar chart is available in the same publication for the isochors.



**Figure 6:** Methane isotherms derived from the SW Equation of State. (Reproduced and modified from [39], with permission of ©1989 AIP Publishing; permission conveyed through Copyright Clearance Center Inc.)

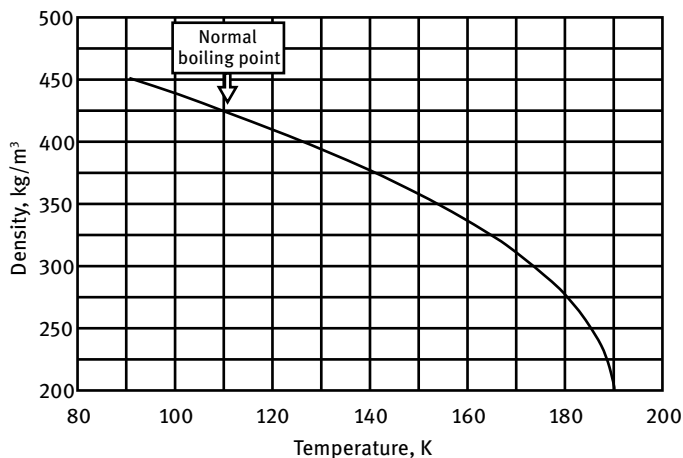
The PVT isotherms of methane and propene have been determined between 1 and 10 kbar at temperatures of 308, 373, and 473 K (35, 100, and 200 °C) [78].

Density measurements on pure methane in the range 273 to 323 K, 0.1 to 12 MPa, and 1 to 1000 kg/m<sup>3</sup> density with a total uncertainty in density less than  $\pm 0.02\%$  used a “Two-Sinker Method,” which is based on Archimedes’ buoyancy principle [79]. Comprehensive ( $P$ ,  $\rho$ ,  $T$ ) measurements on pure methane were taken within the entire working range of the apparatus with respect to temperature and pressure. Truncated virial equations were established for the investigated region of methane and the experimental results were compared with results of previous workers and with current equations of state.

Comprehensive ( $P$ ,  $\rho$ ,  $T$ ) measurements on pure methane (159 values) have been made within the temperature range 240 to 520 K at pressures up to 30 MPa [80]. The

measurements were performed using a single-sinker densimeter that was based on Archimedes' buoyancy principle. The total relative uncertainty of the measurements in the density  $\rho$  was estimated to be  $\leq (1.5 \text{ to } 2) \times 10^{-4} \cdot \rho$  for methane. The measurements were compared with previous results of other experimentalists and with values calculated from current equations of state.

The density of liquid methane along the saturation line under saturation pressure can be simply calculated and graphed using data from the demonstration version of REFPROP (Figure 7).



**Figure 7:** Density of liquid methane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

### 2.1.6.1 Equations of State for Methane

The data on the thermodynamic properties of methane that were available up to the middle of 1991 were reviewed and formed the foundation for a new equation of state in the form of a fundamental equation explicit in the Helmholtz free energy [48, 81]. Independent equations were also included for vapor pressure, saturated liquid and vapor densities, the isobaric ideal gas heat capacity and the melting pressure as functions of temperature. Tables for the thermodynamic properties of methane from 90 to 620 K for pressures up to 1000 MPa were presented. For the density, uncertainties were estimated to be  $\pm 0.03\%$  for pressures below 12 MPa and temperatures below 350 K and  $\pm 0.03\%$  to  $\pm 0.15\%$  for higher pressures and temperatures. For the velocity of sound, the uncertainty ranged from  $\pm 0.03\%$  to  $\pm 0.3\%$  depending on temperature and pressure. Heat capacities may be generally calculated within an uncertainty of  $\pm 1\%$ . To verify the accuracy of the new formulation, the calculated property values were compared with selected experimental results and existing equations of state for methane from the lit-

erature. The new equation of state corresponds to the new International Temperature Scale of 1990 (ITS-90) and can be extrapolated up to pressures of 20000 MPa. After a critical evaluation of all the data it was concluded that measurements before 1950 did not meet the present quality requirements. Therefore, the Setzmann and Wagner 1991 review [48] included only all experimental investigations that had been carried out during the period 1950–1990 or older works that were of essential importance for the characterization of the data situation of single properties of methane.

Table 9 is a summary of the equations of state for methane that have been developed since 1970. All of these wide-range equations of state are based mainly on the  $P\rho T$  data (pressure  $P$ , density  $\rho$ , temperature  $T$ ) published by Douslin et al. [73], Cheng [82], Goodwin and Prydz [71], and Sievers and Schultz [83]. All equations of state listed in Table 9 may contain errors of at least  $\pm 0.2\%$  in density in a wide range of temperatures and pressures.

**Table 9:** Summary of the literature on equations of state for methane.

| References                                       | Temperature range, K | Pressure range, MPa | Structure of the equation           | Number of coefficients |
|--------------------------------------------------|----------------------|---------------------|-------------------------------------|------------------------|
| [84] Bender 1970                                 | 90.66–623            | 0–50                | Extended BWR                        | 20                     |
| [85] Goodwin 1974                                | 90.68–500            | 0–50                | Non-analytic                        | 23                     |
| [86] McCarty 1974                                | 90.68–400            | 0–40                | Extended BWR                        | 32                     |
| [87] Angus, Armstrong, and de Reuck (IUPAC) 1978 | 90.68–421            | 0–1000              | Extended BWR                        | 32                     |
| [88] Sychev et al. 1979                          | 90.68–1000           | 0–100               | Double power expansion              | 54                     |
| [89] Sievers and Schulz 1980                     | 91–625               | 0–50                | —                                   | —                      |
| [90] Kerley 1980                                 | 20–10000             | —                   | —                                   | —                      |
| [91] Ely and Hanley 1981                         | 90.68–500            | 0–260               | 32 Extended BWR                     | —                      |
| [92] Sievers and Schulz 1984                     | 90.68–625            | 0–50                | 20 Extended BWR (Bender)            | —                      |
| [93] Erickson and Leland 1986                    | 90.68–500            | 0–260               | Damping function                    | 32                     |
| [94] Younglove and Ely 1987                      | 90.68–600            | 0–200               | Modified BWR                        | 32                     |
| [95] Kurumov, Olchowy, and Sen-<br>gers 1988     | 187–208              | 4.4–7               | 12 Revised and extended scaling law | —                      |
| [39] Friend, Ely, and Ingham 1989                | 91–600               | 0–100               | Developed for oxygen                | 32                     |

Note: Literature data arranged in chronological order

Data source (in part): [48]

The density of saturated liquid methane between the triple point and the critical point is summarized in Table 10.

**Table 10:** Density of saturated liquid methane.

| Temperature<br>K     | Pressure<br>MPa | Density<br>kg/m <sup>3</sup> |
|----------------------|-----------------|------------------------------|
| 90.694 <sup>a</sup>  | 0.011696        | 451.48                       |
| 100                  | 0.034376        | 438.89                       |
| 110                  | 0.088130        | 424.78                       |
| 120                  | 0.19143         | 409.90                       |
| 130                  | 0.36732         | 394.04                       |
| 140                  | 0.64118         | 376.87                       |
| 150                  | 1.0400          | 357.90                       |
| 160                  | 1.5921          | 336.31                       |
| 170                  | 2.3283          | 310.50                       |
| 180                  | 3.2852          | 276.23                       |
| 190                  | 4.5186          | 200.78                       |
| 190.564 <sup>b</sup> | 4.5992          | 162.66                       |

<sup>a</sup> Triple point<sup>b</sup> Critical point

Data source: [48]

The original report contains 40 tables for a wide range of pressures from 0.101 to 100 MPa. Instead of saturated liquid conditions, the thermodynamic properties of liquid methane at two selected pressures are listed in Table 11.

The density of gaseous methane has been measured in the temperature range 253–423 K (–20 to +150 °C) and in the pressure range 130–690 MPa, using a substitution method [96]. The overall uncertainty in the results was 0.03% at the 95% confidence level. The data were presented in the form of a modified Benedict-Webb-Rubin equation of state and were compared with the results of other workers.

It is difficult enough to obtain accurate equations of state for methane in equilibrium with its environment, but it is even more difficult to describe methane in the superheated liquid state. Measurements of densities of liquid methane in stable and metastable phase states were carried out within the temperature range 144 to 185 K [97]. The depth of penetration into the metastable region was 1.5 MPa and 43.6 K. An equation of state for superheated liquid methane was proposed. The density of the liquid at the line of attainable superheats has been determined. The spinodal curve has been approximated. For compositions within this curve, infinitesimally small fluctuations in composition and density will lead to phase separation via spinodal decomposition.

An equation of state was developed for the thermodynamic properties of methane in the vicinity of the critical point [98]. It incorporated the scaled asymptotic critical behavior predicted theoretically and supplemented a global analytic equation of state for methane developed by Setzmann and Wagner. See also Cheng [82].

**Table 11:** Thermodynamic properties of liquid methane at two selected pressures.

| Temperature<br>K        | Density<br>kg/m <sup>3</sup> | Internal<br>energy<br>kJ/kg | Enthalpy<br>kJ/kg | Entropy<br>kJ kg <sup>-1</sup> K <sup>-1</sup> | $c_v$<br>kJ kg <sup>-1</sup> K <sup>-1</sup> | $c_p$<br>kJ kg <sup>-1</sup> K <sup>-1</sup> | Velocity<br>of sound<br>m/s |
|-------------------------|------------------------------|-----------------------------|-------------------|------------------------------------------------|----------------------------------------------|----------------------------------------------|-----------------------------|
| <b>Pressure 0.1 MPa</b> |                              |                             |                   |                                                |                                              |                                              |                             |
| 90.717                  | 451.50                       | -982.76                     | -982.54           | -7.3866                                        | 2.1678                                       | 3.3674                                       | 1539.0                      |
| 92                      | 449.79                       | -978.44                     | -978.22           | -7.3392                                        | 2.1595                                       | 3.3718                                       | 1527.3                      |
| 94                      | 447.11                       | -971.69                     | -971.47           | -7.2666                                        | 2.1473                                       | 3.3796                                       | 1509.0                      |
| 96                      | 444.41                       | -964.92                     | -964.70           | -7.1954                                        | 2.1356                                       | 3.3883                                       | 1490.4                      |
| 98                      | 441.68                       | -958.14                     | -957.91           | -7.1254                                        | 2.1245                                       | 3.3977                                       | 1471.6                      |
| 100                     | 438.94                       | -951.34                     | -951.11           | -7.0567                                        | 2.1138                                       | 3.4079                                       | 1452.6                      |
| 105                     | 431.95                       | -934.23                     | -934.00           | -6.8897                                        | 2.0883                                       | 3.4363                                       | 1404.2                      |
| 110                     | 424.79                       | -916.97                     | -916.74           | -6.7291                                        | 2.0642                                       | 3.4691                                       | 1354.8                      |
| 111.508 <sup>a</sup>    | 422.59                       | -911.74                     | -911.50           | -6.6818                                        | 2.0572                                       | 3.4799                                       | 1339.7                      |
| <b>Pressure 1 MPa</b>   |                              |                             |                   |                                                |                                              |                                              |                             |
| 90.9478                 | 451.79                       | -982.52                     | -980.31           | -7.3839                                        | 2.1686                                       | 3.3632                                       | 1543.0                      |
| 92                      | 450.39                       | -978.98                     | -976.76           | -7.3451                                        | 2.1618                                       | 3.3666                                       | 1533.5                      |
| 94                      | 447.73                       | -972.26                     | -970.02           | -7.2727                                        | 2.1496                                       | 3.3740                                       | 1515.4                      |
| 96                      | 445.05                       | -965.51                     | -963.27           | -7.2015                                        | 2.1380                                       | 3.3823                                       | 1497.0                      |
| 98                      | 442.34                       | -958.75                     | -956.49           | -7.1317                                        | 2.1269                                       | 3.3913                                       | 1478.4                      |
| 100                     | 439.62                       | -951.97                     | -949.70           | -7.0631                                        | 2.1162                                       | 3.4011                                       | 1459.6                      |
| 105                     | 432.70                       | -934.94                     | -932.63           | -6.8965                                        | 2.0908                                       | 3.4282                                       | 1411.9                      |
| 110                     | 425.61                       | -917.76                     | -915.41           | -6.7363                                        | 2.0667                                       | 3.4593                                       | 1363.2                      |
| 115                     | 418.32                       | -900.42                     | -898.03           | -6.5818                                        | 2.0438                                       | 3.4950                                       | 1313.4                      |
| 120                     | 410.80                       | -882.89                     | -880.45           | -6.4322                                        | 2.0219                                       | 3.5363                                       | 1262.4                      |
| 125                     | 403.01                       | -865.13                     | -862.65           | -6.2869                                        | 2.0010                                       | 3.5848                                       | 1210.2                      |
| 130                     | 394.92                       | -847.12                     | -844.59           | -6.1452                                        | 1.9813                                       | 3.6424                                       | 1156.6                      |
| 135                     | 386.44                       | -828.80                     | -826.21           | -6.0065                                        | 1.9629                                       | 3.7122                                       | 1101.2                      |
| 140                     | 377.51                       | -810.09                     | -807.44           | -5.8700                                        | 1.9460                                       | 3.7984                                       | 1043.7                      |
| 145                     | 368.02                       | -790.90                     | -788.19           | -5.7348                                        | 1.9311                                       | 3.9075                                       | 983.57                      |
| 149.13 <sup>a</sup>     | 359.62                       | -774.57                     | -771.79           | -5.6233                                        | 1.9205                                       | 4.0227                                       | 931.21                      |

<sup>a</sup> Saturation temperature

Data source: [48]

### 2.1.6.2 Densified Liquid Methane

Similar to densified oxygen and densified hydrogen, densified liquid methane has been evaluated for a number of space missions.

Methane gas of 99% purity was condensed to liquid methane, and methane slush was subsequently produced using the freeze-thaw method [99] in the following manner:

- (1) The surface of the liquid was pumped to the triple-point pressure, 11.6 kPa (87.7 mm Hg).
- (2) Pumping was continued until a solid layer formed on the top of the liquid.
- (3) The pumping was stopped and soon the solid layer melted at the Dewar flask walls and settled into the liquid.



Stirring at this time helped to break the solid and encouraged settling. The cycle was then repeated. The slush became more dense and the solid particles no longer tended to settle out of the liquid. An apparatus was assembled that allowed solid particles to be photographed in triple-point liquid with a reference grid in the background. Fresh and aged solid particles were photographed. Photos of the particles indicated a definite aging effect between fresh and 4-h-old particles. Particles of two different size ranges appeared during the production process. One group of particles appeared to be within the range  $\geq 2\text{ mm}$ , and when stirred, these particles settled within a short time (15 s) to the bottom of the Dewar. Another much smaller group of particles, with diameters  $\sim 0.2\text{ mm}$  or less were present immediately after forming solids but coalesced with time.

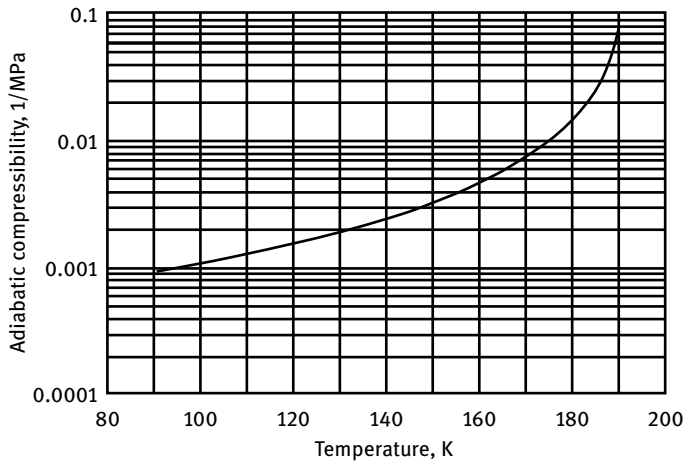
The cryogenic option for an Altair Lunar Lander was envisioned to use liquid oxygen and liquid methane to propel Altair from the lunar surface back to rendezvous with the Orion command module. It was determined that the liquid methane should be densified by subcooling it to 93 K in order to prevent over-pressurization of the propellant tanks during the 210-day stay on the lunar surface. A trade study was conducted to determine the preferred method of producing, loading, and maintaining the subcooled, densified liquid methane onboard Altair from a ground operations perspective [100]. The desired delivery temperature of the methane at 93 K would be only 2.3 K above the methane triple point of 90.7 K. Twenty-six methods of subcooled liquid methane production and delivery along with the associated system architectures were investigated to determine the best solutions to the problem, including slush methane with  $\text{LCH}_4$  at its triple point with 50% solid  $\text{CH}_4$ . The top four cryogenic processing solutions were selected for further evaluation and detailed thermal modeling.

### 2.1.7 Compressibility and Velocity of Sound of Methane

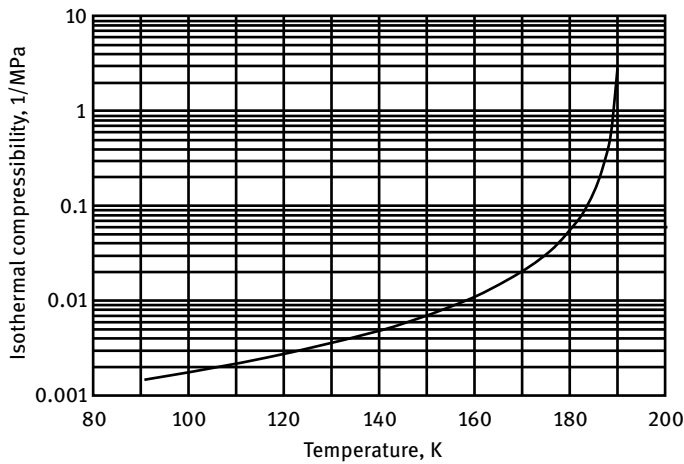
The adiabatic compressibility of liquid methane along the saturation line under saturation pressure is illustrated in Figure 8. The isothermal compressibility of liquid methane along the saturation line under saturation pressure is illustrated in Figure 9. The velocity of sound in liquid methane along the saturation line under saturation pressure is illustrated in Figure 10. Table 12 shows a summary of additional literature on the velocity of sound data in methane.

Sound velocity measurements were carried out in liquid methane between its triple and critical point [57]. Some thermodynamic properties (specific heats, compressibilities, expansion and pressure coefficients) were derived and were in good agreement with the few available and directly measured data.

Sound velocity in liquid methane for pressures up to 200 atm was measured along seven isotherms between the triple point (91 K) and the critical point (191 K) [101]. Adiabatic compressibilities have been calculated by combining these results with density data.

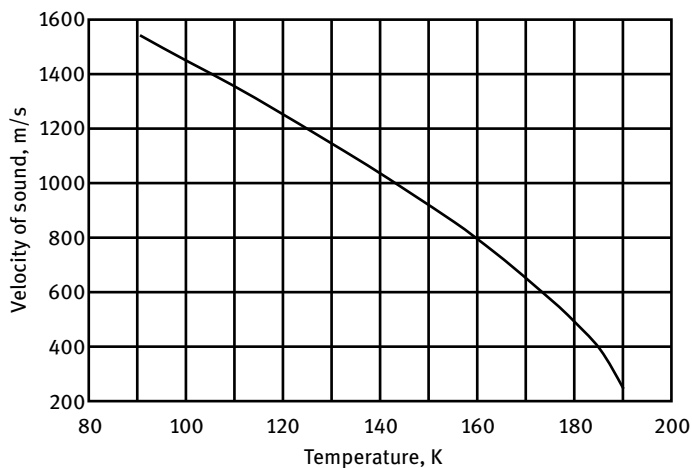


**Figure 8:** Adiabatic compressibility of methane. (Image generated by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)



**Figure 9:** Isothermal compressibility of methane. (Image generated by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

A piezometric method was used to measure the density and isothermal compressibility of liquid methane at  $T = 90\text{--}130\text{ K}$  and  $P$  up to 500 atm [105]. The compressibilities were calculated as a function of  $P$  and  $T$ . The bulk modulus showed a linear dependence on  $P$ . The slopes of these straight lines did not depend on  $T$ . The bulk strengths of methane depended on  $T$  and obeyed the law of corresponding states.



**Figure 10:** Velocity of sound in liquid methane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

**Table 12:** Literature on the velocity of sound in methane.

| References                                | Number of data points | Temperature range K | Pressure range MPa |
|-------------------------------------------|-----------------------|---------------------|--------------------|
| [57] van Dael et al. 1965                 | 28                    | 94–190              | 0.02–4.6           |
| [101] van Itterbeek et al. 1967           | 97                    | 111–190             | 0.01–20            |
| [102] Straty 1974                         | 91                    | 91–300              | 0.01–35            |
| [67] Gammon and Douslin 1976              | 138                   | 113–323             | 0.1–25             |
| [103] Baidakov, Kaverin, and Skripov 1982 | 119                   | 150–183             | 1–4                |
| [104] Sivaraman and Gammon 1986           | 104                   | 193–423             | 1.5–28             |

Data source: [39]

The velocity of sound in saturated and compressed fluid methane was measured on the saturated liquid from 91 to 186 K and on the compressed fluid along selected isotherms from 100 to 300 K at pressures up to about 35 MPa [102]. Data were combined with literature  $P\rho T$  data to obtain the isentropic compressibility and the ratio of the specific heats. Measurements along the higher temperature isotherm were limited to densities greater than about 10 mol/L at 300 K increasing to about 14 mol/L at 210 K owing to the large low pressure sound attenuation in methane.

The velocity of sound and derived values of the constant volume heat capacity in methane were determined as functions of temperature and pressure along the phase

boundaries, at 298 K, and at densities from 0 to 11.6 mol/L for temperatures from 113.5–193.05 K [67]. Velocity dispersion arising from vibrational relaxation, relaxation near the critical point, and relaxation near the triple point were characterized. The results were tested by use of extended thermodynamic scaling representations for the chemical potential  $\mu$ . Within the limits of possible computational errors, the results indicated that along the critical isochore,  $(\partial^2\mu/\partial T^2)_p$  is finite, non-zero, and has a jump discontinuity at the critical temperature that implies that  $\varepsilon = 2$ ,  $(\beta + \alpha) = (1/2)$ , and  $\alpha = (1/7)$ , where  $\alpha$ ,  $\beta$ , and  $\varepsilon$  are scaling exponents.

The principal Hugoniot of liquid methane has been measured between 5 and 43 GPa and a doubly-shocked state has been measured at 91 GPa [106]. The repulsive pair potential for methane was demonstrated to obey the principle of corresponding states.

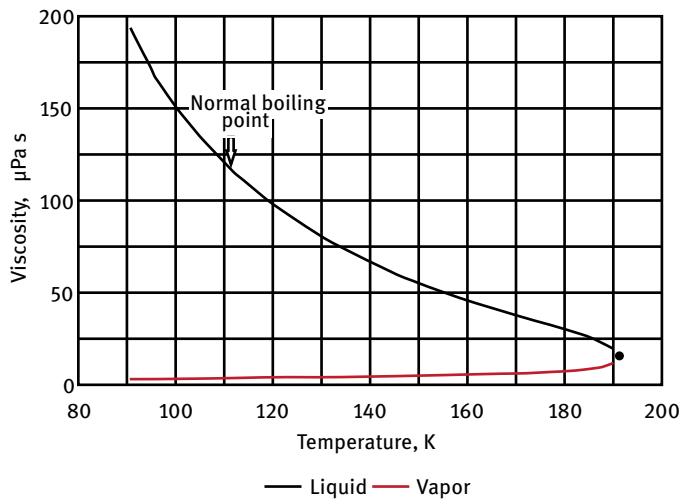
The absolute determination of the refractive index, when combined with an expansion technique for obtaining the higher-order coefficients of the Lorentz-Lorenz expansion, can lead to precise values of density and compressibility [107]. A grating interferometer was used for the refractive index measurements as a function of pressure. The advantage of a grating interferometer was that it performed reversible counting and generated a DC-compensated signal from the interference fringes. The pressure was measured with an interferometer, previously calibrated with an oil-type precision piston gauge. For the precise determination of the compressibility factor, the absolute measurement of the refractive index was combined with the differential technique to determine the refractivity virial coefficients of the Lorentz-Lorenz expansion. The compressibility factors of methane, nitrogen, and their mixtures have been determined at 323.15 K for pressures up to 335 bar. The optical method for the determination of the compressibility factor not only was precise but also had the ability to produce numerous experimental points in a relatively short time compared with other time-consuming methods.

## 2.1.8 Viscosity of Methane

### 2.1.8.1 Viscosity of Liquid Methane

The dynamic viscosity of methane under saturation pressure conditions is illustrated in Figure 11. Table 13 gives the viscosity for the saturated liquid at saturation pressure. The same data are graphed in Figure 12.

In contrast to propane (Vogel et al. 1998) there is no dramatic rise in the viscosity in the liquid phase at low temperatures and high densities. See also Assael et al. [109].

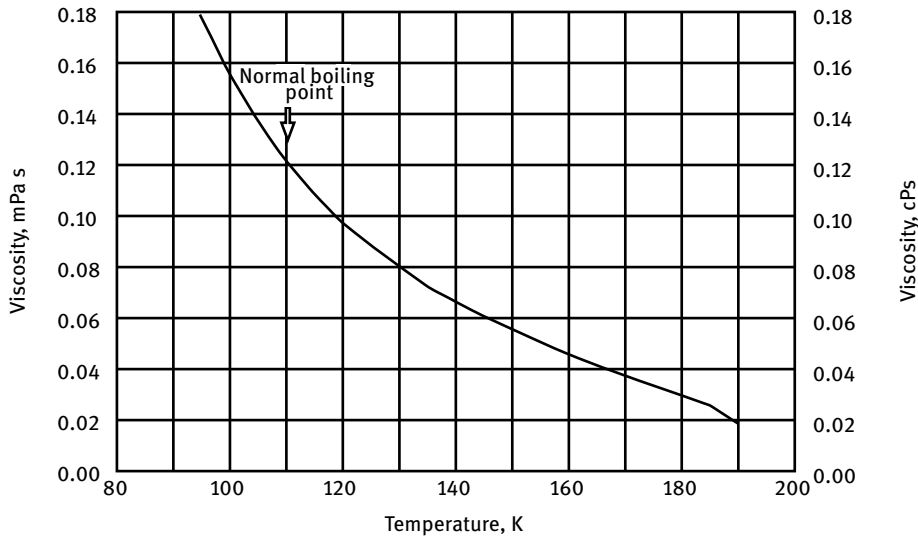


**Figure 11:** Dynamic viscosity of liquid and gaseous methane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

**Table 13:** Density and viscosity of methane-saturated liquid at saturation pressure.

| Temperature<br>K | Density |       | Dynamic viscosity                   |       |
|------------------|---------|-------|-------------------------------------|-------|
|                  | mol/L   | g/mL  | $\mu\text{g cm}^{-1} \text{s}^{-1}$ | cPs   |
| 95               | 27.789  | 0.446 | 1792                                | 0.179 |
| 100              | 27.367  | 0.439 | 1563                                | 0.156 |
| 105              | 26.934  | 0.432 | 1377                                | 0.138 |
| 110              | 26.491  | 0.425 | 1223                                | 0.122 |
| 115              | 26.035  | 0.418 | 1094                                | 0.109 |
| 120              | 25.566  | 0.410 | 984                                 | 0.098 |
| 125              | 25.081  | 0.402 | 889                                 | 0.089 |
| 130              | 24.578  | 0.394 | 807                                 | 0.081 |
| 135              | 24.055  | 0.386 | 734                                 | 0.073 |
| 140              | 23.508  | 0.377 | 669                                 | 0.067 |
| 145              | 22.932  | 0.368 | 611                                 | 0.061 |
| 150              | 22.322  | 0.358 | 558                                 | 0.056 |
| 155              | 21.672  | 0.348 | 509                                 | 0.051 |
| 160              | 20.971  | 0.336 | 464                                 | 0.046 |
| 165              | 20.206  | 0.324 | 421                                 | 0.042 |
| 170              | 19.356  | 0.311 | 380                                 | 0.038 |
| 175              | 18.386  | 0.295 | 340                                 | 0.034 |
| 180              | 17.226  | 0.276 | 300                                 | 0.030 |
| 185              | 15.690  | 0.252 | 256                                 | 0.026 |
| 190              | 12.485  | 0.200 | 187                                 | 0.019 |

Data source: [108]



**Figure 12:** Dynamic viscosity of liquid methane at the saturation line. (Image created by Schmidt 2020 based on data from [108].)

### 2.1.8.2 Viscosity of Gaseous Methane

Sources of viscosity data of methane at elevated pressures are summarized in Table 14.

The viscosity of methane gas can be correlated by the equation

$$\mu(\rho, T) = \mu_0(T) + \mu_1(T)\rho + \Delta\mu'(\rho, T)$$

where  $\mu_0$  is the viscosity of the dilute gas and the term  $\mu_1$  is the first density correction for the moderately dense gas, given by the empirical expression

$$\mu_1(T) = A + B \left[ C - \ln \left( \frac{T}{F} \right) \right]^2$$

where  $T$  is the temperature in kelvin,  $A$ ,  $B$ , and  $C$  are constants and  $F = \epsilon/k = 168.0\text{ K}$  where  $\epsilon$  is the energy parameter of the methane pair potential function and  $k$  is the Boltzmann constant. The term  $\Delta\mu'(\rho, T)$  is expressed empirically by a complicated, empirical equation with many parameters [108, 119]. Similar equations have been derived for thermal conductivity. Calculated viscosity data were tabulated for temperatures between 95 and 500 K and pressures between 0.1 and 50 MPa.

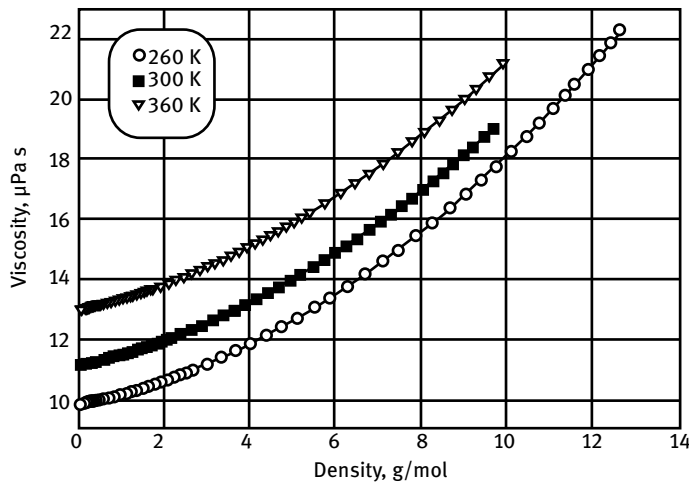
The standard reference viscosity of methane gas at 298 K and 101 kPa is  $11.0769\text{ }\mu\text{Pa}\cdot\text{s}$ .

Figure 13 illustrates the viscosity of gaseous methane as a function of density, which is a function of both temperature and pressure, for three isotherms.

**Table 14:** Sources of viscosity data of methane at elevated pressures.

| References                                 | Number of data points | Temperature range, K | Pressure range, MPa |
|--------------------------------------------|-----------------------|----------------------|---------------------|
| [110] Barua et al. 1964                    | 39                    | 223–423              | 1–18                |
| [111] Carmichael, Berry, and Sage 1965     | 67                    | 278–478              | 0.1–36              |
| [112] Giddings, Kao, and Kobayashi 1966    | 100                   | 283–411              | 0.1–55              |
| [113] Huang, Swift, and Kurata 1966        | 48                    | 103–173              | 0.05–34             |
| [114] Boon, Legros, and Thomaes 1967       | 8                     | 91–114               | 0.01–0.1            |
| [115] Gonzalez, Bukacek, and Lee 1967      | 53                    | 311–444              | 1.4–55              |
| [116] Hellemans, Zink, and van Paemel 1970 | 56                    | 97–187               | 0.04–10             |
| [117] Haynes 1973                          | 20                    | 95–190               | 0.02–4.5            |
| [118] Makita, Tanaka, and Nagashima 1973   | —                     | 273–373              | ≤50                 |
| [119] Hanley, McCarty, and Haynes 1975     | —                     | 95–400               | ≤50                 |
| [108] Hanley, Haynes, and McCarty 1977     | —                     | 95–500               | ≤50                 |
| [120] Diller 1980                          | 141                   | 100–300              | 0.8–31              |
| [121] Vogel et al. 2000                    | 6                     | 260–320              | ≤20                 |
|                                            | 333                   | 340–360              | 20–29               |
| [122] Hellmann et al. 2008                 | —                     | 80–1500              | ≤0.1                |

Data source (in part): [39]



**Figure 13:** Viscosity of gaseous methane as a function of density for three isotherms. (Reproduced and modified from [121], with permission of ©2000 Old City Publishing granted by Dr. Ian Mellanby 10-May-2021.)

2.1.9 Surface Tension of Methane

Data for the surface tension of methane are summarized in Table 15 and illustrated in Figure 14.

Table 15: Surface tension of liquid methane.

| Temperature, K | Surface tension, mN/m |
|----------------|-----------------------|
| 97.0           | 15.64                 |
| 98.5           | 15.44                 |
| 99.1           | 15.17                 |
| 101.8          | 14.68                 |
| 103.0          | 14.38                 |
| 104.7          | 14.20                 |
| 106.5          | 13.90                 |
| 107.7          | 13.52                 |
| 108.7          | 13.50                 |
| 110.8          | 12.99                 |

Data source: [123]

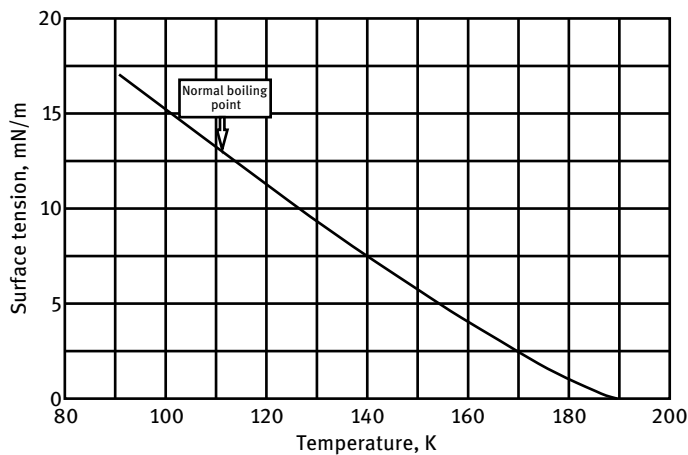


Figure 14: Surface tension of methane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

The differential method of capillary rise was used to determine the temperature dependence of the surface tension of liquid Kr, CH<sub>4</sub>, CD<sub>4</sub>, and LOX over the entire range of temperatures at which they exist in the liquid form at ambient pressure [124]. The results were tabulated and shown graphically along with the other experimental data. The results can be described by the van der Waals equation. The deviations from the



law of corresponding states were discussed for a large number of substances and reasons for the deviations were considered.

The surface tension,  $\sigma$ , versus temperature relations of liquefied gases Ar, Kr, CH<sub>4</sub>, CD<sub>4</sub>, O<sub>2</sub>, CF<sub>4</sub>, and H<sub>2</sub>, were determined by the capillary rise method [125]. The experimental results were used to test the validity of known empirical and semi-empirical equations relating surface tension  $\sigma$  to temperature  $T$ . Based on the free volume theory of liquids, a new equation for  $\sigma$  was derived. The surface tension values calculated from this equation agreed with experimental values only at temperatures below the boiling point.

The surface tension of liquid methane as a function of temperature can be expressed by the equation

$$\eta = 33.97 - 0.1891T$$

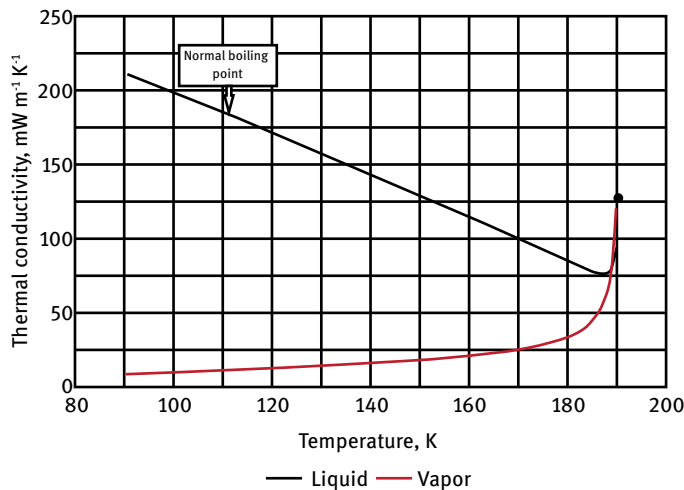
where  $\eta$  is the surface tension in mN/m and  $T$  is the temperature in kelvin [123].

Surface tension liquid acquisition devices can be used within a propellant tank in space to deliver single-phase liquid to the engine in low gravity. One type of liquid acquisition device is a screened gallery whereby a fine mesh screen acts as a “bubble filter” (bubble trap) and prevents the gas bubbles from passing through until a crucial pressure differential condition across the screen, called the bubble point, is reached. Surface tension propellant management devices (PMD) bubble point data were measured in liquid methane for stainless steel Dutch twill screens with mesh sizes of 325 × 2300 and 200 × 1400 wires per inch [126]. Data were presented for both saturated and sub-cooled liquid methane, and were compared with predicted values.

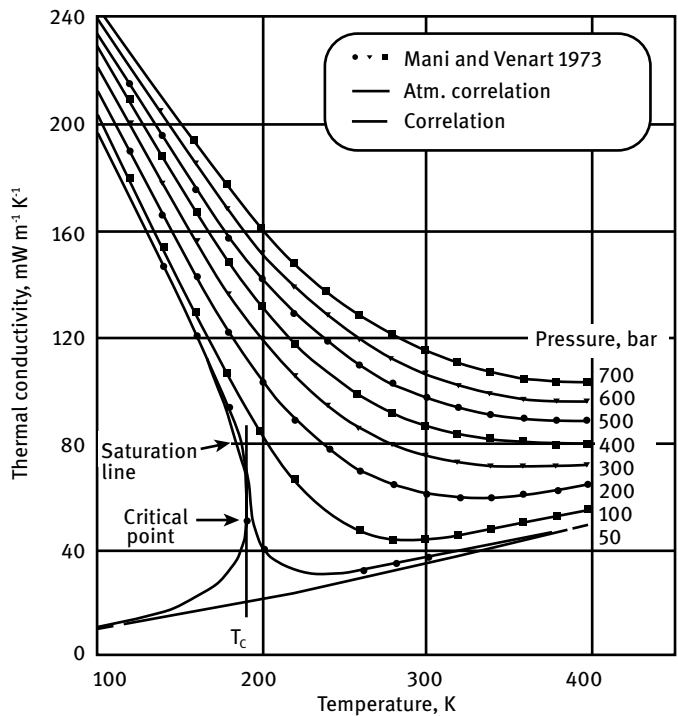
### 2.1.10 Thermal Conductivity of Methane

The thermal conductivity of methane under saturation pressure conditions is illustrated in Figure 15.

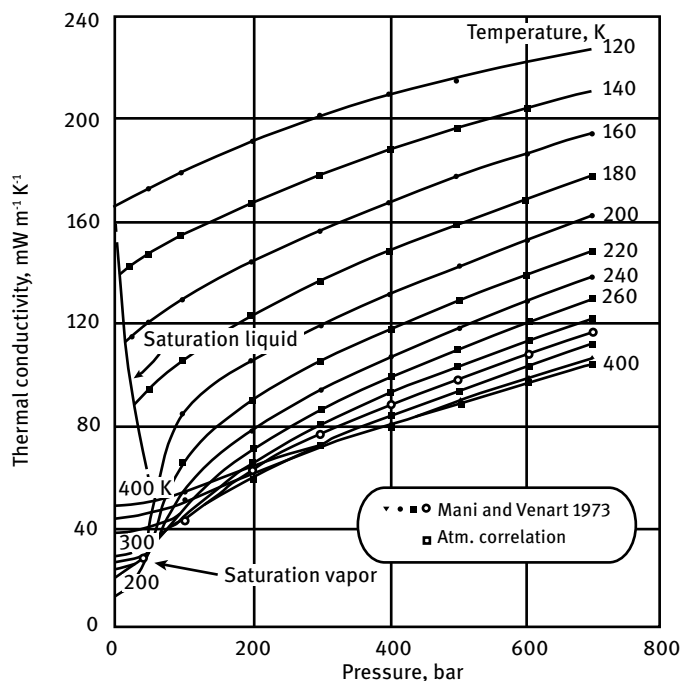
The thermal conductivity of methane was measured in the liquid and dense gaseous states using an absolute transient hot wire apparatus at temperatures between 120 and 400 K and at pressures ranging from 25 to 700 bar, as illustrated in Figures 16 and 17 [127]. Maximum uncertainty in the results due to systematic and random errors in the apparatus and the measurement techniques was less than 1%. Gas-chromatographic analysis of methane samples showed 99.33% methane, 0.56% nitrogen, ethane, and traces of propane. Although several investigators have reported data, very few have covered wide ranges of temperature and pressure. The method used for the present measurements was the solution of the transient true problem for an infinite source of constant heat generation, situated in an unbounded isotropic opaque fluid, initially at local thermodynamic equilibrium. A fine vertical platinum (25  $\mu$ m diameter) wire immersed in the fluid was heated electrically.



**Figure 15:** Thermal conductivity of methane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)



**Figure 16:** Isobars of thermal conductivity of liquid methane as a function of temperature. (Reprinted and modified from [127], with permission by ©1973 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)



**Figure 17:** Isotherms of thermal conductivity of liquid methane as a function of pressure. (Reprinted and modified from [127], with permission by ©1973 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

The temperature transient of this hot wire for large values of dimensionless time was approximated. The temperature rise at the surface of the wire was measured as a function of time. The thermal conductivity may be obtained after correcting for the effects of the finite heat capacity of the wire, non-constant heat generation parasitic heat losses, and radiation (both surface and fluid). Outside the critical region the thermal conductivity of both liquid and dense gaseous methane increased with density and temperature. An enhancement of  $k$  has been observed as the temperature and density approached their critical values. A pre-freezing anomaly is suspected at low temperatures and higher densities in the vicinity of the triple point. The density correlation of the data seems to confirm the existence of the theoretically predicted logarithmic density dependence of thermal conductivity. Table 16 gives a summary of literature sources for thermal conductivity data for methane, arranged in chronological order.

**Table 16:** Sources of thermal conductivity data for methane at elevated pressures.

| References                               | Number of data points | Temperature range, K | Pressure range, Mpa |
|------------------------------------------|-----------------------|----------------------|---------------------|
| [128] Ikenberry and Rice 1963            | 43                    | 99–230               | 0.2–31              |
| [129] Sokolova and Golubev 1967          | 445                   | 109–240              | 0.1–50              |
| [130] Le Neindre et al. 1969             | 193                   | 298–726              | 0.1–125             |
| [131] Tufeu, Le Neindre, and Bury 1969   | 193                   | 298–726              | 0.1–105             |
| [119] Hanley, McCarty, and Haynes 1975   | —                     | 95–400               | 0.1–50              |
| [108] Hanley, Haynes, and McCarty 1977   | —                     | 95–500               | ≤50                 |
| [132] Clifford, Kestin, and Wakeham 1979 | 33                    | 300                  | 1.6–35              |
| [133] Assael and Wakeham 1981            | 13                    | 307                  | 1.8–9.3             |
| [134] Yorizane et al. 1983               | 32                    | 298–323              | 0.1–20              |
| [135] Prasad, Mani, and Venart 1984      | 180                   | 120–400              | 2.6–70              |
| [136] Roder 1984a; [137] Roder 1984b     | 895                   | 110–310              | 0.3–70              |
| [138] Zheng et al. 1984                  | 19                    | 299                  | 0.1–16              |
| [139] Mardolcar and Nieto de Castro 1987 | 37                    | 110–180              | 0.2–10              |
| [140] Patek and Klomfar 2002             | —                     | 290–425              | 0.1–15              |
| [122, 141] Hellmann et al. 2009          | —                     | 80–1500              | —                   |
| [142] Liang and Tsai 2010                | —                     | 200–900              | 0.1                 |

Data source (in part): [39]

The thermal conductivity of methane can be correlated by the equation

$$\lambda(\rho, T) = \lambda_0(T) + \lambda_1(T)\rho + \Delta\lambda'(\rho, T)$$

where  $\lambda_0$  is the thermal conductivity of the dilute gas, the term  $\lambda_1$  is the first density correction for the moderately dense gas, given by the empirical expression

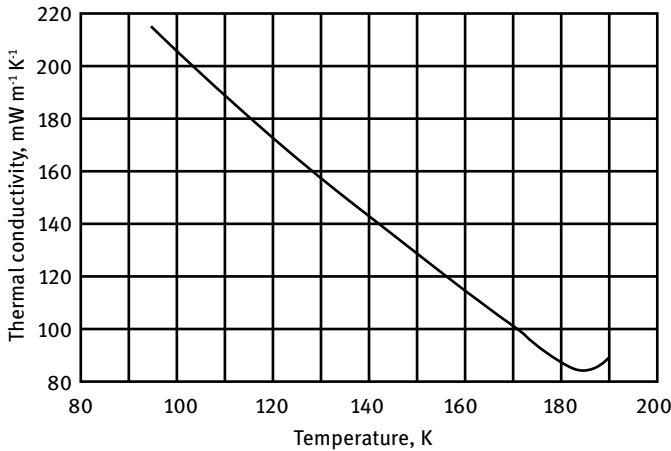
$$\lambda_1(T) = A + B \left[ C - \ln \left( \frac{T}{F} \right) \right]^2$$

where A, B, and C are constants and  $F = \epsilon/k = 168.0$  K where  $\epsilon$  is the energy parameter of the methane pair potential function and  $k$  is the Boltzmann constant. The term  $\Delta\lambda'(\rho, T)$  is expressed empirically by a complicated, empirical equation with many parameters [108, 119]. Similar equations have been derived for viscosity. Calculated thermal conductivity data were tabulated for temperatures between 95 and 500 K and pressures between 0.1 and 50 MPa. Table 17 gives the thermal conductivity for the saturated liquid at saturation pressure. The same data are graphed in Figure 18 for an easy overview.

**Table 17:** Thermal conductivity and density of liquid methane along the saturation line.

| Temperature Density |        |       | Thermal conductivity             |                                                   |
|---------------------|--------|-------|----------------------------------|---------------------------------------------------|
| K                   | mol/L  | g/mL  | $\text{mW m}^{-1} \text{K}^{-1}$ | $\text{kcal h}^{-1} \text{m}^{-1} \text{°C}^{-1}$ |
| 95                  | 27.789 | 0.446 | 215                              | 0.185                                             |
| 100                 | 27.367 | 0.439 | 206                              | 0.177                                             |
| 105                 | 26.934 | 0.432 | 197                              | 0.170                                             |
| 110                 | 26.491 | 0.425 | 189                              | 0.163                                             |
| 115                 | 26.035 | 0.418 | 181                              | 0.156                                             |
| 120                 | 25.566 | 0.410 | 173                              | 0.149                                             |
| 125                 | 25.081 | 0.402 | 165                              | 0.142                                             |
| 130                 | 24.578 | 0.394 | 158                              | 0.136                                             |
| 135                 | 24.055 | 0.386 | 150                              | 0.129                                             |
| 140                 | 23.508 | 0.377 | 143                              | 0.123                                             |
| 145                 | 22.932 | 0.368 | 136                              | 0.117                                             |
| 150                 | 22.322 | 0.358 | 129                              | 0.111                                             |
| 155                 | 21.672 | 0.348 | 122                              | 0.105                                             |
| 160                 | 20.971 | 0.336 | 115                              | 0.099                                             |
| 165                 | 20.206 | 0.324 | 108                              | 0.093                                             |
| 170                 | 19.356 | 0.311 | 101                              | 0.087                                             |
| 175                 | 18.386 | 0.295 | 94                               | 0.081                                             |
| 180                 | 17.226 | 0.276 | 88                               | 0.076                                             |
| 185                 | 15.690 | 0.252 | 84                               | 0.072                                             |
| 190                 | 12.485 | 0.200 | 89                               | 0.077                                             |

Data source: [108]



**Figure 18:** Thermal conductivity of liquid methane along the saturation line. (Image created by Schmidt 2020 based on data from [108].)

#### 2.1.10.1 Thermal Conductivity of Methane in the Supercritical State

The thermal conductivity of methane was measured at temperatures from 308 K down to 190.585 K, which is just 21 mK above the critical temperature, and at densities up to 14 mol/L [143]. The data were obtained with a guarded parallel-plate cell with a cryostat that was built especially for measurements in the critical region of methane. The experimental data had greater accuracy than those reported previously in the literature and enabled an examination of the validity of the currently available theoretical description of the asymptotic and non-asymptotic behavior of the thermal conductivity of fluids in the critical region. Equations for the thermal conductivity of methane within a wide range of temperatures and densities were presented.

Similar data were obtained for an equimolar mixture of methane and ethane very close to the critical point and confirmed that the thermal conductivity of a mixture does not diverge at the vapor-liquid critical point but crosses over to a finite limiting behavior at the critical point [144, 145]. An extension of the mode-coupling theory for dynamic critical phenomena in mixtures gave a good quantitative description of the experimental thermal conductivity data.

The conditions of methane flowing through the cooling jacket of a liquid rocket engine are close to its critical point, complicating cooling analysis. An open-source computational fluid dynamics (CFD) method for analysis of methane cooling channels was validated with experimental data, showing an accuracy within 20 K for wall temperature and 10% for pressure drop [146, 147]. It was shown that the turbulence model had only a limited impact on the simulation results and that the wall function approach generated valid results. A cooling channel analysis was performed to compare two thrust chamber materials. A traditional copper alloy was compared with aluminum as a chamber material for a small moderate-pressure oxygen/methane rocket engine. The analyses showed that aluminum is a feasible chamber material only if a thermal barrier coating is applied. A significantly higher cooling channel pressure drop was incurred for an aluminum chamber than for a copper chamber owing to the lower allowable temperature. See also [109].

#### 2.1.10.2 Thermal Diffusivity of Methane

Thermal diffusivity is defined as thermal conductivity divided by density and specific heat capacity at a constant pressure. The thermal diffusivity of methane along the critical isochore at temperatures to within 0.001 K of the critical temperature was measured by Rayleigh light scattering [148]. The results, corrected to zero wave vector, were compared with values from an expression introduced previously. Agreement was within 10%. Some possible reasons for this discrepancy were given.

#### 2.1.11 Heat Transfer Coefficient of Liquid Methane

The knowledge of the heat transfer coefficient of liquid methane is necessary for the design of cooling systems in regeneratively cooled rocket engines. The modeling of liq-

liquid methane coolant flow is a challenging task because of its particular features, such as the high wall temperature gradient, the high Reynolds number, and the three-dimensional geometry of the passages. In the case of methane as a coolant, a further complication is the trans-critical operating condition of the fluid. In this thermodynamic regime large changes in the fluid properties can greatly influence the coolant flow-field and the heat transfer.

High-pressure methane cooling and coking characteristics were evaluated using stainless-steel-heated tubes at methane bulk temperatures and coolant wall temperatures typical of advanced engine operation, except at lower heat fluxes as limited by the tube material [149, 150]. As expected, no coking was observed. However, coking evaluations need to be conducted with a copper-base surface exposed to the methane coolant at higher heat fluxes approaching those of future high chamber pressure engines.

The heat transfer to liquid methane was studied in a liquid methane cooled thrust chamber [151]. An injector with 18 coaxial elements and two types of combustors, which had the same chamber contour except for chamber length and coolant geometry, were employed for the tests. The chamber pressure was 3.5 to 9.2 MPa and the mixture ratio was 2.7 to 5.2. The characteristic velocity  $c^*$  efficiency achieved was 90 to 95%. The maximum heat flux loaded to the nozzle throat region was approximately 80 MW/m<sup>2</sup>.

A series of heat transfer tests with methane was conducted at pressures of 0.5–30 MPa, flow velocities of 2–106 m/s, and heat fluxes up to 66 MW/m<sup>2</sup> in stainless-steel and copper tubes, and the deposit formation rates for kerosene in tubes were measured [152]. Forced convective heat transfer correlations were obtained for liquid methane, propane, and kerosene, up to extreme heat fluxes at which test tubes burnt out. The test results indicated that heat transfer coefficients of methane and propane decreased at high wall temperatures. No coking was detected in methane tests.

In order to compute methane cooling performance and to solve the thermal problem, a one-dimensional FORTRAN code has been developed [153]. With the integration of CHEMKIN II subroutines, starting from propellant temperatures and mixture ratio the code is capable of calculating chemical equilibrium along the entire thrust chamber (combustion chamber and nozzle). In one example of a cooling system design, methane entered the cooling circuit as a liquid state and owing to heat exchange its temperature rose and its density decreased. However, because pressure is greater than critical pressure ( $P_c = 46.5$  bar), no phase change occurs and methane undergoes supercritical transition ( $T_c = 190.4$  K). In order to predict wall temperatures and to solve the thermal problem, properties of liquid and supercritical methane must be provided.

Measurements were carried out to investigate the pool-boiling behaviors of pure methane and three binary mixtures of methane + ethane, methane + propane, and methane + isobutane, as well as a multi-component mixture of methane, ethane, propane, and isobutane at cryogenic temperatures [154, 155]. The measurements

were performed in a descending heat flux procedure ranging from 250 to 30 kW/m<sup>2</sup> at a fixed pressure of 0.13 MPa. Comprehensive measured data were compared with some existing correlations. The deviations between the measured data and the predicted results were within a  $\pm 25\%$  range.

Liquid methane, which is used for regenerative cooling of rocket thrust chambers can flow in channels at supercritical pressures and in the neighborhood of pseudocritical temperature (near-critical fluid), for instance, in liquid-oxygen/liquid-methane rocket engines with chamber pressures greater than about 50 bar [156]. When the fluid is in such a near-critical condition, deterioration in heat transfer can occur if the heat transfer level is higher than a threshold value. Aiming to improve flow prediction capabilities for the design of such systems, numerical calculations of near-critical fluids flowing in uniformly heated straight tubes were conducted. After code validation against experimental data of near-critical-hydrogen flow, numerical simulations of near-critical-methane flow in heated tubes were carried out, each characterized by a different wall heat flux. The near-critical methane flow condition that exhibited the worst heat transfer deterioration was identified.

Heat transfer measurements in flowing liquid and two-phase methane were conducted at the NASA Glenn Research Center Heated Tube Facility using resistively heated tube sections to simulate conditions encountered in regeneratively cooled rocket engines [157]. Several test runs were conducted using three different diameter Inconel 600 tubes, with nominal inner diameters of 0.57, 1.37, and 1.90 mm (0.0225, 0.054, and 0.075 in). The mass flow rate varied from 2.3 to 31.7 g/s (0.005 to 0.07 lb<sub>m</sub>/s). As the focus was on pressure-fed engines for LOX/LCH<sub>4</sub>, the average test section outlet pressures were targeted to be 1.38 or 3.45 MPa (200 or 500 psia). The heat flux was incrementally increased for each test condition while the test section wall temperatures were monitored. A maximum average heat flux of 1013 W/cm<sup>2</sup> (6.2 BTU in<sup>-2</sup>s<sup>-1</sup>) was achieved and, at times, the temperatures of the test sections reached in excess of 1000 K (1800 °R). The primary objective of the tests was to produce heat transfer correlations for methane in the liquid and two-phase regime. For two-phase flow testing, the critical heat flux values were determined where the fluid transitions from nucleate boiling to film boiling. A secondary goal of the testing was to measure system pressure drops in the two-phase regime.

A numerical study of the turbulent convective heat transfer of cryogenic methane used a horizontal minitube under supercritical pressure and data analysis was based on a complete set of conservation equations and accurate evaluations of the thermophysical properties [158]. The numerical investigations focused on a fundamental understanding of the many key parameters, including the inlet pressure, wall heat flux, inlet velocity, inlet temperature, on the supercritical heat transfer phenomena, and the variations of the Nusselt number. Results indicated that bulk property variations at the pseudocritical temperature under a supercritical pressure would cause local heat transfer deterioration. Increasing the inlet methane pressure would result in improved heat transfer at supercritical pressures, particularly under a high wall heat flux, i.e.,



7 MW/m<sup>2</sup>. The conventional empirical expression, i.e., the Gnielinski equation, cannot be used for the heat transfer predictions of cryogenic methane at supercritical pressures. Instead, a modified heat transfer expression that is applicable to supercritical cryogenic methane was successfully established in this study.

A heat transfer test rig was built with the goal of characterizing the heat transfer characteristics of liquid methane as it passes through a heated channel in the regenerative cooling jacket of a rocket engine [159]. The test rig was designed to replicate the conditions in a regenerative cooling channel in a rocket engine. Experiments were first completed using liquid nitrogen in vacuum, resulting in temperature data that showed evidence for boiling in the channel, causing vapor lock.

The LOX/methane engine firing tests were conducted with a thoroughly instrumented engine with many measurement points [160]. Measurements were made to verify the accuracy of prediction models for coolant pressure drop and increase in coolant temperature. A semi-empirical model predicted a pressure drop and temperature increase correctly, but was not able to correctly predict local temperatures around the nozzle throat.

Three-dimensional numerical analyses have been conducted for turbulent supercritical heat transfer of cryogenic methane flowing in a rectangular engine cooling channel with asymmetric heating on the top channel surface, investigating the effects of operational pressure, wall heat flux, and channel geometric ratio on supercritical heat transfer rates [161]. The results indicated that the operational supercritical pressure and wall heat flux would exert significant influences on supercritical heat transfer through their strong effects on physical property variations. Heat-transfer deterioration could occur during supercritical heat transfer, owing to property variation anomalies near the pseudocritical temperature in a near-wall zone. Increasing the operational supercritical pressure would alleviate heat-transfer deterioration. It was found that a shallow cooling channel performed well for supercritical heat transfer but suffered severe pressure loss. The Bishop heat-transfer correlation was tested to be applicable for supercritical heat-transfer predictions of cryogenic methane under certain conditions.

Numerical simulations of trans-critical methane flow-field in an asymmetrically heated rectangular channel with a high aspect ratio and strong wall temperature differences were carried out by a suitable CFD solver and compared with supercritical methane flow-fields [162]. The aspect ratio effect on methane flow was analyzed by comparison of four different rectangular cooling channel geometries with fixed hydraulic diameter and coolant flows with the same mass flow-rate per unit area that influenced fluid-cooling performance and pressure loss.

Often approximated as pure methane, liquefied natural gas (LNG) is a mixture of methane, other heavier hydrocarbons, and nitrogen. If LNG is to be used in a regeneratively cooled liquid rocket engine, knowledge of the thermodynamic and heat-transfer characteristics when it flows into the cooling channels is of primary importance. A parametric study was carried out to understand how the composition

of LNG can influence the flow in the cooling channels, considering different LNG compositions and heat flux levels [163]. The main concern was chemical composition-induced changes in the pressure drop and cooling capabilities, which are the aspects that have to be controlled in a regenerative cooling system.

The characteristics of film cooling in a LOX/LCH<sub>4</sub> subscale rocket engine chamber with multi-injector elements and two kinds of film-cooling slot dimensions were investigated using a calorimeter chamber in experiments and simulations, in which the finite rate chemistry with a reduced O<sub>2</sub>/CH<sub>4</sub> reaction mechanism was taken into account [164, 165]. The computed wall heat flux and pressure distributions were compared with the experimental results, which overall showed good agreement. A large slot dimension was shown to induce mixing with core flow. This mixing caused a low heat-flux distribution near the face plate along with high combustion efficiency.

The heat-transfer characteristics of liquid methane were investigated as part of the design of a methane-condensing mobile unit to supply the laboratory with liquid methane, including heat-transfer coefficient behavior, non-dimensional correlations, different flow conditions, varied inlet conditions, and varied heat flux for a subscale test article applicable to a regenerative cooled rocket engine cooling channel [166]. Test conditions ranged from 1.03 to 2.07 MPa (150 to 300 psi) supply tank pressure, and heat fluxes of 3.9 to 19 MW/m<sup>2</sup> (2.39 to 11.6 BTU in<sup>-2</sup> s<sup>-1</sup>) at turbulent Reynolds numbers (15000 to 360000), including transient and steady-state heat-transfer response.

Measurements of the steady-state heat-transfer characteristics of liquid methane (LCH<sub>4</sub>) under forced convection were made in a 1.8 × 1.8 mm square channel representative of those found in regeneratively cooled rocket engines [167–169]. A High Heat Flux Test Facility was designed to handle cryogenic fluids while maintaining high heat fluxes between 3.3 and 20.0 MW/m<sup>2</sup>. The average Nusselt number Nu<sub>D</sub> reached as high as 336 and the average Reynolds numbers Re<sub>D</sub> were between 1.9 × 10<sup>4</sup> and 1.6 × 10<sup>5</sup>. A Nusselt number correlation (Nu<sub>0</sub>) used by the NASA Rocketdyne III computer program demonstrated an overprediction inaccuracy primarily with Reynolds numbers within the range 6.0 × 10<sup>4</sup> to 1 × 10<sup>5</sup>, whereas the majority of the overpredictions were between 1 × 10<sup>5</sup> and 1.1 × 10<sup>5</sup>.

The expected wall and coolant behavior of a test article simulating rocket engine cooling channels was analyzed by a three-dimensional conjugate heat transfer model [170]. Different coolant pressure and surface roughness levels were considered in order to understand their influence on the heat-transfer capability of the cooling system. Results showed that heat-transfer deterioration may occur in principle when methane is operated under near-critical conditions. The resultant wall temperature profile peak decreased with increasing coolant pressure and increasing surface roughness.

The steady-state heat transfer characteristics under internal forced convection of liquid methane were experimentally investigated using a rectangular channel with a cross section of 1.8 × 4.1 mm and square channels with a cross section of 3.2 × 3.2 mm [171]. Three square channels had surface finishes typical of milled channels

and another three square channels had internal longitudinal fins. A high heat flux test facility capable of handling cryogenic temperatures, developed for the purpose of simulating the high heat load conditions representative of regeneratively cooled rocket engines, was used in this study. Subcooled film-boiling phenomena were discovered for all the channels tested in this study. Film-boiling onset at critical heat flux correlated with the boiling number  $Bo \sim 0.1$ . The convective Nusselt number followed predicted trends for Reynolds numbers with a wall temperature correction for both the boiling and non-boiling regimes.

A test apparatus has been specifically designed for the purposes of investigating methane heat transfer behavior inside rocket engine cooling channels [172]. The apparatus was composed of a copper-alloy block warmed up by cartridge heaters and of a single channel with rectangular cross section, which was fed with a trans-critical methane flow. Steady-state conditions and channel dimensions were representative of a typical rocket engine cooling channel. Several tests have been conducted with mass flow rates ranging from 10 to 25 g/s, exit pressures from 60 to 150 bar, and inlet temperatures of about 130–140 K. The maximum provided heat flux at the bottom of the channel was  $20 \text{ MW/m}^2$ . Measurements of the channel inlet and exit temperature and pressure, mass flow rate, and wall temperature at different channel locations have provided useful data for the evaluation of heat transfer and pressure loss. In particular, the channel surface roughness induced by the manufacturing process has been estimated and a peculiar Nusselt number correlation has been obtained. This correlation was suitable for describing the thermal behavior of the rectangular cooling channel, including both methane flow and wall.

Methane heat-transfer deterioration can occur in the regenerative cooling channels of LOX/LCH<sub>4</sub> rocket engines with chamber pressures higher than about 50 bar. Aiming to improve the prediction capabilities for the design of cooling systems, a Nusselt number correlation able to describe the convective heat-transfer characteristics of supercritical flow exhibiting deterioration and with negligible buoyancy effects was derived using data from numerical simulations [173]. The adopted numerical solver of the Navier-Stokes equations was first validated against experimental data of near-critical hydrogen in heated tubes and then used to collect heat-transfer data of supercritical methane in a heated tube for different levels of pressure, temperature, and mass flux.

If a cryogenic fluid is used in the cooling jackets of a rocket engine, the coolant may behave as a trans-critical fluid: it may be injected as a liquid and, depending on the heat exchanged with the thrust chamber hot gases, may experience a pseudo-phase change. Finally, it comes out and is sent to the combustion chamber, located downstream, as a supercritical vapor. A breadboard test apparatus was equipped with a rectangular single channel, characterized by dimensions representative of typical rocket engine cooling channels [174]. Inlet temperature and pressure values, ranging from about 120 to 140 K, and from about 10 to 17 MPa respectively were varied one step at a time. A three-dimensional model, including inlet and outlet interfaces showed

very low discrepancies when compared with experimental data. Simulations enabled the description of the thermal stratification as well as the “thermal deterioration” of methane inside a cooling jacket-like channel under supercritical conditions.

A 3D fluid-structural coupled computational methodology was developed to predict the thermal and structural responses of the thrust chamber wall in a LOX/LCH<sub>4</sub> rocket engine under cyclic operating conditions [175]. The thermal and mechanical loads were determined by a validated 3D finite volume fluid-thermal coupled computational method. With the specified loads, a non-linear thermal-structural finite element analysis was applied to obtain the 3D thermal and structural responses.

A study of the non-uniform flow and heat transfer of supercritical cryogenic methane in a heated horizontal circular tube indicated that the peak value of the heat-transfer coefficient appeared near the vicinity of the pseudo-critical point [176]. The Reynolds number monotonically increased with the increase in bulk fluid temperature. However, the Prandtl number exhibited both peak and minima values. Compared with mass fluxes, operating pressures had less of an influence on the heat-transfer performance. Flow stratification phenomena and lateral secondary flows were developed as a result of the combined interaction of buoyancy and gravity. The “flow acceleration” caused by the variation of bulk fluid density had an important effect on the decrease in heat-transfer capacity. Further analysis demonstrated that the Blasius and Han models were able to predict the pressure drop and heat transfer of supercritical cryogenic methane.

Thermal behavior and heat-transfer deterioration of trans-critical methane as well as the fluid state change in regenerative cooling with straight or curved rectangular channels were studied numerically [177]. Simulations were conducted with a finite-volume based CFD solver utilizing reliable turbulence models and thermo-fluidic relations in trans-critical conditions. The known experimental and numerical results of hydrogen inside a heated tube reported in the literature were used for validation of the model. The effects of mass flow rate, outlet pressure, wall temperature, surface roughness, and the channel geometry on the thermal behavior of the coolant fluid were studied in detail. According to the results, variations in the slope of the transport property curves and the inflection point in the density distribution of the coolant flow were proposed as criteria for the recognition of the heat-transfer deterioration and trans-critical regions respectively. The outlet pressure and surface roughness had negligible effects on both methane heat transfer deterioration and trans-critical regions in contrast to the channel curvature, mass flow rate, and wall temperature.

The conjugate heat transfer of liquid methane coolant inside a rectangular channel was studied and the related Nusselt correlations were improved [178]. The compressible methane flow was assumed to enter the cooling channel at supercritical pressure and subcritical temperature such that the coolant flow absorbs heat from the heated walls and exits the channel with a supercritical temperature. An equation solver was developed employing a Semi-Implicit Method for Pressure-Linked Equations-Consistent algorithm accompanied by the appropriate thermodynamic

and transport property relations for the supercritical conditions of the methane coolant. The solver was validated with the experimental data found in the open literature. The behavior of pseudo-critical temperature and density versus pressure were studied and new relations were proposed. The accuracy of different Nusselt relations for estimating the heat-transfer coefficient of methane at supercritical pressures was evaluated. The variation of thermo-fluidic parameter correction factors (i.e., non-dimensional density, temperature, isobaric-specific heat, viscosity, and thermal conductivity) through the cooling channel was investigated. The current Nusselt relations were developed, and improved correlations were proposed for methane at the supercritical pressure inside a rectangular channel. The accuracy of the modified correlations was studied at different outlet pressures, heat transfer rates, and mass flow rates.

The effect of surface roughness on liquid methane ( $\text{LCH}_4$ ) convective heat transfer performance of traditionally and additively manufactured rocket engine cooling channels was studied by conducting high heat flux methane convective cooling tests using a diagnostic system designed and developed to investigate the steady-state heat transfer of cryogenic propellants [179]. This facility was designed to measure the one-dimensional and asymmetric heat flow performance as experienced in regeneratively cooled liquid rocket engine cooling channels. The experiments were performed under the influence of internal forced convection to better simulate the boiling performance in a rocket engine's environment. A total of four samples made of Inconel 625 were tested. Square channels with a cross-section of  $3.2 \times 3.2$  mm and various roughness values were fabricated using conventional milling and advanced 3D printing technologies. Some findings between the experimental Reynolds number and Nusselt number showed that the channels with the  $3.2\text{-}\mu\text{m}$  and  $6.3\text{-}\mu\text{m}$  roughness did not differ significantly in comparison with the smoothest channel ( $0.8\text{-}\mu\text{m}$ ). An increase in heat transfer of more than 100% could be observed with the roughest channel ( $12.5\text{-}\mu\text{m}$ ) during the convective subcooled flow of methane.

### 2.1.12 Critical Constants of Methane

Critical-point measurements reported by various sources are summarized in Table 18.

**Table 18:** Critical point conditions of methane.

| Critical temperature  |              | Critical pressure      |                    | Critical volume | References |
|-----------------------|--------------|------------------------|--------------------|-----------------|------------|
| SI units              | Other units  | SI units               | Other units        | SI units        |            |
| $190.6 \pm 0.3$ K     | $-82.55$ °C  | $46.1 \pm 0.3$ bar     | $45.5 \pm 0.3$ atm | —               | [45]       |
| 190.53 K              | $-82.62$ °C  | 4.596 MPa              | 45.356 atm         | —               | [180]      |
| $190.564 \pm 0.015$ K | $-82.586$ °C | $4.599 \pm 0.003$ MPa  | 45.39 atm          | 0.09860 L/mol   | [9]        |
| 190.53 K              | $-82.62$ °C  | 4.59797 MPa            | 45.378 atm         | 0.09852 L/mol   | [94]       |
| $190.551 \pm 0.01$ K  | $-82.599$ °C | $4.5992 \pm 0.003$ MPa | 45.39 atm          | 0.09863 L/mol   | [39]       |

### 2.1.13 Solubility and Miscibility of Methane

#### 2.1.13.1 Pressurant Gas Solubility

Liquid methane is usually pumped from the propellant tanks into the rocket engine by turbo pumps and not pressure-fed. However, the tanks need to be pressurized with hot methane or an inert gas to provide sufficient net positive suction head to prevent cavitation in the inlet portion and on the blade tips of the pumps. The only gas suitable for the pressurization of liquid methane is helium.

The solubility of helium in liquid methane, liquid hydrogen, and liquid oxygen was described by empirical correlations derived from published experimental data for the mol fraction of these pressurant gases in the liquid phase as a function of temperature and pressure [181]. The correlations were developed to yield accurate estimates of the mol fraction of the pressurant gas in cryogenic liquids at temperature and pressures of interest to rocket propulsion engineers. The helium solubility correlations were of the form

$$\chi = p^* \exp(a + bp^*)$$

where  $\chi$  is the mol fraction solubility of the solute (helium) in the solvent liquid,  $p^*$  is a dimensionless pressure defined as  $p^* = (P - P_0)/P_{\text{REF}}$ , where  $P$  is the total pressure (from the pressurant gas and the vapor pressure of the liquid),  $P_0$  is the saturated vapor pressure of the pure liquid solvent at temperature  $T$ ,  $P_{\text{REF}}$  is a reference pressure defined as equal to 1 MPa, and  $a$  and  $b$  empirically determined, temperature-dependent functions. The coefficient  $b_0$  was determined from the isotherms to be  $b_0 = -0.015$ . For  $b = 0$ , the equation assumes the form of Henry's law. In a graph showing the mol fraction  $\ln(\chi/p^*)$  as a function of pressure for nine different temperatures between 93.2 and 173.2 K, the curves are linear and almost level, indicating minimum dependence of  $\chi$  on pressure. A graph showing the mol fraction  $\ln(\chi/p^*)$  as a function of temperature demonstrated an almost linear increase of  $\ln(\chi/p^*)$  with temperature. More specifically, the equation for the temperature dependence of  $\chi$  based on empirical data becomes

$$\chi = p^* \exp(-13.76 + 0.0748 \times T/\text{K} - 0.000137 \times T^2/\text{K}^2 - 0.015p^*)$$

where the terms in parentheses need to be divided by kelvin and kelvin<sup>2</sup> to make them dimensionless. The helium mol fraction solubility in liquid methane is less than 0.3% in typical propulsion system applications, and the times to reach equilibrium are very long in the absence of active mixing. Considering as an example a tank at the normal boiling point temperature of liquid methane, 111.5 K, and a total pressure of 1.72 MPa (250 psia,  $p^* = 1.62$ ), the equilibrium mol fraction solubility calculated from the above equation is  $\chi = 0.13 \pm 0.006\%$ .

The solubilities of oxygen, argon, carbon monoxide, nitrogen, neon, hydrogen, and helium in liquid methane at temperatures between 90 and 112 K were measured and expressed in logarithmic equations [182]. The solubilities of these gases in liquid methane decrease in the order in which they are listed. The rates of solution of gases

in liquefied natural gas are very high. Only the least soluble gases, neon, hydrogen, and helium, can be used as fuel system pressurants if liquefied natural gas is to be used in aircraft or rockets.

Oxygen, which has a normal boiling temperature of 90 K, would continuously condense in, and be miscible with, liquid methane in all proportions, with liquid methane maintained at 90 K. In a study of the solubility of methane in liquid oxygen, it was concluded that these formed a near-ideal solution at 90 K. Such mixtures, although detonable, have been proposed as monopropellants.

Helium dissolved and saturated in liquid methane may be released as bubbles when the pressure is suddenly lowered and bubbles and two-phase flow interfere with flow rate measurements. The kinetics of the spontaneous boiling of liquid methane saturated with helium has been studied in experiments on measuring the lifetime of the superheated liquid [183]. The temperature dependence of nucleation frequency  $J$  has been determined in a range from  $10^4$  to  $10^8 \text{ s}^{-1} \text{ m}^{-3}$  at pressures of  $P = 1.6$  and  $2.0 \text{ MPa}$  and helium concentrations in liquid methane  $\chi = 0.06$  and  $0.10 \text{ mol-}\%$ . The experimental results were compared with the data of the classical nucleation theory. As in the case of pure methane, the solution superheating temperatures reached in the experiments at  $J > 4 \times 10^6 \text{ s}^{-1} \text{ m}^{-3}$  appeared to be systematically lower (by  $0.6\text{--}1.0 \text{ K}$ ) than their theoretical values. It was shown that the discrepancy between the theoretical and experimental data is associated with the size dependence of the surface tension at the critical bubble-solution interface. See also Sinor [184] and Heck and Hiza [185].

One might also consider hydrogen as a pressurant gas for liquid methane, but it is more soluble than helium [186, 187]. The solubility of helium in liquid methane at 90.3 and 106 K was measured at pressures up to 160 atm. The helium solubility passed through a maximum of 2.7, 5.5, and 6.9 MPa (400, 800, and 1000 psia), within the range of temperatures studied.

### 2.1.13.2 Diluent and Contaminant Solubility

Some nitrogen may be carried over from the production and liquefaction plant and remain dissolved in liquid methane [55]. The specification MIL-PRF-32207 allows 100 to 5000 ppm of nitrogen in the methane, depending on which purity grade is required.

Moisture in methane may precipitate as ice crystals and clog orifices and filter screens. The unexpectedly high solubility of  $\text{H}_2\text{O}$  in liquid methane ( $6.0 \times 10^{-5} \text{ mol}$  fraction) at its normal boiling point of 112 K was determined by using Fourier transform infrared (IR) spectroscopy [188]. The possibilities of experimental artefacts were eliminated via parallel experiments with  $\text{D}_2\text{O}$ . Methane is known to form hydrates at a high pressure, such as at the bottom of oceans. The specification MIL-PRF-32207 limits the allowable moisture content in methane gas to 0.5 to 1 ppm by volume.

### 2.1.14 Thermodynamic Properties of Methane

The thermodynamic properties of methane have been thoroughly investigated for almost a century and are referenced in numerous table works. Most of the published data are for gaseous methane and only relatively few data are for liquid or even solid methane [88, 189, 190].

Thermodynamic properties of methane were described in terms of an equation of state for the real fluid together with an empirical equation for the specific isochoric heat capacity of the ideal gas [92]. The equation of state had a form proposed by Bender with coefficients refitted to precise measurements. In the fluid state for temperatures from 90.68 K (triple-point temperature) to 625 K, densities below 0.46 kg/dm<sup>3</sup> (2.8 times critical density) and pressures below 500 bar, thermodynamic properties of methane were predicted to high accuracy, as shown by comparison with reliable experimental data. Only in the critical region was the accuracy slightly lower. Several equations for the calculation of thermodynamic properties were presented. A comprehensive table was included of the following properties thus calculated at the vapor-liquid coexistence boundary and in the homogeneous region: specific volume, specific enthalpy, specific entropy, velocity of sound, isentropic exponent, and fugacity.

The equation of state and heat capacity of methane were determined at temperatures from 148 to 298 K with pressures up to 1000 MPa following a new computational method [191]. This method was based on the stepwise construction of  $p$ - $T$  isochores starting from an experimental reference  $p$ - $p$  isotherm and using sound speeds in methane as a function of pressure and temperature, together with the experimental heat capacity data of methane at lower pressures. In the region of overlap, the calculated  $\rho p T$  data were found to be in good agreement, namely within 0.08%, with those obtained previously from the most accurate direct measurement reported in the literature.

#### 2.1.14.1 Heat Capacity of Methane

##### Heat Capacity of Liquid Methane

Only a few laboratories have published experimental measurements of heat capacities of methane in the saturation state. The experimental data of the heat capacity along the saturated liquid curve  $C_\sigma$  and of the heat capacity  $C_p$  are summarized in Table 19. The measured data for the isobaric heat capacity of liquid methane are listed in Table 20.

Figure 19 illustrates the heat capacity  $c_p$  of liquid and gaseous methane under saturation pressure conditions. The heat capacities of liquid and gaseous methane are very similar and both increase abruptly as the temperature approaches the critical temperature.

Specific heats of the liquid phase, along the coexistence (saturation) path, are useful for computing thermodynamic properties in compressed liquid states. Data for



**Table 19:** Summary of experimental data for the heat capacity of methane on the saturated liquid line.

| References                     | Number of data points | Temperature range, K |
|--------------------------------|-----------------------|----------------------|
| [192] Wiebe and Brevoort 1930  | 20                    | 97–188               |
| [50] Hestermans and White 1961 | 9                     | 115–188              |
| [54] Cutler and Morrison 1965  | 5                     | 94–107               |
| [193] Younglove 1974           | 66                    | 95–187               |
| [194] Syed et al. 2012         | 14                    | 111–173              |

Data source (in part): [48]

**Table 20:** Experimental isobaric heat capacities of liquid methane.

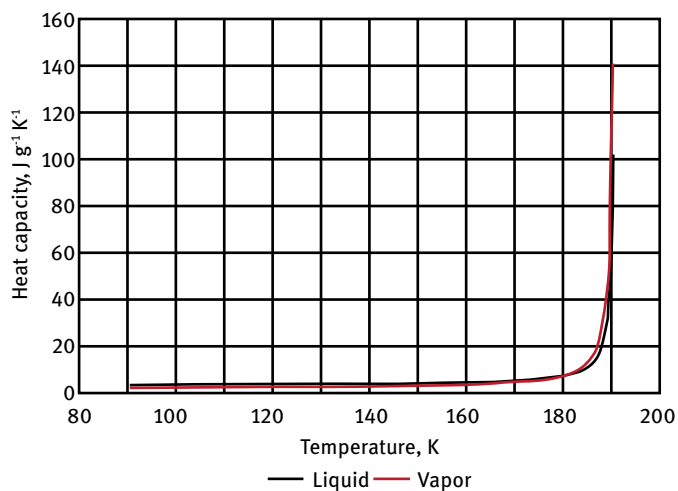
| Temperature<br>K | Pressure<br>MPa | Isobaric heat capacity <sup>a</sup> |                                     |                                     |                                       |
|------------------|-----------------|-------------------------------------|-------------------------------------|-------------------------------------|---------------------------------------|
|                  |                 | J g <sup>-1</sup> K <sup>-1</sup>   | cal g <sup>-1</sup> K <sup>-1</sup> | J mol <sup>-1</sup> K <sup>-1</sup> | cal mol <sup>-1</sup> K <sup>-1</sup> |
| 111.7            | 0.101           | Normal boiling point                |                                     |                                     |                                       |
| 108.15           | 4.23            | 3.391                               | 0.810                               | 54.402                              | 13.002                                |
| 118.15           | 4.27            | 3.462                               | 0.827                               | 55.541                              | 13.275                                |
| 128.15           | 4.33            | 3.555                               | 0.850                               | 57.033                              | 13.631                                |
| 143.15           | 4.35            | 3.701                               | 0.885                               | 59.375                              | 14.191                                |
| 153.15           | 4.34            | 3.942                               | 0.942                               | 63.242                              | 15.115                                |
| 163.15           | 4.39            | 4.220                               | 1.009                               | 67.701                              | 16.181                                |
| 173.15           | 4.38            | 4.854                               | 1.160                               | 77.873                              | 18.612                                |
| 108.15           | 6.30            | 3.373                               | 0.806                               | 54.113                              | 12.933                                |
| 118.15           | 6.35            | 3.435                               | 0.821                               | 55.108                              | 13.171                                |
| 128.15           | 6.40            | 3.532                               | 0.844                               | 56.664                              | 13.543                                |
| 153.15           | 6.34            | 3.801                               | 0.908                               | 60.979                              | 14.574                                |
| 163.15           | 6.47            | 4.021                               | 0.961                               | 64.509                              | 15.418                                |
| 173.15           | 6.45            | 4.424                               | 1.057                               | 70.974                              | 16.963                                |

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.5$  K for  $T < 220$  K,  $u(T) = 0.25$  K for  $T > 220$  K,  $u(p) = 35$  kPa, and combined expanded uncertainty  $Uc(c_p) = 0.02 \cdot c_p$  with a 95% level of confidence.

Data source: [194]

$C_\sigma$  were derived from observations on the two-phase, liquid-vapor system at constant volume by use of accurate PVT data for the two phases (Goodwin [69]). The data were shown in coordinates of  $C_\sigma u^e$  versus  $T$ , the weighted form used for least squares determination of coefficients in

$$C_\sigma = a + bu + \frac{c}{u^e}$$



**Figure 19:** Heat capacity  $c_p$  of liquid and gaseous methane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

where  $C_\sigma$  is the heat capacity in  $\text{J mol}^{-1}\text{K}^{-1}$ ,  $u$  is the reduced temperature  $(T_c - T)/(T_c - T_t)$ , and  $a$ ,  $b$ ,  $c$ , and  $\epsilon$  are constants:

$$a = 29.250$$

$$b = 5.560$$

$$c = 18.924$$

$$\epsilon = 0.55.$$

### Heat Capacity of Gaseous Methane

The ideal gas heat capacity can be derived from statistical mechanical models based on spectroscopic data. The constant pressure heat capacity of methane gas at 298.15 K and 1 bar is  $35.69 \text{ J mol}^{-1}\text{K}^{-1}$ . The gas phase heat capacity of methane as a function of temperature can be calculated from a Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1}\text{K}^{-1}$  and  $\tau$  is the temperature in kelvin divided by 1000 [45]. The constants A through E are listed in Table 21 for two different temperature ranges.

Isobaric heat capacity data of methane were measured, giving 58 data points within the ranges 121–251 K and 3.2–5 MPa [195].

**Table 21:** Constants for methane gas thermodynamic data calculations.

| Temperature range, K | 298–1300  | 1300–6000 |
|----------------------|-----------|-----------|
| A                    | −0.703029 | 85.81217  |
| B                    | 108.4773  | 11.26467  |
| C                    | −42.52157 | −2.114146 |
| D                    | 5.862788  | 0.138190  |
| E                    | 0.678565  | −26.42221 |
| F                    | −76.84376 | −153.5327 |
| G                    | 158.7163  | 224.4143  |
| H                    | −74.87310 | −74.87310 |

Data source: [45]

### 2.1.14.2 Heat of Combustion of Methane

Literature values for the upper heat of combustion of methane are summarized in Table 22. Heat of combustion data for methane from various sources agree fairly well. This is a well-established procedure. See also [196].

**Table 22:** Upper heat of combustion of methane gas.

| SI units             | Other units            | References |
|----------------------|------------------------|------------|
| 890.71 ± 0.38 kJ/mol | 212.88 ± 0.09 kcal/mol | [197]      |
| 890.35 ± 0.30 kJ/mol | 212.80 ± 0.07 kcal/mol | [198]      |
| 891.8 ± 1.1 kJ/mol   | 213.14 ± 0.26 kcal/mol | [199]      |
| 890.16 ± 0.30 kJ/mol | 212.75 ± 0.07 kcal/mol | [200]      |

### 2.1.14.3 Enthalpy of Formation of Methane

Enthalpy of formation data of methane in various physical states are summarized in Table 23.

**Table 23:** Enthalpy of formation of methane.

| Physical state | SI units               | Other units       | References |
|----------------|------------------------|-------------------|------------|
| Gas            | −74.8731 kJ/mol        | −17.895 kcal/mol  | [201]      |
|                | −74.48 ± 0.42 kJ/mol   | −17.80 kcal/mol   | [197]      |
|                | −74.848 ± 0.314 kJ/mol | −17.889 kcal/mol  | [198]      |
|                | −73.39 ± 1.09 kJ/mol   | −17.54 kcal/mol   | [199]      |
|                | −74.6 ± 0.3            | −17.83 kcal/mol   | [202]      |
| Liquid         | −85.31 kJ/mol          | −1271 cal/g       | [203]      |
|                |                        | = −20.39 kcal/mol |            |
|                | −89.233 kJ/mol         | −21.327 kcal/mol  | [204]      |

Molecular mass: 16.0425 g/mol; 62.3344 mol/kg

The standard enthalpy of methane gas as a function of temperature can be calculated from the equation

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - H$$

where  $H^\circ - H^\circ_{298.15}$  is the differential standard enthalpy in kJ/mol and  $\tau$  is the temperature in kelvin divided by 1000. The constants A through H are listed in Table 21 above.

The enthalpy-pressure behavior for methane in the vapor phase was determined with a method based on measurements of the Joule-Thomson throttling effect [205]. Data were measured along six isotherms at 224, 247.50, 273.15, 298.15, 333.25, and 366.70 K. The experimental data and derived enthalpies were represented as polynomial functions of pressure up to a maximum of 100 bar. The enthalpy values were believed to be precise to within 5 J/mol. Comparisons were made with the calorimetric data of Jones et al., the derived enthalpies from the equation of state of Vennix et al. [59, 72] and the values calculated by Harrison et al. [206] from the accurate PVT data of Douslin et al. [73].

#### 2.1.14.4 Enthalpy of Vaporization of Methane

Enthalpy of vaporization data for methane are summarized in Table 24.

**Table 24:** Enthalpy of vaporization of methane.

| Temperature                    |         | Enthalpy of vaporization |          |       | References |
|--------------------------------|---------|--------------------------|----------|-------|------------|
| K                              | °C      | kJ/mol                   | kcal/mol | J/g   |            |
| 111.7 K (normal boiling point) | -161.4  | 8.17                     | 1.953    | 509.3 | [207]      |
| 112                            | -161.1  | 8.2                      | 1.960    | 511.1 | [50]       |
| 130                            | -143.1  | 7.5                      | 1.793    | 467.5 |            |
| 160                            | -113.1  | 5.9                      | 1.410    | 367.8 |            |
| 180                            | -93.1   | 4.0                      | 0.956    | 249.3 |            |
| 90.66                          | -182.44 | 8.661                    | 2.070    | 539.9 | [69]       |
| 110                            | -163.1  | 8.260                    | 1.974    | 514.9 |            |
| 99.54 ( $P = 2.81$ kPa)        | -173.6  | 8.519                    | 2.036    | 531.0 | [45]       |

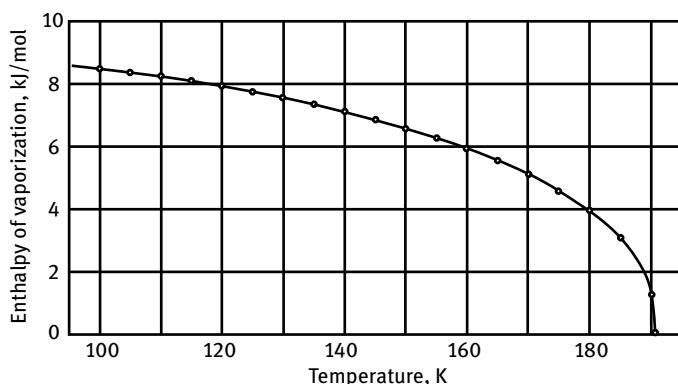
Molecular mass: 16.0425 g/mol; 62.3344 mol/kg

The enthalpy of vaporization of methane at the saturation pressure as a function of temperature within the temperature range 112–180 K can be calculated from the equation

$$(\Delta H)^\circ_{\text{evap.}} = A \exp(-\alpha T_r)(1 - T_r)\beta$$

where  $(\Delta H)^\circ_{\text{evap}}$  is the enthalpy of vaporization in kJ/mol,  $T_r$  is the reduced temperature  $T/T_c$ , and  $T_c$  is the critical temperature in kelvin ( $T_c = 190.6 \text{ K}$ ). The constants are  $A = 10.11$ ;  $\alpha = -0.22$  and  $\beta = 0.388$ .

The enthalpy of vaporization derived from the Clapeyron equation was calculated, tabulated, and graphed for temperatures between 90.66 and 190 K (Figure 20) [69]. The enthalpy of vaporization drops to zero as the temperature approaches the critical point.



**Figure 20:** Enthalpy of vaporization of methane. (Reproduced and modified from [69].)

See also [54]. The entropy of vaporization at 99.54 K is  $85.58 \text{ J mol}^{-1} \text{ K}^{-1}$ . The enthalpy of sublimation of solid methane based on data from 53 to 91 K is  $9.7 \text{ kJ/mol}$  at 72 K [70].

#### 2.1.14.5 Entropy of Methane

The standard entropy of methane gas at 1 bar is  $186.25 \text{ J mol}^{-1} \text{ K}^{-1}$ . The entropy of methane as a function of temperature can be calculated from the equation

$$S^\circ = A \ln(\tau) + B\tau + \frac{C\tau^2}{2} + \frac{D\tau^3}{3} - \frac{E}{2\tau^2} + G$$

where  $S^\circ$  is the standard entropy in  $\text{J mol}^{-1} \text{ K}^{-1}$  and  $\tau$  is the temperature in kelvin divided by 1000. The constants A through G are listed in Table 21.

#### 2.1.15 Molecular Orbital Calculations of Methane

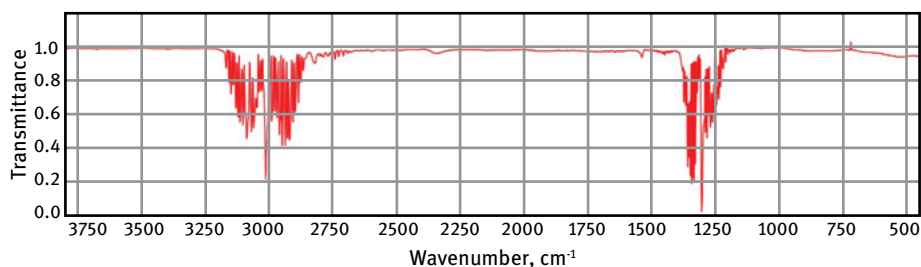
Theoretical thermodynamic properties of methane in the dense gas and liquid states have been calculated by the method of molecular dynamics [208]. The methane pair interactions were modelled using a spherically symmetric m-6-8 potential, and the most significant three-body and quantum effects were included. Agreement between calculated and experimental values for the energy and pressure was generally good

except at low temperatures and high densities. It was not certain if this method could also be used to predict the specific heat at constant volume.

## 2.1.16 Optical, Electrical, and Magnetic Properties of Methane

### 2.1.16.1 Infrared Absorption Spectra of Methane

The gas phase IR absorption spectrum of methane is shown in Figure 21.



**Figure 21:** Infrared absorption spectrum of methane. (Reproduced and modified with permission from [204].)

### 2.1.16.2 Index of Refraction of Liquid Methane

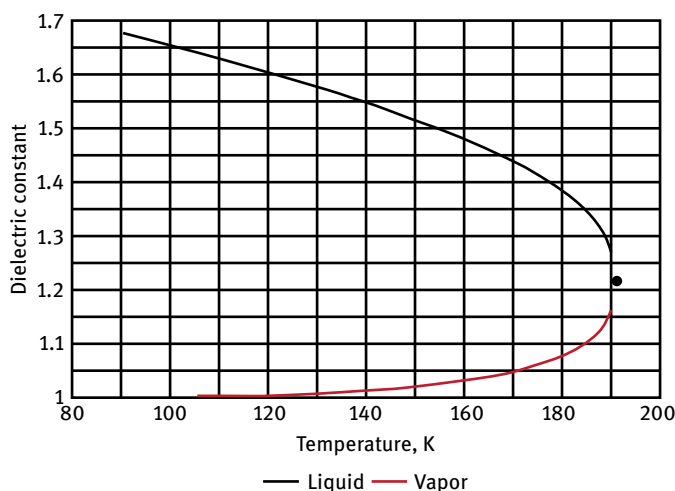
The refractive index of gaseous and liquid methane was measured between 95 and 300 K and at pressures of up to 225 bar (1 bar = 105 Pa) [209]. The measurements were performed at the  $^{198}\text{Hg}$  vapor green line,  $\lambda = 546.2\text{nm}$ , with a Fabry-Perot interferometer referred to vacuum. The refractive index data were combined with the previously measured densities of methane to calculate the Lorenz-Lorentz (LL) function. Refractometric virial coefficients were obtained from analysis of the small ( $\sim 0.5\%$ ) maximum exhibited by the LL function with increasing density.  $B_R$ , the second refractometric virial coefficient, was estimated to be  $\sim 6.0\text{ (cm}^3/\text{mol)}^2$  and was almost independent of temperature between 220 and 300 K. The critical-point refractive index,  $n_c = 1.10333$ , was extrapolated from a rectilinear diameter treatment of the saturated liquid and vapor results. The critical-point refractive index was combined with an estimate of the critical-point (LL) function to yield a critical density of methane,  $\rho_c = 10.16 \pm 0.01\text{ mol/L}$ . The measurement of the refractive index can be used to determine values of density and compressibility [107].

Comprehensive refractive index measurements  $n(P,T)$  were carried out on pure methane in the temperature range from 273 to 373 K and at pressures up to 34 MPa [210]. Two coupled laser interferometers were used for the experiments, one containing methane, the other the reference gas nitrogen maintained at the same pressure and a fixed temperature  $T_o$ , serving as a manometer. The uncertainty of the refractive index was estimated to be less than  $\pm 5 \times 10^{-7}$  at 1 MPa and  $\pm 5 \times 10^{-6}$  at 34 MPa. To measure the higher-order refractivity virial coefficients  $B_R$ ,  $C_R$ , of the

LL expansion, overflow experiments were made on the 323 K isotherm at pressures up to 35 MPa. Within the investigated range of pressure,  $B_R$  and  $C_R$  were the only significant refractivity virial coefficients. A comparison with literature values showed that  $B_R$  and  $C_R$  were independent of temperature within the range 220 to 373 K. On the basis of these  $n(P, T)$  measurements, the density was calculated by including  $B_R$  and  $C_R$ . The uncertainty of the density was estimated to be not greater than  $\pm 0.05\%$ .

### 2.1.17 Dielectric Constant of Liquid Methane

The dielectric constant of liquid and gaseous methane under conditions of saturated pressure is illustrated in Figure 22.



**Figure 22:** Dielectric constant of methane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

## 2.2 Chemical Properties of Methane

### 2.2.1 Reactions of Methane

The primary chemical reactions of methane that are of industrial significance are combustion, steam reforming to syngas, and halogenation for solvents and refrigerants. Attempts have been made to convert methane gas directly to the more storable methanol, but so far the only industrial methane-to-methanol conversion method is by way of syngas.

### 2.2.1.1 Oxidation Reactions of Methane

Methane combustion is the key reaction to using the energy from natural gas in a variety of applications, from home heating furnaces to industrial glass and steel melting furnaces to LNG-driven automobiles and, eventually, rockets.

Partial oxidation of methane to methanol is difficult because the reaction typically progresses all the way to carbon dioxide and water even with an under-stoichiometric supply of oxygen. There have been many attempts to perform a partial oxidation of methane without detracting too much from its heating value, for instance, by converting methane at remote gas wells to methanol that would be easier to store and transport to locations where energy is needed. These efforts have not yet resulted in an economical path to using methane from remote locations that is often flared off because there is no other use for it. Converting methane to synthesis gas and then performing Fischer-Tropsch synthesis resulting in more useful products is done in only a few locations in the world (e.g., Sasol in South Africa).

### 2.2.1.2 Kinetics of Methane Oxidation Reactions

In an effort to advance methane rocket propellant technology, quite often, existing rocket engines originally qualified for operation on kerosene or liquid hydrogen have been converted to operate on methane, although none of those has actually flown in a booster or upper stage. It is important to understand the difference in kinetics between kerosene combustion and methane combustion when designing a LOX/LCH<sub>4</sub> engine. The kinetics of LOX/methane combustion determine the required L\* of a LOX/LCH<sub>4</sub> engine required to achieve complete combustion before the propellant leaves the combustion chamber.

Because the reaction of gaseous oxygen and gaseous methane mixtures is often too fast, frequently transitioning into a detonation, most academic kinetic studies of the O<sub>2</sub>/CH<sub>4</sub> reaction have worked with diluents to slow down the reaction. Diluents often used are inert, non-reactive gases such as helium or argon. Even nitrogen as a diluent may already alter the results of such kinetic studies.

In addition to LOX/LCH<sub>4</sub> and GOX/GCH<sub>4</sub> reaction studies, there are also a multitude of air/CH<sub>4</sub> combustion kinetics studies where nitrogen is sometimes not just a diluent but also a participant in reactions. There are about 50 times more air/CH<sub>4</sub> combustion studies than undiluted O<sub>2</sub>/CH<sub>4</sub> combustion studies, but it is the latter mode of operation that is of interest for the rocket designer.

A comparison of three kinetic mechanisms, Leeds, GRI 3.0, and RAMEC, was made in an effort to find a kinetic model equally suitable for Rocket-Based Combined Cycle (RBCC) engines operating on LOX/LCH<sub>4</sub> or ramjets operating on air/CH<sub>4</sub> [211]. The kinetics mechanism from Leeds was chosen for further usage. The main reasons for this choice were its comparable small size and the fact that its kinetic properties were based more on theoretical and experimental data and less on the simple fitting of data. Furthermore, the Leeds mechanism generally did a better job at predicting ignition delay, which is considered a key feature for rocket applications. In rocket mode, combus-



tion chamber pressure varies between 0.1 MPa during ignition initiation and about 6–10 MPa during steady-state operation. For an air-breathing mode operation (SCRAM-JET mode), the combustion chamber most likely experiences only minor pressure variations during ignition and steady state-operation, i.e., 0.1–0.2 MPa. A chemical model of  $\text{CH}_4$  combustion applicable for CFD simulations of processes in combustors should have between 8 and 12 chemical species. Such kinetic models are called global mechanisms. These models were to be used for predicting ignition delays and laminar flame velocities. The laminar flame velocity is the most important characteristic of a fuel and it can be measured more precisely than the ignition delay time. The experimental flame velocity data typically have errors that do not exceed 10%.

#### **2.2.1.3 Methane Hydrate Formation**

Methane hydrates (also known as methane clathrates) are solid cages of water molecules (ice) that trap single molecules of methane. Methane clathrates have been found in arctic permafrost and beneath the ocean floor within the gas clathrate stability zone, located at high pressures (1 to 100 MPa; the lower end requires a lower temperature) and low temperatures ( $<258\text{ K} = <15^\circ\text{C}$ ; the upper end requires a higher pressure). Methane clathrates can form from biogenic methane, thermogenic methane, or a combination of the two. These deposits are both a potential desirable source of methane fuel as well as a potential unwanted contributor to global warming when they are suddenly released. Solid methane clathrates from moisture in liquefied methane may clog filters and orifices.

#### **2.2.1.4 Combustion of Methane**

The combustion of methane, in particular, flame speeds of pre-mixed and diffusion flames in air or oxygen, will be discussed in a later volume on non-hypergolic bipropellant combinations.

### **2.2.2 Quality Control Specification for Methane**

Procurement by the US Government of methane for rocket applications is governed by Military Specification MIL-PRF-32207 – Propellant, Methane (also Notice 1) [212]. This specification covers two types (Type I: Gas, Type II: Liquid) and three purity grades, as indicated in Table 25.

### **2.2.3 Analysis of Methane**

Another specification for the gas chromatography (GC) analysis of natural gas is the ASTM D 1945 Standard Test Method for Analysis of Natural Gas by Gas Chromatography.

Table 25: Purity requirements for methane per MIL-PRF-32207.

| Component                                                       | Unit                   | Requirements |         |         | Analytical method                   |
|-----------------------------------------------------------------|------------------------|--------------|---------|---------|-------------------------------------|
|                                                                 |                        | Grade 1      | Grade 2 | Grade 3 |                                     |
| Methane assay                                                   | %Vol, min              | 98.7         | 99.9    | 99.97   | GC ASTM D 1945                      |
| Water                                                           | ppmVol, max            | 1            | 0.5     | 0.5     | Hygrometer or electrolytic analyzer |
| Oxygen                                                          | ppmVol, max            | 1            | 1       | 1       | Oxygen analyzer                     |
| Nitrogen                                                        | ppmVol, max            | 5000         | 100     | 100     | GC                                  |
| Carbon dioxide                                                  | ppmVol, max            | 125          | 50      | 50      | IR spectrophotometric at 14.95µm    |
| Other gaseous impurities (e.g.,<br>Ar, H <sub>2</sub> , He, Ne) | ppmVol, max            | 5000         | 125     | 125     | GC ASTM D 1945                      |
| Ethane (C <sub>2</sub> H <sub>6</sub> )                         | ppmVol, max            | 5000         | 500     | 100     | GC ASTM D 1945                      |
| Propane (C <sub>3</sub> H <sub>8</sub> )                        | ppmVol, max            | 3000         | 500     | 100     | GC ASTM D 1945                      |
| Other volatile hydrocarbons                                     | ppmVol, max            | 1            | 1       | 1       | GC with FID                         |
| Total volatile sulfur                                           | ppmVol, max            | 1            | 0.1     | 0.1     | ASTM D 6667                         |
| Non-volatile residue and<br>particulates                        | mg/L, max <sup>a</sup> | 10           | 1       | 1       | Gravimetric                         |

GC = gas chromatography.

<sup>a</sup> Applicable to Type II only.

## 2.2.4 Thermal Stability of Methane

### 2.2.4.1 Coke Deposition During Thermal Decomposition of Methane

Theoretical specific impulse, ignition kinetics, pyrolysis-cracking kinetics, and heat transfer calculations of methane or natural gas in combination with LOX or HTP, in comparison with other fuels such as liquefied petroleum gas, methanol, ethanol, or kerosene, indicated that there should be no soot or coke deposition in regenerative cooling channels of engines operating with methane at 100-atm chamber pressure, but methane entering at 150 K could possibly heat up to above critical-point conditions [213].

The catalytic effects of Inco 718, Inco 600, and A286 are responsible for thermal cracking of pure  $\text{CH}_4$  and may prevent their use as materials for nozzles and combustion chambers [214]. The thermal cracking of pure  $\text{CH}_4$  mechanism was analyzed theoretically and compared with experimental results. The initial temperature of  $\text{CH}_4$  thermal cracking and the coking caused by catalytic activity of the material candidate were explained.

### 2.2.4.2 Radiation Stability of Methane

The radiolysis of methane, presumed to exist in lakes on the moon Titan, under the influence of cosmic radiation, would result in formation of higher hydrocarbons and a tar-like polymer called tholin. It is unlikely that liquid methane stored in orbital propellant depots on Earth or Mars would suffer the same fate, because most of the radiation is shielded by the tank wall material. The radiolysis of methane and other hydrocarbons was already discussed in a previous section, Section 1.2.2.

## 2.3 Compatibility with and Corrosion of Materials in Methane

Experiments were performed in which electrically heated oxygen-free high thermal conductivity = OFHC copper tubes were exposed to flowing high-velocity methane fuels [215]. Significant corrosion was observed during these tests as indicated by recession of the inside tube walls. No corrosion was, however, observed from elevated temperature static exposures of copper specimens to high-pressure liquid natural gas (LNG) and high-purity methane fuels. Mechanisms postulated to explain this corrosion were: (1) sulfur embrittlement, (2) corrosion interactions with high AC currents, (3) erosion-corrosion, (4) electrochemical corrosion, (5) zeta corrosion, and (6) mercury corrosion.

Materials compatibility of hydrocarbon fuels (methane, Mil-Spec RP-1, *n*-dodecane, and propane) in contact with copper-based combustion chamber liner materials (oxygen-free high thermal conductivity = OFHC, NASA-Z, and ZrCu coppers) was tested using two different methods [216, 217]. Static tests, in which copper coupons were exposed to fuel for long periods at constant temperature

and pressure, provided compatibility data in a precisely controlled environment. Dynamic tests, using the Aerojet Carbothermal Test Facility, provided fuel and copper compatibility data under realistic booster engine service conditions. Tests were conducted using very pure grades of each fuel and fuels to which a contaminant, e.g., ethene (ethylene) or methyl mercaptan, was added to define the role played by fuel impurities. It was found that each of the copper materials exhibited similar compatibility behavior. However, there were significant differences among the various hydrocarbon fuels tested. In methane, no carbon deposits were formed up to  $T_{\text{wall}} = 774\text{ K}$  (934 °F) and copper corrosion was observed with sulfur contents down to 1 ppm. Copper(I) sulfide is the corrosion product. Severe corrosion of copper was observed when very small amounts of sulfur impurities (e.g., 1 ppm of methyl mercaptan) were added to the methane. There were subsurface gouges formed in the channel surface during a dynamic test with methane plus 1 ppm methyl mercaptan. In two tests conducted with a relatively high concentration of methyl mercaptan in the methane (200 and 10 ppm respectively) the formation of corrosion product ( $\text{Cu}_2\text{S}$ ) became so massive that it entirely blocked the flow of fuel through the channel.

Dynamic exposure tests using methane and NASA-Z copper test specimen under conditions that simulated those expected in the cooling channels of a regeneratively cooled LOX/hydrocarbon booster engine operating at chamber pressures up to 3000 psi showed that methane with less than 0.5 ppm sulfur contamination has little or no effect on cooling channel performance [218]. At higher sulfur concentrations, severe corrosion of the NASA-Z copper alloy occurred and the copper(I) sulfide  $\text{Cu}_2\text{S}$  layer thus formed impeded mass flow rate and heat transfer efficiency. It was recommended that the methane specification for this end use set the allowable sulfur content at 0.5 ppm (max). As of 1991, bulk high purity liquid methane that met this low sulfur requirement was available from only one producer. It was found that dilute sodium cyanide solutions effectively refurbish sulfur-corroded cooling channels in only 2 to 5 min by completely dissolving all the  $\text{Cu}_2\text{S}$ . Sulfur-corroded/sodium cyanide refurbished channels are highly roughened and the increased surface roughness leads to significant improvements in heat transfer efficiency, but only with an attendant loss in mass flow rate.

## 2.4 Safety Properties of Methane

Methane is non-toxic, an asphyxiant, but it is very flammable and may form explosive mixtures with air. Methane is an asphyxiant if the oxygen concentration in a methane-filled chamber is reduced to below about 16% by displacement [219]. Most people can tolerate a reduction of oxygen concentration from 21 to 16% without ill effects. The concentration of methane at which asphyxiation risk becomes significant is higher than the 5–15% concentration in a flammable or explosive air/methane mixture.

## 2.5 Environmental Effects of Methane

Somebody with the required background knowledge should write a book on the environmental effects of methane. It is unlikely that the increasing use of methane as a rocket propellant will change that assessment. Boiloff from liquid methane storage tanks at rocket launch sites can be flared.

## 2.6 Explosive and Fire Hazards of Methane

Methane emanates continuously from coal deposits underground, in particular wherever coal seams are penetrated with mine shafts and tunnels (galleries) during coal mining activities. Air/methane (“firedamp”) explosions in coal mines have caused thousands of fatalities. Various instruments have been developed to detect methane in the air in coal mines and provide advance warning of flammable conditions. Fire and explosion hazards associated with liquefied natural gas have been thoroughly investigated [220, 221].

### 2.6.1 Limits of Flammability of Gaseous Air/Methane Mixtures

The flammability limits of air/methane mixtures were investigated experimentally at pressures up to 5500 kPa and temperatures up to 473 K (200 °C) [222]. Two different criteria based on the maximum explosion pressure were used to define the flammability limit: the tangent criterion and the min-max criterion. It was shown that the min-max criterion should be used to determine the upper flammability limit (UFL), because the tangent criterion underestimates the UFL at initial pressures higher than ambient. Within the pressure-temperature range tested second-order pressure dependences and linear temperature dependences of the UFL were found. The temperature dependence of the UFL was influenced by the initial pressure, which was in contrast with previous findings.

The UFLs of air/hydrogen, air/methane, air/ethane, air/*n*-butane, and air/ethene (ethylene) were determined experimentally at room temperature (293 K = 20 °C) and initial pressures of 1.0, 0.7, 0.5, 0.3, 0.1, and 0.05 atm [223]. Experiments were conducted in a closed cylindrical stainless steel vessel with an internal diameter of 10 cm and a length of 100 cm with upward flame propagation. The UFL of hydrogen was observed to be inversely proportional to the initial pressure within the range 1.0 to 0.3 atm and proportional to the initial pressure from 0.3 to 0.05 atm. In contrast, the UFLs of the lower alkanes and ethene (ethylene) decreased with the initial pressure. The average flame propagation velocities at UFL concentrations of hydrogen, methane, ethane, *n*-butane, and ethene (ethylene) in air at reduced pressures were also examined. It was found that the flame propagation velocity of hydrogen was larger than those of

the hydrocarbons, increased when the initial pressure decreased from 1.0 to 0.3 atm, and then decreased with further a decrease in pressure. Flame propagation velocities at UFL concentrations of the hydrocarbons decreased with the initial pressure. In a parallel series of experiments, the lower flammability limits (LFLs) of air/hydrogen, air/methane, air/ethane, air/*n*-butane, and air/ethene (ethylene) were also measured in the same closed cylindrical vessel (inner diameter 10 cm, length 100 cm) under the same conditions with upward flame propagation, at room temperature (293 K = 20 °C) and initial pressures of 1.0, 0.7, 0.5, 0.3, and 0.1 atm [224, 225]. The LFL of hydrogen initially decreased with pressure from 1.0 to 0.3 atm, but then the LFL increased with a further decrease in pressure. In contrast, the LFLs of the hydrocarbons increased when the pressure decreased from 1.0 to 0.1 atm, except for methane, for which the LFL did not change with pressure. The adiabatic constant volume flame temperatures at the new measured LFL concentrations of hydrogen and the hydrocarbons were calculated at sub-atmospheric pressure conditions. The behaviors of the adiabatic flame temperatures of hydrogen and the hydrocarbons were similar to those of the LFLs under the influence of low pressures.

### 2.6.2 Minimum Ignition Energy of Methane in Air

The minimum ignition energy of stoichiometric mixtures of methane in air at room temperature and sea level pressure is 0.4 mJ. Expanding the measurements of minimum ignition energy to elevated temperatures and elevated pressures, the minimum ignition energy of air/methane mixtures by spark ignition was measured for different temperatures (303–423 K = 30–150 °C) and different pressures (0.1–0.9 MPa) [226]. The effect of gap width was measured for gap widths between 0.2 and 2.0 mm and the most efficient ignition was with a gap width of 1 mm. Results depended on the width of the electrode gap, which was normally 1 mm for the remainder of the tests. The methane equivalence ratio was maintained at 1.0 (stoichiometric for CO<sub>2</sub>). The minimum ignition energy at 303 K and 0.1 MPa was 0.49 mJ. This compares well with minimum ignition energies reported by earlier authors ranging from 0.28 to 0.50 mJ [227–230]. The minimum ignition energy decreased with increasing pressure or temperature. The minimum ignition energy had a high order exponential relationship with  $1/P^2$ , but an approximately linear inverse relationship with  $1/T$ . At room temperature, the minimum ignition energy decreased in accordance with the equation

$$\text{MIE} = 0.000928 + 0.00489/P^2$$

where MIE is the minimum ignition energy in mJ and  $P$  is the pressure in MPa. With increasing temperature, the influence of pressure on the MIE became less pronounced. The effect of the temperature on the MIE decreased with increasing pressure. See also [231, 232].

### 2.6.3 Spontaneous Ignition of High-Pressure Releases of Methane into Air

The spontaneous self-ignition of high-pressure jets of hydrogen gas released into air has been described in detail in *Encyclopedia of Liquid Fuels*, chapter “Hydrogen.” A similar mechanism may be responsible for spontaneous self-ignition of high-pressure jets of methane or natural gas into surrounding air [233].

### 2.6.4 Accidental Detonation of Gaseous Oxygen/Methane Mixtures

The controlled detonation of air/methane and oxygen/methane mixtures, which may be of interest for use in pulse detonation rocket engines, will be discussed in a later volume on non-hypergolic bipropellant combinations.

Here we are discussing only the hazards and safety aspects of accidental explosions of this type. Detonations may propagate in flowing oxygen/methane mixtures, but always faster than the unburnt gases can flow [234].

During a study of the venting of a fast flame (100–800 m/s) in a round ignition pipe (140 mm I.D.) into a semispherical vessel containing a mixture of the same composition and initial pressure, the flame jet emerging from the pipe interacted with the remains of an unburned starting ring vortex set into motion by the accelerating flame front, and the subsequent intense combustion led to the initiation of an unconfined detonation inside the vessel [235]. A parametric investigation of this phenomenon in nitrogen-diluted (29.4–68.4 vol.-%) stoichiometric mixtures of oxygen/propane has been carried out for a range of exit orifice diameters (50, 101, and 140 mm) under initial pressure of 0.4 and 1 atm. A small number of atmospheric pressure experiments have also been conducted with nitrogen-diluted (33.3–57.1 vol.-%) stoichiometric oxygen/methane mixtures. One criterion, based on the notion of a critical Damköhler number and minimum energy release requirement, has been suggested for the initiation of unconfined detonation by a venting jet flame. All experimental results for a given initial pressure and fuel may be combined into a single curve, separating conditions leading to detonation from those that do not. The critical orifice diameter below which a transition to unconfined detonation does not occur was reduced for a venting fast flame by comparison with a steady detonation wave.

## 2.7 Disposal of Methane

Surplus methane vented from fuel tanks and transfer lines during the initial filling with liquid methane and cooldown can be burned in flare stacks. The design of flare stacks for methane would be similar to those designed for disposal of gaseous hydrogen.

Surplus methane concentrations below the lower flammable limit may have to be destroyed in a thermal oxidizer (also known as thermal incinerator), which is a process unit for air pollution control in many chemical plants that decomposes hazardous

gases at a high temperature and releases them into the atmosphere, but requires additional natural gas to operate the combustion chamber.

## 2.8 Fuel Mixtures with Methane

Methane has been evaluated as a fuel in mixtures with numerous other hydrocarbons and physical properties have been determined, such as in mixtures with ethane, ethene, propane, or butane. There are no obvious advantages of methane/fuel mixtures as rocket fuels over the use of pure methane or liquefied natural gas by itself.

### 2.8.1 Fuel Mixtures of Methane with Ethane

Liquid methane and liquid ethane are miscible over the entire range of compositions. Ethane is the second-most common hydrocarbon constituent of natural gas and is frequently found in liquefied natural gas. The effects of uncontrolled amounts of ethane on the physical properties of methane must be known before one decides to remove ethane from natural gas, prior to using LNG instead of pure methane as a rocket propellant. Although the boiling points of the two hydrocarbons are 72° apart, it is difficult to separate them by simple distillation [236, 237].

Ethane may be added to methane on purpose in order to lower the freezing point and allow the fuel to be cooled to temperatures lower than pure methane and to be densified to densities higher than those possible with pure methane, allowing more fuel to be packed into the same tank volume. Similar methane mixtures with other lower *n*-alkanes also have lower freezing points [238]. A step-by-step variation of the freezing point in the paraffin homologous series was examined to provide reasonably accurate extrapolation of scattered freezing-point data on the methane/*n*-butane mixture to other paraffin hydrocarbon mixtures of methane in which the heavier constituent ranged from ethane to *n*-nonane, inclusive, illustrated in a composite graph of the freezing points of the various binaries with methane, from ethane to *n*-nonane.

Measurements of the thermal conductivity of mixtures of methane and ethane revealed an enhancement in the mixture-critical region, contradicting theoretical predictions [239]. The anomaly was similar in size and temperature dependence to that found for pure fluids.

The thermal conductivity surface for three methane-ethane mixtures with methane mol fractions of 0.69, 0.50, and 0.35 was defined by up to 13 isotherms at temperatures between 140 and 330 K, with pressures up to 70 MPa and densities up to 25 mol/L [240–242]. The measurements were made with a transient hot-wire apparatus covering a wide range of physical states, including dilute gas, single-phase fluid at temperatures above the maxcondentherm, compressed liquid states, and vapor at temperatures below the maxcondentherm. The results showed an enhancement



in the thermal conductivity in the single-phase fluid down to the maxcondentherm temperature, as well as in the vapor and in the compressed liquid.

Comprehensive isochoric ( $P$ ,  $V_m$ ,  $x$ ,  $T$ ) physical state values have been obtained for  $\{x\text{CH}_4 + (1-x)\text{C}_2\text{H}_6\}$  mixtures with  $x = 0.35, 0.50$ , and  $0.69$  at densities ranging from 1 to 25 mol/L [243]. The measurements for each composition covered a temperature range from approximately 100 to 320 K at pressures up to 35 MPa. For each mixture the results were fitted to a 32-term modified Benedict-Webb-Rubin equation of state, supporting further development of an extended corresponding-states model.

A method for predicting transport coefficients of binary molecular liquid mixtures has been verified by measuring the thermal conductivity of liquid methane-ethane mixtures [244].

Measurements of the molar heat capacity at constant volume  $C_V$  of  $\{x\text{CH}_4 + (1-x)\text{C}_2\text{H}_6$ ,  $x = 0.35, 0.50, 0.68\}$  mixtures at 100 to 320 K and at pressures up to 35 MPa were made on samples of constant mass contained by a calorimeter vessel of nearly constant volume [245]. Critical enhancement of heat capacity for each mixture was apparent in the critical-temperature region for constant density and similarly in the critical-density region for constant temperature. Liquid heat capacities at saturation, obtained by extrapolation at constant density, had a minimum for each composition occurring at twice the estimated critical density. Reduced configurational heat capacities at saturation, examined as functions of reduced density  $\rho/\rho_c$ , fell into a family of parallel curves that had minima at  $\rho/\rho_c = 2.0$ .

Velocity of sound data were measured for 13 binary mixtures and 4 multi-component mixtures of natural gas components using a cylindrical cavity over a temperature range from 250 to 350 K and at pressures up to 10 MPa [246]. The binary mixtures were primarily methane-rich, with ethane, nitrogen, carbon dioxide, or propane as the second component. The multi-component mixtures are representative of commercially available gas compositions in the United States and Europe. The data were used to develop and test mathematical models for prediction of the sound speed of natural gas mixtures, within an average uncertainty of 0.1%, over the ranges of pressure, temperature, and composition that encompass the major region of custody transfer for natural gas. This work covered only data for mixtures of  $\text{CH}_4/\text{C}_2\text{H}_6$ ,  $\text{CH}_4/\text{C}_3\text{H}_8$ , not for the pure compounds by themselves.

An equation of state for the thermodynamic properties of mixtures of methane and ethane in the critical region was developed that incorporated the crossover from singular thermodynamic behavior near the locus of vapor-liquid critical points to regular thermodynamic behavior outside the critical region [247]. The equation of state provided a sufficiently accurate representation of the thermodynamic property data for the mixtures within a wide range of temperatures and densities.

Thermal-conductivity measurements for an equimolar mixture of methane and ethane very close to the critical point confirmed that the thermal conductivity of

a mixture does not diverge at the vapor-liquid critical point but crosses over to a finite limiting behavior at the critical point [144]. An extension of the mode-coupling theory for dynamic critical phenomena in mixtures gave a good quantitative description of the experimental thermal conductivity data. The same theory enables one to predict other transport properties of the mixture in the vicinity of the critical point [145].

A single-cycle apparatus was used to measure vapor-liquid equilibrium data for the binary system ( $\text{CH}_4 + \text{C}_2\text{H}_6$ ) over low temperatures of (126 to 140) K and pressures up to 0.64 MPa [248]. The Peng-Robinson model with a modified Huron-Vidal mixing rule and a Wilson model were used to correlate the experimental data for the binary system, and the interactive parameters of the Wilson model were given. The model predicted satisfactory results over the range of experimental temperatures and pressure.

The capillary constant  $a^2$  of ethane-methane solutions was measured and the surface tension  $\sigma$  was calculated within the temperature range 93 to 283 K at pressures from that of saturated vapors of pure ethane to 4 MPa, leading to equations that approximated the temperature, pressure, and concentration dependences of  $a_2$  and  $\sigma$  [249]. The concentration dependence of the surface tension was described based on models of an ideal and a regular solution and the relative adsorption has been calculated.

A specialized cell designed for vapor liquid equilibrium measurements at cryogenic temperatures and high pressures was used to measure new ( $P, T, x, y$ ) data for binary mixtures of methane + ethane, methane + propane, methane + 2-methylpropane (*iso*-butane), and methane + butane from 203 to 273 K at pressures up to 9 MPa [250]. A literature review of vapor liquid equilibrium data for these binary mixtures indicated that a significant number have large uncertainties. However, because estimates of uncertainties in measured phase compositions are often not quantified sufficiently, it can be difficult for equation of state (EOS) developers to identify which data sets are of poor quality. Robust quantitative uncertainties were estimated for the vapor liquid equilibrium data acquired in this work, which allowed the identification of literature data sets that should not be included in future EOS development. The new data were compared with predictions of the Peng-Robinson EOS and the Groupe Européen de Recherche Gazière (GERG-2008) multi-parameter EOS.

Icy bodies in the outer Solar System such as Titan, the largest moon of Saturn, contain simple hydrocarbons, and methane and ethane interact with each other at low temperatures and Titan-like pressures. In mapping the methane-ethane system as a function of composition, it was shown that this is a eutectic system where the freezing point is depressed down to  $71.15 \pm 0.65$  K (whereas pure methane and ethane freeze at 90.56 and 90.09 K respectively), at a mix containing  $64.4 \pm 1.8\%$   $\text{CH}_4$  and  $35.6 \pm 1.8\%$   $\text{C}_2\text{H}_6$  [251].

### 2.8.2 Fuel Mixtures of Methane with Ethene

Fuel mixtures of methane with ethene,  $C_2H_4$ , have not yet been considered as rocket fuels. Mixtures of methane and ethene may be encountered in the products of cracking reactors in petroleum refineries.

The total vapor pressure of liquid mixtures of methane and ethene has been measured as a function of composition at 103.94 and 115.77 K and the results have been used to estimate the excess Gibbs energy at these temperatures [252]. The volume of mixing was determined at 103.94 K and was found to be small and negative. An attempt was made to estimate the value of the molar enthalpy of mixing. The results were interpreted in the light of some simple theories of mixtures, suggesting that this might be a case where the Lorentz rule of combination of collision diameters is valid.

### 2.8.3 Fuel Mixtures of Methane with Propane

Fuel mixtures of methane with propane have not yet been used as rocket fuels. Mixtures of methane with propane may be encountered in the off-gas from petroleum refining processes [54].

The viscosities and densities of methane-propane mixtures were determined at pressures up to 34.5 MPa (5000 psia) for 22.1 and 50.0 mol-% methane over a temperature range from 153 to 311 K (−120 to +37.78 °C) and for 75.3 mol-% methane over a temperature range from 123 to 311 K (−150 to +37.78 °C) [253]. Reproducibility of the viscosity data was  $\pm 2\%$ , and the agreement with literature values was, on average, within  $\pm 2\%$ . The reproducibility of the density data was  $\pm 0.8\%$ , and the agreement with literature values was  $\pm 1.2\%$ .

The total vapor pressure of liquid mixtures of methane and propane has been measured as a function of composition at temperatures of 115 and 135 K [65]. The activity coefficient of methane  $f_1$  and the excess Gibbs function of mixing  $\Delta G$  have been evaluated from the vapor pressure measurements, and the heat of mixing and the excess entropy of mixing have been estimated from the temperature dependence of  $\Delta G$  and compared with direct calorimetric values. Values of the excess thermodynamic functions have been calculated from a simplified version of the Flory theory of mixtures, with allowance for departures from the geometric mean (Berthelot) combining rule. Calculations showed that these deviations were very small, but not negligible.

Isobaric heat capacities  $c_p$  of  $CH_4 + C_3H_8$  mixtures at  $x_1 \approx 0.8$  and  $P \approx 5$  MPa and  $CH_4 + C_4H_{10}$  mixtures at  $x_1 = 0.96, 0.88, \text{ and } 0.60$  were measured at temperatures between 108 and 168 K for liquid mixtures and  $P \approx 5$  MPa [254]. Measurements were made using a specialized calorimeter further modified to prevent preferential condensation of the less volatile component and minimize possible stratification of the mixture during sample loading. Similar differences from the various equations of state were observed for the data of Furtado [255], who measured the  $c_p$  of a mixture with a mol fraction composition of  $0.359 CH_4 + 0.314 C_2H_6 + 0.327 C_3H_8$  at similar temperatures.

#### 2.8.4 Fuel Mixtures of Methane with Butane

Fuel mixtures of methane with butane have not yet been used as rocket fuels. Mixtures of methane with butane may be encountered in the off-gas from petroleum-refining processes. The boiling points of the two liquids are quite different; thus, it should be easy to separate them by distillation.

Bubble-point compositions for the methane-*n*-butane system were measured and combined with dew-point data to give K-values for the methane-*n*-butane system at 278, 255, 244, 233, 222, 211, 200, 190.6, 189, 178, 166, 155, and 144 K (40, 0, -20, -40, -60, -80, -100, -116.6, -120, -140, -160, -180, and -200 °F) from the vapor pressure of *n*-butane up to the critical point or the vapor pressure of methane [66]. Experimental conditions were selected so that direct isobaric observations were also possible.

Isobaric heat capacity measurements of mixtures of liquid methane and liquid butane were already described in the preceding section on methane-propane mixtures [254].

#### 2.8.5 Metal Slurries in Gelled Liquid Methane

The heat of combustion of liquid methane can be increased by suspending metal particles in the liquid methane. In order to prevent the metal particles from settling, the cryogenic liquid methane has to be gelled. It is very difficult to find gelling agents for cryogenic fuels.

### 2.9 Applications of Methane

There are numerous applications of methane as the fuel in rocket propulsion systems, mostly with LOX as the oxidizer. Theoretical performance calculations, design guidelines, and examples of flight applications for the LOX/LCH<sub>4</sub> combination will be provided in a future volume on non-hypergolic bipropellant combinations.

## 3 Ethane

Ethane, C<sub>2</sub>H<sub>6</sub>, CAS RN [74-84-0], is a common constituent of natural gas and is often associated with methane in the various applications of methane. Traces of ethane are not detrimental to the properties of methane as a rocket fuel.

### 3.1 Production and Availability of Ethane

After methane, ethane is the second most prominent constituent of natural gas. Natural gas from different gas fields varies in ethane content from less than 1 vol.-% to

more than 6 vol.-%. Ethane can be prepared by separating it from methane in natural gas by liquefaction and fractionated distillation or swing adsorption on molecular sieves. Ethane is forming lakes on Titan, the moon circling Saturn. Ethane (along with ethene) is formed in the cracking of oil crudes in petroleum refineries. The main use of ethane is to convert it to ethene for polyethylene polymer production. Ethane is unlikely to become a rocket fuel in its own right. It will ride along with methane, only slightly changing the properties of liquid methane, but a contaminant that has to be reckoned with if LNG instead of liquid methane is used as a rocket fuel.

The theoretical ideal work required for liquefaction of ethane starting at 300 K and 101.3 kPa is 353.1 kJ/kg (151.8 BTU/lb).

### 3.2 Physical Properties of Ethane

The physical properties of ethane have been summarized in several useful publications [94, 256, 257].

#### 3.2.1 Freezing Point of Ethane

The freezing point of ethane is at 89.2 K (−183.9 °C). The triple-point properties of ethane are summarized in Table 26.

**Table 26:** Triple-point properties of ethane.

|             |                                             |
|-------------|---------------------------------------------|
| $T_t$       | 90.348 K                                    |
| $P_t$       | $1.1308 \times 10^{-6}$ MPa                 |
| $\rho_{tL}$ | 21.680 mol/dm <sup>3</sup>                  |
| $\rho_{tV}$ | $1.5154 \times 10^{-6}$ mol/dm <sup>3</sup> |

Data source: [94]

#### 3.2.2 Boiling Point of Ethane

The boiling point of ethane is  $184.6 \pm 0.6$  K (−88.5 ± 0.6 °C).

#### 3.2.3 Density and Partial Molar Volumina of Liquid Ethane

The density and surface tension of liquid ethane was measured between 126 and 178 K, as listed in Table 27 [258].

#### 3.2.4 Equation of State for Ethane

A comprehensive study of pressure, volume, temperature relations for ethane included new experimental vapor pressures in relation to the critical, orthobaric

**Table 27:** Density and surface tension of liquid ethane.

| Temperature | Density           | Temperature | Surface tension |        |
|-------------|-------------------|-------------|-----------------|--------|
| K           | g/cm <sup>3</sup> | K           | mN/m            | dyn/cm |
| 126.9       | 0.6081            | 129.2       | 25.00           | 25.00  |
| 133.3       | 0.6017            | 133.2       | 24.54           | 24.54  |
| 135.0       | 0.5997            | 137.1       | 23.72           | 23.72  |
| 138.8       | 0.5951            | 149.1       | 21.75           | 21.75  |
| 141.6       | 0.5934            | 150.6       | 21.68           | 21.68  |
| 143.9       | 0.5900            | 155.9       | 20.71           | 20.71  |
| 148.1       | 0.5860            | 157.5       | 20.46           | 20.46  |
| 149.9       | 0.5831            | 161.3       | 19.86           | 19.86  |
| 157.6       | 0.5752            | 164.4       | 19.28           | 19.28  |
| 164.8       | 0.5677            | 170.3       | 18.31           | 18.31  |
| 167.2       | 0.5651            | 180.6       | 16.63           | 16.63  |
| 189.1       | 0.5630            | —           | —               | —      |
| 171.9       | 0.5599            | —           | —               | —      |
| 174.6       | 0.5572            | —           | —               | —      |
| 176.4       | 0.5551            | —           | —               | —      |
| 178.1       | 0.5527            | —           | —               | —      |
| 179.2       | 0.5516            | —           | —               | —      |
| 183.4       | 0.5478            | —           | —               | —      |

Data source: [258]

densities for the coexistence envelope, with critical constants ( $P_c = 4871.76$  kPa or 48.0807 atm,  $T_c = 305.33$  K,  $V_c = 0.14556$  dm<sup>3</sup>/mol, and  $\rho_c = 6.870$  mol/dm<sup>3</sup>), virial coefficients  $B_0$ ,  $C_0$ , and  $D_0$ , and compression factors  $Z = pV/RT$  in the compressed fluid to 400 atm and 623 K [259]. The effect of gravity on the density of near-critical fluids and the critical point was significant even for small fluid heights (2 cm). The diameter of the coexistence envelope,  $(p_1 + p_g)/2$ , had a gradual curvature at all temperatures up to the critical.

A formulation for the thermodynamic properties of the fluid phase of ethane in the form of a fundamental equation explicit in the Helmholtz energy was presented where the functional form of the residual part was developed using state-of-the-art linear and non-linear optimization algorithms [260]. It contained 44 coefficients that were fitted to selected data for the thermal and caloric properties of ethane both in the single-phase region and on the liquid-vapor phase boundary. The equation of state described the  $ppT$  surface of ethane with an uncertainty in density of less than 0.02–0.03% from the melting line up to temperatures of 520 K and pressures of 30 MPa. In the gaseous and supercritical region, high precision velocity of sound data were represented generally within less than 0.015%. Other reliable data sets were represented within their experimental uncertainties. The primary data, to which the equation was fitted, covered the fluid region from the melting line to temperatures of 675 K and pres-

tures of 900 MPa. Beyond this range, the equation showed reasonable extrapolation behavior up to very high temperatures and pressures.

### 3.2.5 Viscosity of Ethane

The shear viscosity coefficient of compressed gaseous and liquid ethane was measured at temperatures between 95 and 320 K and at pressures up to 30 MPa (4350 psia) with a torsionally oscillating quartz crystal viscometer [261]. The results of the measurements were compared with an equation previously proposed for calculating the viscosity of gaseous and liquid ethane. Differences between the equation and the measurements reported were less than 6%. The largest differences were found at low temperatures and high pressures, and along a supercritical isotherm at 320 K ( $T \approx 1.05T_c$ ).

A set of equations for the viscosity of ethane was based upon a body of experimental data that had been critically assessed for internal consistency and for agreement with theory in the zero-density limit, vapor phase, and critical region [262]. The equation extended over the temperature range from 100 K to the critical temperature in the liquid phase and from 200 K to the critical temperature in the vapor phase. In the supercritical region, the temperature range extends to 1000 K for pressures up to 2 MPa and to 500 K for pressures up to 60 MPa. The ascribed accuracy of the representation varies according to the thermodynamic state from  $\pm 0.5\%$  for the viscosity of the dilute gas near room temperature to  $\pm 3.0\%$  for the viscosity at high pressures and temperatures. Viscosity data generated by the equations at selected temperatures and pressures and along the saturation line were tabulated.

A vibrating-wire viscometer was used to measure the viscosity of gaseous ethane [263]. The experimental data were taken at subcritical temperatures of 290 and 300 K up to 88% of the saturated vapor pressure and at supercritical temperatures of 310, 320, 340, 370, 400, and 430 K at pressures up to a maximum of 30 MPa. The measured data were evaluated using an equation of state by Bücker and Wagner. The viscosity values of the isotherms were correlated as a function of reduced density using a power series expansion. A comparison with correlations from the literature showed deviations up to about 5% in the near critical region and up to 2% at higher densities and temperatures. On the basis of a comparison with direct experimental data from the literature, it was concluded that the new values are the most reliable for an improvement in the viscosity surface correlation of ethane. The measurements were later re-evaluated based on the determination of the wire radius using an improved calibration method [264].

An apparatus combining a vibrating-wire viscometer and a single-sinker densimeter was used to provide accurate  $\eta\rho pT$  data for four isotherms on ethane at 293, 307, and 423 K [265]. The maximum pressure was chosen to be about 95% of the saturated vapor pressure for the subcritical isotherms and a maximum of 30 MPa for the supercritical isotherms. Near the critical region, allocation errors for temperature and pressure have a significant impact on the uncertainty of the experimental densities. The

new viscosity data and additionally re-evaluated earlier data were compared with the viscosity surface correlations by others for ethane and propane as well as with selected experimental data for the low-density region. The new viscosity data should be used to improve the viscosity surface correlations available in the literature.

### 3.2.6 Surface Tension of Ethane

The surface tension of liquid ethane was measured between 129 and 180 K by a capillary rise method where three capillaries with different diameters (0.2, 0.4, and 2 mm) were interconnected and partially filled with liquid [258]. The data are summarized in Table 28.

**Table 28:** Surface tension of ethane.

| Temperature<br>K | Surface tension |        |
|------------------|-----------------|--------|
|                  | mN/m            | dyn/cm |
| 129.2            | 25.00           | 25.00  |
| 133.2            | 24.54           | 24.54  |
| 137.1            | 23.72           | 23.72  |
| 149.1            | 21.75           | 21.75  |
| 150.6            | 21.68           | 21.68  |
| 155.9            | 20.71           | 20.71  |
| 157.5            | 20.46           | 20.46  |
| 161.3            | 19.86           | 19.86  |
| 164.4            | 19.28           | 19.28  |
| 170.3            | 18.31           | 18.31  |
| 180.6            | 16.63           | 16.63  |

Data source: [258]

1 dyn =  $10^{-5}$  N

### 3.2.7 Thermal Conductivity of Ethane

Measurements of the thermal conductivity of ethane up to 5000 psia in the temperature interval between 278 and 444 K (40 and 340 °F) were made with a spherical conductivity cell [266]. The results were only in fair agreement with data of other investigators, which were obtained with entirely different types of instruments. The results were presented in tabular and graphical form. It appeared that the residual thermal conductivity is a single-valued function of weight throughout the range of conditions covered by this investigation. See also [137, 267, 268].

A coaxial cylinder method was used to measure the thermal conductivity of ethane in the pressure range from 10 up to 280 bar and in the temperature range from 308 up to 365 K [269].



The thermal conductivity of ethane in the critical region has been measured with a parallel-plate method as a function of temperature along 11 different isochores so as to obtain detailed information on the enhancement of the thermal conductivity in the critical region [270]. The experimental results appeared to be consistent with a theoretical equation that accounts for both the asymptotic and non-asymptotic critical behavior of the thermal conductivity of fluids in the critical region.

A set of equations for the thermal conductivity of ethane was based upon a body of experimental data that had been critically assessed for internal consistency and for agreement with theory in the zero-density limit and in the critical region [271]. The equations extended over the temperature range from 100 K to the critical temperature in the liquid phase and from 225 K to the critical temperature in the vapor phase. In the supercritical region the temperature range extended to 1000 K for pressures up to 1 MPa and to 625 K for pressures up to 70 MPa. The ascribed accuracy of the representation varied according to the thermodynamic state, from  $\pm 2\%$  for the thermal conductivity of the dilute gas near room temperature to  $\pm 5\%$  for the thermal conductivity at high pressures and temperatures. Thermal conductivity data generated by the equations at selected temperatures and pressures and along the saturation line were tabulated.

### 3.2.8 Critical Constants of Ethane

The critical-point properties of ethane are listed in Table 29.

**Table 29:** Critical-point properties of ethane and methane.

|         | $M$<br>g/mol | $T_c$<br>K          | $P_c$<br>MPa      | $\rho_c$<br>g/cm <sup>3</sup> | $V_c$<br>cm <sup>3</sup> /mol | $Z_c^a$ |
|---------|--------------|---------------------|-------------------|-------------------------------|-------------------------------|---------|
| Methane | 16.043       | $190.564 \pm 0.015$ | $4.599 \pm 0.003$ | $0.1627 \pm 0.0005$           | 98.60                         | 0.286   |
| Ethane  | 30.070       | $305.32 \pm 0.04$   | $4.872 \pm 0.01$  | $0.2066 \pm 0.003$            | 145.5                         | 0.279   |

<sup>a</sup>  $Z_c = P_c V_c / R T_c$ , where  $R = 8.31451 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$

Data source: [9]

Other sources used critical parameters of  $P_c = 4871.76 \text{ kPa}$  or  $48.0807 \text{ atm}$ ,  $T_c = 305.33 \text{ K}$ ,  $V_c = 0.14556 \text{ dm}^3/\text{mol}$ , and  $\rho_c = 6.870 \text{ mol/dm}^3$  [260].

### 3.2.9 Thermodynamic Properties of Ethane

The thermodynamic properties of ethane have been thoroughly investigated and are reported in several sources in the literature [257, 272].

### 3.2.9.1 Heat Capacity of Ethane

Experimental isobaric heat capacities of liquid ethane are listed in Table 30.

**Table 30:** Experimental isobaric heat capacities of liquid ethane.

| Temperature, K | Pressure, MPa | Isobaric heat capacity, J g <sup>-1</sup> K <sup>-1</sup> <sup>a</sup> |
|----------------|---------------|------------------------------------------------------------------------|
| 108.15         | 1.05          | 2.258                                                                  |
| 118.15         | 1.06          | 2.270                                                                  |
| 188.15         | 1.12          | 2.443                                                                  |
| 228.15         | 1.17          | 2.695                                                                  |
| 238.15         | 1.21          | 2.784                                                                  |
| 118.15         | 2.03          | 2.249                                                                  |
| 108.15         | 2.02          | 2.257                                                                  |
| 108.15         | 4.29          | 2.254                                                                  |
| 118.15         | 4.29          | 2.293                                                                  |
| 128.15         | 4.31          | 2.283                                                                  |
| 143.15         | 4.08          | 2.282                                                                  |
| 153.15         | 4.07          | 2.326                                                                  |
| 163.15         | 4.05          | 2.356                                                                  |
| 188.15         | 4.31          | 2.408                                                                  |
| 228.15         | 4.32          | 2.663                                                                  |
| 238.15         | 4.33          | 2.751                                                                  |

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.5$  K for  $T < 220$  K,  $u(T) = 0.25$  K for  $T > 220$  K,  $u(p) = 35$  kPa, and combined expanded uncertainty  $Uc(c_p) = 0.02 c_p$  with a 95% level of confidence.

Data source: [194]

The heat capacities of gaseous ethane have been measured down to 93 K with a low pressure thermal conductivity apparatus [273]. A method of obtaining the heat capacities from the thermal conductivity data was described that does not require a knowledge of the accommodation coefficient  $\alpha$ . The heat capacity results for ethane indicated a potential barrier restricting internal rotation of the two molecule halves with a depth of 11.5 kJ/mol (2.75 kcal/mol).

The specific heats of saturated liquid ethane,  $C_\sigma$ , have been measured at 106 temperatures in the temperature range 93 to 301 K [274]. The specific heats at constant volume,  $C_v$ , have been measured at 19 densities ranging from 0.2 to 3.1 times the critical density, at temperatures between 91 and 330 K, with pressures up to 33 MPa, at 200 PVT states in all. The uncertainty of most of the measurements was estimated to be less than 2.0%. As the critical point was approached, the uncertainty rose to about 5.0%. The results for  $C_\sigma$  for the temperature range 93 to 301 K were represented with an analytical equation as follows:

$$C_\sigma = C_1 + C_2 T + \frac{C_3 T}{(T_c - T)^{0.6}} + \frac{C_4}{T} + \frac{C_5}{T^2}$$

**Table 31:** Constants for saturated heat capacity equation of liquid ethane.

| Constant | Value             |
|----------|-------------------|
| $C_1$    | 0.2264822683E+02  |
| $C_2$    | 0.8796160711E-01  |
| $C_3$    | 0.1090640627E+01  |
| $C_4$    | 0.5371201054E+04  |
| $C_5$    | -0.2123389640E+06 |

Data source: [274]

where  $T_c$  is the critical temperature, 305.33 K and values of the coefficients are given in Table 31. At 298 K the vapor pressure was 4.2086 MPa, the density was 10.426 mol/L, and the measured saturated heat capacity was 167.24 J mol<sup>-1</sup> K<sup>-1</sup>.

Additional data on the heat capacity of ethane are available from Wiebe et al. [275] and Witt and Kemp [276]. Isobaric enthalpy increment measurements were made on liquid ethane over the temperature range 146.0 to 256.2 K and pressure ranges 1.16 to 5.07 MPa using an electrically heated flow calorimeter [277].

### 3.2.9.2 Heat of Combustion of Ethane

The upper heat of combustion of gaseous ethane is 1560.69 ± 0.25 kJ/mol (373.01 ± 0.06 kcal/mol) [197].

### 3.2.9.3 Enthalpy of Vaporization of Liquid Ethane

The enthalpy of vaporization of ethane at the normal boiling point (184 K) is 14.703 kJ/mol (3.514 kcal/mol).

### 3.2.10 Dielectric Constant of Liquid Ethane

The dielectric constant of ethane in the saturated liquid and compressed fluid states was measured at temperatures between 95 and 323 K and at pressures ranging up to 390 bar [278]. The data were combined with accurate density data from several sources to produce the Clausius-Mossotti function over a wide range of temperature and density. An analytical expression of the Clausius-Mossotti function was given, and the consistency of the available density data was examined.

## 3.3 Flammability Limits of Ethane

The flammable limits of ethane in air with upward propagation are from 3.0 to 12.4 vol.-% C<sub>2</sub>H<sub>6</sub> in air. The autoignition temperature is 788 K (515 °C). Limits of flammability of ethane in other oxidizing atmospheres have been measured as well [279].

### 3.4 Fuel Mixtures with Ethane

Fuel mixtures of ethane with methane were already discussed in this chapter, Section 2.8.1 on methane.

The heat of combustion and the specific impulse of ethane can be increased by suspending metal particles in the liquid fuel. In order to prevent the metal particles from settling, the liquid fuel has to be gelled. It is difficult to find suitable gelling agents for cryogenic propellants.

Aluminized ethane and propane gels have been evaluated along with other gelled hydrocarbon fuels [280, 281]. The gellants included alkoxides and silica-based materials. Hexane, ethane, propane, and hydrogen were gelled and their rheological properties were determined: shear stress versus shear rate and their attendant viscosities. Gellant concentrations were varied from 0.75 to 3.05 mass-%. The metal-loaded dispersions exhibited pseudoplastic behavior similar to that observed for the neat gels. The ethane gel had a much thicker consistency than the propane gel, as is evident by the higher  $k$  value ( $0.47 \text{ Pa}\cdot\text{s}^{0.22}$  versus  $0.22 \text{ Pa}\cdot\text{s}^{0.22}$ ), where  $k$  is a measure of viscosity.

## 4 Propane

Propane,  $\text{C}_3\text{H}_8$ ,  $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_3$ , dimethylmethane, CAS RN [74-98-6], is a colorless, odorless gas that is most frequently used as a compressed gas liquid at room temperature. The vapor pressure of propane at 298 K is 0.94844 MPa (9.36 atm = 137 psia). Because propane can be handled as a liquid at room temperature it would make it easier to handle as a rocket propellant than methane or ethane, which requires cryogenic handling apparatus. A common name for liquid propane is liquefied petroleum gas.

Propane can be separated from natural gas and gas released when crude oil is brought to the surface. Propane and propylene are formed during the cracking of crude oil to produce lighter (gasoline) fractions. The ideal work required for liquefaction of propane starting at 300 K and 101.3 kPa is 140.4 kJ/kg (60.4 BTU/lb).

### 4.1 Physical Properties of Propane

The free mini-REFPROP computer program, which can be downloaded from the National Institute of Standards and Technology (NIST) website [38], contains propane as an example. It can instantly create physical and thermochemical property tables and graphs for a wide range of temperatures. The thermophysical properties of propane are reported in Younglove and Ely [94]. The physical properties of propane are summarized in Table 32.

**Table 32:** Physical properties of propane.

| Property                                                       | SI units                                  | Other units                                                   | References |
|----------------------------------------------------------------|-------------------------------------------|---------------------------------------------------------------|------------|
| Molecular mass                                                 | 44.0956 g/mol                             | 22.678 mol/kg                                                 | [45]       |
| Freezing point                                                 | 85.46 K                                   | −187.69 °C                                                    |            |
| Boiling point                                                  | 231.1 ± 0.2 K                             | −42 °C                                                        |            |
| Density, liquid, at 293 K                                      | 0.50028 g/cm <sup>3</sup>                 | 31.23 lb/ft <sup>3</sup>                                      | [38]       |
| Viscosity, liquid, at 293 K and saturation pressure            | 102.55 μPa s                              | 0.10255 cPs                                                   |            |
| Viscosity, gas, at 205 K                                       | 8.01 μPa s                                | 0.008 cPs                                                     |            |
| Vapor pressure                                                 | 8.56 bar at 293 K                         | 124 psia at 68 °F                                             | [45]       |
| Thermal conductivity, liquid at 293 K, and saturation pressure | 96.144 mW m <sup>−1</sup> K <sup>−1</sup> | 0.05558 BTU h <sup>−1</sup> ft <sup>−1</sup> °F <sup>−1</sup> | [38]       |
| Heat capacity, $C_p$ , liquid, at 230 K                        | 98.36 J mol <sup>−1</sup> K <sup>−1</sup> | 23.5 cal mol <sup>−1</sup> °C <sup>−1</sup>                   | [45]       |
| Heat capacity, $C_p$ , gas, at 298 K                           | 73.60 J mol <sup>−1</sup> K <sup>−1</sup> | 17.6 cal mol <sup>−1</sup> °C <sup>−1</sup>                   |            |
| Enthalpy of formation at 298 K, liquid                         | −119.8 ± 0.59 kJ/mol                      | −28.6 kcal/mol                                                |            |
| Enthalpy of formation at 298 K, vapor                          | −104.7 ± 0.50 kJ/mol                      | −25.0 kcal/mol                                                |            |
| Enthalpy of fusion at 85 K                                     | 3.51 kJ/mol                               | 0.84 kcal/mol                                                 |            |
| Heat of evaporation at 231.1 K                                 | 19.04 kJ/mol                              | 4.55 kcal/mol                                                 |            |
| Heat of combustion                                             | −2219.2 ± 0.46 kJ/mol                     | 530 kcal/mol                                                  |            |
| Critical temperature                                           | 369.9 ± 0.2 K                             | 96.8 °C                                                       |            |
| Critical pressure                                              | 42.5 ± 0.1 bar                            | 616 psia                                                      |            |
| Critical density                                               | 5.1 ± 0.4 mol/L                           | 0.225 g/cm <sup>3</sup>                                       |            |

#### 4.1.1 Freezing Point of Propane

The triple point properties of propane are listed in Table 33. Other sources reported a triple-point temperature of  $85.525 \pm 0.005$  K [282].

**Table 33:** Triple-point properties of propane.

|             |                                              |
|-------------|----------------------------------------------|
| $T_t$       | 85.47 K                                      |
| $P_t$       | $1.6850 \times 10^{-10}$ MPa                 |
| $\rho_{tL}$ | 16.636 mol/dm <sup>3</sup>                   |
| $\rho_{tV}$ | $2.3775 \times 10^{-10}$ mol/dm <sup>3</sup> |

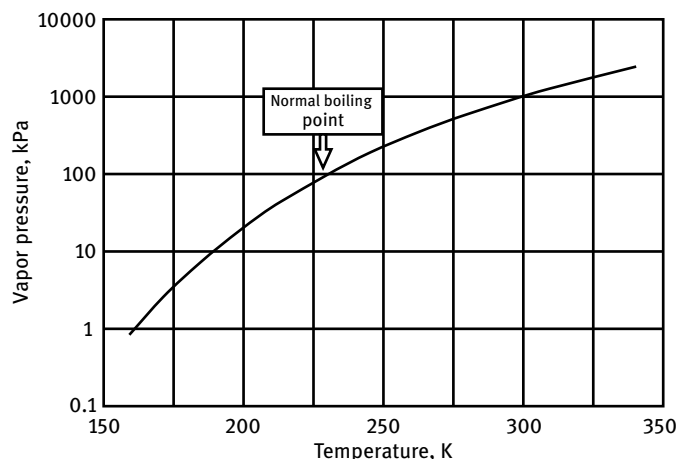
Data source: [94]

#### 4.1.2 Boiling Point of Propane

The boiling point of propane is 231.0679 K (−42.08 °C) [283]. The density of liquid propane at boiling point is 13.1687 mol/L.

### 4.1.3 Vapor Pressure of Propane

The vapor pressure of propane is illustrated in Figure 23.



**Figure 23:** Vapor pressure of propane. (Image created by Schmidt 2020 based on National Institute of Standards and Technology data.)

The vapor pressure of propane within the range 230.6 to 320.7 K (above the normal boiling point) can be calculated from the Antoine equation

$$\log P = A - B/(T + C) = 3.98292 - [819.296/(T - 24.417)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

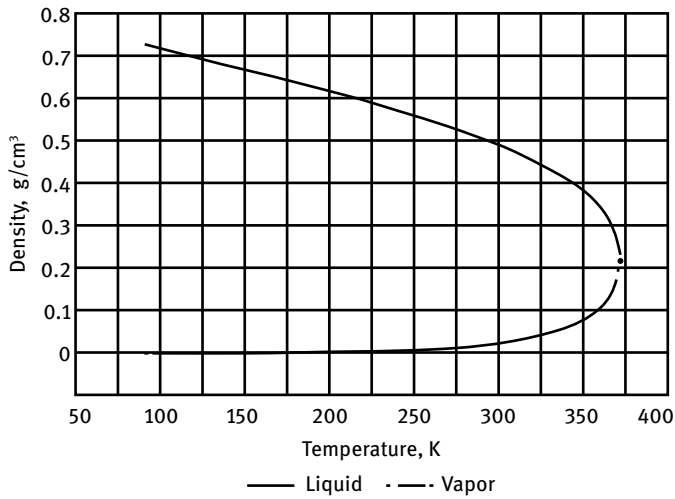
The vapor pressure of propane within the range 166.02 to 231.41 K (below the normal boiling point) can be calculated from the Antoine equation

$$\log P = A - B/(T + C) = 4.01158 - [834.26/(T - 22.763)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. This equation gives a vapor pressure of 8.56 bar (124 psia) at 293 K (20 °C) and 9.73 bar (141 psia) at 298 K (25 °C). These two equations were used in constructing Figure 23.

### 4.1.4 Density of Propane

The density of liquid and vapor propane under saturation conditions as a function of temperature is illustrated in Figure 24.

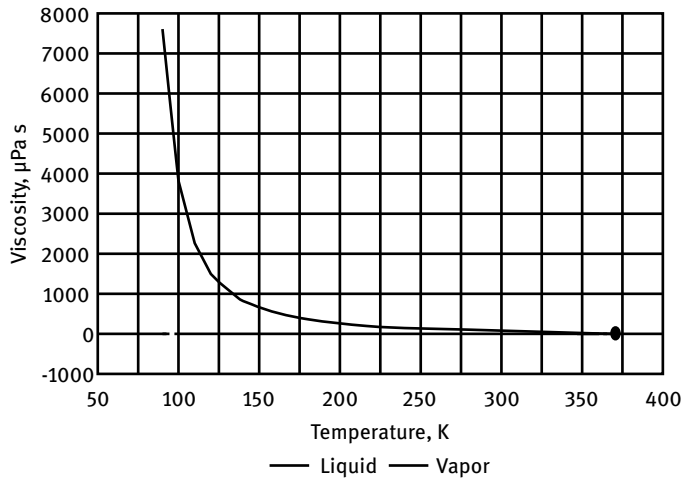


**Figure 24:** Density of saturated propane. (Image created by Schmidt 2020 based on National Institute of Standards and Technology data.)

#### 4.1.5 Viscosity of Propane

The viscosity of propane under saturation conditions as a function of temperature is illustrated in Figure 25.

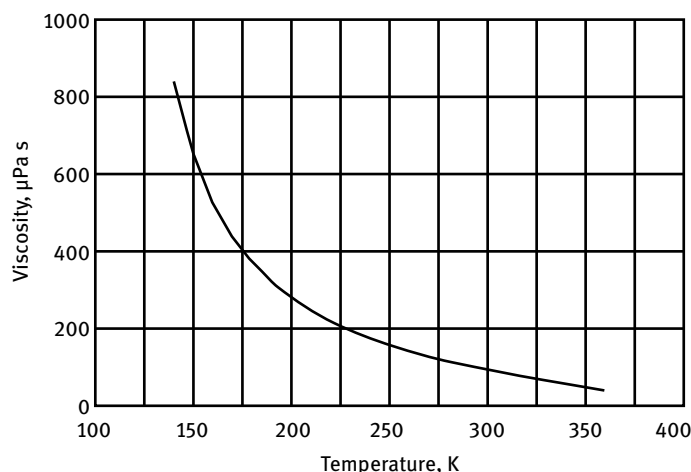
The viscosity of propane was measured in the liquid and gas phases at pressures up to 34.5 MPa (5000 psia) in the temperature interval between 278 and 478 K (40 and



**Figure 25:** Viscosity of saturated propane. (Image created by Schmidt 2020 based on National Institute of Standards and Technology data.)

400 °F) [284]. These measurements served to corroborate and extend the results reported in more extensive investigations carried out with entirely different types of instruments. For the most part, satisfactory agreement between several sets of investigations has been found. However, earlier measurements carried out with a rolling-ball viscometer indicated that the latter type of instrument is entirely unsuitable for measurements in the gas phase. Utilizing the current experimental data obtained for propane along with those that have been recorded in connection with the viscosity of ethane and *n*-butane, a comparison was made with the data reported by several investigators using various types of instruments.

Viscosity and thermal conductivity of gaseous and liquid propane have been measured and represented by empirical functions developed in previous work [285]. Tables of values were presented for the range 140–500 K and for pressures up to 50 MPa (500 atm). The viscosities were estimated to have uncertainties of about  $\pm 5\%$ . Dynamic viscosity of liquid propane is illustrated in Figure 26. The data in Figures 25 and 26 are essentially identical.



**Figure 26:** Viscosity of liquid propane along the saturation line. (Image created by Schmidt 2020 based on data from [285])

High-precision viscosity measurements on gaseous propane were performed in a quartz oscillating-disk viscometer with small gaps from room temperature up to about 625 K and for densities between 0.01 and 0.05 mol/L [286]. The experimental data were evaluated with a first-order expansion, in terms of density, for the viscosity. Reduced values of the second viscosity virial coefficients deduced from the zero-density and initial-density viscosity coefficients for propane and for higher *n*-alkanes were in close agreement with the theoretical representations. A new representation of the viscosity of propane within the limit of zero density was



provided using the new experimental data and some data sets from the literature. The universal correlation based on the extended principle of corresponding states extended over the temperature range 293 to 625 K with an uncertainty of  $\pm 0.5\%$  and deviated from earlier representations by about 1% at the upper temperature limit. The standard reference viscosity of propane gas at 298 K and 101 kPa is 8.1327  $\mu\text{Pa}\cdot\text{s}$ .

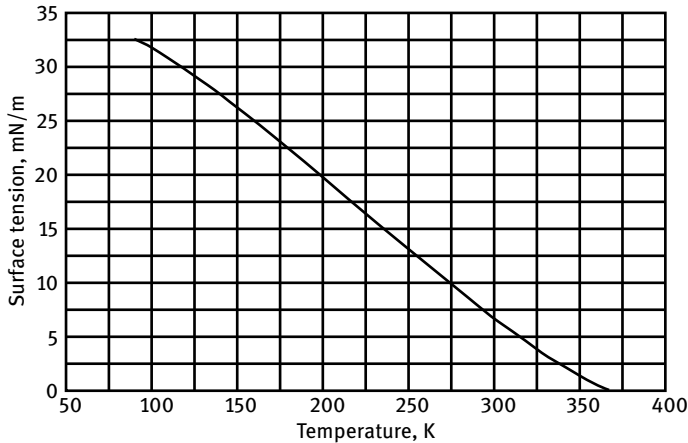
A different representation of the viscosity of propane included a zero-density correlation and an initial-density dependence correlation based on the kinetic theory of dilute gases [287]. The higher density contributions of the residual viscosity in the representation were formed by a combination of double polynomials in density and reciprocal temperature, and a free-volume term with a temperature-dependent close-packed density. The full surface correlation was based on a set of primary experimental data selected as a result of a critical assessment of the available information from 37 original viscosity studies, referring to 96 citations altogether. The validity of the representation extended from the triple point to 600 K and 100 MPa in accordance with the modified Benedict-Webb-Rubin equation of state. Tables of the viscosity according to the representative equations at selected temperatures and pressures and along the saturation line provided easy reference as well as a validation of computer codes. A re-evaluation of the viscosity data concerned the determination of the wire radius using an improved calibration [288].

An apparatus combining a vibrating-wire viscometer and a single-sinker densimeter was used to provide accurate  $\eta p p T$  data for four isotherms on ethane at 293, 307, and 423 K and five isotherms on propane at 273, 298, 366, 373, and 423 K [265]. The maximum pressure was chosen to be about 95% of the saturated vapor pressure for the subcritical isotherms and a maximum of 30 MPa for the supercritical isotherms. Near the critical region, allocation errors for temperature and pressure have a significant impact on the uncertainty of the experimental densities. The new viscosity data and earlier data that had also been re-evaluated were compared with the viscosity surface correlations by others for ethane and propane as well as with selected experimental data for the low-density region. These viscosity data can be used to improve the viscosity surface correlations available in the literature.

Another viscosity formulation for propane, using the reference equation of state for its thermodynamic properties by Lemmon, McLinden, and Wagner [289] and valid in the fluid region from the triple-point temperature to 650 K and pressures up to 100 MPa was based on a zero-density contribution and one for the critical enhancement, each based on experimental data [290]. The higher-density contributions were correlated as a function of the reciprocal reduced temperature  $\tau = T_c/T$  and of the reduced density  $\delta = \rho/\rho_c$  ( $T_c$  = critical temperature,  $\rho_c$  = critical density). The final formulation included 17 coefficients inferred by applying a linear optimization algorithm. Tables of viscosity data computed for the most recent formulation were given in an appendix for the single-phase region, for the vapor-liquid phase boundary, and for the near-critical region. See also [113].

#### 4.1.6 Surface Tension of Propane

The surface tension of propane along the saturation boundary under saturation pressure is illustrated in Figure 27.



**Figure 27:** Surface tension of propane. (Image created by Schmidt 2020 based on National Institute of Standards and Technology RefProp data.)

#### 4.1.7 Thermal Conductivity of Propane

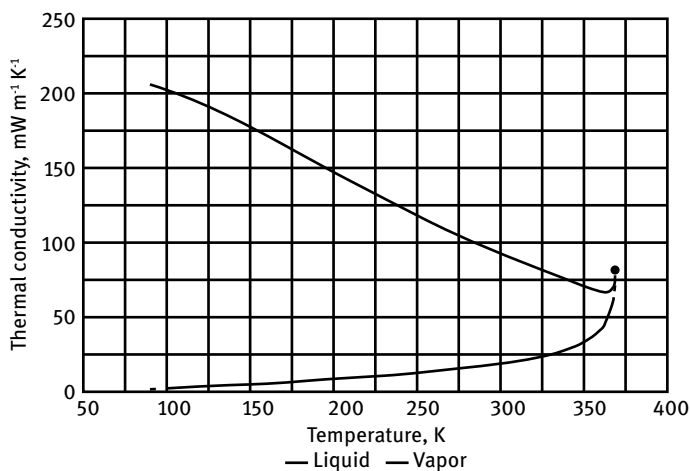
The thermal conductivity of propane under saturated liquid and vapor conditions is illustrated in Figure 28. The two curves for liquid and vapor propane meet at the critical point.

From RefProp, a calculation of the thermal conductivity of liquid propane at the saturation pressure at 295 K gives  $95.196 \text{ mW m}^{-1} \text{ K}^{-1}$  and the thermal conductivity of the saturated pressure gas phase above it is  $18.505 \text{ mW m}^{-1} \text{ K}^{-1}$ .

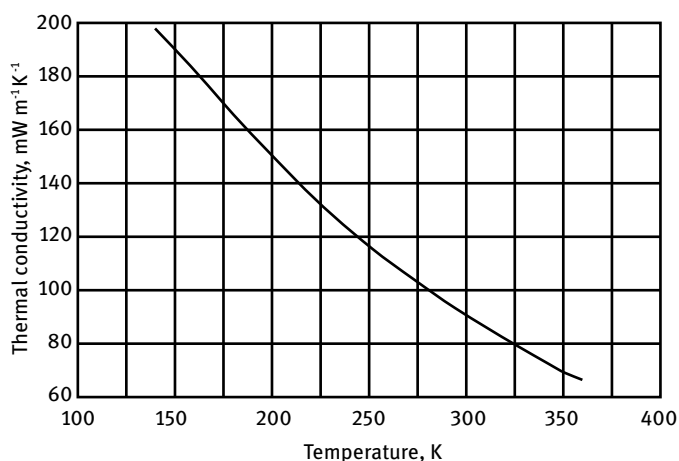
The thermal conductivity of propane was measured in both gas and liquid regions at temperatures and pressures above and below the critical point [291]. Five isotherms at 323, 341, 360, 379, and 413 K (122, 154, 189, 222, and 284 °F), and at pressures from 0.1 to 28.6 MPa (1 to 282 atm) were measured.

Thermal conductivity of gaseous and liquid propane have been measured and represented by empirical functions developed in previous work [286]. Tables of values were presented for the range 140–500 K and for pressures up to 50 MPa (500 atm). The thermal conductivity of liquid propane is illustrated in Figure 29. The data in Figures 28 and 29 are essentially identical.

The thermal conductivity of propane along seven isotherms from 110 to 300 K at pressures up to 70 MPa, with densities within the range 11–16.5 mol/L ( $0.484\text{--}0.726 \text{ g/cm}^3$ ) was measured and compared with literature data for liquid propane [137, 292].



**Figure 28:** Thermal conductivity of saturated liquid and gaseous propane. (Image created by Schmidt 2020 based on National Institute of Standards and Technology RefProp data.)



**Figure 29:** Thermal conductivity of liquid propane along the saturation line. (Image created by Schmidt 2020 based on data from [285].)

A coaxial cylinder method was used to measure the thermal conductivity of propane in the pressure range from 1 to about 70 MPa and in the temperature range from room temperature to 578 K (305 °C), extending data coverage to the critical region [293].

Thermal conductivity of propane was measured over the temperature range 192–320 K, at pressures up to 70 MPa, and densities to 15 mol/L, using a transient line-source instrument [294]. The experimental results were presented in the form of

a correlation together with other available data in the range 110–580 K up to 70 MPa, including the anomalous critical region.

Experimental data on the thermal conductivity of gaseous propane, covering a temperature range of 110 to 700 K and a pressure range of 0.1 to 70 MPa, were used together with previously available data to develop an improved empirical equation for the thermal conductivity of gaseous and liquid propane [295]. The quality of the new data was such that the thermal conductivity correlation for propane was estimated to have an uncertainty of about  $\pm 5\%$  at a 95% confidence level, with the exception of points near the critical point, where the uncertainty of the correlation increased to  $\pm 10\%$ .

Additional experimental data on the thermal conductivity of propane allowed improved correlations to be developed. Previous correlations had been limited by a lack of thermal conductivity data for the vapor at temperatures below 300 K and liquid data near the critical point. In addition, significant discrepancies were noted in the thermal conductivity of high-temperature dilute gas. Measurements over the temperature range from the triple point at 85.5 to 600 K and the pressure range 0.1 to 70 MPa were estimated to have an uncertainty of 1% for measurements removed from the critical point and at pressures above 1 MPa, which increases to 3% in the critical region and 4% at low pressures ( $<1$  MPa) [296]. These experimental data were used together with previously available data to develop improved correlations for the thermal conductivity of propane.

Measurements of the thermal conductivity of propane over the temperature range from 370.83 to 381.00 K, and the pressure range 0.1 to 15 MPa were performed in a coaxial cylinder cell operating under steady-state conditions and were extended along eight quasi-isotherms to above the critical temperature [297]. The parameters of a background equation were determined from experimental data in order to analyze the critical enhancement of the thermal conductivity as a function of temperature and density. On the basis of the measurement of more than 500 experimental points, a phenomenological equation was provided to describe the thermal conductivity of propane, from the critical temperature 369.825 to 600 K and densities up to  $550 \text{ g/cm}^3$ . This equation can be generalized to calculate the supercritical behavior of the thermal conductivity for any fluid.

#### 4.1.8 Heat Transfer Coefficient of Liquid Propane

Heat transfer characteristics of propane were experimentally evaluated in heated tube tests [298–300]. Forced convection heat transfer coefficients were determined over the range of fluid conditions covering operating condition from 3.1 to 12.4 MPa (450 to 1800 psia), 116 to 394 K ( $-250$  to  $+250$  °F), and 15 to 45 m/s (50 to 150 ft/s), with wall temperatures from ambient to 922 K (1200 °F), and heat fluxes to  $1634 \text{ W/cm}^2$  ( $10 \text{ BTU in}^{-2} \text{ s}^{-1}$ ). Nucleate boiling and coking were also evaluated. Coking occurred over a wide temperature range. Coking rate was comparable with published data for RP-1. Propane purity affected the rate but not the threshold temperature of coking.

When testing a LOX/propane rocket engine, carbon deposition in the acoustic cavities was extensive to the point that acoustic damping capabilities could be lost. Burnout heat flux was found to be considerably higher than an extrapolation of available low heat flux data would have predicted. Operating with propane at subcritical pressures was unacceptable because of low burnout heat flux. The low wall temperature threshold determined for the coking of propane, combined with the incompatibility of commercial propane with copper, the material of choice for high pressure regeneratively cooled chambers because of its high thermal conductivity, may eliminate propane as a candidate propellant for certain applications. Otherwise, propane would offer a desirable combination of high combustion performance and high mass density.

A series of heat transfer tests with propane was conducted at pressures of 0.5–30 MPa, flow velocities of 2–106 m/s, and heat fluxes up to 66 MW/m<sup>2</sup> in stainless-steel and copper tubes, and the deposit formation rates for kerosene in tubes were measured [152]. Forced convective heat transfer correlations were obtained for liquid methane, liquid propane, and kerosene, up to extreme heat fluxes at which test tubes burnt out. The test results indicated that heat transfer coefficients of methane and propane decreased at high wall temperatures.

#### 4.1.9 Critical Constants of Propane

The critical constants of propane and butane are listed in Table 34. Other sources gave  $T_c = 369.80$  K,  $P_c = 42.3974$  bar,  $\rho_c = 4.96$  mol/L [69].

**Table 34:** Critical-point properties of propane and butane.

|         | $M$<br>g/mol | $T_c$<br>K   | $P_c$<br>MPa | $\rho_c$<br>g/cm <sup>3</sup> | $V_c$<br>cm <sup>3</sup> /mol | $Z_c^a$ |
|---------|--------------|--------------|--------------|-------------------------------|-------------------------------|---------|
| Propane | 44.097       | 369.83 ± 0.1 | 4.248 ± 0.01 | 0.220 ± 0.003                 | 200                           | 0.277   |
| Butane  | 58.123       | 425.12 ± 0.1 | 3.796 ± 0.01 | 0.228 ± 0.003                 | 255                           | 0.274   |

<sup>a</sup>  $Z_c = P_c V_c / R T_c$ , where  $R = 8.31451$  Pa m<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>

Data source: [9]

#### 4.1.10 Thermodynamic Properties of Propane

An equation of state was developed for the thermodynamic properties of propane that was valid for temperatures from the triple-point temperature (85.525 K) to 650 K and for pressures up to 1000 MPa [289]. The formulation can be used for the calculation of all thermodynamic properties, including density, heat capacity, velocity of sound, energy, and saturation properties. Comparisons with available experimental data established the accuracy of calculated properties. The approximate uncertainties of properties calculated with the new equation are 0.01 to 0.03% in density below 350 K, 0.5% in

heat capacities, 0.03% in the velocity of sound between 260 and 420 K, and 0.02% in vapor pressure above 180 K. Deviations in the critical region were higher for all properties except for vapor pressure.

#### 4.1.10.1 Heat Capacity of Propane

Experimental isobaric heat capacities of liquid propane are listed in Table 35.

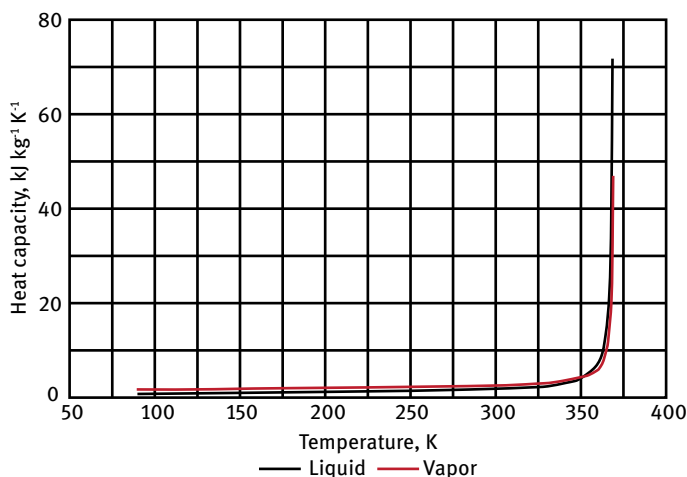
**Table 35:** Experimental isobaric heat capacities of liquid propane.

| Temperature, K | Pressure, MPa | Isobaric heat capacity, $\text{J g}^{-1} \text{K}^{-1}$ |
|----------------|---------------|---------------------------------------------------------|
| 108.15         | 1.16          | 1.927                                                   |
| 118.15         | 1.17          | 1.922                                                   |
| 128.15         | 1.18          | 1.934                                                   |
| 143.15         | 1.13          | 1.960                                                   |
| 153.15         | 1.19          | 1.987                                                   |
| 163.15         | 1.17          | 1.995                                                   |
| 188.15         | 1.19          | 2.067                                                   |
| 228.15         | 1.15          | 2.239                                                   |
| 238.15         | 1.11          | 2.296                                                   |
| 248.15         | 1.16          | 2.349                                                   |
| 258.15         | 1.16          | 2.396                                                   |
| 108.15         | 3.68          | 1.966                                                   |
| 118.15         | 3.65          | 1.975                                                   |
| 128.15         | 3.67          | 1.957                                                   |
| 128.15         | 3.64          | 1.965                                                   |
| 143.15         | 3.69          | 1.966                                                   |
| 228.15         | 3.67          | 2.232                                                   |
| 238.15         | 3.68          | 2.284                                                   |
| 248.15         | 3.67          | 2.317                                                   |
| 258.15         | 3.68          | 2.361                                                   |
| 108.15         | 5.16          | 1.965                                                   |
| 118.15         | 5.18          | 1.974                                                   |
| 128.15         | 5.19          | 1.963                                                   |
| 143.15         | 5.18          | 1.963                                                   |
| 153.15         | 5.20          | 2.011                                                   |
| 163.15         | 5.21          | 2.026                                                   |
| 188.15         | 5.22          | 2.066                                                   |
| 228.15         | 5.22          | 2.225                                                   |
| 238.15         | 5.22          | 2.282                                                   |
| 248.15         | 5.19          | 2.301                                                   |
| 258.15         | 5.22          | 2.353                                                   |
| 108.15         | 5.33          | 1.923                                                   |
| 118.15         | 5.43          | 1.938                                                   |
| 128.15         | 5.43          | 1.940                                                   |

Standard uncertainties  $u$  are  $u(T) = 0.5 \text{ K}$  for  $T < 220 \text{ K}$ ,  $u(T) = 0.25 \text{ K}$  for  $T > 220 \text{ K}$ ,  $u(p) = 35 \text{ kPa}$ , and combined expanded uncertainty  $Uc(c_p) = 0.02 c_p$  with a 95% level of confidence.

Data source: [194]

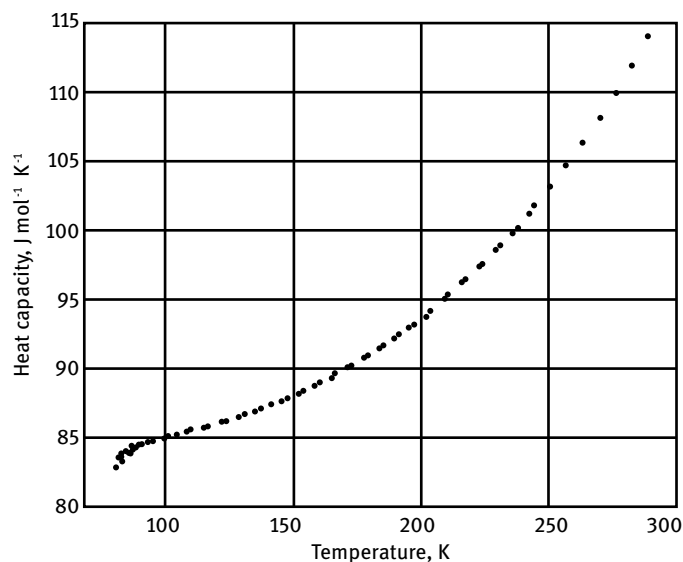
The heat capacity of propane is illustrated in Figure 30. The two curves for liquid and gaseous propane run very close to each other.



**Figure 30:** Heat capacity  $c_p$  of liquid and vapor propane at saturation point. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

Experimental specific heats for saturated liquid propane along the coexistence path have been determined from the triple-point temperature (85 K) to 289 K (Figure 31) [283]. Specific heats for the compressed liquid at a constant molar volume have been determined along isochors at nine different densities ranging from near the triple-point liquid density to about twice the critical-point density (at pressures up to 300 bar). Comparisons with previous experimental and/or derived data showed agreement within combined uncertainties of about 3%.

Molar heat capacities at constant volume ( $C_V$ ) from 85 to 345 K with pressures to 35 MPa were measured with an adiabatic calorimeter for pure propane [301]. The high purity of the samples was verified by chemical analysis. Measurements were conducted on liquid propane in equilibrium with its vapor and on compressed liquid samples along isochors. Heat capacity results were reported for two-phase ( $C_{V(2)}$ ), saturated liquid ( $C_{\sigma}$ ), and single-phase ( $C_V$ ) isochors. Vapor pressure data were based on measurements of  $C_{V(2)}$  along a two-phase isochore. Measurements were also made to determine the triple-point temperature of  $85.525 \pm 0.005$  K and heat of fusion of  $3508 \pm 20$  J/mol for propane near its triple point. The principal sources of uncertainty in  $C_V$  were the temperature rise measurement and the change-of-volume work adjustment.



**Figure 31:** Specific heat of saturated liquid propane. (Reproduced and modified from [69].)

#### 4.1.10.2 Heat of Combustion of Propane

The upper heat of combustion of propane gas is  $2219.17 \pm 0.46$  kJ/mol ( $530.39 \pm 0.11$  kcal/mol) [197].

#### 4.1.10.3 Enthalpy of Formation of Propane

The standard enthalpy of formation of liquid propane at 298 K is  $-119.8 \pm 0.59$  kJ/mol ( $-28.6$  kcal/mol). The standard enthalpy of formation of propane vapor at 298 K is  $-104.7 \pm 0.50$  kJ/mol ( $-25.0$  kcal/mol).

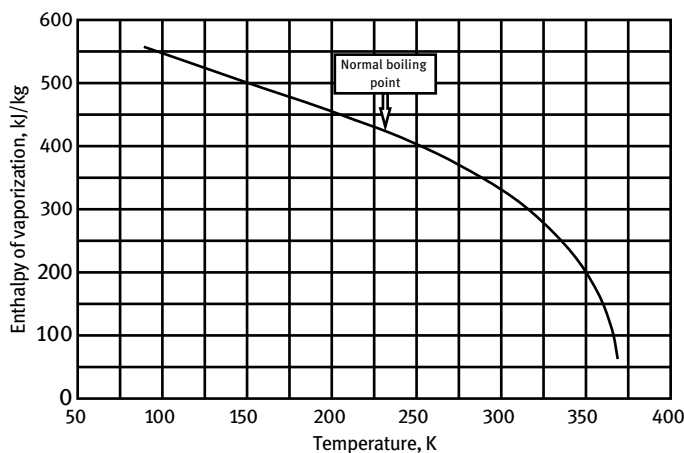
#### 4.1.10.4 Enthalpy of Fusion of Propane

The heat of fusion of propane is  $3508 \pm 20$  J/mol ( $0.84$  kcal/mol) [301].

#### 4.1.10.5 Enthalpy of Vaporization of Liquid Propane

The enthalpy of vaporization of propane at the normal boiling point at 231.1 K and 101 kPa is 19.04 kJ/mol (4.55 kcal/mol). The dependence of the enthalpy of vaporization on temperature (and pressure) under saturation conditions is illustrated in Figure 32. The enthalpy of vaporization approaches zero as the temperature increases to near the critical temperature.





**Figure 32:** Enthalpy of vaporization of propane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

## 4.2 Chemical Properties of Propane

### 4.2.1 Thermal Decomposition and Coke Deposition of Propane

A high-pressure fuel coking test apparatus was used to evaluate thermal decomposition (coking) limits and carbon deposition rates in heated copper tubes for commercial-grade propane [302]. Tests were conducted using JP-7 and chemically pure propane as being representative of more refined cuts of the baseline fuels. A parametric evaluation of fuel thermal stability was performed at pressures of 136 to 340 atm, bulk fuel velocities within the range 6–30 m/s and tube wall temperatures within the range 422–811 K. The effect of the inside wall material on deposit formation was evaluated in selected tests using nickel-plated tubes. The carbon deposition rates for the propane fuels were generally higher than those obtained for either of the kerosene fuels at any given wall temperature. Plating the inside wall of the tubes with nickel was found to significantly reduce carbon deposition rates for RP-1 fuel.

The heat transfer characteristics of propane at subcritical and supercritical pressure were experimentally evaluated using electrically heated Monel K-500 tubes [303, 304]. A design correlation for supercritical heat transfer coefficient was established using the same approach previously applied to supercritical oxygen. Flow oscillations were observed and the onset of these oscillations at supercritical pressures correlated with wall-to-bulk temperature ratio and velocity. The critical heat flux measured at subcritical pressure correlated with the liquid velocity and subcooling. Long-duration tests under fixed heat flux conditions were conducted to evaluate coking on the coolant side tube wall. Coking rates comparable with those with RP-1 were observed.

#### 4.2.2 Radiolysis of Propane

Methane and propane radiolysis reactions go by different routes. A comparative study of variations of  $G(H_2)$  with respect to temperature at very small conversions in a hydrocarbon in which abstraction is believed to predominate at room temperature ( $C_3H_8$ ) and in  $CH_4$  might provide more definitive insight into the question of the apparent inertness of methane to H atom attack [21].

Propane or methane, ethane, or ethene were irradiated to study radiation effects on stored liquid propellants on spacecraft with auxiliary RTG or nuclear power sources [23, 24]. Radiation experiments with propane at the higher dose rate were done in 1100F aluminum vessels to see if there were any obvious effects attributable to container materials. Samples of the gas above liquid propane at 195 K ( $-78^\circ\text{C}$ ) were analyzed by mass spectrometry (MS). The results showed the major gaseous products to be unsaturated  $C_2$  compounds, acetylene and ethene. Methane was also always present in significant quantities. The surprising result in these analyses was the general absence of hydrogen. From the amount of unsaturated compounds present there should have been easily discernible amounts of hydrogen. One might suspect that the hydrogen reacted with the titanium vessel in which the irradiation was performed. Such a reaction is less likely with an aluminum vessel, however, but there was no difference. Low-dose-rate experiments were also conducted with liquid propane in titanium vessels for a period of almost 4 months at an average dose rate of  $4.80 \times 10^3$  rad/h.

#### 4.3 Materials Compatibility with Propane

Materials compatibility of hydrocarbon fuels (propane, methane, Mil-Spec RP-1, and *n*-dodecane) in contact with copper-based combustion chamber liner materials (OFHC, NASA-Z, and ZrCu coppers) was tested using two different methods [216]. Static tests, in which copper coupons were exposed to fuel for long durations at constant temperature and pressure, provided compatibility data in a precisely controlled environment. Dynamic tests, using the Aerojet Carbothermal Test Facility, provided fuel and copper compatibility data under realistic booster engine service conditions. Tests were conducted using very pure grades of each fuel and fuels to which a contaminant, e.g., ethene or methyl mercaptan, was added to define the role played by fuel impurities. It was found that each of the copper materials exhibited similar compatibility behavior. However, there were significant differences among the various hydrocarbon fuels tested. In propane, no carbon deposits were formed up to  $T_{\text{wall}} = 736$  K ( $865^\circ\text{F}$ ) and copper corrosion was observed in all tests with sulfur contents down to 1 ppm. Copper(I) sulfide is the corrosion product.

## 4.4 Safety Properties of Propane

### 4.4.1 Toxicity of Propane

Propane, like most lower hydrocarbons, is mostly acting as an asphyxiant and narcotic when inhaled at concentrations of several percent by volume in air. The NIOSH REL is 1000 ppm (1800 mg/m<sup>3</sup>) and the OSHA TWA is also 1000 ppm (1800 mg/m<sup>3</sup>). It has been reported that brief inhalation exposures up to 10000 ppm propane in air caused no symptoms in humans.

Propane is a simple asphyxiant and does not present an Immediately Dangerous to Life and Health (IDLH) hazard at concentrations below its lower explosive limit (LEL). The original IDLH was based on the LEL of 21000 ppm rounded down to 20000 ppm, but it was later lowered to 2100 ppm which is 10% of the LEL.

Commercially sold propane is scented with an odorant for safety reasons to make leaks more readily detectable before they reach the flammable range.

### 4.4.2 Flammable Range of Propane

The flammable range of propane is from 2.1 to 9.5 vol.-% in air. The lower temperature limit of flammability is at 171 K (−102 °C). The autoignition temperature in air is 723 K (450 °C).

### 4.4.3 Detonation of Air/Propane Mixtures

During a study of the venting of a fast flame (100–800 m/s) in a round ignition pipe (140 mm I.D.) into a semispherical vessel containing a mixture of the same composition and initial pressure, the flame jet emerging from the pipe interacted with the remains of an unburned starting ring vortex set into motion by the accelerating flame front, and the subsequent intense combustion lead to the initiation of an unconfined detonation inside the vessel [235]. A parametric investigation of this phenomenon in nitrogen-diluted (29.4–68.4 vol.-%) stoichiometric mixtures of oxygen/propane has been carried out for a range of exit orifice diameters (50, 101, and 140 mm) under initial pressure of 0.4 and 1 atm. A small number of atmospheric pressure experiments have also been conducted with nitrogen-diluted (33.3–57.1 vol.-%) stoichiometric oxygen/methane mixtures. A criterion, based on the notion of a critical Damköhler number and minimum energy release requirement, has been suggested for the initiation of unconfined detonation by a venting jet flame. All experimental results for a given initial pressure and fuel may be combined into a single curve, separating conditions leading to detonation from those that do not. The critical orifice diameter below which a transition to unconfined detonation does not occur was reduced for a venting fast flame by comparison with a steady detonation wave.

#### 4.5 Gelled Propane

The performance of propane and other hydrocarbons as fuels in bipropellant rocket engines can be increased by the addition of metal powders with high heats of combustion and high densities. In order to prevent the solid particles from settling during storage, the liquid needs to be gelled. Several gelling agents have been proposed for propane [305, 306]. The bipropellant system may be, but need not be, hypergolic (depending on the type of oxidizer used).

### 5 Butane and Pentane

Butane or pentane have not yet been used as fuels in rocket propellants. A hydrogen peroxide/butane dual mode bipropellant thruster named Halcyon has been proposed by Tesseract/Benchmark Space Systems. Traces of butane or pentane may be found in other hydrocarbons used as rocket fuels. Information on these hydrocarbons can be obtained from other literature sources.

#### 5.1 Physical Properties of Butane and Pentane

Thermophysical properties of *n*-butane are summarized in [94, 307, 308]. The heats of combustion and enthalpies of formation of ten gaseous C<sub>4</sub> hydrocarbons were measured in a calorimeter at ambient pressure [309]. The enthalpy of formation of *n*-butane vapor is  $-127.1 \pm 0.7$  kJ/mol ( $-30.37 \pm 0.16$  kcal/mol).

### Higher (C>5) Aliphatic Hydrocarbons

#### 6 Hexane

Hexanes, C<sub>6</sub>H<sub>14</sub>, and heptanes, C<sub>7</sub>H<sub>16</sub>, are typical constituents of gasoline, but are not used as rocket fuels in the pure state. Hexane has five isomers. *n*-Hexane, CAS RN 110-54-3, is often used as a model compound to determine the physical properties of hydrocarbons in gasoline in a more reproducible manner. *n*-Hexane is used as a constituent in gasoline surrogate mixtures. Because hexane is more readily available in pure form than other hydrocarbons, it is often used for thermal decomposition studies that are also useful for evaluating the thermal decomposition of other hydrocarbon rocket fuels.

## 6.1 Physical Properties of Hexane

The physical properties of *n*-hexane are listed in Table 36.

**Table 36:** Physical properties of *n*-hexane.

| Property                                               | SI units                                   | Other units                                                                   | References    |
|--------------------------------------------------------|--------------------------------------------|-------------------------------------------------------------------------------|---------------|
| Molecular mass                                         | 86.1754 g/mol                              | 11.6042 mol/kg                                                                | [45]          |
| Freezing point                                         | 178 ± 1 K                                  | −95 °C                                                                        | [45]          |
| Boiling point                                          | 341.9 ± 0.3 K                              | 68.8 °C                                                                       | [45]          |
| Density at 303 K                                       | 0.66 g/cm <sup>3</sup>                     | 41.2 lb/ft <sup>3</sup>                                                       | [310]         |
| Compressibility at 303 K                               | 1.569 × 10 <sup>−9</sup> Pa <sup>−1</sup>  | 1.59 × 10 <sup>−4</sup> atm <sup>−1</sup>                                     | [310]         |
| Viscosity at 298 K                                     | 294 μPa s                                  | 0.294 cPs                                                                     | [311]         |
| Viscosity at 213 K                                     | 8.9 × 10 <sup>−4</sup> Pa s                | 0.89 cPs                                                                      | [312]         |
| Vapor pressure at 298 K                                | 0.200 bar                                  | 150 mm Hg                                                                     | [45]          |
| Surface tension at 298 K                               | 18.43 mN/m                                 | 18.43 dyn/cm                                                                  | [311]         |
| Thermal conductivity, liquid at 303 K                  | 0.1381 W m <sup>−1</sup> K <sup>−1</sup>   | 3.30 × 10 <sup>−4</sup> cal cm <sup>−1</sup> °C <sup>−1</sup> s <sup>−1</sup> | [310]         |
| Heat capacity, <i>C<sub>p</sub></i> , liquid, at 298 K | 195.52 J mol <sup>−1</sup> K <sup>−1</sup> | 46.7 cal mol <sup>−1</sup> °C <sup>−1</sup>                                   | [45]          |
| Enthalpy of formation at 298 K, liquid                 | −198.7 ± 0.67 kJ/mol                       | −47.49 kcal/mol                                                               | [45]          |
| Enthalpy of formation at 298 K, vapor                  | −167.1 kJ/mol<br>−167.31 kJ/mol            | −39.94 kcal/mol<br>−39.99 kcal/mol                                            | [45]<br>[203] |
| Enthalpy of fusion at 177 K                            | 13.079 kJ/mol                              | 3.126 kcal/mol                                                                | [45]          |
| Heat of evaporation at NBP <sup>a</sup>                | 28.85 kJ/mol                               | 6.89 kcal/mol                                                                 | [45]          |
| Upper heat of combustion                               | 4163 ± 20 kJ/mol                           | 995 kcal/mol                                                                  | [45]          |
| Critical temperature                                   | 507.6 ± 0.5 K                              | 234.6 ± 0.5 °C                                                                | [45]          |
| Critical pressure                                      | 30.2 ± 0.4 bar                             | 29.8 atm                                                                      | [45]          |
| Critical density                                       | 2.71 ± 0.02 mol/L                          | 0.233 g/cm <sup>3</sup>                                                       | [45]          |

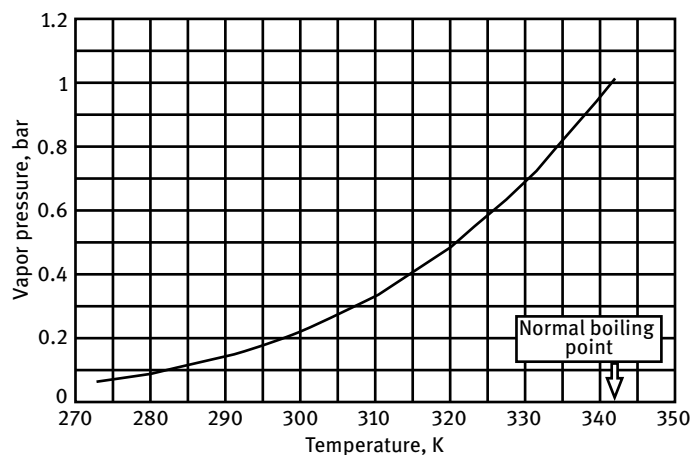
<sup>a</sup> NBP = normal-boiling point

The vapor pressure of *n*-hexane within the range 286.18–342.69 K can be calculated using an Antoine equation

$$\log P = 4.00266 - [1171.53 / (T - 48.784)]$$

where *P* is the pressure in bar and *T* is the temperature in kelvin. This vapor pressure function for temperatures below the NBP is illustrated in Figure 33.

Reference equations for the thermal conductivity of *n*-hexane were based in part upon a body of experimental data that had been critically assessed for internal consistency and for agreement with theory whenever possible [313]. In the case of the thermal conductivity of dilute gas, a theoretically based correlation was adopted in order to extend the temperature range of the experimental data. In the critical region, the experimentally observed enhancement of the thermal conductivity was well rep-



**Figure 33:** Vapor pressure of *n*-hexane. (Image created by Schmidt 2020 based on National Institute of Standards and Technology data.)

resented by theoretically based equations containing just one adjustable parameter. The correlations were applicable for the temperature range from the triple point to 600 K and pressures up to 500 MPa.

## 7 Heptane

Heptanes,  $C_7H_{16}$ , are typical constituents of gasoline. Heptane has 12 isomers. *n*-Heptane, CAS RN [142-82-5], is a natural constituent of many gasolines and jet engine fuels and is often used as a model compound to determine the physical properties of hydrocarbons in gasoline in a more reproducible manner. *n*-Heptane is used as a constituent in gasoline surrogate mixtures. Heptane may be present as the low boiling fraction of kerosenes used as jet fuels or rocket propellants. Because heptane is more readily available in pure form than other hydrocarbons, it is often used for thermal decomposition studies that are also useful for evaluating the thermal decomposition of other hydrocarbon rocket fuels.

### 7.1 Physical Properties of Heptane

The physical properties of *n*-heptane are listed in Table 37. The boiling points of hydrocarbons are usually divided into a lower range for gasolines and an upper range for kerosenes. The boiling points of heptanes are more in the boiling range of gasolines than that of kerosenes.

**Table 37:** Physical properties of *n*-heptane.

| Property                                                | SI units                                   | Other units                                                                   | References |
|---------------------------------------------------------|--------------------------------------------|-------------------------------------------------------------------------------|------------|
| Molecular mass                                          | 100.2019 g/mol                             | 9.9798 mol/kg                                                                 | [45]       |
| Freezing point                                          | 182.6 ± 0.4 K                              | −90.5 ± 0.4 ± 0.3 °C                                                          | [45]       |
| Boiling point                                           | 371.5 ± 0.3 K                              | +98.4 °C                                                                      | [45]       |
| Density at 303 K                                        | 0.684 g/cm <sup>3</sup>                    | 42.7 lb/ft <sup>3</sup>                                                       | [310]      |
| Compressibility at 303 K                                | 1.322 × 10 <sup>−9</sup> Pa <sup>−1</sup>  | 1.34 × 10 <sup>−4</sup> atm <sup>−1</sup>                                     | [310]      |
| Viscosity at 298 K                                      | 386 μPa s                                  | 0.386 cPs                                                                     | [311]      |
| Surface tension at 293 K                                | 20.14 mN/m                                 | 20.14 dyn/cm                                                                  | [312]      |
| Surface tension at 313 K                                | 18.18 mN/m                                 | 18.18 dyn/cm                                                                  |            |
| Surface tension at 333 K                                | 16.22 mN/m                                 | 16.22 dyn/cm                                                                  |            |
| Surface tension at 353 K                                | 14.26 mN/m                                 | 14.26 dyn/cm                                                                  |            |
| Thermal conductivity, liquid at 303 K                   | 0.1397 W m <sup>−1</sup> K <sup>−1</sup>   | 3.34 × 10 <sup>−4</sup> cal cm <sup>−1</sup> °C <sup>−1</sup> s <sup>−1</sup> | [310]      |
| Heat capacity, <i>C<sub>p</sub></i> , liquid, at 298 K  | 224.64 J mol <sup>−1</sup> K <sup>−1</sup> | 58.47 cal mol <sup>−1</sup> °C <sup>−1</sup>                                  | [45]       |
| Enthalpy of formation, vapor at 298 K                   | −187.8<br>± 0.79 kJ/mol                    | −44.88 kcal/mol                                                               | [45]       |
| Enthalpy of formation, liquid at 298 K                  | −224.4<br>± 0.79 kJ/mol                    | −53.63 kcal/mol                                                               | [45]       |
| Enthalpy of fusion at 182.55 K                          | 14.037 kJ/mol                              | 3.35 kcal/mol                                                                 | [45]       |
| Heat of evaporation at NBP                              | 31.77 kJ/mol                               | 7.59 kcal/mol                                                                 | [45]       |
| Upper heat of combustion                                | 4817 ± 8 kJ/mol                            | 1151 ± 2 kcal/mol                                                             | [45]       |
| Index of refraction, <i>n<sub>D</sub></i> <sup>20</sup> | 1.38756                                    | —                                                                             | [314]      |
| Critical temperature                                    | 540 ± 2 K                                  | 267 ± 2 °C                                                                    | [45]       |
| Critical pressure                                       | 27.4 ± 0.3 bar                             | 27.04 ± 0.3 atm                                                               | [45]       |
| Critical density                                        | 2.35 ± 0.07 mol/L                          | 0.235 g/cm <sup>3</sup>                                                       | [45]       |

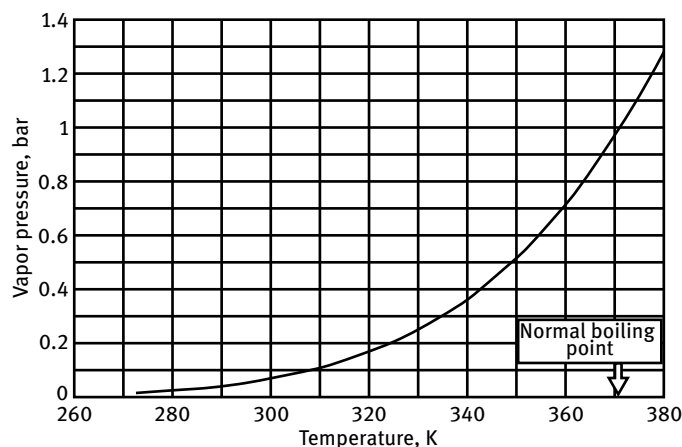
The vapor pressure of *n*-heptane in the range 299.07–372.43 K can be calculated using an Antoine equation

$$\log P = 4.02832 - [1268.636 / (T - 56.199)]$$

where *P* is the pressure in bar and *T* is the temperature in kelvin. The vapor pressure of *n*-heptane below its normal boiling point at 101 kPa is illustrated in Figure 34.

The viscosities of *n*-heptane and *n*-octane and their binary mixtures were measured as part of calibrating a two-capillary viscometer [315].

Equations for the thermal conductivity of *n*-heptane were based in part upon a body of experimental data that had been critically assessed for internal consistency and for agreement with theory whenever possible [316]. In the case of the thermal conductivity of dilute gas, a theoretically based correlation was adopted in order to extend the temperature range of the experimental data. In the critical region, the experimentally observed enhancement of the thermal conductivity was well represented by theoretically based equations containing just one adjustable parameter.



**Figure 34:** Vapor pressure of *n*-heptane. (Image created by Schmidt 2020 based on National Institute of Standards and Technology data.)

The correlations were applicable for the temperature range from the triple point to 600 K and pressures up to 250 MPa.

*n*-Heptane is often used as a well-defined model compound for mixtures of hydrocarbons. Additional information on heat transfer to *n*-heptane is published in Greenfield [317] and Seader and Wagner [318].

The rate of evaporation of *n*-heptane droplets and other fuels in rocket engines determines the required characteristic length of rocket combustion chambers [319, 320].

## 7.2 Chemical Properties of Heptane

Pure *n*-heptane is not used as a rocket propellant, but it is often used as a well-defined model compound for mixtures of hydrocarbons.

### 7.2.1 Thermal Decomposition of *n*-Heptane

The thermal decomposition of *n*-heptane was studied because it is often a constituent of surrogate fuel mixtures with controlled composition or it is part of the light boiler fraction in other hydrocarbon mixtures obtained by the refining of petroleum.

### 7.2.2 Pyrolysis of *n*-Heptane

The pyrolysis of both saturated and unsaturated *n*-heptane was evaluated via shock tube over a pressure range of 25–50 atm and a temperature range of 1000–1350 K, with reaction times ranging from 1 to 3 ms [321]. Pyrolysis products consisted of several



species that included acetylene, ethane, ethene, propene, allene, propyne, 1-butene, 1-pentene, and 1-hexene owing to the thermal decomposition of *n*-heptane. It was observed that there was no pressure dependence for the decomposition of *n*-heptane and formation of acetylene at reflected shock pressures of 25 and 50 atm. This was probably because the reacting species were at the high-pressure limit.

Single pulse shock-tube oxidation and pyrolysis experiments with *n*-heptane were conducted at a nominal pressure of 3.95 atm over a temperature range of 900–1500 K examining how ignition delay may be influenced by the interactive chemistry of alkanes and their pyrolytic and oxidative decomposition products [322]. *n*-heptane pyrolysis led to the formation of methane, ethene, acetylene, and propylene. It was found that heptane, ethene, heptane-ethene, and heptane-ethene-methane mixtures had similar CO<sub>2</sub> formation temperatures. This suggested that the primary reasons for the difference in ignition delay of the individual constituents and their mixtures are the reactions of the parent fuel leading to formation of the smaller molecules and the thermochemistry of the system.

A study of the kinetics and product distribution during the cracking of heptane in the presence of steam was performed in a flow reactor under atmospheric pressure within a temperature range of 953–1033 K (680–760 °C), with a mass ratio of steam to heptane of 3:1 [323]. The overall decomposition of heptane was represented by a first-order reaction with activation energy of 249.1 kJ/mol and a frequency factor of  $3.13 \times 10^{13} \text{ s}^{-1}$ . The reaction products were analyzed using GC, the main product being ethene. A molecular reaction scheme, which consisted of a primary reaction and 24 secondary reactions between primary products, was used for modelling the experimental product yields.

*n*-Heptane is a key straight chain paraffin in the fossil-fuel industry. Pyrolysis of *n*-heptane at a high temperature was investigated by a series of ReaxFF-based reactive molecular dynamic simulations [324]. The pyrolysis intermediate reactions, important product/intermediate distributions, and corresponding kinetics behaviors were systematically analyzed at an atomistic level. The results indicated that the entire pyrolysis process is radical-dominated. The unimolecular dissociation was the main pathway of *n*-heptane decomposition. Initiation of the decomposition was mainly through C–C bond fission. Central C–C bonds would dissociate prior to the terminal ones. The apparent activation energy extracted from these computer simulations was 180–226 kJ/mol (43–54 kcal/mol) in the temperature range 2400–3000 K, which was reasonably consistent with the experimental results. Results of the pyrolysis of heptane can then be compared with the thermal decomposition of higher alkanes, such as *n*-dodecane found in RP-1 or RP-2.

## 8 Octane

Octanes,  $C_8H_{18}$ , are typical constituents of gasoline. Octane has 20 isomers. *n*-Octane, CAS RN [111-65-9], is often used as a model compound to determine the physical properties of hydrocarbons in gasoline in a more reproducible manner. *n*-Octane is used as a constituent in gasoline surrogate mixtures. *Iso*-octane is used to measure the tendency of internal combustion engines toward “knocking,” premature ignition by adiabatic compression before the spark plug is energized. The tendency of gasoline to cause knocking in a reciprocating compression combustion engine is expressed by the Octane Number.

### 8.1 Physical Properties of *n*-Octane

The physical properties of *n*-octane are listed in Table 38.

**Table 38:** Physical properties of *n*-octane.

| Property                                         | SI units                                   | Other units                                                                          | References |
|--------------------------------------------------|--------------------------------------------|--------------------------------------------------------------------------------------|------------|
| Molecular mass                                   | 114.2285 g/mol                             | 8.7544 mol/kg                                                                        | [45]       |
| Freezing point                                   | $216.3 \pm 0.3$ K                          | $-56.8^\circ\text{C}$                                                                | [45]       |
| Boiling point                                    | $398.7 \pm 0.5$ K                          | $+125.6^\circ\text{C}$                                                               | [45]       |
| Vapor pressure at 298 K                          | 0.01848 bar                                | 14 mm Hg                                                                             | [45]       |
| Density at 293 K                                 | $0.7025 \text{ g/cm}^3$                    | $43.85 \text{ lb/ft}^3$                                                              | [311]      |
| Compressibility at 293 K                         | $1.003 \times 10^{-9} \text{ Pa}^{-1}$     | $1.016 \times 10^{-4} \text{ atm}^{-1}$                                              | [310]      |
| Viscosity at 300 K and 10 MPa                    | $553.6 \mu\text{Pa s}$                     | 0.554 cPs                                                                            | [325]      |
| Thermal conductivity, liquid at 303 K            | $0.1452 \text{ W m}^{-1} \text{ K}^{-1}$   | $3.47 \times 10^{-4} \text{ cal cm}^{-1} \text{ }^\circ\text{C}^{-1} \text{ s}^{-1}$ | [310]      |
| Thermal conductivity, liquid at 300 K and 10 MPa | $128.36 \text{ mW m}^{-1} \text{ K}^{-1}$  | $0.0742 \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ }^\circ\text{F}^{-1}$              | [325]      |
| Heat capacity, $C_p$ , liquid, at 298 K          | $255.68 \text{ J mol}^{-1} \text{ K}^{-1}$ | $61.11 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$                             | [45]       |
| Enthalpy of formation, vapor at 298 K            | $-208.7 \text{ kJ/mol}$                    | $-49.88 \text{ kcal/mol}$                                                            | [45]       |
| Enthalpy of formation, liquid at 298 K           | $-250.3 \pm 1.8 \text{ kJ/mol}$            | $-59.82 \text{ kcal/mol}$                                                            | [45]       |
| Enthalpy of fusion at 182.55 K                   | $20.74 \text{ kJ/mol}$                     | $4.96 \text{ kcal/mol}$                                                              | [45]       |
| Heat of evaporation at NBP                       | $34.41 \text{ kJ/mol}$                     | $8.22 \text{ kcal/mol}$                                                              | [45]       |
| Upper heat of combustion                         | $5430 \pm 100 \text{ kJ/mol}$              | $1298 \pm 24 \text{ kcal/mol}$                                                       | [45]       |
| Critical temperature                             | $568.9 \pm 0.5 \text{ K}$                  | $295.8 \pm 0.5^\circ\text{C}$                                                        | [45]       |
| Critical pressure                                | $24.9 \pm 0.1 \text{ bar}$                 | $24.6 \pm 0.1 \text{ atm}$                                                           | [45]       |
| Critical density                                 | $2.034 \pm 0.007 \text{ mol/L}$            | $0.232 \text{ g/cm}^3$                                                               | [45]       |

The vapor pressure of *n*-octane in the range 326.08–399.72 K can be calculated using an Antoine equation

$$\log P = 4.04867 - [1355.126 / (T - 63.633)]$$

where  $P$  is the pressure in bar and  $T$  is the temperature in kelvin.

Polynomial equation correlations for the thermal conductivity of the pure fluids *n*-octane, *n*-nonane, and *n*-decane that are valid over a wide range of fluid states, from dilute gas to dense liquid, including an enhancement in the critical region were derived from literature data for octane and two other hydrocarbons [325]. The correlations represented the thermal conductivity to within the uncertainty of the best experimental data and will be useful for researchers working on thermal conductivity models for other hydrocarbon mixtures.

The thermal conductivity of liquid *n*-octane, a pure hydrocarbon often used as a model substance in heat transfer studies, is  $0.14528 \text{ W m}^{-1} \text{ K}^{-1} = 3.47 \times 10^{-4} \text{ cal cm}^{-1} \text{ }^{\circ}\text{C}^{-1} \text{ s}^{-1}$  [310].

## 9 Decane

Decane,  $\text{C}_{10}\text{H}_{22}$ , CAS RN [124-18-5], is often used as a model compound of uniform chemical composition for simulating mixtures of hydrocarbons in kerosenes. For this reason it is important to have a complete set of physical properties for *n*-decane and some of its isomers.

### 9.1 Physical Properties of Decane

The enthalpy of vaporization of *n*-decane at 298 K is  $51.42 \pm 0.26 \text{ kJ/mol}$  [326]. The heat of sublimation of *n*-decane at 298 K is  $80.3 \text{ kJ/mol}$ .

#### 9.1.1 Thermal Conductivity of Decane

Polynomial equation correlations for the thermal conductivity of the pure fluids *n*-octane, *n*-nonane, and *n*-decane that are valid over a wide range of fluid states, from dilute gas to dense liquid, including an enhancement in the critical region, were derived from literature data for decane and two other hydrocarbons [325]. The correlations represented the thermal conductivity to within the uncertainty of the best experimental data and will be useful for researchers working on thermal conductivity models for other hydrocarbon mixtures. A sample point at 300 K and 10 MPa is for a fluid that has a thermal conductivity of  $132.80 \text{ mW m}^{-1} \text{ K}^{-1}$ , a viscosity of  $926.37 \text{ } \mu\text{Pa s}$ , and a density of  $5.1504 \text{ mol/L}$ .

### 9.1.2 Heat Transfer Properties of Decane

Turbulent heat transfer of hydrocarbon fuels at supercritical pressure plays a crucial role in the regenerative cooling of aerospace propulsion systems. Flow dynamics in transient heat transfer of *n*-decane at a supercritical pressure of 5 MPa were numerically investigated, focusing on the effects of a number of key influential parameters, including the surface heat flux, surface heating rate, cooling tube length, and inlet flow velocity, on the transient responding behaviors [327]. The results indicated that the transient responding process is dictated by two fundamental mechanisms: the initial thermoacoustic oscillation, which is caused by strong fluid thermal expansion, and the subsequent transient convection. The thermoacoustic oscillating magnitude increased as the surface heat flux, surface heating rate and cooling tube length were increased, but it decreased as the inlet flow velocity was increased. The surface heating rate and cooling tube length exerted strong influences on the oscillating frequency of the thermoacoustic wave. The cooling tube length and inlet flow velocity significantly affected the second-stage transient convective process and thus the total transient responding time, which both increased as the cooling tube length was increased and/or the inlet flow velocity was decreased. The results are helpful for a fundamental understanding of the transient heat transfer mechanisms relevant to regenerative rocket engine cooling processes.

Supercritical pressure hydrocarbon fuels have shown deteriorated heat transfer rates and instabilities for some flow conditions. The flow and heat transfer instabilities in supercritical pressure *n*-decane were investigated experimentally with pressures of 2.5 and 3.0 MPa and inlet temperatures of 293–498 K (16–225 °C) [328]. The heat flux was slowly increased to observe the flow at different stages, as well as to obtain the boundary lines for a stability map. Seven stages were observed with different stability features. The transition to turbulence was found to be the main reason for the instability for stage b with slightly irregular oscillations, whereas dramatic variations of the thermal properties caused Helmholtz oscillations with regular frequencies and large amplitudes. The heat transfer deterioration, in conjunction with an instability with buoyancy owing to the density variation, was found to be the reason. Higher pressures, inlet mass flow rates or fluid temperatures or downward flow weakened the instabilities; thus, these remedies should be used in engineering designs to reduce the heat transfer deterioration and instability. The stability map provided further support for the non-linear dynamic theory explaining the oscillations.

## 9.2 Chemical Properties of Decane

### 9.2.1 Thermal Decomposition of Decane

The flow and heat-transfer behavior of thermal cracking *n*-decane was investigated experimentally and numerically [329]. An electrically heated vertical tube (inner diameter 2 mm) was used to study thermal cracking of supercritical pressure *n*-decane at various pressures, temperatures, and resident times. The results showed that the second-order reactions increased the formation rates of the light products (especially CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>) for conversions greater than 13%, whereas the heavy product (C<sub>5</sub>–C<sub>9</sub>) formation rates were decreased. A global reaction model was given for *n*-decane conversions less than 13%, including 18 main product species. A computational fluid dynamics (CFD) model was developed using the real thermal properties and coupled with fuel flow, heat transfer, and wall thermal conduction. Three turbulence models were tried out and then compared with the experimental results. The predicted fuel and wall temperatures were in good agreement with experimental data. The results also showed that *n*-decane continues to crack with almost half of the *n*-decane conversion in the connection pipe. Thus, the thermal cracking in the connection pipe should be more carefully analyzed in cracking models.

The pyrolysis mechanism of *n*-decane as a component of some rocket fuels was studied at 773–943 K in a flow reactor under pressures of 3, 4, and 5 MPa [330]. GC/MS was used to analyze the pyrolysis products, which were mainly alkanes from C<sub>1</sub>–C<sub>9</sub> and alkenes from C<sub>2</sub>–C<sub>9</sub>. A kinetic model containing 164 species and 842 reactions was developed and validated by experimental results including the distributions of products and the chemical heat sink of fuel. The decomposition pathways of *n*-decane were illustrated through reaction flux analysis. It was concluded that the C<sub>4</sub>–C<sub>9</sub> alkanes are mainly generated by the recombinations of alkyls, whereas the small alkanes (C<sub>1</sub>–C<sub>3</sub>) are formed by H-abstraction reactions by C<sub>1</sub>–C<sub>3</sub> alkyl radicals. The applicability of previous models to supercritical pressure and high fuel concentration conditions was criticized. In contrast, the performance of the new model in reproducing the experimental data was reasonably good.

The supercritical pyrolysis and endothermicity capacity of *n*-decane were studied under different pressures [331]. Experimental results indicated that the main gaseous products are small molecular hydrocarbons (methane, ethane, ethene). Ethene and propene were the most abundant components under this set of experimental conditions. It was noticed that the influence of pressure on the production of ethene is greater than that of any others. The increase in pressure increased the conversion of fuel to enhance its endothermicity, but the increase in pressure also decreased the alkene/alkane ratio, which has negative effect on the improvement of the chemical heat sink capacity of the fuel. The influence of pressure on the endothermicity of *n*-decane is not a simple effect of promotion or inhibition, but differs within different temperature ranges.

A study of the global pyrolytic reaction mechanism of *n*-decane for problems with mild endothermic pyrolysis at supercritical pressures was based on the fact that the high-molecular-weight alkane or alkene components in a thermally decomposed *n*-decane mixture possess similar thermophysical properties [332]. They can thus be grouped together and represented by a single light species with similar properties. Numerical tests indicated that a reduced 12-species reaction mechanism for mild cracking of *n*-decane represents a reasonable choice in terms of model accuracy and efficiency. The reduced pyrolytic reaction mechanism was employed to study the effect of mild thermal decomposition of *n*-decane on turbulent convective heat transfer at supercritical pressures. The wall heat flux into the coolant can thus be increased significantly at high fluid temperatures, due mainly to heat absorption resulting from endothermic pyrolytic reactions.

The effect of pyrolysis and coke deposition of *n*-decane on heat-transfer performance was examined in a series of experiments at pressures of 1, 2.5, and 4 MPa in a resistance-heated tube to simulate conditions encountered in regenerative cooling engines with a length range of 30–100 cm [333]. The bulk inlet and outlet temperatures of fuel were held constant at 753 K (480 °C) and 803–1053 K (530–780 °C) respectively in the test section. The heat transfer coefficients were dependent on both pressure and heat flux, and there was a critical heat flux at about 0.4–0.5 MW/m<sup>2</sup> for sub- and super-critical pressures. Relatively low pressure during pyrolysis had great advantages under the condition of relatively high heat flux because of the higher heat transfer coefficients and reduced coking.

The pyrolysis of helium-seeded *n*-decane as a surrogate of the *n*-alkane fraction of JP-8 was studied over a temperature range of 1100–1600 K at a pressure of 80 kPa (600 mm Hg) [334]. The nascent products were identified *in situ* in a supersonic molecular beam via single photon vacuum ultraviolet photoionization coupled with a mass spectroscopic analysis of the ions in a reflectron time-of-flight mass spectrometer. The initial reaction products formed in the decomposition of *n*-decane, including radicals and thermally labile closed-shell species, effectively exclude mass growth processes. Eighteen different products were identified: molecular hydrogen (H<sub>2</sub>), C<sub>2</sub> to C<sub>7</sub> 1-alkenes (ethene [C<sub>2</sub>H<sub>4</sub>] to 1-heptene [C<sub>7</sub>H<sub>14</sub>]), C<sub>1</sub>–C<sub>3</sub> radicals (methyl [CH<sub>3</sub>], vinyl [C<sub>2</sub>H<sub>3</sub>], ethyl [C<sub>2</sub>H<sub>5</sub>], propargyl [C<sub>3</sub>H<sub>3</sub>], allyl [C<sub>3</sub>H<sub>5</sub>]), small C<sub>1</sub>–C<sub>3</sub> hydrocarbons (methane [CH<sub>4</sub>], acetylene [C<sub>2</sub>H<sub>2</sub>], allene [C<sub>3</sub>H<sub>4</sub>], methylacetylene [C<sub>3</sub>H<sub>4</sub>]), along with higher-order reaction products (1,3-butadiene [C<sub>4</sub>H<sub>6</sub>], 2-butene [C<sub>4</sub>H<sub>8</sub>]). On the basis of electronic structure calculations, *n*-decane decomposes initially by C–C bond cleavage (excluding the terminal C–C bonds) producing a mixture of alkyl radicals from ethyl to octyl. These alkyl radicals are unstable under experimental conditions and rapidly dissociate by C–C bond β-scission to split ethene (C<sub>2</sub>H<sub>4</sub>) plus a 1-alkyl radical with the number of carbon atoms reduced by two and 1,4-, 1,5-, 1,6-, or 1,7-H shifts followed by C–C β-scission producing alkenes from propene to 1-octene in combination with smaller 1-alkyl radicals. The higher alkenes become increasingly

unstable with rising temperature. When the C—C  $\beta$ -scission continues all the way to the propyl radical ( $\text{C}_3\text{H}_7$ ), it dissociates producing methyl ( $\text{CH}_3$ ) plus ethene ( $\text{C}_2\text{H}_4$ ). At higher temperatures, hydrogen atoms can abstract hydrogen from  $\text{C}_{10}\text{H}_{22}$  to yield *n*-decyl radicals, whereas methyl ( $\text{CH}_3$ ) can also abstract hydrogen or recombine with hydrogen to form methane. These *n*-decyl radicals can decompose via C—C-bond  $\beta$ -scission to  $\text{C}_3$  to  $\text{C}_9$  alkenes.

A three-dimensional (3D) model was developed for numerically investigating the flow and heat transfer of pyrolytically reacted *n*-decane with pyrolytic coking in the engine cooling tube under supercritical pressure [335]. The one-step global pyrolytic reaction mechanism and the kinetic coking model were incorporated into the numerical model to simulate the pyrolysis and pyrolytic coking process of *n*-decane. The numerical method was validated based on the good agreement between the current predictions and the experimental data. Numerical studies of the characteristics of pyrolysis and surface coking rate at the start time under various outer wall heat fluxes ranging from 1.2 to 1.8 MW/m<sup>2</sup> have been conducted under 5 MPa pressure. Results revealed that heat flux has a significant effect on the pyrolytic reaction and the distribution of the pyrolytic coking rate. In order to better understand the complicated unsteady physicochemical process, further investigations on coupling relationships between the turbulent flow, heat transfer, pyrolysis, and pyrolytic coking in 20 min under a high heat flux of 1.8 MW/m<sup>2</sup> have been performed. It was found that surface coking deteriorated the cooling ability of *n*-decane. The mechanisms of these physicochemical phenomena were analyzed in detail, which will be very helpful in the design of regenerative cooling channels.

A molecular kinetic model was developed to describe the thermal cracking of *n*-decane at supercritical pressures [336]. The apparent kinetic parameters at different pressures were optimized. Following model validation, the role of pressure on the chemical heat absorption rate during *n*-decane pyrolysis was investigated using a one-dimensional plug flow model. It was found that the heat absorption rate first increased and then slightly decreased as the temperature increased at all pressures. The highest chemical heat absorption rate was located at a conversion of 41.81, 53.34, and 59.40% at 3, 4, and 5 MPa respectively. In addition, the effect of pressure on *n*-decane pyrolysis was quantitated using the equivalent temperature. Under the simulation conditions considered in the present study, each 1-MPa increase in pressure produced the same conversion as a temperature decrease of 6.5–10 K. In order to extrapolate the kinetic model to a wider range of pressure conditions, a model extrapolation method based on the activation volume was proposed.

In another modeling approach for the thermal cracking of hydrocarbon fuels at supercritical pressures, the thermal cracking process was treated as an infinite number of continuous microreactions at different fuel conversions, in which the stoichiometric coefficients of each species were expressed by continuous differentiable functions of the fuel conversion to consider the effects of secondary reactions [337]. A set of thermal cracking experimental results involving *n*-decane was used as an example to show

how to establish the differential global reaction model with variable stoichiometric coefficients. The differential global reaction model was implemented in a computational fluid dynamics simulation to predict *n*-decane thermal cracking coupled with flow, heat transfer, and wall thermal conduction in a cooling channel. The results showed that the differential global reaction model could more accurately predict the species mass fractions than existing global reaction models, especially for conditions when the secondary reactions strongly impact the thermal cracking. The stoichiometric coefficients of the differential global reaction model determined from the thermal cracking experiments only required the species mass/molar fractions. Therefore, the modeling method can be easily extended to other hydrocarbon fuels.

### 9.2.2 Catalytic Decomposition of *n*-Decane

*n*-Decane decomposition, an endothermic reaction, can be accelerated by catalysts. MoO<sub>3</sub>/Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> composite oxides with various MoO<sub>3</sub> content were prepared and used for *n*-decane cracking under supercritical conditions [338]. The experiments showed that the catalyst with 8.3 mass-% MoO<sub>3</sub> exhibited the highest catalytic cracking activity among all catalysts, leading to a gas yield increased by 14.6% at 973 K (700 °C), and the heat sink capability increased by 0.39 MJ/kg compared with thermal cracking.

Monometallic and bimetallic Pt/Ni catalysts supported on La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> modified by MoO<sub>3</sub> were evaluated for catalytic cracking of *n*-decane [339]. The results showed that the bimetallic catalyst had better catalytic cracking activity than other catalysts and exhibited the best high-temperature stability. The cracking activity of the bimetallic catalyst was due to unique acidity, higher resistance against sintering of active phases, finely dispersed active metals, enhanced metal-support interaction and synergistic effects between Pt and Ni.

## 10 *n*-Dodecane

*n*-Dodecane, C<sub>12</sub>H<sub>26</sub>, CAS RN [112-40-3], is an oily hydrocarbon with properties very similar to those of rocket propellants RP-1 and RP-2. When formulating surrogate hydrocarbon mixtures simulating RP-1 or RP-2, *n*-dodecane was often chosen as the third most prevalent hydrocarbon in the synthetic mixture. Because *n*-dodecane is a key component of RP-1 and RP-2, it is important to have a complete set of properties for the pure compound in order to identify the contributions this constituent makes to the hydrocarbon mixtures. If certain physical properties for RP-1 or RP-2 are not available in text books or from the literature, the next best option to not having any properties at all is to use the properties of *n*-dodecane as a substitute for those real-life hydrocarbon mixtures. This is the reason why this book contains a fairly detailed summary of the properties of this hydrocarbon.



## 10.1 Preparation of *n*-Dodecane

*n*-Dodecane and many other C<sub>12</sub> alkanes are constituents of petroleum distillates derived from crude oil by either distillation or cracking.

## 10.2 Physical Properties of *n*-Dodecane

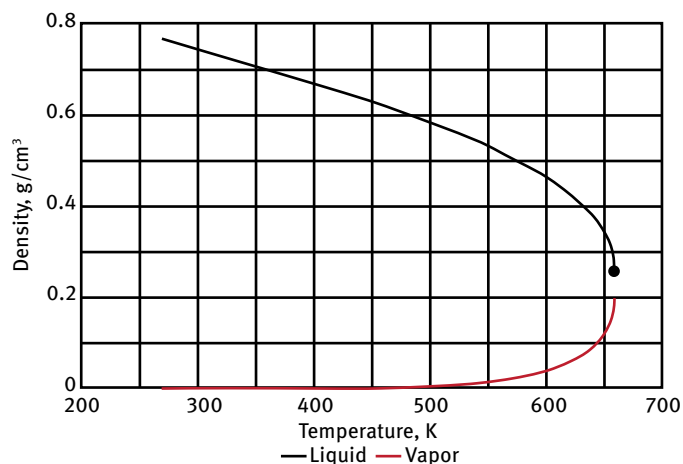
The physical properties of *n*-dodecane are summarized in Table 39.

**Table 39:** Physical properties of *n*-dodecane.

| Property                                         | SI units                                   | Other units                                                  | References |
|--------------------------------------------------|--------------------------------------------|--------------------------------------------------------------|------------|
| Molecular mass                                   | 170.3348 g/mol                             | 5.8708 mol/kg                                                | [45]       |
| Freezing point                                   | 263.5 ± 0.3 K                              | −9.6 ± 0.3 °C                                                |            |
| Boiling point                                    | 489 ± 2 K                                  | 216 ± 2 °C                                                   |            |
|                                                  | 489.4 K                                    | 216.2 °C                                                     | [312]      |
| Density at 298 K                                 | 0.7548 g/cm <sup>3</sup>                   | 47.12 lb/ft <sup>3</sup>                                     | [45]       |
| Velocity of sound, liquid at 298 K               | 1280.9 m/s                                 | 4213 ft/s                                                    | [45]       |
| Dynamic viscosity at 298 K, liquid               | 1360.7 μPa s                               | 1.3607 cPs                                                   |            |
| Kinematic viscosity at 298 K, liquid             | 0.018246 cm <sup>2</sup> /s                | 1.8246 cSt                                                   |            |
| Vapor pressure at 298 K                          | 0.017656 kPa                               | 0.13 mm Hg                                                   |            |
| Thermal conductivity, liquid at 298 K            | 135.30 mW m <sup>−1</sup> K <sup>−1</sup>  | 0.0782 BTU h <sup>−1</sup> ft <sup>−1</sup> °F <sup>−1</sup> | [45]       |
| Heat capacity, C <sub>p</sub> , liquid, at 298 K | 2.2119 J g <sup>−1</sup> K <sup>−1</sup>   | 0.5286 cal g <sup>−1</sup> °C <sup>−1</sup>                  | [45]       |
|                                                  | 375.37 J mol <sup>−1</sup> K <sup>−1</sup> | 89.71 cal mol <sup>−1</sup> °C <sup>−1</sup>                 | [45]       |
| Enthalpy of formation, vapor at 298 K            | −290.9 ± 1.4 kJ/mol                        | −69.53 kcal/mol                                              |            |
| Enthalpy of formation, liquid at 298 K           | −352.1 ± 1.4 kJ/mol                        | −84.15 kcal/mol                                              |            |
| Heat of sublimation                              | 100.2 kJ/mol                               | 23.95 kcal/mol                                               |            |
| Enthalpy of fusion at 263.1 K                    | 35.7 kJ/mol                                | 8.53 kcal/mol                                                |            |
| Heat of evaporation at NBP                       | 61 ± 1 kJ/mol                              | 14.58 kcal/mol                                               |            |
| Heat of evaporation at 415 K                     | 51.6 kJ/mol                                | 12.33 kcal/mol                                               |            |
| Upper heat of combustion                         | 8086.0 ± 1.2 kJ/mol                        | 1933 kcal/mol                                                |            |
| Critical temperature                             | 658.2 ± 0.9 K                              | 385.1 °C                                                     | [45]       |
| Critical pressure                                | 18.10 bar                                  | 263 psia                                                     |            |
| Critical volume                                  | 1.3 ± 0.1 mol/L                            | 0.287 g/cm <sup>3</sup>                                      |            |

### 10.2.1 Density of *n*-Dodecane

The density of *n*-dodecane as a function of temperature under saturation pressure conditions is shown in Figure 35.

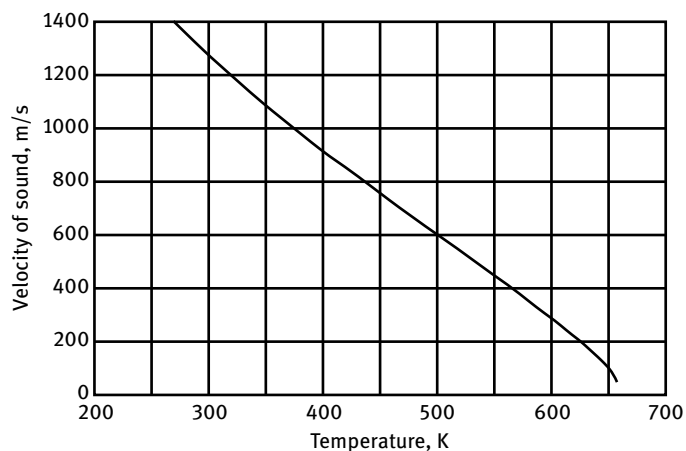


**Figure 35:** Density of *n*-dodecane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

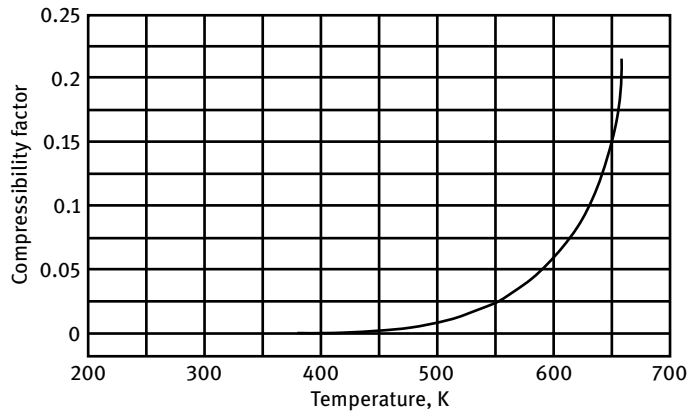
### 10.2.2 Compressibility and Velocity of Sound of *n*-Dodecane

The velocity of sound in liquid *n*-dodecane as a function of temperature is shown in Figure 36.

The compressibility factor of *n*-dodecane,  $Z = P/\rho RT$ , is derived from velocity of sound measurements. As one can see in Figure 37, its trend is the opposite of that of the velocity of sound.



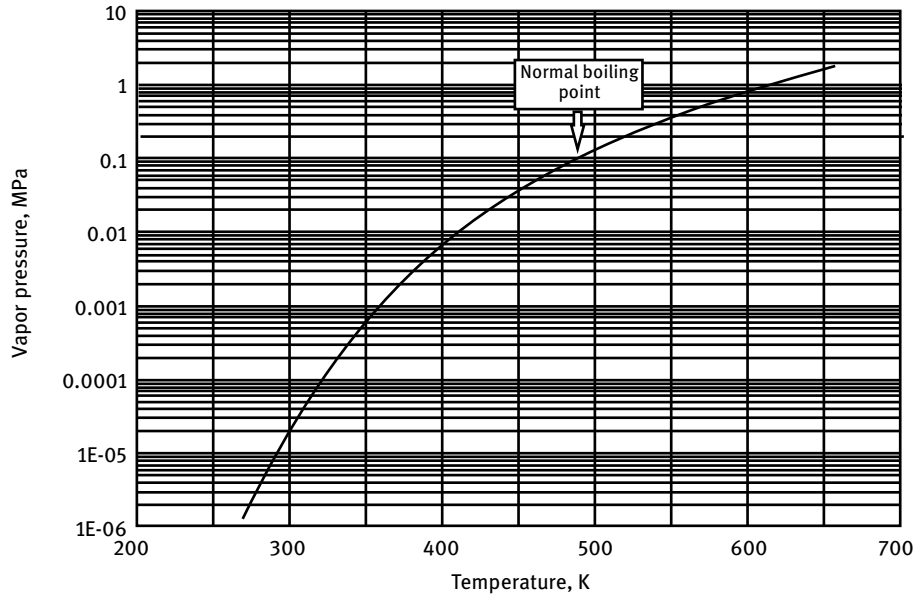
**Figure 36:** Velocity of sound in liquid *n*-dodecane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)



**Figure 37:** Compressibility factor of liquid *n*-dodecane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

### 10.2.3 Vapor Pressure of *n*-Dodecane

The vapor pressure of *n*-dodecane as a function of temperature is illustrated in Figure 38.



**Figure 38:** Vapor pressure of *n*-dodecane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

The vapor pressure of *n*-dodecane can be calculated from the Antoine equation

$$\log P = A - B/(T + C) = 6.109514 - [1628.949/(T - 92.4917)]$$

where  $P$  is the vapor pressure in kPa and  $T$  is the temperature in kelvin [314].

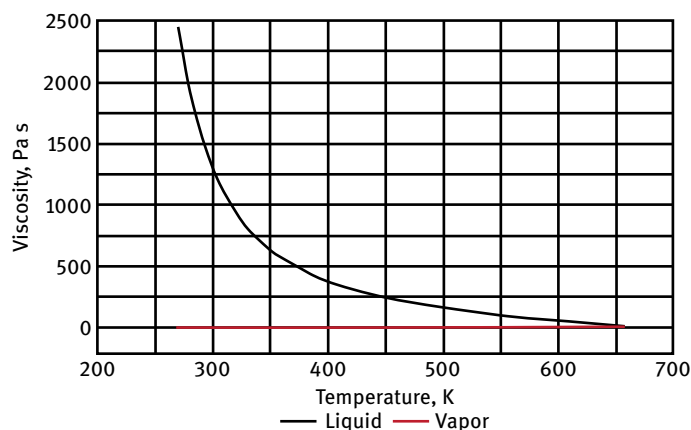
Another Antoine equation for the temperature range 400–490 K gives the vapor pressure of *n*-dodecane as

$$\log P = A - B/(T + C) = 4.10549 - [1625.928/(T - 92.839)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin (NIST).

### 10.2.4 Viscosity of *n*-Dodecane

Viscosity measurements have been made on nine pure hydrocarbon liquids, including dodecane, at six temperatures ranging from 288 to 408 K (15 to 135 °C) and at pressures as high as 4000 bars [340]. The dynamic viscosity of *n*-dodecane under saturation pressure conditions as a function of temperature is illustrated in Figure 39.



**Figure 39:** Dynamic viscosity of *n*-dodecane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

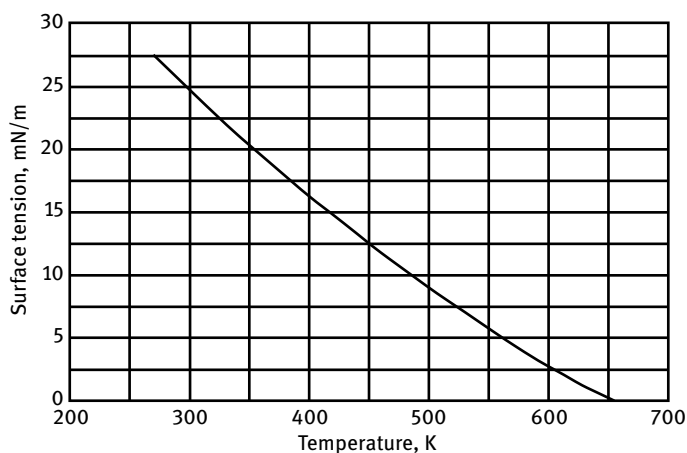
Correlations for the viscosity and thermal conductivity of *n*-dodecane that are valid over a wide range of fluid states were developed based on surveyed literature data [341]. The new correlations were applicable from the triple point (263.59 K) to 800 K, and at pressures up to 200 MPa. The viscosity correlation had an estimated uncertainty of 0.5% along the saturation boundary in the liquid phase, 3% in the compressed liquid region, and 3% in the vapor (where the uncertainties can be considered as estimates of a combined expanded uncertainty with a coverage factor of 2). The thermal conductivity correlation had an estimated uncertainty of 4% along

the liquid saturation boundary and in the compressed liquid, and ~5% in the vapor region.

The dynamic viscosities of *n*-dodecane were measured at temperatures between 303 and 693 K and pressures up to 10 MPa using a dual-capillary viscometer [342]. The accuracy of the dual-capillary viscometer was improved by considering centrifugal effects and the thermal expansion of the capillary. The combined relative standard uncertainty in the dynamic viscosity was 0.58–2.92%. This study provided new data for checking the accuracy of Huber's correlations at supercritical pressures, and a small portion of the data points at supercritical conditions where few experimental data had been reported so far. The average absolute deviation between the experimental data and the calculated data from Huber's correlations was 0.97%, and the maximum absolute deviation was 6.79%. In the near-critical and supercritical region, the accuracy of viscosities of *n*-dodecane needs more experimental data for verification and to extend the theories.

### 10.2.5 Surface Tension of *n*-Dodecane

The surface tension of *n*-dodecane as a function of temperature (under saturation pressure conditions) is illustrated in Figure 40.



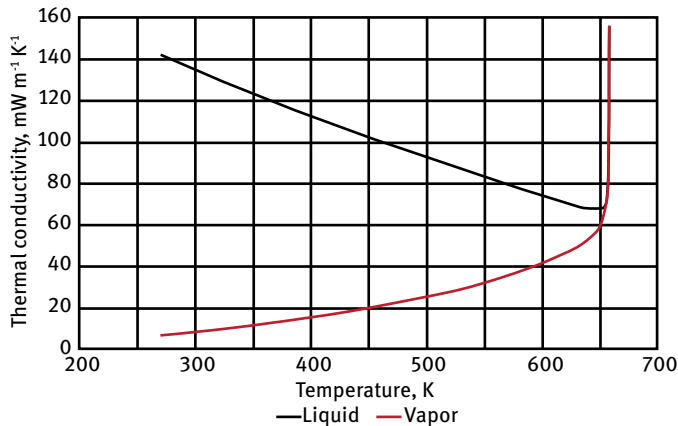
**Figure 40:** Surface tension of *n*-dodecane as a function of temperature. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

### 10.2.6 Thermal Conductivity of *n*-Undecane and *n*-Dodecane

This particular publication is for undecane and not for dodecane but it is referenced here because the physical properties of the two hydrocarbons are very similar. Assael et al. presented wide-ranging correlations for the viscosity and thermal conductivity of *n*-undecane based on critically evaluated experimental data [343]. The correlations

were designed to be used with an equation of state that is valid from the triple point to 700 K, at pressures up to 500 MPa, with densities below  $776.86 \text{ kg/m}^3$ . Both correlations behaved in a physically reasonable manner when extrapolated to the full range of the equation of state, but care must be taken when using the correlations outside of the validated range. The uncertainties will be larger outside of the validated range and also in the critical region.

The thermal conductivity of *n*-dodecane under saturation pressure conditions is illustrated in Figure 41.



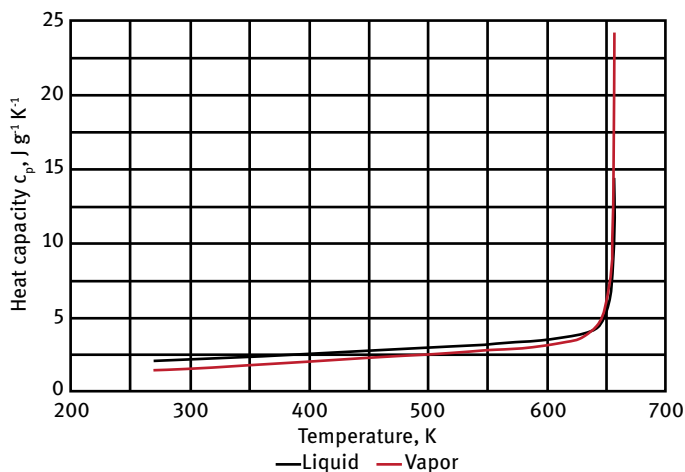
**Figure 41:** Thermal conductivity of *n*-dodecane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

## 10.2.7 Thermodynamic Properties of *n*-Dodecane

### 10.2.7.1 Heat Capacity of *n*-Dodecane

The heat capacity  $c_p$  of *n*-dodecane as a function of temperature under saturated conditions is illustrated in Figure 42. This property is required for calculating heat transfer and fuel temperature rise in cooling channels of rocket engines. The curves for heat capacities of liquid and vapor dodecane under saturation conditions are close together and then increase abruptly as they approach the critical temperature.

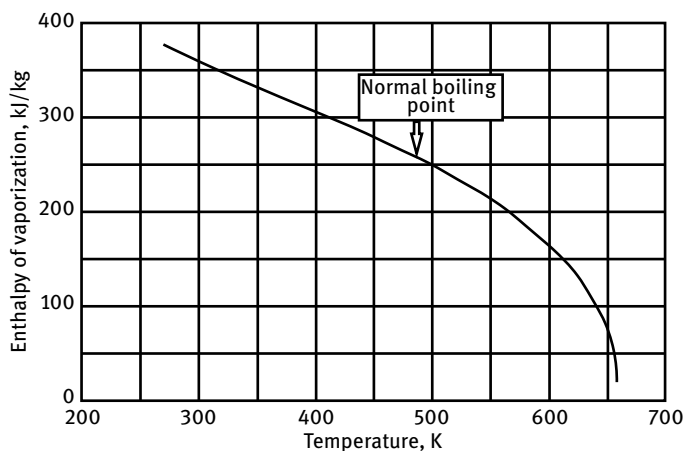
An equation of state has been developed to represent the thermodynamic properties of all liquid, vapor and supercritical states of *n*-dodecane [344]. Experimental data used to develop the equation included pressure-density-temperature state points, vapor pressures, isobaric and saturation heat capacities, heats of vaporization, and velocities of sound. The uncertainties of properties calculated using the equation were: 0.2% in density at pressures up to 200 MPa, and 0.5% at higher pressures up to 500 MPa; 1% in heat capacity; 0.5% in the velocity of sound; and 0.2% in vapor pressure. Deviations of calculated properties from available experimental data in the critical region were higher for all properties except for vapor pressure.



**Figure 42:** Heat capacity  $c_p$  of *n*-dodecane. (Image created by Schmidt 2020 based on data from National Institute of Standards and Technology RefProp.)

#### 10.2.7.2 Enthalpy of Vaporization of *n*-Dodecane

The heat of sublimation of *n*-dodecane is 100.2 kJ/mol at 298 K and 101.7 kJ/mol at 263 K. The enthalpy of vaporization of *n*-dodecane at 298 K was reported to be  $61.52 \pm 0.62 \text{ kJ/mol} = 361 \text{ kJ/kg}$  (Nelson and Chickos [326]). The enthalpy of vaporization of *n*-dodecane under saturation pressure conditions as a function of temperature is illustrated in Figure 43. The enthalpy of vaporization drops to near zero as the temperature approaches the critical point, the same as is observed for most fluids.



**Figure 43:** Enthalpy of vaporization of *n*-dodecane. (Image created by Schmidt 2020 based on data from NIST RefProp.)

### 10.2.8 Physical Properties of *n*-Dodecane Mixtures

RP-1 and RP-2 are hydrocarbon mixtures containing *n*-dodecane. *n*-Dodecane has been mixed with other hydrocarbons to make surrogate fuels with properties similar to those of RP-1 or RP-2 [345].

## 10.3 Chemical Properties of *n*-Dodecane

### 10.3.1 Thermal Decomposition of Dodecane

Although pure dodecane is not used as a rocket fuel, its thermal decomposition has been thoroughly investigated because it is a constituent of RP-1 and RP-2 and many other kerosene blends. The thermal cracking of *n*-dodecane was investigated using additives [346].

Pseudo-first-order-rate constants for the decomposition of *n*-dodecane at 623 and 673 K were measured in a batch reactor pressurized to 9.2 MPa (91 atm) with nitrogen or hydrogen [347]. Dodecane is thermally stable below 600 K, whereas under more severe conditions it is thermolyzed to give a series of paraffins and olefins up to C<sub>22</sub>, but with C<sub>13</sub> missing. High-pressure reaction favors the formation of saturated hydrocarbons and shifts the product distribution toward heavier components. The yield of paraffin plus olefin of the same carbon number decreased with increasing molecular weight, and the yield of the olefin was slightly higher than that of its paraffin counterpart. These observations can be interpreted by a free-radical-chain mechanism with certain modifications. Hydrogen participates in dodecane thermolysis reactions through radical-capping reactions. The pseudo-first-order rate law applies to dodecane disappearance.

In a study of the vapor-phase thermolysis of several straight-chain alkanes and their mixtures, including C<sub>9</sub>, C<sub>12</sub>, C<sub>13</sub>, C<sub>16</sub>, and C<sub>22</sub>, in a flowing tube reactor at atmospheric pressure and temperatures from 623 to 893 K, the thermolysis of unbranched alkanes yielded a series of 1-alkenes as major products [14]. The 1-alkene selectivity strongly depended upon pressure: the lower the pressure, the higher the selectivity.

Micro-reactor studies of *n*-dodecane decomposition rates in nitrogen at pressures of 0.69 to 1 MPa (6.8 to 9.9 atm) and temperatures of 673 to 723 K were carried out as part of an evaluation of hydrogen donors as stabilizers that would retard the decomposition of kerosenes [348, 349]. The most important conclusion of this work was that within the temperature range 673–723 K (400–450 °C), 1,2,3,4-tetrahydroquinoline (THQ) was by far the best thermal stabilizer that had been discovered up to that time and it was significantly more effective than benzyl alcohol.

Kinetics of the thermal decomposition of C<sub>10</sub>–C<sub>14</sub> *n*-alkanes and their mixtures was studied under near-critical and supercritical conditions [16]. Supercritical-phase thermal decomposition of *n*-alkanes can be represented well by an apparent first-order kinetics, even though the decomposition was not a true first-order process. A generalized expression was developed to predict the apparent first-order rate



constants for the decomposition of  $C_8$ - $C_{16}$  *n*-alkanes at 698 K (425 °C). Pressure had a significant effect on the apparent first-order rate constant in the near-critical region. This large pressure effect can be attributed to the significant changes in density and possibly to the changes in the rate constants of elementary reactions with pressure in the near-critical region. Individual compounds interacted with each other in the thermal reaction of *n*-alkane mixtures. The overall first-order rate constants for decomposition of *n*-alkane mixtures can be predicted satisfactorily from the rate constants for pure compounds.

Solid coke deposits from thermal stressing of a jet fuel model compound, *n*-dodecane, were studied in the presence of three initiator additives, 1-nitropropane (NP), triethylamine (TEA), or 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TEMPO), to show the role of initiators in the carbon deposition during the thermal cracking of jet fuels [350]. It was found that the thermal cracking rate of *n*-dodecane was enhanced by the initiators in the following order, TEMPO > NP > TEA, and that TEMPO and TEA remarkably inhibited the formation of pyrolytic deposits by 30–50% at a similar conversion level. Temperature-programmed oxidation of deposits indicated that reactive deposition can be reduced slightly by TEMPO and TEA, but the less reactive deposits are reduced because of possible radical scavenging or the hydrogen donation effect, resulting from the decomposition of TEMPO and TEA. Scanning electron microscopy (SEM) showed that TEA and NP also have a significant effect on the deposit morphologies. Those same results were also observed in the thermal stressing of Chinese RP-3 fuel with initiators.

Various additives were tested in the hope that they would prevent the formation of carbonaceous deposits during thermal stressing of hydrocarbons at high temperatures (>773 K = >500 °C) [351]. Three hydrogen donors, tetralin (THN),  $\alpha$ -tetralone (THNone), and benzyl alcohol, and two organic selenides, diphenyl selenide ( $Ph_2Se$ ) and diphenyl diselenide ( $Ph_2Se_2$ ), as well as their mixtures, were selected as thermally stable additives to inhibit the deposition from the thermal stressing of *n*-dodecane and Chinese RP-3. It was found that the amount of solid deposits from thermal stressing of RP-3 was reduced by 77.0% with the additive of  $Ph_2Se_2$ /THN/THNone. It was found that hydrogen donor THN/THNone and organic selenides possibly reduce the carbon deposits by retarding the thermal cracking rate, blocking surface catalysis, and depressing the reactivity of sulfur with the surface metals, as well as their synergistic effect. The morphologies of deposits also dramatically changed after adding organic selenides or hydrogen donors.

An experimental and computer modelling study of the pyrolysis of *n*-dodecane used a stainless steel isothermal plug flow reactor at temperatures of 950, 1000, and 1050 K and atmospheric pressure, with GC analysis of the end products showing mainly methane, ethane, and alkenes from  $C_2$  to  $C_{10}$  [352]. A detailed kinetic model containing 1175 reactions has been produced using EXGAS software. This model was able to represent with reasonable accuracy the experimental results, both for the

conversion of *n*-dodecane and for the formation of products, as well as literature data obtained from other sources measured at 623 to 823 K.

The thermal decomposition of *n*-dodecane was measured in a jet-stirred reactor at temperatures from 773 to 1073 K, with residence times between 1 and 5 s and at atmospheric pressure [353]. The products of the reaction were mainly hydrogen, methane, ethane, 1,3-butadiene, and 1-alkenes from ethene to 1-undecene. For higher temperatures and residence times acetylene, allene, propyne, cyclopentene, 1,3-cyclopentadiene, and aromatic compounds from benzene to pyrene through naphthalene have also been observed. A previously published detailed kinetic model of the thermal decomposition of *n*-dodecane generated using EXGAS software has been improved and completed by a sub-mechanism explaining the formation and the consumption of aromatic compounds.

A two-wavelength, mid-IR optical absorption diagnostic was developed for simultaneous temperature and *n*-dodecane vapor concentration measurements in an aerosol-laden shock tube. Shock tube studies of the high-temperature (1100 to 1300 K) decomposition of *n*-dodecane were completed within the pressure range 0.3 to 6 atm [354]. Fourier transform infrared absorption spectra for the temperature range 323 to 773 K were used to select the two wavelengths (3409 and 3432 nm). Shock-heated mixtures of *n*-dodecane vapor in argon were then used to extend absorption cross-section data at these wavelengths to 1322 K. At high temperatures, pseudo-first-order decomposition rates were extracted from time-resolved concentration measurements, and data from vapor and aerosol shocks were found to be in good agreement. Notably, the *n*-dodecane concentration measurements exhibited slower decomposition than predicted by models using two published reaction mechanisms, illustrating the need for further kinetic studies of this hydrocarbon. These results demonstrated the potential of multi-wavelength mid-IR laser sensors for hydrocarbon measurements in environments with time-varying temperature and concentration.

Supercritical additive-promoted thermal cracking of a jet fuel model compound, *n*-dodecane, was studied in the presence of several sensitizing additives, such as 1-nitropropane, triethylamine, and 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane in view of improving the heat sink of jet fuel [355]. It was found that the remarkable promoting effects of the initiative additives on the cracking rates, compared with the thermal cracking of pure *n*-dodecane, were observed up to 20–150% in the following order: 1-nitropropane > 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane > triethylamine. Comparisons of product distributions from the thermal cracking of *n*-dodecane with and without initiators indicated that initiator type had a slight effect on the selectivity of the gas products, but a non-negligible effect on the distributions of liquid products. Apparent first-order kinetics were used to describe the supercritical initiative thermal cracking of *n*-dodecane, and the apparent cracking activation energy of pure *n*-dodecane was 256.56 kJ/mol, which decreased to 185.80 kJ/mol by the addition of 1-nitropropane, 196.05 kJ/mol by the addition of

3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane, and 242.83 kJ/mol by the addition of triethylamine.

An HZSM-5 zeolite coating was applied to the inner surface of a microchannel reactor by a washcoating method to improve the cracking rate of supercritical hydrocarbon fuels [356]. Thermal or catalytic cracking of *n*-dodecane was experimentally investigated in the stainless steel microchannel reactor coated with HZSM-5 coatings under supercritical conditions ( $p > 4$  MPa,  $T > 723$  K =  $> 450$  °C). It was found that cracking of *n*-dodecane was enhanced more than 100% by HZSM-5 coatings in 30-min reaction test run durations at 798 and 823 K (525 and 550 °C), despite gradual deactivation of catalytic activity due to coke deposition from pyrolysis and acid-catalyzed reactions. Cokes deposited in the microchannels with and without HZSM-5 coating were characterized by SEM and temperature-programmed oxidation, indicating that HZSM-5 coating effectively reduced formation of filamentous cokes and damage on the micro channel surface by shielding surface metals, for as long as the temperature was higher than 873 K (600 °C) at least.

The initiation mechanisms and kinetics of pyrolysis and combustion of *n*-dodecane were investigated by using reactive molecular dynamics (ReaxFF MD) simulation and chemical kinetic modeling [357]. From ReaxFF MD simulations, it was found that the initiation mechanisms of the pyrolysis of *n*-dodecane proceeds mainly through two pathways: **(1)** the cleavage of C—C bonds to form smaller hydrocarbon radicals, and **(2)** the dehydrogenation reaction to form an H radical and the corresponding  $n\text{-C}_{12}\text{H}_{25}$  radical. Another pathway is the H-abstraction reactions by small radicals including H, CH<sub>3</sub>, and C<sub>2</sub>H<sub>5</sub>, which are the products after the initiation reaction of *n*-dodecane pyrolysis. ReaxFF MD simulations lead to reasonable Arrhenius parameters compared with experimental results based on first-order kinetic analysis of *n*-dodecane pyrolysis, even when the density/pressure effects on the pyrolysis of *n*-dodecane were analyzed. By appropriate mapping of the length and time from macroscopic kinetic modeling to ReaxFF MD, a simple comparison of the conversion of *n*-dodecane from ReaxFF MD simulations and that from kinetic modeling was performed. When studying the oxidation of *n*-dodecane by ReaxFF MD simulations, it was found that formaldehyde molecule is an important intermediate in the oxidation of *n*-dodecane, which has been confirmed by kinetic modeling, and ReaxFF leads to reasonable reaction pathways for the oxidation of *n*-dodecane. These results indicated that ReaxFF MD simulations can give an atomistic description of the initiation mechanism and product distributions of pyrolysis and combustion for hydrocarbon fuels, and can be further used to provide a molecular-based robust kinetic reaction mechanism for chemical kinetic modeling of hydrocarbon fuels.

High pressure *n*-decane and *n*-dodecane shock tube decomposition experiments were conducted to assist in the development of a Jet A surrogate kinetic model [358]. In the formulation of surrogate mixtures for Jet-A, *n*-decane or *n*-dodecane represents the normal paraffin class of hydrocarbons present in kerosene fuels. The experimental

work on both *n*-alkanes was performed in a heated high-pressure single-pulse shock tube. Experimental data on both *n*-decane and *n*-dodecane oxidation and pyrolysis were obtained for temperatures from 867 to 1739 K, pressures from 19 to 74 atm, reaction times from 1.15 to 3.47 ms, and equivalence ratios from 0.46 to 2.05, and  $\infty$ . Both *n*-decane and *n*-dodecane oxidation showed that the fuel decays through thermally driven oxygen-free decomposition under the conditions studied. This observation prompted an experimental and modeling study of *n*-decane and *n*-dodecane pyrolysis using a revised *n*-decane/*iso*-octane/toluene surrogate model. The surrogate model was extended to *n*-dodecane in order to facilitate the study of the species and the 1-olefin species quantified during the pyrolysis of *n*-dodecane and *n*-decane were revised with additional reactions and reaction rate constants modified by rate constants taken from the literature. When compared against a published generalized *n*-alkane model and the original and revised surrogate models, the revised (based on our experimental work) and extended surrogate model showed improvements in predicting 1-olefin species profiles from pyrolytic and oxidative *n*-decane and *n*-dodecane experiments.

An investigation of temperature-dependent products in the pyrolysis of helium-seeded *n*-dodecane, which represents a surrogate of the *n*-alkane fraction of JP-8, was performed in a high-temperature chemical reactor over a temperature range of 1200 to 1600 K at a pressure of 600 mm Hg, with *in situ* identification of the nascent products in a supersonic molecular beam using single photon vacuum ultraviolet photoionization coupled with the analysis of the ions in a reflectron time-of-flight mass spectrometer [359]. The initial decomposition products of *n*-dodecane, including radicals and thermally labile closed-shell species, were probed in experiments, which effectively excluded mass growth processes. A total of 15 different products were identified, such as molecular hydrogen,  $C_2$  to  $C_7$  1-alkenes,  $C_1$ – $C_3$  radicals, small  $C_1$ – $C_3$  hydrocarbons (acetylene,  $C_2H_2$ , allene,  $C_3H_4$ , methylacetylene,  $C_3H_4$ ), as well as the reaction products (1,3-butadiene, 2-butene) attributed to higher-order processes. Electronic structure calculations combined with RRKM/master equation of rate constants for relevant reaction steps showed that *n*-dodecane decomposes initially by a non-terminal C–C bond cleavage and produces a mixture of alkyl radicals from ethyl to decyl with approximately equal branching ratios. The alkyl radicals appear to be unstable under the experimental conditions and to rapidly dissociate either directly by C–C bond  $\beta$ -scission to produce ethene plus a smaller 1-alkyl radical with the number of carbon atoms diminished by two or via hydrogen shifts followed by C–C  $\beta$ -scission producing alkenes from propene to 1-nonene together with smaller 1-alkyl radicals. The C–C  $\beta$ -scission continues all the way to the propyl radical, which dissociates to methyl plus ethene. In addition, at higher temperatures, another mechanism can contribute, in which hydrogen atoms abstract hydrogen from  $C_{12}H_{26}$ , producing various *n*-dodecyl radicals and these radicals then decompose by C–C bond  $\beta$ -scission to  $C_3$  to  $C_{11}$  alkenes.

*n*-Dodecane was selected as a surrogate for kerosene and it was subjected to a series of thermal cracking experiments at supercritical pressure [360]. According to variations in chemical heat sink, fuel-conversion rate, and gas-production rate, the thermal cracking of *n*-dodecane was divided into three regions: primary, secondary, and severe. In the primary cracking region, the fuel-conversion rate was lower than 13%, and the liquid products contained only chain alkanes and alkenes. Owing to the mass fraction of main products being proportional to the fuel-conversion rate, a one-step global reaction kinetic scheme was constructed. The secondary cracking region was characterized by a rapidly increasing chemical heat sink, fuel-conversion rates, and gas-production rates with increasing fuel temperature, and the appearance of monocyclic aromatic hydrocarbons and cycloalkenes. A kinetic model containing three reactions was proposed for this region. This also considered the thermal decomposition of chain alkanes and alkenes, which resulted in the formation of monocyclic aromatic hydrocarbons and cycloalkenes. Severe cracking was observed for fuel-conversion rates above 71% where a rapid increase in the concentration of monocyclic and polycyclic aromatic hydrocarbons occurred. The increasing rate of chemical heat sink slowed in this region, which was characterized by the formation of monocyclic and polycyclic aromatic hydrocarbons and coke. A three-dimensional numerical model was built for the primary and secondary cracking regions, taking the effects of the flow, heat transfer, and thermal cracking of *n*-dodecane into consideration. Predicted values for the outlet temperature, fuel-conversion rate, and distribution of the main species in all tested cases agreed well with the experimental results, validating the numerical model and kinetics for the primary and secondary thermal cracking of *n*-dodecane.

### 10.3.2 Oxidation of *n*-Dodecane

Oxidation of *n*-dodecane may come from dissolved oxygen when in contact with air or in a rocket engine. Rocket engine operations with kerosenes will be discussed in a future volume on non-hypergolic bipropellant combinations. Here, we are only looking at some of the chemical kinetics of dodecane oxidation, in particular, some that may lead to the formation of soot (coke).

A single, compact, and reliable chemical mechanism was proposed that can accurately describe the oxidation of a wide range of fuels, which are important components of surrogate fuels for kerosenes [361]. A well-characterized mechanism appropriate for the oxidation of smaller hydrocarbon species and several substituted aromatic species, ideally suited as a base to model surrogates, has been extended to describe the oxidation of *n*-dodecane, which is often used in diesel and jet fuel surrogates. To ensure compactness of the kinetic scheme, a short mechanism for the low-to high-temperature oxidation of *n*-dodecane was extracted from a scheme detailed earlier and integrated in a systematic way into the base model. Rate changes based on rate recommendations from the literature were introduced to the resulting chemical

mechanism in a consistent manner, which improved the model predictions. Thorough validation of the revised kinetic model was performed using a wide range of experimental conditions and data sets.

Pyrolysis and oxidation kinetics of *n*-dodecane within the temperature range 1000–1300 K were investigated in a Variable Pressure Flow Reactor facility where the reactor environment is vitiated and the experiments were conducted at atmospheric pressure [362]. Species time-history data were collected for *n*-dodecane and oxygen, as well as for 12 intermediate and product species over a span of 1- to 40-ms residence times using real-time GC. The experimental data were compared against the predictions of four detailed kinetic models. The results showed that the hydrocarbon oxidation proceeds through an early pyrolytic stage, where the fuel breaks down into smaller hydrocarbon fragments, including mostly  $C_{2-4}$  alkenes, and a late oxidation stage where the fragments oxidize to CO. The kinetic models were observed to diverge notably in their predictions from one another. The flow reactor data were used to demonstrate how model uncertainty minimization can improve model predictions. It was shown that after uncertainty minimization against a selected set of *n*-dodecane combustion data, the predictions of the resulting optimized model were improved notably for all existing *n*-dodecane data sets tested, including those of the current flow reactor study that were not part of the optimization target list.

#### 10.4 Safety Properties of *n*-Dodecane

The average flash point of *n*-dodecane tested by several laboratories was 358 K (85°C) [363].

### 11 Hexadecane

Hexadecane, also known as cetane,  $C_{16}H_{34}$ , CAS RN [544-76-3] is a viscous oily hydrocarbon with a melting point of 291 K (18°C = 64°F) and a boiling point of 560 K (287°C = 549°F). The cetane number is a measure of the ease of ignition and combustion of diesel fuel by adiabatic compression. Cetane ignites very easily under adiabatic compression; for this reason, it was assigned a cetane number of 100, and serves as a reference for other fuel mixtures. Hexadecane is not used as a rocket propellant as such, but is a natural constituent of RP-1, RP-2, and many of the JP fuels.

#### 11.1 Physical Properties of Hexadecane

*n*-Hexadecane is a constituent of RP-1 and RP-2 and it is important to have physical properties for the pure compound before using it as a constituent of surrogate fuel

mixtures. A correlation for the viscosity of *n*-hexadecane was based upon a set of experimental data that had been critically assessed for internal consistency and for agreement with theory [3]. It is applicable within the temperature range from the triple point to 673 K at pressures up to 425 MPa and along the saturation line.

A wide-ranging correlation for the thermal conductivity of *n*-hexadecane based on critically evaluated experimental data was designed to be used with an equation of state, and covered a range from the triple point up to 700 K and pressures up to 50 MPa [364]. The correlation behaved in a physically reasonable manner when extrapolated to the full range of the equation of state, but the uncertainties are larger outside of the validated range, and deviations are large in the critical region.

## 11.2 Thermal Decomposition of Hexadecane

A pyrolysis reaction system that provided better control than the tubular flow reactors of previous researchers was used to study the ultrapyrolysis kinetics of *n*-hexadecane [365]. Ultrapyrolysis, or ultra-rapid pyrolysis, refers to thermal cracking under conditions of high temperatures, very short reaction times, high heating rates, and rapid product quench. Millisecond furnaces operating under such conditions have demonstrated significantly higher ethene yields owing to improved selectivity. The automated micro-reaction system used a Curie point pyrolyzer to rapidly heat microgram *n*-hexadecane samples to high temperatures. The Curie point phenomenon ensured that a reproducible and well-defined temperature was attained. A rapid direct quench system was used to stop the reactions and transfer the products to the analyzer. *n*-Hexadecane was pyrolyzed at 849–1115 K (576–842 °C) for 100–3200 ms. Peak ethene production (28 mass-%) was observed at ultrapyrolytic conditions of 1115 K (842 °C) and 500 ms. A first-order kinetic analysis performed on the pyrolysis data yielded an activation energy of 165 kJ/mol (39.4 kcal/mol).

Thermal cracking of *n*-hexadecane was carried out in a tubular flow reactor at 653–723 K (380–450 °C), 13.9 MPa, and residence times ranging from 0.06 to 2.0 h, giving conversions of 1.5–10% [366]. Primary reaction products were C<sub>1</sub> to C<sub>14</sub> *n*-alkanes and C<sub>2</sub> to C<sub>15</sub> α-olefins, in agreement with a free-radical chain mechanism. Under high-pressure conditions, addition of radicals to α-olefins became significant. Addition of parent hexadecyl radicals to α-olefins resulted in the formation of alkyl hexadecanes within the range C<sub>18</sub> to C<sub>31</sub>. Addition of lower primary alkyl radicals to α-olefins gave higher *n*-alkanes, including *n*-C<sub>15</sub> and *n*-C<sub>17</sub>. Addition of lower secondary alkyl radicals resulted in the formation of C<sub>7</sub> to C<sub>17</sub> branched alkanes. A simple kinetic model based on a free-radical mechanism was developed to account for the observed product distributions and overall *n*-C<sub>16</sub> conversion.

Thermal cracking of *n*-hexadecane within the mild temperature (603–648 K = 330–375 °C) range was investigated in liquid and gas phases [367]. The kinetics of liquid-phase cracking were shown to be very similar to those of gas-phase cracking.

However, the pattern and distribution of the products were greatly phase dependent. In liquid-phase cracking, there was an equimolar distribution of *n*-alkane and 1-alkene products within the  $C_3$ – $C_{13}$  range at low conversion. When the conversion was increased, more alkanes than alkenes were produced. To the contrary, more alkenes than alkanes were always determined in products from gas-phase cracking. Liquid-phase cracking gave a low selectivity of gas products and a high selectivity of addition compounds ( $C_{18}$ – $C_{30}$ ), whereas gas-phase cracking produced a large amount of gas products and no addition compounds. The phase dependence of products was interpreted in terms of a low concentration of hexadecane, under which  $\beta$ -scission would occur more preferentially than in the liquid phase. Reaction mechanisms were suggested based on the product analysis to account for the different cracking behaviors of liquid-phase and gas-phase cracking.

Pyrolysis experiments on *n*-hexadecane were conducted at 673–723 K and *n*- $C_{16}$  concentrations of 0.07–1.47 mol/L by using batch-type reactors [282]. The main products of *n*- $C_{16}$  pyrolysis were *n*-alkanes and 1-alkenes under all the reaction conditions. The 1-alkene/*n*-alkane ratio decreased with increasing *n*- $C_{16}$  concentration at all the reaction temperatures. The rate of *n*- $C_{16}$  pyrolysis increased to a maximum and then decreased with increasing *n*- $C_{16}$  concentration. The activation energy of the overall rate constant of *n*- $C_{16}$  pyrolysis was 196 kJ/mol at 0.07 mol/L of *n*- $C_{16}$  concentration and 263 kJ/mol at 0.22 mol/L. A mathematical model for the pyrolysis was developed to describe these phenomena and the radical network reaction, including initiation, isomerization,  $\beta$ -scission, H abstraction, and termination. The effect of radical size on the rates of bimolecular reactions (H abstraction and termination) was important for a correct quantitative description. Comparison between the experimental data and the model showed that the rates of bimolecular reactions were inversely proportional to the carbon number *i* of radical  $R_i$ . The model was able to predict product distribution and *n*- $C_{16}$  pyrolysis rates within a wide range of temperatures (603–893 K) and *n*- $C_{16}$  concentrations ( $6.86 \times 10^{-3}$  to 2.48 mol/L). The model can even describe the pyrolysis kinetics of *n*- $C_{10}$  to *n*- $C_{25}$  by considering the carbon number of the hydrocarbon.

## 12 Branched Chain Aliphatic Hydrocarbons

Branched chain hydrocarbons not only had better octane numbers for combustion in internal combustion engines in automobiles and airplanes (better than straight-chain molecules), but they were also expected to burn more smoothly (less combustion instabilities) in rocket engines. One of the synthetic branched-chain hydrocarbons considered as a replacement for RP-1 in ATLAS rocket engines was “tetraisobutylene” and its heat transfer properties were measured [368]. An analytical and experimental investigation was made of the heat-transfer characteristics of tetraisobutylene to determine the potential of this fuel as a replacement for RP-1 in an Atlas engine with FLOX oxidizer. Under regenerative cooling conditions of surface and fluid temperature, the



heat sink from the endothermic dissociation of this fluid could not be realized. Experiments also evaluated the heat-transfer characteristics of RP-1 at fluid temperatures over 422 K (300 °F).

Isobutylene can be polymerized and results in the formation of oily, liquid oligomers that can be separated by fractionated distillation or used as mixtures. Oligomers described in the literature include diisobutylene, triisobutylene, and tetraisobutylene [369]. Triisobutylene consists of a mixture of three isomers, 1,1-dineopentylethene, 1-methyl-1-neopentyl-2-*tert*-butylethene, and 1,1-dimethyl-2,2-di-*tert*-butylethene [370, 371].

Oligopropylenes, such as the trimer and the tetramer, had exceptionally high autoignition temperatures in air when tested in a spontaneous ignition test apparatus [372].

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# Alkenes and Alkynes

## Introduction

The *Encyclopedia of Liquid Fuels* contains eight chapters that deal with hydrocarbon fuels. It was necessary to sub-divide the topic of hydrocarbon fuels into several smaller sections that were easier to arrange in alphabetical order in five subvolumes of equal size. The titles of the eight hydrocarbon chapters are: “Alkanes,” “Alkenes and Alkynes,” “Aromatic Hydrocarbons,” “Cycloaliphatic Hydrocarbons,” “Hydrocarbons,” “Jet Fuels,” “Kerosenes,” and “Ramjet Fuels.”

## 1 Unsaturated Hydrocarbons: Alkenes and Dienes

Alkenes, also called *olefins*, contain at least one carbon-to-carbon double bond, making them *unsaturated compounds*. The general formula for alkenes with one double bond is  $C_nH_{2n}$ . If they contain two, three, or more double bonds, they are called *dienes*, *trienes*, or *polyenes*, respectively. If the double bonds in a chain alternate with single bonds, they are termed *conjugated double bonds*. Such bonds share electron clouds, causing quantum mechanical resonance, which increases the thermal stability but also the reactivity of molecules containing conjugated double bonds. Alkenes with one or more double bonds are more susceptible than alkanes to autoxidation and resin formation, an undesirable property for jet engine fuels and rocket fuels alike. Alkenes with one or more double bonds are more reactive than either alkanes or aromatics, and their presence will reduce the storability of liquid fuels.

Depending on the application of the fuel, the presence or absence of double bonds is encouraged or avoided. In one wants a polyunsaturated hydrocarbon fuel capable of hypergolic ignition with WFNA or mixed acid, one looks for a molecule with many double bonds. If one wants a storable hydrocarbon fuel without resin formation due to autoxidation, one minimizes the content of double bonds.

The formation of double and triple bonds increases the enthalpy of formation of alkanes, as shown in Table 1. However, the loss of hydrogen may outweigh the gain in energy released when one applies the rocket propulsion specific impulse formula in the search for better rocket propellants.

The increased energy content of ethene increases the specific impulse of LOX/ethene over that of LOX/ethane or LOX/kerosene. The chamber temperature is hotter than the LOX/ethane flame.

Alkenes containing two or more conjugated double bonds may be reactive enough that they will ignite hypergolically with WFNA or RFNA or mixed acid, but they may also spontaneously polymerize and thus cannot be stored without forming resins that would clog orifices.

**Table 1:** Enthalpies of formation of alkanes, alkenes, and alkynes.

| Compound             | Enthalpy of formation, liquid |                | Enthalpy of formation, gas |               | References |
|----------------------|-------------------------------|----------------|----------------------------|---------------|------------|
|                      | kJ/mol                        | kcal/mol       | kJ/mol                     | kcal/mol      |            |
| Ethane               | −99.97 (calc.)                | −23.89 (calc.) | −84.67 ± 0.49              | −20.24 ± 0.12 | [1]        |
|                      | −103.819                      | −24.81         | −83.852                    | −20.04        | [2]        |
| Ethylene (ethene)    | +38.4 (calc.)                 | +9.18 (calc.)  | +52.4 ± 0.5                | +12.52 ± 0.12 | [1]        |
|                      | +33.945                       | +8.11          | +52.5                      | +12.55        | [2]        |
|                      | +33.92                        | +8.11          | —                          | —             | [3]        |
| Acetylene            | +211.1 (calc.)                | +50.45 (calc.) | +227.4 ± 0.8               | +54.35 ± 0.19 | [1]        |
|                      | +207.599                      | +49.62         | +228.2                     | +54.54        | [2]        |
|                      | +206.1                        | +49.3          | +226.7                     | +54.2         | [3]        |
| Allene               | —                             | —              | +190.92                    | +45.63        | [2]        |
| <i>n</i> -Butane     | −148.8 (calc.)                | −35.56 (calc.) | −125.6 ± 0.67              | −30.02 ± 0.16 | [1]        |
|                      | −150.664                      | −36.01         | −125.79                    | −30.06        | [2]        |
| 1-Butene             | −23.43 (calc.)                | −5.60 (calc.)  | −0.63 ± 0.79               | −0.15 ± 0.19  | [1]        |
|                      | −25.173                       | −6.02          | −0.54                      | −0.13         | [2]        |
| <i>cis</i> -2-Butene | −31.7 (calc.)                 | −7.58 (calc.)  | −7.7 ± 1.3                 | −1.84 ± 0.31  | [1]        |
|                      | —                             | —              | −7.4                       | −1.77         | [2]        |
| Butadiene            | +90.5 ± 0.96                  | +21.63 ± 0.23  | +108.8 ± 0.79              | +26.00 ± 0.19 | [1]        |
|                      | —                             | —              | +110                       | +26.29        | [2]        |

(calc.) indicates that this number was calculated by subtracting the enthalpy of vaporization from the enthalpy of formation of the vapor

The use of butadiene and substituted butadienes as hypergolic fuels in combination with WFNA or RFNA was patented, but has never found any application [4].

## 2 Ethene (Ethylene)

Ethene (ethylene) has gained importance as the fuel in pulse detonation engines, rotating detonation engines, and in monopropellant mixtures with nitrous oxide.

### 2.1 Production and Availability of Ethene

Ethene is an important feedstock for the chemical and polymer industry and is produced in megaton quantities by cracking petroleum in refineries.

## 2.2 Physical Properties of Ethene

Physical properties of ethene are summarized in [5, 6]. They are also listed in Table 2.

**Table 2:** Physical properties of ethene.

| Property                                | SI units                                  | Other units                                                   | References |
|-----------------------------------------|-------------------------------------------|---------------------------------------------------------------|------------|
| Molecular mass                          | 28.0532 g/mol                             | 35.6465 mol/kg                                                | [1]        |
| Freezing point                          | 103.7 K                                   | −169.4 °C                                                     |            |
| Boiling point                           | 169 ± 1 K                                 | −104 ± 1 °C                                                   |            |
|                                         | 169.4 K                                   | −103.7 °C                                                     | [7]        |
| Density, liquid, at 169 K               | 0.5657 g/cm <sup>3</sup>                  | —                                                             |            |
| Density, liquid, at 103 K               | 0.6585 g/cm <sup>3</sup>                  | —                                                             |            |
| Viscosity, liquid, at 165 K             | 186.32 μPa s                              | 0.186 cPs                                                     | [8]        |
| Viscosity, gas, at 298 K and 0.1 MPa    | 9.2398 μPa s                              | 0.009 cPs                                                     |            |
| Thermal conductivity, liquid, at 165 K  | 191.95 mW m <sup>−1</sup> K <sup>−1</sup> | 0.11098 BTU h <sup>−1</sup> ft <sup>−1</sup> °F <sup>−1</sup> |            |
| Heat capacity, $C_p$ , gas, at 298 K    | 42.90 J mol <sup>−1</sup> K <sup>−1</sup> | 10.25 cal mol <sup>−1</sup> °C <sup>−1</sup>                  | [1]        |
| Heat capacity, $C_p$ , liquid, at 170 K | 67.4 J mol <sup>−1</sup> K <sup>−1</sup>  | 16.11 cal mol <sup>−1</sup> °C <sup>−1</sup>                  |            |
| Enthalpy of formation, liquid           | +38.4 (calc.)                             | +9.18 (calc.)                                                 |            |
| Enthalpy of formation, gas, at 298 K    | +52.4 ± 0.5 kJ/mol                        | +12.52 ± 0.12 kcal/mol                                        |            |
| Enthalpy of fusion at 103.97 K          | 3.351 kJ/mol                              | 0.801 kcal/mol                                                |            |
| Enthalpy of vaporization at 169 K       | 13.544 kJ/mol                             | 3.237 kcal/mol                                                |            |
| Heat of combustion, upper               | 1411.20 ± 0.30 kJ/mol                     | 337.3 ± 0.1 kcal/mol                                          |            |

### 2.2.1 Vapor Pressure of Ethene

The vapor pressure of ethene in the range 149–188 K can be calculated from the Antoine equation:

$$\log(P) = A - [B/(T + C)] = 3.87261 - [584.146/(T - 18.307)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

### 2.2.2 Viscosity of Ethene

Data for the viscosity and thermal conductivity coefficients of gaseous and liquid ethene were evaluated and represented by polynomial empirical functions [8]. The data were represented in graphs as a function of density rather than as a function of temperature, which would have been more convenient. Tables of values were presented for the temperature range 110–500 K and for pressures up to 50 MPa (500 atm). The viscosity of liquid ethene at 165 K is 186.32 μPa s, and the viscosity of ethene gas at 298 K is 9.2398 μPa s.

### 2.2.3 Surface Tension of Ethene

Data for the surface tension of liquid ethene are summarized in Table 3.

**Table 3:** Surface tension of liquid ethene.

| Temperature, K | Surface tension, mN/m |
|----------------|-----------------------|
| 114.1          | 26.09                 |
| 115.8          | 25.76                 |
| 117.3          | 25.49                 |
| 119.1          | 25.09                 |
| 120.1          | 24.96                 |
| 121.7          | 24.65                 |
| 123.1          | 24.38                 |

Data source: [9]

The surface tension of liquid ethene as a function of temperature can be expressed by the equation

$$\eta = 47.68 - 0.1893T$$

where  $\eta$  is the surface tension in mN/m and  $T$  is the temperature in kelvin.

### 2.2.4 Thermal Conductivity of Ethene

Data for the thermal conductivity coefficients of gaseous and liquid ethene were evaluated and represented by polynomial empirical functions [8]. The data were represented in graphs as a function of density rather than as a function of temperature, which would have been more convenient. Tables of values were presented for the temperature range 110–500 K and for pressures up to 50 MPa (500 atm). The anomalous contribution to the thermal conductivity in the vicinity of the critical point was included. The thermal conductivity of liquid ethene at 165 K is  $191.95 \text{ mW m}^{-1} \text{ K}^{-1}$  and the thermal conductivity of ethene gas at 300 K is  $20.56 \text{ mW m}^{-1} \text{ K}^{-1}$ .

The thermal conductivities of ethene and propene were measured as a function of temperature and density from 110 to 520 K at pressures up to 200 MPa [10]. The resulting correlations were valid from 180 to 625 K and up to 50 MPa, but they also behaved in a physically reasonable manner down to the triple point and may be used at pressures up to 100 MPa. For both fluids, uncertainties in the critical region were very large, since the thermal conductivity approached infinity at the critical point and was very sensitive to small changes in density.

The thermal conductivity of ethene was measured in a coaxial cylinder cell operating under steady-state conditions along eight quasi-isotherms above the critical temperature over the temperature range from 283 to 425 K and the pressure range from 0.1 to 100 MPa [11].

### 2.2.5 Critical Constants of Ethene

The critical point properties of ethene are as follows:

$$T_c = 282.34 \text{ K}$$

$$\rho_c = 0.215 \text{ g/cm}^3 \quad (7.66 \text{ mol/L})$$

$$P_c = 5.0390 \text{ MPa} \quad (49.73 \text{ atm})$$

$$M = 28.054$$

### 2.2.6 Thermodynamic Properties of Ethene

Fundamental equations for the thermodynamic properties of ethene from the freezing line to 450 K and at pressures up to 260 MPa included independent equations for the vapor pressure of the saturated liquid and vapor densities as functions of temperature, and for the ideal gas heat capacity [12, 13]. The coefficients of the fundamental equation were determined by a weighted least-squares fit to selected  $P - \rho - T$  data and saturated liquid and saturated vapor density data to define the phase equilibrium criteria for coexistence,  $C_v$  data, velocity of sound data, and second virial coefficient data. The fundamental equation and the derivative functions were used to calculate the internal energy, enthalpy, entropy, isochoric heat capacity ( $C_v$ ), isobaric heat capacity ( $C_p$ ), and velocity of sound. Tables of thermodynamic properties of ethene were assembled for liquid and vapor states within the range of validity of the fundamental equation.

## 2.3 Chemistry of Ethene

### 2.3.1 Reactions of Ethene

Ethene is capable of polymerizing under a variety of conditions. The most important polymerization process is the synthesis of polyethylene, the most widely used plastic foil for packaging and building materials. Precautions should be taken during the storage and transport of liquid ethene to avoid catalytic contaminants [14].

### 2.3.2 Analysis of Ethene

The easiest method of performing occasional spot checks of the ethene concentration in air in the workplace is to use gas detection tubes made from glass tubes containing an indicator (supported on a granular material) that changes color when exposed to ethene. Such tubes are available from Draeger, MSA, Kitagawa, and others. Gas detection tubes are sensitive to as little as 0.2 ppm  $\text{C}_2\text{H}_4$  and can measure up to 2500 ppm  $\text{C}_2\text{H}_4$  with ten strokes. Draeger ethene gas detection tubes are available for two ranges of concentrations (Table 4).



**Table 4:** Draeger ethene gas detection tube concentration ranges.

| Tube designation | Concentration range | Draeger part number |
|------------------|---------------------|---------------------|
| Ethene 0.1/a (5) | 0.2–5 ppm           | 81 01 331           |
| Ethylene 50/a    | 50–2500 ppm         | 67 28 051           |

Data source: [15]

## 2.4 Safety Properties of Ethene

### 2.4.1 Limits of Flammability of Ethene

The limits of flammability of ethylene in oxygen, air, and air/nitrogen mixtures were measured at elevated temperatures and pressures in a 3 L spherical bomb [16]. The limits in oxygen were determined at 353, 393, and 423 K (80, 120, and 150 °C) and over the pressure range 932–3550 kPa (135–515 psia). The limits in air and air/nitrogen mixtures were determined at 101, 310, and 932 kPa (14.7, 45, and 135 psia) and at 293 and 523 K (20 and 250 °C). The upper limit in oxygen was raised by increasing either the temperature or pressure, but the effect of the pressure was small above 2.07 MPa (300 psia). The upper limit in air was also raised by increasing either temperature or pressure, and the critical oxygen concentration was reduced under the same conditions. Explosions in oxygen/ethylene mixtures close to the upper limit of flammability at high pressures gave abnormally high explosion pressures. This effect was attributed to the energy released by the decomposition of ethylene and the formation of significant quantities of methane.

Mixtures of ethylene with small amounts of oxygen are used as the feed for the synthesis of ethylene oxide, but these mixtures are potentially flammable. The flammabilities of oxygen/ethylene mixtures with different diluents (nitrogen, carbon dioxide, methane) were measured at up to 523 K (250 °C) and 2.03 MPa (20 atm) [17].

The upper flammability limit of ethene/air/nitrogen mixtures under flow conditions was measured with the gas mixtures flowing through an explosion tube with a length of 3.0 m and a diameter of 21 mm [18]. An electrically heated wire was used as the ignition source. Experiments were performed at pressures of 5 and 10 bar, with gas temperatures between 298 and 573 K (25 and 300 °C), and with the ignitor wire oriented horizontally and vertically. Three different phenomena were observed: a negligible reaction, a local reaction, and an explosion. The negligible reaction region occurred at power supply rates to the wire below a critical value. Above this critical value, either a local reaction or an explosion took place. The critical oxygen concentration that separated the local reaction and explosion regimes depended on the experimental conditions used (i.e., the gas composition, pressure, temperature, wire size and orientation, and gas velocity). An increase in pressure increases the upper flammability limit. Obviously, the upper flammability limit is influenced by the gas velocity. Under flow conditions, the explosion region becomes smaller and shifts to higher oxygen con-

centrations. This is important for applications in the chemical industry that depend on partial oxidation reactions of ethylene.

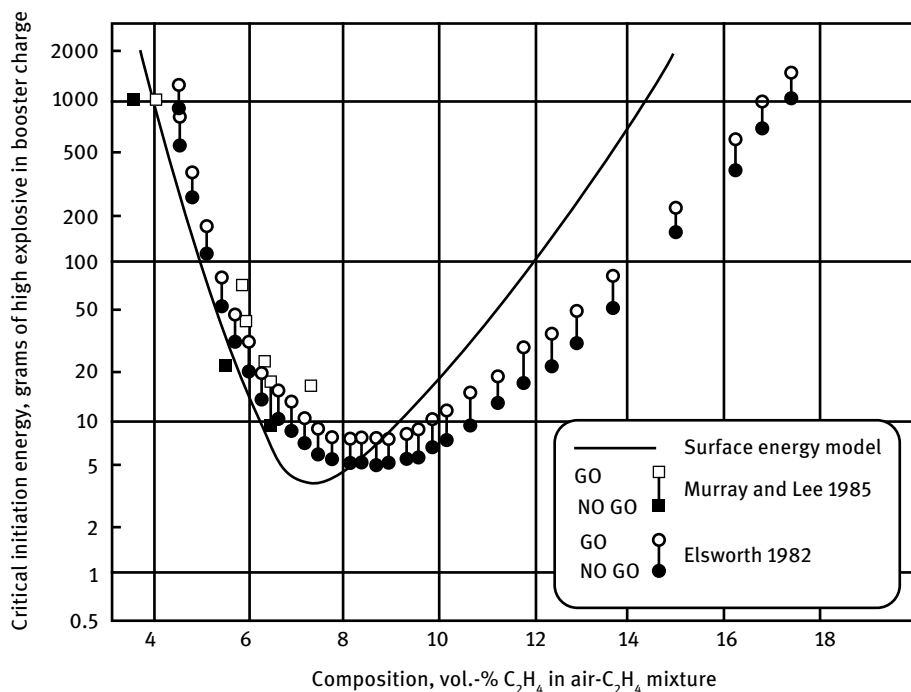
#### 2.4.2 Critical Diameter for the Propagation of Air/Ethene Explosions

Knowledge of the critical diameter for the propagation of detonations is required for the design of flame arrestors and detonation arrestors. The critical diameter is the tubing or orifice diameter below which detonation from a donor section cannot propagate into an acceptor section of detonable gas [19]. A series of field tests was performed to obtain the critical tube diameter ( $d_c$ ) for air/ethylene mixtures by investigating the diffraction of detonations from tubes into large plastic bags simulating an unconfined fuel/air cloud. The critical air/ethylene compositions for successful re-establishment of detonation upon emerging from tubes with diameters of 0.31, 0.45, 0.89, and 1.36 m were determined by monitoring the diffracted detonation wave in the bag. High-speed cinematography of the diffracted wave showed that re-establishment of detonation occurs via one or more re-ignition centers at sites along the head of the expansion wave that originates at the area change. The characteristic transverse wave spacings,  $S$ , associated with the detonations were measured from smoked foils mounted in the tubes. These measurements demonstrated that the empirical relation  $d_c = 13S$  provided a good correlation between the critical tube diameter and the cell size over a wide range of ethylene/air compositions. Based on these tests, it was concluded that the critical tube and critical orifice diameters are equal.

A similar experimental study has been carried out to investigate the transmission of a planar detonation wave through an orifice into an unconfined medium [20]. Mixtures of  $C_2H_4 + 3(O_2 + \beta N_2)$  for a range of nitrogen concentrations corresponding to  $1 \leq \beta \leq 3.76$  and at an initial pressure of 1 atm were used in the experiments. It was found that the critical diameter for transmission through an orifice is identical to that for a straight tube and that both follow the empirical correlation of  $d_c \cong 13\lambda$ . Transmission through square, triangular, elliptical, and rectangular orifices has led to the development of a correlation based on the effective diameter similar to that for a circular geometry (i.e.,  $d_{eff} \cong 13\lambda$ ). The effective diameter is defined as the mean value of the longest and shortest dimensions of the orifice shape.

#### 2.4.3 Critical Initiation Energy for Air/Ethene Explosions

Critical initiation energy results for a range of air/hydrocarbon mixtures are shown in Figure 1. This graph presents a comparison of critical initiation energy data for the air/ethene system derived from the experiments of Murray et al. [21] with more recent data obtained by Guirao, Knystautas, and Lee [22]. The agreement between both sets of data is good. This information would be useful for the design of pulsed detonation engines or rotating detonation engines that operate on air/ethene.



**Figure 1:** Variation of the critical energy for the direct initiation of spherical detonation with the fuel percentage in ethylene/air mixtures at NTP. (Reproduced and modified from Figure 15 of [22].)

#### 2.4.4 Deflagration-to-Detonation Transitions in Air/Ethylene Gas Mixtures

A series of single-shot experiments were conducted to characterize the deflagration-to-detonation transition (DDT) of air/ethene mixtures in a 45 × 45-mm square tube that was 1.65 m long [23]. Obstacles are important for inducing the DDT; this fact can be used advantageously in pulse detonation engines.

### 3 Propene (Propylene)

Propene (C<sub>3</sub>H<sub>6</sub>, CAS RN [115-07-1]) has been selected as a rocket propellant fuel by Vector Launch Inc. of Tucson, AZ in 2018. It was to be used as the fuel in combination with LOX for its planned Vector-R and Vector-H launch vehicles. Very little is known about their rationale for selecting propene over propane or kerosene. Prior to that, propene had been considered as a fuel to use in combination with hydrogen peroxide [24].

### 3.1 Physical Properties of Propene

The physical properties of propene are summarized in Table 5.

**Table 5:** Physical properties of propene.

| Property                                       | SI units                                  | Other units                                  | References |
|------------------------------------------------|-------------------------------------------|----------------------------------------------|------------|
| Molecular mass                                 | 42.0797 g/mol                             | 23.7644 mol/kg                               | [1]        |
| Freezing point                                 | 87.9 K                                    | −185.2 °C                                    |            |
| Boiling point                                  | 225.6 ± 0.6 K                             | −47.5 ± 0.6 °C                               |            |
| Density, liquid, at 293 K                      | 0.5193 g/cm <sup>3</sup>                  | —                                            | [25]       |
| Vapor pressure at 293 K                        | 1016 kPa                                  | 147 psia                                     | [1]        |
| Heat capacity, $C_p$ , liquid, at 298 K        | 102 J mol <sup>−1</sup> K <sup>−1</sup>   | 24.38 cal mol <sup>−1</sup> °C <sup>−1</sup> |            |
| Heat capacity, $C_p$ , gas, at 298 K           | 64.32 J mol <sup>−1</sup> K <sup>−1</sup> | 15.37 cal mol <sup>−1</sup> °C <sup>−1</sup> |            |
| Enthalpy of formation at 298 K, liquid (calc.) | −1.91 kJ/mol                              | −0.456 kcal/mol                              |            |
| Enthalpy of formation at 298 K, vapor          | +20.41 kJ/mol                             | +4.878 kcal/mol                              |            |
| Enthalpy of fusion at 88.2 K                   | 2.93 kJ/mol                               | 0.700 kcal/mol                               |            |
| Enthalpy of vaporization at 225.5 K            | 18.42 kJ/mol                              | 4.402 kcal/mol                               |            |
| Heat of combustion, gas                        | 2057.8 kJ/mol                             | 491.8 kcal/mol                               |            |
| Critical temperature                           | 365.2 ± 0.8                               | 92.1 °C                                      |            |
| Critical pressure                              | 46.0 ± 0.3 bar                            | 45.4 ± 0.3 atm                               |            |
| Critical density                               | 5.42 ± 0.03 mol/L                         | —                                            |            |

## 4 Acetylene and Acetylene Derivatives

Acetylene and acetylene compounds (*alkynes*) contain at least one triple bond between two carbon atoms,  $\text{—C}\equiv\text{C—}$ , and have the general formula  $\text{C}_n\text{H}_{2n-2}$ . The name acetylene is specifically used to designate the simplest member of the series, also known as ethyne ( $\text{C}_2\text{H}_2$ ;  $\text{HC}\equiv\text{CH}$ ). Acetylene and many acetylene compounds have very high enthalpies of formation and very high heats of combustion, making them suitable fuels to reach very high flame temperatures but not necessarily high specific impulses unless a hydrogen carrier is added to the formulation.

The CH group adjacent to a triple bond in acetylene or terminal alkynes is more acidic than any other hydrocarbon bond and can form stab-sensitive explosive metal salts with silver or copper.

Instead of physically dissolving acetylene in other fuels, it has been proposed that high-energy fuels could be synthesized by introducing the alkyne group  $\text{—C}\equiv\text{CH}$  as a substituent into other hydrocarbons, amines, or hydrazines. Alkyne molecules with one or two attached nitrile groups have extremely high flame temperatures (see the chapter “Cyano Compounds and Nitriles” in *Encyclopedia of Liquid Fuels*).

It has also been proposed that alkyne groups could be introduced into solid propellant binders to give them more energy [26, 27].

Although the primary objective was to develop fuels for air-breathing turbo jet engines or bipropellant rocket systems, tests by other laboratories indicated that acetylenic hydrocarbons also have interesting possibilities for monopropellant and ramjet engine systems [28]. Some of the acetylenic compounds investigated are listed in Table 6.

**Table 6:** Properties of acetylene derivatives.

| Compound                                                               | Density<br>at 293 K | Melting point |       | Boiling point      |                     | Net heat of<br>combustion |        |
|------------------------------------------------------------------------|---------------------|---------------|-------|--------------------|---------------------|---------------------------|--------|
|                                                                        |                     | K             | °F    | K                  | °F                  | MJ/kg                     | BTU/lb |
| 3,6-Dimethyl-2,6-octadiene-4-yne                                       | 0.807               | 213           | -76   | 446                | 343                 | 42.316                    | 18205  |
| 1,6-Heptadiyne                                                         | 0.805               | 188           | -121  | 387                | 237                 | 43.118                    | 18550  |
| Methyl vinyl acetylene<br>(2-methyl-1-butene-3-yne)                    | 0.680 at<br>11 °C   | <193          | <-112 | 307                | 93                  | 43.746                    | 18820  |
| Methyl divinyl acetylene<br>(2-methyl-1,5-hexadiene-3-yne)             | 0.781               | <208          | <-85  | 381                | 226                 | 42.481                    | 18276  |
| Dimethyl divinyl diacetylene<br>(2,7-dimethyl-1,7-octadiene-3,5-diyne) | 0.843               | 267           | 22    | 314 at<br>0.07 kPa | 106 at<br>0.5 mm Hg | 41.840                    | 18000  |
| 1,3-Hexadiyne                                                          | 0.796               | <208          | <-85  | 320 at<br>15 kPa   | 117 at<br>113 mm Hg | 43.776                    | 18833  |
| For comparison:<br>Kerosene JP4                                        | 0.78                |               |       |                    |                     | 42.769                    | 18400  |

Data source: [28]

The most promising of these compounds appeared to be dimethyl divinyl diacetylene, which rendered JP-4 hypergolic with both WFNA and RFNA when present in concentrations as low as 15% by volume. Methyl divinyl acetylene also appeared quite promising, since it exhibited excellent low-temperature ignition characteristics. Methyl divinyl acetylene had an ignition delay of 5.5 ms at 219 K (-65 °F) with RFNA as the oxidizer, while the ignition delay of triethylamine was 29 ms in the same apparatus. The cap sensitivities of the acetylenic compounds were tested with 10-mL samples in a glass test tube inserted into a lead pipe. Exploding compounds were incrementally diluted with hexane until the no-detonation point was reached. Insensitive acetylenic compounds were sensitized by the incremental addition of

peroxy butane until the mixture became sensitive. Dimethyl divinyl diacetylene showed greater sensitivity than peroxy butane.

Cyclopropylacetylene has a density of  $0.773 \text{ g/cm}^3$  at 293 K. Dipropargylether has a density of  $0.924 \text{ g/cm}^3$  at 293 K. Deterioration of acetylenic compounds during storage is mainly caused by polymerization and peroxidation. In general, acetylenic compounds that are not conjugated and contain no double bonds are the most stable. A series of tests have been run to determine the relative stabilities of many of the acetylenic compounds. Samples were heated at 344 K (71 °C) for 5 days and were then analyzed for polymer content [29]. A variety of propargyl compounds have been evaluated as high energy density materials [30].

## 4.1 Acetylene

Acetylene itself ( $\text{HC}\equiv\text{CH}$ ,  $\text{C}_2\text{H}_2$ , ethyne, CAS RN [74-86-2]) can be liquefied only under extreme precautions. Liquid acetylene is very explosive and it is not suitable for use as a rocket propellant [31]. Interestingly, solutions of acetylene in liquid ammonia are stable enough and have been tested as rocket propellants. We therefore give a summary of the properties of acetylene below, even though this chemical will not be used as a rocket propellant in the pure state.

### 4.1.1 Production of Acetylene

Acetylene is easily produced by reacting calcium carbide with water. Prior to the availability of acetylene in compressed gas cylinders with a solvent, it was common practice to have calcium carbide acetylene gas generators at metalworking shops where oxygen/acetylene welding torches were used.

### 4.1.2 Physical Properties of Acetylene

The physical properties of acetylene are summarized in Table 7.

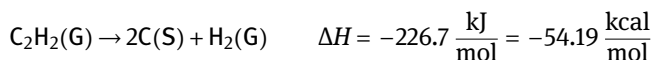
**Table 7:** Physical properties of acetylene.

| Property                                   | SI units                | Other units    | References |
|--------------------------------------------|-------------------------|----------------|------------|
| Molecular mass                             | 26.0373 g/mol           | 38.4064 mol/kg | [1]        |
| Freezing point                             | 171.65 K                | -101.5 °C      |            |
| Boiling point                              | 189 K                   | -84 °C         |            |
| Density, liquid, at 193 K (under pressure) | 0.612 g/cm <sup>3</sup> | —              |            |
| Critical temperature                       | 308.3 ± 0.1 K           | 35.2 ± 0.1 °C  | [1]        |
| Critical pressure                          | 61.38 ± 0.10 bar        | 890 psia       |            |
| Critical volume                            | 0.1122 L/mol            | —              |            |

### 4.1.3 Chemical Properties of Acetylene

#### 4.1.3.1 Thermal Decomposition of Acetylene

The thermal decomposition of acetylene usually proceeds with explosive force, so it is difficult to obtain kinetic rate information unless the reactive gas is highly diluted. The thermal decomposition of acetylene is used on an industrial scale for producing very pure carbon black called acetylene black. In theory, the reaction proceeds as the reverse of the formation of acetylene from the elements:



Under real-life conditions, the decomposition products contain ethylene and methane.

The pyrolysis of acetylene/argon mixtures has been investigated in the temperature range 1400–2500 K using shock wave heating [32]. Time-resolved emission and absorption spectra, measurements of reflected shock velocities, and an analysis of the products of the reaction have been used to follow the rate of loss of acetylene. The average activation energy over the temperature range from 600 to 2500 K was approximately 163 kJ/mol (39 kcal/mol), and there is evidence that the same mechanism is dominant over the entire range of temperatures.

The activation energies of first- and second-order acetylene decomposition reactions in acetylene/argon mixtures in shock tube experiments were 109 and 138 kJ/mol (26 and 33 kcal/mol), respectively [33].

#### 4.1.3.2 Reactions of Acetylene

Acetylene is a weak acid and, as such, forms salts with strong bases. Sodium acetylide is relatively stable, but silver acetylide is very shock and friction sensitive, similar to silver azide and lead azide.

In an attempt to prepare acetylide salts of strong organic bases as propellant ingredients, solutions of sodium acetylide in liquid ammonia were reacted with guanidinium(1+) sulfate or tetramethylammonium chloride, but the only products were the sodium salts and acetylene gas. The affinity of the acetylide anion for protons was higher than its affinity for organic base cations [34, 35].

Instead of synthesizing acetylides, they were successful in synthesizing salts of propiolic acid (acetylene carbonic acid), such as tetramethylammonium propiolate  $\text{HC}\equiv\text{C}-\text{COO}[\text{N}(\text{CH}_3)_4]$  [36]. The melting point of the salt in a sealed capillary tube was 408 K (135 °C). Decarboxylation of the salt did not yield any tetramethylammonium acetylide, only the evolution of acetylene. The presence of an acetylenic function was demonstrated by the formation of a precipitate when ammoniacal silver nitrate was added to an aqueous solution of the compound.

#### 4.1.4 Detonation of Acetylene in the Absence of Air

It has been shown that explosive acetylene decomposition may occur in the deflagration mode and detonation mode. The term deflagration is understood to refer to flame propagation at variable velocity, depending on the operating conditions. Acetylene can detonate in the liquid or gaseous state even in the absence of air. The detonation of air/acetylene mixtures will be discussed in the chapter “Non-hypergolic Combinations with Oxygen” in a future volume to be published as a part of the *Encyclopedia of Rocket Propellants*. In acetylene, the formation of a detonation wave and energy release are due to the condensation of supersaturated carbon vapor rather than exothermic oxidation reactions, in contrast to most other gas detonation processes. The detonability of acetylene increases sharply with pressure. Acetylene compressed to pressures above 60 atm combusts spontaneously.

##### 4.1.4.1 Detonation of Liquid Acetylene

The detonability of liquid acetylene severely limits the use of acetylene as a fuel gas and feedstock for chemical syntheses because it cannot be stored safely in the liquid state. See Section 4.1.7.3.

##### 4.1.4.2 Detonation of Gaseous Acetylene

Older sources reported that the lower pressure detonation and combustion limits of gaseous acetylene were considerably above 1 atm, and that the upper detonation limit of acetylene/oxygen mixtures at 1 atm was 92 vol.-% acetylene. It was later shown that stable detonations can occur at much lower pressures and at much higher acetylene concentrations. It was found that, depending upon the diameter of the detonation tube, 1–3 g of high explosive such as tetryl will initiate a stable detonation wave in acetylene at an initial pressure as low as 80 kPa (60 cm Hg) [37].

The observed velocity of detonation in acetylene gas initially at 8 atm was found to be  $1817 \pm 7$  m/s in a 12-mm (0.5-in.) diameter pipe and  $1870 \pm 22$  m/s in a 25-mm (1.0-in.) diameter pipe [38]. These results led to an estimate of 1923 m/s for the limiting velocity at infinite diameter. A theoretical value of 2053 m/s was calculated from the Chapman–Jouget theory of detonation. The properties of detonation waves in compressed acetylene were therefore found to be substantially in accord with theory, although there was a discrepancy of 130 m/s between the measured and calculated velocity. Possible reasons for this discrepancy were discussed.

Experiments in small-diameter tubes under pressure indicated an inverse relationship between tube diameter and the critical pressure of detonation wave propagation in gaseous acetylene [39]. With tubes 3 and 8 mm in diameter, the critical pressures were 22.5 and 16 atm, respectively. Exceeding these critical pressures by 1 atm would lead to detonation propagation in acetylene in 50% of cases; exceeding them by 4 atm would lead to propagation in 90% of the tests.

In a study of the mechanism of the explosive decomposition of acetylene it was found that the particle size of the carbon formed by the explosive decomposition of



acetylene in tubes at pressures above atmospheric pressure increased as the propagation rate of the flame front increased [40]. This was explained by heat losses through emission from the front. A study relating the acetylene decomposition temperature to the particle size of the carbon formed used an injection method where a portion of acetylene was introduced into a previously heated evacuated volume, and the gaseous and solid products were examined after decomposition.

In many cases, the process of acetylene decomposition is accompanied by superhigh pressures that are 300–400 times higher than the initial pressure of the gas. An experimental investigation of transient flame modes of acetylene decomposition was conducted to explain the superhigh pressures and to list conditions for DDT transient regimes [41]. The experiments were performed in rectangular tubes with cross-sections of  $219 \times 8.5$ ,  $120 \times 10$ , and  $75 \times 13$  mm and lengths of 124, 36, and 32.6 m, respectively. Explosive acetylene decomposition was initiated at the tube end by heating a Nichrome wire. The reaction zone traversed the last third of the tube with a velocity of 250–333 m/s. In sufficiently long tubes this process transitions to detonation.

The detonation of acetylene is sustained by the energy derived from the condensation of carbon. The formation of a condensation detonation wave has been experimentally observed in the shock-induced thermal decomposition of acetylene. A stable detonation wave in a 20%  $C_2H_2$ /80% Ar mixture was obtained at an initial pressure behind the shock wave of no less than 30 atm [42]. The main kinetic characteristics of the pyrolysis of acetylene – the period of the induction of condensation and the growth rate constant of condensed particles – have been determined. Condensation stages characterized by significant heat release occur very rapidly (faster than  $10^{-5}$  s) in so-called explosive condensation. An analysis of the results indicated that the reactions leading to the growth of large polyhydrocarbon molecules, which precede the formation of condensed carbon particles, constitute the limiting stage of the process that determines the possibility of the formation of the condensation detonation wave in acetylene. An increase in pressure was accompanied by a sharp narrowing of the induction region and a transition of the process to the condensation detonation wave.

The initiation energy required to initiate acetylene explosive decay is dependent on the amount of water vapor present. Hydrogen peroxide vapor has a similar effect [43]. In an analysis of kinetic data using theoretical concepts regarding the dominant role of chain processes in gas combustion, it was concluded that water vapor and hydrogen peroxide vapor can have a promoting effect on the explosive decomposition of acetylene. This prediction contradicted earlier conclusions that were based on the thermal theory of combustion, which stated that water can only exert a diluting effect on acetylene decomposition. More recent experiments confirmed that it is possible to initiate acetylene decomposition in the presence of water vapor or hydrogen peroxide at an ignition energy 100 times lower than that of the explosive decomposition of dry acetylene at atmospheric pressure. Other data in the literature indicated that acetylene explosiveness is largely determined by humidity.

#### 4.1.5 Speed of Acetylene Decomposition Flames

The burning velocity of acetylene decomposition flames increased markedly with pressure in the range 202–1013 kPa (2–10 atm) [44]. Neither the straightforward burning velocity vs pressure plot nor the corresponding log-log plot gave a tolerably straight line, so there appears to be no simple analytical expression relating burning velocity and pressure for this flame. The burning velocity data for acetylene and methylacetylene are summarized in Table 8. The quenching diameter of the acetylene flame at 205 kPa (2.02 atm) was approximately 0.6 cm. The measured brightness temperature of the acetylene decomposition flame at 10 atm was 2140 or 3160 K assuming that no energy is lost as radiation.

**Table 8:** Burning velocities of acetylene and methylacetylene decomposition flames.

| Fuel                   | Acetylene |      |      |      |      | Methylacetylene |      |      |
|------------------------|-----------|------|------|------|------|-----------------|------|------|
| Pressure, atm abs.     | 2.02      | 4.06 | 6.10 | 8.14 | 10.2 | 10              | 20   | 40   |
| Tube diam., cm         | 2.12      | 1.04 | 0.67 | 0.55 | 0.36 | 1.4             | 0.7  | 0.3  |
| Area flame/area tube   | 5.14      | 2.83 | 2.50 | 2.0  | 2.0  | 7.4             | 5.8  | 4.9  |
| Linear speed, cm/s     | 14.7      | 15.8 | 16.2 | 15.9 | 17.1 | 15.0            | 12.5 | 10.9 |
| Burning velocity, cm/s | 2.8       | 5.6  | 6.5  | 7.9  | 8.5  | 2.0             | 2.1  | 2.2  |

Data source: [44]

A method of stabilizing a pure acetylene decomposition flame on a burner over a range of temperatures and pressures has been developed [45]. Its safety depends on the use of a specialized flow and compressor system. The variation of the burning velocity with temperature and pressure was determined not only for acetylene but also for a series of air/hydrocarbon mixtures in order to test both the apparatus and the method of interpretation. The tasks were: (1) to develop a flow system that terminates in a burner, will meter and deliver acetylene safely at a range of pressures and temperatures over which the gas can decompose spontaneously, and prevents flashback; (2) to develop a burner on which an acetylene decomposition flame can be stabilized in a form suitable for accurate burning velocity measurements at a range of pressures and temperatures; and (3) to determine burning velocities at various temperatures and pressures for several air/hydrocarbon mixtures and then for acetylene by itself. An analysis of the acetylene decomposition results yielded effective orders and activation energies that differed substantially from those of low-temperature pyrolysis as well as shock-tube studies. A proposed reaction mechanism, which is likely to be dominant only in the presence of flames and the absence of soot deposits, accounts for these differences as well as for the numerical values obtained. In the presence of soot, an alternative heterogeneous surface reaction is likely to become important. Based on the dependence of burning velocity on the inlet gas temperature, with decomposition at pressures be-

tween 2.5 and 3.3 atm and burning velocities of between 7.3 and 16.6 cm/s, an activation energy of 90.4 kJ/mol (21.6 kcal/mol) was proposed for a first-order reaction.

Acetylene decomposition flame propagation was numerically analyzed and was found to be the result of a condensation reaction. Condensation processes provide reaction heat and act as a driving force for  $C_2H_2$  flame propagation. Some kinetic models can predict the burning velocity of the acetylene decomposition flame, but the model did not demonstrate the relatively strong positive pressure dependence of burning velocity observed experimentally [46]. Heat-release kinetics indicated a two-stage process. The first stage corresponds to heat release due to the formation of benzene and other polyaromatics, and the second stage of heat release corresponds to soot inception and carbonization processes. It was demonstrated that the burning velocity is sensitive to the surface growth rate constant. The use of a simplified presentation of the surface growth process explained the positive thermal feedback in the heat generation in the flame reaction zone.

#### **4.1.5.1 Speed of Acetylene Combustion Flames**

Flame speeds and critical diameters for the propagation of acetylene combustion flames in air or oxygen will be discussed in more detail in a future chapter “Non-hypergolic Combinations with Oxygen.” Often these flames are characterized using the same type of equipment used for acetylene decomposition flames.

#### **4.1.6 Handling of Acetylene**

Chemical reactions involving acetylene under pressure are extremely dangerous and must be carried out with all necessary safety precautions. A system has been designed for experiments with liquid acetylene under pressure [47].

#### **4.1.7 Safety Properties of Acetylene**

##### **4.1.7.1 Flammability Limits of Acetylene in Air**

The flammable range of acetylene in air is 2.5–100 vol.-%. The autoignition temperature is 578 K (305 °C).

##### **4.1.7.2 Ignition Energy for Acetylene Decomposition**

The critical pressure for the decomposition of acetylene initiated by a melting platinum wire at 288 K (15 °C) was reported as 1.4 bar. Later, when an initiation energy of 1200 J was used instead of 1 J, the critical pressure dropped to 0.65 bar from 1.6 bar. A more powerful chemical igniter that provided 2400 J was able to initiate the propagation of acetylene decomposition at pressures as low as 0.54 bar [48].

##### **4.1.7.3 Detonability of Acetylene**

Accidental detonation of acetylene has been the cause of numerous industrial accidents.

A plan to load supercritical acetylene into a sounding rocket and release it into the stratosphere to study the chemiluminescence of the reaction between acetylene and atomic oxygen was proposed. To assess the feasibility of loading supercritical acetylene into a large tank and releasing it at high rates, samples of supercritical acetylene with densities in the range from 0.208 to 0.256 g/cm<sup>3</sup> (13–16 lb/cu.ft) were subjected to high temperature, explosive shock, mechanical shock, ignition by flame, and rapid venting operations [49]. The results of these tests showed that supercritical acetylene presents no more of an explosive hazard than TNT and that sounding rocket experiments could be made with supercritical acetylene loaded into a payload tank.

#### 4.1.8 Acetylene Fuel Mixtures

Acetylene/ethane mixtures with only a few percent oxygen have been patented as gun propellants [50]. The main fraction of the energy released is derived from the decomposition of acetylene, with the oxygen only aiding in the ignition.

Alkylhydrazines are good solvents for acetylene when acetylene needs to be removed from a gas stream [51].

In 2012 it was reported that the Russian rocket engine manufacturer Energomash had started the development of a new rocket engine that could vastly reduce the cost of rocket launches and avoid the need to produce cryogenic hydrogen for fuel. Instead, the rocket was described as using “a completely novel fuel mixture of acetylene and ammonia (*atsetam*).” The properties of acetylene/ammonia mixtures are described in detail in the chapter “Ammonia” in *Encyclopedia of Liquid Fuels*.

Ammonia and acetylene are miscible over the entire range of compositions. Ammonia is a protophilic compound of average basicity, while acetylene is a proton-donating compound with weakly acidic character. The hydrogen that forms the hydrogen bond between the two molecules comes from the acetylene and not from the ammonia, and extends from the acetylene molecule to the free electron pair on the nitrogen atom. Spectral analysis revealed that acetylene binds to ammonia through a weak hydrogen bond (C—H...N) to form a C<sub>3v</sub>-symmetric top, consistent with previous microwave and IR spectroscopic studies at 3 μm. The acetylene/ammonia system shows small negative deviations from Raoult’s law. Such deviations, as foreseen, increase as the temperature decreases and must be ascribed to both chemical and physical ammonia–acetylene interactions.

##### 4.1.8.1 Physical Properties of Acetylene Mixtures

The objective when developing acetylene/fuel mixtures is to find a mixture that is less detonable than acetylene by itself but still benefits from the high energy contributed by the C≡C triple bond. Ideally, the added fuel should be rich in hydrogen such that acetylene raises the heat of combustion and the added fuel lowers the mean molecular weight of the exhaust products, resulting in a better specific impulse of the mixture.

Prior to considering them as rocket fuels, ammonia/acetylene mixtures were used as solvents for acetylene in organic synthesis reactions where the use of undiluted acetylene might constitute an explosion hazard [47]. Vapor–liquid equilibrium data on the acetylene/ammonia system for seven isotherms in the range 213–298 K (–60 to +25 °C) and at 1–32 atm were measured and interpreted according to the thermodynamics of associated systems. It was shown that thermodynamic consistency could be achieved by assuming the formation of a bimolecular complex between acetylene and ammonia. Equilibrium constants for this complex in the liquid phase were derived and related to the corresponding gas-phase values known from the literature.

Ammonia/acetylene fuel mixtures had been burned with oxygen in the laboratory, but no rocket engine tests were documented prior to the Russian studies. The theoretical rocket performance of LOX/NH<sub>3</sub>-C<sub>2</sub>H<sub>2</sub> combinations was calculated [52]. We are looking forward to reading reports that this propellant combination has actually flown.

Acetylene is very soluble in *N*-methylpyrrole and similar *N*-alkylpyrroles, and such solutions could be used as rocket fuels [53]. The Bunsen coefficient (the volume of gas at 101 kPa and 273 K per volume of solvent) of acetylene in *N*-methylpyrrole is 7.3. In the petroleum industry, *N*-methylpyrrole can be used to selectively wash acetylene from a product gas mixture. Such solutions would be hypergolic rocket fuels with WFNA or RFNA used as the oxidizer.

## 4.2 Methylacetylene

One of the better-characterized alkynes is methylacetylene (propyne, H<sub>3</sub>C–C≡CH, C<sub>3</sub>H<sub>4</sub>, CAS RN [74-99-7]). In the liquid state, it is not quite as sensitive as liquid acetylene. In either case, one must avoid the formation of metal acetylides.

It has been stated that although methylacetylene has a high monopropellant specific impulse and a high fuel specific impulse, it suffers from the disadvantages of having a high vapor pressure and a low density. One way of overcoming these difficulties would involve blending methylacetylene with other high-energy compounds that have low vapor pressures. The vapor pressures of a number of blends were calculated according to Raoult's law, and the monopropellant specific impulses were calculated for blends that have vapor pressures of 413 kPa (60 psia) at 311 K (100 °F).

### 4.2.1 Production of Methylacetylene

Methylacetylene and certain diolefins, such as allene, can be made by the thermal cracking of branched chain monoolefins, in particular isobutylene [54, 55]. Isobutane mixtures containing steam are heated for 0.05–0.5 s at 1073–1173 K (800–900 °C) and about 101 kPa (1 atm) of pressure, then cooled rapidly to give allene and methylacetylene. Yields are highest at limited (e.g., 28%) conversions.

Hydrocarbons of the acetylene and cyclopropane families, by virtue of their extra energy, yield fuels that have higher specific impulses and increased reactivity (resulting in smoother combustion in engines) than conventional rocket or aviation fuels. Possible methods of producing such fuels were reviewed, and several commercial processes were described [56]. One fuel of interest was 2-methyl-1,5-hexadiene-3-yne [57].

A mixture of 30% 2,7-dimethyl-1,7-octadiene-3,5-diyne in 2-methyl-1-butene-3-yne has good ignition properties, low thermal and shock sensitivities, and a low freezing point ( $<233\text{ K} = <-40^\circ\text{F}$ ) [58].

Allene can be isomerized to methylacetylene at  $425\text{--}683\text{ K}$  ( $150\text{--}410^\circ\text{C}$ ) in the presence of alumina. Allene is passed over  $\text{Al}_2\text{O}_3$  at  $483\text{ K}$  ( $210^\circ\text{C}$ ) at a space velocity of  $825\text{ h}^{-1}$  to make methylacetylene [59]. Allene and methylacetylene can be made by the catalytic conversion of isobutylene and propylene [60].

#### 4.2.2 Physical Properties of Methylacetylene

The physical properties of methylacetylene are summarized in Table 9.

**Table 9:** Physical properties of methylacetylene.

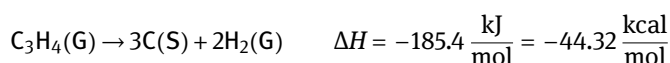
| Property                                   | SI units                                   | Other units                                     | References |
|--------------------------------------------|--------------------------------------------|-------------------------------------------------|------------|
| Molecular mass                             | 40.0639                                    | 24.9601 mol/kg                                  | [1]        |
| Freezing point                             | $170.2 \pm 0.6\text{ K}$                   | $-102.9^\circ\text{C}$                          |            |
| Boiling point                              | $250.0 \pm 0.5\text{ K}$                   | $-23^\circ\text{C}$                             |            |
| Density                                    | $0.6711\text{ g/cm}^3$ at $248.9\text{ K}$ | $0.6711\text{ g/cm}^3$ at $-24.2^\circ\text{C}$ | [29]       |
| Vapor pressure                             | 507 kPa at $293\text{ K}$                  | 5 atm at $20^\circ\text{C}$                     |            |
| Enthalpy of formation, gas                 | $+185.4 \pm 0.88\text{ kJ/mol}$            | $+44.3 \pm 0.2\text{ kcal/mol}$                 | [1]        |
| Enthalpy of formation, liquid              | $+162.4\text{ kJ/mol}$ (calc.)             | $+38.8\text{ kcal/mol}$                         |            |
| Enthalpy of vaporization at $242\text{ K}$ | $23.0\text{ kJ/mol}$                       | $5.50\text{ kcal/mol}$                          |            |
| Critical temperature                       | $402.4 \pm 0.2\text{ K}$                   | $129.3 \pm 0.2^\circ\text{C}$                   | [1]        |
| Critical pressure                          | $56.3 \pm 0.2\text{ bar}$                  | $817 \pm 3\text{ psia}$                         |            |
| Critical volume                            | $0.1635\text{ L/mol}$                      | —                                               |            |

#### 4.2.3 Chemical Properties of Methylacetylene

##### 4.2.3.1 Thermal Decomposition of Methylacetylene

Methylacetylene may self-decompose under certain conditions. Methylacetylene has been investigated as a monopropellant, but has never found application as such [61] (see the chapter “Organic Monopropellants” in *Encyclopedia of Monopropellants*).

Theoretically, the decomposition reaction proceeds as the reverse of the formation of methylacetylene from the elements:



Under real-life conditions, the decomposition products contain ethylene, methane, and a little ethane.

#### 4.2.3.2 Burning Velocity of Methylacetylene Decomposition Flames

The burning velocity of methylacetylene decomposition flames is listed in Table 8 above. The burning velocity of the methylacetylene flame varies little, if at all, in the range 1–4 MPa (10–40 atm) [44]. The quenching diameter of the methylacetylene decomposition flame at 1 MPa (10 atm) is less than 0.3 cm.

#### 4.2.4 Safety Properties of Methylacetylene

The lower limit of methylacetylene combustion in air with upward propagation is 1.7 vol.-%. This is an extremely low lower limit. The upper limit is 100%. Methylacetylene will burn in the absence of air, which is why it is considered a monopropellant.

##### 4.2.4.1 Toxicity of Methylacetylene

Rats were exposed to average concentrations of 42000 ppm methylacetylene for 6 h in an acute toxicity test, and rats and dogs were exposed to 28700 ppm 6 hours a day, 5 days a week for 6 months in chronic tests [62]. Exposure to the acute concentration resulted in almost complete anesthesia in all the animals within 95 min. The majority of the animals had recovered completely 40 min after the cessation of exposure. Exposure to the chronic concentration caused the dogs to lose weight during the first 6 weeks of exposure, after which they regained their initial weight. Both levels of exposure produced ataxia, mydriasis, salivation, and anesthesia, and it was noted that the response to exposure became less severe in dogs. With rats, the most significant sign of toxicity was death, which occurred in 8 out of 20 animals.

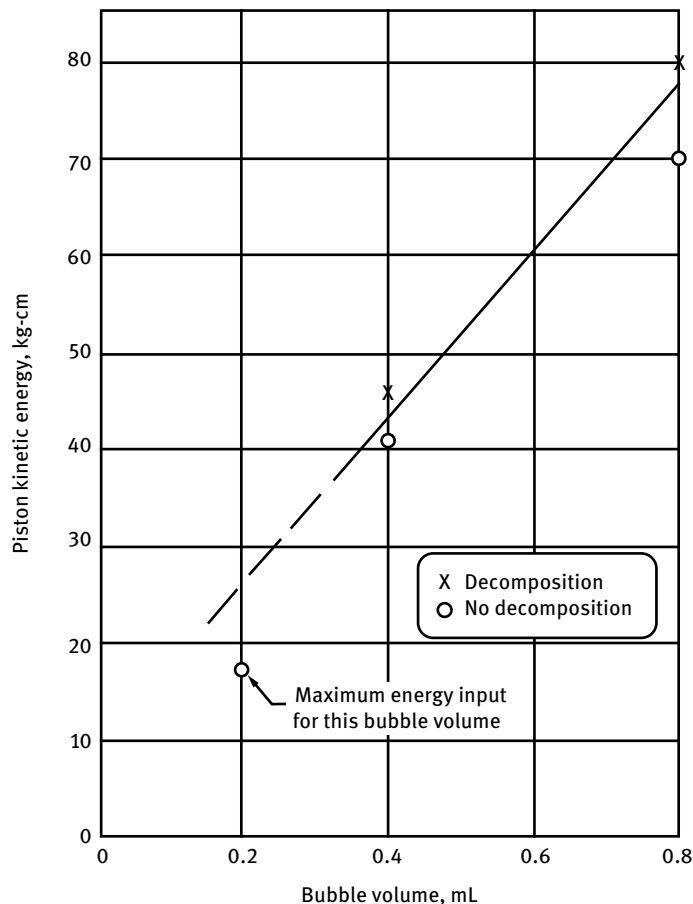
In Europe, the MAK of 1000 ppm was based on an earlier TLV of 1000 ppm, but this was later repealed [63].

##### 4.2.4.2 Explosive Hazards of Methylacetylene

Undiluted liquid methylacetylene is shock sensitive and will explode if heated rapidly [64]. Construction materials that come into contact with methylacetylene must not contain any copper.

The adiabatic compression sensitivities of several monopropellants, including methylacetylene, were tested in a rapid compression test apparatus where a gas bubble in contact with the propellant was compressed rapidly by a gas-driven piston [65]. The mass and velocity of the piston were analogous to the mass and velocity of a slug of liquid propellant flowing in a propellant feed system against a dead-end pipe. The minimum compressive energy per gas bubble volume required to initiate propellant decomposition was used as the safety criterion. The most sensitive sample tested was a mixture of ethyl nitrate and propyl nitrate ( $4.8 \pm 0.8$  kg-cm/mL). Methylacetylene was made to decompose with bubble volumes of 0.8 and 0.4 mL.

For those tests, the liquid sample was loaded at 233 K ( $-40^{\circ}\text{C}$ ) and fired at 243 K ( $-30^{\circ}\text{C}$ ). Decompositions were indicated by the presence of a compacted carbon pellet in the sample holder. The sensitivity of methylacetylene was only marginal,  $86 \pm 12 \text{ kg}\cdot\text{cm}/\text{mL}$  (Figure 2).



**Figure 2:** Adiabatic compression sensitivity of methylacetylene. (Republished and modified from Figure 12 on page 197 of [65] with permission from the American Institute of Aeronautics and Astronautics; permission was conveyed through Copyright Clearance Center Inc.)

## 4.2.5 Combustion of Methylacetylene

### 4.2.5.1 Flammable Range of Methylacetylene in Air

The lower limit of flammability of methylacetylene in air is 1.7 vol.-% [66]. There is no upper limit because methylacetylene will decompose even in the absence of air or oxygen.



#### 4.2.5.2 Explosive Sensitivity of Methylacetylene

The adiabatic compression sensitivity of methylacetylene was tested in an adiabatic compression sensitivity tester developed by Aerojet and compared to those of *n*-propyl nitrate, nitromethane, and a mixture of 60% ethyl nitrate/40% propyl nitrate [65]. The apparatus consisted of a pneumatically driven piston that rapidly compressed a gas bubble above a liquid propellant sample. In a few cases, the apparatus was also inverted, pushing the liquid upward into the gas (vapor) bubble. The sensitivity was expressed in terms of the piston kinetic energy divided by the size of the gas bubble, which is the slope of a straight line separating the go from the no-go areas in an *x-y* chart. The results are summarized in Table 10. In this series of tests, methylacetylene was the least sensitive chemical, so it required the highest compression energy to initiate an explosion.

**Table 10:** Adiabatic compression sensitivity of methylacetylene in comparison to those of other monopropellants.

| Compound                                        | Adiabatic compression sensitivity, $\text{kg cm mL}^{-1}$ |
|-------------------------------------------------|-----------------------------------------------------------|
| Methylacetylene                                 | $86 \pm 12$                                               |
| Mixture of 60% ethyl nitrate/40% propyl nitrate | $4.0 \pm 0.8$                                             |
| <i>n</i> -Propyl nitrate                        | $6.7 \pm 1.2$                                             |
| Nitromethane                                    | $10.4 \pm 1.7$                                            |

Data source: [65]

In a series of detonability tests in heavy-walled confined tubes with unsymmetrical dimethylhydrazine (UDMH), nitromethane, ethylene oxide, and methylacetylene, only nitromethane detonated completely [67].

#### 4.2.6 Applications of Methylacetylene

Methylacetylene had been evaluated as a fuel for a helicopter with blades propelled by tip-mounted ramjets [68–70].

Range calculations were made for a long-range air-breathing missile that employed a ram rocket as the power plant [71]. The ram rocket power plant was adapted to the structure of the TRITON missile, a ramjet with a range of 2000 miles and a baseline design that used JP-1 as a fuel. Methylacetylene was used to illustrate potential fuel improvements. The results of the investigation indicated that the ram rocket could achieve the same range as the rocket-boosted ramjet with a lower total take-off weight.

#### 4.2.7 Properties of Methylacetylene Mixtures

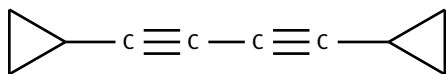
Methylacetylene/propane/propadiene (MAPP) gas is a stabilized mixture of methylacetylene and propadiene. Alkane and alkene hydrocarbons are added as stabilizers. The stabilizers serve to render the methylacetylene and propadiene shock insensitive and ensure that their concentrations remain nearly uniform at all times during the vaporization of the mixture. MAPP gas is transported and stored as a liquid under its own vapor pressure. Its transportation, storage, and handling characteristics are the same as those of liquefied petroleum gas. It has a characteristic odor that is detectable at concentrations as low as 100 ppm in air. Stabilized liquefied MAPP liquid and MAPP gas vapor are insensitive to shock [72].

Rats, guinea pigs, rabbits, and dogs were exposed 7 h per day, 5 days per week for a period of 16 weeks to either 5000 or 1000 ppm of a mixture of saturated and unsaturated C3 and C4 hydrocarbons (MAPP Industrial Gas<sup>®</sup>) [73]. There were no adverse effects on either sex of any species exposed to 1000 ppm, as determined by growth, mortality, body and organ weights, clinical and biochemical determinations, urinalysis, hematological examination, and gross and microscopic pathological examination. Results of a limited sensory perception study of humans indicated that some persons could detect 25 ppm and most would detect 100 ppm. The odor was found to be strong at 1000 ppm and quite objectionable at higher concentrations.

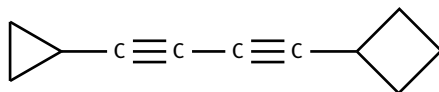
The flammable limits of MAPP gas in air are 2 and 13 vol.-%. MAPP/air mixtures have been evaluated as fuel/air explosives.

#### 4.3 Diacetylenes

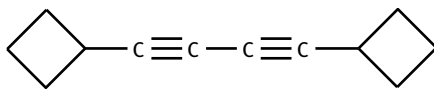
Several dialkylbutane-1,3-diyne fuels have been patented and are considered to be hypergolic with IRFNA [74]. Examples of this type of fuel are shown below:



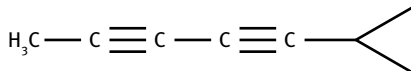
1,4-Dicyclopropyl-1,3-butadiyne, 4-Cyclopropylbuta-1,3-diynylcyclopropane



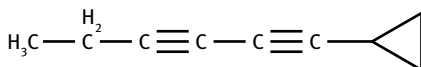
1-Cyclobutyl-4-cyclopropyl-1,3-butadiyne, 4-cyclopropylbuta-1,3-diynylcyclobutane



1,4-Dicyclobutyl-1,3-butadiyne, 4-cyclobutylbuta-1,3-diynylcyclobutane



1-Methyl-4-cyclopropyl-1,3-butadiyne, 1-Cyclopropylpenta-1,3-diyne, Penta-1,3-diynylcyclopropane



1-Ethyl-4-cyclopropyl-1,3-butadiyne, Hexa-1,3-diynylcyclopropane

The compound shown first is 1,4-dicyclopentyl-1,3-butadiyne (CAS RN [114546-62-2], empirical formula  $C_{10}H_{10}$ , formula weight 130.19 g/mol).

Compounds that contain several acetylene linkages in the molecule are called oligoalkadiynes. Macrocyclic oligoalkadiynes have been synthesized [75]. Apart from strong electronic interactions, spirocyclopropanated macrocyclic oligodiacetylenes are also highly energetic compounds. When struck too powerfully with a spatula, the samples decompose immediately, forming a cloud of black soot.

#### 4.4 1,7-Octadiyne

Octadiyne ( $C_8H_{10}$ , CAS RN [871-84-1]) has been tested with LOX as the oxidizer in a side-by-side comparison with RP-1 in a 220-N (50-lbf) rocket engine [76]. Its density is 1.8% less than that of RP-1, and its specific impulse is 3% better than RP-1.

##### 4.4.1 Physical Properties of 1,7-Octadiyne

The boiling point of 1,7-octadiyne at atmospheric pressure is 408–409 K (135–136 °C). The density at 294 K is 0.817 g/cm<sup>3</sup>. The flash point is at 296 K (23 °C). The index of refraction  $n_D^{20}$  is 1.4464. The standard enthalpy of formation is +334 kJ/mol (+79.9 kcal/mol). The heat of combustion is 44.85 MJ/kg (19297 BTU/lb).

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# Alkylboranes

## Introduction

Alkylboranes share many properties, such as pyrophoricity, with their parent compounds, the inorganic boranes described in *Encyclopedia of Liquid Fuels* chapter “Boranes.” Their parent element, boron, is described in chapter “Boron.” Alkylboranes, boranes and elemental boron all share the common disadvantage of diboron trioxide deposition in the combustion products, possibly leading to clogged orifices and nozzle throats.

## 1 Alkylboranes

Alkylboranes, also called boron alkyls, are compounds where the alkyl groups are directly bound to the central boron atom by way of a C–B bond [1–3]. Alkylpentaboranes and alkyldecaboranes were manufactured on a large scale in the past but are no longer in use. Similar to the chapter on fluorine compounds as rocket propellants, this chapter on alkylboranes is now mostly of historical interest. A detailed write-up in book format of the US borane effort covering the years from 1950 to 1965 is the most comprehensive summary ever published on this exciting period of borane fuel development [4]. A subsequent anecdotal and historical account of the US borane program written by an experienced insider makes very entertaining reading [5]. We wish that there were similar easy-to-read books on the history of some of the other rocket propellants, such as the early years of hydrazines and hydrogen peroxide.

Hydrogen atoms in diborane can be gradually replaced by alkyl groups to form alkylidiboranes. After replacing more than four of the hydrogen atoms in diborane by alkyl groups, there are not sufficient hydrogen atoms to maintain the hydrogen bridge between the two boron atoms, and the molecule splits into fragments that contain only one boron atom per molecule. These are called alkylboranes instead of alkylidiboranes.

Alkylboranes and alkyl aluminum compounds will probably not be used as main rocket propellants, but they have been used as ignition aids for the hypergolic slug ignition of bipropellant rocket engines with non-hypergolic oxidizers such as LOX. They have also been evaluated as fuels in air-breathing ramjets or afterburners.

The different types of alkylboranes where R is an alkyl group (most often an ethyl group that can be attached by reacting boranes with ethylene) are listed below:

|                                |                                                  |
|--------------------------------|--------------------------------------------------|
| Alkylboranes (boron trialkyls) | $\text{BR}_3$                                    |
| Alkylidiboranes                | $\text{B}_2\text{H}_{(6-n)}\text{R}_n \ (n < 4)$ |
| Alkylpentaboranes              | $\text{B}_5\text{H}_{(9-n)}\text{R}_n$           |
| Alkyldecaboranes               | $\text{B}_{10}\text{H}_{(14-n)}\text{R}_n$       |

In 1952, the United States started a major effort to develop *high-energy fuels* (HEF) or *exotic fuels* as replacements for common kerosene jet fuels under the code name ZIP. These compounds were intended to have much higher heats of combustion and could burn at lower pressures, thus giving airplanes greater ranges and allowing them to fly at higher altitudes (out of reach of the enemy's interceptor fighter jet planes at that time) [6, 7].

These fuels were prepared by the alkylation of diborane with subsequent pyrolysis, or by the pyrolysis of diborane to pentaborane(9) and decaborane(14) with subsequent alkylation of these products. A whole family of alkylborane fuels was investigated that were generally referred to by code names assigned by the Air Force: HEF-1 (ethylidiborane), HEF-2 (propylpentaborane), HEF-3 (ethyldecaborane), HEF-4 (methyldecaborane), and HEF-5 (ethylacetylenedecaborane). The HEF fuel that was produced in the largest quantities was HEF-3. Another family of boron fuels were known as Hi-Cal fuels. The Air Force's program was largely devoted to HEF-3. The B-70 (XB-70) design originally used the J93-GE-5 engine with HEF-3 in the afterburners fed from separate fuel tanks. The General Electric J93 jet engine used on the B-70 and F-108 was designed to use HEF-3 in its afterburner section only. This avoided some of the main problems with HEF. By burning it only in the afterburners, the problem with oxide slag buildup on the turbine blades was eliminated, and since the afterburners were only used for takeoff and high-speed flight, the problems with the exhaust were greatly reduced. However, this meant that the advantages of using HEF-3 were also greatly reduced as it was used only part of the time instead of all the time. By using it for only one portion of the engine, and only during certain portions of the flight regime, the range was only extended by about 10%. There were also studies on the use of HEF-3 in the BOMARC ramjets, as well as studies into its use by the US Navy's aircraft carrier fleet to power high-performance aircraft, but these programs all died out and were discontinued. In the end, the problems with burning HEF throughout the entire turbojet engine turned out to be impossible to solve. At best, the HEF fuels could be used in the afterburner. Removing the oxide buildup on the turbine blades and housing was difficult. These issues, combined with the high cost of producing the fuel and its toxicity issues, seriously hampered the competitiveness of HEF-ZIP fuel. In 1959, the Air Force eventually canceled the boron fuel program altogether, after which it found only small-scale use as a rocket fuel. These fuels never saw flight applications. The expensive boron fuel production plants were first mothballed and eventually dismantled without ever having operated at full capacity [8, 9].

## 2 Trialkylboranes

The most frequently used term for  $\text{BR}_3$  compounds is trialkylboranes. Occasionally they are also called boron trialkyls or trialkylboron compounds. The name trialkylboron could be used in analogy to trialkylaluminum. Very rarely, the term trialkyl-

alane is used for those aluminum compounds. Also, in the antiquated literature, one might also find the use of the term trialkylborine.

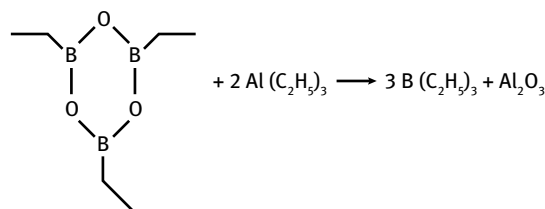
Boron is trivalent in all of its organic compounds. Trialkylborane compounds with small alkyl groups are pyrophoric in air and can be used as ignition fluids with LOX and other non-hypergolic combinations. They have not been used as the main rocket fuel.

Trimethylborane or boron trimethyl,  $(\text{CH}_3)_3\text{B}$ , is a colorless gas at room temperature which ignites spontaneously in air. It has the shortest ignition delay of all trialkylboranes.

Triethylborane or boron triethyl,  $(\text{C}_2\text{H}_5)_3\text{B}$ , is a colorless liquid at room temperature. It ignites instantly as soon as air comes into contact with the liquid and burns with a beautiful green flame (truly a “green” propellant). Mixtures of triethylborane and triethylaluminum are used as hypergolic slug ignition fluids for rocket engines, with LOX used as the oxidizer. One of the launch vehicles that uses this mode of ignition is the Falcon 9 from Space-X. Triethylborane can be used as the initiator for polymerizations. Triethylborane-induced polymerizations typically involve free radicals.

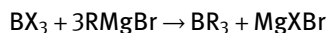
## 2.1 Preparation of Trialkylboranes

Triethylborane, also known as triethyl boron, boron triethyl, or triethylborine,  $(\text{C}_2\text{H}_5)_3\text{B}$ ,  $\text{C}_6\text{H}_{15}\text{B}$ , TEB, CAS RN [97-94-9], can be prepared by the reaction of triethylboroxol with triethylaluminum [10, 11]:



This method avoids the use of halogenides. Triethylboroxol can be made from  $\text{B}_2\text{O}_3$  and triethylborane such that 3 moles of triethylborane are ultimately obtained for each mole of triethylborane used as a starting reactant. This can be used as a step in the production of diborane from boron trioxide, assuming that sufficient triethylaluminum is available.

The traditional method of preparing trialkylboranes is the reaction of boron trihalogenides (as etherates) with Grignard reagents:



Triethylborane, tri-*n*-propylborane, and tri-*n*-butylborane were prepared by the reaction of boron trifluoride etherate with alkyl magnesium bromides [12, 13]. Using this method, triethylborane and tri-*n*-propylborane were obtained at purities of 99.8 and 99.7 mol-%, respectively, but the tri-*n*-butylborane was not pure since it decomposed during distillation. The hydroboration of ethylene gives triethylborane [14].

## 2.2 Physical Properties of Trialkylboranes

The physical properties of triethylborane are compiled in Table 1. The boiling point of triethylborane listed in the NIST Chemistry WebBook [15] and accredited to Kostryukov, Samorukov et al. [16], shown as 321.81 K, is incorrect.

**Table 1:** Physical properties of triethylborane.

|                                                     | SI units                                                               | Other units                                                                    | References           |
|-----------------------------------------------------|------------------------------------------------------------------------|--------------------------------------------------------------------------------|----------------------|
| Molecular mass                                      | 97.994 g/mol<br>= 10.204 mol/kg                                        |                                                                                | [15]                 |
| Freezing point                                      | 178 K<br>180.22 K                                                      | −95 °C<br>−92.93 °C                                                            | [17]<br>[12]         |
| Boiling point                                       | 367–368 K<br>368.1 K<br><del>321.81 K</del>                            | 94 to 95 °C<br>95.0 °C                                                         | [10]<br>[12]         |
| Density (at 25 °C)                                  | 0.678 g/cm <sup>3</sup>                                                | 42.33 lb/ft <sup>3</sup>                                                       | [18]                 |
| Density (at 20 °C)                                  | 0.6850 g/cm <sup>3</sup>                                               | 42.76 lb/ft <sup>3</sup>                                                       | [12]                 |
| Vapor pressure (at 20 °C)                           | 5.68 kPa                                                               | 42.6 mm Hg                                                                     | [18]                 |
| Viscosity (at 20 °C)                                | 0.0003 N s m <sup>−2</sup>                                             | 0.30 cPs                                                                       | [18]                 |
| Surface tension (at 30 °C)                          | 0.01984 N/m                                                            | 19.84 dyn/cm                                                                   | [18]                 |
| Index of refraction ( $n_D^{20}$ )                  | 1.3971<br>1.3971                                                       | —<br>—                                                                         | [18]<br>[12]         |
| Dielectric constant (at 20 °C)                      | 1.974                                                                  | —                                                                              | [12]                 |
| Molar heat capacity (at 25 °C)                      | 237 J mol <sup>−1</sup> K <sup>−1</sup>                                | 56.65 cal mol <sup>−1</sup> °C <sup>−1</sup>                                   | [18]                 |
| Enthalpy of formation ( $\Delta H_f^{298}$ ) liquid | −196 kJ/mol<br>−197.5 ± 15.5 kJ/mol                                    | −46.8 kcal/mol<br>−47.2 ± 3.7 kcal/mol                                         | [18]<br>[19]         |
| Enthalpy of formation ( $\Delta H_f^{298}$ ) vapor  | −159 kJ/mol                                                            | −38.0 kcal/mol                                                                 | [18]                 |
| Upper heat of combustion                            | 46.5 kJ/g<br>40.04 kJ/g<br>4975.6 ± 15.1 kJ/mol<br>= 50.77 ± 0.15 kJ/g | 11.12 kcal/g<br>20670 BTU/lb<br>1189.2 ± 3.6 kcal/mol<br>= 12.13 ± 0.04 kcal/g | [18]<br>[12]<br>[19] |

A similar complete set of physical properties of tri-*n*-propylborane are available in Rosenblum and Allen [12], but they are not included here because this trialkylborane is less likely to be used as a rocket propellant. Its enthalpy of formation is  $-271 \text{ kJ/mol}$  ( $-64.7 \text{ kcal/mol}$ ). The standard enthalpy of formation of liquid trimethylborane (under pressure) is  $-145.6 \text{ kJ/mol}$  ( $-34.8 \text{ kcal/mol}$ ).

The vapor pressure of triethylborane can be calculated from an Antoine equation (shown in the NIST Chemistry WebBook [15] but referenced from very old data):

$$\log p = 2.91408 - [753.261/(T - 112.631)]$$

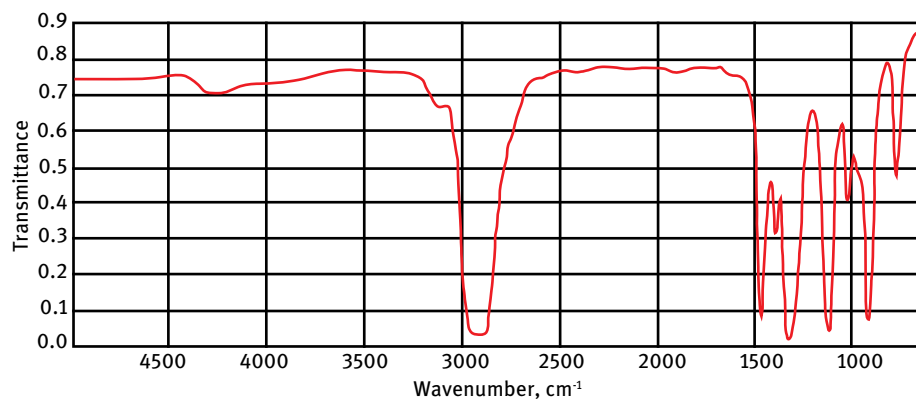
where  $p$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. Another source gave the vapor pressure as

$$\log p = 7.4856 - 1704.1/T$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.

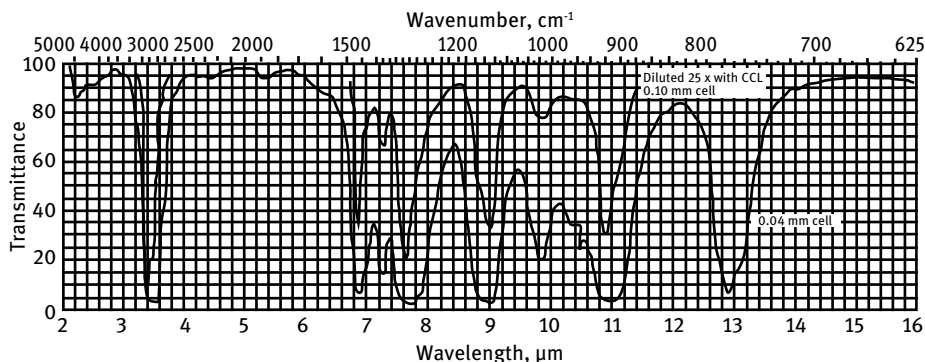
### 2.3 Optical Properties of Alkylboranes

The IR spectrum of triethylborane is shown in Figure 1.



**Figure 1:** IR spectrum of triethylborane. (Reproduced and modified with permission from [20].)

A similar IR spectrum of triethylborane is shown in Figure 2 for two different triethylborane concentrations. Tentative assignments of the observed bands in the IR [21] and Raman spectra [22] of triethylborane were made by comparison with the spectra of trimethylborane and ethane.



**Figure 2:** IR spectrum of triethylborane. (Reproduced and modified from [12])

## 2.4 Thermodynamic Properties of Alkylboranes

The heat of combustion is an important property when evaluating any of these compounds for use as fuels for air-breathing jet engines. It is often difficult to obtain accurate data in a calorimeter because the solid combustion products undergo secondary reactions with condensates while the bomb cools down. In many cases it was necessary to extrapolate the enthalpies of formation from other data. Pertinent literature containing thermodynamic data on alkylboranes are summarized in Table 2.

**Table 2:** Literature on the thermodynamic properties of alkylboranes.

| Author(s)                    | Year | Short title                                                                                                     | References |
|------------------------------|------|-----------------------------------------------------------------------------------------------------------------|------------|
| Waszeciak and McCarthy       | 1953 | <i>Determination of heats of combustion of compounds containing boron</i>                                       | [23]       |
| Joyner, Adams, and Galbraith | 1954 | <i>Methods of estimating heats of combustion</i>                                                                | [24]       |
| Wallenstein and Prosen       | 1954 | <i>Bond energies and heats of formation of some boron compounds</i>                                             | [25]       |
| Wagman et al.                | 1954 | <i>Thermodynamic properties of boron compounds</i>                                                              | [26]       |
| Altshuller                   | 1955 | <i>Calculated heats of formation and combustion of boron compounds</i>                                          | [27]       |
| Bauer                        | 1958 | <i>Energetics of the boranes. V. Prediction of heats of formation. Interconversion of the hydrides of boron</i> | [28]       |

Table 3 is a summary of the literature containing measured thermodynamic data on boranes and alkylboranes. Table 4 provides a summary of theoretically predicted thermodynamic data on alkylboranes.

**Table 3:** Measured thermodynamic data on boranes and alkylboranes.

| Physical state                                             | Liquid                |                 | Vapor     |             |
|------------------------------------------------------------|-----------------------|-----------------|-----------|-------------|
| Compound                                                   | Enthalpy of formation |                 |           |             |
|                                                            | kJ/mol                | kcal/mol        | kJ/mol    | kcal/mol    |
| B <sub>2</sub> H <sub>6</sub>                              | —                     | —               | 32        | 7.53        |
| B <sub>5</sub> H <sub>9</sub>                              | 33                    | 7.8             | 63        | 15          |
| B <sub>10</sub> H <sub>14</sub>                            | 33 (crystalline)      | 8 (crystalline) | 109       | 26          |
| (CH <sub>3</sub> ) <sub>3</sub> B                          | −144 ± 15             | −34.5 ± 3.5     | −123 ± 15 | −29.3 ± 3.5 |
| (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B            | −196 ± 20             | −46.8 ± 4.7     | −159 ± 20 | −38 ± 4.7   |
| (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> B            | −96 ± 33              | −23 ± 8         | −59 ± 33  | −14 ± 8     |
| ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> B | −272                  | −65             | −226      | −54         |
| ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> B | −167 ± 33             | −40 ± 8         | −121 ± 33 | −29 ± 8     |
| ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> B | −351 ± 18             | −83.9 ± 4.2     | −296 ± 18 | −70.8 ± 4.2 |

Data source: [27]

**Table 4:** Summary of thermodynamic data on alkylboranes and boranes.

|                                                                             | Enthalpy of formation ( $\Delta H_f^{298}$ ) |                     |                  |                  | Heat of combustion ( $\Delta H_{\text{comb}}$ )<br>(forming amorphous B <sub>2</sub> O <sub>3</sub> ) |       |         |       |
|-----------------------------------------------------------------------------|----------------------------------------------|---------------------|------------------|------------------|-------------------------------------------------------------------------------------------------------|-------|---------|-------|
|                                                                             | kJ/mol                                       |                     | kcal/mol         |                  | MJ/kg                                                                                                 |       | kcal/kg |       |
|                                                                             | Liquid                                       | Vapor               | Liquid           | Vapor            | Liquid                                                                                                | Vapor | Liquid  | Vapor |
| B(CH <sub>3</sub> ) <sub>3</sub>                                            | -146.4                                       | -121.3              | -35              | -29              | 47.66                                                                                                 | 47.86 | 11780   | 11910 |
| B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>                              | -146.4 <sup>a</sup>                          | -108.8 <sup>a</sup> | -35 <sup>a</sup> | -26 <sup>a</sup> | 46.23                                                                                                 | 46.69 | 11390   | 11440 |
| B( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub>                   | -217.6 <sup>a</sup>                          | -171.5 <sup>a</sup> | -52 <sup>a</sup> | -41 <sup>a</sup> | 45.31                                                                                                 | 45.56 | 11050   | 11160 |
| B( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>                   | -372.4 <sup>a</sup>                          | -318.0 <sup>a</sup> | -89 <sup>a</sup> | -76 <sup>a</sup> | 72.38                                                                                                 | 72.80 | 10830   | 10890 |
| B <sub>2</sub> H <sub>6</sub>                                               | +16.7                                        | +31.4               | +4               | +7.5             | 57.40                                                                                                 | 57.86 | 17300   | 17400 |
| B <sub>2</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>                 | -58.6                                        | -33.5               | -14              | -8               | 52.59                                                                                                 | 52.76 | 13720   | 13830 |
| B <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> | -129.7                                       | -96.2               | -31              | -23              | 49.96                                                                                                 | 50.50 | 12570   | 12610 |
| B <sub>2</sub> H <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> | -200.8                                       | -159.0              | -48              | -38              | 48.58                                                                                                 | 49.04 | 11940   | 12070 |
| B <sub>2</sub> H <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> | -272.0                                       | -221.8              | -65              | -53              | 67.57                                                                                                 | 68.12 | 11610   | 11720 |
| B <sub>5</sub> H <sub>9</sub>                                               | +32.6                                        | +62.8               | +7.8             | +15.0            | 62.76                                                                                                 | 63.22 | 16150   | 16280 |
| B <sub>5</sub> H <sub>8</sub> CH <sub>3</sub>                               | -29.3                                        | +4.2                | -7               | +1               | 59.75                                                                                                 | 60.21 | 15000   | 15110 |
| B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub>                 | -62.8                                        | -25.1               | -15              | -6               | 57.66                                                                                                 | 58.12 | 14280   | 14390 |
| B <sub>5</sub> H <sub>8</sub> C <sub>3</sub> H <sub>7</sub>                 | -79.5                                        | -37.7               | -19              | -9               | 65.56                                                                                                 | 66.19 | 13780   | 13890 |
| B <sub>10</sub> H <sub>14</sub>                                             | -32.6 <sup>b</sup>                           | +108.8              | -8 <sup>b</sup>  | +26              | 63.22                                                                                                 | 63.68 | 15670   | 15820 |
| B <sub>10</sub> H <sub>13</sub> CH <sub>3</sub>                             | -4.2 <sup>c</sup>                            | +50.2               | -1 <sup>c</sup>  | +12              | 61.38                                                                                                 | 61.84 | 15110   | 15220 |
| B <sub>10</sub> H <sub>13</sub> C <sub>2</sub> H <sub>5</sub>               | -37.7 <sup>c</sup>                           | +20.9               | -9 <sup>c</sup>  | +5               | 59.91                                                                                                 | 60.42 | 14670   | 14780 |
| B <sub>10</sub> H <sub>13</sub> C <sub>3</sub> H <sub>7</sub>               | -54.4 <sup>c</sup>                           | -8.4                | -13 <sup>c</sup> | -2               | 49.29                                                                                                 | 49.83 | 14320   | 14440 |

<sup>a</sup> Experimental data<sup>b</sup> Two different experimental data reported<sup>c</sup> Average data

Data source: [27]



An empirical formula for estimating the heat of vaporization of alkylboranes has been derived:

$$(\Delta H)_{\text{evap.}} = 2 + \Sigma(\text{B,C})$$

where  $\Sigma(\text{B,C})$  is the sum of the boron and carbon atoms in the molecule and  $(\Delta H)_{\text{evap.}}$  is the heat of vaporization in kcal/mol. Table 5 gives a comparison of values extrapolated using the above formula with experimentally determined heats of evaporation of boron compounds.

**Table 5:** Comparison of extrapolated and measured heats of evaporation of boron compounds.

| Gross formula                                  | Extrapolated |          | Measured |          |
|------------------------------------------------|--------------|----------|----------|----------|
|                                                | kJ/mol       | kcal/mol | kJ/mol   | kcal/mol |
| B <sub>2</sub> H <sub>6</sub>                  | 17           | 4        | 14.4     | 3.45     |
| B <sub>4</sub> H <sub>10</sub>                 | 25           | 6        | 27.1     | 6.47     |
| B <sub>5</sub> H <sub>11</sub>                 | 29           | 7        | 30.1     | 7.2      |
| B <sub>10</sub> H <sub>14</sub>                | 50           | 12       | 50.8     | 12.13    |
| B(CH <sub>3</sub> ) <sub>3</sub>               | 25           | 6        | 0.8      | 0.2      |
| B(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> | 38           | 9        | 36.8     | 8.8      |

Data source: [27]

The heats of combustion of trimethylborane (liquid), triethylborane (liquid), and tri-*n*-butylborane (liquid) to form crystalline boric acid, liquid water, and gaseous carbon dioxide were found to be  $2989.4 \pm 22.4$  kJ/mol ( $714.48 \pm 5.36$  kcal/mol),  $4975.6 \pm 15.1$  kJ/mol ( $1189.2 \pm 3.6$  kcal/mol), and  $8901.0 \pm 10.2$  kJ/mol ( $2127.4 \pm 2.4$  kcal/mol), respectively [19]. These data were used along with the heats of formation of boric acid, carbon dioxide, and water to calculate the standard enthalpies of formation of liquid trimethylborane, triethylborane, and tri-*n*-butylborane:  $-145.6 \pm 22.6$ ,  $-197.5 \pm 15.5$ , and  $-348.1 \pm 10.5$  kJ/mol at 298 K, respectively ( $-34.79 \pm 5.40$ ,  $-47.2 \pm 3.7$  and  $-83.2 \pm 2.5$  kcal/mol at 25°C, respectively). See also [16, 29–32].

## 2.5 Molecular Structure of Triethylborane

The molecule of triethylborane is very symmetrical (Figure 3). There is free rotation around the C–C axis in the pendant ethyl groups.

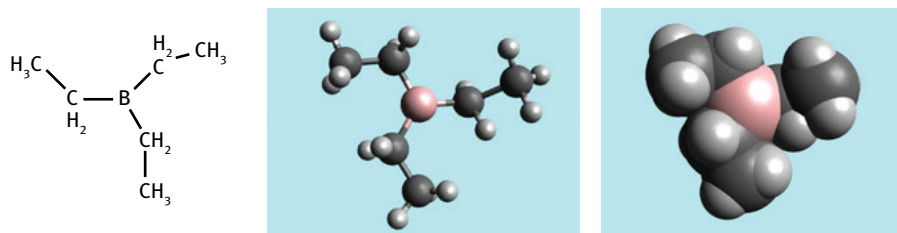


Figure 3: Molecular structure of triethylborane.

## 2.6 Chemical Properties of Alkylboranes

Triethylborane is thermally stable and can be stored indefinitely without undergoing any chemical changes. It ignites spontaneously in air and burns with a green flame. It is not miscible with water and is resistant to hydrolysis, which is a distinct difference from the behavior of triethylaluminum. In chemical commerce, triethylborane is sold as a 11–14-% solution in tetrahydrofuran. Solutions of triethylborane with <14 mass-% in THF are non-pyrophoric in air. Slow exposure to air will oxidize triethylborane solutions to borinic esters and other borate ester materials. Triethylborane does not react readily with atmospheric moisture or water in a THF solution.

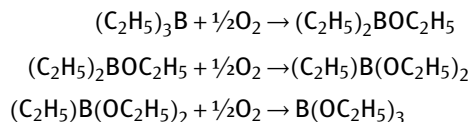
### 2.6.1 Thermal Stability of Alkylboranes

A mechanism was proposed for the thermal decomposition of aluminum and boron alkyls and for the reverse reaction, the addition of olefins to metal hydrides [33]. These reactions were shown to be non-radical in nature and they may proceed through a cyclic intermediate.

### 2.6.2 Autoignition of Alkylboranes

Triethylborane is pyrophoric and ignites spontaneously in air or in contact with liquid oxygen and other oxidizers [34, 35].

Triethylborane vapor, at concentrations exceeding 1150–1300 ppm, undergoes complete spontaneous combustion in air to form boron oxide,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ . At concentrations below 1150 ppm, triethylborane rapidly oxidizes in air to diethylethoxyborane, then ethyldiethoxyborane, and ultimately to triethoxyborane.



The lowest autoignition temperature of cooled triethylborane in air is  $253\text{ K} = -20^\circ\text{C}$ .

For higher molecular mass alkylboranes, the spontaneous ignition delay increases with the length of the alkyl group, so that when liquid tri-*n*-butylborane is exposed to air, there is an induction period of several seconds before ignition occurs.

### 2.6.3 Analysis of Alkylboranes

The number of alkyl groups in alkylboranes can be determined by titration with peroxybenzoic acid. For elementary analysis, the sample is combusted in a CHN analyzer, water and carbon dioxide are absorbed in phosphorus pentoxide and Ascarite, and the boric acid residue is titrated acidimetrically after the addition of mannitol [36]. This method is applicable to all organic boron compounds, even to boric acid esters.

A cartridge that contains a mixture of 15% triethylaluminum and 85% triethylborane, called TEA/TEB, is used as a hypergolic igniter for many LOX/kerosene or LOX/LH2 rocket engines. Quality control of the 15/85 mixture of triethylaluminum and triethylborane is fundamental to ensuring the reliability of engine ignition. Prior to each launch, an infrared spectrophotometric procedure based upon 5 years of studying the correlation between absorbance differences and ignition delay data utilizing the C—C stretching mode at  $10.1\text{--}10.2\text{ }\mu$  for triethylaluminum, and the  $\text{CH}_3$  rocking mode at  $9.7\text{--}9.8\text{ }\mu$  for triethylborane was used for quality assurance [37].

## 2.7 Handling of Alkylboranes

Because most dialkyl and trialkyl boranes, in particular triethylborane, are pyrophoric, they can be handled only under an inert gas (argon, nitrogen) [38]. Argon is preferred because it is heavier than air and it is less likely that air will intrude into the apparatus when the purge gas flow rate is too slow. Transport and storage containers should have two outlets, one for pressurization with an inert gas and the other a dip tube for the withdrawal of liquid.

Alkylboranes with longer alkyl groups are not as reactive in air as triethylborane and autoxidize only slowly without autoignition.

Triethylborane and triethylaluminum have been patented as ignition fluids for solid rocket motors [39].

## 2.8 Toxicity of Trialkylboranes

In earlier investigations, rats were exposed to triethylborane (TEB) via either the i.p., i. g., or inhalation route [40]. The 4-h inhalation LC50 of what was reported to be pure TEB vapor was nominally 700 ppm. However, these data have been considered suspect because the TEB in the exposure environment was not characterized quantita-

tively nor qualitatively and the temporal stability of the exposure concentration was not monitored. Most of it will have been oxidized by the time it was inhaled by the animals.

Clinical symptoms of personnel accidentally exposed to triethylborane indicated that TEB vapors induced both central nervous system and respiratory dysfunction. A renewed investigation was undertaken to re-evaluate the acute inhalation toxicity of TEB in rats exposed for 1 h [41]. It is known that triethylborane is labile in air, undergoing a series of rapid oxidations; thus the toxicity of similar concentrations of TEB vapor (actually TEB oxidation products) was examined at two time points subsequent to the initiation of the spontaneous oxidation process. The acute inhalation toxicity of TEB and its oxidation products was determined not only as a function of concentration but also as a function of time after the initiation of oxidation. Atmospheres with fresh or oxidized TEB at its highest-attainable non-combustive concentration proved to be pneumo- and hepatotoxic as well as lethal. During initial exposure to 900 ppm TEB, 21 of 23 animals expired. The overall LC50 for TEB was 738 ppm.

### 3 Alkyldiboranes

There are mono-, di-, tri-, and tetraalkyldiboranes. In alkyldiborane compounds, some of the hydrogen atoms are bonded to boron and some to carbon. The last two hydrogens of  $B_2H_6$  cannot be replaced because they perform the bridge bonding between the two boron atoms. Alkyldiboranes are pyrophoric in air, similar to trialkylboranes, and can be used for the hypergolic ignition of rocket engines. Alkyldiboranes are more difficult to prepare than trialkylboranes, thus it is less likely that they will be used as rocket propellants.

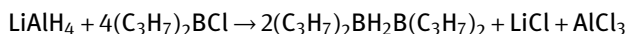
#### 3.1 Preparation of Alkyldiboranes

Alkyldiboranes can be prepared by the reduction of trialkylboron compounds, by the co-proportionation of a mixture of diborane and trialkylboron compounds, or by the addition of ethylene to diborane. Dialkyldiboranes form symmetrical and unsymmetrical isomers where the two alkyl groups can be on the same boron atom or on different boron atoms.

A mixture of ethyldiboranes were prepared by reacting gaseous diborane and ethylene that were passed through a tube containing a catalyst [42]. The product mixture of mostly *unsym*-diethyldiborane was condensed and recovered in a trap cooled with dry ice, mixed with diborane, and stored at 293–298 K (20–25°C) in a stainless steel container. During storage, a slow reaction occurred in which monoethyldiborane was formed. This product was periodically removed and purified by distillation at low temperatures. When monoethyldiborane was warmed to 298 K

(25°C), a disproportionation reaction took place with the formation of an equilibrium mixture of diborane and *sym*-diethyldiborane, which were easy to separate. The vapor pressure of *sym*-diethyldiborane was 4.8 kPa at 273 K (36 mm Hg at 0°C).

Tetraalkyldiboranes can be obtained by the action of lithium aluminum hydride on the dialkylboron chloride in ether solution [43]:



The alkylation of diborane by reaction with trimethylborane and the decomposition of monomethyldiborane leads to mixtures of alkyldiboranes [44]. See also [45].

### 3.2 Physical Properties of Alkyldiboranes

Table 6 is a summary of the physical properties of some of the more common alkyldiboranes.

The lower heat of combustion of liquid tetraethyldiborane to form steam and solid  $\text{B}_2\text{O}_3$  is  $47865 \pm 293 \text{ kJ/kg} = 11440 \pm 70 \text{ kcal/kg} = 20600 \pm 130 \text{ BTU/lb}$  (corrected for incomplete combustion) [47]. At lower temperatures, boron trioxide and water form boric acid, which changes the overall heat release.

**Table 6:** Physical properties of alkyldiboranes.

| Molecular formula                                                       | Melting point |        | Boiling point         |                       | Vapor pressure at specified temperature | Temperature | Vapor pressure at specified temperature |     | Temperature |
|-------------------------------------------------------------------------|---------------|--------|-----------------------|-----------------------|-----------------------------------------|-------------|-----------------------------------------|-----|-------------|
|                                                                         | K             | °C     | K                     | °C                    |                                         |             | mm Hg                                   | °C  |             |
| $\text{CH}_3\text{B}_2\text{H}_5$                                       | —             | —      | —                     | —                     | 7.3                                     | —           | 55                                      | —78 | —           |
| $(\text{CH}_3)_2\text{BH}\cdot\text{BH}_3$                              | 123           | −150   | 270.4                 | −2.6                  | 1.3                                     | 195         | 10                                      | −78 | —           |
| $(\text{H}_3\text{CBH}_2)_2$                                            | 149.1         | −123.9 | 277.9                 | 4.9                   | 0.9                                     | 195         | 7                                       | −78 | —           |
| $(\text{H}_3\text{C})_2\text{BH}\cdot\text{H}_2\text{BCH}_3$            | 150.1         | −122.9 | 318.5                 | 45.5                  | 16.3                                    | 273         | 123                                     | 0   | —           |
| $[(\text{H}_3\text{C})_2\text{BH}]_2$                                   | 200.5         | −72.5  | 341.6                 | 68.6                  | 6.4                                     | 273         | 48                                      | 0   | —           |
| $\text{C}_2\text{H}_5\text{B}_2\text{H}_5$                              | —             | —      | —                     | —                     | 0.9                                     | 195         | 7                                       | −78 | —           |
| $(\text{C}_2\text{H}_5)_2\text{BH}\cdot\text{BH}_3$                     | —             | —      | 340                   | 67                    | 6.1                                     | 273         | 46                                      | 0   | —           |
| $[(\text{C}_2\text{H}_5)\text{BH}_2]_2$                                 | —             | —      | 335 <sup>a</sup>      | 62 <sup>a</sup>       | —                                       | —           | —                                       | —   | —           |
| $(\text{C}_2\text{H}_5)_2\text{BH}\cdot\text{H}_2\text{BC}_2\text{H}_5$ | 224.8         | −48.3  | —                     | —                     | 0.5                                     | 273         | 4                                       | 0   | —           |
| $[(\text{C}_2\text{H}_5)_2\text{BH}]_2$                                 | 216.6         | −56.5  | 444                   | 171 <sup>a</sup>      | 0.1                                     | 273         | 0.5                                     | 0   | —           |
| $n\text{-C}_3\text{H}_7\text{B}_2\text{H}_5$                            | —             | —      | —                     | —                     | 0.8                                     | 213         | 6.2                                     | −60 | —           |
| $[(n\text{-C}_3\text{H}_7)_2\text{BH}]_2$                               | —             | —      | 307 K<br>at<br>130 Pa | 34°C<br>at<br>1 mm Hg | 2.8                                     | 279         | 21                                      | 6   | —           |

<sup>a</sup> Extrapolated

Data source: [46]

Other alkyldiboranes with a gross formula of  $B_2C_4H_8$  were formed by the reaction of diborane with a mixture of acetylene and ethylene. The resulting alkyldiboranes were spontaneously inflammable in air and had a heat of combustion of  $48455 \pm 349 \text{ kJ/kg} = 20850 \pm 150 \text{ BTU/lb}$  [48]. A similar alkyldiborane with a gross formula of  $B_2C_8H_{22}$  was formed by the reaction of diborane with 1,3-butadiene. It reacted rapidly in air, ignited spontaneously in an oxygen-enriched atmosphere, and had a heat of combustion of  $44330 \pm 349 \text{ kJ/kg} = 19075 \pm 150 \text{ BTU/lb}$  [49].

Frequency assignments, including some of the B–C stretching frequencies, were made for the IR spectra of tri-, tetramethyl-, and ethyldiboranes together with some of their boron-deuterated and  $^{10}\text{B}$  isotopic derivatives, and were compared to the Raman spectrum of tetramethyldiborane [50, 51].

For alkyldiboranes, the vibrational frequencies of the terminal B–H bonds lie in the range  $2500\text{--}2600 \text{ cm}^{-1}$  in their IR absorption and Raman spectra, while those of the bridge B–H bonds are in the range  $1500\text{--}1600 \text{ cm}^{-1}$  in their IR spectra.

Vibrational assignments were made, using both IR and Raman data, for the Raman spectra of liquid tetramethyldiborane and 1,1-dimethyldiborane at 203 K ( $-70^\circ\text{C}$ ), and the polarization states of these two alkyldiboranes were investigated qualitatively [52]. The corresponding results were also obtained for monomethyldiborane and trimethyldiborane [53]. Characteristic frequencies of the methyldiboranes showed trends with increasing methyl substitution.

The microwave spectra of ten isotopomers of monomethyldiborane and *unsym*-dimethyldiborane were measured in the region between 18.5 and 40 GHz, and all atom–atom distances and bond angles were derived from these data [54, 55]. The bridge  $B\cdots H_2\cdots B$  group appeared to be displaced toward the methyl group. Thermodynamic properties of several alkyldiboranes are listed in Table 7.

**Table 7:** Enthalpies of formation of alkyldiboranes.

| Compound             | Formula                   | Liquid |          | Vapor  |          |
|----------------------|---------------------------|--------|----------|--------|----------|
|                      |                           | kJ/mol | kcal/mol | kJ/mol | kcal/mol |
| Methyldiborane       | $H_3CB_2H_5$              | –58.6  | –14      | –35.6  | –8.5     |
| 1,2-Dimethyldiborane | $H_3CHBH_2BHCH_3$         | –130   | –31      | –100   | –24      |
| 1,1-Dimethyldiborane | $(H_3C)_2BH_2BH_2$        | –130   | –31      | –199   | –24      |
| Trimethyldiborane    | $(H_3C)_2BH_2BHCH_3$      | –201   | –48      | –171.5 | –41      |
| Tetramethyldiborane  | $(H_3C)_2BH_2B(CH_3)_2$   | –272   | –65      | –234   | –56      |
| Ethyldiborane        | $H_3CCH_2B_2H_5$          | –58.6  | –14      | –33.5  | –8       |
| 1,1-Diethyldiborane  | $(H_3CCH_2)_2BH_2BH_2$    | —      | —        | –125   | –29.768  |
| Triethyldiborane     | $(H_3C)_2BH_2BHC_2H_5$    | –201   | –48      | –159   | –38      |
| Tetraethyldiborane   | $(H_3C)_2BH_2B(C_2H_5)_2$ | –272   | –65      | –222   | –53      |

Data sources: [4,27]

Raman spectra (liquid and solid) and IR spectra (gas and solid) have been measured for samples of *trans*-1,2-dimethyldiborane and *cis*-1,2-dimethyldiborane [56]. Previous spectroscopic work that was originally thought to focus mainly on the *cis* form, is now believed to represent spectra of an equilibrium mixture of both forms.

The molecular geometries, force fields, and IR absorption intensities of diborane and methyldiborane have been predicted from *ab initio* calculations [57]. The theoretical geometries revealed slight distortion of the diborane ring bond angles, by 1–2°, on methylation. The calculated value of the threefold barrier for methyl torsion was nearly 8.5 kJ/mol.

### 3.3 Reactions with Alkyldiboranes

In their chemical properties, the alkyldiboranes are similar to the trialkylboranes; for instance, they autoignite in air at room temperature. However, they are more reactive when they come in contact with water and quickly hydrolyze.

The gas-phase oxidation of *sym*-diethyldiborane has been studied under both explosive and non-explosive conditions [42, 58]. With excess oxygen, the non-explosive reaction was a partial oxidation to form ethyl metaborate and hydrogen. The rate of disappearance of *sym*-diethyldiborane in the slow partial oxidation was found to be zero order in oxygen and first order in *sym*-diethyldiborane. The partial oxidation reaction proceeded via the formation of an unstable intermediate.

Chemical and physical evidence supports the structure  $[(\text{CH}_3)_2\text{B}(\text{NH}_3)_2]^+[\text{H}_2\text{B}(\text{CH}_3)_2]^-$  for the unstable product of the direct reaction of ammonia and tetramethyldiborane [59]. The reaction of ammonia with an ethereal solution of  $(\text{CH}_3)_2\text{BH}_2(\text{CH}_3)_2$  gives the non-electrolyte  $(\text{CH}_3)_2\text{BHNH}_3$ .

## 4 Alkylpentaboranes

Alkylpentaboranes were produced in substantial quantities during the boron fuel program for the XB-70 high-altitude/long-range bomber. HEF-2 consisted of a mixture of alkylpentaboranes, most likely propylpentaborane [60].

Although ethylpentaborane is more easily prepared and purified than ethyldeca-borane, the latter is more attractive as a high-energy fuel for air-breathing engines because of its lower vapor pressure, higher heat of combustion, higher density, better thermal and hydrolytic stability, and the greater ease of handling of decaborane and its derivatives. The combustion of alkylboranes is of most interest in air-breathing engines and not in rocket engines.

## 4.1 History of the Borane Fuels Program

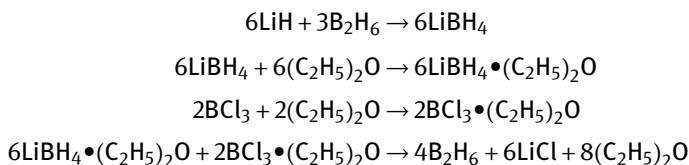
A complete history of the borane fuels program in the United States during the 1950s would fill an entire book and span chapters on all three main boranes (diborane, pentaborane, decaborane) and their alkyl derivatives. The most complete account of the activities during that period is offered in [4]. The following information was extracted from that source. It is included in this discussion of alkylpentaboranes because one of the main ingredients of the HEF fuels was an alkylpentaborane; otherwise, the historical account would have included in the section on alkyldecaboranes. In 1952, the United States Navy (Bureau of Aeronautics) commenced *Project Zip* to develop borane-based fuels with physical properties similar to hydrocarbon jet fuels but substantially higher energies and densities. It was envisaged that such fuels would extend the range, speed, and maximum cruising altitude of existing or planned long-range bombers. Callery Chemical Company and the Olin Mathieson Chemical Corporation were awarded multi-million dollar contracts for the development of these new fuels. Later, in 1957, smaller contracts were given to the Aerojet General Corporation and to AFN, Inc. (a team comprising American Potash and Chemical Corporation, Food Machinery, Inc., and National Distillers). Callery Chemical Company and the Olin Mathieson Chemical Corporation outlined very broad competitive programs for the synthesis of the new high-energy fuels. As the feasibility of the programs proved encouraging, the effort was divided between the United States Navy (*Project Zip* of Callery Chemical Company) and the United States Air Force (*Project HEF*) in 1956. Each of the prime contractors enlisted the help of many subcontractors. Among these subcontractors were industrial research laboratories, research institutes, universities, and private research laboratories. Indeed, during the mid-1950s, the work assumed the character of a crash program similar to the Manhattan Project. It soon became apparent that in order to obtain the desired physical properties, the new fuel would probably need to consist of alkylated derivatives of the boranes. Producing alkylated boranes from borate ores necessitated raising boron from a low-energy oxidized state to a high-energy fuel, and the processes used to achieve this in the two projects were quite different. Olin Mathieson considered the synthesis and demonstration of a usable fuel to be of prime importance; Callery Chemical Company, however, believed that economic feasibility deserved as much emphasis as the synthesis of the fuel. As a result of this divergence in approach, the dissimilarity of the processes became evident. This divergence was particularly evident in the preparation of the earliest alkylated boranes. Olin Mathieson preferred to focus on the preparation of higher boranes, particularly pentaborane(9) and decaborane, and their subsequent alkylation. Callery Chemical Company favored the alkylation of diborane with subsequent pyrolysis to higher alkylated boranes. These process differences make it difficult to compare the chemistry



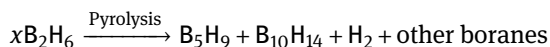
involved in them. It is regrettable that much of this excellent, original, and creative work was never reported because of the pressures of the times and because it was performed under proprietary or national security restrictions. This small area of boron chemistry was advanced by an unusual amount of research effort in a very short time. When the program was concluded, the attentions of these organized groups of scientists and engineers turned to other tasks, and many lost their jobs. Knowledge of borane chemistry has been markedly advanced by all these efforts, as have associated laboratory techniques and theoretical concepts. The research expenditure on these programs, although large, represented only a small portion of the total cost and was certainly justified by the results. The following sections describe the synthetic routes used by the various chemical companies. The initial steps (lower step numbers), starting from borax ores, have been omitted here; it is assumed that the boron trichloride (trichloroborane) and triethylborate were derived from that source. Lithium hydride and sodium hydride were prepared from the elements.

#### 4.1.1 Olin Mathieson Chemical Corporation Process

**Step (3):** Preparation of diborane from lithium hydride and trichloroborane:



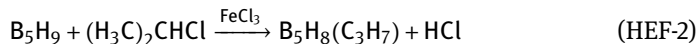
**Step (4):** Formation of pentaborane(9) and decaborane(10) from diborane:



This step was very complex and had not been entirely elucidated. The kinetics and mechanism are described in other sources. The *hot tube* pyrolysis method was used.

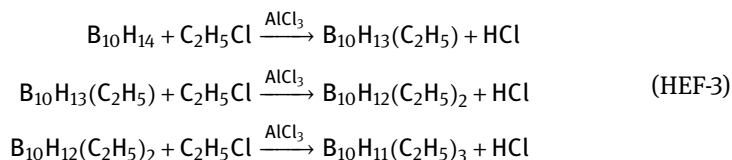
**Step (5):** Preparation of propylpentaborane(9) (HEF-2).

Pentaborane(9) was successfully alkylated to propylpentaborane(9) in the presence of ferric chloride as a catalyst. Aluminum chloride could have been used as a catalyst instead, but it could not be separated from the product.



**Step (6):** Preparation of ethyldecaboranes (HEF-3).

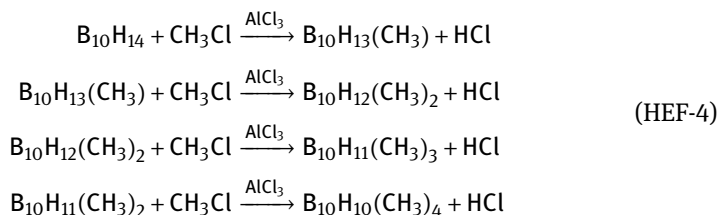
Decaborane can be ethylated in the presence of aluminum chloride to yield mono-, di-, and triethyldecaborane:



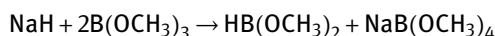
40–50% conversion was obtained in this process. HEF-3 contained mono-, di-, and triethyldecaborane in the ratio 65 : 30 : 5.

**Step (7):** Preparation of methyldecaboranes.

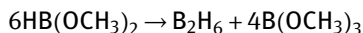
Mono-, di-, tri-, and tetramethyldecaborane were formed from decaborane and methyl chloride in the presence of aluminum chloride. The mass ratio of these materials in the order given was 67 : 24 : 7 : 2.

**4.1.2 Callery Chemical Company**

A different approach to the synthesis of alkylboranes was taken at Callery Chemical Company.

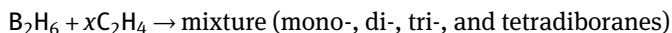
**Step (4):** Preparation of dimethoxyborane:**Step (5):** Preparation of diborane.

The disproportionation of dimethoxyborane to diborane proceeded readily with nearly 100% conversion. The disproportionation was favored by increased pressure and temperature.

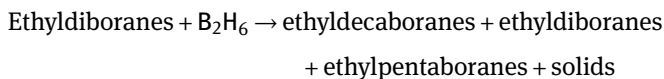


**Step (6):** Preparation of ethyldiboranes.

When allowed to react at 308 K (35 °C) and 69 kPa gauge (10 psig), diborane and ethylene yielded a mixture of ethyldiboranes. This reaction was 95% complete with respect to diborane and complete with respect to ethylene. Between 2 and 3 moles of ethylene were used per mole of diborane.

**Step (7):** Preparation of crude ethyldecaboranes (HiCal-2).

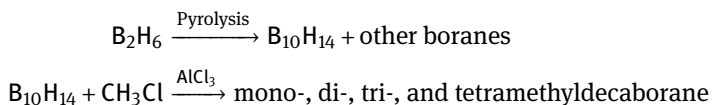
Additional diborane was added to mixed ethyldiboranes at 343 K (70 °C) and 2.76 MPa gauge (400 psig) to yield a mixture of ethyldecaboranes and ethylpentaboranes. The excess ethyldiboranes were removed by distillation, and the resulting product was HiCal-2.

**Step (8):** Preparation of refined ethyldecaboranes (HiCal-3).

Dissolved solids were removed by precipitating and diluting with 20 volumes of pentane and filtering. The pentane was removed by stripping with an inert gas to yield HiCal-3.

**Step (9):** Preparation of methyldecaboranes (HiCal-4).

Diborane from Step (5) was pyrolyzed to decaborane and other boranes and the decaborane was methylated over an aluminum chloride catalyst with a reported yield of 60–85% methyldecaboranes. A mixture of mono-, di-, tri-, and tetramethyldecaboranes was reported, but the composition was not given.



Other methods were tested at Stauffer-Aerojet Chemical Company and at a team called AFN, Inc. (a team of chemical companies formed by American Potash and Chemical Corporation, Food Machinery, Inc., and National Distillers), but they did not advance beyond the pilot plant scale. The final fuel objectives at AFN, Inc. were the preparation of HEF-4 or pentaborane(9).

## 4.2 Production of Alkylpentaboranes

Alkylpentaboranes can be prepared by the addition of alkenes to pentaborane or by the pyrolysis of diborane in the presence of trialkylboron compounds. The reaction of diborane with trimethylborane at 508–573 K (235–300 °C) leads to the formation of about 5% methylpentaborane in addition to pentaborane as the main product [61]. The mixture contains two isomers of methylpentaborane that can be separated by low-temperature fractionation. The less volatile isomer has a vapor pressure of 2.7 kPa (20 mm Hg) at 273 K (0 °C).

Several reactions of pentaborane(9) that lead to alkylpentaboranes have already been discussed in the section on the reactions of pentaborane with organic compounds. The addition of alkenes to pentaborane is catalyzed by amines (e.g., trimethylamine, pyridine) [62, 63]. Isobutylpentaborane, which has a vapor pressure of 0.67 kPa at 298 K (5 mm Hg at 25 °C), can be made by reacting pentaborane(9) with isobutylene [64]. The use of tetrahydrofuran as a solvent improves the alkylpentaborane yield [65].

Reactions involving alkene addition to pentaborane can be catalyzed by Friedel–Crafts catalysts such as  $\text{AlCl}_3$  [66]. The ethyl group in ethylpentaborane is located preferentially in the apex (apical position), i.e., the ethyl group is attached to the boron atom of the pentaborane molecule, which is not in the plane of the base of the pyramid in which the boron atoms are located. Ethylpentaborane can be prepared by reacting ethylene with pentaborane in the presence of a Friedel–Crafts catalyst, e.g., anhydrous aluminum chloride. The reaction takes place in a nickel–chromium alloy vessel at a pressure in excess of 354 kPa (3.5 atm) and a temperature of 318–333 K (45–60 °C).

The addition of propylene to pentaborane(9) at 433–468 K (160–195 °C) can be catalyzed by magnesium silicate catalysts [67].

Another production method for alkylpentaboranes is the alkylation of pentaborane by alkyl halogenides in the presence of Friedel–Crafts catalysts [68, 69]. The reaction of 2*B*-methylpentaborane with chloromethane in the presence of  $\text{AlCl}_3$  leads to the formation of 1,2-dimethylpentaborane. Alkylpentaboranes often undergo intramolecular rearrangements.

The reaction of pentaborane and ethylene oxide resulted in a viscous yellow liquid that was not pyrophoric in air [70].

The reaction of methyl chloride with pentaborane in the presence of  $\text{AlCl}_3$  at 373 K for 3 h gives a good yield of 1*B*-methylpentaborane. If 1*B*-methylpentaborane is heated to 473 K (200 °C) overnight, it rearranges itself to form 2*B*-methylpentaborane [71]. The rate of apex-to-base rearrangement is retarded if the number of substituents is increased [72].

Butylpentaborane and tributylborane were prepared from pentaborane(9) and isobutylene [73]. Mono-*sec*-butylpentaborane(9) has a vapor pressure of 0.5 kPa at

298 K (4 mm Hg at 25 °C), and monopropylpentaborane(9) has a vapor pressure of 0.9 kPa at 293 K (7 mm Hg at 20 °C).

It is possible to synthesize alkylpentaboranes with two pentaborane entities in the molecule that are connected by an alkane chain. 1,4-Dipentaboranylbutane can be obtained by the reaction of butadiene with pentaborane [74, 75].

The preparation of dipentaborylmethane by reacting pentaborane with dichloromethane in the presence of aluminum chloride gave poor yields of less than 1% [76]. No dipentaborylethane resulted from the reaction of pentaborane with 1,2-dichloroethane or 1,2-dibromoethane. Instead, these reactions produced ethylpentaborane in yields of up to 47%.

The complex product obtained by reacting ethylene with diborane has been shown by vapor-phase chromatography to include, among others, two homologous series, namely ethylpentaboranes(9) and ethyldecaboranes(11). At 673 K (400 °C), diborane and ethylene predominantly produce triethylborane. However, when heated, diborane decomposes to give higher boron hydrides, and while triethylborane is an alkylating agent, borane and ethylene might be expected to give ethyl derivatives of the higher boron hydrides under suitable conditions [77, 78].

Aluminum-chloride-catalyzed Friedel–Crafts reactions have generally been used to prepare alkylpentaboranes and alkyldecaboranes, although several methyl derivatives were obtained by simultaneous pyrolysis and alkylation using trimethylboron. It was possible to isolate two isomeric monomethyl pentaboranes. One of the isomers, which had a vapor pressure of 4.67 kPa at 273 K (35 mm Hg at 0 °C), was identical to the apically substituted product obtained by Friedel–Crafts methylation of pentaborane. Propyl pentaborane is the major constituent (70–85%) of boron fuel, HEF-2. The material also contains dipropylpentaborane (15–25%) and pentaborane (3–5%).

A slurry of  $\text{AlCl}_3$  in pentaborane rapidly absorbs ethylene gas, forming monoethylpentaborane(9) [79].

### 4.3 Physical Properties of Alkylpentaboranes

The physical properties of ethylpentaborane(9) are listed in Table 8.

Methylpentaborane freezes at 216 K (–57 °C) and boils at 348 K (75 °C). 1,4-Dipentaboranylbutane has a boiling point of 333–353 K at 267–67 Pa (60–80 °C at 2–0.5 mm Hg) [74]. The heats of combustion of alkylpentaboranes and alkyldecaboranes are listed in Table 9. Table 10 gives a comparison of the physical properties of alkylpentaboranes and alkyldecaboranes. Thermodynamic properties of alkylpentaboranes are listed in Table 11.

**Table 8:** Physical properties of ethylpentaborane.

| Property            | SI units                   | Other units              | References |
|---------------------|----------------------------|--------------------------|------------|
| Freezing point      | 178 K                      | −95 °C                   |            |
| Boiling point       | 288 K at 1.87 kPa          | 15 °C at 14 mm Hg        |            |
| Density ( $\rho$ )  | 0.68 g/cm <sup>3</sup>     | 42.45 lb/ft <sup>3</sup> | [66]       |
| Kinematic viscosity | 0.005472 m <sup>2</sup> /h | 1.52 cSt                 |            |
| Heat of combustion  | 59831 kJ/kg                | 14300 kcal/kg            | [66]       |
| Vapor pressure      | 1.57 kPa at 273 K          | 11.8 mm Hg at 0 °C       |            |
|                     | 6.76 kPa at 303.4 K        | 50.7 mm Hg at 30.3 °C    |            |
|                     | 101 kPa at 376.6 K         | 760 mm Hg at 103.5 °C    |            |

**Table 9:** Heats of combustion of alkylboranes to crystalline B<sub>2</sub>O<sub>3</sub>.

|             | Unsubstituted |        | Methyl |        | Ethyl |        | Propyl |        |
|-------------|---------------|--------|--------|--------|-------|--------|--------|--------|
|             | kJ/kg         | BTU/lb | kJ/kg  | BTU/lb | kJ/kg | BTU/lb | kJ/kg  | BTU/lb |
| Pentaborane | 68337         | 29400  | 63224  | 27200  | 60202 | 25900  | 58110  | 25000  |
| Decaborane  | 66245         | 28500  | 64153  | 27600  | 62061 | 26700  | 60434  | 26000  |

Data source: [80]

**Table 10:** Physical properties of ethylpentaborane and methyl- and ethyl-decaborane.

| Property                   | Ethylpentaborane | Methyldecaborane     | Ethyldecaborane      |
|----------------------------|------------------|----------------------|----------------------|
| Vapor pressure, mm Hg      | 29 at 19.5 °C    | Less than 2 at 25 °C | Less than 3 at 25 °C |
| Boiling point, °C          | 104              | 223                  | 217                  |
| Melting point, °C          | −85              | −4 to −12            | −25                  |
| Density, g/cm <sup>3</sup> | 0.68             | 0.8 (HEF-4)          | 0.80–0.82 (HEF-3)    |
| Viscosity, cSt             | 0.66 at 20 °C    | 9 at 25 °C (HEF-4)   | 9 at 25 °C (HEF-3)   |

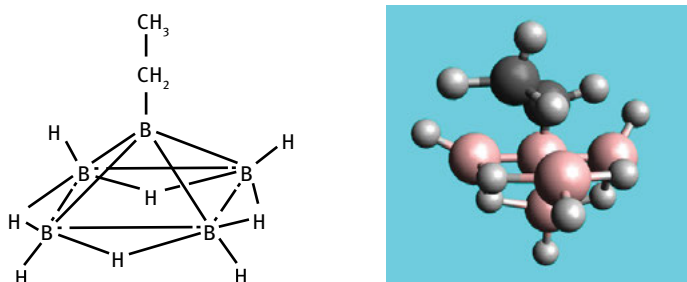
Data source: [80]

**Table 11:** Enthalpies of formation of alkylpentaboranes.

| Compound          | Formula                                                         | Liquid |          | Vapor  |          |
|-------------------|-----------------------------------------------------------------|--------|----------|--------|----------|
|                   |                                                                 | kJ/mol | kcal/mol | kJ/mol | kcal/mol |
| Methylpentaborane | H <sub>3</sub> CB <sub>5</sub> H <sub>8</sub>                   | −29.3  | −7       | +4.2   | +1       |
| Ethylpentaborane  | H <sub>3</sub> CCH <sub>2</sub> B <sub>5</sub> H <sub>8</sub>   | −62.8  | −15      | −25.1  | −6       |
| Propylpentaborane | (H <sub>3</sub> C) <sub>2</sub> CHB <sub>5</sub> H <sub>8</sub> | −79.5  | −19      | −37.7  | −9       |

Data sources: [4,27]

Ethyldecaborane is more stable than ethylpentaborane with respect to hydrolysis and thermal decomposition. The molecular structure of ethylpentaborane is similar to that of bromopentaborane [81]. From analyzing the infrared spectrum of pentaborane, the ethyl group in ethylpentaborane was found to be located at the apical position of the pentaborane molecule (Figure 4) [82]. The infrared spectra of pentaborane, bromopentaborane, methylpentaborane, and ethylpentaborane in the ranges 1900–400 and 3000–2500  $\text{cm}^{-1}$  were measured and compared. The spectra of methylpentaborane and ethylpentaborane were observed to be very similar. The structure of *n*-propylpentaborane (HEF-2) would be similar to that of ethylpentaborane.



**Figure 4:** Molecular structure of ethylpentaborane

The apex-basal dimethylpentaborane 1,2-( $\text{CH}_3$ )<sub>2</sub>B<sub>5</sub>H<sub>7</sub> was shown by XRD to rearrange itself into the dibasal isomer 2,3-( $\text{CH}_3$ )<sub>2</sub>B<sub>5</sub>H<sub>7</sub>, in which the methyl groups are on adjacent basal B atoms of the square-pyramidal B<sub>5</sub> unit [83]. The space group of crystalline 2,3-dimethylpentaborane is *Pm* $\bar{c}$ *n*, and there are four molecules in the unit cell. The unit cell parameters are:  $a = 12.55 \text{ \AA}$ ,  $b = 6.39 \text{ \AA}$ , and  $c = 9.10 \text{ \AA}$ .

#### 4.4 Reactions of Alkylpentaboranes

The thermal decomposition of ethylpentaborane at 458–517 K (185–244 °C) leads to non-volatile polymers, hydrogen, methane, and traces of decaborane [84]. The thermal decomposition of ethylpentaborane at temperatures of 458–517 K (185–244 °C) has a reaction order of approximately 1.5. Ethylpentaborane has a greater rate of decomposition than pentaborane itself [85].

1-Alkylpentaboranes rearrange themselves into 2-alkylpentaboranes when heated to 473 K (200 °C) [71]. This can be a deliberate, pre-planned step in the synthesis of 2-alkylpentaboranes from pentaborane.

The products of the decomposition of propylpentaborane (HEF-2) in the range 420–463 K (147 to 190 °C) were hydrogen, hydrocarbons, and a solid, non-volatile, yellow boron hydride [86]. The following equation that may be used to calculate the ap-

proximate time required to decompose 20% of propyl pentaborane as a function of temperature was developed:

$$\log(t_{20} - 2) = 7.85 \times \frac{10^3}{T} - 16.3$$

where  $t_{20}$  is the time required for 20% decomposition in minutes and  $T$  is the temperature in kelvin.

#### 4.5 Toxicity of Alkylpentaboranes

Alkylpentaboranes are somewhat less toxic than pentaborane itself. The toxicity hazards of HEF-2 necessitated extensive precautions during the handling of these exotic jet engine fuels and ultimately contributed to the termination of the boron fuels program [87, 88].

Acute and subacute studies on HEF have established a linear relationship between serum borane levels and clinical signs of toxicity [89]. Repeated exposure to low levels resulted in tissue accumulation and the appearance of toxic effects as a function of time and dose. The accumulation of HEF in tissues limited the usefulness of the biological index test procedure as a diagnostic aid in cases of chronic human exposure during work hours.

### 5 Alkyldecaboranes

Alkyldecaboranes were the mainstay of the boron high-energy fuels (HEF) program. While HEF-2 consisted of propylpentaborane, HEF-3 was a mixture of ethyldecaboranes. HEF-5 may have consisted of a butyldecaborane. Hi-Cal was a mixture of two components.

HEF-3, a boron fuel that was once commercially available in the US, consisted of decaborane (6.8%), monoethyldecaborane (69.4%), diethyldecaborane (22.4%), and triethyldecaborane (1.4%). Another boron fuel from a commercial source in the US, HiCal-3, was prepared by the simultaneous ethylation and pyrolysis of diborane and ethylene and contained mono- and polyethylated decaborane as well as the corresponding derivatives of pentaborane.

#### 5.1 Production of Alkyldecaboranes

Both Olin Mathieson and Callery Chemical Company constructed large facilities for the synthesis of alkylboranes on an industrial scale. Olin Mathieson built a facility at Niagara Falls, NY and Callery built a facility near Muskogee, OK. They also built an ad-



jacent facility for producing ethylene that was needed to alkylate the boranes. Callery later became a division of Mine Safety Appliances Company and then a subsidiary of Ascensus.

Alkyldecaboranes can be prepared by the reaction of decaborane with alkyl halogenides and anhydrous aluminum chloride [90], by the pyrolysis of diborane and trialkylborane or alkylidiboranes at 373–773 K (100–500 °C) in a reactor with a short dwell time [91], from decaborane and ethylene [92], from decaborane with Grignard compounds [93], from decaborane and metal-organic compounds, e.g., ethyl lithium [94], from diborane and alkylidiborane in an autoclave at high pressure and high temperature [95], or by high-pressure reaction of diborane and ethylene [96]. The reaction of diborane with ethylene can proceed explosively at high pressure. See also [77, 78].

## 5.2 Physical Properties of Alkyldecaboranes

Monoethyldecaborane boils at 368–388 K (97–115 °C) at a reduced pressure of 466 Pa (3.5 mm Hg). HiCal-2 is a mixture of several alkyldecaboranes. As summarized in Table 12, an elemental chemical analysis of HiCal-2 was performed, and its heat of combustion, vapor pressure, decomposition, freezing point, density, self-ignition temperature, flash point, and blow-out velocity were determined [97]. When conducting blowout velocity tests with this fuel, considerable difficulties were encountered

**Table 12:** Properties of HiCal-2.

| Property                                                                                                      | SI units                                                         | Other units                                                          |
|---------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|----------------------------------------------------------------------|
| Elemental chemical analysis                                                                                   |                                                                  |                                                                      |
| Boron                                                                                                         | 53.60 mass-%                                                     | —                                                                    |
| Carbon                                                                                                        | 32.33 mass-%                                                     | —                                                                    |
| Hydrogen                                                                                                      | 13.51 mass-%                                                     | —                                                                    |
| Net heat of combustion of liquid fuel to gaseous carbon dioxide, liquid water, and solid boric oxide at 25 °C | 53831 kJ/kg                                                      | 23159 BTU/lb                                                         |
| Density                                                                                                       | 841 kg/m <sup>3</sup> at 293 K<br>838 kg/m <sup>3</sup> at 298 K | 0.841 g/cm <sup>3</sup> at 20 °C<br>0.838 g/cm <sup>3</sup> at 25 °C |
| Freezing point                                                                                                | No true freezing point found                                     |                                                                      |
| Self-ignition temperature in air                                                                              | 398 K                                                            | 125 °C                                                               |
| Vapor pressure curve, mm Hg                                                                                   | —                                                                | $\log P_v = -7825/2.303RT + 6.240$                                   |
| Flash point                                                                                                   | 290 K                                                            | 17 °C                                                                |
| Extrapolated boiling point                                                                                    | 509 K                                                            | 236 °C                                                               |
| Decomposition, °C                                                                                             | >433 K                                                           | >160                                                                 |

Data source: [97]

because of foreign matter in the fuel. Filters in the transfer lines became clogged with a solid and gelatinous material.

Table 13 is a summary of the physical properties of ethyldecaborane and diethyldecaborane. The original source has additional data for a wider temperature range of 273–333 K (0–60 °C).

Thermodynamic properties of alkyldecaboranes are listed in Table 14.

**Table 13:** Physical properties of 1-ethyldecaborane and 1,2-diethyldecaborane.

| Compound              | Property            | Temperature |    | Property value          |
|-----------------------|---------------------|-------------|----|-------------------------|
|                       |                     | K           | °C |                         |
| 1-Ethyldecaborane     | Density             | 293         | 20 | 0.816 g/cm <sup>3</sup> |
|                       | Freezing point      | —           | —  | 193 K = –80 °C          |
|                       | Boiling point       | —           | —  | 490 K = 217 °C          |
|                       | Vapor pressure      | 333         | 60 | 0.84 mm Hg              |
|                       | Kinematic viscosity | 293         | 20 | 7.62 cSt                |
|                       | Absolute viscosity  | 293         | 20 | 6.22 cPs                |
|                       | Heat of evaporation | —           | —  | 13.8 kcal/mol           |
| 1,2-Diethyldecaborane | Density             | 293         | 20 | 0.828 g/cm <sup>3</sup> |
|                       | Boiling point       | —           | —  | 465 K = 192 °C          |
|                       | Vapor pressure      | 333         | 60 | 0.27 mm Hg              |
|                       | Kinematic viscosity | 293         | 20 | 6.35 cSt                |
|                       | Absolute viscosity  | 293         | 20 | 5.26 cPs                |
|                       | Heat of evaporation | NBP         |    | 18.1 kcal/mol           |

Data source: [98].

**Table 14:** Enthalpies of formation of alkyldecaboranes.

| Compound         | Formula                                                           | Liquid |          | Vapor  |          |
|------------------|-------------------------------------------------------------------|--------|----------|--------|----------|
|                  |                                                                   | kJ/mol | kcal/mol | kJ/mol | kcal/mol |
| Methyldecaborane | H <sub>3</sub> CB <sub>10</sub> H <sub>13</sub>                   | –37.7  | –9       | +20.9  | +5       |
| Ethyldecaborane  | H <sub>3</sub> CCH <sub>2</sub> B <sub>10</sub> H <sub>13</sub>   | –4.2   | –1       | +50.2  | +12      |
| Propyldecaborane | (H <sub>3</sub> C) <sub>2</sub> CHB <sub>10</sub> H <sub>13</sub> | –54.4  | –13      | +8.4   | +2       |

Data sources: [4,27]

### 5.3 Chemical Properties of Alkyldecaboranes

#### 5.3.1 Ignition of Alkyldecaboranes

Alkyldecaboranes autoxidize readily in contact with air. A mixture of 4% decaborane, 61% ethyldecaborane, 29% diethyldecaborane, and 6% triethyldecaborane autoignites in air at 403 K (133 °C). Autoignition may be an undesirable hazard. The autoignition temperature can be increased (i.e., the mixture can be made safer to handle) by the addition of trace iodine [99].

#### 5.3.2 Thermal Decomposition of Alkyldecaboranes

The kinetics of the thermal decomposition of 2-ethyldecaborane in a static system in the temperature range 483–503 K (210–230 °C) and at 2-ethyldecaborane pressures of 13.3–80 kPa (100–600 mm Hg) were examined [100]. The rate of decomposition, which initially leads to decaborane and diethyldecaboranes, is second order with respect to 2-ethyldecaborane. The activation energy was  $165 \pm 2$  kJ/mol ( $39.5 \pm 0.5$  kcal/mol). In the later stages of the decomposition, the reaction deviates from a second-order dependence due to side reactions that give non-volatile solid hydrides, alkylated non-volatile solid hydrides, hydrogen, methane, and a little ethane. 1,2-diethyldecaborane was always present in the products in greater concentrations than 2,4-diethyldecaborane.

The thermal stabilities of a commercial grade of ethyl decaborane (HEF-3) and of decaborane were investigated at temperatures of 475 and 525 K (202 and 252 °C) [101]. The decomposition products were hydrogen and a boron hydride, which was a solid or viscous liquid. Ethyl decaborane also yielded methane and/or ethane. For HEF-3, the following equation that allows the time required to decompose 20% of the ethyl decaborane at any other temperature to be calculated was developed:

$$\log(t_{20\%} - 2) = 7.12 \times \frac{10^3}{T} - 13.3$$

where  $T$  is the temperature in kelvin and  $t$  is the decomposition time of 20% of HEF-3 in minutes.

#### 5.3.3 Analysis of Alkyldecaboranes

Many of the HEF fuels were mixtures or contained contaminants that needed to be analyzed. HiCal-3 was expected to contain unreacted pentaborane as a contaminant. A combination GC/IR method was developed that was capable of detecting small amounts of pentaborane in HiCal-3 [102].

The boron contents of alkyldecaboranes and similar non-volatile boron compounds can be determined by oxidizing the sample with alkaline potassium persulfate and performing a potentiometric titration of the boric acid formed, with the acidity enhanced by the addition of mannitol [103].

### 5.4 Handling of Alkyldecaboranes

All alkylboranes, whether they are alkylpentaboranes or alkyldecaboranes, must be handled with extreme care [104]. The hazards of HEF-2 are similar to those of pentaborane itself. Spilled HEF-2 may autoignite at any moment. Spilled HEF-2 should first be diluted with a high-boiling kerosene and then flushed with a dilute aqueous ammonia solution. HEF-3 and HEF-4 do not autoignite as readily as HEF-2. The main hazard during the handling of HEF-3 or HEF-4 is accidental contact with the skin and resorption through it, resulting in severe chronic poisoning.

### 5.5 Toxicity of Alkyldecaboranes

The LD50 of boron fuels of the HEF-3 or Hi-Cal type in rats is 13 mg/kg for intravenous (*i.v.*) injection and 317–500 mg/kg for slow resorption through the skin. The LC50 for a 4-h inhalation period is 23 ppm.

The recommended first-aid treatment for splashes of HEF fuels on the skin is flushing of the affected area with a 2.8% aqueous ammonia solution or with a triethanolamine solution.

See also [105, 106] for brain and central nervous system effects of borane fuels.

Applying 0.1–0.012 cm<sup>3</sup> of HEF-3 daily to the skin of rats proved fatal after several days [107]. When symptoms were severe, the doses were adjusted downward to maintain severe intoxication, and daily exposure continued for 2 or 4 weeks in order to study its effects on the central nervous system. Intoxication developed in three stages: (1) hyperexcitation with coordinated movements or twitching and aggressive behavior after a few hours; (2) depression interrupted by agitation accompanied by ataxia; and finally (3) coma. The first two stages were reversible. Convulsions occurred only after massive lethal doses. Repeated subliminal doses produced sudden intoxication after several symptom-free days. Nuclei of nerve cells were enlarged and neurons with reduced chromatin or a disorganized chromatin pattern seemed more frequent.

## 6 Other Boron-Containing Organic Compounds

Boron, either in the elemental state or in boron hydrides or boron-organic compounds, is a preferred fuel ingredient for rocket propellants because of its light weight and high heat of combustion, mainly due to the highly negative enthalpy of formation of the boron trioxide (B<sub>2</sub>O<sub>3</sub>) that forms as a combustion product.

## 7 Boron-Containing Polymers

Low molecular weight alkylboranes are liquids or even gases, but higher molecular weight alkylboranes and polyalkylboranes are solids that can be formulated into solid propellants. Boron-containing polymers can serve as binders and at the same time increase the heats of combustion and the specific impulses of solid propellants as compared to solid propellants formulated with polymeric hydrocarbon binders. The use of boron-organic compounds as binders will also increase the burning rates of those propellants compared to the burning rates of baseline hydrocarbon-bonded propellants.

Polymeric (BNH) compounds form upon the thermolysis and dehydrogenations of ammonia borane or borine hydrazine [108], but they are brittle and have no strength. One intermediate,  $\text{H}_2\text{BNHNHBH}_2$ , exists mostly in a polymeric form.

## 8 Carboranes

The discovery of the icosahedral *closo*-1,2-dicarbadoecaborane(12),  $1,2\text{-C}_2\text{B}_{10}\text{H}_{12}$ , led to the rapid development of carborane chemistry [109]. The discovery of the base-promoted degradation of isomeric *closo*- $\text{C}_2\text{B}_{10}\text{H}_{12}$  cages provided one of the most important carborane anion systems, isomeric [*nido*- $\text{C}_2\text{B}_9\text{H}_{12}$ ]<sup>−</sup> anions. Carboranes have been extensively tested as burning-rate-accelerating additives in solid propellants. Many dicarbaboranes exist as isomers that differ in the relative locations of the carbon centers. The boron atoms and the associated hydrogen atoms are not identified in the schematic of a carborane molecule shown in Figure 5.

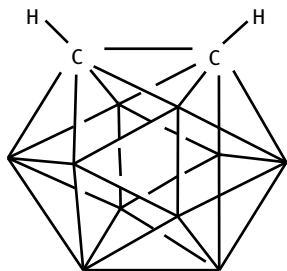


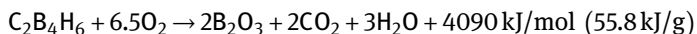
Figure 5: Structure of *ortho*-carborane.

*n*-Hexylcarborane, CAS RN [20740-05-0], is a burning rate catalyst for solid propellants. There were very ambitious projects to scale up the production of *n*-hexylcarborane to 13 metric tons per year [110]. A production facility like this would consume a substantial amount of diborane to make decaborane as an intermediate. The decaborane would then be reacted with 1-octyne to make *n*-hexylcarborane. The plan was to construct the plant next to an existing diborane production facility. The

principal hazards identified were the toxicity of borane and the fire hazard due to flammable materials and solvents.

The relative toxicities of technical grade *n*-hexylcarborane (NHC), carboranyl-methylethyl sulfide, and carboranylmethylpropyl sulfide were investigated using rats, guinea pigs, rabbits, and dogs [111]. Each compound produced primary irritation when applied to the intact and abraded skin of rabbits. Data indicated only a minor toxic hazard would be expected from acute accidental ingestion. Acute vapor and aerosol inhalation exposures of animals to the three compounds resulted in no deleterious effect. Respiratory irritation with some minimal lung damage and transient eye effects occurred in dogs and rats as a result of repeated exposure to aerosols of NHC for 6 h/d, 5 d/week for 6 weeks at concentrations of 77 and 245 mg/m<sup>3</sup>.

Carborane-4,1,6-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>, is pyrophoric in air, similar to pentaborane, and reacts violently with water. Carboranes may be suitable as additives to conventional fuels to ease their ignition and widen the range of operating pressures, allowing jet aircraft to fly at higher altitudes. The ignition delay of air/carborane mixtures is shorter than that of air/H<sub>2</sub> or air/hydrocarbon mixtures by one and three orders of magnitude, respectively [112]. The limiting ignition stage is the pyrolysis of carborane. The carborane-6 molecule has an octahedral structure whose apexes are occupied by boron and carbon atoms. A structure of this type presumes a high degree of electron localization in the boron-carbon skeleton. Therefore, carborane-4, like the higher carboranes, is a quasi-aromatic system. There are two isomers: 1,6- and 1,2-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>. The combustion of carborane-4 proceeds in accordance with the following equation:



The ignition delay of carborane-4/oxygen/argon mixtures behind reflected waves in a shock tube at 700–1600 K and 0.05–0.15 MPa was measured experimentally, and the kinetics of the initial stage of carborane oxidation were derived from these data [113]. The initial products of carborane oxidation were predicted from a semiempirical MNDO quantum-chemical method. A kinetic scheme for the promoted ignition of stoichiometric oxygen/carborane-4/argon mixtures in the presence of isopropyl nitrate (to promote additions) at a temperature of 600–1300 K and under a pressure of 0.1 ± 0.02 MPa was derived and compared to experimental results [114].

The heats of combustion, formation, and sublimation of *o*- and *m*-carboranes were determined calorimetrically, and it was confirmed that *o*-carborane is less thermodynamically stable than *m*-carborane [115].

## 9 Other Boron Compounds

Adducts between borane and trinitromethyl anions have been characterized and could be used as rocket propellants [116].

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# Alkylhydrazines

## Introduction

There are three chapters relating to alkylhydrazines in *Encyclopedia of Liquid Fuels*, with the titles “Alkylhydrazines” (the chapter at hand), “Dimethylhydrazines,” and “Methylhydrazine.” The current chapter deals with alkylhydrazines in general and alkylhydrazines other than methylhydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH), or symmetrical dimethylhydrazine (SDMH). It also contains a short section on arylhydrazines. All alkylhydrazines are potentially valuable rocket propellant fuels. Alkylhydrazines can contain one to four alkyl groups attached to the hydrazine molecule, replacing one or more hydrogens in  $N_2H_4$  with an alkyl group. For dialkylhydrazines, the two alkyl groups can be attached to either the same nitrogen atom (unsymmetrical dialkylhydrazines, *N,N*-dialkylhydrazines, 1,1-dialkylhydrazines) or to different nitrogen atoms (symmetrical dialkylhydrazines, *N,N'*-dialkylhydrazines, 1,2-dialkylhydrazines). Alkylhydrazines have been called hydrazinoalkanes, but that is an antiquated nomenclature, just like the name “diamine” should no longer be used for hydrazine. The properties of the parent compound, hydrazine, are summarized in the chapter “Hydrazine” of the *Encyclopedia of Liquid Fuels*.

## 1 Alkylhydrazines

The primary objective of this chapter on alkylhydrazines is to summarize the physical and chemical properties and uses of organic hydrazine-derivative fuels. It also includes the higher and substituted alkylhydrazines that do not belong in either of the chapters on mono- or dimethylhydrazines. A book many times the size of the current book volume would have to be written if all organic hydrazine derivatives had to be included. However, this is not necessary because some excellent summaries of organic hydrazine derivatives have already been published, and because only a selected few are used as rocket fuels. The second edition of the book *Hydrazine and Its Derivatives* contains detailed information on all alkylhydrazines, including those of interest as rocket propellants. Other sources (some more historical) of information on alkylhydrazines can be found in [1–12].

Our discussion of organic hydrazine derivatives and their preparation in this chapter is thus restricted to alkylhydrazines that have been considered or have actually been used as rocket propellants. Many other hydrazine derivatives have found applications as herbicides or pharmaceuticals or plastic processing ingredients, and in some instances have benefited from the ready availability of hydrazines that were initially prepared as a result of the missile and space programs. There are many

**Table 1:** Physical properties of methylhydrazines in comparison to hydrazine.

| Property                              | Unit                                                 | N <sub>2</sub> H <sub>4</sub> | MMH                     | UDMH                    | SDMH                    |
|---------------------------------------|------------------------------------------------------|-------------------------------|-------------------------|-------------------------|-------------------------|
| Molecular mass                        | g/mol                                                | 32.0453                       | 46.0724                 | 60.0986                 | 60.0986                 |
| Melting point                         | K                                                    | 275.16                        | 220.78                  | 215.94                  | 264.3                   |
|                                       | °C                                                   | 2.01                          | -52.37                  | -57.21                  | -8.88 ± 0.04            |
|                                       | °F                                                   | 35.6                          | -62.27                  | -70.97                  | 16.02                   |
| Boiling point                         | K                                                    | 387.37                        | 360.80                  | 335.47                  | 354.6                   |
|                                       | °C                                                   | 114.2                         | 87.65                   | 62.32                   | 81.5 °C at<br>753 mm Hg |
|                                       | °F                                                   | 237.6                         | 189.77                  | 144.18                  | 179                     |
| Vapor pressure                        | kPa                                                  | 1.89                          | 6.6                     | 22.3                    | 9.32 kPa                |
|                                       | mm Hg                                                | 14.19                         | 49.47                   | 167.1                   | 69.9                    |
|                                       | psia                                                 | 0.274                         | 0.957                   | 3.23                    | 1.35                    |
| Density, liquid                       | g/cm <sup>3</sup> (lb/ft <sup>3</sup> )              | 1.0037<br>(62.659)            | 0.8702<br>(54.32)       | 0.7861<br>(49.073)      | 0.8274                  |
| Viscosity, liquid                     | cPs                                                  | 0.913                         | 0.775                   | 0.492                   | —                       |
| Surface tension                       | mN/cm =<br>dyn/cm × 10 <sup>2</sup>                  | 0.6645                        | 0.3383                  | 0.2409                  | —                       |
| Thermal conductivity, liquid          | cal cm <sup>-1</sup> K <sup>-1</sup> s <sup>-1</sup> | 1.17 × 10 <sup>-3</sup>       | 5.92 × 10 <sup>-4</sup> | 3.76 × 10 <sup>-4</sup> | —                       |
| Heat capacity, liquid                 | J g <sup>-1</sup> K <sup>-1</sup>                    | 3.0778                        | 2.9296                  | 2.945                   | —                       |
|                                       | cal g <sup>-1</sup> °C <sup>-1</sup>                 | 0.7356                        | 0.7002                  | 0.704                   | —                       |
| Enthalpy of formation, liquid         | kJ/mol                                               | +50.434                       | +54.835                 | +51.626                 | +50.6                   |
|                                       | kcal/mol                                             | +12.054                       | +13.106                 | +12.339                 | +12.1                   |
| Heat of fusion, solid                 | kJ/mol                                               | 12.657                        | 10.420                  | 10.073                  | 13.788 ± 0.02           |
|                                       | kcal/mol                                             | 3.025                         | 2.4905                  | 2.4074                  | 3.2955 ± 0.005          |
| Heat of vaporization at normal bp     | kJ/mol<br>(kcal/mol)                                 | 39.079 (9.34)                 | 37.212<br>(8.894)       | 32.623<br>(7.797)       | —                       |
| Standard entropy, liquid              | J mol <sup>-1</sup> K <sup>-1</sup>                  | 121.21                        | 165.93                  | 200.24                  | —                       |
|                                       | cal mol <sup>-1</sup> °C <sup>-1</sup>               | 28.97                         | 39.66                   | 47.86                   | —                       |
| Standard entropy, vapor               | J mol <sup>-1</sup> K <sup>-1</sup>                  | 238.4                         | 301.3                   | 304.72                  | —                       |
|                                       | cal mol <sup>-1</sup> °C <sup>-1</sup>               | 56.97                         | 72.02                   | 72.83                   | —                       |
| Dielectric constant, liquid           |                                                      | 51.7                          | 19                      | —                       | —                       |
| Dipole moment, liquid                 | Debye units                                          | 1.84                          | 1.68                    | 1.72                    | —                       |
| Index of refraction (n <sub>D</sub> ) |                                                      | 1.4683                        | 1.4284                  | 1.4053                  | 1.4039                  |

Note: All listed property values (except for the heat of vaporization) were obtained at 298 K (25 °C)

methods for the production of alkylhydrazines [13], but only a few of those have actually advanced to the level of industrial-scale production.

### 1.1 Physical Properties of Alkylhydrazines

Table 1 gives a juxtaposition of physical properties of several alkylhydrazines with those of their parent compound, anhydrous hydrazine,  $\text{N}_2\text{H}_4$ . Additional physical properties are listed in individual tables in the following sections on specific alkylhydrazines.

### 1.2 Molecular Structure of Alkylhydrazines

The  $^{14}\text{N}$  nuclear quadrupole resonance spectra at 77 K of several hydrazines were analyzed in the framework of a semi-empirical theory that was extended to cover the case of large asymmetry parameters for the molecules [14]. The atomic-orbital occupation numbers obtained by this analysis were linked with the hydrogen-bonding configuration in the solid state. The results indicated that the hydrogen-bonding ability of the amino nitrogen exceeds that of the substituted nitrogen atom and decreases in the order: hydrazine > alkyl hydrazines > *N*-amino heterocycles > aryl hydrazines. See also [15, 16].

### 1.3 Thermal Stability of Alkylhydrazines

Replacing one or more hydrogens on hydrazine with alkyl groups can improve the thermal stability of this molecule. Some of the cyclic hydrazines have remarkable thermal stability. In most instances, the thermolysis of hydrazine compounds starts with the breaking of the N—N bond.

### 1.4 Toxicity of Alkylhydrazines

Some alkylhydrazines, predominantly 1,2-dimethylhydrazine, symmetrical dimethylhydrazine, SDMH, are distinctly carcinogenic, but not all alkylhydrazines are in the same hazard category [17]. For UDMH, the hazard is higher for its autoxidation product, *N*-nitrosodimethylamine,  $(\text{CH}_3)_2\text{NNO}$ , NDMA, than for the pure alkylhydrazine from which it is derived. In many instances, NDMA was present in UDMH of poor quality, and the toxicity reported in the literature may have been caused by the NDMA contaminant, and not by UDMH itself. Many of the early toxicity studies used UDMH of



inferior quality, UDMH made from NDMA, or they deliberately used the same poor-quality stuff that the soldiers might be exposed to at the missile launch sites.

Alkylhydrazines such as methylhydrazine derivatives occur naturally in mushroom poisons such as gyromitrin [18]. A phenylhydrazine derivative, agaritine, occurs naturally in the commonly eaten brown cap mushrooms.

## 2 Methylhydrazine

See the separate chapter on methylhydrazine in *Encyclopedia of Liquid Fuels*.

## 3 Dimethylhydrazines

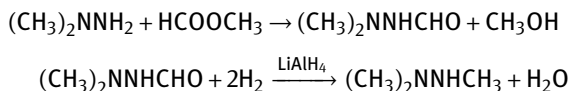
See the separate chapter on dimethylhydrazines in *Encyclopedia of Liquid Fuels*.

## 4 Trimethylhydrazine

Trimethylhydrazine and tetramethylhydrazine have not been used as rocket propellants. They may be encountered as contaminants in UDMH that was prepared by direct methylation of hydrazine. In the search for less toxic replacements for UDMH, trimethylhydrazine and tetramethylhydrazine were good candidates due to their lower vapor pressure and reduced tendency to form nitrosoamines, but no efforts have been made to produce and test them on a larger scale. Trimethylhydrazine or tetramethylhydrazine may be less toxic than UDMH. When looking for methods for the disposal of surplus UDMH by conversion to a useful product, the methylation of UDMH to make trimethylhydrazine or tetramethylhydrazine may be an option if new applications for trimethylhydrazine or tetramethylhydrazine can be found.

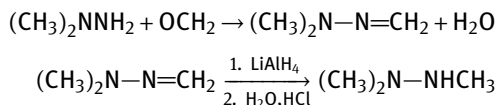
### 4.1 Preparation of Trimethylhydrazine

Trimethylhydrazine can be obtained in 63.8% yield by reduction of 1,1-dimethyl-2-formylhydrazine with lithium aluminum hydride [19], which is prepared from UDMH and methyl formate:



Continuation of this methylating reaction using trimethylhydrazine instead of UDMH as a starting material leads to tetramethylhydrazine.

Trimethylhydrazine and tetramethylhydrazine were first prepared in 1952 [20, 21]. These compounds were not accessible by direct methylation of hydrazine with dimethyl sulfate. Instead, trimethylhydrazine was prepared by reduction of formaldehyde 1,1-dimethylhydrazone (methylene-dimethylhydrazine) with lithium aluminum hydride:



Trimethylhydrazine can be prepared in two steps from UDMH, using an easy-to-scale-up procedure that avoided difficult acid–base extractions [22]. The procedure provided trimethylhydrazine as a solution in 1,4-dioxane.

## 4.2 Physical Properties of Trimethylhydrazine and Tetramethylhydrazine

For the sake of saving space, the physical properties of trimethylhydrazine and tetramethylhydrazine have been combined here in one place, Table 2. The properties are quite different from those of MMH or UDMH, illustrating the effect of progressive methylation on the physical properties of the hydrazine ( $\text{H}_2\text{NNH}_2$ ) molecule.

The IR and Raman spectra of liquid and gaseous trimethylhydrazine have been measured, and can be used to check for the presence of trimethylhydrazine as an impurity in UDMH [28]. The vapor-phase spectra of trimethylhydrazine reported there were later shown to be mostly those of oxidation products such as methylene dimethylhydrazine (formaldehyde dimethylhydrazone) [29]. The later study used a 10-cm cell and scanned spectra from 2 to 15  $\mu\text{m}$ . Their liquid trimethylhydrazine spectra agreed with those reported by Shull et al., but the vapor spectra were quite different.

### 4.2.1 Molecular Structure of Trimethylhydrazine

Trimethylhydrazine can exist as stereoisomers: *cis*-trimethylhydrazine and *trans*-trimethylhydrazine. Using *ab initio* calculations of the trimethylhydrazine molecule, it was shown that the *anti* and *syn* conformers occupy energy maxima when the molecule is rotating around the N–N bond [30].

## 4.3 Chemical Properties of Trimethylhydrazine

The autoxidation of trimethylhydrazine leads to formaldehyde dimethylhydrazone [29]. Trimethylhydrazine can be identified by its mass spectrum [31]. Trimethylhydrazinium nitrate, perchlorate, dinitramide, azide, nitroformate, and 5-aminotetrazolate have been characterized as energetic materials [32].

**Table 2:** Physical properties of trimethylhydrazine and tetramethylhydrazine.

| Property              | Empirical formula | Compound name        | SI units                                         | Other units                                 | References |
|-----------------------|-------------------|----------------------|--------------------------------------------------|---------------------------------------------|------------|
| Melting point         | $C_3H_{10}N_2$    | Trimethylhydrazine   | $155 \pm 10$ K                                   | $-118 \pm 10$ °C                            | [21]       |
|                       |                   |                      | 201.24                                           | -71.9                                       | [23, 24]   |
|                       | $C_4H_{12}N_2$    | Tetramethylhydrazine | 169 K                                            | -104 °C                                     | [25]       |
| Boiling point         | $C_3H_{10}N_2$    | Trimethylhydrazine   | 346 K at 97 kPa                                  | 73 °C at 730 mm Hg                          | [21]       |
|                       | $C_3H_{10}N_2$    |                      | 332 K at 98.6 kPa                                | 59 °C at 740 mm Hg                          | [26]       |
|                       | $C_4H_{12}N_2$    | Tetramethylhydrazine | 344–345 K                                        | 71–72 °C                                    | [19]       |
|                       | $C_4H_{12}N_2$    |                      |                                                  | at 760 mm Hg                                |            |
| Density               | $C_4H_{12}N_2$    |                      | 345.9 K                                          | 72.9 °C at 760 mm Hg                        | [25]       |
|                       | $C_3H_{10}N_2$    | Trimethylhydrazine   | 0.814 g/cm <sup>3</sup> at 291 K                 | —                                           | [26]       |
|                       | $C_3H_{10}N_2$    | Trimethylhydrazine   | 0.7794 g/cm <sup>3</sup> at 293 K                | —                                           | [21]       |
|                       | $C_4H_{12}N_2$    | Tetramethylhydrazine | 0.768 g/cm <sup>3</sup> at 297 K                 | —                                           | [19]       |
| Heat capacity         | $C_3H_{10}N_2$    | Trimethylhydrazine   | 186 J mol <sup>-1</sup> K <sup>-1</sup> at 298 K | 44.5 cal mol <sup>-1</sup> °C <sup>-1</sup> | [27]       |
| Enthalpy of formation | $C_4H_{12}N_2$    | Tetramethylhydrazine | +47.9 kJ/mol                                     | +11.4 kcal/mol                              | [25]       |
| Heat of fusion        | $C_3H_{10}N_2$    | Trimethylhydrazine   | 9.485 kJ/mol                                     | 2267 cal/mol                                | [24]       |
| Heat of vaporization  | $C_3H_{10}N_2$    | Trimethylhydrazine   | 33.26 ± 0.03 kJ/mol                              | 7949 ± 7 cal/mol                            | [24]       |
| Index of refraction   | $C_3H_{10}N_2$    | Trimethylhydrazine   | 1.4040 at 293 K                                  | —                                           | [21]       |
|                       | $C_3H_{10}N_2$    | Trimethylhydrazine   | 1.406 at 291 K                                   | —                                           | [21]       |
|                       | $C_4H_{12}N_2$    | Tetramethylhydrazine | 1.40138 at 298 K                                 | —                                           | [19]       |

#### 4.4 Toxicity of Trimethylhydrazine

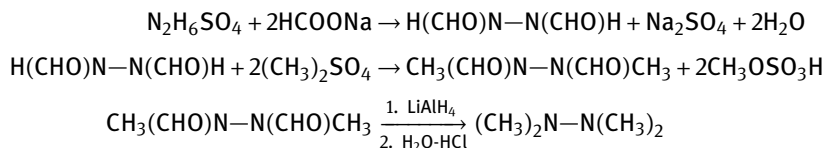
The reason for studying the toxicities of trimethylhydrazine and tetramethylhydrazine was to see if reducing the number of reactive N—H bonds in hydrazines would also reduce their toxicity. Giving 0.05% trimethylhydrazine hydrochloride solution to Swiss mice with their drinking water throughout their lives increased the incidence of blood vessel tumors from 5 (control group) to 85, lung tumors from 22 to 44, and kidney tumors from 0 to 6 [33, 34]. Histopathologically, tumors were classified as angiosarcomas of blood vessels and adenomas of the lungs and kidneys. Similar results were obtained with trimethylhydrazine in Syrian golden hamsters [35].

## 5 Tetramethylhydrazine

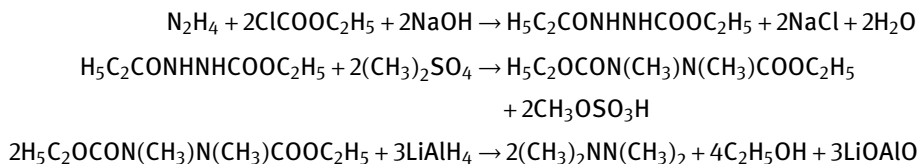
Tetramethylhydrazine is not likely to be used as a rocket propellant. It is more difficult to prepare than UDMH. Tetramethylhydrazine may be a contaminant in UDMH that was prepared by direct methylation of hydrazine or MMH. Tetramethylhydrazine may be less toxic than UDMH.

### 5.1 Preparation of Tetramethylhydrazine

The first preparation of tetramethylhydrazine started with hydrazine, and involved converting it to the 1,2-diformylhydrazine by reaction with sodium formate, methylating the two free NH groups with dimethyl sulfate, and reducing the formyl groups with lithium aluminum hydride [21]:



The yield in this lengthy process was only very low (15%). Other investigators followed a different route by using methyl formate instead of sodium formate and again reducing the formyl compound with lithium aluminum hydride [19]. The yield was 55% in the last step and 63.5% in the first step, resulting in an overall yield of 35%. Tetramethylhydrazine and methyl iodide or bromide form crystalline pentamethylhydrazonium salts. The mechanism of the reaction of trimethylhydrazine with formic acid and subsequent reduction with formaldehyde under the evolution of carbon dioxide is not quite clear, but the product is tetramethylhydrazine, which can be distilled from the mixture of reaction products as an azeotrope with water [36]. Very good yields (35% based on hydrazine as a starting material) can be obtained by reacting hydrazine hydrate with chloroformic acid ethyl ester, methylating with dimethyl sulfate, and reducing with lithium aluminum hydride [37]:



Eleven different tetraalkylhydrazines, most of them including heterocyclic rings, have been prepared by using cyanoborohydride in place of lithium aluminum hydride as a reducing agent [38]. The yield ranged from 27 to 59%.

Tetramethylhydrazine was first prepared in 1952 [20, 21]. This compound was not accessible by direct methylation of hydrazine with dimethyl sulfate.

Tetramethyltetrazene, readily prepared by oxidation of UDMH (see *Encyclopedia of Liquid Fuels*, chapter Dimethylhydrazines), will split off molecular nitrogen by photolytic decomposition under UV light, resulting in the formation of tetramethylhydrazine [39, 40].

Hydrazine hydrate and formamide were used as starting materials to form *N,N'*-diformylhydrazine and then reacted with dimethyl sulfate to make *N,N'*-dimethyl-*N,N'*-diformylhydrazine by methylation. Finally, reduction by lithium aluminum hydride yielded tetramethylhydrazine in an overall yield of 15% [41].

## 5.2 Physical Properties of Tetramethylhydrazine

Physical properties of tetramethylhydrazine are included in Table 2 above. The IR spectra of trimethylhydrazine and tetramethylhydrazine are included in a catalog of IR spectra for the qualitative analysis of gases [42]. This useful summary also includes IR spectra of 30 other compounds found in propellant mixtures. Tetramethylhydrazine showed absorption bands at the following wavenumbers (in  $\text{cm}^{-1}$ ) [25]: 3000(vs), 2960(vs), 2830(vs), 2780(vs), 1450(vs), 1231(vs), 1201(w), 1151(vs), 1089(s), 1026(vs), 969(w), 712(s), 508(s), and 435(w). An extended scan of spectra of gaseous and solid tetramethylhydrazine in the far IR in comparison to Raman spectra provided some insight into the molecular structure of tetramethylhydrazine [43]. Most of the fundamental vibrations could be assigned to specific bonds and atom groups in the molecules. Tetramethylhydrazine exists in the *gauche* conformation and has  $C_2$  symmetry in all phases. Like hydrazine itself, tetramethylhydrazine also exists preferentially in the *gauche* form and has  $C_2$  symmetry in all phases.

The IR spectrum of gaseous tetramethylhydrazine has been measured from 4500 to  $400\text{ cm}^{-1}$  using a conventional prism spectrometer [44]. The region below  $1500\text{ cm}^{-1}$  has also been investigated in the liquid and solid states, in solution, and in the gas phase at 393 K (120 °C). The spectra in the gaseous and condensed phases were similar, with the exception of a few bands, and possible reasons for their appearance were suggested. No alteration in the spectrum occurred with a change in temperature, which can be attributed to the occurrence of more than one structural isomer.

### 5.2.1 Molecular Structure of Tetramethylhydrazine

The molecular structure of tetramethylhydrazine has been investigated by electron diffraction in the gas phase [45]. Diffraction intensities can be explained by a mixture of *gauche* and *trans* conformations in a 70:30% ratio. The structure parameters are  $r(\text{C}-\text{H}) = 1.096\text{ \AA}$ ,  $r(\text{C}-\text{N}) = 1.463\text{ \AA}$ ,  $r(\text{N}-\text{N}) = 1.410\text{ \AA}$ ,  $\angle\text{NCH} = 108.6^\circ$ ,  $\angle\text{CNC} = 110.8^\circ$ , and  $\angle\text{NNC} = 113.5^\circ$ . For the *gauche* conformation, the dihedral angle between two vicinal methyl groups was  $78.5^\circ$ .

Based on Molecular Mechanics 3 (MM3) computational studies, the theoretical N—N bond length for tetramethylhydrazine is  $1.436 \times 10^{-10}$  m, indicating that experimental values ( $1.401 \times 10^{-10}$  m) probably err on the low side [46].

### 5.3 Toxicity of Tetramethylhydrazine

Given the tumor-inducing activities of the three lower methylhydrazines, it is not surprising to find that there was the same effect with tetramethylhydrazine when using Swiss mice as test animals [47]. Tetramethylhydrazine hydrochloride predominantly produced blood vessel tumors in 92% of the mice. Trimethylhydrazine or tetramethylhydrazine are not nearly as active carcinogens as SDMH.

## 6 Other Alkylhydrazines and Their Salts

Besides methyl hydrazines, alkylhydrazines with longer alkyl chains and arylhydrazines have been considered as rocket fuels. They do not exhibit any advantage over methylhydrazines and have never seen flight use. Some of the other alkylhydrazines and their hydrazides are being used for the synthesis of heterocyclic compounds.

*tert*-Butylhydrazinium azide [*tert*-BuNH<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>[N<sub>3</sub>]<sup>−</sup> was prepared from *tert*-butylhydrazine and hydrazoic acid [48, 49]. *N,N,N*-Trimethylhydrazinium azide [NH<sub>2</sub>-N(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>[N<sub>3</sub>]<sup>−</sup> was prepared via the reaction of silver azide with *N,N,N*-trimethylhydrazinium iodide. Both salts were characterized by XRD, IR, Raman, and multinuclear <sup>1</sup>H-, <sup>13</sup>C-, and <sup>14</sup>N-NMR spectroscopy.

### 6.1 Alkenylhydrazines

Vinylhydrazines and allylhydrazines could be used as intermediates for the synthesis of alkylhydrazines with substituents other than hydrogen in the alkyl groups by addition to the double bond(s) in the alkenyl rests. They could also be used as hypergolic fuels in place of or in mixtures with other alkylhydrazines. If vinylhydrazine or its salts could be polymerized without breaking the N—N bond, one could make a polyvinylhydrazine that should be a good solid-propellant binder [50].

It was not possible to make methylvinylhydrazine by partial reduction of methylvinyl nitrosamine [51, 52]. Instead, 1-ethyl-1-methylhydrazine was obtained.

The reaction of triallylamine with hydroxylamine-*O*-sulfonic acid gave a salt of triallylhydrazine and the triallylhydrazine itself was liberated by reaction with sodium methoxide [53]. Triallylhydrazine was separated by distillation at 358 K at 5 kPa (85 °C at 37 mm Hg). *N,N*-dimethyl-*N'*-allylhydrazine was obtained by a similar method.

## 6.2 Alkynylhydrazines

Hydrazines with extremely high heat of combustion values are obtained by substituting one or several hydrogens with alkynyl (alkyne) groups. Alkynylamines were already examined for the same reason. Alkynylhydrazines were patented as high-energy rocket fuels [54]. According to that patent, (2-propynyl)hydrazine and 1,1-bis-(2-propynyl)hydrazine freeze at approximately 213 and 228 K (−60 and −45°C) and boil at 336–339 K at 2.26 kPa pressure (63–66°C at 17 mmHg pressure) or at 334–336 K at 0.5 kPa pressure (61–63°C at 4 mmHg pressure), respectively. Dimethyl(2-propynyl)amine and allyl-di(2-propynyl)amine freeze at approximately 229 K (−44°C) and 213 K (−60°C), respectively. The compounds possess very high heats of combustion, as shown in Table 3.

**Table 3:** Heats of combustion of alkynylhydrazines.

| Compound                         | Heat of combustion |         |
|----------------------------------|--------------------|---------|
|                                  | kJ/kg              | kcal/kg |
| (2-Propynyl)hydrazine            | 32635              | 7800    |
| 1,1-Bis(2-propynyl)hydrazine     | 37070              | 8860    |
| 1-Methyl-1-(2-propynyl)hydrazine | 34895              | 8340    |
| 1-Ethyl-1-(2-propynyl)hydrazine  | 36230              | 8660    |
| Methyl-di-(2-propynyl)hydrazine  | 41000              | 9800    |
| Dimethyl-(2-propynyl)hydrazine   | 39960              | 9550    |

Data source: [54]

Direct alkylation of hydrazine hydrate in ethanol with propargyl bromide gives 2-propynylhydrazine and 1,1-di(2-propynyl)hydrazine [55]. Efforts, not always successful, were made to synthesize monopropargylhydrazine and *N*-methyl-*N*-propargylhydrazine [56]. Monopropargylhydrazine and unsymmetrical dipropargylhydrazine were evaluated as hypergolic rocket fuels [57].

## 6.3 Preparation of Other Alkylhydrazines

There are 20 conceivable methyl- and ethyl-substituted hydrazines. Only three are available commercially: MMH, UDMH, and SDMH. Until 1973, only 12 additional ones were described in the literature. When the need arose to investigate all 20 compounds, the missing (previously unknown) five alkylhydrazines were synthesized using standard routes [58, 59]. The new hydrazines and their methods of synthesis are summarized in Table 4.

Table 4: Summary of reactions used in syntheses of methyl- and ethyl-substituted hydrazines.

|                             |                                                |                                                        |                                       |                                                                |                                            |                                              |                                         |                                            |
|-----------------------------|------------------------------------------------|--------------------------------------------------------|---------------------------------------|----------------------------------------------------------------|--------------------------------------------|----------------------------------------------|-----------------------------------------|--------------------------------------------|
| $\text{Me}_2\text{NNH}_2$   | $\xrightarrow{\text{CH}_2\text{O}}$            | $\text{Me}_2\text{NN}=\text{CH}_2$                     | $\xrightarrow{\text{LiAlH}_4}$        | $\text{Me}_2\text{NNHMe}$                                      | $\xrightarrow{\text{EtOCHO}}$              | $\text{Me}_2\text{NN}=\text{MeCHO}$          | $\xrightarrow{\text{LiAlH}_4}$          | $\text{Me}_2\text{NNHMe}_2$                |
| $\text{Me}_2\text{NNHMe}$   | $\xrightarrow{\text{Ac}_2\text{O}}$            | $\text{Me}_2\text{NN}(\text{Ac})\text{Me}$             | $\xrightarrow{\text{LiAlH}_4}$        | $\text{Me}_2\text{NNEtMe}$                                     |                                            |                                              |                                         |                                            |
| $\text{EtNHCONHET}$         | $\xrightarrow{\text{NaNO}_2}$                  | $\text{EtN}(\text{NO})\text{CONHET}$                   | $\xrightarrow{\text{Zn, HOAc}}$       | $\text{EtN}(\text{NH}_2)\text{CONHET}$                         | $\xrightarrow{\text{H}_2\text{O, HCl}}$    | $\text{EtNHNH}_2$                            | $\xrightarrow{\text{NaOH}}$             | $\text{EtNHNH}_2$                          |
| $\text{MeNHNH}_2$           | $\xrightarrow{\text{Ac}_2\text{O}}$            | $\text{MeNAcNH}_2$                                     | $\xrightarrow{\text{CH}_3\text{CHO}}$ | $\text{MeNAcN}=\text{CHCH}_3$                                  | $\xrightarrow{\text{NaBH}_4, \text{EtOH}}$ | $\text{MeN}(\text{Ac})=\text{NHET}$          | $\xrightarrow{\text{H}_2\text{O, HCl}}$ | $\text{MeNHNHET}$                          |
| $\text{NH}_2\text{NH}_2$    | $\xrightarrow{\text{CH}_3\text{CHO}}$          | $\text{CH}_3\text{CH}=\text{N}=\text{N}-\text{CHCH}_3$ | $\xrightarrow{\text{LiAlH}_4}$        | $\text{EtNHNHET}$                                              |                                            |                                              |                                         | $\xrightarrow{\text{NaOH}}$                |
| $\text{Me}_2\text{NNH}_2$   | $\xrightarrow{\text{CH}_3\text{CHO}}$          | $\text{Me}_2\text{NN}=\text{CHCH}_3$                   | $\xrightarrow{\text{LiAlH}_4}$        | $\text{Me}_2\text{NNHET}$                                      | $\xrightarrow{\text{Ac}_2\text{O}}$        | $\text{Me}_2\text{NN}(\text{Ac})\text{Et}$   | $\xrightarrow{\text{LiAlH}_4}$          | $\text{Me}_2\text{NNAEt}_2$                |
| $\text{EtNH}_2$             | $\xrightarrow{\text{C}_6\text{H}_5\text{CHO}}$ | $\text{PhCH}=\text{N}=\text{Et}$                       | $\xrightarrow{\text{MeSO}_4}$         | $[\text{PhCH}=\text{N}^+(\text{Me})\text{Et}]=\text{MeSO}_4^-$ | $\xrightarrow{\text{H}_2\text{O}}$         | $[\text{EtMeN}^+\text{H}_2]=\text{MeSO}_4^-$ | $\xrightarrow{\text{NaNO}_2}$           | $\text{EtMeNNO}$                           |
| $\text{EtMe}_2\text{NNH}_2$ | $\xrightarrow{\text{CH}_2\text{O}}$            | $\text{EtMeNN}=\text{CH}_2$                            | $\xrightarrow{\text{LiAlH}_4}$        | $\text{EtMeNNHMe}$                                             | $\xrightarrow{\text{Ac}_2\text{O}}$        | $\text{EtMeNN}=\text{Me}(\text{Ac})$         | $\xrightarrow{\text{LiAlH}_4}$          | $\text{EtMeNNEtMe}$                        |
| $\text{Et}_2\text{NH}$      | $\xrightarrow{\text{NaNO}_2, \text{HCl}}$      | $\text{EtMeNN}=\text{CH}_2$                            | $\xrightarrow{\text{CH}_3\text{MgI}}$ | $\text{EtMeNNHET}$                                             |                                            |                                              |                                         |                                            |
|                             |                                                | $\text{Et}_2\text{NNO}$                                | $\xrightarrow{\text{Zn, HOAc}}$       | $\text{Et}_2\text{NNH}_2$                                      | $\xrightarrow{\text{CH}_3\text{O}}$        | $\text{Et}_2\text{NN}=\text{CH}_2$           | $\xrightarrow{\text{LiAlH}_4}$          | $\text{Et}_2\text{NNHMe}_2$                |
|                             |                                                |                                                        |                                       |                                                                |                                            |                                              |                                         | $\xrightarrow{\text{Ac}_2\text{O}}$        |
|                             |                                                |                                                        |                                       |                                                                |                                            |                                              |                                         | $\text{Et}_2\text{NN}(\text{Ac})\text{Me}$ |
|                             |                                                |                                                        |                                       |                                                                |                                            |                                              |                                         | $\xrightarrow{\text{LiAlH}_4}$             |
|                             |                                                |                                                        |                                       |                                                                |                                            |                                              |                                         | $\text{Et}_2\text{NN}(\text{Et})\text{Me}$ |
|                             |                                                |                                                        |                                       |                                                                |                                            |                                              |                                         | $\xrightarrow{\text{LiAlH}_4}$             |
|                             |                                                |                                                        |                                       |                                                                |                                            |                                              |                                         | $\text{Et}_2\text{NNEt}_2$                 |

<sup>a</sup> Legend: Ac = acetyl, Et = ethyl, Me = methyl, Ph = phenyl

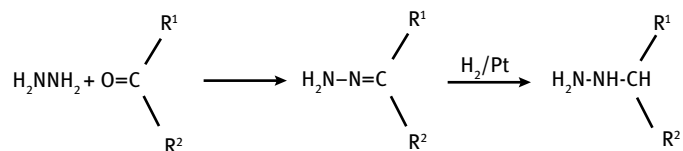


Lithium aluminum hydride proved to be a useful synthetic tool during this effort because it reduces formaldehyde hydrazones to methylhydrazines and acethydrazides to ethylhydrazines. These methods were preferred over the direct alkylation because they result in fewer by-products.

When preparing tetraalkylhydrazines by  $\text{LiAlH}_4$  reduction of acylhydrazines, the products were frequently contaminated by trialkylhydrazine formed by cleavage of the *N*-acyl bond. This unwanted by-product was converted to a high-boiling acetyl derivative with acetic anhydride, and then the lower-boiling tetraalkylhydrazine, which does not react with acetic anhydride, could be removed by distillation.

### 6.3.1 Preparation of Other Alkylhydrazines (Monoalkylhydrazines)

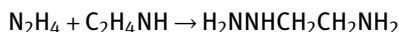
Higher alkylhydrazines and substituted hydrazines are not used as rocket propellants but are sometimes investigated in stability and molecular structure studies comparing them to MMH or UDMH. All alkylhydrazines are useful reactants in the synthesis of heterocyclic compounds with two or more nitrogens in the ring. Higher alkylhydrazines and substituted hydrazines can frequently be prepared by using the same methods used for MMH. In addition, other methods have been described that produce only poor yields for the lowest member of the alkylhydrazine family. Some of these methods can be used to synthesize alkylhydrazines with substituents in the alkyl group, resulting in more energetic or less toxic hydrazines. A very comprehensive survey article on the preparation and reactions of monoalkylhydrazines contained 363 references [7]. The following hydrazone method can be used, which can start with hydrazine hydrate instead of anhydrous hydrazine:



Reaction rates and activation energies for the reactions of chloramine with *n*-propylamine, *n*-butylamine, or di-*n*-propylamine in liquid ammonia solvent, leading to *n*-propylhydrazine, *n*-butylhydrazine, or *N,N*-di-*n*-propylhydrazine, showed that replacement of the hydrogen in ammonia by an alkyl group greatly enhances the reactivity of the amino compound toward chloramine [60]. At 223 K, replacement of one hydrogen by propyl increased the reaction rate 140-fold. Replacement of two hydrogens by propyl groups increased the rate of reaction with chloramine 460-fold. These reactions led to substituted alkylhydrazines in good yields, although the yields were limited by side reactions of product hydrazines with chloramine. The reaction of amines with chloramine proved to be a generally useful method for the synthesis of alkylhydrazines, as illustrated by the conversion of *n*-hexylamine and cyclohexy-

lamine to the corresponding hydrazines, allylamine to allylhydrazine, ethanolamine to  $\beta$ -hydroxyethylhydrazine, ethylenediamine to  $\beta$ -aminoethylhydrazine, and morpholine to *N*-aminomorpholine [61]. The reaction of glycine with chloramine did not give the desired hydrazinoacetic acid, because the mixture decomposed prematurely. Piperylhydrazine can be obtained by bubbling a chloramine-ammonia mixture at a rate of 0.8 mM/min through 150 mL of piperidine for 45 min, removing the amine salt by filtration and unreacted piperidine by distillation [62]. The yellow oily distillation residue was reacted with benzaldehyde to extract the piperylhydrazine as the corresponding hydrazone in 50% yield. 2-Pentylhydrazine can be obtained by reducing the hydrazone of methyl propyl ketone with hydrogen and platinum oxide [63]. The same method has been used for 3-cyclohexyl-2-propylhydrazine [64]. Sterically bulky groups (*tert*-butyl or benzyl) favor monosubstitution. Although the yields were not economically attractive, the following monoalkylhydrazines have been prepared from the corresponding alkyl bromides and a fivefold molar excess of hydrazine: ethylhydrazine, *n*-butylhydrazine, and *n*-nonylhydrazine [65]. Alkylation of hydrazine hydrate with  $\text{ClCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$  leads to  $\beta$ -diethylaminoethylhydrazine,  $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NHNH}_2$ , a potential rocket fuel [66].

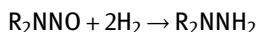
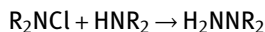
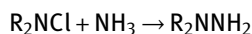
The reaction of aziridine (ethyleneimine) with hydrazine produces  $\beta$ -aminoethylhydrazine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHNH}_2$ , also a potential rocket fuel [67, 68]:



A homologous series of *n*-aliphatic hydrazines, ethyl- through *n*-amyl hydrazines, and isopropyl hydrazine and hydroxyethylhydrazine were prepared from the corresponding amines [1]. The yields were typically around 40% of the theoretically expected yields. The most convenient way to isolate the new hydrazines was in the form of their sparingly soluble oxalates.

### 6.3.2 Preparation of Other Dialkylhydrazines

Some of the methods described for UDMH and SDMH are also applicable to higher dialkyl hydrazines. The following reactions have been used to prepare unsymmetrical dialkylhydrazines:



The Sisler process can be modified by reacting chlorine with a secondary amine first and then reacting the substituted chloramine with aqueous or anhydrous ammonia in the presence of caustic [69–71] or reacting a dialkylchloramine with an excess of ammonia in a pressure bomb [72].

The following alkylhydrazines have been prepared by reaction of chloramine with anhydrous primary and secondary amines: methylhydrazine; ethylhydrazine; isopropylhydrazine; *unsym*-dimethylhydrazine; *unsym*-diisopropylhydrazine; and *N*-aminopiperidine [62]; as well as cyclohexylhydrazine, and butylhydrazine [73]. Surprisingly, the reaction of chloramine with diethylamine resulted only in the formation of monoethylhydrazine because of the loss of an ethyl group. This is in contrast to the formation of 1,1-dimethylhydrazine, 1,1-diethylhydrazine, 1,1-di-*n*-propylhydrazine, and di-*n*-butylhydrazine in 40–50% yield by reaction of chloramine and secondary amines in aqueous solution [74]. The 1,1-dialkylhydrazines were identified as the sparsely soluble oxalates.

Like UDMH itself, most other unsymmetrical dialkylhydrazines can be prepared by reduction of the corresponding secondary nitrosamines. The methods described in the literature vary mostly with regard to the reducing agent used. Thus 1,1-diethylhydrazine was obtained in 75% yield by reduction of the nitrosamine with aluminum flakes and sodium hydroxide [75, 76]. 1,1-Diisopropylhydrazine,  $[(\text{H}_3\text{C})_2\text{C}]_2\text{NNH}_2$ , CAS RN [921-14-2], with a boiling point of 315–316 K at 1.7–2.1 kPa (42–43 °C at 13–16 mm Hg), was prepared by the same method. The catalytic reduction of nitrosamines with hydrogen on a palladium catalyst is applicable to higher dialkylhydrazines as well [77]. The following 1,1-dialkylhydrazines were prepared from the corresponding secondary amines by nitrosation with  $\text{NaNO}_2\text{-HCl}$ , separation of the nitrosamine, and reduction with zinc amalgam [78]: 1,1-diethylhydrazine, 1-methyl-1-*n*-propylhydrazine, 1-methyl-1-isopropylhydrazine, 1-methyl-1-*n*-butylhydrazine, 1-methyl-1-isobutylhydrazine, 1,1-di-*n*-propylhydrazine, and di-*n*-butylhydrazine. Reduction of *N*-nitrosodialkylamines with lithium aluminum hydride in ether gave 1,1-diethylhydrazine or 1,1-diisopropylhydrazine in 55–58% yield [79].

1,1-Diethylhydrazine was obtained by thermal decomposition and treatment with alkali of what was called *diethyl hydroxyurea*,  $(\text{C}_2\text{H}_5)_2\text{N-CO-NHOH}$  [80]. Its reaction product with phenyl isocyanate was a well-crystallized derivative,  $\text{C}_6\text{H}_5\text{-N=C=N-N}(\text{C}_2\text{H}_5)_2$ , melting point 398 K.

The reaction of primary amines with hydroxylamine-*O*-sulfonic acid that leads to alkyl- and arylhydrazines can also be applied to secondary amines to form 1,1-dialkylhydrazines in good yields [81]. 1,1-Diethylhydrazine, 1,1-di-*n*-butylhydrazine, and *N*-aminopiperidine have been prepared by this route. The reaction of hydroxylamine-*O*-sulfonic acid with tertiary amines gave quaternary hydrazinium compounds, such as 1,1,1-trimethylhydrazinium iodide from trimethylamine, hydroxylamine-*O*-sulfonic acid, and hydrogen iodide. These hydrazinium salts can also be precipitated as their well-crystallized oxalates or picrates.

A useful source of free alkyl radicals for kinetic studies is the thermolysis of azoalkanes. Azoalkanes are obtained in over 90% yield by oxidation of 1,2-dialkylhydrazines with mercury(II) oxide in water. 1,2-Diethylhydrazine was prepared in 80% yield by reduction of ethylideneazine with lithium alanate [82]. The azine was first made by reacting an excess of acetaldehyde with hydrazine hydrate.

1,2-Di-*n*-propylhydrazine was prepared by similar methods in 77% yield, and 1,2-diisopropylhydrazine in 81% yield. Mixed dimethyl alkylhydrazines (e.g., 1-ethyl-2,2-dimethylhydrazine) were obtained by reduction of 1-acetyl-2,2-dimethylhydrazine [83].

Direct alkylation with alkylhalogenides, as already discussed for trimethyl and tetramethylhydrazine, can be used to synthesize the higher trialkyl- and tetraalkylhydrazines, also in mixed configurations. Reacting unsymmetrical dibutylhydrazine in ethylene glycol dimethyl ether with butyl bromide in the presence of sodium hydride gave tributylhydrazine in 54% yield and tetrabutylhydrazine in 6% yield [84].

### 6.3.3 Preparation of Dialkynylhydrazines

Triple  $C\equiv C$  bonds derived from acetylene derivatives can increase the energy content of molecules. Thus, instead of physically mixing acetylene and hydrazine, the triple bonds can be included in the alkyl (i.e., alkynyl) groups attached to hydrazine. Monopropargylhydrazine and unsymmetrical dipropargylhydrazine were evaluated as rocket fuels [57].

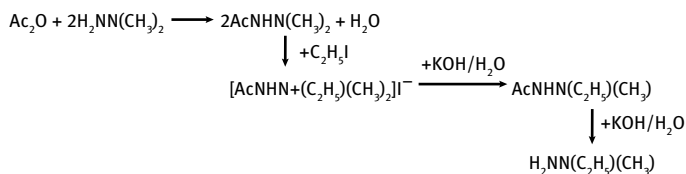
## 6.4 Preparation and Properties of Tri- and Tetraalkylhydrazines

The preparation of trimethylhydrazine and tetramethylhydrazine is described in Section 4.1. Here we discuss tri- and tetraalkylhydrazines with alkyl groups other than methyl. The reaction of chloramine with tertiary amines results in the formation of 1,1,1-trisubstituted hydrazinium salts [85–87]. The salts of trimethyl-, triethyl-, tri-*n*-propyl-, tri-*n*-heptyl-, 1,1-dimethyl-1-phenyl-, and 1,1-diethyl-1-phenylhydrazine have been characterized as chlorides, hexafluorophosphates, picrates, nitrates, and perchlorates. A summary of quaternary hydrazine compounds was compiled [88]. Paired with different anions, such as dicyanomethanide, some of these quaternary salts can serve as ionic liquids.

In analogy to quaternary ammonium salts, quaternary hydrazinium salts can be converted to hydrazinium hydroxides by reaction with silver oxide. The same method can also be applied to obtain quaternary hydrazinium salts of long-chain aliphatic hydrazines.

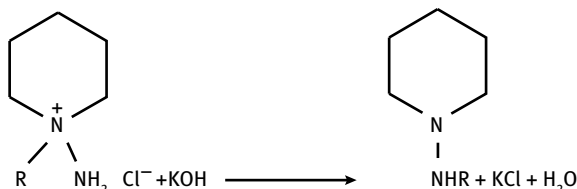
Tetraalkylhydrazines can be prepared by photolysis of tetraalkyltetrazenes [39, 89]. Tetramethylmethylenediamine and trimethyltrimethylenetriamine were formed as byproducts.

An amino (hydrazino) group can be protected from unwanted alkylation by acetylation. Acetodimethylhydrazide, obtained from UDMH and acetic anhydride, can be alkylated with ethyl iodide to form a quaternary compound which, on hydrolysis and elimination of one methyl group, gives 1-methyl-1-ethylhydrazine [90]:



The procedure can be repeated with the elimination of the second methyl group, resulting in 1,1-diethylhydrazine-. Similarly, methylpropylhydrazine and 1,1-dipropylhydrazine have been prepared in good yields. 1,2-Diethyl-1,2-dimethylhydrazine can be prepared by reduction of 1,2-diacetyl-1,2-dimethylhydrazine [83].

Substituted *N*-amino-piperidine derivatives were prepared by reaction of quaternary hydrazinium salts with aqueous NaOH, KOH, or Na<sub>2</sub>CO<sub>3</sub> [91]:



where R = methyl, isopropyl, cyclohexyl.

## 6.5 Preparation of Alkylene Dihydrazines

The simplest alkylene dihydrazine, methylene dihydrazine, was prepared by reaction of hydrazine with tris(chloromethyl)amine or the boron trifluoride BF<sub>3</sub> adduct of 1,3,5-trimethylhexahydro-*s*-triazine and characterized spectroscopically [92]. The reaction between methylhydrazine and tris(chlormethyl)amine gave 1,4-dimethylhexahydro-*s*-tetrazine.

Methylene dihydrazine is not very stable. Its homologue, 1,2-dihydrazinoethane (also called ethylene dihydrazine, EDH), can be prepared from 1,2-dichloroethane and an excess of hydrazine hydrate, and has been evaluated as a hypergolic rocket fuel on its own or in mixtures with UDMH [93, 94].

The reduction of nitrosamines can also be used to synthesize aliphatic dihydrazines, aminohydrazines, and aminodihydrazines of general structure H<sub>2</sub>NNR(CH<sub>2</sub>)<sub>*n*</sub>NRX with R = methyl, ethyl, *n*-propyl, or isopropyl groups, *n* = 2 or 3, and X = H or NH<sub>2</sub> [95]. The hydrazines were characterized in the form of their dihydrazones with 4-nitrobenzaldehyde and of hydrazides of aliphatic carbonic acids, and can be used as hypergolic fuels.

## 7 Omega-Substituted C<sub>2</sub>–C<sub>5</sub> Alkylhydrazines

Alkylhydrazines with alkyl groups that contain two to five carbon atoms are of less interest as rocket propellants but are included here mostly for comparison and because of theoretical studies. 1,1-Diethylhydrazine, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NNH<sub>2</sub>, C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>, CAS RN [616-40-0], *M* = 88.15 g/mol, might be a substitute for UDMH with lower vapor pressure and almost equal rocket performance. Very little work has been done on 1,1-diethylhydrazine. Its boiling point is 372 K (99 °C) and its density is 0.8004 g/cm<sup>3</sup> at 293 K (20 °C).

The enthalpy of formation of *N,N'*-di-*n*-butylhydrazine vapor is –59.4 kJ/mol.

If simple alkyl substitution of hydrogens in hydrazine does not result in alkylhydrazine fuels with the desired attributes, the physical and chemical properties of alkylhydrazines can be modified further by substituting hydrogens in the alkyl group with additional hydroxyl, amino, cyano, azido, or hydrazino groups. Alpha substitution in methylhydrazines is not possible because double substitution on methyl groups makes these compounds very unstable. Beta and higher (omega) substitution in higher (C<sub>*n* ≥ 2</sub>) alkylhydrazines leads to a group of alkylhydrazines with interesting physical properties – in particular, much lower vapor pressures, which makes them easier to handle than MMH or UDMH. Typically, only monoalkylhydrazines are modified in this manner, but di-, tri-, and tetraalkylhydrazines could be modified in the same way.

If the alkyl group in C<sub>*n* ≥ 2</sub> alkylhydrazines is substituted, substitution could occur on the alpha-, beta-, or omega carbon atom. For substituted ethylhydrazines, substitution typically occurs at the beta- (2-) position. To avoid confusion, one should always include the position designator beta- or 2- when describing 2-hydroxyethylhydrazine or 2cyanoethylhydrazine-. However, the 2- designator is often omitted because it is known that alpha-substituted hydroxyalkylhydrazines are unstable.

### 7.1 Preparation of Substituted Alkylhydrazines

Substitution of hydrogens in the alkyl groups in alkylhydrazines creates new compounds that have interesting new properties yet inherit the reactivity of alkylhydrazines. These substitutions are typically made on alkyl groups with two or more carbons in the alkyl chain. Substituted methylhydrazines are not very stable. The substituting groups introduced into the new molecules are typically hydroxyl, amino, nitrile, and cyano groups, and are typically in the terminal ω-position, not in the proximal α position.

Monoalkylhydrazines that have a functionalized alkyl group and a formula of H<sub>2</sub>N–NH–R, in which R can be a C<sub>2</sub>–C<sub>6</sub> alkenyl radical, C<sub>2</sub>–C<sub>6</sub> alkynyl radical, or linear or branched C<sub>2</sub>–C<sub>6</sub> alkyl radical carrying at least one functional group selected from a group consisting of OH, C<sub>2</sub>–C<sub>6</sub> alkoxy, C=NH, C≡N, phenoxy, and COOH, can

be synthesized by: **(1)** synthesizing the monoalkylhydrazine  $\text{H}_2\text{N}-\text{NH}-\text{R}$  by reacting a monochloramine with an anhydrous amine of formula  $\text{H}_2\text{N}-\text{R}^2$ ; then **(2)** demixing the solution into an organic phase and an aqueous phase by adding anhydrous sodium hydroxide under cooling; and finally **(3)** isolating the monoalkylhydrazine of formula  $\text{H}_2\text{N}-\text{NH}-\text{R}$  from the organic phase [96].

## 7.2 2-Hydroxyethylhydrazine

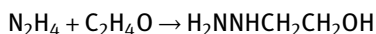
2-Hydroxyethylhydrazine, also known as  $\omega$ -hydroxyethylhydrazine, 2-hydrazinoethanol, 2-hydrazonoethanol, HEH,  $\text{H}_2\text{NNHCH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_2\text{H}_8\text{N}_2\text{O}$ , CAS RN [109-84-2], was produced in industrial quantities while it was still being used as a growth retardant to achieve the simultaneous blooming of pineapple plants, compressing the harvest time to a few days instead of several weeks [97, 98]. It is also used as an intermediate in the synthesis of veterinary medicines (furazolidone) and other heterocyclic compounds. Surprisingly, HEH was detected as a naturally occurring antioxidant in the hexane extract of *Cassia fistula* and in the ethanol extract of *Cassia alata* leaves [99, 100]. There are many other naturally occurring hydrazine derivatives, but this one came as a surprise, and may need to be confirmed by other methods.

Only 25 years ago, the HEH nitrate salt was recognized as a potential rocket propellant (monopropellant) ingredient, which has revived the interest in this chemical [101]. In the interim, numerous publications have studied the properties and potential applications of HEH nitrate (see Section 7.2.5.1 on Hydroxyethylhydrazinium Nitrate). Monopropellants containing 2-hydroxyethylhydrazinium nitrate (HEHN) will be described in the chapter “Hydroxylammonium Nitrate-Based Monopropellants” in *Encyclopedia of Monopropellants*.

### 7.2.1 Preparation of 2-Hydroxyethylhydrazine

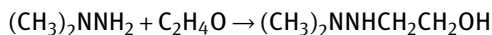
Hydroxyethylation of hydrazine is achieved relatively easily by reacting it with ethylene oxide, resulting in gradual substitution of one or two hydrogen(s) by the hydroxyethyl group.

Hydroxyethylhydrazine free base can be prepared by reaction of ethylene oxide with a large excess of hydrazine or hydrazine hydrate [102]. Instead of alkylating hydrazine with alkyl halogenides or sulfates, alkylation with bifunctional alkylating agents will result in substituted alkylhydrazines that are useful intermediates in organic synthesis. Reaction of an excess of hydrazine or hydrazine hydrate with ethylene oxide at low pressure gives  $\beta$ -hydroxyethylhydrazine [102]:



This reaction has to be carried out with extreme safety precautions because both reactants are monopropellants in their own right and might explode if overheated. Each of the reactants by themselves have caused numerous accidental explosions. The reaction does not stop at the monosubstituted hydrazine; the nucleophilic ethylene oxide will seek out the free electron pair in HEH and quickly form a disubstituted hydrazine. The more prevalent secondary product forms mostly by 1,1-disubstitution, with only a little forming by 1,2-disubstitution. The difficulty of this reaction is to prevent more than one hydroxyethyl group from attaching itself to the hydrazine molecule. If multiple substitution is not prevented, the resultant dihydroxyethylhydrazines (two possible isomers) are undesirable contaminants in the HEH product.

Hydroxyethyl (hydroxyalkyl) groups can be introduced into substituted hydrazines by reaction with ethylene oxide (or similar alkylloxiranes) [103]:



Hydroxyethylhydrazine free base was available in the US in large quantities while it was still being used as a growth retardant of pineapple and other fruit, allowing all fruit to ripen at the same time and facilitating the harvest. Toxicity considerations have caused farmers to discontinue this application and the chemical is no longer in use, resulting in a supply problem. Hydroxyethylhydrazine was an intermediate in the preparation of a nitrofuran anti-bacterial agent used mostly in veterinary medicine, but that was not sufficient to entice the US chemical industry to keep it in production. For several years, the only source was a chemical company in Mexico, and lately even that source has dried out.

Two different methods for the synthesis of hydroxyethylhydrazine that avoid the use of ethylene oxide were evaluated and compared: Raschig synthesis (the reaction of monochloramine and ethanolamine) and alkylation of hydrazine hydrate by chloroethanol [104]. For the Raschig synthesis, a kinetic and mechanistic study of the reactions of formation and degradation made it possible to identify the products and to establish a reaction model. The optimum conditions for synthesis were defined, as well as the approach to extraction operations. The second part of the thesis examined the alkylation of hydrazine hydrate by chloroethanol with and without the presence of a strong base. The rate laws of the mono- and dialkylation were given. This work was supplemented by a calorimetric study of the enthalpy of solvation and reaction.

The synthesis of HEH by reaction of 2-chloroethanol,  $\text{ClCH}_2\text{CH}_2\text{OH}$ , with an excess of hydrazine also often leads to disubstituted hydrazine instead of only the desired monosubstituted product [105]. To optimize yields of HEH, a study of the kinetics of the reaction of  $\text{N}_2\text{H}_4$  with 2-chloroethanol with and without sodium hydroxide was carried out. The reaction kinetics of the synthesis of 2-hydroxyethylhydrazine (HEH) by alkylation of  $\text{N}_2\text{H}_4$  with 2-chloroethanol with and without sodium hydroxide were derived from a set of experiments [105]. In both cases, the yield of HEH was diminished by a follow-on HEH alkylation (or dialkylation of  $\text{N}_2\text{H}_4$ ), leading to the formation of two unwanted isomers: 1,1-di(hydroxyethyl)hydrazine and



1,2-di(hydroxyethyl)hydrazine. In this study, hydrazine and hydroxyalkylhydrazine alkylations followed SN2 reactions triggered directly by 2-chloroethanol or indirectly in the presence of a strong base by ethylene oxide, an intermediate compound formed by reaction of 2-chloroethanol with alkali. The kinetics were studied in diluted media by quantifying HEH and 2-chloroethanol by GC and GC-MS. The energy of activation parameters of each reaction and the influence of a strong base on the reaction mechanisms were determined. A global mathematical treatment was applied for each alternative reaction, which allowed the reactions to be modeled as a function of reactant concentrations and temperature. In the case of direct alkylation by 2-chloroethanol, simulations were established for semi-batch and batch syntheses, and simulation results were confirmed in experiments for concentrated solutions ( $1.0\text{ M} \leq [\text{2-chloroethanol}]_0 \leq 3.2\text{ M}$  and  $15.7\text{ M} \leq [\text{N}_2\text{H}_4]_0 \leq 18.8\text{ M}$ ). Simulation permitted the prediction of the momentary concentrations of reagents and products, in particular the ethylene oxide concentration in the case of indirect alkylation (this concentration should be kept as low as possible).

2-Hydroxyethylhydrazine can be made by a modified Raschig synthesis, which is the reaction of monochloramine on ethanolamine. The formation of HEH was monitored by UV spectrometry, and the influences of temperature and pH were measured to better understand the kinetics of this reaction [106]. The primary reaction is an SN2-type mechanism, whereas the main unwanted secondary reaction is the oxidation of HEH by monochloramine. This reaction was also monitored by UV spectrometry, and the oxidation product was identified by GC-MS analysis, showing the formation of hydroxyethylhydrazone. The reaction mechanisms and the rate constants were determined, and the results permitted the main reactions occurring during HEH synthesis to be established. These reactions were validated in a concentrated medium with a systematic study of the influences of the molar ratio ( $[\text{HEH}]_0/[\text{NH}_2\text{Cl}]_0$ ), the final sodium hydroxide concentration, and the temperature. A comparison was made with the other (previously published) synthetic process, the alkylation of hydrazine by either chloroethanol or epoxide.

Unless one maintains a very low HEH concentration in the reaction mixture, di(2-hydroxyethyl)hydrazine is always an undesirable by-product of HEH production. Commercially available HEH is only advertised as a 90–95 or 95–98% purity product. Because of the uncertain supply situation for HEH in the US and the resulting dependence on foreign imports, plans have been developed to establish a domestic HEH production facility to satisfy the anticipated HEH and HEHN needs of the US aerospace industry and government agencies [107–109]. The design followed the process outlined in US Pat. 2660607 [102]. The process design was supposed to meet the following constraints:

- (1) The plant should have a minimum production capacity of 200 metric tons per year (MTPY) of HEH.
- (2) The HEH should have a purity of 99% or greater.

The economic analysis was based on many overly optimistic assumptions. In particular, a domestic HEH supply is useless without a simultaneous reliable domestic source of electronic-grade, high-purity, sulfur-free HAN. See also [110].

### 7.2.2 Physical Properties of 2-Hydroxyethylhydrazine

Compared to other alkylhydrazines, HEH is very viscous. Physical properties of HEH are listed in Table 5.

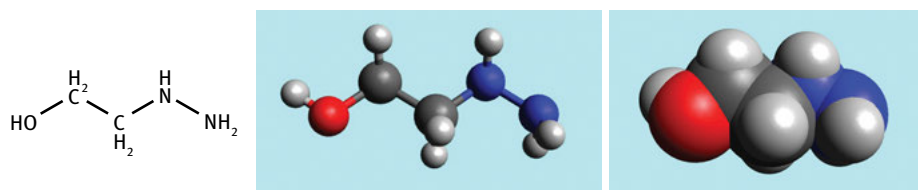
**Table 5:** Physical properties of 2-hydroxyethylhydrazine.

| Property                                 | SI units                                                 | Other units                                                  |
|------------------------------------------|----------------------------------------------------------|--------------------------------------------------------------|
| Molecular mass                           | 76.098 g/mol                                             | 13.141 mol/kg                                                |
| Glass transition temperature             | 201 K                                                    | –72 °C                                                       |
| Boiling point                            | 492 K (dec.)<br>428–433 K at 4.2 kPa<br>413 K at 1.2 kPa | 219 °C (dec.)<br>155–160 °C at 32 mm Hg<br>140 °C at 9 mm Hg |
| Density at 298 K                         | 1.1176 g/cm <sup>3</sup>                                 | 69.77 lb/ft <sup>3</sup>                                     |
| Vapor pressure at 298 K                  | 0.5 Pa                                                   | 0.004 mm Hg                                                  |
| Viscosity at 298 K                       | 0.113 Pa s                                               | 113 cPs                                                      |
| Dynamic viscosity at 298 K               | 0.147 Pa s                                               | 147 cPs                                                      |
| Heat of combustion                       | 23.043 kJ/g                                              | 5.5075 kcal/g                                                |
| Enthalpy of formation $\Delta H_f^{298}$ | –175.3 kJ/mol                                            | –41.9 kcal/mol                                               |

Data source: Olin Chemicals data sheet (unpublished data)

#### 7.2.2.1 Molecular Structure of 2-Hydroxyethylhydrazine

The hydroxyl group is attached to the ethyl substituent in the terminal ( $\omega$ -) position, identified as 2- or  $\beta$ -hydroxyethyl. Theoretically, the hydroxyl group could also be in the 1- or  $\alpha$ -position, but this molecule would be less stable. The molecular structure of 2-hydroxyethylhydrazine is illustrated in Figure 1.



**Figure 1:** Molecular structure of 2-hydroxyethylhydrazine.

Hydroxymethylmethylhydrazine, another isomer with the same empirical formula ( $C_2H_8N_2O$ ), is not stable.

### 7.2.3 Chemical Properties of 2-Hydroxyethylhydrazine

#### 7.2.3.1 Thermal Stability of 2-Hydroxyethylhydrazine

During the attempted distillation of 2-hydroxyethylhydrazine, brisk gas evolution occurred at about 488 K (215 °C), and a mixture of liquids with boiling points in the range 353–423 K (80–150 °C) were distilled [111]. The residue then charred with some violence. Purification of the distilled liquid gave methylhydrazine (MMH) in 25% yield, which was identified by its boiling point, as well as hydrogen sulfate and hydrogenoxalate salts. This is not a good method to make MMH. In this and subsequent decompositions, the presence of 2-aminoethanol was established, and ammonia and hydrazine were identified in the gaseous effluent. Neutral gases were also evolved but were not identified. In order to prevent the decomposition of HEH, it should be distilled only under reduced pressure. Safe distillation conditions are 413 K at 1.2 kPa (140 °C at 9 mm Hg).

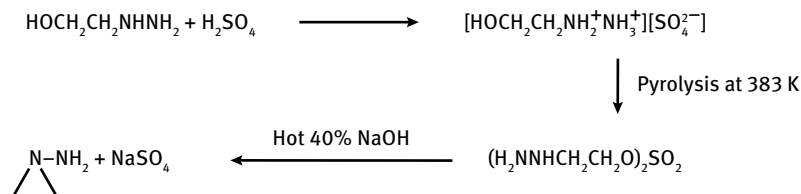
For comparison, the thermal decomposition of 1-hydrazino-2-propanol,  $H_2NNHCH_2CHOHCH_3$ , proceeded more smoothly than with 2-hydrazinoethanol, little gas was evolved, and no violent decompositions occurred.

#### 7.2.3.2 Reactions of 2-Hydroxyethylhydrazine

2-Hydroxyethylhydrazine is a useful intermediate in the synthesis of numerous heterocyclic compounds.

The reaction of HEH with acetylene led to an unexpected product, 1-ethyl-3-methyl-1*H*-pyrazole, in 39% yield [112]. The reaction also yielded the expected (2-vinyloxy)hydrazine in lower yield. A similar reaction was carried out in benzene in the presence of anhydrous cadmium acetate as catalyst, and separation of the reaction mixture by vacuum distillation gave isomeric acetaldehyde *N*-(2-hydroxyethyl)hydrazones and 43% ethylidene-2-methyloxazolidin-3-amine [113].

2-Hydroxyethylhydrazine can be the starting ingredient of an interesting cyclization reaction leading to *N*-aminoaziridine [114]:



HEH is a reducing agent. HEH has been evaluated as a less toxic replacement for hydrazine in nuclear fuel element reprocessing for the reduction of actinide elements such as neptunium.

### 7.2.3.3 Analysis of 2-Hydroxyethylhydrazine

2-Hydroxyethylhydrazine can be analyzed by completing an acidimetric titration with methyl orange indicator followed by oxidimetric titration with potassium periodate in borate-, acetate-, or bicarbonate-buffered solution [115].

Contaminants detected in industrial samples of HEH by GC analysis were hydrazine, water, ethylene glycol, and “high boilers” that cannot be separated from each other by simple distillation [116]. The high boilers consisted of mostly 1,1-di(2-hydroxyethyl)hydrazine with some 1,2-di(2-hydroxyethyl)hydrazine. A third constituent of the high boilers peak was possibly 2-(2-hydroxyethoxy)ethylhydrazine, HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>NHNH<sub>2</sub>. A technical-grade HEH sample contained only 83% HEH and 15% high boilers.

### 7.2.4 Toxicity of 2-Hydroxyethylhydrazine

2-Hydroxyethylhydrazine free base (in solution) was at one time widely used as a growth retardant of pineapple, but it is suspected to cause tumors in hamsters, but not in mice. It has since been withdrawn from this agricultural application. Solutions of 0.015% 2-hydroxyethylhydrazine were given continuously in the drinking water of 6- and 5-week-old Syrian golden hamsters and Swiss mice for the remainder of their lifetimes [117]. In treated hamsters, 6% of the females and 10% of the males developed hepatomas, whereas the corresponding incidence among untreated controls was 0% in females and 1% in males. The chemical did not increase the incidence of other tumors in hamsters; nor did it result in a detectable tumorigenic effect in mice.

The toxicity of 2-hydroxyethylhydrazine (2-hydrazinoethanol) was investigated in turkey poults 2–6 weeks post-hatch [118]. Significant depression of body weight was evident at concentrations of the chemical as low as 10 ppm. Severe anorexia closely paralleled a highly significant decrease in water intake. A significant increase in the ratio of granulocytes to agranulocytes was seen in poults fed the chemical at a dose of 50 ppm. Under the conditions of this experiment, none of the tissues sampled exhibited pathologic changes consistent with HEH injury. See also [119].

### 7.2.5 2-Hydroxyethylhydrazinium Salts

The HEH salts of several energetic anions, including the HEH nitrate, perchlorate, dinitramide, and nitroformate, were prepared and characterized.

### 7.2.5.1 2-Hydroxyethylhydrazinium Nitrate

2-Hydroxyethylhydrazinium nitrate (HEHN) has gained importance as the water-soluble fuel salt in monopropellants in combination with hydroxylammonium nitrate (HAN) as the oxidizer. Several non-toxic (low vapor pressure) monopropellants have been formulated with HAN and HEHN. One of these, AF-M315E, was the first non-toxic monopropellant launched on a US satellite (GPIM). HEHN is very efficient at lowering the melting point of ADN, and ADN/HEHN binary eutectics (without solvent) have been considered as ionic liquid monopropellants.

### 7.2.5.2 Preparation of 2-Hydroxyethylhydrazinium Nitrate

Hydroxyethylhydrazinium nitrate (HEHN) can be prepared by slowly neutralizing diluted hydroxyethylhydrazine with diluted nitric acid and then stripping off the water at reduced pressure in a Rotavapor. Even after removing all of the water from a HEHN solution, HEHN stays behind as a viscous syrup. The resultant syrup residue does not want to crystallize and often remains in a supercooled ionic liquid state for a long time. For subsequent use as a fuel for monopropellants, it is not necessary to obtain HEHN in the crystallized form as long as one knows how much water is clinging tenaciously to the residue.

The preparation of HEHN as well as the hydroxyethylhydrazinium perchlorate, dinitramide, and nitroformate in millimolar quantities can be done using the simple methods described in a patent [120]. Because the reaction is exothermic, it has to be conducted in a solvent diluent (methanol, ethanol, isopropanol, *n*-propanol, *n*-butanol, water, or acetonitrile) and with active cooling to prevent overheating and decomposition of HEHN. With the stronger acids, HEH will form not only the mononitrate and monoperchlorate but also the dinitrate and the diperchlorate. The monobasic salts of HEH are viscous oils, but the dibasic salts are crystalline solids that are extremely shock and friction sensitive.

If larger quantities of HEHN are needed, the methods for HEH neutralization and HEHN production can be patterned after the methods used for making triethanolammonium nitrate (TEAN), which was once used as an ingredient in the production of XM46 liquid gun propellant.

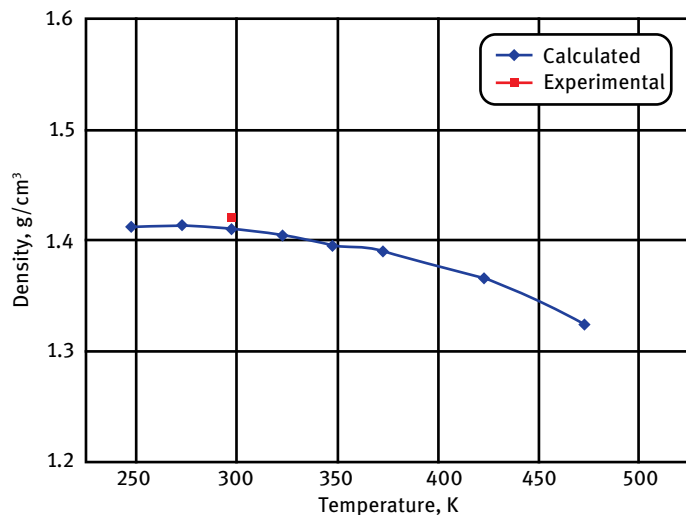
### 7.2.5.3 Physical Properties of 2-Hydroxyethylhydrazinium Nitrate

2-Hydroxyethylhydrazinium(1+) nitrate has an unusually low melting point (<248 K) and has been classified as an ionic liquid. The viscosity of molten HEHN at 298 K (25 °C) is 248 mPa s (248 cPs).

### Molecular Structure of 2-Hydroxyethylhydrazinium Nitrate

Computational chemistry has been used to help explain the unusual behavior of HEHN with regard to its melting point and density. It was hoped that the structure and low-temperature melting point of HEHN could be copied by other ionic liquids that were intended as energetic ionic liquids and rocket propellants.

2-Hydroxyethylhydrazinium nitrate is a low-melting ionic liquid that has considerable potential for energetic materials applications. Although little experimental data are available in the literature, predictions were made concerning the physical and dynamical properties of this ionic liquid based on previous validation of the molecular force field [121]. As shown in Figure 2, the theoretical liquid density decreases linearly with increasing temperature. The experimentally determined [120] density at 298 K of  $1.42 \text{ g/cm}^3$  is in excellent agreement with the value predicted from simulation,  $1.428 \text{ g/cm}^3$ .



**Figure 2:** Computed density of hydroxyethylhydrazinium nitrate as a function of temperature. (Reproduced and modified from [121].)

The ionic liquid HEHN is expected to exhibit strong hydrogen bonding in the liquid phase. The interaction between the nitrate oxygen atoms and either the hydroxyl hydrogen or the amine hydrogens of 2-HEH<sup>+</sup> showed that the N–H···O interaction was far weaker than the O–H···O interaction. The former occurred at  $\sim 1.9 \text{ \AA}$ , while the latter occurred at the much shorter distance of  $\sim 1.5 \text{ \AA}$ . The  $1.5 \text{ \AA}$  hydrogen bond is very short relative to hydrogen bonds in general, which suggests that this interaction is very strong in the liquid. This was supported by the sharpness and intensity of the  $g(r)$  curve for this peak relative to the N–H···O interaction. The correlations at about  $3.5$  to  $4 \text{ \AA}$  are associated with the neighboring oxygens of the nitrate anion. 2-HEHN is an ionic liquid that is dominated by hydrogen bonding due to the presence of many significant donor/acceptor sites.

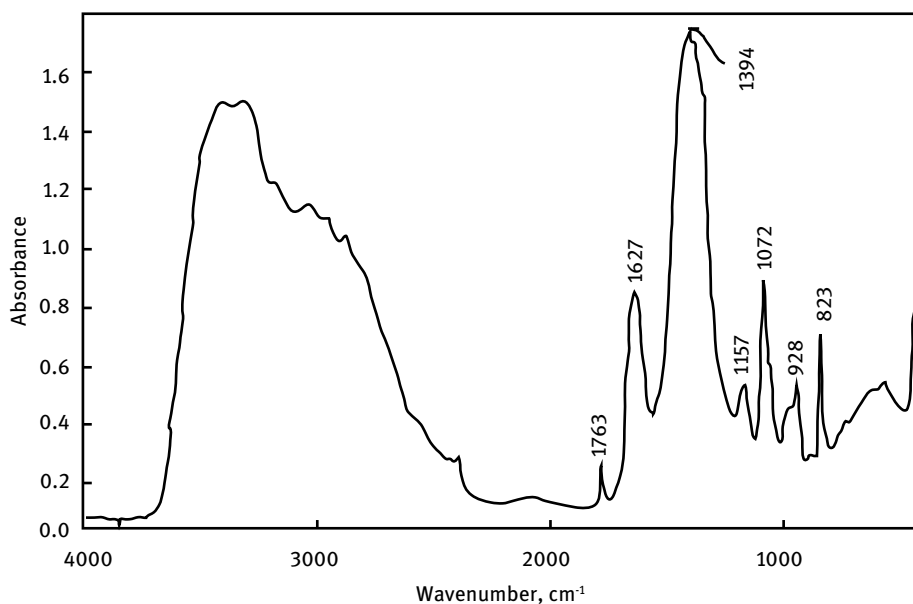
### Computational Chemistry Calculations of the HEHN Molecular Structure

Force-field (FF) computations were performed for hydrazine and organic hydrazine derivatives, including MMH, UDMH, monoethylhydrazine, and 2-hydroxyethylhydrazine [122]. The FF computations successfully reproduced a range of equilibrium properties, including vapor–liquid coexistence densities, vapor pressures, enthalpies of vaporization, and critical properties. Using this as a basis, a FF method was also developed for the protonated forms of these species, i.e., hydrazinium cations. Properties of 1:1 energetic salts formed by pairing these cations with the nitrate anion were computed and compared with a limited amount of experimental data. The simulations indicated that the ionic liquid 2-HEHN has significantly slower dynamics than the other hydrazinium ILs.

### Optical Properties of Hydroxyethylhydrazinium Nitrate

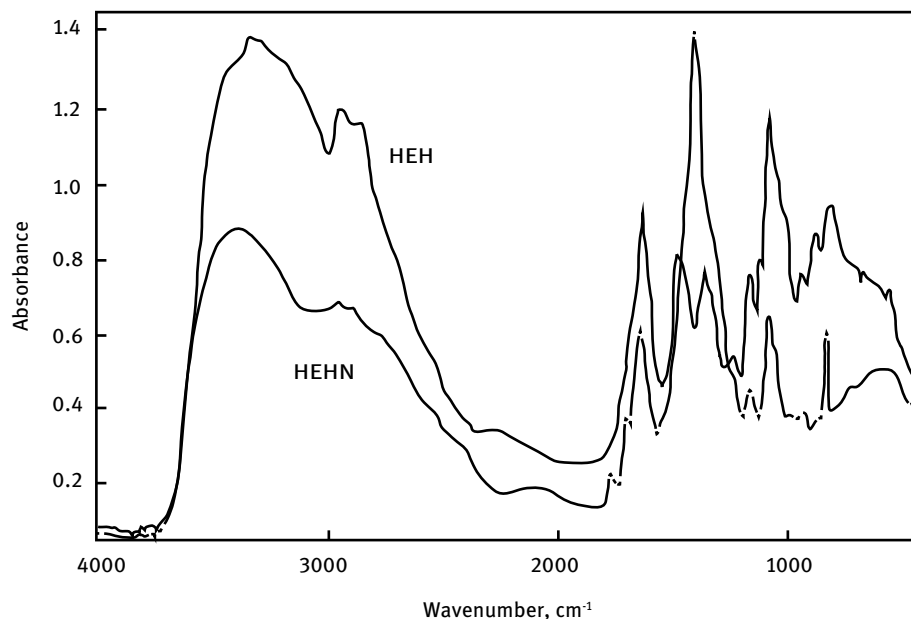
#### IR Absorption Spectra of HEHN

The IR spectrum of HEHN shown in Figure 3 has absorption peaks at 1763, 1627, 1394, 1157, 1072, 928, and 823  $\text{cm}^{-1}$ .



**Figure 3:** IR spectrum of 2-hydroxyethylhydrazinium nitrate. (Reproduced and modified from [123].)

The IR spectrum of HEHN is compared to that of HEH in Figure 4; the main difference is the strong absorption peak at 1394  $\text{cm}^{-1}$  due to the nitrate ion. Other samples showed this peak at 1376  $\text{cm}^{-1}$ .



**Figure 4:** Comparison of the IR spectra of HEH and HEHN. (Reproduced and modified from [123].)

### Thermodynamic Properties of Hydroxyethylhydrazinium Nitrate

The most important thermodynamic property of HEHN needed for theoretical rocket performance calculations is its standard enthalpy of formation in the solid or molten state. It helps to have accurate numbers for the standard enthalpy of formation for the parent hydrazine, HEH. Many organizations have used HEHN standard enthalpies of formation of  $-452 \text{ kJ/mol} = -108 \text{ kcal/mol}$  for theoretical performance calculations.

Various extrapolations have been made. One frequently used method is to compare the molar enthalpies of formation of free liquid amines and free liquid hydrazines to those of their solid nitrates and apply a constant conversion addition (subtraction).

#### 7.2.5.4 Chemical Properties of 2-Hydroxyethylhydrazinium Nitrate

2-Hydroxyethylhydrazinium nitrate is an ionic liquid that does not readily crystallize at room temperature. Molten HEHN or concentrated solutions of HEHN can be decomposed on Shell 405 catalysts [124, 125]. The 2-hydroxyethylhydrazinium dinitrate reacts with Shell 405 catalyst in a similar fashion. It should be mentioned that HEHN has been considered not only as a water-soluble fuel in monopropellants but also as a liquid fuel in bipropellant combinations. HEHN and HEHN solutions in acetone have also been considered as a liquid bipropellant fuel in combination with RFNA, NTO, or 98% HTP [123].



### Thermal Decomposition of 2-Hydroxyethylhydrazinium Nitrate

It is impossible to crystallize HEHN at room temperature and it has a glass transition at 216.2 K (−56.9 °C). In the DSC, HEHN showed an onset of exotherm at 442 K (169 °C) and a peak of exotherm at 471 K (198 °C). Although HEHN will probably not be used as a rocket propellant by itself, it is important to have information on its thermal decomposition. The results of these tests with HEHN by itself will then be compared to similar tests where HEHN is mixed with oxidizers such as HAN or AN. For the same reason, strand burning rates of HEHN by itself have been measured so that they can be compared to strand burning rates of monopropellants containing HEHN.

Confined rapid thermolysis (CRT) with two synergistic diagnostic tools, a Fourier transform infrared (FTIR) spectrometer and a time-of-flight mass spectrometer (ToFMS), were used to study the temporal evolution of gases from the condensed phase during the thermal decomposition of HEHN, and to compare this to the decomposition of AN [126]. High heating rates (2000 K/s) could be achieved by enclosing a small sample volume within a confined space. Decomposition of HEHN was assumed to proceed by three different reactions. The processes governing the decomposition of several energetic compounds were found to be autocatalytic in nature, and the autocatalytic agents were the strong  $\text{HNO}_3$  acids generated by the initial decomposition step. The estimated Arrhenius-type parameters of HEHN decomposition are listed in Table 6.

**Table 6:** Estimated Arrhenius-type parameters of HEHN decomposition.

| Reaction                                                                                                                                          | $E_a$ , kJ/mol | Pre-exponential coefficient $A$ |
|---------------------------------------------------------------------------------------------------------------------------------------------------|----------------|---------------------------------|
| $\text{HEHN} \rightarrow \text{HEH} + \text{HNO}_3$                                                                                               | 183.0          | $2 \times 10^{16}$              |
| $\text{HEHN} + \text{HNO}_3 \rightarrow \text{HEH} + 2\text{HNO}_3$                                                                               | 124.8          | $3.9 \times 10^{12}$            |
| $\text{HEH} + \text{HNO}_3 \rightarrow 2.5\text{H}_2\text{O} + 0.42\text{N}_2\text{O} + 1.08\text{N}_2 + 0.042\text{O}_2 + \text{CH}_3\text{CHO}$ | 24.3           | $8.3 \times 10^5$               |

Data source: [126]

Using these parameters, the predicted evolution of decomposition products and the measured concentration profiles agreed fairly well. The activation energy for the unimolecular step in HEHN decomposition was computed to be slightly higher than that of HN. The reaction rate constants for the unimolecular step for HEHN were found to be to two orders of magnitude higher than those of AN.

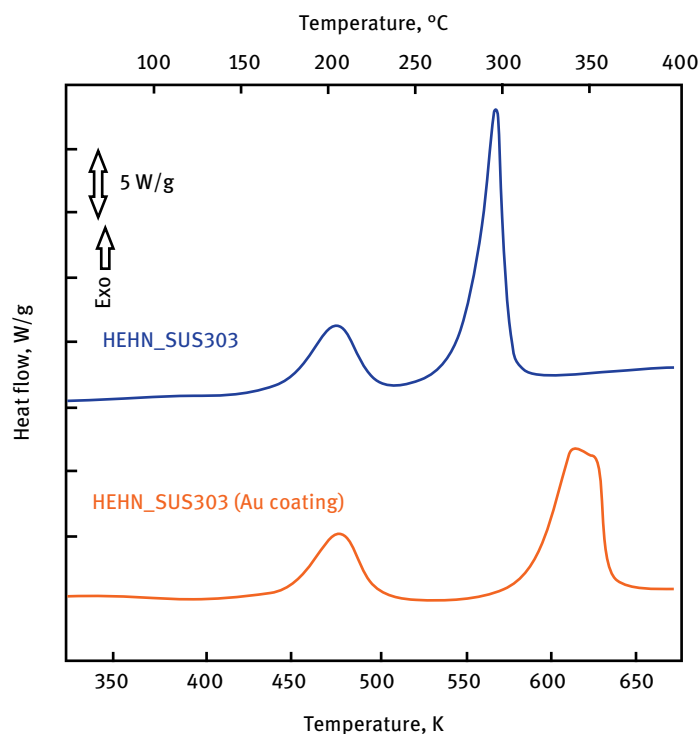
The thermal decomposition of HEHN was studied using TGA and FTIR spectroscopy [127]. At a heating rate of 10 K/min, two distinct periods of mass loss were observed. First, the mass decreased by 10% in the temperature range of 313–353 K (40–80 °C), which was attributed to the evaporation of water absorbed by the sample. Next, the mass dropped by 75% between 453 and 513 K (180 and 240 °C) because of

HEHN decomposition. The identified product gases were N<sub>2</sub>O, CO<sub>2</sub>, NH<sub>3</sub>, HNO<sub>3</sub>, and NO<sub>2</sub>. Approximately 15% of the initial mass was found to remain in the crucible after 513 K (240 °C). The kinetic rate equation for HEHN decomposition at 50 bar and 561 K, derived from confined rapid thermolysis, was

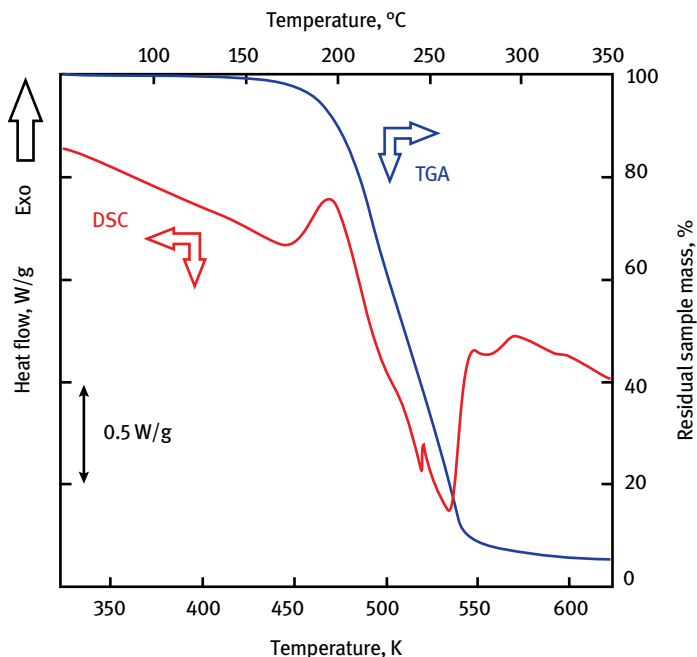
$$k = 2 \times 10^{16} \text{ s}^{-1} \exp \left( - (183 \text{ kJ mol}^{-1} / RT) \right) = 0.183 \text{ s}^{-1}$$

In a different study of the thermal decomposition of HEHN in a DSC with a heating rate of 5 K/min., there were two exotherms. The onset of the first exotherm was at 443 K (170 °C) and the maximum of the first exotherm peak was at 473 K (200 °C) [128]. The onset of the second exotherm was at 523 K (250 °C) and the maximum of the second exotherm peak was at 563 K (290 °C). When the test was repeated in gold-plated DSC crucibles, the first exotherm was shifted a little and the second exotherm was shifted substantially towards higher temperatures, and the rate of heat release was lower (Figure 5).

The DSC-TGA at a heating rate of 5 K/min initially showed a slow material loss (moisture?), then a substantial material loss beginning at 473 K (200 °C) accompanied



**Figure 5:** DSC thermogram of HEHN decomposition. (Reproduced and modified from [128], with permission granted by Professor Kento Shiota, 24 May 2021.)



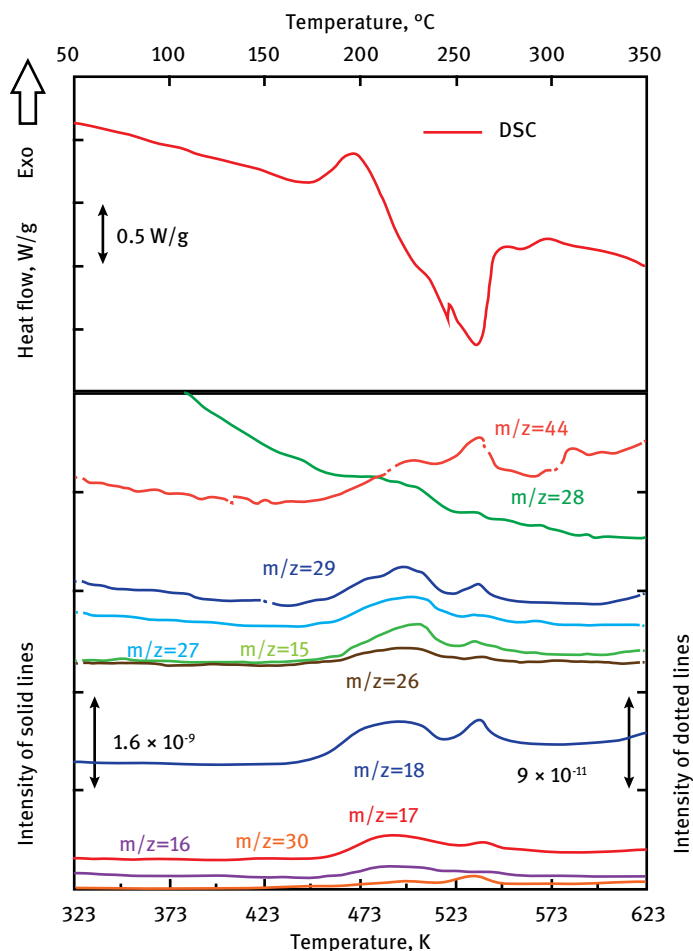
**Figure 6:** DSC-TGA thermogram of HEHN decomposition. (Reproduced and modified from [128], with permission granted by Professor Kento Shiota, 24 May 2021.)

by a single exotherm, and then endothermic decomposition until only 5% material remained in the pan (Figure 6).

The composition of the gases evolved during decomposition of HEHN and the variation in gas composition with time and temperature were monitored by MS. The main products were nitrogen ( $m/z = 28$ ), water ( $m/a = 18$ ), and carbon dioxide ( $m/z = 44$ ) (Figure 7). See also [129].

While Figures 5 and 6 above show the heat flow during DTA and the mass loss during TGA at only one fixed heating rate, a more detailed investigation showed heat flow and mass loss curves during heating of HEHN at four different heating rates (Figures 8 and 9) [130, 131]. The shapes of the curves and the onsets of exotherms depend significantly on the heating rate. The two-stage nature of the decomposition reactions is best shown at slow heating rates.

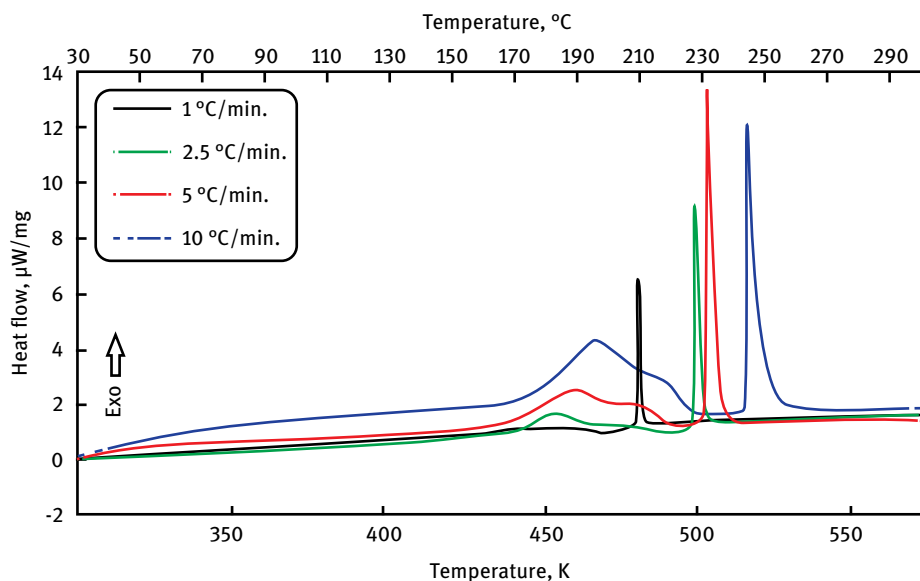
All the techniques used (TGA, DSC, MS, and FTIR spectroscopy) clearly show the existence of two stages of HEHN thermal decomposition. The apparent activation energies determined by a model-based thermal analysis,  $113.7 \pm 1.7$  kJ/mol for the first stage and  $123.6 \pm 2.5$  kJ/mol for the second stage, are relatively close to the value of 124.8 kJ/mol obtained by Chowdhury and Thynell for step 2 in their reaction mechanism (autocatalytic reaction between HEHN and  $\text{HNO}_3$ ).



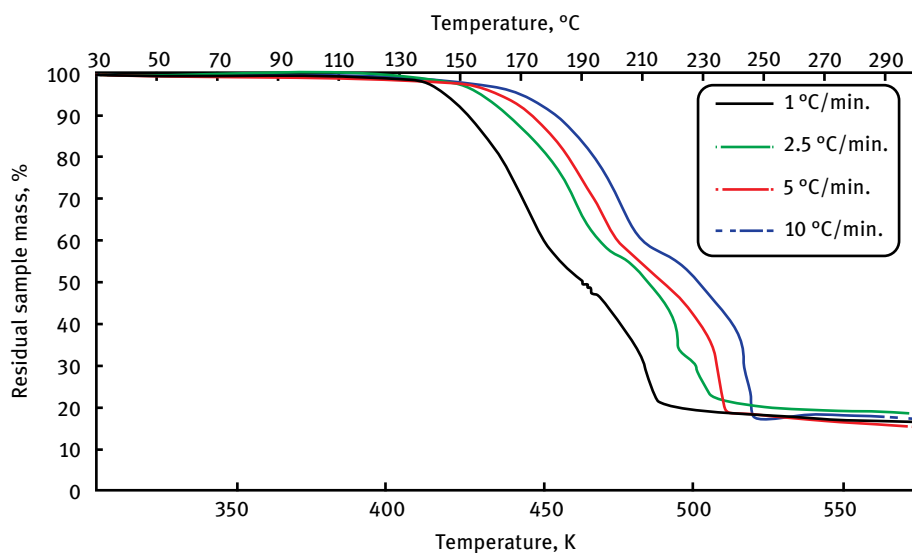
**Figure 7:** Composition of the gases evolved during decomposition of HEHN. (Reproduced and modified from [128], with permission granted by Professor Kento Shiota, 24 May 2021.)

#### 7.2.5.5 Strand Burning of 2-Hydroxyethylhydrazinium Nitrate

Although HEHN could not sustain ignition at atmospheric pressures despite repeated attempts, it combusted at chamber pressures of 10 and 15 bar with surrounding atmospheres of air and nitrogen, respectively. The effects of variation of pressure on combustion of HEHN strands were studied at pressures ranging from atmospheric to 90 bar [127]. Immediately after ignition, the monopropellant flame above the liquid surface was maintained by the decomposition of HEHN in the condensed phase. Linear burning rates and temperature distributions during combustion of these formulations were investigated with air or nitrogen as the surrounding atmospheres and compared to those of Otto Fuel-II, a torpedo propellant. The intermediate pressure burning range



**Figure 8:** DSC curves of HEHN decomposition at heating rates of 1, 2.5, 5, and 10 °C/min. (Reprinted and modified from [130], with permission from ©2020 Elsevier; permission conveyed through RightsLink.)



**Figure 9:** TGA curves of HEHN decomposition at four different heating rates. (Reprinted and modified from [130], with permission from ©2020 Elsevier; permission conveyed through RightsLink.)

of HEHN extended from 10 to 50 bar, beyond which abrupt rises in the luminosity and temperature of the monopropellant flame were recorded. The low-pressure deflagration limit (LPDL), which determines the low-pressure limit for self-sustained combustion of a propellant, was found to be 15 and 25 bar for HEHN and Otto Fuel-II, respectively. HEHN at 10 bar did not sustain combustion under repeated attempts. The burning rates of HEHN in two different pressure regimes and two different atmospheres are compared to those of Otto Fuel-II and isopropyl nitrate in Table 7.

**Table 7:** Strand burning rates of HEHN in comparison to those of Otto Fuel-II and isopropyl nitrate.

| Compound        | Atmosphere | Pressure, bar | Burning rate laws            |
|-----------------|------------|---------------|------------------------------|
| HEHN            | Air        | 20–50         | $r = 0.032 \times p^{1.15}$  |
| HEHN            | Air        | 60–90         | $r = 0.331 \times p^{0.58}$  |
| HEHN            | Nitrogen   | 20–50         | $r = 0.043 \times p^{1.10}$  |
| HEHN            | Nitrogen   | 70–90         | $r = 0.560 \times p^{0.45}$  |
| For comparison: |            |               |                              |
| IPN             | Air        | 10–50         | $r = 0.0046 \times p^{1.54}$ |
| Otto Fuel-II    | Air        | 20–100        | $r = 0.0063 \times p^{1.31}$ |

Data source: [127]

Theoretical rocket performance calculations indicated that at a chamber pressure of 2 MPa and a nozzle area ratio of 50, the vacuum specific impulse of HEHN would be 252.2 s, better than that of anhydrous hydrazine.

#### 7.2.5.6 Toxicity of 2-Hydroxyethylhydrazinium Nitrate

HEHN and other potential ingredients for hydrazine monopropellant replacements were examined for their toxicity to liver tissue. *In vitro* rat hepatocyte toxicity and bacteria (*Salmonella*) genotoxicity assays were performed on 13 high-energy chemicals that were candidates for potential replacement monopropellants for hydrazine [132, 133]. The chemicals were mostly hydrazine derivatives and amino compounds in the form of their nitrate salts, including HN and HEHN. Responses to hydrazine were used as reference values for ranking the other chemicals. The results in hepatocytes showed a dose-dependent decrease in mitochondrial activity, an increase in lactate dehydrogenase leakage, and depletion of glutathion levels. According to the MTT assay, the hydrazine-containing compounds were the most toxic (HN > DEHN > DHTN > MMHN > HEHN > DAGN > NAGN), and amino-containing compounds and triazole-containing compounds were less toxic. The order of toxicity of hydrazine derivatives in reducing glutathion GSH levels was DHTN > HN > DEHN > MMHN > HEHN > DAGN > NAGN. Results of genotoxicity tests (Ames assay) indicated that HEHN is not mutagenic. Similar measurements were made in another study of HEHN and other chemicals intended as

hydrazine monopropellant or fuel replacements [134]. Quantitative structure–activity relationships for these nitrate salts were derived from *in vitro* toxicity endpoints in primary cultures of isolated rat hepatocytes, and molecular descriptors were obtained using *ab initio* molecular orbital theory [135]. Appendix F of [136] contains a brief summary of the toxicity of HEHN, also published as a separate report [137].

#### 7.2.5.7 Safety Properties of 2-Hydroxyethylhydrazinium Nitrate

The impact sensitivities of three different HEHN samples measured at one laboratory ranged from 44 to 50 kg-cm. The friction sensitivity of HEHN ranged from 176 to 223 N.

#### 7.2.5.8 Applications of 2-Hydroxyethylhydrazinium Nitrate

*Encyclopedia of Monopropellants* will contain a detailed summary of the application of HEHN as a fuel in non-toxic monopropellants, most of which use HAN as the oxidizer. HEHN solutions in UDMH have been considered as hypergolic fuels in bipropellant engines [138]. UDMH/HEHN blends containing a minimum of 30 mass-% UDMH were found to be hypergolic with RFNA or WFNA, respectively.

HEHN by itself and in mixtures with HAN has been tested as a working fluid in electrospray colloid thrusters [139]. The gas-phase behavior of HEHN ions and clusters is important for understanding its potential as an electrospray thruster propellant. The unimolecular dissociation pathways of two clusters were experimentally observed, and theoretical modeling of hydrogen bonding and dissociation pathways was used to help explain those observations.

#### 7.2.5.9 Propellant Mixtures with 2-Hydroxyethylhydrazine

The chapter “Dimethylhydrazines” in *Encyclopedia of Liquid Fuels* includes a summary of fuel blends containing HEH. HEH has been added to UDMH in an effort to decrease its volatility. Physical properties of UDMH/HEH mixtures have been determined for mixtures containing 0–50 mass-% HEH [140, 141].

### 7.3 1,1-Di(2-hydroxyethyl)hydrazine

Unless one always maintains an excess of hydrazine hydrate and a very low HEH concentration in the reaction mixture, 1,1-di(hydroxyethyl)hydrazine is inevitably an undesirable by-product of HEH production. The second ethylene oxide molecule attaches itself at the nitrogen with the lowest electron concentration, which is the one that already carries an alkyl group. Commercial HEH may contain up to 13% of 1,1-di(hydroxyethyl)hydrazine along with a small amount of its isomer 1,2-di(hydroxyethyl)hydrazine.

## 7.4 2-Aminoethylhydrazine

2-Aminoethylhydrazine, also known as  $\beta$ -aminoethylhydrazine, 1-amino-2-hydrazinoethane, 1,2,6-triazahehexane; ethanamine, 2-hydrazino-; AEH,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHNH}_2$ ,  $\text{C}_2\text{N}_3\text{H}_9$ , CAS RN [14478-61-6], should make a good hypergolic rocket fuel, but it is not readily available and there is no record that it has ever been tested for that application. AEH is isomeric with dimethylenetriamine (1,3,6-triazahehexane), which is not very stable.

Aminoethylhydrazines can be prepared by reaction of ethylenimine or alkylaziridines with excess hydrazine hydrate or substituted hydrazines [142]. Hydrazine hydrate (80%, 900 g) was heated to 363 K (90 °C), then 250 g ethylenimine was dropped in with stirring. After completion of the addition, the temperature was raised to 393 K (120 °C) within 2 h and kept there for 1 h. Distillation gave 245 g 2-aminoethylhydrazine, whose boiling point was 359–360 K at 1.8 kPa (86–87 °C at 14 mm Hg), and 42 g *N,N*-di(2-aminoethyl)hydrazine, CAS RN [89282-54-2P], whose boiling point was 389–391 K at 533 Pa (116–118 °C at 4 mm Hg). (3-Aminopropyl)hydrazine, with a boiling point of 356–357 K at 1.8 kPa (83–84 °C at 13.5 mm Hg), and *N,N*-bis(3-aminopropyl)hydrazine were prepared analogously. The ternary amine (2-diethylaminoethyl)hydrazine has a boiling point of 385–387 K at 6.7 kPa (112–114 °C at 50 mm Hg), and aminoethyl(diethylaminoethyl)hydrazine has a boiling point of 397–399 K at 1.7 kPa (124–126 °C at 13 mm Hg).

Known synthetic procedures for AEH were rechecked, and that of Eiter and Truscheit [142] yielded 42.5% 2-aminoethylhydrazine, AEH,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHNH}_2$ , and 17.5% 1,1-di-(2-aminoethyl)hydrazine ( $\text{H}_2\text{NCH}_2\text{CH}_2$ )<sub>2</sub>NNH<sub>2</sub>, whereas that of Kloes and Offe [66] gave only 23.5% AEH [143]. AEH can be characterized by the melting points of its salts: the dichloride of AEH melts at 442–444 K (169–171 °C); the dioxalate of AEH melts at 469 K (196 °C) (decomp.); and the dipicrate of AEH melts at 448–449 K (175–176 °C) (decomp.)

The yield of AEH was as high as 62% when  $\text{H}_2\text{NCH}_2\text{CH}_2\text{OSO}_3\text{H}$  was refluxed first with 4 mol 80% hydrazine hydrate and then reacted with 2 mol NaOH dissolved in 4.5 mol hydrazine hydrate instead of  $\text{H}_2\text{O}$  [144].

## 7.5 2-Cyanoethylhydrazine and Cyanomethylhydrazine

Similar to hydroxyethylation of hydrazine by reaction with ethylene oxide, cyanoethylation is possible by reacting hydrazine with acrylic nitrile [145]. 2-Cyanoethylhydrazine (CEH) was made by reaction of 0.58 mol of a 64% hydrazine solution (i.e., 100% hydrazine hydrate) and 0.5 mol of acrylonitrile. The addition was carried out over a period of 2 h with a maximum temperature of 294 K (21 °C). The resulting mixture was vacuum distilled at 3.5 mm Hg. The first cut of water and hydrazine was discarded and a middle cut consisting of 2-cyanoethylhydrazine boiling at 378 K at



253 Pa (105 °C at 1.9 mm Hg) was collected. It was characterized by NMR, IR, elemental analyses, and its heat of combustion. A similar reaction of MMH with acrylonitrile gave 1-methyl-1-cyanoethylhydrazine (MCEH), which was vacuum distilled at 342 K at 127 Pa (69 °C at 0.95 mm Hg). The product of the reaction of 0.5 mol UDMH in 40 mL of water at 360 K (87 °C) with 0.5 mol acrylonitrile for 2 h, with the temperature reaching that of reflux, was vacuum distilled at 530 Pa (4 mm Hg). The first cut was removed and discarded, and a second fraction with a boiling point of 350–354 K (77–81 °C) at a pressure of 530 Pa (4 mm Hg) was 1,1-dimethyl-2-cyanoethylhydrazine (DMCEH). This product was characterized by NMR, IR, and elemental analyses. The heat of combustion was determined in order to calculate the enthalpy of formation for the product. Cyanoethylhydrazines would perform well as low-vapor-pressure hypergolic fuels for RFNA, but they are not very stable and discolor during storage. Properties of low-volatility  $\omega$ -substituted alkylhydrazines are listed in Table 8.

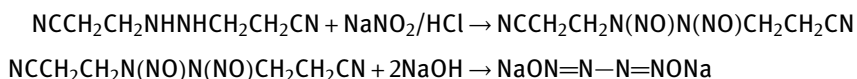
**Table 8:** Properties of low-volatility  $\omega$ -substituted alkylhydrazines.

| Property                              | CEH                                          | MCEH                                         | DMCEH                                         | HEH                                            |
|---------------------------------------|----------------------------------------------|----------------------------------------------|-----------------------------------------------|------------------------------------------------|
| CAS RN                                | 353-07-1                                     | 352-90-9                                     | 22705-94                                      | 8 109-8-42                                     |
| Gross formula                         | C <sub>3</sub> H <sub>7</sub> N <sub>3</sub> | C <sub>4</sub> H <sub>9</sub> N <sub>3</sub> | C <sub>5</sub> H <sub>11</sub> N <sub>3</sub> | C <sub>2</sub> H <sub>8</sub> N <sub>2</sub> O |
| Molecular mass, g/mol                 | 85.11                                        | 99.13                                        | 113.16                                        | 76.10                                          |
| Boiling point, °C at mm Hg            | 85 at 0.35                                   | 95 at 10                                     | 80 at 4                                       | 140 at 9                                       |
| Enthalpy of formation, kJ/mol         | +77.0                                        | +126                                         | +165                                          | −194                                           |
| Enthalpy of formation, kcal/mol       | +18.4                                        | +30.2                                        | +39.5                                         | −46.4                                          |
| Density, g/cm <sup>3</sup> , at 293 K | 1.055                                        | 0.9737                                       | —                                             | 1.113                                          |
| Dynamic viscosity, cPs, at 293 K      | —                                            | 4.19                                         | —                                             | —                                              |

Data source: [145]

Reaction of UDMH with bromoacetonitrile makes 1-cyanomethyl-1,1-dimethylhydrazinium bromide, [(CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>CN)NH<sub>2</sub>]Br, which can be converted to energetic salts based on the [(CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>CN)NH<sub>2</sub>]<sup>+</sup> cation and nitrate, perchlorate, azide, 5-aminotetrazolate, and picrate anions [146]. The melting and decomposition points of these compounds were determined by DSC, and sensitivities to impact, friction, and ESD were measured. See also [147–150].

Nitrosation of 1,2-bis(2-cyanoethyl)hydrazine yields 1-nitroso- and 1,2-dinitroso-1,2-bis(2-cyanoethyl)hydrazines. Decyanoethylation of 1-nitroso-1,2-bis(2-cyanoethyl)hydrazine resulted in formation of sodium azide. Dinitrosohydrazine salts were synthesized by dealkylation of 1,2-dinitroso-1,2-bis(2-cyanoethyl)hydrazine [151]:



## 7.6 2-Azidoethylhydrazine

2-Dimethylaminoethylazide (DMAZ) is simple to prepare and is hypergolic with IRFNA, but there is a significant ignition delay. The replacement of the tertiary amine nitrogen in DMAZ with 1,1-dimethyl hydrazine was expected to result in 1,1-dimethyl-2-(2-azidoethyl)hydrazine, (H<sub>3</sub>C)<sub>2</sub>NNHCH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>, DMAEH, which was predicted to have better rocket performance than DMAZ. DMAEH is anticipated to have a lower vapor pressure than hydrazine. Several attempts at synthesizing DMAEH by different routes have ultimately failed, as only traces of a product were seen at most [152–154]. The end product in most reactions was a solid quaternary salt with the positive charge on the same nitrogen that was also carrying the two methyl groups. In all cases UDMH acted as a strong nucleophile. Attempts to make 2-azidoethylhydrazine, H<sub>2</sub>NNHCH<sub>2</sub>CH<sub>2</sub>N<sub>3</sub>, by starting with hydrazine instead of UDMH also failed. Intermediates for the synthesis were 2-azidoethyl *p*-toluenesulfonate or 1-azido-2-chloroethane with leaving groups such as *p*-toluenesulfonate (*tosylate*) or a halide. It was hoped that either one would react with UDMH to produce the desired DMAEH energetic fuel.

A three-step reaction sequence was developed, beginning with the reaction of UDMH and chloroacetyl chloride with 1,1-dimethyl-2-[2-chloroethyl]hydrazine as an intermediate [155]. Regardless of the conditions (temperatures, reaction times, and varying reactant concentrations) applied, yields were consistently low (18% max.). The hydrazone was formed, but only accompanied by copious amounts of glyoxal bis-(dimethylhydrazine) as a by-product, from which it was difficult to separate.

In analogy to 2-azidoethanol and DMAZ, which have been extensively studied as potential rocket propellants, computational chemistry predicted that 2-hydrazinoethyl azide (2-azidoethylhydrazine, DMAEH) should be a very energetic molecule. In support of experimental efforts to make DMAEH, quantum chemical calculations using a density functional theory method and charge density analysis of amine-azide-based propellants (DMAZ, DMAEH, 2-azido-*N,N*-dimethylcyclopropanamine, 2-azido-*N*-methylcyclobutanamine, and 2-azidocyclopentanamine) were carried out to understand the geometry, bond topological, electrostatic, and energetic properties of each [156]. The electron density distributions revealed the nature of the chemical bonding in these molecules. The charge concentration of the N–N bond attached to the dimethylamino group in DMAEH is very small, confirming that this bond is the weakest among the molecules. The charge imbalance parameters of the molecules showed that the DMAEH molecule is the least sensitive in this series. Surprisingly, upon comparing band-gap energies among the linear molecules, one would predict that DMAZ (4.42 eV) would be less stable than DMAEH (5.58 eV).

## 7.7 Chloromethyldimethylhydrazine

The reaction of UDMH with excess dichloromethane led to the formation of the chloride salt of the 1-(chloromethyl)-1,1-dimethylhydrazinium cation  $[(\text{CH}_3)_2\text{N}(\text{CH}_2\text{Cl})\text{NH}_2]\text{Cl}$ . The metathetical reaction of this intermediate salt with a suitable silver salt provided the nitrate, perchlorate, azide, dicyanamide, and sulfate salts, which were ionic liquids [157].

## 8 1,2-Dihydrazinoethane

Alkylhydrazines with only one hydrazino group per molecule are discussed above. Similar to polyaminoalkanes, we can also make polyhydrazinoalkanes with two or more hydrazino groups attached to a hydrocarbon alkane backbone. Such compounds may have physical properties that make them more desirable than either MMH or UDMH. The simplest representative of this group is 1,2-dihydrazinoethane, but more complex hydrazines such as 1,2,3,4-tetrahydrazinobutane have also been proposed as rocket fuels. Ethylene dihydrazine was initially considered for use as a liquid propellant approximately 50 years ago because of its high apparent density ( $1.09 \text{ g/cm}^3$ ) and positive enthalpy of formation ( $+155 \text{ kJ/mol}$ ;  $+37 \text{ kcal/mol}$ ) [158].

### 8.1 Preparation of 1,2-Dihydrazinoethane

1,2-Dihydrazinoethane, also known as ethylenedihydrazine, 1,2,5,6-tetraazahexane; hydrazine, 1,1'-(1,2-ethanediy)bis-;  $\text{H}_2\text{NNHCH}_2\text{CH}_2\text{NHNH}_2$ ,  $\text{C}_2\text{H}_{10}\text{N}_4$ , EDH, CAS RN [6068-98-0], has been evaluated as a substitute for UDMH or as an additive to UDMH. However, EDH has a substantially higher viscosity than either hydrazine or UDMH. 1,2-Dihydrazinoethane (also called ethylenedihydrazine, EDH) was prepared from 1,2-dichloroethane and an excess of hydrazine hydrate, and has been evaluated as a hypergolic rocket fuel on its own or in mixtures with UDMH [93, 94]. The reactants are immiscible and had to be stirred for 24 h below 312 K. After the reaction mixture became homogeneous, indicating completion of the reaction, the excess hydrazine hydrate was removed by distillation and the product had to be separated from hydrazinium chloride in the residue and recrystallized as the EDH dichloride salt. 1,4-Diaminopiperazine formed as an unwanted by-product. Even in the presence of a large excess of hydrazine, this and other polymeric by-products formed in the reaction. An alternate method of extracting the desired product involved adding sodium hydroxide to the reaction mixture to neutralize hydrochloric acid and liberate all hydrazines, followed by fractionated vacuum distillation. Reported yields were only 52% of the theoretical yield [158]. EDH has not been commercially available since the early 1960s, when Dow Chemical discontinued its pilot plant operation in

Pittsburgh, CA. When it was commercially available, the EDH was of poor quality. The purification of distilled EDH was achieved by formation and recrystallization of either its hydrochloride or oxalate salt. Purification of the oxalate salt was substantially more efficient and was eventually selected as the method of choice. Purification was monitored by neutralization of the oxalate salt followed by capillary column GC analysis of the liberated EDH. One recrystallization from alcohol/water increased the purity from 87% to a nominal 95%. A second recrystallization gave better than 99% pure EDH. The final isolation was achieved by vacuum distillation. The overall yield of this high-purity EDH (> 99%), based on the starting material ethylene dichloride, was only 19.5%.

The structure of the polymer formed as a byproduct during the reaction of ethylene halogenides and hydrazine hydrate has not been identified. Formation of the otherwise useless polymer is maximized if a ternary amine is added to the reaction mixture [159]. Reduction of the polymer with hydrogen did not give the expected ethylenediamine, indicating it does not have a simple linear structure.

The first step of the synthesis of alkylenedihydrazines often leads to the chloride salts of the desired product. The free bases can be liberated by reaction with alkali metal alkoxides. For instance, an excess of a salt was treated with alkali metal alcoholates to give the free bases  $\text{H}_2\text{NNH}(\text{CH}_2)_n\text{NHNH}_2$ . Thus, 102.4 g ethylenedihydrazine dichloride salt ( $n = 2$ ) was added to a solution of 99.5 g  $\text{PrONa}$  in 400 mL  $\text{PROH}$  at 293–298 K (20–25 °C), the suspension was stirred at room temperature for 4 h, the  $\text{NaCl}$  was filtered off, and the filtrate was distilled to give 29.5 g EDH with a boiling point of 361–362 K at 27 Pa (88–89 °C at 0.2 mm Hg),  $n_D^{22} = 1.522$ ,  $\rho = 1.095 \text{ g/cm}^3$  at 22 °C [160].

The isolation and characterization of trimethylene hydrazine and the search for better syntheses for ethylenedihydrazine did not lead to wider use of these chemicals [56].

1,2-Dihydrazino ethane is an alternative low-vapor-pressure (compared to UDMH) hydrazine fuel for hypergolic storable bipropellant combinations. It has been evaluated as a low-vapor-pressure replacement for MMH or UDMH. Aerojet formulated a hypergolic fuel mixture containing EDH and hydrazine in the 1960s [158]. It was intended as a high-density replacement for Aerozine-50.

The reaction of 1,2-dichloroethane with MMH results in the *N*-methyl-substituted dihydrazinoethane  $\text{H}_3\text{CN}(\text{NH}_2)(\text{CH}_2)_2\text{N}(\text{NH}_2)\text{CH}_3$ , which can be used as a low-vapor-pressure substitute for MMH with no loss in rocket performance [161]. Another bishydrazine that was prepared was 1,1'-(butan-1,4-diyl)bis(1-methylhydrazine),  $\text{H}_3\text{CN}(\text{NH}_2)(\text{CH}_2)_4\text{N}(\text{NH}_2)\text{CH}_3$ . Other low-vapor-pressure alkylhydrazines evaluated as substitutes for MMH had  $\beta$ -aminoethyl or  $\beta$ -azidoethyl substituents.

## 8.2 Physical Properties of 1,2-Dihydrazinoethane Mixtures

The physical properties of EDH/hydrazine mixtures are summarized in Table 9. The freezing point of the binary system shows a minimum near 80% EDH. Solutions with EDH have a tendency to supercool and it is difficult to determine the freezing points.

**Table 9:** Freezing points, densities, and viscosities of 1,2-dihydrazinoethane/hydrazine mixtures.

| EDH, % by mass                                | 0      | 20    | 40    | 60    | 80    | 100  |
|-----------------------------------------------|--------|-------|-------|-------|-------|------|
| Freezing point, °C                            | +1.5   | −8    | −15   | −30   | −33   | +8   |
| Freezing point, K                             | 274.65 | 265   | 258   | 243   | 240   | 291  |
| Density, g/cm <sup>3</sup> , at 298 K = 25 °C | 1.005  | 1.016 | 1.035 | 1.048 | 1.073 | 1.09 |
| Viscosity, cPs, at 298 K = 25 °C              | 0.9    | 20    | 22    | 25    | 36    | 90   |

Data source: [94]

## 8.3 Physical Properties of 1,2-Dihydrazinoethane

Physical properties of 1,2-dihydrazinoethane are listed in Table 10.

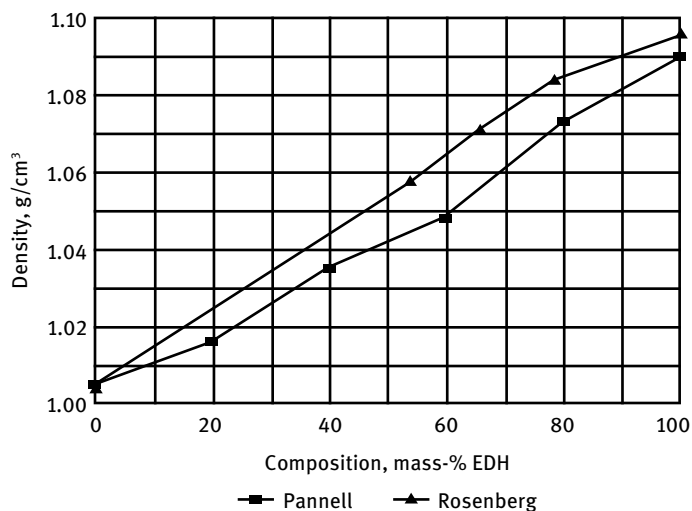
**Table 10:** Physical properties of 1,2-dihydrazinoethane.

| Property              | SI units                         | Other units            |
|-----------------------|----------------------------------|------------------------|
| Molecular mass        | 90.13 g/mol                      | 11.095 mol/kg          |
| Freezing point        | 285.9 K                          | +12.8 °C               |
| Boiling point         | ~515 K                           | ~242 °C (uncertain)    |
| Density               | 1.096 g/cm <sup>3</sup> at 298 K | —                      |
| Vapor pressure        | 10.6 Pa at 334 K                 | 0.08 mm Hg at 61 °C    |
| Viscosity             | 90 mPa s                         | 90 cPs                 |
| Heat of combustion    | 26.09 kJ/g                       | 6235.9 ± 2.7 cal/g     |
| Enthalpy of formation | +137.7 ± 2.1 kJ/mol              | +32.91 ± 0.49 kcal/mol |
| Heat of vaporization  | 77.0 kJ/mol                      | 18.4 kcal/mol          |

Data source: [158]

### 8.3.1 Densities of 1,2-Dihydrazinoethane/N<sub>2</sub>H<sub>4</sub> Mixtures

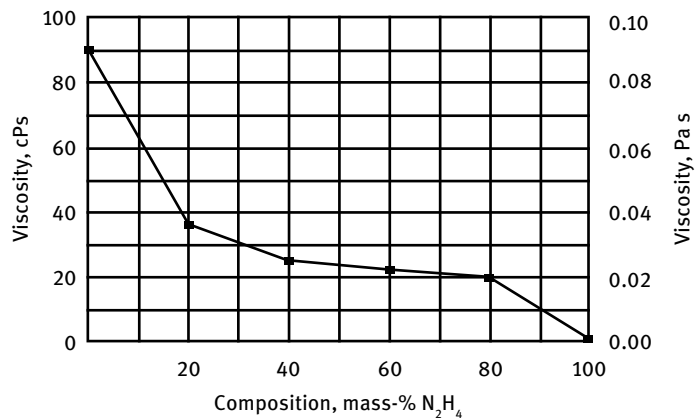
Higher densities at similar elemental compositions (carbon contents) can be achieved by replacing UDMH in Aerozine-50 with 1,2-dihydrazinoethane (EDH). Densities of this blend, as shown in Figure 10, increase with increasing EDH content. The EDH/AH mixture is known by the designation A-67, Aerozine-67, which is a solution of 32.8 mass-% ethylene dihydrazine in hydrazine. The density of A-67 is 1.071 g/cm<sup>3</sup> at 298 K (25 °C). The heat of solution of EDH in hydrazine is minimal, +9.3 cal/mol at 65.7–34.3 mass-% EDH-AH.



**Figure 10:** Comparison of density data for 1,2-dihydrazinoethane/hydrazine mixtures. (Image created by Schmidt 2016 based on data from [94] and [158].)

### 8.3.2 Viscosities of 1,2-Dihydrazinoethane/ $\text{N}_2\text{H}_4$ Mixtures

Replacing UDMH in Aerozine-50 with a less volatile alkyldiazine such as 1,2-dihydrazinoethane can reduce the vapor toxicity hazard somewhat, but the viscosity increases dramatically, as illustrated in Figure 11.



**Figure 11:** Viscosity of 1,2-dihydrazinoethane/hydrazine mixtures. (Image created by Schmidt 2016 based on data from [94].)

## 8.4 Chemical Properties of 1,2-Dihydrazinoethane

GC analysis of a commercial sample of EDH (distilled once before) showed that the retention times of the four main components were sufficiently close to indicate that purification by fractional distillation would not be successful. The mononitrate of 1,2-dihydrazinoethane has an unusually low melting point and remains a liquid at room temperature. It has all the properties of an ionic liquid.

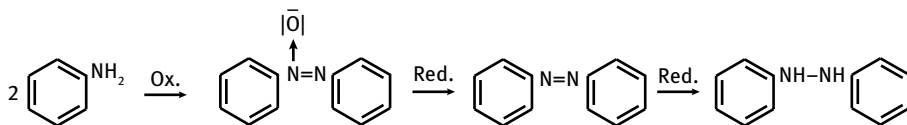
## 9 Cyclic Hydrazines

Heterocyclic hydrazines, rings with two adjacent nitrogen atoms, are heterocyclic compounds and are covered in the chapter “Heterocyclic and Heterocycloaliphatic Amines” in *Encyclopedia of Liquid Fuels*.

## 10 Arylhydrazines

Although arylamines like toluidine and xylydine have been used as rocket fuels, arylhydrazines have not. Arylhydrazines are more difficult to prepare than arylamines and are more susceptible to autoxidation.

Historically, much more information has been published about the preparation and chemistry of arylhydrazines than about their aliphatic counterparts. The main cause of this is the close interconnection between aromatic hydrazines and their respective azo compounds, which are useful intermediates for dyes and pharma products. The transitions between amine, azoxy, azo, and hydrazo compounds are easily achieved by progressive oxidation and reduction, respectively:



Arylhydrazines are not generally prepared by direct arylation of hydrazine with arylhalogenides, at least not unless the halogen is sufficiently activated by neighboring groups, such as in 2,4-dinitrochlorobenzene, which reacts with hydrazine to form 2,4-dinitrophenylhydrazine, a widely used reagent for the identification of compounds containing carbonyl groups. The halogen in the vicinity of the heterocyclic nitrogen in 2-chloropyridine or 2-chlorophthalazine is also sufficiently active to give the corresponding hydrazines by direct substitution.

Several books and survey articles on organic hydrazines, in particular aromatic hydrazines, have already been published, and we are not attempting to repeat that material herein.

When viewing the toxicity of hydrazines as a family, it is interesting to note that phenylhydrazine is a constituent of agaritine, a glucoside found in the common brown cap mushroom *Agaricus bisporus*, which is consumed in tonnage quantities by the entire world population, apparently without any undue toxic effects. Fresh mushrooms contain about 0.4–0.7 g agaritine/kg = 0.04–0.07 mass-% dry mushroom (we assume 0.055% on average). The annual US cultivated brown cap mushroom consumption is 800 million lb = 362000000 kg wet. Assuming 10% moisture, that is 326000000 kg dry mass containing 180000 kg agaritine, which contains 20880 kg  $N_2H_3$  entity. According to this calculation, more  $N_2H_3$  is eaten than is used as a rocket propellant. Agaritine has been shown to be broken down by enzymes in animal kidneys into the toxic metabolites 4-(hydroxymethyl)phenylhydrazine and 4-(hydroxymethyl)benzenediazonium ion. These metabolites have been shown to cause stomach cancer in mice.

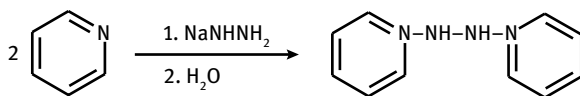
## 11 Alicyclic Hydrazines

The energy content of alkylhydrazines can be increased by replacing *n*-alkyl groups with alkyl groups that contain stressed rings. 1,4-Di(hydrazomethyl)cubane was prepared by reduction of 1,4-cubanedicarboxylic acid dihydrazide with an excess of  $BH_3 \cdot THF$  etherate [162]. The hydrazines were not stable at room temperature but were isolated as their salts. The dihydrazine dioxalate was the most stable salt isolated, but the diacetate, ditriflate, disulfate, and dinitrate were also prepared. The dinitrate was a white solid with a melting point of 468–469 K (195–196 °C). The diperchlorate and dinitroformate salts decomposed after several hours at room temperature.

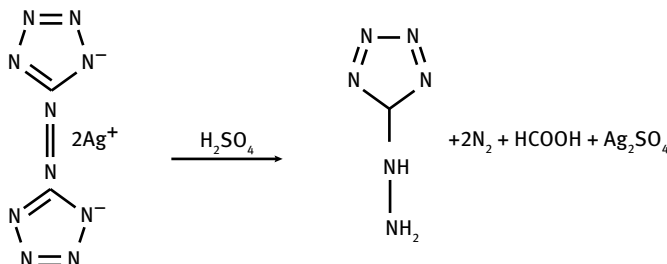
## 12 Heterocyclic Hydrazines

2-Pyridylhydrazines can be prepared in 36% yield by the direct introduction of hydrazine as sodium hydrazide into pyridine (Py) and subsequent hydrolysis with water [163]. Even better yields (62 and 58%, respectively) can be obtained from 4-methylpyridine or 2,4-dimethylpyridine. Sodium methylhydrazide and sodium *N,N*-dimethylhydrazide give the corresponding disubstituted (26%) and trisubstituted (33%) hydrazines, respectively [164]. The reaction of sodium hydrazide with aromatic nitrogen heterocycles produces hydrazo compounds:





Various azotetrazole salts are used as percussion initiators. Disposal of these salts by treatment with dilute mineral acid may not be without danger because, in the case of silver azotetrazole, a hypersensitive compound may form [165]. Hydrolysis of azotetrazole anion in boiling dilute sulfuric acid gives 5-hydrazinotetrazole, nitrogen, and formic acid:



3,6-Dihydrazino-1,2,4,5-tetrazine would be a good constituent of gas generator propellants due to its high nitrogen content (79%) and high enthalpy of formation (+519 kJ/mol). It can be prepared by reaction of 3,6-diamino-1,2,4,5-tetrazine with hydrazine [166]. Alicyclic hydrazines are the parent compounds of a large family of 1,2-diazoles and 1,2-diazanes [167].

## 13 Alkyldiazenes and Azoalkanes

### 13.1 Alkyldiazenes

#### 13.1.1 Preparation of Alkyldiazenes

Alkyldiazenes ( $\text{R}-\text{N}=\text{NH}$  compounds with one alkyl group, not with two, as in azoalkanes) are not very stable, but the methyl esters of the alkyl azocarbonic acids  $\text{R}-\text{N}=\text{N}-\text{COOCH}_3$  are stable. Boiling points and IR spectra of several alkyl esters of azocarbonic acids ( $\text{R}=\text{H}$ , cyclopropyl, Me, Et, *i*-Pr, *i*-Bu, and *t*-Bu) were determined [168]. These served as intermediates when preparing short-lived diazenes, the IR spectra of which were measured on cooled samples in frozen matrices. Diazenes are likely intermediates in the Wolff-Kishner reaction. They also form as intermediates in the oxidation of alkylhydrazines.

## 13.2 Azoalkanes

Azoalkanes exist in two structural isomers where the two alkyl groups are either on the same side (*cis*) or on opposite sides (*trans*) of the plane defined by the double bond.

### 13.2.1 Preparation of Azoalkanes

Azoalkanes,  $R-N=N-R$ , are obtained as intermediates in the oxidation of 1,2-dialkylhydrazines. The simplest member of this group is azomethane. Azomethane was detected in the exhaled air of 1,2-dimethylhydrazine-treated rats [169]. Azomethane may form as an unwanted intermediate during industrial MMH synthesis by the Raschig route, and may have been the cause of accidents in MMH production plants. In contrast to the azoaranes (aromatic azo compounds), the azoalkanes are unstable and may decompose explosively. This explosive property is similar to that of diazomethane  $H_2CN_2$ , which is usually handled only in dilute solutions.

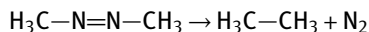
### 13.2.2 Physical Properties of Azomethane

Azomethane can be recognized by its Raman spectrum, which is quite different from that of SDMH [170].

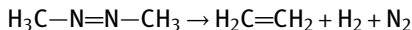
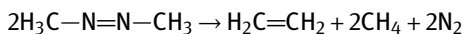
### 13.2.3 Decomposition of Azomethane

Azomethane,  $H_3C-N=N-CH_3$ ,  $C_2H_6N_2$ , is a relatively simple molecule, but notoriously unstable. One would not want to use it as a rocket propellant, and one must avoid its formation as a byproduct of other reactions by all means. The decomposition of azomethane is discussed here only because the accumulation and explosive decomposition of azomethane is a potential problem in the production of MMH and has been the cause of accidents.

Similar to methyl azide, which also has no practical application value, azomethane decomposition was studied mostly to satisfy academic curiosity. It is a ready source of methyl radicals, which can trigger all kinds of other reactions. In addition to studying the decomposition of azomethane in the homogeneous gas phase, many studies also looked at the decomposition of azomethane adsorbed on metal surfaces. Azomethane decomposition was once studied because someone was planning to use it as a rocket propellant (which is NOT a good idea!). The kinetics of azomethane decomposition have been studied extensively because, similar to dinitrogen pentoxide, it is a relatively simple reaction. The decomposition of azomethane is a reaction of first order, but the rate decreases at low pressure [171, 172]. The main reaction during decomposition of azomethane leads to ethane and nitrogen:



Side reactions lead to ethylene and methane or to ethylene and hydrogen:



Ethane and nitrogen are reaction products in the decomposition of azomethane, but adding ethane and nitrogen to the azomethane before heating it had little effect on the kinetics and did not retard the decomposition reaction [173].

Helium addition activated azomethane, being 0.12 times as effective as azomethane itself. If the azomethane decomposition is a chain reaction, the chain is very short, and its length is independent of temperature and pressure over the range studied [174].

The products of low-pressure decomposition of azomethane were analyzed by fractionated condensation at dry ice and liquid nitrogen temperatures [175].

The activation energy of azomethane decomposition in the temperature range 563–613 K (290–340 °C) is 220 kJ/mol (52.5 kcal/mol). Tetramethylhydrazine may form as an intermediate during the reaction [176].

Azomethane decomposition can also be initiated by photolysis [177]. The quantum yield of nitrogen formation was found to be unity and independent of temperature.

The rapid pyrolysis of azomethane was studied in a shock tube over the temperature range 800–1300 K [178]. Concentrations of the azomethane in argon were 1–3%. The rate of decomposition in the incident shock region was followed spectrophotometrically at  $\lambda = 338$  nm. It was estimated that, under shock conditions, the depletion of the reactant due to a chain mechanism was negligible compared to that due to the unimolecular decomposition. Due to the exothermicity of the overall reaction (products:  $\text{N}_2$  and  $\text{C}_2\text{H}_4$ ), only average rate constants could be evaluated from the recorded oscilloscope traces. These were found to fall well within the extrapolations of the two most recent low-temperature studies, based on a strict Arrhenius rate vs temperature relationship.

The explosive decomposition of azomethane was studied experimentally in an apparatus that permitted the simultaneous, time-resolved measurement of pressure, the local gas temperature at the center of a spherical reaction vessel, and the local gas temperature near the vessel wall [179]. The explosion-limit pressure could be bracketed closely, and the pre-explosion pressure and temperature rise, the maximum stable temperature rise, the length of the induction period, and the course of the fast but non-explosive decomposition were measured at temperatures from 605 to 714 K and for some mixtures with added  $\text{H}_2$ , He,  $\text{N}_2$ , and NO. NO was added as a free-radical scavenger. At temperatures between 636 and 687 K, the records indicated a thermal explosion, i.e., the temperature at the center rose exponentially just before the onset of explosion and a large maximum temperature rise of 40–45 °C was measured for the

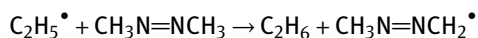
slow reaction just below the limit. From the temperature dependence of the limit, the maximum temperature rise, and the temperature rise well below the limit as a function of initial concentration, an activation energy of 134 kJ/mol (32 kcal/mol) was obtained, in marked disagreement with a literature value of 213 kJ/mol (51 kcal/mol) from slow isothermal decomposition.

The decomposition of azomethane is a complex process, but work showed that the residual fully NO-inhibited reaction has all the features of a unimolecular reaction. This residual reaction was treated using a quantum mechanical harmonic version of a theory of unimolecular reactions [180]. Extrapolation to infinite pressure gave

$$\log k_{10\infty} = 17.32 - 55500/2.303RT$$

In accordance with the high pre-exponential factor (and hence high entropy of activation), a very loose activated complex was postulated, involving free rotations of the two methyls and the central nitrogen. Two models of this complex were considered: one having a planar methyl and the other a tetrahedral methyl. Theory also predicted an activation energy fall-off with pressure that is, on the whole, in accord with the rather limited experimental data.

The thermal decomposition of azomethane has been studied in a static system at temperatures between 523 and 593 K (250 and 320 °C) and at pressures between 0.67 and 53.6 kPa (5 and 402 mm Hg), with particular attention paid to identification of products [181]. Major products, in decreasing order of importance, were nitrogen, methane, ethane, methylethyldiimide, dimethylhydrazone, propane, tetramethylhydrazine, ethylene, methylpropyldiimide, and methylethylhydrazone. Carbon balance at the lowest pressure and highest temperature was 92%, but decreased with increasing pressure and decreasing temperature owing to the formation of a polymer. A fairly simple mechanism should account reasonably well in the decomposition for a short chain reaction propagated by the free radical  $\text{CH}_3\text{N}=\text{NCH}_2^\bullet$ , and for the five most abundant products except ethane. It turns out that there may be a second source of ethane:



Ethyl radicals are also shown to be responsible for the formation of propane, ethylene, methylethylhydrazone, and methylpropyldiimide. The radical  $\text{CH}_3\text{N}=\text{NCH}_2^\bullet$  decomposes to  $\text{CH}_3 + \text{CH}_2 + \text{N}_2$ , and the methylene radical (probably both singlet and triplet) can yield  $\text{C}_2\text{H}_5^\bullet$  at low pressure and high temperature and mostly polymer at high pressure and low temperature.

The rate constant of azomethane decomposition in argon was measured at temperatures of 820–1400 K, pressures of 0.25–7.5 atm, and initial azomethane concentrations of 40–2000 ppm [182]. The amount of azomethane reacted was estimated via UV absorption at the vacuum UV boundary ( $\lambda = 198 \text{ nm}$ ), and the concentration of  $\text{CH}_3^\bullet$  radicals resulting from azomethane decomposition was monitored by absorption at

$\lambda = 216$  nm. The observed temperature dependence of the azomethane decomposition apparent rate constant,

$$k_1 = 10^{11.3} \exp(-33.5/RT) \text{ s}^{-1}$$

was in good agreement with the literature. The low values of the activation energy and pre-exponential factor are unusual for classical monomolecular decomposition. This confirms the assumption that azomethane decomposition at high temperatures takes place via a concerted mechanism.

The decomposition of azomethane has been investigated over a wide range of different conditions and in the presence of various additives, but what is really needed is a study of the effect of azomethane on the decomposition of methylhydrazine and *vice versa*. Such a study has not yet been done. Methyl radicals formed during the decomposition of azomethane are likely to trigger the decomposition of MMH. Active intermediates in the decomposition of azomethane most likely also play a role in the decomposition of MMH, SDMH, and UDMH.

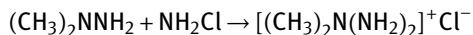
## 14 Alkyltriazanes and Alkyltriazenes

Connecting alkyl groups to a chain of three nitrogen atoms could lead to NH homologues of alkylhydrazines, but connecting three nitrogen atoms in a row leads to unstable compounds unless they are stabilized by resonance with adjacent aromatic structures. In that case, there is usually a  $\text{—N=N—}$  double bond in the chain. Triazenes are more stable than triazanes.

### 14.1 Preparation of Alkyltriazenes

Surprisingly, the reaction of UDMH and chloramine does not lead to dimethyltriazene; a sequence of reactions leads to tetramethyltetrazene as the ultimate product [183]. The chloramine acts just like an oxidant, and the same result can be achieved by using another oxidizer.

While the free dimethyltriazane is not stable, stable 2,2-dimethyltriazanium chloride can be prepared by the reaction of UDMH with chloramine [184]:



If samples of this salt are needed for comparison purposes, it can be prepared in good yield by reaction of UDMH with chloramine in ethereal solution. It is stable at room temperature and reacts with neither ammonia nor UDMH. It can be recrystallized from UDMH, in which it is moderately soluble. Replacing the chloride anion with trinitroformate ion results in the formation of an energetic salt.

1,3-Dialkyltriazenes  $R-NH-N=N-R$  (e.g., 1,3-dimethyltriazene) can be obtained as a magnesium complex intermediate by reacting methyl azide with a Grignard reagent. The solution in ether can be kept at low temperature, but the free pure triazene is unstable. Trimethyltriazene complexes with the chlorides of copper(I), zinc, boron, aluminum, silicon, tin, titanium, zirconium, and phosphorus were found to be stable (at least below 373 K) and were well characterized [185].

*Ab initio* and DFT methods were used to compute the theoretical enthalpies of formation of solid ionic compounds derived from nitrogen-rich salts of the 2,2-dimethyltriazanium cation and other nitrogen-rich ionic compounds [186]. The crystal structure and hydrogen-bonding networks of the nitroformate salt of the 2,2-dimethyltriazanium cation were selected as examples for detailed discussion.

## 14.2 Alkyltriazanium and Alkyltriazenium Salts

The enthalpies of formation of dimethyltriazanium salts were calculated from the heats of combustion and solution (in  $H_2O$ ) [187, 188] (Table 11).

**Table 11:** Enthalpies of formation of dimethyltriazanium salts.

| Compound name                  | Formula                     | Enthalpies of formation |          |
|--------------------------------|-----------------------------|-------------------------|----------|
|                                |                             | kJ/mol                  | kcal/mol |
| Dimethyltriazanium chloride    | $[Me_2N(NH_2)_2]^+ Cl^-$    | -88.6                   | -21.17   |
| Dimethyltriazanium nitrate     | $[Me_2N(NH_2)_2]^+ NO_3^-$  | -145.7                  | -34.82   |
| Dimethyltriazanium perchlorate | $[Me_2N(NH_2)_2]^+ ClO_4^-$ | -69.7                   | -16.66   |
| Dimethyltriazanium ion         | $[Me_2N(NH_2)_2]^+$         | -101.6                  | 24.29    |

Data source: [187]

Triazenes can be stabilized by attaching heterocyclic rings to either end in the 1,3-positions such that the electron cloud of the  $-N=N=N-$  bridge interacts by resonance with the electron clouds in the ring systems, forming compounds such as 1,3-bis(1-methyltetrazol-5-yl)triaz-1-ene and 1,3-bis(2-methyltetrazol-5-yl)triaz-1-ene by diazotization of 1-methyl-5-aminotetrazole or 2-methyl-5-aminotetrazole using only half an equivalent of sodium nitrite [189].

## 14.3 Nitrotriazanes and Nitrotriazenes

Attaching one or two nitro groups to triazane or triazene creates molecules that contain four or even five nitrogen atoms in a chain. An attempt was made to synthesize the ammonium salt of 1,3-dinitrotriazene, (also known as dinitramidoamine,

di(nitramido)amine, and 1,1,5,5-tetraoxoazapentene(2)), but without success [190]. Theoretical calculations were performed in an effort to see if it might be more stable than ADN, which contains just one or two fewer nitrogens. This salt is also known by its acronym, ADNA, but it remains elusive.

## 15 Tetraalkyltetrazenes

### 15.1 Preparation of Tetraalkyltetrazenes

Tetramethyl-2-tetrazene, also known as  $(\text{H}_3\text{C})_2\text{N}=\text{N}=\text{N}(\text{CH}_3)_2$ ,  $\text{C}_4\text{H}_{12}\text{N}_4$ , TMTZ, CAS RN [39247-67-1],  $M = 116.168 \text{ g/mol} = 8.6080 \text{ mol/kg}$ , has been considered as a low-vapor-pressure replacement for MMH or UDMH in hypergolic bipropellant combinations [191].

Tetramethyl-2-tetrazene usually forms as an unwanted autoxidation product in UDMH that has been exposed to air for too long. The contamination of UDMH by tetramethyl-2-tetrazene is usually quickly recognized as it causes yellow discoloration. It has a characteristic absorption band at  $2360 \text{ \AA}$ .

Tetramethyl-2-tetrazene (and similarly tetraethyl-2-tetrazene) can be prepared by oxidation of UDMH (or 1,1-diethylhydrazine) in ether by gradual addition of mercury(II) oxide [39, 192]. It boils at  $305 \text{ K}$  at  $2 \text{ kPa}$  ( $32^\circ\text{C}$  at  $15 \text{ mm Hg}$ ) and has a UV absorption maximum at  $277 \text{ nm}$  in ethanol. The shape of the absorption spectrum differs in solvents of different acidities. Tetramethyltetrazene forms salts and adducts, some of which are stable enough that melting points can be obtained: picrate (m.p.  $353 \text{ K}$ ), hydrogen oxalate, and 1:1 adducts with  $\text{CdCl}_2$ ,  $\text{CdBr}_2$ , and  $\text{HgCl}_2$ . Oxidation of 1,1-dialkylhydrazines with potassium bromate leads to tetraalkyltetrazenes [193, 194].

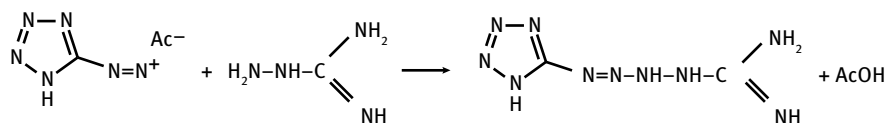
Tetramethyl-2-tetrazene was initially obtained as a pale-yellow liquid by oxidation of UDMH with  $\text{HgO}$ . The use of toxic and expensive  $\text{HgO}$  can be avoided by oxidizing UDMH with chloramine instead of  $\text{HgO}$  [195–199]. The UDMH solution should be acidified to a slightly basic pH by addition of hydrochloric acid. TMTZ spontaneously demixes from the aqueous medium and can be easily separated from the unreacted UDMH, which can be recycled. The crude TMTZ is 95% pure and the yield is 90%. A potential by-product of the reaction of UDMH with chloramine is formaldehyde dimethylhydrazone [200].

The otherwise very unstable tetramethyltetrazene can be stabilized by forming Lewis-type complexes with Lewis acids, such as trimethylaluminum or triethylaluminum [201]. The adducts are clear, colorless liquids that can be distilled under high vacuum. Similar compounds can be obtained with hydrazine and alkylhydrazines [202]. TMTZ forms a simple salt with hydrochloric acid and a quaternary salt with methyl iodide where the positive charges are located at the two terminal nitrogen atoms [203].

The dimerization of 1,1-dimethyldiazonium and 1,1-diethyldiazonium ions resulted in the random formation of tetramethyltetrazene, 1,1-diethyl-4,4-dimethyltetrazene, and tetraethyltetrazene [204]. Even three-component (Me, Et, Pr) and four-component (Me, Et, Pr, and Bu) mixtures were studied, and mixtures of up to ten different tetraalkyltetrazenes were successfully separated.

Tetramethyltetrazene has been proposed as a hypergolic fuel substitute for the more volatile and more toxic MMH or UDMH. The energy content of tetramethyltetrazene can be improved by replacing one or more methyl groups by azidomethyl groups [205]. The most energetic derivative is 1,1',4,4'-tetraazidomethyl-2-tetrazene (TMTZ), which can be made using the iodosylbenzene/trimethylsilyl azide couple. This one-step synthesis has led to two azido derivatives: 1-azidomethyl-1',4,4'-trimethyl-2-tetrazene (MATMTZ) and 1,4-di(azidomethyl)-1,4-dimethyl-2-tetrazene (DADMTZ). The decomposition of these two compounds in solution at different temperatures was studied using proton NMR analysis and quantitative NMR. Results showed that DADMTZ was more stable than MATMTZ.

Aminoguanidine is a useful intermediate for the synthesis of numerous high-nitrogen compounds. Aminoguanidine sulfate or hydrogen carbonate and sodium nitrite react in a slightly acidified (with acetic acid) solution to form “tetracene” through aminotetrazole and its diazo salt [206, 207]:



The more accurate designation for this compound is 1-(5-tetrazolyl)-4-guanyltetrazene. It forms shock-sensitive heavy-metal salts with silver or copper.

5,5'-Azobistetrazole and its heavy-metal salts are friction sensitive and are used in percussion primers. Azotetrazole is made by oxidizing aminotetrazole in alcoholic solution with permanganates or peroxydisulfates [208] (see also the chapter “Heterocyclic and Heterocycloaliphatic Amines” in *Encyclopedia of Liquid Fuels*). Azotetrazole is acidic and forms highly energetic salts with a variety of bases. The acid hydrolysis of azotetrazole (5,5'-azoditetrazole) anion with dilute acids gives 5-hydrazinotetrazole. However, other high-nitrogen products have also been isolated, one of which is explosive [165].

## 15.2 Physical Properties of Tetramethyltetrazene

The heat of combustion of tetramethyltetrazene is  $3521 \pm 1 \text{ kJ/mol}$  ( $841.47 \pm 0.21 \text{ kcal/mol}$ ). From this number, the enthalpy of formation can be calculated as  $\Delta H_f^{298} = +231.5 \text{ kJ/mol} = +55.34 \text{ kcal/mol}$  [209]. Other sources list exactly the same enthalpy of formation [210].



Boiling points of tetramethyltetrazene at different pressures have been reported. Boiling at 403 K (130 °C) at sea-level pressure results in decomposition. It is safe to distil it at 317 K at 4 Pa (44 °C at 30 mm Hg). Tetramethyl-2-tetrazene boils at 305 K at 2 kPa (32 °C at 15 mm Hg) and has a UV absorption maximum at 277 nm in ethanol [192]. The shape of the absorption spectrum differs in solvents of different acidities. Tetramethyltetrazene forms salts and adducts, some of which are stable enough that melting points can be obtained, for instance a picrate with a melting point of 353 K, a hydrogen oxalate, and 1:1 adducts with  $\text{CdCl}_2$ ,  $\text{CdBr}_2$ , and  $\text{HgCl}_2$ . Titration of tetramethyltetrazene with a Lewis acid ( $\text{BF}_3$  etherate in benzene or  $\text{AlCl}_3$  in chloroform) using crystal violet as an indicator gave sharp end points at molecular ratios of 1:1.

The density of pure TMTZ was  $\rho = 0.899 \text{ g/cm}^3$ , close to that of MMH ( $0.880 \text{ g/cm}^3$ ) [199]. In the IR spectrum, it exhibited a medium band at  $1467 \text{ cm}^{-1}$  ( $\text{N}=\text{N}$ ) and one very sharp band at  $995 \text{ cm}^{-1}$ . In the DSC, TMTZ melted at ca. 248 K (–25 °C) and decomposed at around 426 K (153 °C). The UV spectrum in an aqueous buffered solution (borax buffer, pH 9) featured two absorption bands at 248 nm ( $\epsilon = 5234 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and 277 nm ( $\epsilon = 7170 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), but only one band was observed in ether (279 nm,  $\epsilon = 9450 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). From the heat of combustion determined in a calorimeter, a standard enthalpy of formation of liquid TMTZ of  $214.37 \text{ kJ/mol}$  ( $51.20 \text{ kcal/mol}$ ) was calculated, which was in the same range as a literature value of  $55.34 \text{ kcal/mol}$ . The vapor pressure of TMTZ at 293 K (20 °C) was 875 Pa (6.57 mm Hg), lower than that of hydrazine and much lower than that of MMH. MMH had a vapor pressure of 4.98 kPa at 293 K (37.35 mm Hg at 20 °C).

Tetramethyl-2-tetrazene and tetraethyl-2-tetrazene in ethanol have absorbance maxima at 277 and 285 nm with molar absorptivities of  $8.3 \times 10^3$  and  $7.6 \times 10^3$ , respectively [192].

Repetitive recording of tetramethyltetrazene spectra in aqueous solution as a function of pH showed that the peak at 277 nm/pH 8.89 is eventually replaced by a peak at 248 nm/pH 3.34 with two distinct isosbestic points at 260 and 210 nm [211].

### 15.3 Decomposition of Tetramethyltetrazene

Some of the radicals and molecule fragments that occur during UDMH decomposition can again be observed during thermal decomposition of tetramethyltetrazene [212]. Fifty-four mass spectrometer runs were carried out at six different temperatures. At 2.4 Pa (0.018 Torr) and 400–420 K, the reaction was first order and the rate equation was

$$\log k = 11.64 - \frac{31900}{2.303RT} \quad \text{s}^{-1}$$

The activation energy was  $133 \text{ kJ/mol}$  ( $31.9 \text{ kcal/mol}$ ). This reaction is of interest for the preparation of tetramethylhydrazine.

Tetramethyltetrazene will decompose as soon as it comes into contact with monometallic noble metal (Pt and Ir) or bimetallic (Pt-Cu and Pt-Zn) catalysts deposited on alumina [213]. The addition of a transition metal such as Zn on Pt/Al<sub>2</sub>O<sub>3</sub> enhances the catalytic activity. A catalyst able to decompose TMTZ at 373 K (100 °C) (no less than 70 °C below the thermal decomposition temperature) was thus obtained and catalyzed the formation of molecular nitrogen, amines, and tetramethylhydrazine. See also [214].

#### 15.4 Toxicity of Tetramethyltetrazene

One of the autoxidation products of UDMH is tetramethyltetrazene, TMTZ, which is a contaminant of UDMH, and may also form in the blood and plasma of UDMH-treated animals.

Intraperitoneal administration of <sup>15</sup>N isotope-labeled TMTZ was performed in mice to define its toxicokinetics and tissue distribution [196, 215]. In two separate test series, mice were injected with TMTZ at a dose of 300 mg/kg and were sacrificed after 1 and 14 d, respectively, and blood and tissue samples were analyzed. A liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) assay was developed to determine TMTZ levels in biological samples. The elimination rate constant suggested that TMTZ was very quickly eliminated from the body. The results of tissue distribution experiments indicated that TMTZ underwent rapid distribution into limited organs such as the liver, kidney, and brain. Administration of TMTZ did not cause death or loss of weight in the mice examined. The mice also did not behave differently than usual, or relative to the control population.

Various cellular animal and human models were exposed to TMTZ and to the reference compound MMH to test their cytotoxicities [216]. There were no cytotoxic effects following exposure to TMTZ in animal as well as human models. The TMTZ molecule had little impact on cellular viability and proliferation of rodent and human dermal and hepatic cell models. TMTZ did not produce any metabolomic effects and appeared to be a promising alternative to MMH.

#### 15.5 Applications of Tetramethyltetrazene

Tetramethyltetrazene has been tested as a hypergolic fuel with IRFNA in a 1100-N (250-lb<sub>f</sub>) rocket engine at 2.07 MPa (300 psi) chamber pressure, and compared to anhydrous hydrazine and UDMH [217]. Six test firings with O/F ratios from 2.42 to 3.19 gave a specific impulse near to 215 s, less than that of hydrazine or UDMH.

While tetrazoles and tetrazole derivatives are surprisingly stable and widely used in various propellant formulations, the open-chain tetrazenes lack stability and must be stabilized by attaching groups that lead to resonance stabilization of the molecule.

One exception is 1,1,4,4-tetramethyltetrazene(2), which is an oxidation product of UDMH and is readily available. Tetramethyltetrazene has even been suggested as a low-volatility replacement for UDMH in hypergolic propellant combinations [217–219].

## 15.6 Alkyltetrazanium and Alkyltetrazenium Salts

Salts derived from alkyltetrazenes with chloramine and strong acids, in particular oxyacids, have been examined as potential propellant ingredients. These include the salts derived from 1,1,4,4-tetramethyl-2-tetrazene and nitric, perchloric, picric, and hydrazoic acids [203, 220]. Most of these syntheses start out by oxidizing UDMH, which leads to the formation of 1,1,4,4-tetramethyl-2-tetrazene.

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# Amides and Imides

## 1 Amides

Amides contain the  $\text{—CO—NH—}$  linkage and are usually formed from carboxy acids or carbonyl chlorides with amines or ammonia. Polyamides such as Nylon are known as polymers with very desirable mechanical properties, although they are not used as binders in rocket propellants. Imides contain a  $\text{C=NH}$  linkage and will be discussed in the section “Imides” following the section “Amides.”

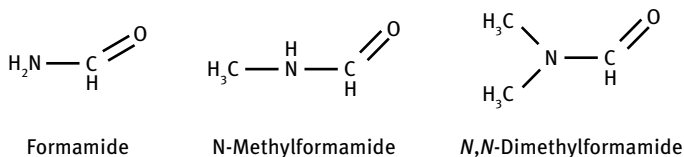
The sections “Amides” and “Imides” are arranged in order by the number of carbon atoms in the core of the molecule next to the  $\text{—CO—NH}_2$  group (not including the carbon in the  $\text{—CO—NH}_2$  group in the total count).

Amides and imides carrying nitro groups, such as nitroguanidine, are of particular interest as energetic materials. Many of these compounds described in this section were primarily developed as explosives, but they can potentially be used as replacements for RDX or nitroguanidine, NQ, in composite modified double-base (CMDB) propellants, or as triple-base propellants. Most amides and imides and their salts are useful sources of nitrogen in gas generants for airbag inflators.

## 2 Formamide and Formamide Derivatives

### 2.1 Formamide

Formamide,  $\text{HCONH}_2$ ,  $\text{CH}_3\text{NO}$ , CAS RN [75-12-7], also known as methanamide, is an amide derived from formic acid,  $\text{HCOOH}$ . It could also be considered as the aldehyde of an amino group. The molecular structures of formamide and its two methyl derivatives are shown below.



Formamide is a clear liquid which is miscible with water in all proportions and has an ammonia-like odor. When heated with dehydrating agents, it converts to hydrocyanic acid,  $\text{HCN}$ . It can be used as a non-aqueous solvent, but as such does not have the same desirable solvent properties as its dimethyl derivative, dimethylformamide (see section “Dimethylformamide”). It can dissolve all compounds that would also dissolve in water. Orbital Technologies Corp. (Orbitec Inc.) of Madison, WI, has made a monopropellant consisting of 67.5 mass-% ADN and 32.5 mass-% formamide, and

a Swedish patent was filed for an ADN/formamide monopropellant. No other uses as a propellant ingredient are known.

## 2.2 Methylformamide

*N*-Methylformamide,  $\text{CH}_3\text{NHCHO}$ ,  $\text{C}_2\text{H}_5\text{NO}$ , monomethylformamide, MMF, NMF, CAS RN [2921-57-5] or [123-39-7], molecular mass: 59.0672 g/mol, is a colorless, nearly odorless liquid at room temperature. It is miscible with water in all proportions. NMF is mainly used as a reagent in various organic syntheses. It finds only limited applications as a highly polar solvent in comparison to the more frequently used dimethylformamide. The industrial or chemical laboratory uses of NMF are far fewer than those for either formamide or dimethylformamide (DMF). DMF is favored over NMF as a solvent due to its greater stability.

NMF has a density of  $1.011\text{ g/cm}^3$ , freezes at 269 K ( $-4^\circ\text{C} = 25^\circ\text{F}$ ), and boils at 455.7 K ( $182.6^\circ\text{C} = 360.6^\circ\text{F}$ ). The heat capacity is  $125.2\text{ J K}^{-1}\text{ mol}^{-1}$ . The heat of vaporization is  $56.2\text{ kJ/mol}$ .

Although the fuel component of the Swedish ADN-based monopropellant FLP-106 at first had not been identified by its inventors, all indications are that it is *N*-methylformamide. The enthalpy of formation of NMF could not be found in the literature, but the performance calculations in [1, 2] used a value of  $-258.2\text{ kJ/mol}$  which corresponds to  $-61.7\text{ kcal/mol}$ . Other sources [3] gave the enthalpy of formation of *N*-methylformamide as  $-4188\text{ J/g} = -247.4\text{ kJ/mol}$ . It is not known why the two numbers are so different and which is more accurate.

## 2.3 Dimethylformamide

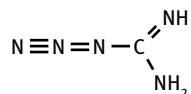
Dimethylformamide, also known as *N,N*-dimethylformamide,  $(\text{CH}_3)_2\text{NCHO}$ ,  $\text{C}_3\text{H}_7\text{NO}$ , DMF, CAS RN [68-12-2], is a colorless liquid which is miscible with water and the majority of organic liquids in all proportions. DMF is a common non-aqueous solvent for chemical reactions because it can dissolve ionic as well as non-polar reactants and bring them into contact with each other. Pure dimethylformamide is odorless, whereas technical grade or degraded samples often have a fishy (mousy) smell due to an impurity of dimethylamine. Dimethylformamide is a polar (hydrophilic) aprotic solvent with a high boiling point. Dimethylformamide has a density of  $0.948\text{ g/cm}^3$ , freezes at 212.7 K ( $-60.5^\circ\text{C} = -76.8^\circ\text{F}$ ), and boils at 426 K ( $152$  to  $154^\circ\text{C}$ ). The refractive index  $n_D^{20}$  is 1.4305 and the viscosity is  $0.92\text{ mPa s}$  (at 293 K =  $20^\circ\text{C}$ ). The standard enthalpy of formation is  $-239.4 \pm 1.2\text{ kJ/mol}$ .

Dimethylformamide has not been used as a rocket fuel, but it has been used widely as a solvent in the synthesis of more energetic fuels, such as organic azides and glycidyl azide polymer (GAP). It may be present as a contaminant in those fuels stemming

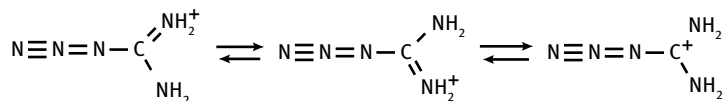
from its use as a solvent, which is difficult to remove due to its low vapor pressure (516 Pa at 298 K). Dimethylformamide may be used as a solvent in the demilitarization of solid propellant rocket motors.

## 2.4 Azidoformamide

Azidoformamide,  $\text{N}_3\text{C}(=\text{NH})\text{NH}_2$ ,  $\text{CH}_3\text{N}_5$ , has been combined with several oxygen- and nitrogen-rich energetic acids to form azidoformamidinium salts. Azidoformamide is an isomer of aminotetrazole. When looking at the structure of azidoformamide,



one would guess that this compound should be called azidoformimide instead of azidoformamide, and that its salts should be called azidoformidinium instead of azidoformamidinium, because azidoformamide contains an imide  $>\text{C}=\text{NH}$  grouping instead of the  $>\text{C}=\text{O}$  group that is found in amides. The azidoformamidinium ion is resonance stabilized because the positive charge can reside on either of the two aminoimino nitrogens or on the carbon, giving a nearly symmetrical carbonium ion:



Azidoformamide itself, the free base, is not very stable. The salts are more stable than the free base from which they are derived. The decomposition of the azidoformamidinium ion proceeds via hydrogen azide and cyanamide, and ends up with ammonium cyanide, ammonium azide, and nitrogen.

### 2.4.1 Azidoformamidinium Nitrate

Azidoformamidinium nitrate can be obtained by reacting aminoguanidinium bicarbonate with sodium nitrite and nitric acid. Azidoformamidinium nitrate forms a double salt in 1:1 molar ratio with guanidinium nitrate [4].

### 2.4.2 Azidoformamidinium Perchlorate

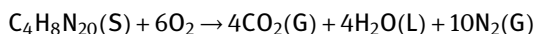
The highly explosive azidoformamidinium perchlorate was obtained by the reaction of the hydrazine group of aminoguanidinium perchlorate with  $\text{HNO}_2$  formed from potassium nitrite in dilute aqueous perchloric acid solution [5]. After filtration of  $\text{KClO}_4$ , the

product was isolated simply by removing the solvent. The structure of the perchlorate salt in the crystalline state was determined using low-temperature single-crystal X-ray diffraction (XRD), indicating an orthorhombic structure. The crystallographic data of azidoformamidinium perchlorate are summarized in Table 22 (in Section 12.2 “Aminoguanidinium Perchlorate”). The crystals were very sensitive to impact or friction.

### 2.4.3 Azidoformamidinium Dinitramidate

The highly energetic isomers azidoformamidinium dinitramide and 5-aminotetrazolium dinitramide were synthesized by the reaction of potassium dinitramide and azidoformamidinium perchlorate or 5-aminotetrazolium perchlorate, respectively [6]. Both compounds have an oxygen balance of 0.0%, which means they are perfectly balanced to burn to nothing but CO<sub>2</sub> and H<sub>2</sub>O (besides N<sub>2</sub>).

The properties of bis(azidoformamidinium) 5,5'-azotetrazolate (AFZT) are listed in tables and illustrated in figures in *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic and Heterocycloaliphatic Amines” under the section “Tetrazole Compounds.” Following its synthesis, AFZT had to be isolated and dried very rapidly after crystallization, as the product decomposed in solution [7]. AFZT dissolved in DMSO was completely decomposed within 10 min under formation of nitrogen. The controlled combustion of AFZT in a calorimeter takes place according to



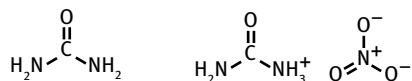
### 2.4.4 Formamidinium Salts

Formamidinium nitroformate,  $[\text{NH}_2\text{CHNH}_2]^+[\text{C}(\text{NO}_2)_3]^-$ , was prepared by a simple metathetical reaction, the crystal structure was examined by XRD, nuclear magnetic resonance (NMR), and Raman and infrared (IR) spectroscopy, and the enthalpy of formation was predicted by computational chemistry [8]. All the nitroformate salts had higher predicted detonation pressures and velocities than trinitrotoluene (TNT). Formamidinium nitroformate was thermally less stable than 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), but also less sensitive to friction and impact.

## 3 Urea

Urea, also known as carbamide, carbonyldiamide, (H<sub>2</sub>N)<sub>2</sub>CO, CH<sub>4</sub>N<sub>2</sub>O, CAS RN [57-13-6], is more widespread as a product of living beings' metabolism than as a rocket propellant ingredient. Urea can be formed by decomposition of ammonium cyanate or by reaction of liquid ammonia and liquid carbon dioxide under pressure (via ammonium carbonate and ammonium carbamate). Urea is used as a fertilizer and as a building block of polymers (urea-formaldehyde resins). Urea forms monovalent and divalent salts with strong acids. Some of those salts with oxidizing acids like nitric acid

or perchloric acid are potential explosives and propellant ingredients. Some chemists call the urea salts “uronium” salts, but this name is very uncommon.



Urea and urea nitrate

Urea has a density of 1.32 g/cm<sup>3</sup> and melts at 406–409 K (133–135 °C) with partial decomposition. Extended heating of molten urea results in loss of ammonia and the formation of biuret (see Section 4 “Biuret and Urea Derivatives”).

Mixtures of urea and ammonium nitrate used in the synthesis of nitroguanidine are potentially explosive even in aqueous solution.

Urea added to solid propellants can act as a coolant and would slow down the burning rate. It might also reduce the muzzle flash for gun propellants in barrel weapons. Urea is also able to act as a stabilizer for double-base propellants because it will effectively neutralize and destroy (scavenge) nitrous acid formed during storage and aging of nitrate ester-based propellants. However, its ethyl and phenyl derivatives are better suited to this task because they are liquids and more easily dispersed in the propellant blend than a solid. Urea has been added to emulsion explosives based on ammonium nitrate as a stabilizer to protect against the formation of free acids during storage and emplacement.

Alkyl- and aryl-substituted urea derivatives are widely used as stabilizers in nitrocellulose-based propellants because they can scavenge nitrous oxides and retard further decomposition of the propellant. The applications of alkyl- and aryl-substituted urea derivatives as stabilizers will be summarized in a future set on solid propellants.

*Diesel exhaust fluid* is an aqueous urea solution made with 32.5% high-purity urea and 67.5% deionized water and injected into the exhaust from diesel engines to reduce NO<sub>x</sub> emissions.

Urea that is to be used for propellants and explosives must meet purity requirements of MIL SPEC DOD-U-10866D (17 April 1979) Urea, Technical (Metric) or MIL-DTL-10866E Note 1 (Jul 2010).

### 3.1 Urea Nitrate

The most thoroughly investigated salt of urea is urea nitrate, [(NH<sub>2</sub>)<sub>2</sub>COH<sup>+</sup>][NO<sub>3</sub><sup>-</sup>], CH<sub>5</sub>N<sub>3</sub>O<sub>4</sub>, UN, CAS RN [124-47-0], which is also a potential explosive. Urea nitrate has been considered as a rocket propellant ingredient for low-flame-temperature propellants. Urea nitrate may also be called “uronium nitrate.” A common abbreviation is UN.

### 3.1.1 Preparation of Urea Nitrate

Urea nitrate can be prepared from urea and >95%  $\text{HNO}_3$  white fuming nitric acid in acetic acid as a solvent [9]. Acetic acid is a solvent for urea, but a non-solvent for urea nitrate.

It would be undesirable or even ill advised to have to heat a reacting mixture of incompletely dissolved urea and nitric acid to 378–408 K (105–135 °C) to achieve a uniform reaction mixture [10]. At those temperatures, incipient decomposition will spoil the product.

In industry, most of the UN made by one of these methods is subsequently used for making nitrourea.

Not for rocket propellant applications but for academic studies of crystal structure by the Weissenberg single-crystal XRD method, may it be desirable to grow large single crystals of urea nitrate. This is possible by evaporating a solution that contains UN in nitric acid solutions [11]. Large, perfect crystals of UN were obtained by the addition of concentrated nitric acid to an aqueous solution of the salt followed by spontaneous evaporation. The angles of the crystal faces were then measured in a goniometer. See also [12].

### 3.1.2 Physical Properties of Urea Nitrate

The physical properties of UN are summarized in Table 1. Table 2 gives a comparison of the physical properties of UN and nitrourea. Nitrourea can be made from UN.

**Table 1:** Physical properties of urea nitrate.

| Property                                 | SI units                   |             | Other units                   |                 | References |
|------------------------------------------|----------------------------|-------------|-------------------------------|-----------------|------------|
| Molecular mass                           | 123.1 g/mol                |             | 8.1235 mol/kg                 |                 |            |
| Melting point                            | 428–429 K                  |             | 155–156 °C                    |                 | [13]       |
|                                          | 425 K                      |             | 152 °C (dec.)                 |                 | [14]       |
| Density                                  | 1.68 g/cm <sup>3</sup>     |             | 0.0607 lb/in. <sup>3</sup>    |                 | [15]       |
| Vapor pressure at 298 K                  | 3.94 × 10 <sup>-5</sup> Pa |             | 2.96 × 10 <sup>-7</sup> mm Hg |                 | [16]       |
| Heat of combustion at const. vol.        | 551.9 kJ/mol               | 4484 kJ/kg  | 1071.7 cal/g                  | 131.9 kcal/mol  | [17]       |
| Heat of explosion                        | 329.1 kJ/mol               | 2673 kJ/kg  | 639 cal/g                     | 78.66 kcal/mol  | [17]       |
| Enthalpy of formation $\Delta H_f^{298}$ | -563 kJ/mol                | -4573 kJ/kg | -134 kcal/mol                 | -1093 cal/g     | [18]       |
|                                          | -561.4 kJ/mol              | -4561 kJ/kg | -1090 kcal/kg                 | -134.2 kcal/mol | [17]       |
| Enthalpy of sublimation                  | 79 ± 5.4 kJ/mol            |             | 18.88 ± 1.29 kcal/mol         |                 | [14, 20]   |
|                                          | 167 kJ/mol                 |             | 39.91 kcal/mol                |                 | [16]       |

**Table 2:** Comparison of physical properties of urea nitrate and nitrourea.

|                                                  | Urea nitrate                                                    | Nitrourea                  |
|--------------------------------------------------|-----------------------------------------------------------------|----------------------------|
| Melting point                                    | 430–432 K = 157–159 °C                                          | 426–428 K = 153–155 (dec.) |
| Density, g/cm <sup>3</sup>                       | 1.67 ± 0.011                                                    | 1.73 ± 0.026               |
| DSC 20°/min, onset of dec. °C                    | ~433 K = ~160                                                   | ~413 K = ~140              |
| TGA dec., °C, wt. loss, %                        | 433 K = 160 °C, 40%                                             | 433 K = 160 °C, 100%       |
| IR, cm <sup>-1</sup>                             | 3500, 3200, 2410 broad,<br>1704, 1568, 1426, 1298<br>1605, 1305 | 3400–2700 multiple peaks   |
| <sup>1</sup> H NMR [D <sub>6</sub> ]acetone, ppm | 8                                                               | 7, 12                      |
| <sup>13</sup> C NMR [D <sub>6</sub> ]DMSO, ppm   | 163                                                             | 151                        |
| <b>Solubility, mg/mL</b>                         |                                                                 |                            |
| Water                                            | 167.2 ± 0.5                                                     | 20 ± 2                     |
| Ethanol                                          | 14.2 ± 0.1                                                      | 17.2 ± 0.6                 |
| Methanol                                         | 54.8 ± 0.9                                                      | 43 ± 8                     |
| Acetone                                          | 10.4 ± 0.2                                                      | 41 ± 5                     |

Data source: [19]

The sublimation UN in a continuously pumped vacuum was measured using a thermogravimetric method in the temperature range 329–370 K (56–97 °C) and the enthalpy of sublimation was  $79 \pm 5.4$  kJ/mol [20]. There are four good reasons why the weight loss was exclusively due to sublimation: Firstly, 100% weight loss was possible (no residue). Secondly, the operating temperature was well below the lowest possible decomposition temperature of about 378 K (105 °C). Thirdly, a sample was placed in a glass tube and evacuated continuously with about one third of the tube being inserted in boiling water (367 K = 94 °C). The UN disappeared from the bottom of the sample cell and condensed on the cooler walls of the upper part of the sample cell which were kept at room temperature. The sublimate added up to about 95% of the initial sample weight, and on the basis of XRD and IR measurements, it was found to be pure urea nitrate. Fourthly, a sample was heated at 339 K (66 °C) under continuous vacuum in the thermogravimetric system and the residues after 8 and 69% weight loss were collected separately and analyzed by IR. The IR patterns of both of these residues were the same and matched exactly that of the original urea nitrate, showing that no decomposition had occurred.

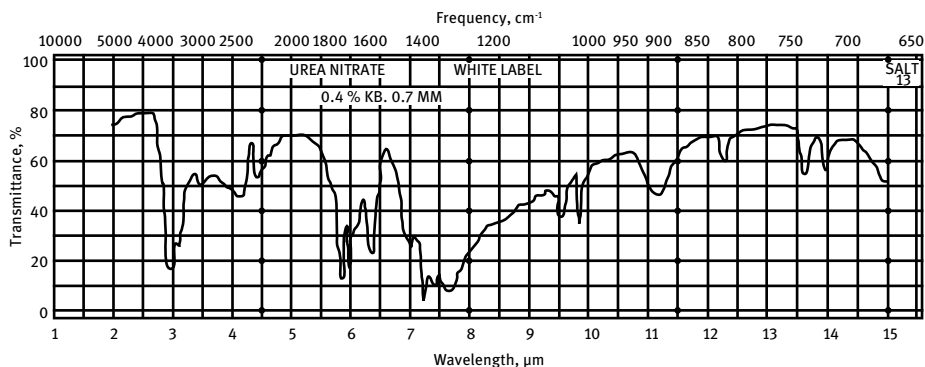
The vapor pressure of UN was measured at 353–393 K (80–120 °C) using an isothermal thermogravimetric weight-loss method and compared to that of guanidinium nitrate and ammonium nitrate (AN) [16]. The Clapeyron equation for UN vapor pressure is

$$\ln P = 57.377 - 20131/T$$

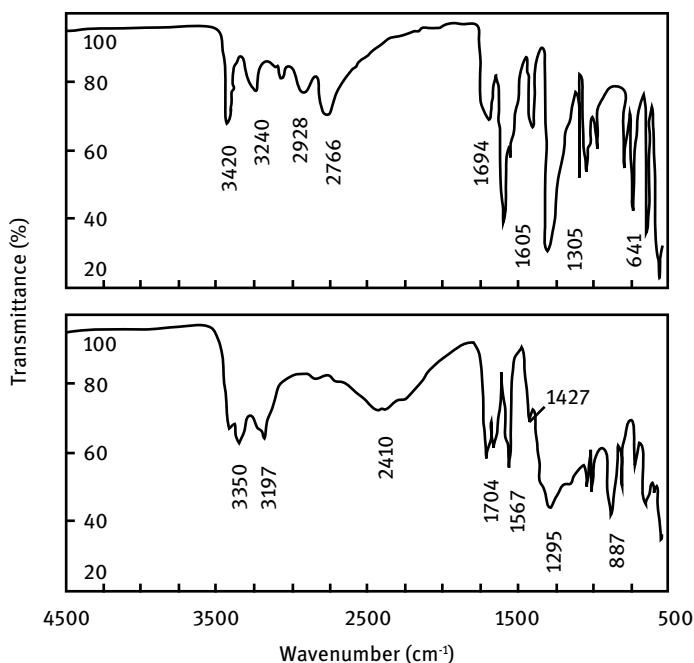
where  $P$  is the pressure in Pa and  $T$  is the temperature in kelvin. For a temperature of 298 K, this equation gives a vapor pressure of  $3.94 \times 10^{-5}$  Pa =  $2.96 \times 10^{-7}$  mm Hg. From the slope of this equation, an enthalpy of sublimation was calculated as 167 kJ/mol.



Urea nitrate is hygroscopic; the mass gain at 298 K (25°) is +0.76% at 90% R.H. and +23.2% at 100% R.H. The IR spectrum of UN is shown in Figure 1 (from [21]). Nitrourea is formed by dehydration of UN. Figure 2 gives a comparison of the IR spectra of nitrourea (top) and urea nitrate (bottom).



**Figure 1:** Infrared spectrum of urea nitrate. (Reproduced and modified from [21].)



**Figure 2:** Comparison of the IR spectra of recrystallized nitrourea (top) and recrystallized urea nitrate (bottom). (Republished and modified from [19], with permission of ©2013 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

### 3.1.2.1 Crystal Structure of Urea Nitrate

The crystal structure of UN was determined by neutron diffraction [22]. Urea nitrate crystallizes in a monoclinic structure with symmetry  $P2_1/c$  and lattice parameters  $a = 9.5434(6)$ ,  $b = 8.2010(5)$ ,  $c = 7.4982(4)$  Å, and  $\beta = 124.246^\circ$ . The crystal structure shows a layer arrangement with all atoms approximately at  $z = 1/4$  or  $1/2$ . The acidic proton is on the carbonyl oxygen atom with an O—H distance of  $1.006(3)$  Å and forms a hydrogen bond to a nitrate oxygen atom with an O—H...O distance of  $2.596(2)$  Å. Four other hydrogen bonds of the type N—H...O join the uronium and nitrate ions into a two-dimensional network. The only forces between the layers are of the van der Waals type.

These results agree quite well with data obtained by XRD [15]. The space group of the crystal is  $P2_1/c$ . The cell dimensions and their standard deviations are  $a = 9.527 \pm 0.007$ ,  $b = 8.203 \pm 0.005$ , and  $c = 7.523 \pm 0.006$  Å;  $\beta = 124.37 \pm 0.05^\circ$ . With four molecules in the unit cell, the calculated XRD density is  $1.68 \text{ g/cm}^3$ . The pycnometric experimental value is  $1.69 \text{ g/cm}^3$ . See also [12, 23–25].

The electronic structure of UN has been calculated by the SCC-DV-Xa quantum chemical method and its IR and UV absorption bands and XPS binding energy were investigated [26].

An examination of UN crystals at pressures up to 26 GPa using Raman spectroscopy and XRD exhibited a supramolecular structure with the uronium cation and nitrate anion held together by multiple hydrogen bonds in the layer [27]. The irreversible phase transition in the range 9–15 GPa has been confirmed by experimental results and was proposed to stem from rearrangements of hydrogen bonds indicating a new phase.

### 3.1.3 Chemical Properties of Urea Nitrate

Urea nitrate as a propellant ingredient is slightly under-oxidized, but it has a good nitrogen content. The oxygen balance of UN is  $-6.5\%$  and the nitrogen content is  $34.14 \text{ mass-\% N}$ .

#### 3.1.3.1 Analysis and Detection of Urea Nitrate

In the wake of widespread use of UN in unauthorized production of clandestine explosives, a need has arisen to identify this chemical in luggage taken on airplanes and other modes of transportation. All methods of explosive detection have been tested for their sensitivity toward UN and other explosives likely to be found in or on the hands of terrorists.

This includes electrospray ionization mass spectrometry [28]. The structure of the ions was deduced using measurements of isotopically labeled UN. Urea nitrate was detected and identified in real-world criminal cases using this method.

A sensitive, specific, and simple spot plate color indicator test for UN is based on the formation of a red pigment upon the reaction between UN and *p*-di-

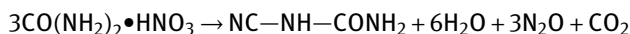
methylaminocinnamaldehyde (*p*-DMAC) under neutral conditions [29]. Urea itself did not give a red color with *p*-DMAC under the same conditions. Other potential sources of a false-positive response, e.g., common fertilizers, did not produce the red color with *p*-DMAC. Exhibits collected from ten terrorist cases were tested with *p*-DMAC. The results were in full agreement with those obtained by more sophisticated instrumental techniques including GC/MS, XRD, and IR.

It has already been mentioned that UN is a powerful improvised explosive sometimes used by terrorists. It is difficult to identify UN in post-explosion debris, since only a very small fraction survives the blast. Also, in the presence of water, it readily dissociates to its original components, i.e., urea and nitric acid. Post-blast debris of UN can be confused with ammonium nitrate, the main solid product of UN thermal decomposition. In a comprehensive study towards identification of UN in post-blast traces, a spectrophotometric technique for quantitative determination of UN was developed, and conditions were found for extraction and separation of unexploded surviving traces of urea nitrate [30].

In a similar effort, the residues were extracted with hot acetone, and the extract HPLC-chromatographed on Chromosorb [31]. The eluent was analyzed by LC/MS using atmospheric pressure chemical ionization (APCI). By applying this technique, it was possible to identify UN in actual exhibits from crime scenes.

### 3.1.3.2 Thermal Stability of Urea Nitrate

The kinetics of isothermal decomposition of UN, which melts with decomposition at 425 K (152 °C), was studied in open air in the temperature range 379–423 K (106–150 °C) by TGA [14]. GC analysis of product gases indicated the formation of CO<sub>2</sub>, N<sub>2</sub>O, and traces of water vapor as product gases. A pasty amorphous residue was found to be cyanourea based on wet chemical and infrared analysis. The reaction for decomposition of UN in open air is most likely



The weight loss–time curve exhibited an acceleratory region extending almost to the end of the main reaction (35% decomposition) and followed a third-order nucleation model obeying the relation

$$\alpha^{\frac{1}{3}} = K(t - t_0)$$

where  $\alpha$  = fraction of sample reacted at time  $t$ ,  $K$  = reaction rate constant, and  $t_0$  = induction time with an enthalpy of activation of  $H_a = 27.6 \pm 1.2$  kcal/mol. The rate of decomposition was slightly accelerated in He atmosphere and slightly retarded in N<sub>2</sub>O and CO<sub>2</sub> atmospheres, while water vapor drastically reduced the rate. Urea nitrate thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out both in air and under an atmosphere of nitrogen using 5-mg samples at a linear heating rate of 10 °C/min [32]. Urea nitrate started to decompose at 398 K (125 °C) and there was a break in the weight loss curve at 428 K (155 °C), showing about 40% weight

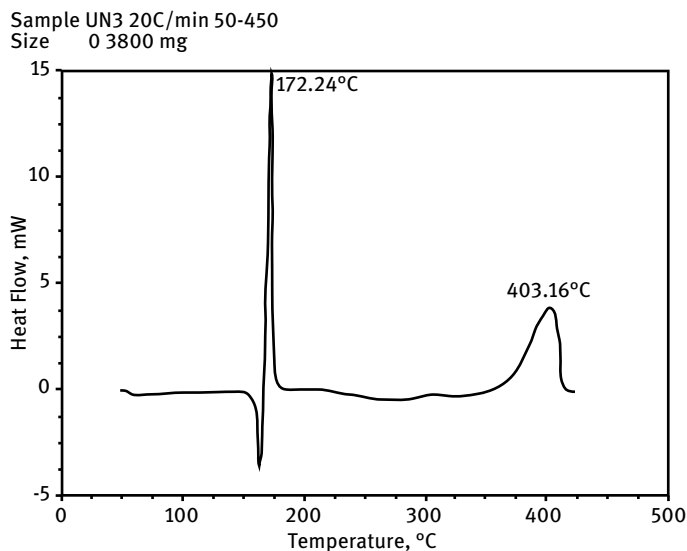
loss. The decomposition was rapid up to 548 K (275 °C) and about 95% of the initial mass volatilized by the time the sample reached 548 K (275 °C). No residue remained at 598 K (325 °C). In a separate test, a known amount of UN was heated and kept at 413 K (140 °C) and the residue obtained was examined. The weight loss observed was 35%, corresponding to the calculated weight loss of 35% for the anticipated formation of  $\text{NH}_4\text{NO}_3$  from urea nitrate. The IR spectrum of the residue resembled that of  $\text{NH}_4\text{NO}_3$ . The DTA showed three exothermic peaks at 428, 448, and 558 K (155, 175, and 285 °C) and an endotherm at 433 K (160 °C). The initial exotherm was attributed to the expulsion of  $\text{HOCN}$  and was more pronounced in air than in nitrogen. In the mass spectrum there was no molecular peak corresponding to urea nitrate,  $m/e$  123, and there were no mass peaks above  $m/e$  61,  $[(\text{CH}_2\text{N})_2\text{COH}]^+$ . The major fragments were  $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  derived primarily from nitrate, and  $\text{H}_2\text{NCN}$ ,  $\text{HNCO}$ ,  $\text{NCO}$ , and  $\text{OC}(\text{NH}_2)$  fragments obtained from the cation moiety. On a hot plate with rapid heating, the deflagration point was 459 K (186 °C = 367 °F). See also [23, 33].

The initial steps in the decomposition process of UN were studied by using *ab initio* calculations [34]. To determine the most favorable reaction pathway of decomposition, geometries, structures, and energies were evaluated for reactants, products, intermediates, and transition states of the proposed pathways. It was found that there is a reaction path for the endothermic channel with a potential energy barrier of 47.8 kcal/mol. Although a considerable difference was found between the actual crystal structure and the optimized structure of UN, these results strongly suggested that decomposition occurs via internal hydrogen transfer from one amino group to the other  $-\text{NH}_2$  group to produce  $\text{NH}_3$ . These calculated results seem to support the experimental results observed during the thermal decomposition of UN by using T-jump/Fourier-transform IR spectroscopy (FTIR).

Electronic structure calculations were performed to investigate the initial steps in the gas-phase decomposition of urea and urea nitrate [35]. Gaseous UN formed by the association of urea and  $\text{HNO}_3$  has two isomeric forms, both of which are acid–base complexes stabilized by the hydrogen bonding interactions involving the acidic proton of  $\text{HNO}_3$  and either the O or N atoms of urea, with binding energies of 13.7 and 8.3 kcal/mol, respectively, and with estimated standard enthalpies of formation ( $\Delta H_f^{298}$ ) of  $-102.3$  and  $-97.1$  kcal/mol, respectively. Both isomers can undergo relatively facile double proton transfer within cyclic hydrogen-bonded structures. In both cases,  $\text{HNO}_3$  plays a catalytic role for the (1,3) H-shifts in urea by acting as a donor of the first and an acceptor of the second proton transferred in a relay fashion. The  $\text{HNO}_3$ -catalyzed breakdown of urea to  $\text{HNCO}$  and  $\text{NH}_3$  is predicted to be the most favorable decomposition pathway for gaseous UN. Thus,  $\text{HNCO} + \text{NH}_3 + \text{HNO}_3$  and their association products (e.g., ammonium nitrate and isocyanate) are expected to be the major initial products of UN decomposition. This is consistent with experimental T-jump/FTIR data [33].

The decomposition of UN has been determined with isothermal heating followed by quantification of both remaining nitrate and remaining base [36]. Activation ener-

gies determined for urea for nitrate and urea itself were 158 and 131 kJ/mol, with the pre-exponential factors being  $1.39 \times 10^{12} \text{ s}^{-1}$  and  $2.66 \times 10^9 \text{ s}^{-1}$ , respectively. These pairs of Arrhenius constants predict decomposition rates less than a factor of two apart. Literature values for ammonium nitrate decomposition indicate that it should decompose somewhat slower than UN and faster than guanidinium nitrate. Differential scanning calorimetry (DSC) also indicated this ordering but suggested that UN is substantially less stable than was observed in the isothermal experiments. The thermal stability of guanidinium nitrate was measured as part of the same study. A DSC thermogram of UN sealed in glass capillary tubes heated at a rate of  $20^\circ\text{C}/\text{min}$  is shown in Figure 3.



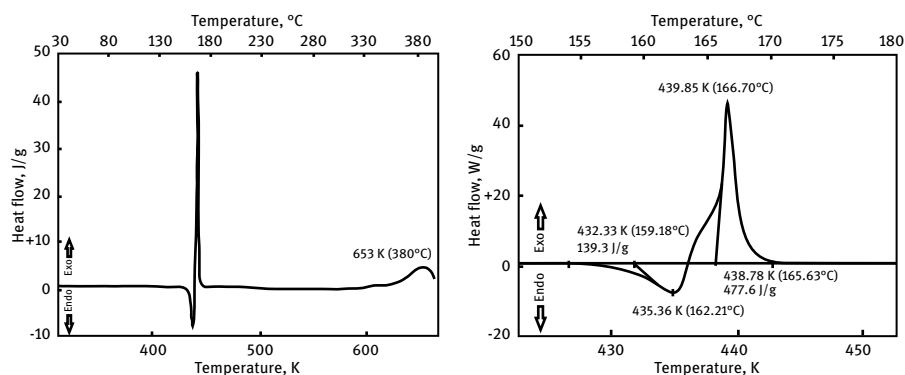
**Figure 3:** Thermogram of urea nitrate in a glass capillary tube. (Republished and modified from [36], with permission of ©2009 Taylor & Francis, [www.tandfonline.com](http://www.tandfonline.com).)

The decomposition of UN at high temperatures was studied using adiabatic and non-isothermal calorimetry techniques [13]. Gas species released were identified and quantified *in situ* using TGA-IR spectroscopy/MS. A decomposition mechanism at high temperature was proposed based on the nature and sequences of gaseous species observed. Non-isothermal decomposition kinetics of UN were measured using preset constant heating rates to give activation energies of  $E_a = 206$  and  $113 \text{ kJ/mol}$  with pre-exponential factors  $\ln Z = 47$  and  $21 \text{ min}^{-1}$ , in a closed and open system, respectively. In these systems the major UN decomposition step is strongly coupled to an endothermic dissociation reaction. Species remaining after this exothermic decomposition showed only minor exothermicity at higher temperatures. This is contrasted with the onset of

adiabatic decomposition, which occurred  $\sim 30^\circ\text{C}$  below the apparent melting point of 428–429 K (155–156  $^\circ\text{C}$ ).

In a parallel study, when studying the aging and slow degradation of UN at temperatures below the melting point at 373 K (100  $^\circ\text{C}$ ) by using thermal analysis and spectroscopic methods including IR, Raman,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR techniques, it was found that UN was completely degraded after 72 h at 100  $^\circ\text{C}$  into a mixture of solids (69%) and released gaseous species (31%) [37]. The remaining solid mixture was composed of ammonium nitrate, urea, and biuret, while unreacted residual nitric and isocyanic acids as well as traces of ammonia were released as gaseous species at 373 K (100  $^\circ\text{C}$ ). The thermal stability of UN under less extreme storage conditions (323 K = 50  $^\circ\text{C}$ ) was also examined by isothermal nano-calorimetry.

In a repeat of an earlier study, the thermogram of UN showed a melt endotherm near 435 K = 162  $^\circ\text{C}$  and a sharp exotherm immediately thereafter at 440 K = 167  $^\circ\text{C}$  [19]. A secondary broader exotherm was observed around 653 K = 380  $^\circ\text{C}$  (Figure 4). The thermogram on the right is the same initial event shown at different scale expansions, revealing a shoulder before the exotherm gets into full swing. The decomposition of UN leads to a mixture of ammonium isocyanate, biuret, melamine, cyanourea, and cyanuric acid.



**Figure 4:** DSC thermograms of urea nitrate decomposition, scan rate 10 K/min (Republished and modified from [19], with permission of ©2013 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

In the 373 K (100  $^\circ\text{C}$ ) thermal stability heat test, no acid and no explosion were observed within 300 min. In the 408 K (135  $^\circ\text{C}$ ) heat test, some acid was detected within 30 min, but no explosion occurred within 300 min.

### 3.1.3.3 Thermal Stability of Urea Nitrate/Metal Complexes

The thermal stability of the Fe and Cr complex nitrates of urea was investigated by DTA and TGA [38]. The coordination of urea to a metal ligand sphere increased its thermal stability. The thermal stability of the Cr complex was greater than that of Fe complex. The Fe complex decomposed not to  $\text{Fe}_2\text{O}_3$  but to  $\text{Fe}(\text{NO}_3)_2$ , while the Cr complex decomposed to  $\text{Cr}_2\text{O}_3$  during the isothermal decomposition over the temperature range of 433 to 493 K (160 to 220 °C). A first-order equation can best describe the decomposition reaction for both complexes. The activation energies were 160.4 kJ/mol for the Fe complex and 174.0 kJ/mol for the Cr complex. It was suggested that the nitrate ions in the Fe nitrate complex participated only partially in the reaction.

### 3.1.4 Safety Properties of Urea Nitrate

Urea nitrate is known as an explosive material, but not commercially used as such. The friction sensitivity and the shock sensitivity were low [39]. The critical shock initiation pressure of UN (bulk density  $0.68 \text{ g/cm}^3$ ) was measured in a card gap test and shown to be 2.2–2.6 GPa.

In the Bundesanstalt für Materialforschung und -prüfung (BAM) impact test apparatus, no reaction was noted at impact energies up to 49 Nm. Likewise, in the BAM friction sensitivity test apparatus, no reaction was noted at pistil loads up to 353 N.

In the Picatinny friction sensitivity apparatus, loads of up to 36 kp = 353 N pistil load gave no reaction. In the Picatinny impact sensitivity apparatus, impacts of up to  $5 \text{ kp} \cdot \text{m} = 49 \text{ Nm}$  gave no reaction [17].

### 3.1.5 Explosive Performance of Urea Nitrate

Detonation velocities of UN were measured in various cylindrical containers with composition C-4 as a booster. It was shown that the detonation velocity of UN is typical for a steady-state detonation. Detonation velocities of samples confined in a steel tube could reach 5000 m/s [39]. The effects of bulk density, charge diameter, and degree of confinement on detonation velocity were studied.

Other sources give the detonation velocity as 3400 m/s at a packing density of  $0.85 \text{ g/cm}^3$  in a 30-mm diameter paper tube when driven by 1.5 g of mercury fulminate, and 4700 m/s at a packing density of  $1.20 \text{ g/cm}^3$  in a 30-mm diameter steel tube when initiated by 1.5 g of mercury fulminate [17].

In the lead block test, the explosion of UN will increase the cavity volume by  $270 \text{ cm}^3/10 \text{ g}$ . See also [40].

### 3.1.6 Other Applications for Urea Nitrate

Because both urea and nitrate ion are good sources of nitrogen in fertilizers, urea nitrate in the dry state would make a good fertilizer. However, for safety reasons, it would have to be diluted substantially with inert materials (limestone, dolomite) to desensitize the pure compound. Aqueous solutions of urea nitrate and ammonium nitrate with 28–32% usable nitrogen are widely used as fertilizers. There is concern that urea nitrate may form inadvertently in fertilizer mixtures containing both urea and ammonium nitrate. Such mixtures may be detonable.

## 3.2 Urea Perchlorate

Urea perchlorate,  $\text{H}_2\text{NCONH}_3\text{ClO}_4$ ,  $\text{CH}_5\text{N}_2\text{O}_5\text{Cl}$ , CAS RN [1872-07-6], forms colorless, very hygroscopic crystals that explode upon ignition without burning. The oxygen balance for complete combustion to  $\text{CO}_2$  is positive +4.98%. The nitrogen content is 17.46% N. Urea perchlorate may be useful as an explosive, but it is too sensitive to be used as a rocket propellant.

Urea perchlorate melts at 356 K (83 °C) and starts decomposing at 413 K (160 °C). It is quite soluble in water: at 293 K (20 °C), 958 g urea perchlorate will dissolve in 100 g water and the density of the saturated aqueous solution at 293 K (20 °C) is 1.6226 g/cm<sup>3</sup>. The impact sensitivity of the saturated solution was six negatives (no fires) out of six tests with a 5-kg hammer dropped from 60 cm.

### 3.2.1 Detonability of Urea Perchlorate Solutions

Numerous patents have been issued for the use of urea perchlorate solutions in combination with organic fuels as liquid explosives [41, 42]. The detonability of aqueous solutions/suspensions of organic amine perchlorates was studied in steel and glass ampules with an electric detonator with or without an intermediate hexogen booster. The isochoric detonation temperature of aqueous solutions of urea perchlorate was 1700–1740 K, and the upper concentration limit of  $\text{H}_2\text{O}$  below which the solutions retained their detonation capacity was 22–23%  $\text{H}_2\text{O}$  [43]. In a 28-mm I.D. steel tube with a tetryl booster, no stable reaction wave was observed in this solution.

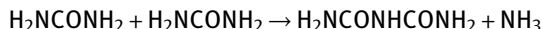
## 3.3 Urea Dinitramide

Urea dinitramide,  $[\text{H}_2\text{NCONH}_3^+][\text{N}_3\text{O}_4^-]$ ,  $\text{CH}_5\text{N}_5\text{O}_5$ , melts at 371–373 K (98–100 °C) [44].



## 4 Biuret and Urea Derivatives

Biuret, imidodicarbonic diamide, 2-imidodicarbonic diamide, carbamylurea,  $\text{H}_2\text{NCO-NHCONH}_2$ ,  $\text{C}_2\text{H}_5\text{N}_3\text{O}_2$ , molecular mass: 103.08 g/mol, CAS RN [108-19-0], is formed when urea is heated and one mol of ammonia is split off.



Biuret is a crystalline solid similar to urea. The enthalpy of formation is  $\Delta H_f^{298}(\text{S}) = -563.7 \pm 2.1 \text{ kJ/mol}$ . Biuret itself has not been used as a propellant ingredient, but several high-energy compounds are based on biuret.

### 4.1 Dinitrobiuret

Dinitrobiuret, also known as 1,5-dinitrobiuret; 1-nitro-3-(nitrocarbamoyl)urea, imidodicarbonic diamide, *N,N'*-dinitro-; *N,N*-dinitrodicarbonimidic diamide,  $\text{O}_2\text{NNHCONH-CONHNO}_2$ ,  $\text{C}_2\text{H}_3\text{N}_5\text{O}_6$ , DNB, CAS RN [671181-09-2], is a very powerful energetic additive and relatively easy to obtain. DNB has an approximate planar structure (Figure 5).

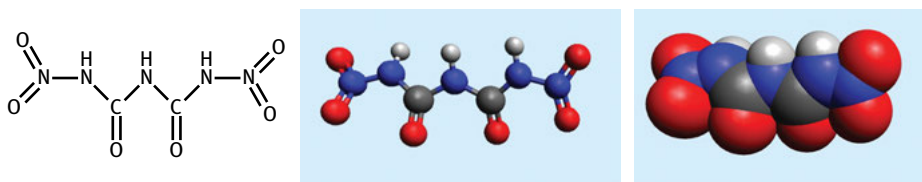
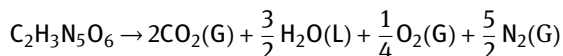


Figure 5: Molecular structure of dinitrobiuret.

The standard enthalpy of formation ( $\Delta H_f$ ) was calculated from quantum mechanical considerations to be  $-353 \text{ kJ/mol}$  ( $-1829 \text{ kJ/kg}$ ). The enthalpy ( $\Delta H_r$ ) for the reaction of DNB(s)



was determined to be  $1003 \pm 39 \text{ kJ/mol}$  ( $5195 \pm 200 \text{ kJ/kg}$ ) using bomb calorimetry. DNB detonated strongly in the steel sleeve test, without the need of adding any additional oxidizer. The detonation velocity and detonation pressure were calculated to be  $8.66 \text{ mm/s}$  and  $33.9 \text{ GPa}$ , respectively.

The calculated theoretical enthalpy of formation of dinitrobiuret is  $-353 \text{ kJ/mol} = -1829 \text{ kJ/kg}$  [45–47]. Dinitrobiuret has a slightly positive oxygen balance of  $+4.1\%$ . The predicted detonation velocity and detonation pressure of DNB was calculated using the empirical equations by Kamlet and Jacobs and obtained as  $D = 8.66 \text{ mm}/\mu\text{s}$ ,

$P = 33.9$  GPa. Other data reported for the heat of combustion of dinitrobiuret are 851 kJ/mol (203.3 kcal/mol) [48].

The thermal decomposition of mononitrobiuret (MNB) and 1,5-dinitrobiuret was investigated by TGA and DSC and the gaseous decomposition products were identified by mass spectrometry (MS) and IR [49]. Decomposition appeared in both cases to be initiated by the release of nitramine. The gaseous products after the exothermic decomposition were similar for MNB and DNB. The decomposition of MNB leads to the formation of urea, biuret, triuret, tetrauret, and cyanuric acid.

Computer simulations were performed for decomposition of 1,5-dinitrobiuret over a temperature range from 4000 to 6000 K, aimed at providing insight into decomposition mechanisms [50]. The trajectories revealed various decomposition paths and reproduced the products (including HNCO,  $N_2O$ ,  $NO_2$ , NO, and  $H_2O$ ) observed in pyrolysis experiments. Decomposition starts with elimination of  $NO_2$  from DNB, followed by consecutive elimination of two isocyanic acid (HNCO) molecules from the derivative intermediate. According to computer predictions of the weakest link, the dominant initial decomposition path corresponds to elimination of  $HNNO_2H$  via a concerted mechanism where the molecular decomposition is accompanied with intra-molecular H-atom transfer from the central nitrogen to the terminal nitro oxygen. Other important paths correspond to elimination of  $NO_2$  and  $H_2NNO_2$ .  $NO_2$  elimination is a simple N–N bond scission process.

The combustion dynamics of 1,5-dinitrobiuret with nitric acid have been examined by computer methods using reactive molecular dynamics simulations [51]. The simulations showed that at certain compositions of the mixture, reaction kinetics result in a very sharp release of thermal energy, which can be associated with spontaneous ignition or hypergolicity.

Calculations showed that the pseudo-*trans* conformer of 1,5-dinitrobiuret is the most stable form of the isolated molecule, while the pseudo-*cis* conformer is about 7.5 kJ/mol higher in energy [52]. The structure of gaseous 1,5-dinitrobiuret is different from that in the crystal state, where the molecules have pseudo-*cis* conformation. The value of enthalpy of formation of gaseous 1,5-dinitrobiuret ( $-257 \pm 5$  kJ/mol) was calculated from isodesmic reactions. Combining this value with the empirically estimated enthalpy of sublimation, the enthalpy of formation of crystalline 1,5-dinitrobiuret was predicted to be  $-415 \pm 15$  kJ/mol. The energy of the weakest N– $NO_2$  bond was 190–200 kJ/mol.

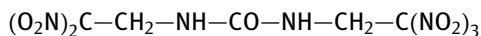
It had been proposed that an important step for the hypergolic ignition of ionic liquid bipropellants composed of nitric acid and dicyanamide salts is the activation and dissociation of the 1,5-dinitrobiuret anion formed from dicyanamide [53].

A quasi-classical direct dynamics simulation computation was supposed to explain the intermediates formed in the hypergolic ignition reaction [54–56].

Mononitrobiuret (MNB) and 1,5-dinitrobiuret (DNB) are tetrazole-free, nitrogen-rich energetic compounds. A comprehensive *ab initio* kinetics study on the thermal decomposition mechanisms of MNB and DNB has been carried out [57].

## 4.2 Nitroalkylurea Derivatives

Bis(2,2,2-trinitroethyl)urea, also known as di(2,2,2-trinitroethyl)urea, BTNEU,  $C_5H_6N_8O_{13}$ , is one of the few explosives that is exactly stoichiometric oxygen balanced (oxygen balance:  $\pm 0\%$ ) for combustion to carbon dioxide and water. It has a nitrogen content of 29.02 mass-% N.



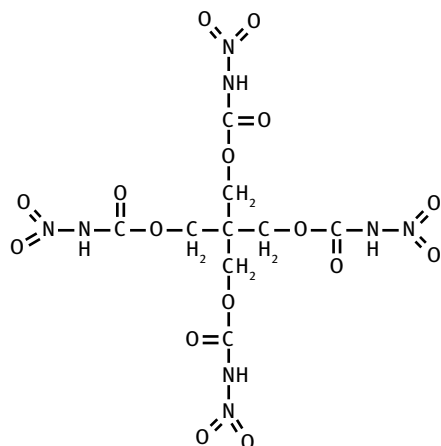
It has a molecular mass of 386.15 g/mol and an enthalpy of formation of  $-199.2 \text{ kcal/kg} = -833.2 \text{ kJ/kg} = -321.7 \text{ kJ/mol} = -76.9 \text{ kcal/mol}$ .

## 5 Carbamic Acid Derivatives

Carbamic acid,  $H_2N-COOH$ , CAS RN [463-77-4] itself is not stable, but many of its salts have been prepared and some have been evaluated as propellant ingredients. It is a zwitter between an amide and a carboxylic acid. Carbamic acid is an intermediate in the production of urea, which involves the reaction of carbon dioxide and ammonia. The gross formula of carbamic acid,  $CH_3NO_2$ , is the same as that of nitromethane, but the compound is much less energetic than nitromethane, due to the fact that the oxygens are attached to carbon and not to nitrogen. Carbamate linkages can be found in insecticides, polymers, and some metabolic intermediates. The medicinal use of ethyl carbamate (urethane) was discontinued after ethyl carbamate was identified as a carcinogen. The widespread presence of ethyl carbamate in alcoholic beverages and fermented food was first discovered during the mid-1980s and continues to be a matter of concern.

Ammonium carbamate can hydrolyze to ammonium carbonate or dissociate reversibly to ammonia and carbon dioxide. When heated in a pressure autoclave it converts irreversibly to urea and water, which is an industrial process for making urea. Ammonium carbamate has been used as a subliming solid in low-thrust rocket engines.

The reaction of alcohols with chlorosulfonyl isocyanate forms alkyl carbamates which can be nitrated with mixed acid to form energetic nitrocarbamates [58]. Polyols like pentaerythritol can be converted to a tetracarbamate and nitrated to give pentaerythritol tetranitrocarbamate, [3-(nitrocarbamoyloxy)-2,2-bis(nitrocarbamoyloxymethyl)propyl]-*N*-nitrocarbamate



The density of pentaerythritol tetranitrocarbamate is  $1.77 \text{ g/cm}^3$  at 100 K ( $-173^\circ\text{C}$ ). It did not melt, but started to decompose at 469 K ( $196^\circ\text{C}$ ) which is 30 degrees better than pentaerythritol tetranitrate (PETN). The enthalpy of formation is  $-1311 \text{ kJ/mol}$ .

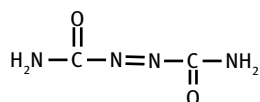
The reaction of urea with trinitromethane and acetaldehyde forms *N,N'*-bis(1,1,1-trinitroprop-2-yl)urea which can be converted to 1,1,1-trinitroprop-2-yl carbamate and 1,1,1-trinitroprop-2-yl nitrocarbamate which can be used as energetic additives or explosives [59].

2,2,2-Trinitroethyl carbamate was obtained by the reaction of 2,2,2-trinitroethyl chloroformate with aqueous ammonia. The nitration of 2,2,2-trinitroethyl carbamate with anhydrous nitric acid and sulfuric acid yielded 2,2,2-trinitroethyl nitrocarbamate, which has potential as a perchlorate-free highly energetic dense oxidizer with a high oxygen balance of  $\Omega(\text{CO}_2) = +14.9\%$  [60]. The thermal stability was studied using DSC and the energies of formation and detonation parameters were calculated.

## 5.1 Azodicarbonamide and Hydrazodicarbonamide

### 5.1.1 Azodicarbonamide

Azodicarbonamide, also known as azobisformamide, 1,1'-azobisformamide, 1,2-diazenedicarboxamide, azodicarbonic acid diamide, carbamoyliminurea,  $\text{C}_2\text{H}_4\text{N}_4\text{O}_2$ , CAS RN [123-77-3],



is produced in tonnage quantities and used widely as a blowing agent for foamed plastics. It can be used as a coolant and source of nitrogen in rocket propellants, gun pro-

pellants, and solid gas generant formulations. Solid gas generant formulations containing azodicarbonamide will be discussed in future volumes on solid propellants and gas generants as part of the *Encyclopedia of Rocket Propellants*.

Azodicarbonamide is manufactured by the reaction of dihydrazinium sulfate and urea at high temperature and under pressure. The product of this reaction is then oxidized using sodium chlorate or free chlorine and centrifuged to yield a slurry containing azodicarbonamide. The slurry is washed to remove impurities and dried to obtain the azodicarbonamide powder. This is then pulverized before packaging. It can also be produced by electrochemical oxidation [61]. Azodicarbonamide that is labeled with the radioisotope  $^{14}\text{C}$  for metabolic fate and toxicity studies can be made by reaction of hydrazinium sulfate with potassium [ $^{14}\text{C}$ ]cyanate, followed by oxidation of the resulting biurea [62].

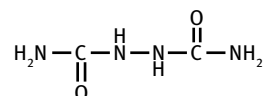
Azodicarbonamide is a light yellow to orange powder with a decomposition temperature of 477–481 K (204–208 °C = 400–410 °F), depending on the rate of heating. It is available in various particle size ranges down to 3.5  $\mu\text{m}$  for applications as a foaming agent in the plastics industry. It is poorly soluble in water at room temperature (50 mg/L), although it is slightly soluble in hot water. The standard enthalpy of formation of azodicarbonamide is  $-292\text{ kJ/mol}$  ( $-69.91\text{ kcal/mol}$ ) [63].

There have been several deflagrations in azodicarbonamide storage warehouses when the material was improperly stored in oversize containers.

Azodicarbonamide is used as a flour-bleaching agent and a bread dough conditioner, speeding up the bread making process in a bread factory. Azodicarbonamide reacts with moist flour as an oxidizing agent. The main reaction product is biurea, a derivative of urea, which is stable during baking. Secondary reaction products include semicarbazide and ethyl carbamate. Both of those are potentially toxic and one seriously wonders how this chemical is allowed to be in bread and eaten by the entire population at large. Azodicarbonamide is not authorized for use as a food additive in Australia and the European Union, so why is it safe to use it in the United States? In the United States, azodicarbonamide has a Generally Recognized As Safe (GRAS) status and is allowed to be added to flour at levels up to 45 ppm [64].

### 5.1.2 Hydrazodicarbonamide

Hydrazodicarbonamide, also known as carbamoylaminourea, ureidourea, 1,2-hydrazinedicarboxamide,  $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ , CAS RN [110-21-4],



melts at 521 K (248 °C) and the standard enthalpy of formation of hydrazodicarbonamide is  $-499\text{ kJ/mol}$  ( $-119.19\text{ kcal/mol}$ ; [63]).

Hydrazodicarbonamide can be prepared by reaction of urea and hydrazine in an acidic medium [65]. It is an intermediate in the preparation of azodicarbonamide. Hydrazodicarbonamide would be a good coolant and ingredient for gas generants, but there are no known applications and it is not produced in as large quantities as azodicarbonamide. Numerous patent applications list hydrazodicarbonamide along with azodicarbonamide as a gas generant ingredient.

## 6 Semicarbazide

Semicarbazide,  $\text{H}_2\text{NNHCONH}_2$ ,  $\text{CH}_5\text{N}_3\text{O}$ , CAS RN [57-56-7] is a white crystalline powder that is widely used as a metal ion-complexing reagent in analytical chemistry. It forms stable complexes with most transition metals. Semicarbazide melts at 369 K (96 °C) and has a density of  $1.484 \text{ g/cm}^3$ . It is soluble in water and somewhat soluble in ethanol.

Semicarbazide forms a nitrate salt with nitric acid. The dry nitrate salt melts at 396 K (123 °C) with decomposition. Semicarbazide also forms a perchlorate salt with perchloric acid. The dry perchlorate salt melts at 551 K (278 °C) with explosion.

Semicarbazide chloride has been suggested as a burning rate suppressant, but there are no known actual uses of any of these salts.

## 7 Carbohydrazide

Carbohydrazide, also known as *N,N'*-diaminourea,  $\text{H}_2\text{NNHCONHNH}_2$ ,  $\text{C}_1\text{H}_6\text{N}_4\text{O}_1$ , CHZ, CAS RN [479-18-7], has a higher nitrogen content than urea and makes a good coolant for gas generants. Carbohydrazide can be used as an oxygen scavenger in boiler-feed water treatment for power plants. In those applications, it is a non-volatile alternative to volatile hydrazine hydrate. At high temperatures such as those in a boiler, carbohydrazide reacts with oxygen to form water, nitrogen, and urea.

### 7.1 Preparation of Carbohydrazide

Carbohydrazide can be prepared by hydrazinolysis of dimethyl carbonate or ethylcarbazate with hydrazine hydrate in aqueous solution [66].

### 7.2 Physical Properties of Carbohydrazide

Carbohydrazide melts at 425–427 K (152–154 °C) and has a density of  $1.616 \text{ g/cm}^3$  at 293 K (20 °C).

The molecular structures of gaseous isomers and the crystalline state of carbohydrazide were examined by quantum mechanical methods [67]. Three stable isomers were located on the energy potential curve. The structure in the crystal is the most stable one. The vibrational frequencies were predicted and agreed well with the experimental data.

### 7.3 Chemical Properties of Carbohydrazide

Carbohydrazide is a weak base and forms monobasic and dibasic salts with strong acids. The salts may be called diaminouronium salts, but this is a very uncommon name. The salts with oxidizing inorganic acids are of interest as propellant ingredients. Carbohydrazide metal complexes were proposed as gas generants for automobile air bag inflators, such as the carbohydrazide Mg complex [68, 69] or Cd perchlorate complexes [70].

Carbohydrazide forms complexes (similar to semicarbazide) with many metal ions. These metal ions can catalyze the combustion of carbohydrazide in the presence of suitable oxidizers, leading to nitrogen-rich gases suitable for inflation of automobile-occupant restraint systems.

The specific heat capacities of four carbohydrazide nitrate energetic coordination compounds  $[M(CHZ)_3](NO_3)_2$ , ( $M = Mn, Co, Zn, Ni$ ) were determined by DSC and curve-fit regression equations for the specific heat capacity as a function of temperature were obtained [71]. For all except  $Zn(CHZ)_3(NO_3)_2$ , the specific heat capacity of the compounds changed substantially, and one or more peaks appeared in the curves of the specific heat capacity. In TGA at 473 K (200 °C), only  $Co(CHZ)_3(NO_3)_2$  lost 8.6% of its mass. FTIR spectra were not the same at different temperatures; therefore, it is possible that polymorphic crystal transformations resulted in the changes of specific heat capacities.

#### 7.3.1 Carbohydrazide Salts

Carbohydrazide(1+) nitrate, diaminouronium(1+) nitrate, an energetic salt, was compared with EDDN and ethylenediamine diperchlorate (EDDP) and in a study on the effect of the molecular structure of energetic materials on the burning rate [72]. With an excess of strong nitric acid, carbohydrazide can also form carbohydrazidium(2+) dinitrate [73].

Carbohydrazidium(2+) dinitrate crystallized with one molecule of water as hydrate [74]. This salt is completely insensitive towards impact and friction, but, unfortunately, when heated it already decomposes at 388 K (115 °C).

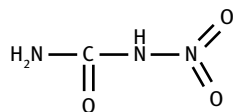
Diaminouronium nitrate, diaminouronium dinitrate monohydrate, and diaminouronium perchlorate were synthesized by acidification of carbohydrazide [75]. The bis-perchlorate salt could not be isolated due to its high hygroscopicity.

The salts were fully characterized using XRD, NMR, and IR spectroscopy, MS, DSC, and elemental analysis. The sensitivities towards impact were 9J, 40J, and 2J, respectively. The sensitivities towards friction were 288 N, 360 N, and 5 N, respectively (BAM methods).

## 8 Nitrourea and Dinitrourea

### 8.1 Nitrourea

Nitrourea,  $\text{CH}_3\text{N}_3\text{O}_3$ , CAS RN [556-89-8], is a crystalline, colorless solid.



Nitrourea must not be confused with urea nitrate. Both substances form similar-looking, clear, colorless crystals, and are potentially explosive and can be converted into each other by dehydration or hydrolysis. If sufficiently desensitized and diluted, nitrourea could possibly be used as a propellant ingredient, but no applications are known.

#### 8.1.1 Preparation of Nitrourea

Nitrourea can be synthesized by dehydration of urea nitrate with sulfuric acid or acetic anhydride and acetic acid at 333 K (60 °C). It can be recrystallized from glacial acetic acid.

#### 8.1.2 Physical Properties of Nitrourea

The physical properties of nitrourea are summarized in Table 2 (“Physical Properties of Urea Nitrate” in the “Urea Nitrate” section) and here in Table 3. Other data reported for the heat of combustion of nitrourea are 553 kJ/mol (132.3 kcal/mol) [48].

The IR spectrum of nitrourea was already shown in Figure 2 in comparison to the spectrum of urea nitrate. Both urea nitrate and nitrourea have absorption bands around  $1700\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ) and in the high and low end of  $1300\text{ cm}^{-1}$  (NO), but urea nitrate is clearly distinguished by the broad band around  $2400\text{ cm}^{-1}$ . Nitrourea differs from urea nitrate between  $3400$  and  $2765\text{ cm}^{-1}$ , where at least five bands are resolved. Raman spectra of urea, urea nitrate, nitrourea, and AN are given in [19]. A similar IR spectrum and also a UV spectrum of nitrourea is shown in [76].

A theoretical analysis of the molecular structure of nitrourea and its possible tautomers was performed using Hartree–Fock and density functional theory (DFT), re-



**Table 3:** Physical properties of nitrourea.

| Property              | SI units                       |             | Other units       |              | References |
|-----------------------|--------------------------------|-------------|-------------------|--------------|------------|
| Molecular mass        | 105.1 g/mol                    |             | 9.5147 mol/kg     |              |            |
| Oxygen balance        | −7.6%                          |             | —                 |              | [18]       |
| Melting point         | 432 K (dec.)                   |             | 159 °C (dec.)     |              | [18]       |
|                       | 426–428 K (dec.)               |             | 153–155 °C (dec.) |              | [19]       |
| Density               | 1.73 ± 0.026 g/cm <sup>3</sup> |             | —                 |              | [19]       |
| Enthalpy of formation | −282 kJ/mol                    | −2688 kJ/kg | −67.5 kcal/mol    | −642.5 cal/g | [18]       |
| Enthalpy of formation | −281.3 kJ/mol                  | −2676 kJ/kg | −67.23 kcal/mol   | −639.7 cal/g | [17]       |

sulting in optimized geometries, vibrational frequencies, and some thermodynamic values in their ground states [77].

Computational modeling of the structures and properties of a series of nitro-substituted urea derivatives indicated that nitrated urea molecules have specific enthalpies of decomposition commensurate with current high-energy materials [78].

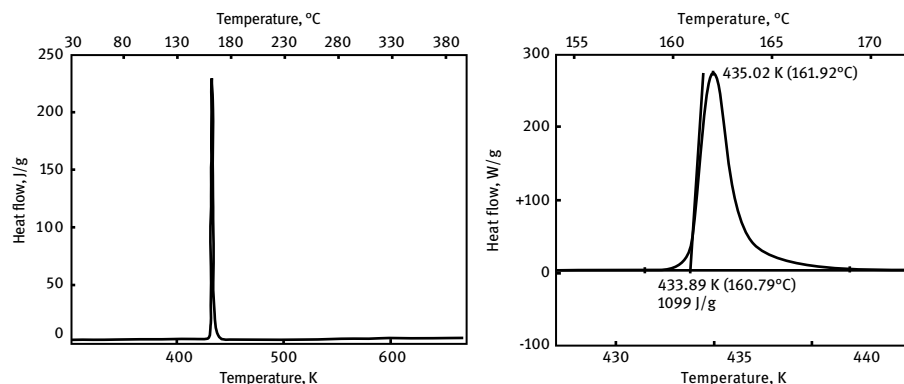
### 8.1.3 Chemical Properties of Nitrourea

Nitrourea has an only slightly negative oxygen balance of −7.6% and contains 39.95 mass-% nitrogen. It is a powerful explosive and potentially suitable as a propellant ingredient. Nitrourea is soluble and stable in benzene, diethyl ether, or chloroform, but it reacts with water. The solubility of nitrourea in water is 20 mg/mL. It tends to decompose spontaneously with moisture. *N*-Substituted-*N*-nitroureas are more hydrolytically stable. Dinitrourea also is very sensitive to hydrolysis.

When heated on a hot-stage microscope, nitrourea decomposed without melting and no solid residue remained, but in the DSC pan, a small amount of black residue was formed. In the DSC, a single sharp exotherm for nitrourea was observed at about 435 K (162 °C; Figure 6). The figure to the right shows the same event with different scale expansions. While the DSC of urea nitrate showed an endothermic melt, the nitrourea did not. The nitrourea energy released, according to DSC, was about double the energy of urea nitrate (1100 vs. 480 J/g).

### 8.1.4 Safety Properties of Nitrourea

In the Picatinny drop-weight sensitivity test apparatus with a 2-kg mass, only incomplete ignition occurred at 18 in (for comparison: 50% point for TNT is at 16 in). In the lead block test, the cavity was expanded by 310 cm<sup>3</sup>, which is 94% of the expansion typical for picric acid.



**Figure 6:** DSC Thermograms of nitrourea, scan rate 10 K/min. (Republished and modified from [19], with permission of ©2013 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

## 8.2 Dinitrourea

Dinitrourea, also known as 1,3-dinitrourea, *N,N'*-dinitrourea,  $\text{O}_2\text{NNHCONHNO}_2$ ,  $\text{CH}_2\text{N}_4\text{O}_5$ , DNU, CAS RN [176501-96-5], is a useful precursor in the synthesis of aliphatic and cyclic nitramine energetic compounds. It can also be used to prepare the parent compound, nitramide  $\text{H}_2\text{NNO}_2$ . An excellent summary review with 40 references of the synthesis, properties, structure, and reactions of *N,N'*-dinitrourea was published in 2013 [79].

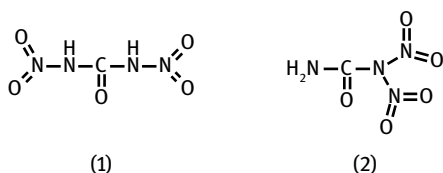
### 8.2.1 Preparation of Dinitrourea

Dinitrourea can be prepared by stepwise nitration of urea with 100%  $\text{HNO}_3$ /20% oleum via mononitrourea as an intermediate. DNU was obtained in 95% yield via direct nitration of urea with a mixture of equal parts of 98%  $\text{HNO}_3$  and 20% oleum [80]. The stirred mixture of acids was cooled at 258 to 263 K ( $-15$  to  $-10^\circ\text{C}$ ) and urea was dosed at such a rate as to keep the reaction temperature below 273 K ( $0^\circ\text{C}$ ). The stirring was continued for 30 min at 273 to 268 K ( $0$  to  $-5^\circ\text{C}$ ). The precipitate of crude DNU was filtered, rinsed cold, and used as the starting material in further reactions. At room temperature, particularly in the presence of water and traces of acids, DNU underwent decomposition, which may lead to spontaneous ignition. Pure DNU has an ignition temperature of  $420 \pm 9$  K ( $147 \pm 9^\circ\text{C}$ ). The stability of DNU strongly depends on its purity. The crude, separated DNU still containing nitrating acids, kept at 298 K ( $25^\circ\text{C}$ ) for 20 min, may undergo self-ignition. Attempts at DNU purification by recrystallization from diethyl ether and careful drying in a vacuum were unsuccessful. Partial hydrolysis of substrate occurred during formation of DNU salts. Besides  $\text{CO}_2$ , nitramine was the main hydrolysis by-product and it decomposed into  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ .

The diammonium salt of dinitrourea was obtained in direct synthesis from crude DNU and aqueous ammonia (13%) at 293 K (20 °C). The product precipitated as a colorless solid. The ammonium salts originating from acidic impurities of DNU remained in the supernatant solution. The product was separated by filtration, washed a few times with ice-cold water, and dried in a vacuum desiccator over silica gel.

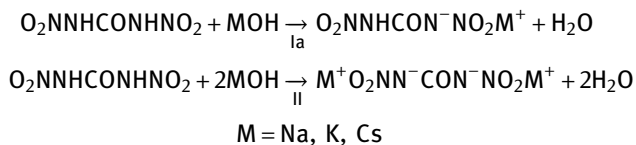
Under similar conditions (similar to those described in [80]), namely 100%  $\text{HNO}_3$ /20% oleum (V/V) ratio = 0.6/1, temperature of the first stage at 258 K (−15 °C) and temperature of the second stage at 278 K (+5 °C), reaction time 50 min, the yield of dinitrourea was 83.2% of theory [81]. The thermodynamic properties at different temperatures were obtained from vibrational analysis. Results showed that dinitrourea has two stable conformations with an energy difference of 12.621 kJ/mol. The calculated vibrational frequencies and intensities of DNU IR spectra were in good agreement with the experimental values.

Depending on the reaction conditions and the type of nitrating agent used, not only the symmetrical dinitrourea (**1**), but also the unsymmetrical dinitrourea with two geminal nitro groups (**2**) may be formed



The 1,1-dinitrourea (**2**) is not stable, but it is an important intermediate in the synthesis of dinitramides (see *Encyclopedia of Oxidizers*, chapter “Dinitramide Oxidizers”).

A study of the hydrolysis of *N,N'*-dinitrourea resulted in the development of a convenient method for synthesizing nitramide on the basis of urea and the discovery of new reactions of nitramide [82, 83]. The availability of *N,N'*-dinitrourea salts made it possible to synthesize new nitramine compounds [84]. Symmetric *N,N'*-dinitrourea is a fairly strong dibasic acid which is capable of undergoing stepwise ionization with formation of acid and neutral salts:



The existence of acid salts of the **I** type was proved by physical methods. Neutral salts **II** were formed on prolonged heating of aqueous solutions of acid salts. The reaction of *N,N'*-dinitrourea with hydrazine yielded 4-nitrosemicarbazide, and the reaction with hydroxylamine lead to *N*-hydroxy-*N'*-nitrourea.

Reactions of *N,N'*-dinitrourea with formaldehyde, depending on the conditions of the reaction, may lead to formation of various hydroxymethyl derivatives of *N*-nitroamines and products of their further condensations [85]. The condensation of *N,N'*-dinitrourea with formaldehyde at a molar ratio of 1:1 in aqueous solution in the presence of sulfuric acid at 293–353 K (20–80 °C) gave an oily substance whose IR spectrum suggested the presence of CH<sub>2</sub>, OH, NH, and NNO<sub>2</sub> groups. Its UV spectrum contained an absorption near 226–228 nm, which was characteristic of the expected product *N,N'*-dinitromethylenediamine.



Treatment of this product with KOH yielded a dipotassium salt with yields up to 89%, depending on the temperature and reaction time.

### 8.2.2 Physical Properties of Dinitrourea

Dinitrourea melts at 474–477 K (101–104 °C) in a capillary and at 480–483 K (107–110 °C) on a hot-stage microscope. The density is 1.98 g/cm<sup>3</sup> at room temperature. Dinitrourea is soluble in water, acetonitrile, alcohols, ether, ethyl acetate, cyclohexanone, THF, DMSO or nitric acid. However, aqueous solutions of DNU decompose quickly.

### 8.2.3 Decomposition of Dinitrourea

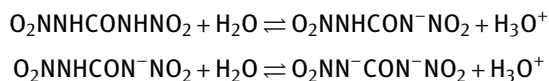
The thermal decomposition of the diammonium salt of DNU proceeded in stages: the first mol of NH<sub>3</sub> was removed at up to 383 K (110 °C; weight loss 10%, 9.24% calcd.) [80]. The second much faster stage of decomposition was connected with releasing the second mol of ammonia, until at 403 K (130 °C), the total weight loss was ~18%. At the end of the second stage the decomposition of DNU itself began and ended at 413 K (140 °C), with a spontaneous complete decomposition of the sample. A much more thermostable compound is the potassium salt of DNU. The beginning of the decomposition was observed at 408 K (135 °C), but ignition did not take place below around 463 K (190 °C). A hexamethylenetetramine salt of dinitrourea was obtained in a reaction of crude DNU with a 15 mass-% aqueous solution of (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> at 293 K (20 °C). It was not as stable as the potassium salt.

The lack of stability of DNU reported by Syczewski, Cieslowska-Glinska, and Boniuk in [80] was later disputed. Later investigators found that when DNU was very pure, it could indeed be stored at room temperature [86]. In the DSC at a heating rate of 10 °C/min, the exotherm started at 373 K (100 °C) and was very steep at 393 K (120 °C). The ignition temperature in a Wood's metal bath was at 364–366 K (91–93 °C). The activation energy by DSC was 104 kJ/mol and from the ignition delay it came out to be 78 kJ/mol. The measured density was 1.98 g/cm<sup>3</sup> at 298 K (25 °C). The drop-weight impact sensitivity was 5 J (for comparison: RDX 7 J) and the friction sensitivity was 76 N (for comparison: RDX 120 N). See also [87].

The thermal decomposition mechanism of DNU was studied by temperature-programmed *in situ* pyrolytic FTIR spectroscopy [88]. The results showed that the nitro group of the DNU molecule is initially broken, followed by a rearrangement. All the decomposition reactions had gone to completion before the sample reached 373 K (100 °C), resulting in the formation of N<sub>2</sub>O, NO<sub>2</sub>, CON, HNCO, and NO<sub>2</sub>NH<sub>2</sub>. Theoretical calculations confirmed that the *syn*, *anti* conformations play a key role in the decomposition process and that the N—N bonds were broken firstly with the increase of temperature. The plotted potential energy curve via the corresponding bond length showed that cleavage of the N—N bond in the condensed phase of DNU was a highly reversible process and a typical radical recombination reaction with zero barriers in the initial step. The final products of N<sub>2</sub>O, NO<sub>2</sub>, HNCO, and NO<sub>2</sub>NH<sub>2</sub> were formed by  $\alpha$ -cleavage or hydrogen atom rearrangement of the radicals that were formed in the initial step.

### 8.2.4 Salts of Dinitrourea

Dinitrourea is a fairly strong acid. The  $pK_a$  value of the first stage of ionization is  $pK_{a1} = -0.13$ . The  $pK_a$  value of the second stage of ionization is  $pK_{a2} = 4.87$ :



The behavior of dinitrourea and its potassium and dipotassium salts in different solvents have been studied by IR and UV spectroscopy [89]. In different media, dinitrourea can exist in several tautomeric forms. An XRD study of the potassium and dipotassium salts of dinitrourea revealed a tendency toward equalization of the bond lengths of the C—N<sup>−</sup>—NO<sub>2</sub> fragments compared to those of C—NH—NO<sub>2</sub>, which agreed with the results of quantum chemical calculations.

The crystal structure of DNU was determined by single-crystal XRD and was found to be orthorhombic; space group: *Fdd2*,  $a = 12.0015(9) \text{ \AA}$ ,  $b = 17.6425(13) \text{ \AA}$ ,  $c = 4.5555(4) \text{ \AA}$ ,  $V = 964.57 \text{ \AA}^3$ ,  $Z = 8$ ,  $T = 90 \text{ K}$ ,  $\rho_{\text{XRD}} = 2.067 \text{ g/cm}^3$  [90]. The heat of formation ( $\Delta H_f^{298}$ ) of DNU vapor in the gas phase was calculated to be 24.88 kJ/mol using a method based on isodesmic reactions. Eleven mono-organic salts of DNU were prepared in acetonitrile and characterized via NMR spectra, elemental analyses, and DSC. Derivatives of 1,2,4-triazolium salts of DNU exhibited densities ranging from 1.75 to 1.86 g/cm<sup>3</sup> and detonation properties comparable to those of RDX and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX).

Ten DNU dianionic salts formed by the metathesis of tetrazolium and guanidinium sulfates with *in situ*-generated barium DNU in aqueous solution were examined for impact sensitivity, NMR, elemental analysis, IR, DSC, and TGA [91]. Bis(guanylguanidinium) DNU dianionic salt crystallized in the triclinic space group *P*-1. The detonation pressures calculated for these salts range from 19.6 to 29.1 GPa,

and the detonation velocities ranged from 7521 to 8908 m/s, which make them competitive energetic materials. The DNU dianion compares very favorably with dinitramide as a novel oxidative species.

Six energetic DNU ionic salts were prepared by the reaction of ethylenediamine (EDA) and derivatives of triazole and imidazole with *N,N'*-dinitrourea [92]. Among them, EDA gave diacidic salt and other derivatives gave monoacidic salts. The effects of solvent, reaction temperature, and time on yield of salt from 4-aminotriazole and DNU were analyzed. The yield could be up to 85% in acetonitrile and 71% in ethanol at 10 °C for a 2-h reaction time. Generally, polar solvents with high dielectric constants were beneficial to the salt-forming reaction. The structures of all salts prepared were confirmed by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. The thermal stability of most salts surpassed that of DNU. For instance, EDA-DNU salt started to decompose at 398 K (125 °C; approximately 55 °C higher than DNU).

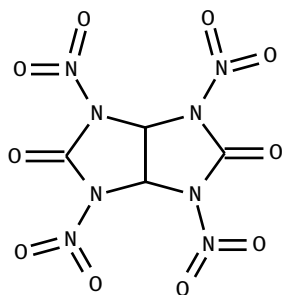
Additional information on salts formed from DNU is referenced in [79]. The IR spectrum of the crystalline monopotassium salt indicated that one of the two nitramine groups, which is not involved in salt formation, has the true structure of a nitramine (doublet: 1620, 1600 cm<sup>-1</sup>), and the proton participates in either inter- or intra-molecular hydrogen bonding with oxygen atoms of the nitro and carbonyl groups, as the proton's vibrational frequency decreased to 3180, 3220 cm<sup>-1</sup>. The IR spectrum of the dipotassium salt of DNU differed from both the IR spectrum of DNU and that of the DNU monopotassium salt. The difference lies, first, in lacking any band within the region of 3600–3000 cm<sup>-1</sup> (N–H group and hydroxonium ion) and within the region of 1530–1620 cm<sup>-1</sup> (asymmetric vibrational frequencies of the nitro group), and second, in the observed vibrational frequencies for both nitro groups in the *aci*-form N=NO(OK)(1390, 1380, and 1210 cm<sup>-1</sup>).

### 8.3 Ring-Shaped Nitrourea and Dinitrourea Derivatives

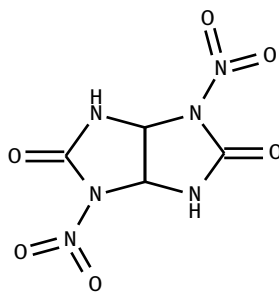
Instead of leaving the amide group dangling at the end of the linear molecule, there are several ways to close the ring using the terminal –NH<sub>2</sub> group and performing an –NH– ring closure. Compounds that contain the –NH–CO–NH– sequence in small ring structures are sometimes called **urils**, to indicate their relationship to **urea** H–NH–CO–NH–H. Energetic compounds are then obtained by replacing the hydrogen on the NH group and converting the amido groups to nitramino –N(NO<sub>2</sub>) groups. These compounds could be discussed in later chapters in this book under nitramines (*Encyclopedia of Liquid Fuels*, chapter “Nitramines”) or heterocyclic amines (chapter “Heterocyclic Amines”), but because of their close relationship to **urea**, they are already discussed here.

The earliest and best-known examples of bicyclic mono- and dinitroureas were 1,3,4,6-tetranitroglycouril (TNGU) and 1,4-dinitroglycouril (DNGU or DINGU) [93–97]. TNGU can be processed in prilled particle form [98]. This spherical morphology was

significantly less sensitive to impact, friction, and electrostatic discharge than crystalline TNGU made according to literature methods. DNGU was first described in 1888, but received little attention until 90 years later.



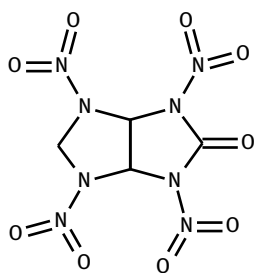
TNGU



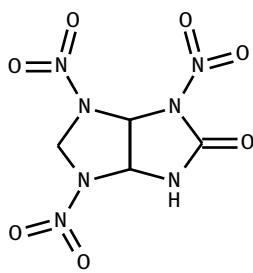
DNGU

Both TNGU and DNGU have high crystal densities (2.04 and 1.98 g/cm<sup>3</sup>, respectively). TNGU is unstable in the presence of water and hydrolyzes [99], while DNGU decomposes only slowly even in boiling water. DNGU has a significantly higher drop hammer value (i.e., less sensitive) than TNGU and is more stable. DNGU has been proposed as an RDX and TNT replacement. When compacted to a bulk density of 1.94 g/cm<sup>3</sup>, TNGU exhibited a detonation velocity of 9073 m/s. DNGU has no melting point before decomposition. DNGU has a sharp exothermic transition at 518–523 K (245–250 °C). The impact sensitivity was 80–100 cm in the Holston apparatus (for comparison: RDX: 17 cm) and the friction sensitivity was 360 N (for comparison: RDX: 164 N).

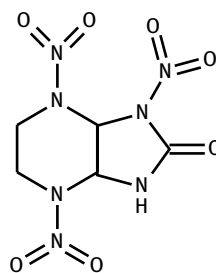
Similar uriles with only one carbonyl group and the other carbonyl group replaced by a methylene bridge also have good explosive properties. These compounds contain only one  $\text{—N(NO}_2\text{)—CH}_2\text{—N(NO}_2\text{)—}$  nitramide sequence instead of three as in RDX or four as in HMX.



K55

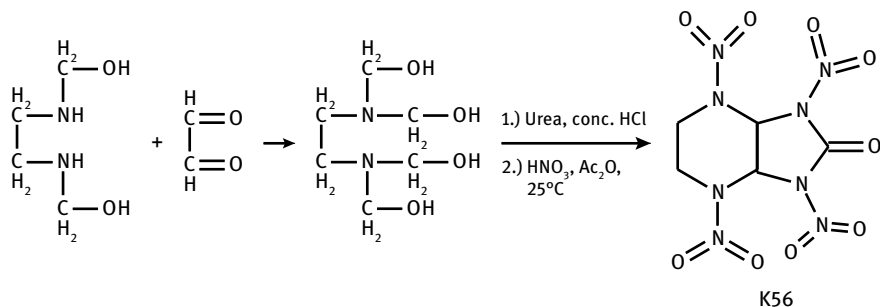


HK55

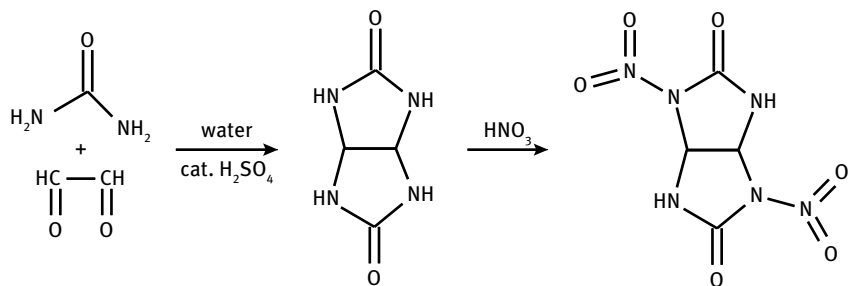


HK56

Pagoria et al. [100] also prepared K-56 in a shorter synthesis route from 1,4-diformyl-2,3-dihydropiperazine, which undergoes a condensation reaction with urea (in aq. HCl) to yield 2,5,7,9-tetrahydro-2,5,7,9-tetrazabicyclo(4.3.0)nonane-8-one dihydrochloride, followed by nitration with fuming nitric acid and acetic anhydride. Another nitrolysis agent is trifluoromethanesulfonic acid anhydride/20%  $\text{N}_2\text{O}_5$ /fuming nitric acid. K-56 has a density of  $1.969 \text{ g/cm}^3$ , while HK-56 has a density of  $1.84 \text{ g/cm}^3$  [100].



DNGU can be produced by a simple nitration of glycoluril, which is very inexpensive [101]. Glycoluril can be produced from very inexpensive materials (urea and glyoxal). Glycoluril is commercially available and the cost of DNGU was estimated to be between that of RDX and that of HMX. Yields are typically 90–95%, with purities 99%.



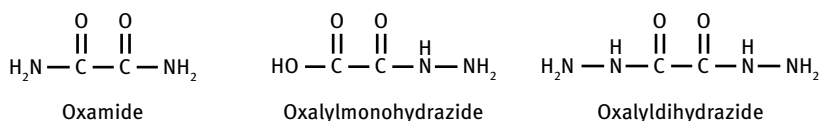
Continued nitration of DINGU leads to the tetranitramine also called SORGUYL (same as TNGU). SORGUYL has a very high density ( $2.01 \text{ g/cm}^3$ ) and a very high detonation velocity ( $9150 \text{ m/s}$ ).

Tetranitrodiglycoluril (TNDGU) can be synthesized from glycoluril dimer [102]. TNDGU is a primary explosive with a density of  $1.93 \text{ g/cm}^3$  and a detonation velocity of  $8305 \text{ m/s}$ . It will probably not be used as a rocket propellant.



## 9 Oxamide and Oxalyldihydrazide

The three compounds oxamide, oxalylmonohydrazide (oxalic acid monhydrazide), and oxalyldihydrazide (oxalic acid dihydrazide) are useful high-nitrogen compounds and are used as coolants for gas generants. Physical properties of these compounds are listed in Table 4. Additional information on oxamide is found in [103]. Procurement and purity requirements of oxamide are covered by specifications AS-1871 and MIL-O-60863.



**Table 4:** Properties of oxamide, oxalylmonohydrazide, and oxalyldihydrazide.

|                          | Oxamide                                                     | Oxalylmonohydrazide                                         | Oxalyldihydrazide                                           |
|--------------------------|-------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| Empirical formula        | C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> | C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sub>3</sub> | C <sub>2</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub> |
| CAS RN                   | 471-46-5                                                    | —                                                           | 996-98-5                                                    |
| Molecular mass           | 88.066 g/mol                                                | 104.07 g/mol                                                | 118.1 g/mol                                                 |
| Nitrogen content, mass-% | 31.81                                                       | 26.92                                                       | 47.44                                                       |
| Melting point, K         | 623                                                         | —                                                           | 513 (dec.)                                                  |
| Melting point, °C        | 350                                                         | —                                                           | 240 (dec.)                                                  |
| Enthalpy of formation    | −508 kJ/mol                                                 | —                                                           | −295 kJ/mol                                                 |
|                          | −121.5 kcal/mol                                             | —                                                           | −70.5 kcal/mol                                              |
|                          | −1380 cal/g                                                 | —                                                           | −597 cal/g                                                  |

The protonation of oxalyldihydrazide with nitric acid gives oxalyldihydrazinium nitrate (OHN) and dinitrate (OHDN) [104]. The synthesis is very simple and can be carried out on large scales and with very good yields. OHN and OHDN were intensively characterized by low-temperature XRD, NMR, and vibrational spectroscopy. These salts could be used as ingredients in energetic formulations due to their low sensitivities and high nitrogen contents. Their thermal stability was investigated by DSC and the salts were very thermally stable.

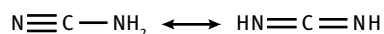
## 10 Cyanamide

Cyanamide, also known as cyanamid, carbamonitrile, H<sub>2</sub>N—C≡N, CAS RN [420-04-2] is an important intermediate in the synthesis of high-nitrogen compounds like triaminoguanidine and its salts, and readily cyclizes to heterocyclic compounds with nitrogen(s) in the ring. It forms colorless, hygroscopic crystals. Cyanamide as an acid

forms ionic liquid salts that are under consideration as low-volatility hypergolic fuels with less toxicity than alkylhydrazines. The cyanamide anion is sometimes called a cyanamidate anion. Cyanamide in aqueous solution is stable at pH < 5, but will dimerize to dicyandiamide at pH 8–9.5.

Calcium cyanamide was once used as a fertilizer before nitrogen from the Haber–Bosch synthesis of ammonia became the main source of fertilizer nitrogen.

Cyanamide contains both a nucleophilic and an electrophilic group within the same molecule, and so cyanamide undergoes various reactions with itself. Cyanamide exists as two tautomers



the cyanamide form and the carbondiimide form. The  $\text{N}\equiv\text{CNH}_2$  form dominates, but in a few cases, the imide configuration forms the path for reactions.

Cyanamide dimerizes readily to give 2-cyanoguanidine (dicyandiamide, see section “Dicyandiamide (2-Cyanoguanidine)”) and trimerizes to a cyclic trimer which is called melamine. Unstabilized cyanamide may polymerize spontaneously while stored at room temperature. Therefore, most cyanamide is not stored as such, but converted to dicyandiamide or melamine for further use. A large American chemical company once carried the term “Cyanamid” in its name. The physical properties of cyanamide are summarized in Table 5.

**Table 5:** Properties of cyanamide.

| Property              | SI units                            | Other units                                 | References |
|-----------------------|-------------------------------------|---------------------------------------------|------------|
| Molecular mass        | 42.0400 g/mol                       | 23.787 mol/kg                               | [105]      |
| Melting point         | 315 K                               | 42 °C                                       | [106]      |
| Boiling point         | 356 K at 6.7 Pa<br>413 K at 2.5 kPa | 83 °C at 0.05 mm Hg<br>140 °C at 18.7 mm Hg | [106]      |
| Density               | 1.282 g/cm <sup>3</sup>             | —                                           | [106]      |
| Enthalpy of formation | +58.79 kJ/mol                       | +14.05 kcal/mol                             | [105]      |
| Heat of fusion        | 8.76 kJ/mol at 317 K                | 2.09 kcal/mol at 44 °C                      | [105]      |
| Heat of sublimation   | 75.2 kJ/mol at 290 K                | 17.97 kcal/mol at 17 °C                     | [105]      |

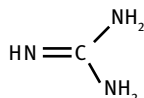
When stored under moist conditions, cyanamide degrades via hydrolysis to urea. Heating cyanamide in an autoclave can form graphitic carbon nitride (g  $\text{C}_3\text{N}_4$ ).

## Imides

Imides contain the  $>\text{C}=\text{NH}$  group where an amide would contain a  $>\text{C}=\text{O}$  group. Imides are of more interest as propellants than the  $>\text{C}=\text{O}$  compounds from which they are often derived because they have higher enthalpies of formation and a better fuel value. Nobody likes  $>\text{C}=\text{O}$  bonds in a fuel.

## 11 Guanidine

Guanidine,  $\text{H}_2\text{NC}=\text{NH NH}_2$ ,  $\text{C}_1\text{H}_5\text{N}_3$ , CAS RN [113-00-8], itself, the free base, is rarely used as an ingredient in rocket propellants because it is not as stable as the guanidinium salts derived from it.



Guanidinium salts have a useful high nitrogen content and a remarkable thermal stability. Actually, guanidine is amphoteric and can form salts with both acids and with very strong bases. Alkali metal guanidates have been prepared and characterized.

Guanidine melts and decomposes at 323 K ( $50^\circ\text{C} = 122^\circ\text{F}$ ). The heat of combustion is 1052 kJ/mol and the standard enthalpy of formation  $\Delta H_f^{298}$  is  $-56$  kJ/mol. The  $\text{p}K_a$  of guanidine in water is 13.6, meaning that guanidine is a very strong base. Guanidine free base is difficult to obtain in the pure state and that difficulty has delayed the characterization of its molecular structure [107–109]. The crystal structure consists of two Y-shaped symmetry-independent molecules in the unit cell that are interconnected by a hydrogen bonding network, which results in a layered structure. Pure guanidine crystallizes in the orthorhombic space group *Pbca* (No. 61) with the cell parameters of  $a = 8.5022(2) \text{ \AA}$ ,  $b = 9.0863(2) \text{ \AA}$ ,  $c = 15.6786(4) \text{ \AA}$  at 100 K,  $Z = 16$ , with two Y-shaped molecules in the asymmetric unit [110].

The theoretical gas-phase enthalpies of formation of guanidine and its ten amino and nitro derivatives were calculated using an isodesmic reaction method [111]. The enthalpies of sublimation were estimated within the framework of the Politzer approach that combined the empirical equation for enthalpy of sublimation with the quantum mechanical calculations of the electronic properties of the molecular surfaces. The enthalpies of sublimation of mono-, di-, and triaminoguanidine were calculated using experimental data for their salts. On the basis of the calculated enthalpies of formation in the gaseous state and enthalpies of sublimation values, the solid-phase enthalpies of formation were estimated for all guanidine derivatives. Results from a predictive model agreed with available experimental data for guanidine, nitroguanidine, and some of their derivatives.

Guanidine free base would never be used as a fuel in rocket propellants, but it is a good intermediate in the synthesis of heterocyclic compounds and special guanidinium salts.

Fluorination of urea or guanidine was intended as a step in the synthesis of energetic difluoroamino compounds. However, side reactions prevented formation of the desired products. The reaction of guanidine in solution with  $\text{ClO}_3\text{F}$  did not give the desired *N*-fluoro- or *N,N'*-difluoroguanidine, but instead yielded guanidinium salts  $\text{C}(\text{NH}_2)_3^+\text{X}^-$  ( $\text{X} = \text{F}, \text{ClO}_4$ ) [112, 113].

### 11.1 Guanidinium Salts

Guanidine is a strong base and forms salts with many acids, even weak proton donor acids. Many of the salts are thermally stable and contain a high nitrogen content, making them promising ingredients for propellants and gas generators. Table 6 is a summary of CAS registry numbers, gross formulae, molecular mass, oxygen balance, and nitrogen content of guanidinium nitrate and a few derived compounds. See also [114].

Table 7 is a summary of the melting points of guanidinium salts.

**Table 6:** Molecular mass, nitrogen content, and oxygen balance of guanidinium nitrates.

| Name                        | CAS RN     | Gross formula                              | Molecular mass | Oxygen balance, % | Nitrogen content, mass% |
|-----------------------------|------------|--------------------------------------------|----------------|-------------------|-------------------------|
| Guanidinium nitrate         | 506-93-4   | $\text{C}_1\text{H}_6\text{N}_4\text{O}_3$ | 122.0833       | -26.2             | 45.89                   |
| Aminoguanidinium nitrate    | 10308-82-4 | $\text{C}_1\text{H}_7\text{N}_5\text{O}_3$ | 137.10         | -29.2             | 51.08                   |
| Diaminoguanidinium nitrate  | 37160-07-9 | $\text{C}_1\text{H}_8\text{N}_6\text{O}_3$ | 152.11         | -31.6             | 55.25                   |
| Triaminoguanidinium nitrate | 4000-16-2  | $\text{C}_1\text{H}_9\text{N}_7\text{O}_3$ | 167.13         | -33.5             | 58.67                   |

**Table 7:** Summary of melting points of guanidinium salts.

| Compound name           | Gross formula                                 | Melting point |          | References |
|-------------------------|-----------------------------------------------|---------------|----------|------------|
|                         |                                               | K             | °C       |            |
| Guanidinium perchlorate | $\text{CH}_6\text{N}_3\text{O}_4\text{Cl}$    | 528           | 255      | [115]      |
| Guanidinium nitrate     | $\text{CH}_6\text{N}_4\text{O}_3$             | 488           | 215      | [18]       |
| Guanidinium carbonate   | $\text{C}_3\text{H}_{12}\text{N}_6\text{O}_3$ | 471           | 198      | [106]      |
| Guanidinium picrate     | $\text{C}_7\text{H}_8\text{N}_6\text{O}_7$    | 606           | 333 dec. | [18]       |
| Guanidinium dinitramide | $\text{C}_1\text{H}_6\text{N}_6\text{O}_4$    | 421           | 148      | [116]      |

## 11.2 Guanidinium Nitrate

Guanidinium nitrate,  $[\text{C}^+(\text{NH}_2)_3]\text{NO}_3^-$ ,  $\text{CH}_6\text{N}_4\text{O}_3$ , guanidine nitrate, GuN, GN, CAS RN [506-93-4], is a thermally very stable high-nitrogen compound. It contains a good amount of nitrogen (45.89% N), is used in gas generants for airbag inflators, and was used as the main ingredient in high-temperature explosives. It is the starting material for production of nitroguanidine.

### 11.2.1 Production of Guanidinium Nitrate

Guanidinium nitrate can be prepared by reacting cyanamide or dicyandiamide with nitrate in liquid ammonia [117]. Liquid ammonia is a solvent for cyanamide, dicyandiamide, and ammonium nitrate. Guanidinium nitrate can be prepared by fusing dicyandiamide with ammonium nitrate, which results in ammeline and ammelide as contaminant by-products. The mixtures of AN with any organic compounds like dicyandiamide are potentially explosive, in particular in the presence of organic contaminants. Another method used the reaction of urea and ammonium nitrate with silica gel as a catalyst, and the kinetics of the reaction were followed by measuring the formation of  $\text{NH}_3$  [118]. The optimum temperature for the maximum yield of guanidinium nitrate from urea and AN using silica gel as catalyst and with a given ratio of urea and AN had to be determined. See also [119, 120]. The effect of the mixture ratio of raw materials, reaction time, temperature, activity of the catalyst, and other parameters on the synthesis of GuN from urea and ammonium nitrate in the presence of catalyst and conversion of urea were investigated [121, 122]. The most favorable process conditions have advantages of economic raw materials and high yield.

### 11.2.2 Physical Properties of Guanidinium Nitrate

Table 8 gives a summary of the physical properties of GuN.

**Table 8:** Physical properties of guanidinium nitrate.

| Property                | SI units                    | Other units                    | References |       |
|-------------------------|-----------------------------|--------------------------------|------------|-------|
| Molecular mass          | 122.0833 g/mol              | 8.1911 mol/kg                  | —          | [105] |
| Melting point           | 488 K                       | 215 °C                         | 419 °F     | [18]  |
|                         | 487.17 K                    | 214.02 °C                      | 417 °F     | [123] |
|                         | 485.43                      | 212.28 °C                      | 414 °F     | [36]  |
| Density                 | 1.436 g/cm <sup>3</sup>     | —                              | —          | [124] |
|                         | 1.4365 g/cm <sup>3</sup>    | —                              | —          |       |
| Vapor pressure at 298 K | 2.66 × 10 <sup>−18</sup> Pa | 1.99 × 10 <sup>−20</sup> mm Hg | [16]       |       |

### 11.2.2.1 Vapor Pressure of Guanidinium Nitrate

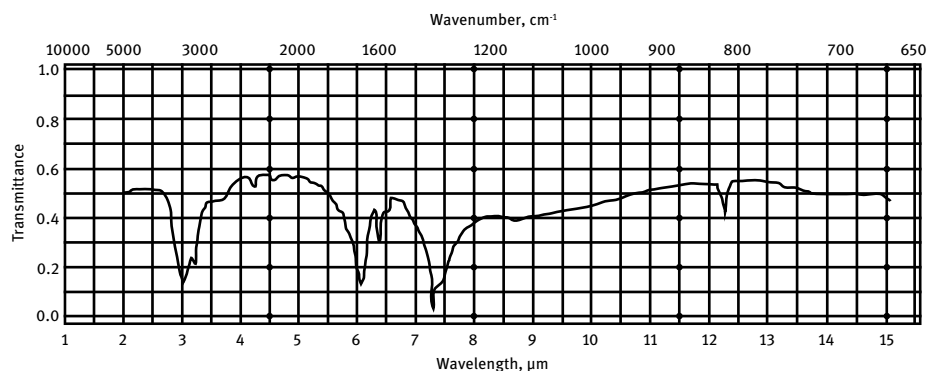
The vapor pressure of GuN was measured at 478–498 K (205–225 °C) using an isothermal thermo-gravimetric weight-loss method and compared to that of urea nitrate and AN [16]. The Clapeyron equation for GuN vapor pressure is

$$\ln P = 72.189 - 33589/T$$

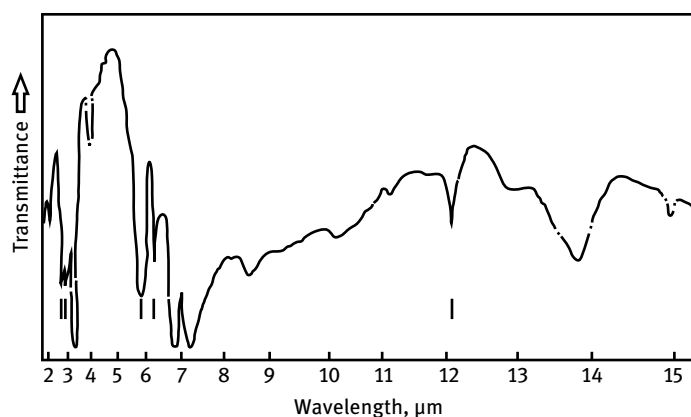
where  $P$  is the pressure in Pa and  $T$  is the temperature in kelvin. For a temperature of 298 K, this equation gives a vapor pressure of  $2.66 \times 10^{-18}$  Pa =  $1.99 \times 10^{-20}$  mm Hg. From the slope of this equation, the enthalpy of sublimation was calculated as 279 kJ/mol.

### 11.2.2.2 IR Spectra of Guanidinium Nitrate

Infrared spectra of GuN are shown in Figures 7 and 8.



**Figure 7:** Infrared spectrum of guanidinium nitrate. (Reproduced and modified from [21].)



**Figure 8:** Infrared spectrum of guanidinium nitrate. (Reproduced and modified from [125], with permission from Levering Estate.)

The IR spectra of GuN, aminoguanidinium nitrate, diaminoguanidinium nitrate, triaminoguanidinium nitrate, and several other compounds of interest are shown in Figure 8, 18, 21, and 24 [125–127]. The spectra were taken as a suspension of the compound to be studied in white mineral oil, and mineral oil absorption is always superimposed on the spectrum of the other compound. The main oil bands are shown as dotted lines, while the bands considered to be due to the compound under study are marked with a small vertical line. For the 20 guanidine derivatives presented in the paper, a strong absorption band was found in the region of 5.95 to 6.02  $\mu\text{m}$  in all but four cases; in these cases, a band was observed a few hundredths of a micron on either side of this region. As this band is in the region of the spectrum characteristic of double bonds, it has been attributed to the C=NH group present in all guanidine derivatives.

### 11.2.2.3 Thermodynamic Properties of Guanidinium Nitrate

Table 9 gives a summary of the thermodynamic properties of GuN.

**Table 9:** Thermodynamic properties of guanidinium nitrate.

| Property                  | SI units         |               | Other units              |              | References |
|---------------------------|------------------|---------------|--------------------------|--------------|------------|
| Molecular mass            | 122.0833 g/mol   | 8.1911 mol/kg |                          |              | [105]      |
| Enthalpy of formation     | –386.9           | –3169.2 kJ/kg | –92.47                   | –757.4 cal/g | [128,      |
|                           | $\pm 0.7$ kJ/mol |               | $\pm 0.17$ kcal/mol      |              | 129]       |
|                           | –387 kJ/mol      | –3170.1 kJ/kg | –92.5 kcal/mol           | –757.7 cal/g | [18]       |
|                           | –389             | 3186 kJ/kg    | $-93 \pm 0.93$ kcal/mol  | –761.7 cal/g | [130]      |
|                           | $\pm 3.9$ kJ/mol |               |                          |              |            |
| Heat of fusion            | –387.2 kJ/mol    | 3171 kJ/kg    | –92.54 kcal/mol          | –758 cal/g   | [124]      |
|                           | 24.8 kJ/mol      | 203 kJ/kg     | 5.86 kcal/mol            | 48 cal/g     | [18]       |
|                           | 25.27 kJ/mol     | 207 kJ/kg     | 6.04 kcal/mol            | 49.5 cal/g   | [123]      |
| Heat of sublimation       | 279 kJ/mol       | 2285 kJ/kg    | 66.7 kcal/mol            | 546 cal/g    | [16]       |
| Heat of combustion        | 869.4 kJ/mol     | 7122 kJ/kg    | 207.8 kcal/mol           | 1702 cal/g   |            |
|                           | 864.1 kJ/mol     | 7079 kJ/kg    | 206.53                   | 1692 cal/g   | [128,      |
|                           |                  |               | $\pm 0.17$ kcal/mol      |              | 129]       |
|                           | 811.7 kJ/mol     | 6648.8        | 194 kcal/mol             | 1589 cal/g   | [131]      |
|                           |                  | $\pm 5$ kJ/kg |                          |              |            |
| Heat of solution in water | 41.00 kJ/mol     | 335.9 kJ/kg   | $9.80 \pm 0.01$ kcal/mol | 80.3 cal/g   | [128, 129] |

### Enthalpy of Formation of Guanidinium Nitrate

Because of interference due to the formation of nitric acid during combustion of GuN in a combustion bomb in a calorimeter, the heat of reaction of guanidinium perchlorate with nitric acid and the heat of reaction of GuN with perchloric acid in solution was measured and used to calculate the enthalpy of formation of GuN [130]. The heats of solution of the various reactants were determined in separate experiments for a wide range of dilutions. The experiments gave a value of  $-389 \pm 3.9$  kJ/mol ( $-93 \pm 0.93$  kcal/mol) for the standard enthalpy of formation of GuN. The same method was also used to obtain the enthalpy of formation of guanidinium perchlorate.

Enthalpies of formation and solution of guanidinium, aminoguanidinium, and triaminoguanidinium nitrate were determined by combustion and solution calorimetry methods [131]. Enthalpies of formation of the respective cations by themselves in infinitely diluted aqueous solution were then calculated using the known enthalpy of formation of the nitrate ion ( $-206.8$  kJ/mol =  $-49.44$  kcal/mol). The upper heats of combustion in a constant-volume calorimetric bomb, the enthalpies of formation, and the enthalpies of solution of the three nitrate salts are summarized in Table 10.

**Table 10:** Heats of combustion, enthalpies of formation, and enthalpies of solution of guanidinium and mono- and triaminoguanidinium nitrates.

| Compound                    | Heat of combustion<br>$\Delta U_{\text{Comb}}$ |                  | Enthalpy of formation<br>$\Delta H_f^{298}$ |                   | Enthalpy of solution<br>$\Delta H_{\text{sol}}^{298}$ |                  |
|-----------------------------|------------------------------------------------|------------------|---------------------------------------------|-------------------|-------------------------------------------------------|------------------|
|                             | J/g                                            | cal/g            | kJ/mol                                      | kcal/mol          | kJ/mol                                                | kcal/mol         |
| Guanidinium nitrate         | $6648.8 \pm 5$                                 | $1703.7 \pm 1.1$ | $-387 \pm 0.5$                              | $-92.48 \pm 0.13$ | $41.0 \pm 0.08$                                       | $9.80 \pm 0.02$  |
| Aminoguanidinium nitrate    | $8184 \pm 9.6$                                 | $1956.0 \pm 2.3$ | $-279 \pm 0.67$                             | $-66.62 \pm 0.16$ | $49.0 \pm 0.04$                                       | $11.71 \pm 0.01$ |
| Triaminoguanidinium nitrate | $9804 \pm 5$                                   | $2343.3 \pm 1.3$ | $-50.2 \pm 0.8$                             | $-12.01 \pm 0.19$ | $52.9 \pm 0.12$                                       | $12.65 \pm 0.03$ |

Data source: [131]

#### 11.2.2.4 Solubility of Guanidinium Nitrate

Guanidinium nitrate is not very soluble in water and can be easily purified by recrystallizing from water. Based on very old data, the solubility of GuN in water is 160 g/kg  $\text{H}_2\text{O}$  at 293 K (20 °C), 470 g/kg  $\text{H}_2\text{O}$  at 328 K (55 °C), and 2000 g/kg  $\text{H}_2\text{O}$  at 373 K (100 °C). In boiling ethanol, one can dissolve 130 g GuN in 1 kg  $\text{C}_2\text{H}_5\text{OH}$  at 351 K (78 °C).

Using a gravimetric method, solubilities of GuN in water, methanol, ethanol, *n*-propanol, and acetone at temperatures ranging from 278 to 333 K at atmospheric pressure were experimentally measured [123]. Melting temperature,  $T_m$ , and fusion enthalpy,  $\Delta H_f$ , of guanidinium nitrate were determined using DSC. Dissolution of GuN in all examined solvents was found to be endothermic and entropically favorable. The measured solubility data were combined with calculated ideal solubility data to



calculate activity coefficients at infinite dilution. Solubility data for GuN in water, methanol, and ethanol are summarized in Table 11. The heat of dissolution of GuN in water is 24.41 kJ/mol, in methanol 23.80 kJ/mol, and in ethanol 23.23 kJ/mol.

**Table 11:** Solubility of guanidinium nitrate in three different solvents.

| Water          |                                        | Methanol       |                                        | Ethanol        |                                        |
|----------------|----------------------------------------|----------------|----------------------------------------|----------------|----------------------------------------|
| Temperature, K | Solubility, mol fraction $\times 10^2$ | Temperature, K | Solubility, mol fraction $\times 10^2$ | Temperature, K | Solubility, mol fraction $\times 10^2$ |
| 278.25         | 0.90                                   | 278.25         | 0.63                                   | 278.05         | 0.30                                   |
| 283.35         | 1.12                                   | 283.25         | 0.75                                   | 283.15         | 0.37                                   |
| 288.25         | 1.36                                   | 288.25         | 0.92                                   | 288.35         | 0.43                                   |
| 292.95         | 1.57                                   | 293.25         | 1.07                                   | 293.15         | 0.51                                   |
| 298.25         | 1.90                                   | 298.35         | 1.26                                   | 298.25         | 0.62                                   |
| 303.15         | 2.22                                   | 303.15         | 1.48                                   | 303.25         | 0.70                                   |
| 308.35         | 2.62                                   | 308.35         | 1.74                                   | 308.25         | 0.81                                   |
| 313.05         | 3.02                                   | 313.15         | 1.98                                   | 313.05         | 0.94                                   |
| 318.25         | 3.49                                   | 318.25         | 2.27                                   | 318.05         | 1.08                                   |
| 323.25         | 4.01                                   | 323.35         | 2.64                                   | 323.25         | 1.24                                   |
| 328.35         | 4.63                                   | 328.05         | 3.05                                   | 328.35         | 1.43                                   |
| 332.85         | 5.11                                   | 278.25         | 0.63                                   | 278.05         | 0.30                                   |

Data source: [123]

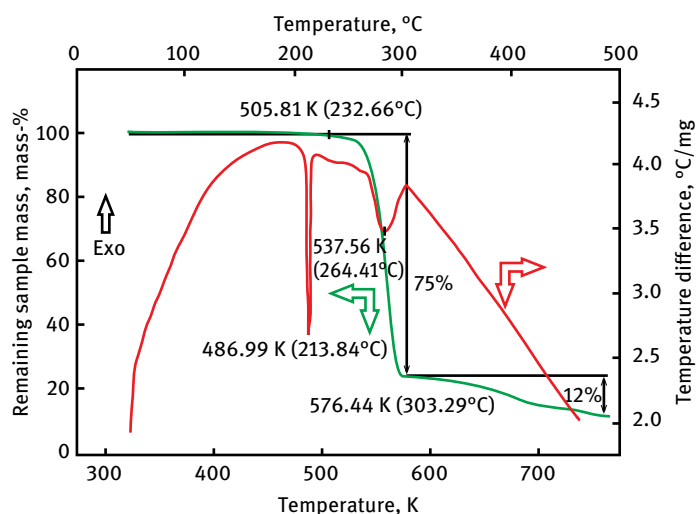
### 11.2.3 Thermal Stability of Guanidinium Nitrate

The TGA showed that GuN started losing weight at 503 K (230 °C) and the decomposition was fast between 548 and 598 K (275–325 °C) [132]. Compared to all other organic nitrate salts, this is a very high decomposition temperature. Guanidinium nitrate is thermally very stable. The weight loss was slow in the temperature range 598–773 K (325–500 °C). No residue was left behind at 773 K (500 °C), which suggested that the entire mass had been converted into gaseous products. The activation energy calculated by analyzing was 192.5 kJ/mol (46 kcal/mol). The DTA showed an endotherm at 483 K (210 °C) and an exotherm at 578 K (305 °C). As the compound melts at 483 K (210 °C) and since there is no weight change around this temperature, the endothermic peak is due to the melting of GuN. Analyzing the decomposition products in a mass spectrometer at 503 K (230 °C), there was no indication of a molecular peak corresponding to GuN, which suggests that the decomposition process occurs through a proton transfer mechanism as observed in similar onium-type salts. It is interesting to note that the fragmentation product, cyanamide ( $m/e = 42$ ), undergoes dimerization to cyanoguanidine ( $m/e = 84$ ) and trimerization to melamine ( $m/e = 126$ ).

Infrared spectroscopy measurements of the kinetics and decomposition pathways of aqueous GuN solutions at 513–573 K (240–300 °C) and 275 bar showed that the decomposition of GuN was catalyzed by the formation of  $\text{NH}_3$  [133]. The reaction

scheme involved deprotonation of the guanidinium ion by  $\text{NH}_3$  to produce neutral guanidine, which hydrolyzed to form urea as the rate-determining step. The subsequent hydrothermolysis chemistry followed that of urea. Thus, although the overall decomposition rate of GuN was slower than that of urea, the Arrhenius parameters for the step for formation of  $\text{CO}_2$  from GuN and urea were similar ( $E_a \approx 66 \text{ kJ/mol}$ ,  $\ln A \approx 19 \text{ s}^{-1}$ ).

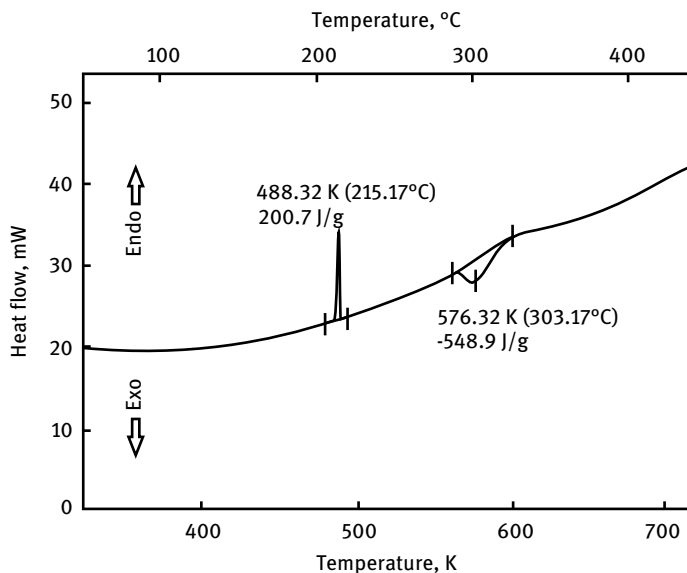
The first endothermic peak seen at 487 K (214 °C) in the DTA thermogram of GuN at a heating rate of  $2^\circ/\text{min}$  is the phase change from solid to liquid (Figure 9) [134]. After this phase change, a very slow decomposition reaction occurred. The major decomposition of GuN began only at 505 K (232 °C) and was complete at 576 K (303 °C; 75% weight loss). The remaining 25% weight residue decomposed endothermically at higher temperature.



**Figure 9:** DTA-TGA thermogram of guanidinium nitrate. (Republished and modified from [134], with permission of ©2009 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

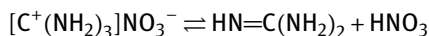
The DSC thermogram recorded at a heating rate of  $10^\circ\text{C}/\text{min}$  in nitrogen atmosphere showed a similar behavior (Figure 10). The melting endotherm appeared between 475 and 493 K (202 and 220 °C), with a peak temperature at 488 K (215 °C). The exotherm between 563 and 598 K (290 and 325 °C), with a peak temperature at 576 K (303 °C), indicated that the slow decomposition of GuN took place at a higher temperature as compared to that of TAGZ (see Section 14.5 “Triaminoguanidinium Azide” below).

The decomposition of GuN was examined by isothermal heating followed by quantification of both remaining nitrate and remaining base [36]. Activation energies determined for GuN were 199 and 191 kJ/mol with pre-exponential factors  $1.94 \times$

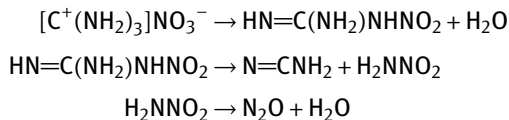


**Figure 10:** DSC thermogram of guanidinium nitrate. (Republished and modified from [134], with permission of ©2009 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

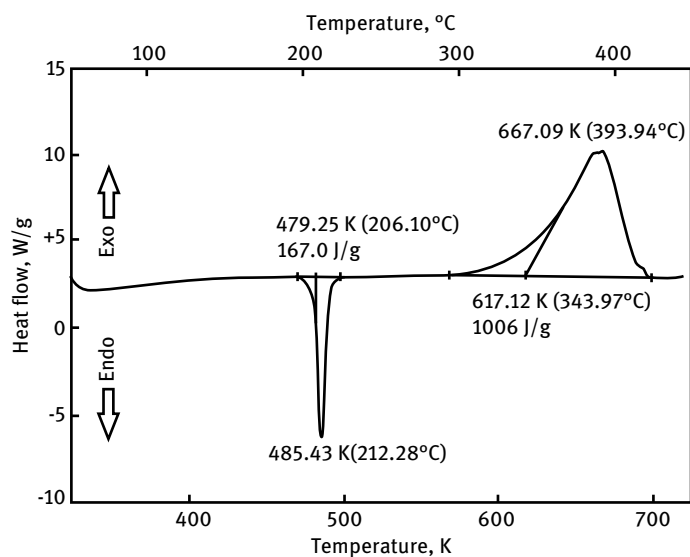
$10^{15} \text{ s}^{-1}$  and  $3.20 \times 10^{14} \text{ s}^{-1}$  for nitrate and guanidine, respectively. Decomposition products, both gaseous and condensed, were analyzed and decomposition routes were suggested. Experimental results indicated that  $\text{NO}_2^+$  might be generated during the decomposition. This mechanism appeared to differ from that of the analogous nitro derivatives. For guanidinium nitrate, several possible decomposition routes can be envisioned: A decomposition pathway for GuN proceeding via dissociation to nitric acid would be analogous to that proposed for AN and UN. This is essentially the reversal of GuN synthesis. Dissociation



and subsequent decomposition of nitric acid and reaction with ammonia would explain the observed acceleration in the presence of acids. Nitroguanidine can be formed by dehydration of GuN and its decomposition also produces ammeline and melamine. Subsequent reaction would give cyanamide and nitramine, which rapidly undergo further decomposition



Cyanamide can combine to give a multitude of cyclic products. Unlike AN and UN, GuN decomposition is accelerated by basic species as well as by acids. Reaction pathways involving water loss would explain such sensitivity. Nitroguanidine may also be formed by the dehydration of GuN. Its decomposition also produces ammeline and melamine. Subsequent reactions would give cyanamide and nitramine, which rapidly undergo further decomposition. A DSC thermogram of GuN decomposition in sealed glass capillary tubes under nitrogen at a heating rate of 20°/min is shown in Figure 11.



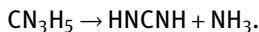
**Figure 11:** DSC thermogram of guanidinium nitrate decomposition. (Republished and modified from [36], with permission of ©2009 Taylor & Francis, [www.tandfonline.com](http://www.tandfonline.com).)

The thermal decomposition of GuN was analyzed using a combined experimental and computational approach [135]. Concurrent TGA-FTIR-MS experiments were carried out at three different heating rates under closed- and open-crucible conditions. A two-stage decomposition process was observed, and the major gases evolved were found to be  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_2$ , and  $\text{CO}_2$ . Results of quantum mechanics-based *ab initio* computations indicated that decomposition of GuN is not initiated in the condensed phase, because the guanidinium cation and the nitrate anion are highly stable. The most likely mechanism involves isomerization of GuN followed by a proton transfer in the gas phase to yield nitric acid and guanidine. These products then further react to form nitroguanidine (NQ) and  $\text{H}_2\text{O}$ . NQ dissociates via several competing pathways to yield  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ .  $\text{HNO}_3$  formation and decomposition can help to explain  $\text{NO}_2$  formation. The residue left towards the end of TGA can be attributed to dimerization and trimerization reactions of cyanamide. See also [136].

The thermal decomposition of GuN and basic cupric nitrate (GuN/BCN) mixtures in five different mass ratios intended to be used as gas-generating agents for airbag inflation was investigated by TGA-DSC-MS-FTIR and automatic calorimeter [137]. It was shown that the onset reaction temperatures of GuN/BCN mixtures were lower than that of GuN alone. The thermal decomposition of GuN/BCN mixtures could be subdivided into three stages, including the dissociation and escape of crystal water, solid (GuN)-solid (BCN) phase reaction, and liquid (GuN)-solid (BCN) phase reaction. When the mass ratio of GuN/BCN was 62.24/37.73, the largest value of the reaction heat was measured at 3152.7 J/g, with  $N_2$  and  $H_2O$  as the major gases produced during thermal decomposition.

A combined TGA/DSC/FTIR investigation indicated that the GuN/BCN mixture underwent endothermic decomposition at 443 K (170 °C) and exothermic decomposition at 481 K (208 °C), which was accompanied by 66% mass loss [138]. The decomposition gases,  $CO_2$ ,  $N_2O$ , and  $H_2O$ , were detected via FTIR spectrum. Because  $N_2O$  was not detected in the hot combustion gas, it was suggested that the detected  $N_2O$  was generated at a low temperature and decomposed in high-temperature combustion. See also [139].

The decomposition mechanism of GuN was investigated by quantum chemistry calculations and optimized structures of reactants, products, and transition states were obtained and the total electron energies and free energies of these structures were calculated [140]. In the initial decomposition pathway of GuN, two mechanisms occur in parallel:  $CN_3H_5$  decomposition and the interaction between  $CN_3H_5$  and  $HNO_3$ . The former mechanism has three pathways and each of these schemes provided the same global reaction:



Other pathways for neutral monomolecular decomposition are **(1)** neutral-neutral bimolecular decomposition ( $CN_3H_5 + CN_3H_5$ ) and **(2)** cation-neutral bimolecular reaction ( $CN_3H_6^+ + CN_3H_5$ ). The latter reaction has four pathways and each of these schemes provided the same global reaction:



Based on the calculated energy barrier results,  $HNO_3$ -catalyzed monomolecular decomposition for  $CN_3H_5$  decomposition and  $N_2O_5/CN_3H_5$  schemes for the interaction between  $CN_3H_5$  and  $HNO_3$  are the most plausible mechanisms.

The thermal decomposition of GuN was studied at different linear heating rates of 5, 10, 15, and 20 K/min. [141]. The average extrapolated TGA mass loss onset temperature was 580 K. The average activation energies were 140.43 or 137.82 kJ/mol, respectively, depending on the method used for data reduction. The spontaneous ignition temperatures were 530 and 548 K, respectively.

### 11.2.3.1 Thermal Stability of Guanidinium Nitrate Mixtures

Mixtures of AN and GuN have better thermal stability than AN alone [142]. The kinetics of heat release during the thermal decomposition of GuN and AN and their mixtures in the liquid phase in a calorimeter were studied by DSC. The temperature dependence of the kinetic constants in these equations gives the activation energy. The oxidation rate constants of guanidinium and ammonium cations with molecular nitric acid in aqueous nitric acid solutions were calculated by solution of the reverse problem for salt melts. The temperatures and  $\Delta H$  values of melting of the initial salts and their eutectic mixture were determined. The DSC of AN/GuN eutectics still shows the somewhat weakened phase transitions of AN at 327 and 362 K (54 and 89 °C) [143].

A eutectic mixture of 85 parts aminoguanidinium nitrate and 15 parts GuN melts at 399 K (126 °C). Eutectic mixtures of aminoguanidinium nitrate with AN, also stabilized with small amounts of potassium nitrate and bonded with polyvinyl alcohol, were patented as airbag inflator gas generants [144].

Sealed-cell DSC, TGA-DTA-IR, and TGA-DTA-MS were used to study the thermal decomposition of 1,2,4-triazole-3-one (TO) and GuN mixtures which can be used as gas generants in airbag inflators [145]. The endothermic peak and onset of exotherm temperatures of TO/GuN mixtures were lower than those of individual TO and GuN pure compounds.

### 11.2.4 Toxicity of Guanidinium Nitrate

#### 11.2.4.1 Oral Toxicity of Guanidinium Nitrate

The acute oral toxicity of GuN was determined in male and female albino Sprague–Dawley rats administered a single dose by oral gavage [146]. The median lethal doses (MLD) were  $989.6 \pm 68.7$  mg/kg in male rats and  $729.8 \pm 34.3$  mg/kg in female rats. Clinical signs were behavioral changes (e.g., inactive, irritable, disoriented, hyperactive, ataxic) and were observed in 63 of 99 animals dosed with GuN. These observations suggested that guanidine nitrate is a slightly toxic compound with a primary effect on the central nervous/neuromuscular system.

In similar tests with male and female ICR mice, the median lethal dose was 1105 mg/kg for male mice and 1028 mg/kg for female mice [147]. Clinical signs included behavioral changes, hunched posture, and changes in reflex activity. Behavioral changes observed were irritability, inactivity, disorientation, hyperactivity, jumping, tremors, twitching, head tilt, catalepsy, and ataxia. The lethality and clinical signs were observed primarily during the first 24 h after dosing. These results place GuN in the slightly toxic category.

#### 11.2.4.2 Dermal Toxicity of Guanidinium Nitrate

The 24-h acute dermal toxicity of GuN was determined in rabbits [148]. No compound-related deaths or clinical signs other than dermal irritation were observed at a limit dose of 2 g/kg during this study. In a similar test, guinea pigs received three weekly

induction doses of 10% GuN solutions and, after a 2-week delay, a challenge dose at the same concentration [149, 150]. No evidence of GuN-induced skin sensitization was obtained in this study.

The eye irritation potential of GuN was determined in rabbits by a modified Draize method [151]. GuN caused mild-to-moderate irritation (erythema and chemosis of the conjunctiva, iritis, and corneal lesions).

The primary dermal irritation potential of GuN was determined in rabbits using a modified Draize method [152]. The compound was classified as a severe primary irritant with corrosive properties. Erythema, edema, and eschar formation was detected 24, 48, and 72 h after dosing. Irreversible skin damage was apparent at the time of sacrifice, 14 d after dosing.

### **11.2.5 Safety Properties of Guanidinium Nitrate**

#### **11.2.5.1 Shock Sensitivity of Guanidinium Nitrate**

The impact sensitivity of GuN in the BAM apparatus gave no reaction at impact energies up to 50 Nm. Likewise, in the BAM friction sensitivity tester, no reaction was observed at pistil loads up to 353 N.

#### **11.2.5.2 Detonability of Guanidinium Nitrate**

In a hazards analysis and safety design of facilities for manufacturing nitroguanidine by the urea/ammonium nitrate (U/AN) and the British aqueous fusion (BAF) processes, critical diameter, propagation, sensitivity, and thermal characteristics of a number of mixtures and compounds representative of selected streams in the processes were determined [153]. Critical diameter tests indicated that streams from the evaporator outlet, mixed reactor feed, and the liquid reactor outlet of the U/AN process will propagate detonation when initiated with a booster and that they are mass detonable. Propagation in 5.08-cm (2-in) pipes was not complete on any mixture containing  $\geq 25\%$  water. For comparison, the process streams in the wet guanidine nitrate mixtures used in the BAF process are not detonable. This is also true of cold melts (molten mixtures allowed to cool) in the event of plant shutdown. The sensitivity data on GuN alone showed that it is a relatively low-order explosive when compared to TNT, but that it is mass detonable. The detonation velocity of dense GuN would be 3700 m/s.

In the lead block test, the cavity is only slightly enlarged and the volume increase is  $240 \text{ cm}^3/10 \text{ g}$ . This is about 10% of the enlargement created by TNT.

#### **11.2.6 Applications of Guanidinium Nitrate**

Guanidinium nitrate samples from six different manufacturers representing at least two different synthetic processes were examined for gas generants in airbag inflators [154]. The two synthetic routes differed in starting materials, one being the fairly common dicyandiamide (DCDA) condensation with AN method while the other utilized urea and AN. Samples were first chemically and physically characterized and then

processed in a gas generant composition. Significant gas generant final property differences were noted as a function of GuN synthesis route. In general, material from the DCDA process, which represented the baseline, was found to be quite sensitive to source and impurity levels. Material prepared by the urea route appeared to possess higher purity than material manufactured by the DCDA process and tended to exhibit higher process viscosities and lower burning rates. The effect of the addition of various impurities to the GuN based on original sample analysis was also explored with respect to gas generant processing and ballistic properties, in an attempt to identify critical components requiring control.

Guanidinium nitrate was the main ingredient of a high-temperature-resistant explosive in a homogeneous molten mixture with sodium, potassium, and calcium nitrates that has been used for stimulating geothermal steam wells at very hot downhole temperatures [155].

### 11.3 Guanidinium Perchlorate

Guanidinium perchlorate, also known as guanidine perchlorate; guanidine, mono-perchlorate;  $\text{CH}_6\text{N}_3\text{O}_4\text{Cl}$ , GuP, GP, CAS RN [10308-84-6], is a thermally very stable high-nitrogen compound. It contains a good amount of nitrogen (26.35% N).

#### 11.3.1 Production of Guanidinium Perchlorate

Guanidinium perchlorate can be prepared by melting dicyandiamide with ammonium perchlorate (AP) or by metathetical reactions, like reacting guanidinium chloride with sodium perchlorate [156] or barium perchlorate in aqueous solutions. The metathetical reaction of guanidinium sulfate and barium perchlorate is quantitative and the product is easily separated from the precipitated barium sulfate [157]. A very straightforward preparation for the formation of guanidinium perchlorate is the reaction of guanidinium carbonate with perchloric acid in aqueous solution.

#### 11.3.2 Physical Properties of Guanidinium Perchlorate

Table 12 gives a summary of the physical properties of guanidinium perchlorate. Guanidinium perchlorate is a white, crystalline (cubic lattice), non-hygroscopic salt. Guanidinium perchlorate melts at 518–519 K (245–246 °C; [157]). Other reports state that it melts at 521 K (248 °C) and is thermally stable up to 650 K. A literature report of a GuP melting point of 451 K (178 °C) must have been in error and most likely was for an impure salt. The melting point of anhydrous GuP is close to that of  $\text{LiClO}_4$ , which is the only alkali metal perchlorate that melts without decomposition. At 453–455 K (180–182 °C), GuP undergoes a phase transition, but both phases possess a cubic crystal structure. The pycnometric density of GuP is  $1.743 \pm 0.04 \text{ g/cm}^3$  and the XRD density is  $1.772 \text{ g/cm}^3$ .



**Table 12:** Physical properties of guanidinium perchlorate.

| Property              | SI units                       | Other units     | References       |
|-----------------------|--------------------------------|-----------------|------------------|
| Molecular mass        | 159.5 g/mol                    | 6.269 mol/kg    | —                |
| Melting point         | 513 K                          | 240 °C          | 464 °F [18]      |
|                       | 518–519 K                      | 245–246 °C      | 473–475 °F [157] |
| Density               | 1.743 ± 0.04 g/cm <sup>3</sup> | —               | —                |
| Enthalpy of formation | −310 ± 2.9 kJ/mol              | −74.10          | −465 cal/g [130] |
|                       |                                | ± 0.55 kcal/mol |                  |

### 11.3.2.1 Crystal Structure of Guanidinium Perchlorate

A single-crystal X-ray analysis has shown that GuP crystallizes in the rhombohedral system with space group  $R3$  and hexagonal unit cell dimensions  $a = 7.606(2) \text{ \AA}$ ,  $c = 9.121(2) \text{ \AA}$ , and  $Z = 3$  [158]. Both the guanidinium cation and the perchlorate anion have a threefold symmetry axis and form hydrogen-bonded layers in which the N—H...O hydrogen bond is 3.06 Å in length. Nuclear magnetic resonance studies carried out on the polycrystalline compound revealed a considerable reduction in the second moment from 19.5 to 3.2 G<sup>2</sup> between 170 and 250 K, approaching zero above 454 K, as well as an asymmetrical T1 plot with a single minimum of 14 ms at 310 K. The nature of the solid-solid phase transition at 454 K appears to be related to the onset of cationic self-diffusion. A later refinement of the crystallographic data suggested the space group  $R3m$  rather than  $R3$  [159].

Guanidinium perchlorate undergoes a pressure-induced phase transition at high pressures up to ~11 GPa in a supramolecular structure held together by hydrogen bonding and electrostatic interactions [160]. *In situ* Raman spectroscopy and synchrotron XRD experiments have revealed a subtle phase transition accompanied by the symmetry transformation from  $R3m$  to  $C_2$ , evidenced by changes in both Raman and XRD patterns at 4.5 GPa. The phase transition is attributed to the competition between hydrogen bonds and close packing of the supramolecular structure at high pressure. Hydrogen bonds evolved into a distorted state through the phase transition, accompanied by a reduction in the separation of oppositely charged ions in adjacent sheet motifs.

Guanidinium perchlorate is a multi-axial ferroelectric material with a very high phase transition temperature of 454 K. This unusual dielectric property is one reason the GuP crystal structure has been thoroughly investigated, beyond the type of information needed to use it as a rocket propellant.

Guanidinium perchlorate single crystals were grown from aqueous solutions by low-temperature solution growth techniques and the cell parameters were measured using XRD [161]. The optical transmittance window and the lower cutoff wavelength were identified by UV-visible-near-IR (UV-VIS-NIR) spectral analysis. The dielectric constant was measured over a wide range of frequencies (100–5 MHz) and decreased

from 550 to 100 over this frequency range. The thermal stability of the crystals was studied using TGA (see Section 11.3.3.1).

### 11.3.2.2 Solubility of Guanidinium Perchlorate

GuP is somewhat soluble in water. The solubility is 31 mass-% GuP at 298 K (25 °C) and 11.5 mass-% at 273 K (0 °C). At 11.69 mass-%, GuP forms a eutectic with water which melts at 269.9 K (−3.2 °C) [157]. GuP crystallizes without water of hydration. GuP is very soluble in acetone (40.3 mass-% GuP at 298 K). In methanol at room temperature, only 30.2 mass-% GuP goes into solution.

The solubility of GuP in perchloric acid goes through a minimum and then rises to 36% in the anhydrous acid. A salt crystallizing from a saturated solution of GuP in perchloric acid was analyzed and turned out to be the guanidinium(2+) diperchlorate.

### 11.3.2.3 Melting Point of Guanidinium Perchlorate Mixtures

Guanidinium perchlorate forms a eutectic with AP at 9 mol-% AP, which melts at 490 K (217 °C) [162]. Guanidinium perchlorate/lithium perchlorate mixtures have a single eutectic at 49.5 mol-% LiClO<sub>4</sub> melting at 378 K (105 °C), and do not form double salts [163]. A break in the liquidus curve at 84.7 mol-% GuP at 454 K (181 °C) is due to the polymorphic transition of GuP. The referenced publication contains a graph illustrating the phase diagram for the entire range of compositions. These eutectic mixtures are useful as rocket propellants [164, 165].

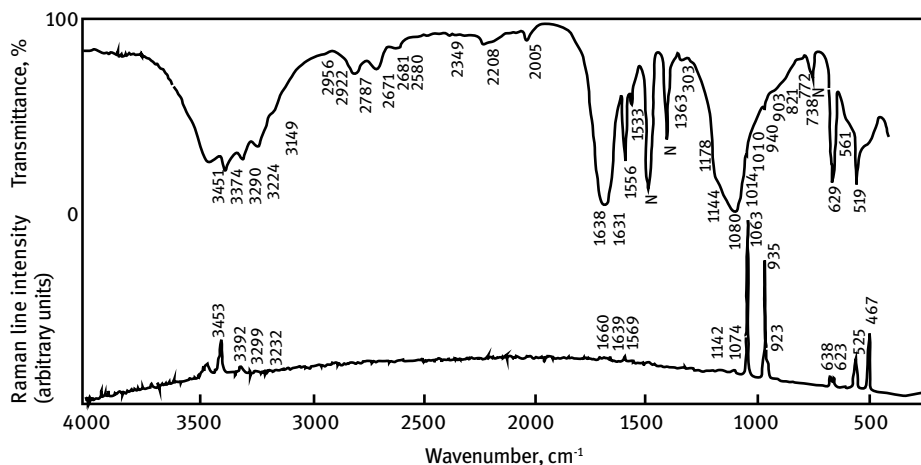
The eutectic formed with GuP and tetrabutylammonium perchlorate consists of 35.5 mol-% [(NH<sub>2</sub>)<sub>3</sub>C]ClO<sub>4</sub> + 64.5 mol-% [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]ClO<sub>4</sub>, and is an ionic liquid that melts at 255 K (82 °C) [166].

### 11.3.2.4 Vibrational Spectra of Guanidinium Perchlorate

The Raman and IR spectra of GuCl and GuP and their deuterated isotopomers were recorded at 300–3600 cm<sup>−1</sup> [167]. The solution IR spectra were independent of the anion present and are influenced by H-bonding in the solvents.

Near-IR spectra of guanidinium perchlorate (GuP) single crystals were recorded at 10 K in polarized light [168]. GuP contains planar guanidinium ions which lie on trigonal sites and are hydrogen bonded to the anions. The spectrum of guanidinium nitrate was also recorded, but its structure was not known at that time. The spectra showed clearly the effects of hydrogen bonding on the crystal structure.

The IR spectra of guanidinium compounds show very strong bands of stretching C–N vibrations ( $\nu_{\text{as}}\text{CN}$ ) in the range 1680–1570 cm<sup>−1</sup>. Bands in the IR spectrum at 1631 and 1556 cm<sup>−1</sup> with Raman counterparts observed at 1660 and 1639 cm<sup>−1</sup> were assigned to  $\nu_{\text{as}}\text{CN}$  type vibrations (Figure 12) [169, 170]. The phase transitions observed at 451 and 453 K were confirmed by IR spectra. The temperature changes in IR spectra suggested that the mechanism of phase transition is the result of forces derived by weak



**Figure 12:** Infrared and Raman spectrum of guanidinium perchlorate. (Reprinted and modified from [170], with permission from ©2013 Elsevier; permission conveyed through RightsLink.)

hydrogen bonds. When embedded in KBr for measuring IR absorption, there may be chemical interaction between GuP and the embedding material that distorts the spectra [161].

#### 11.3.2.5 Thermodynamic Properties of Guanidinium Perchlorate

Because of interference due to the formation of acids during combustion of GuN or GuP in a combustion bomb in a calorimeter, the heat of reaction of guanidinium carbonate with barium perchlorate in solution was measured and used to calculate the enthalpy of formation of GuP [130]. The heats of solution of the various reactants were determined in separate experiments for a wide range of dilutions. The standard enthalpy of formation of solid guanidinium carbonate was taken from other sources ( $-971 \text{ kJ/mol} = -232.2 \text{ kcal/mol}$ ) and served as starting point for the calculations, resulting in a value of  $-310 \pm 2.9 \text{ kJ/mol}$  ( $-74.10 \pm 0.55 \text{ kcal/mol}$ ) for the standard enthalpy of formation of solid GuP and  $40.58 \pm 0.38 \text{ kJ/mol} = 10.416 \pm 0.092 \text{ kcal/mol}$  for the heat of solution of GuP in water. Other sources state an enthalpy of formation of GuP of  $-311.08 \text{ kJ/mol} = -1950 \text{ kJ/kg} = -74.35 \pm 0.22 \text{ kcal/mol} = -466 \text{ cal/g}$  [128, 129], which represents good agreement between the two sets of data.

#### 11.3.3 Chemical Properties of Guanidinium Perchlorate

Guanidinium perchlorate is not as hygroscopic as lithium or magnesium perchlorate. It is soluble in warm water. In spite of the presence of the powerful perchlorate anion, GuP is still slightly under-oxidized, with an oxygen balance of  $-5.0\%$ .

### 11.3.3.1 Thermal Stability of Guanidinium Perchlorate

The thermal decomposition of GuP was investigated by TGA, DTA, MS analysis of volatile decomposition products, and X-ray diffractometry of the crystals [115]. Guanidinium perchlorate undergoes a crystallographic phase transformation at 453 K (180 °C) before melting at 528 K (255 °C). It appears that both the room-temperature and the high-temperature modification crystallize in a cubic lattice. Guanidinium perchlorate decomposes exothermally into gaseous products in the temperature range from 548 to 598 K (275–325 °C). The MS results suggest that the compound undergoes thermal decomposition into neutral particles which are then vaporized, ionized, and oxidized. One of the fragments, cyanamide, was found to undergo trimerization to give melamine. Melamine is thermally very stable (see *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic and Heterocycloaliphatic Amines,” Section 18.4.2).

When GuP is heated at or below 573 K (300 °C) for several hours, it suffers only a very slight loss of weight. Above 673 K (400 °C) ignition occurs, but always after a definite period of inhibition, and with the formation of a yellow solid residue. In the range 573–673 K (300–400 °C), decomposition proceeds at a measurable rate and the reaction goes to completion [156]. The following mechanism was proposed for the decomposition of the salt: (a) Ammonia is evolved, cyanamide and perchloric acid being formed; (b) cyanamide undergoes self-condensation, e.g., to melamine; and (c) these condensation products are oxidized in stages by perchloric acid or ammonium perchlorate to the gaseous products found, amongst them hydrogen chloride, which may eventually combine with ammonia to form ammonium chloride.

Induction periods before ignition at 663–713 K (390–440 °C) were somewhat shorter than the induction periods of AP under similar conditions [171]. The rate constant,  $k$ , for the medium temperature range may be expressed by the equation

$$k = 2.4 \times 10^{11} e^{\frac{-32400}{RT}}$$

where  $k$  is the rate constant in %/min. The temperature dependence of the induction period indicated an activation energy of 127.6 kJ/mol (30.5 kcal/mol). Addition of metal oxide catalysts shortens the induction period and lowers the onset of exotherms. For example, mixtures of GP with CuO, Ag<sub>2</sub>O, Hg<sub>2</sub>O, and MoO<sub>3</sub> exploded at 573, 593, 618, or 618 K (300, 320, 345, or 345 °C), respectively.

DTA thermograms of GuP showed two endotherms and one exotherm [157]. A distinct, reversible endotherm at 453–455 K (180–182 °C) was assigned to a reversible phase transition. This phase transition was also observed in GP/LiClO<sub>4</sub> mixtures. The second endotherm at 521 ± 2 K (248 ± 2 °C) was due to melting. The final exotherm peaking at 665 K (392 °C) was due to decomposition which started at 573 K (300 °C). Other DTA thermograms of GuP reported two exotherms, one at 590 K (317 °C) and another at 623 K (350 °C) [172].

Pure GuP decomposed very slowly at 513–553 K (240–280 °C). The thermal stability of an 80 mass-% AP/20% guanidinium perchlorate mixture was studied by TGA in the temperature range from 523 to 553 K (250–280 °C [162]). Guanidinium perchlorate/AP

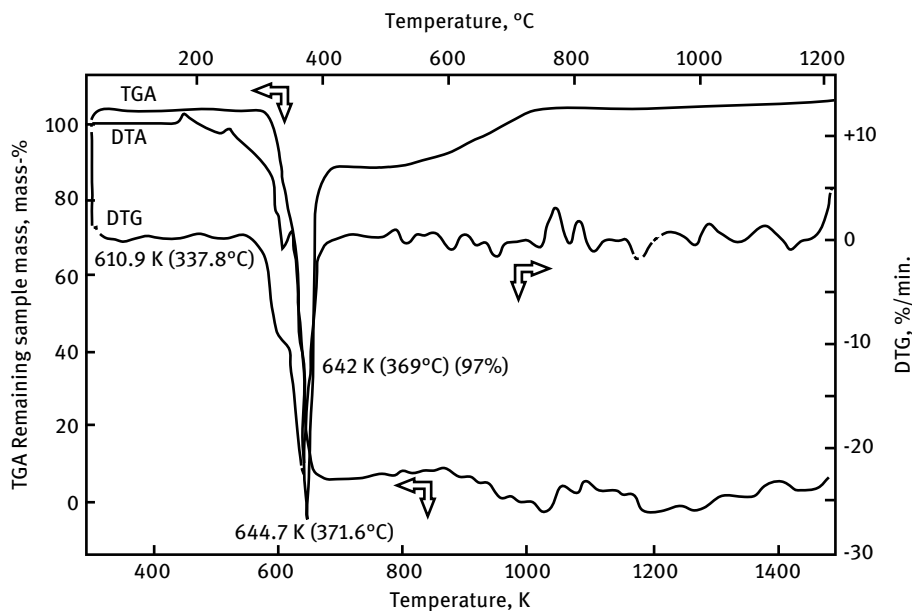
mixtures decompose more readily than pure GuP. After a lengthy induction period, the process begins to accelerate rapidly. The temperature dependence of the first-order rate constant (after 5% conversion) can be expressed by

$$k = 10^{12.3} \exp \left[ -41000 \pm \frac{2000}{RT} \right]$$

where  $k$  is the rate constant in  $\text{s}^{-1}$  and  $T$  is the temperature in kelvin.

The qualitative composition of the gaseous products of GuP thermal decomposition and the effect of  $\text{Fe}_2\text{O}_3$  and  $\text{ZnO}$  additives on decomposition were studied by MS [173, 174]. The decomposition of GuP at temperatures 573 K (300 °C) gave  $\text{NH}_4\text{Cl}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$ ; while at temperatures 573 K (300 °C),  $\text{NH}_4\text{Cl}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  were formed. Smaller amounts of  $\text{Cl}_2$ ,  $\text{HClO}_4$ ,  $\text{ClO}$ ,  $\text{ClO}_2$ , and  $\text{ClO}_3$  were detected.

The TGA-DTA-DTG thermograms for GuP crystals in a nitrogen atmosphere at a heating rate of 20 °C/min are shown in Figure 13 [161]. Guanidinium perchlorate started to decompose at about 610 K (337 °C). There was no endotherm indicating any loss of water of hydration from the crystal lattice below 573 K (300 °C). Further mass loss occurred in small steps due to the release of volatile substances in the compound, probably ammonia and oxides of chlorine. TGA showed that a complete mass loss took place at near 642 K (369 °C). The endothermic peak at 644.7 K (371.6 °C)



**Figure 13:** DTA, TGA, and DTG thermograms of guanidinium perchlorate decomposition. (Reprinted and modified from [161], with permission from ©2011 Elsevier; permission conveyed through RightsLink.)

occurred at the same temperature as the mass loss in the TGA. Some guanidinium salts emit cold light during thermal decomposition [175].

### 11.3.4 Strand Burning Rates of Guanidinium Perchlorate

Burning rates of formulated solid propellants containing GuP will be discussed in a future set of several volumes on solid propellants and gas generants to be published as part of the *Encyclopedia of Rocket Propellants*. Here we look only at strand burning rates of the pure compound in isolation. The dependence of strand burning rates on pressure was studied for a series of organic perchlorates including GuP in the pressure range 0.1–40 MPa (1–400 atm) [176]. Equations describing burning dependence on pressure were obtained for a systematic series of perchlorates of aliphatic amines, aliphatic polyamines, aromatic amines, amidines, and heterocyclic amines. Organic perchlorates burned several times faster than their nitrate analogs.

### 11.3.5 Safety Properties of Guanidinium Perchlorate

Guanidinium perchlorate was synthesized from guanidinium carbonate and  $\text{HClO}_4$  and its explosive properties were studied [177]. The impact sensitivity was  $\sim 150$  kg-cm (classified grade 6 in Japan Industrial Standard), the BAM friction sensitivity was  $\sim 24$  kg, the ballistic mortar value was 128 (TNT = 100), the decomposition temperature was 653 K (380 °C), and the maximum detonation velocity was 6.3 km/s.

### 11.3.6 Explosive Performance of Guanidinium Perchlorate

Guanidinium perchlorate is a powerful explosive and in the lead block test, the cavity volume expansion was  $400 \text{ cm}^3/10 \text{ g}$ . The detonation velocity was 6000 m/s at a packing density of  $1.15 \text{ g/cm}^3$ , and 7150 m/s at a packing density of  $1.67 \text{ g/cm}^3$  [178]. In the drop-weight sensitivity test, GuP was more sensitive than picric acid. The drop-weight sensitivity in the Bu Mines apparatus was 50 cm with a 2-kg mass (for comparison: picric acid 85 cm under the same conditions).

Guanidinium perchlorate can be synthesized from guanidinium carbonate and dilute perchloric acid. The structure, morphology, thermal decomposition, and thermal stability of guanidinium perchlorate were examined by XRD, elemental analysis, IR spectrometry, scanning electron microscopy (SEM), TGA, and DSC [179]. The XRD and IR spectra of the products were almost identical, regardless of whether the molar ratio of guanidinium carbonate to  $\text{HClO}_4$  was 1 : 2 or 1 : 4. Elemental analysis identified all products as  $\text{CH}_6\text{O}_4\text{N}_3\text{Cl}$ . Guanidinium perchlorate is a relatively insensitive explosive. Its sensitivity is significantly less than that of PETN. With different packing densities, detonation velocities of pure and aluminum-dusted guanidinium perchlorate were about 5500 m/s. The addition of 5 mass-% aluminum powder had little effect on the detonation velocity.

### 11.3.7 Applications of Guanidinium Perchlorate

Guanidinium perchlorate has been evaluated as an ingredient in high-temperature explosives and gas generators for airbag inflation.

The eutectic mixture of GuP and  $\text{LiClO}_4$  is less sensitive than GuP and can be safely used in propellant formulations [164, 165]. The impact sensitivity of a 57.5 GuP + 42.5  $\text{LiClO}_4$  mixture with a melting point of 383 K (110 °C) is 120 cm with a 2-kg mass versus 5 cm for GuP alone.

## 11.4 Other Guanidinium Salts

The stability of the guanidinium ion and its high nitrogen content were the motivation for developing other guanidinium salts with better properties (in some respects, except price) than guanidinium nitrate.

Some guanidinium salts are capable of forming ionic liquids, depending on the anion they are coupled with [180]. Guanidinium dicyanamide and guanidinium octahydrotriborate are ionic liquids melting below 330 K (57 °C).

A double salt of GuN and nitroguanidinium nitrate consists of alternating layers of guanidinium and nitroguanidinium cations, these cations being parallel to each other within the layers and perpendicular in adjacent layers [181]. The layers are connected by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds to nitrate anions, forming an infinite three-dimensional framework. These hydrogen bond patterns are closely related to those of GuN.

### 11.4.1 Guanidinium Dinitramide

Guanidinium dinitramide, guanidinium dinitramide,  $[(\text{NH}_2)_2\text{C}=\text{NH}_2]^+\text{N}(\text{NO}_2)_2^-$ ,  $\text{C}_1\text{H}_6\text{N}_6\text{O}_4$ , GuDN, GDN, CAS RN [170515-96-5], can be prepared by mixing ammonium dinitramide (ADN) and guanidinium chloride in water. However, it is more likely that this reaction would be conducted in the opposite direction as a means to prepare ADN from the less soluble and easily separable GuDN. GuDN melts at 412 K (139 °C), which is substantially higher than the melting point of ADN or HDN, but lower than the melting point of GuN.

In the preparation of ADN, instead of trying to isolate the product as the very soluble ADN, it is easier to isolate the dinitramide salt in the form of the poorly soluble guanidinium dinitramide which precipitates, is filtered, washed, dried, and can later be converted to ADN [182].

Unlike alkali metal dinitramide salts, guanidinium dinitramide does not exhibit abnormal solid-phase decomposition rates. The rates in vacuum and in air are equal, and no increase in the rate is observed at the point of the eutectic melting with guanidinium nitrate (401 K = 128 °C). The rate in the solid state is 400 times slower than in the liquid phase.

Guanidinium dinitramide melts at 421 K (148 °C) [116]. Other sources give a melting point of 417 K (144 °C) [183].

Guanidinium dinitramide (GuDN) was prepared by mixing ADN and guanidinium chloride in water. The thermal behavior of GuDN was studied under non-isothermal conditions by DSC and TGA/DTG [184]. The apparent activation energy ( $E_{\text{act}}$ ) and the pre-exponential constant ( $A$ ) of the exothermic decomposition reaction of GuDN were 118.75 kJ/mol and  $10^{10.86} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion ( $T_b$ ) of GuDN was 437 K (164 °C). The heat capacity of GuDN was determined by the micro-DSC method, and the molar heat capacity was  $234.76 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  at 298.15 K. The adiabatic time-to-explosion of GuDN was estimated to be somewhere between 405 and 455 s (but this depends on the surface: volume ratio of the sample container!).

Guanidinium dinitramide crystallizes in the triclinic space group with cell dimensions  $a = 8.325(2) \text{ \AA}$ ,  $b = 9.301(2) \text{ \AA}$ ,  $c = 9.868(2) \text{ \AA}$ ,  $\alpha = 84.73(3)^\circ$ ,  $\beta = 69.25(3)^\circ$ ,  $\gamma = 67.55(3)^\circ$ , while hydroxyguanidinium dinitramide crystallizes in the non-centric monoclinic space group  $Pc$  with cell dimensions  $a = 7.098(2) \text{ \AA}$ ,  $b = 3.5160(10) \text{ \AA}$ ,  $c = 14.358(3) \text{ \AA}$ ,  $\beta = 98.940(10)^\circ$  [185]. The structures contain protonated amine cations and dinitramide anions linked by hydrogen bonding. In both structures the conformations adopted by the dinitramide anions can be related to the types of hydrogen bonds it forms with the surrounding amine cations.

Guanidinium dinitramide was prepared by mixing ammonium dinitramide and guanidinium chloride in water, and its structure was determined by single-crystal XRD [186]. The crystal is triclinic, space group  $P1$ , with crystal parameters of  $a = 0.8332(5) \text{ nm}$ ,  $b = 0.9306(6) \text{ nm}$ ,  $c = 0.9878(6) \text{ nm}$ ,  $\alpha = 84.659(11)^\circ$ ,  $\beta = 69.213(12)^\circ$ ,  $\gamma = 67.451(12)^\circ$ ,  $V = 0.6605(7) \text{ nm}^3$ ,  $Z = 4$ , and  $D_{\text{calc}} = 1.671 \text{ g/cm}^3$ . Based on DSC and TGA/DTG results, its thermal decomposition process takes place in four stages, where the third stage is an intense exothermic decomposition process. The apparent activation energy and pre-exponential constant of the exothermic decomposition reaction are 118.75 kJ/mol and  $10^{10.86} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion is 437 K (164 °C). GuDN has a better thermal stability than ADN.

Enthalpies of formation and solution of guanidinium, aminoguanidinium, and triaminoguanidinium salts of nitric and dinitramidic acids were determined by combustion and solution calorimetry methods [131]. The enthalpies of formation of the respective cations by themselves in infinitely diluted aqueous solution were then calculated using the known enthalpy of formation of the nitrate ion ( $-206.8 \text{ kJ/mol} = -49.44 \text{ kcal/mol}$ ). The upper heats of combustion in a constant volume calorimetric bomb, the enthalpies of formation, and the enthalpies of solution of guanidinium, aminoguanidinium, and triaminoguanidinium dinitramide are summarized in Table 13. Of all the compounds studied in this paper, triaminoguanidinium dinitramide is the only one with a positive enthalpy of formation.

The thermal decomposition of GuDN was studied under non-isothermal conditions by DSC and TGA/DTG [184]. The apparent activation energy ( $E$ ) and pre-



**Table 13:** Heats of combustion, enthalpies of formation, and enthalpies of solution of guanidinium and mono- and triaminoguanidinium dinitramides.

| Compound                        | Heat of combustion<br>$\Delta U_B$ |                  | Enthalpy of formation<br>$\Delta H_f^{298}$ |                   | Enthalpy of solution<br>$\Delta H_s^{298}$ |                  |
|---------------------------------|------------------------------------|------------------|---------------------------------------------|-------------------|--------------------------------------------|------------------|
|                                 | J/g                                | cal/g            | kJ/mol                                      | kcal/mol          | kJ/mol                                     | kcal/mol         |
| Guanidinium dinitramide         | 6649 $\pm$ 5                       | 1589.1 $\pm$ 1.2 | -157.9 $\pm$ 0.6                            | -37.75 $\pm$ 0.15 | 53.9 $\pm$ 0.08                            | 12.88 $\pm$ 0.02 |
| Aminoguanidinium dinitramide    | 8184 $\pm$ 9.6                     | 1956.0 $\pm$ 2.3 | -43.6 $\pm$ 0.67                            | -10.44 $\pm$ 0.16 | 56.5 $\pm$ 0.04                            | 13.50 $\pm$ 0.01 |
| Triaminoguanidinium dinitramide | 9804 $\pm$ 5.4                     | 2343.3 $\pm$ 1.3 | +183.2 $\pm$ 1.1                            | +43.79 $\pm$ 0.26 | 61.5 $\pm$ 0.04                            | 14.69 $\pm$ 0.01 |

Data source: [131]

exponential constant ( $A$ ) of the exothermic decomposition stage of GuDN were 118.75 kJ/mol and  $10^{10.86} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion of GuDN was 437 K (164 °C). The standard molar heat capacity was  $234.76 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  at 298 K.

Other reported data for the enthalpy of formation of guanidinium dinitramide are remarkably similar: -168 kJ/mol (-40.1 kcal/mol) as reported by [44], and -169 kJ/mol (-40.7  $\pm$  1.5 kcal/mol; meas.) as reported by [187].

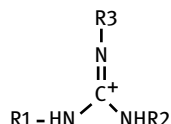
Guanidinium dinitramide can be synthesized from guanidinium carbonate. When using this method, two different crystalline forms ( $\alpha$ -type and  $\beta$ -type) may be obtained depending on the type of applied solvents and synthesis and recrystallization conditions [188]. During crystallization, water might become trapped in a crystal lattice between inner molecules. Despite having the same chemical composition, Raman IR and TGA-DSC revealed different physical characteristics of the two forms. Peaks of Raman shift near  $1000 \text{ cm}^{-1}$  implied different chemical structures. The  $\beta$ -type is thermally more stable than the  $\alpha$ -type. Thermal analysis revealed an exotherm peak temperature of 428.8 K (155.7 °C) for  $\alpha$ -type but one of 464.7 K (191.6 °C) for  $\beta$ -type. The exotherm heat release caloric value of  $\alpha$ -type was 536.4 J/g, which was 2.5 times smaller than that of the  $\beta$ -type, which was 1310 J/g. While the synthesized GDN of  $\alpha$ -type showed a steep exothermic decomposition, the  $\beta$ -type decomposed slowly after melting through an endothermic process. This implied that despite the same molecular structural formula, some different thermal properties are obtained depending on synthesis conditions.

Five different types of guanidinium dinitramide (GuDN-I, II, III, IV, V) were synthesized using different starting materials such as guanidinium acetate, chloride, carbonate, nitrate, or sulfate [189]. Intermediates and products formed in these processes were identified and their thermal properties and chemical structures were examined. The absorption peaks measured by FTIR were assigned to guanidinium ion (3452, 3402, 3354, 3278,  $1642 \text{ cm}^{-1}$ ) and to dinitramide ion (3208, 1570, 1492,

1416, 1337, 1179, 1000  $\text{cm}^{-1}$ ). The activation energies of GuDN thermal decomposition determined by DTA from exothermic reactions at above 426 K (153 °C) differed only very little:  $E_a = 222.8 \text{ kJ/mol} = 53.26 \text{ kcal/mol}$  (GuDN-I),  $213.1 \text{ kJ/mol} = 50.94 \text{ kcal/mol}$  (GuDN-II),  $219 \text{ kJ/mol} = 52.34 \text{ kcal/mol}$  (GuDN-III),  $260.2 \text{ kJ/mol} = 62.19 \text{ kcal/mol}$  (GuDN-IV),  $231.4 \text{ kJ/mol} = 55.32 \text{ kcal/mol}$  (GuDN-V). See also [190–192].

#### 11.4.2 Guanidinium Nitroformate

Although several energetic salts containing the nitroformate anion have been reported in the literature, so far only one compound, hydrazinium nitroformate, HNF, has gained practical application. Since its discovery in 1951, as of 2006, more than 80 publications have since appeared, showing that there is continued interest in investigating the properties and new applications of HNF. Along the same line of investigation, guanidinium nitroformate monohydrate (GNFH), aminoguanidinium nitroformate (AGNF), diaminoguanidinium nitroformate (DAGNF), and triamino-guanidinium nitroformate (TAGNF) have been prepared and characterized [193–195]. The following abbreviations are used for the four compounds:



Abbreviations used: GNFH AGNF DAGNF TAGNF

GNFH:  $\text{R1} = \text{R2} = \text{R3} = \text{H}$  plus  $\text{H}_2\text{O}$

AGNF:  $\text{R1} = \text{NH}_2$ ,  $\text{R2} = \text{R3} = \text{H}$

DAGNF:  $\text{R1} = \text{R2} = \text{NH}_2$ ,  $\text{R3} = \text{H}$

TAGNF:  $\text{R1} = \text{R2} = \text{R3} = \text{NH}_2$

Guanidinium nitroformate was obtained according to the literature procedure as the monohydrate (GNFH), whereas AGNF, DAGNF, and TAGNF were obtained as the water-free species and were reported for the first time in 2006. Guanidinium nitroformate crystallized from aqueous solutions with one molecule of water as hydrate  $\text{C}_2\text{H}_6\text{N}_6\text{O}_6 \cdot \text{H}_2\text{O} = \text{C}_2\text{H}_8\text{N}_6\text{O}_7$ . This may explain the different melting points given for guanidinium nitroformate, with the hydrate melting point listed as 383–390 K (110–117 °C) and the anhydrous salt supposedly melting at 401 K (128 °C). All of the compounds were obtained as bright yellow solids in high yields by the reaction of either the potassium or silver salt of nitroform with the corresponding guanidinium chloride in acetonitrile. All four compounds and melamine nitroformate have been characterized using single-crystal XRD (Table 14) as well as multi-nuclear NMR spectroscopy, IR and Raman spectroscopy, MS, DSC (at five different heating rates), and elemental analysis.

**Table 14:** Crystal structure and physical properties of guanidinium nitroformates.

| Parameter                          | GNFH                                                        | AGNF                                                        | DAGNF                                                       | TAGNF                                                       |
|------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| Formula                            | C <sub>2</sub> H <sub>8</sub> N <sub>6</sub> O <sub>7</sub> | C <sub>2</sub> H <sub>7</sub> N <sub>7</sub> O <sub>6</sub> | C <sub>2</sub> H <sub>8</sub> N <sub>8</sub> O <sub>6</sub> | C <sub>2</sub> H <sub>9</sub> N <sub>9</sub> O <sub>6</sub> |
| Formula weight                     | 228.14                                                      | 225.15                                                      | 240.16                                                      | 255.18                                                      |
| Crystal system                     | monoclinic                                                  | triclinic                                                   | monoclinic                                                  | triclinic                                                   |
| Space group                        | <i>C2/c</i> (No.15)                                         | <i>P</i> $\bar{1}$ (No.2)                                   | <i>P2<sub>1</sub>/n</i> (No.14)                             | <i>P</i> $\bar{1}$ (No.2)                                   |
| GOOF <sup>a</sup>                  | 1.072                                                       | 1.086                                                       | 1.168                                                       | 1.099                                                       |
| Density, exptl., g/cm <sup>3</sup> | 1.695                                                       | 1.766                                                       | 1.702                                                       | 1.689                                                       |
| Volume, Å <sup>3</sup>             | 894.15(8)                                                   | 423.29(9)                                                   | 937.1(2)                                                    | 501.7(2)                                                    |
| $\gamma$ , °                       | 90.0                                                        | 9.61(1)                                                     | 90.00                                                       | 111.10(2)                                                   |
| $\beta$ , °                        | 101.132(2)                                                  | 84.425(9)                                                   | 105.336(8)                                                  | 95.03(2)                                                    |
| $\alpha$ , °                       | 90.0                                                        | 84.567(9)                                                   | 90.00                                                       | 105.49(2)                                                   |
| <i>c</i> , Å                       | 7.7556(5)                                                   | 11.320(1)                                                   | 11.416(1)                                                   | 8.515(2)                                                    |
| <i>b</i> , Å                       | 14.3541(7)                                                  | 7.559(1)                                                    | 7.7524(8)                                                   | 8.347(2)                                                    |
| <i>a</i> , Å                       | 8.1859(4)                                                   | 5.0690(7)                                                   | 10.980(1)                                                   | 8.021(2)                                                    |
| <i>Z</i>                           | 4                                                           | 2                                                           | 4                                                           | 2                                                           |
| Melting point, °C                  | 69                                                          | 71                                                          | 80                                                          | 84                                                          |
| DSC, (2 °C/min)                    | 113 (decomp.)                                               | unstable at room temperature                                | 82 (decomp.)                                                | 104 (decomp.)                                               |

<sup>a</sup> GOOF = goodness of fit

Data source: [193]

Infrared and Raman spectra of the four (amino)guanidinium nitroformates were measured and tabulated, also in comparison to spectra obtained from ANF, HNF, and melamine nitroformate (Table 15). The <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR shifts of all of these salts are also available.

The sensitivity properties of GNFH, AGNF, DAGNF, and TAGNF were measured in order to establish safe handling procedures for these compounds in comparison to HNF. Two different instruments were used to determine the friction and impact sensitivity: the Bundesanstalt für Materialforschung und Prüfung (BAM) drop hammer (BAM fh [Fallhammer]) and friction tester (BAM ft). In the series of increasing nitrogen content from GNFH to TAGNF, the materials became more sensitive to impact and friction. GNFH was found to meet the criteria of the United Nations (UN) Recommendations for the Transport of Dangerous Goods, with a friction sensitivity of greater than 360 N and an impact sensitivity of greater than 29.6 J (1 J = 1 Nm). In contrast, great care should be taken when handling the other salts, which are considerably more sensitive: In the series of increasing nitrogen content from GNFH to TAGNF, the materials became more sensitive to impact and friction. The sensitivity of TAGNF was about the same as that of dry HNF (Table 16).

Table 15: IR and Raman spectra of four (amino)guanidinium nitroformates.

| GNFH                                                                                                                                                                                                                                          |                                                                                                                                                                                                                      | AGNF                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                            | DAGNF                                                                                                                                                                                                                                                                  |                                                                                                                                   | TAGNF                                                                                                                                                                                                             |                                                                                                                                                                                          |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| IR spectra                                                                                                                                                                                                                                    | Raman spectra                                                                                                                                                                                                        | IR spectra                                                                                                                                                                                                                                  | Raman spectra                                                                                                                                                                                                                                              | IR spectra                                                                                                                                                                                                                                                             | Raman spectra                                                                                                                     | IR spectra                                                                                                                                                                                                        | Raman spectra                                                                                                                                                                            |
| Wave number $\nu$ , $\text{cm}^{-1}$                                                                                                                                                                                                          | Wave number $\nu$ , $\text{cm}^{-1}$                                                                                                                                                                                 | Wave number $\nu$ , $\text{cm}^{-1}$                                                                                                                                                                                                        | Wave number $\nu$ , $\text{cm}^{-1}$                                                                                                                                                                                                                       | Wave number $\nu$ , $\text{cm}^{-1}$                                                                                                                                                                                                                                   | Wave number $\nu$ , $\text{cm}^{-1}$                                                                                              | Wave number $\nu$ , $\text{cm}^{-1}$                                                                                                                                                                              | Wave number $\nu$ , $\text{cm}^{-1}$                                                                                                                                                     |
| 3397 (m),<br>3280 (w),<br>3197 (w),<br>2917 (w),<br>2851 (w),<br>1662 (m),<br>1640 (m),<br>1513 (m),<br>1495 (m),<br>1421 (m),<br>1358 (w),<br>1272 (s),<br>1177 (m),<br>1144 (w),<br>976 (w),<br>866 (w),<br>794 (m),<br>733 (m),<br>515 (w) | 3287 (3),<br>1528 (11),<br>1470 (10),<br>1388 (63),<br>1299 (37),<br>1244 (35),<br>1155 (46),<br>1055 (12),<br>1013 (63),<br>868 (100),<br>789 (15),<br>728 (13),<br>533 (24),<br>472 (25),<br>442 (15),<br>252 (17) | 3447 (m),<br>3362 (m),<br>3297 (m),<br>2917 (w),<br>2846 (w),<br>2181 (w),<br>1657 (s),<br>1512 (s),<br>1495 (s),<br>1421 (m),<br>1272 (s),<br>1177 (s),<br>984 (w),<br>943 (w),<br>866 (w),<br>794 (m),<br>733 (m),<br>614 (w),<br>499 (w) | 3282 (1),<br>1487 (10),<br>1465 (6),<br>1380 (76),<br>1333 (10),<br>1277 (100),<br>1244 (56),<br>1197 (16),<br>1163 (17),<br>960 (10),<br>869 (93),<br>793 (13),<br>788 (13),<br>721 (11),<br>501 (19),<br>445 (15),<br>273 (18),<br>262 (16),<br>156 (12) | 3432 (m),<br>3307 (s),<br>3247 (w),<br>2978 (w),<br>2554 (w),<br>2175 (w),<br>1682 (s),<br>1621 (m),<br>1512 (s),<br>1495 (s),<br>1421 (s),<br>1352 (w),<br>1270 (s),<br>1177 (s),<br>992 (m),<br>957 (m),<br>869 (w),<br>794 (s),<br>733 (s),<br>653 (w),<br>549 (w); | 3299 (3),<br>1379 (66),<br>1247 (100),<br>1184 (33),<br>1158 (25),<br>873 (81),<br>793 (12),<br>725 (9),<br>277 (19),<br>152 (14) | 3317 (m),<br>3210 (s),<br>1683 (m),<br>1614 (w),<br>1513 (s),<br>1421 (m),<br>1333 (w),<br>1276 (s),<br>1177 (s),<br>1127 (m),<br>951 (m),<br>871 (w),<br>793 (s),<br>733 (s),<br>638 (w),<br>603 (m),<br>483 (w) | 3287 (6),<br>1648 (25),<br>1461 (16),<br>1437 (15),<br>1385 (71),<br>1331 (38),<br>1260 (27),<br>1153 (67),<br>868 (100),<br>789 (19),<br>735 (6),<br>470 (34),<br>430 (24),<br>152 (20) |

Data source: [195]

Table 16: Comparison of safety properties, HNF vs. guanidinium nitroformates.

|                            | HNF<br>no | GNFH<br>no | AGNF<br>yes | DAGNF<br>yes | TAGNF<br>no |
|----------------------------|-----------|------------|-------------|--------------|-------------|
| Hygroscopic                |           |            |             |              |             |
| Melting point, °C          | 110–124   | 110–117    | —           | 80           | 84          |
| Decomp. point, °C          | 110–124   | —          | 71          | 82           | 104         |
| Impact sensitivity, Nm     | 2–15      | 30         | 10          | 5–6          | 2–2.5       |
| Friction sensitivity, N    | 14–36     | 360        | 144         | 32–40        | 20–24       |
| Density, g/cm <sup>3</sup> | 1.86      | 1.70       | 1.77        | 1.70         | 1.69        |

Data source: [193]

The onset and point of maximum thermal decomposition of the five salts were monitored using differential scanning calorimetry. Thermal stability improved in the sequence AGNF DAGNF TAGNF. A good example for the effect of different heating rates on the shape of the thermograms of aminoguanidinium nitroformate is shown in Figure 19 (in section “Aminoguanidinium Nitroformate”).

Guanidinium trinitromethanide (nitroformate) monohydrate has been obtained from guanidinium chloride and either potassium trinitromethanide or iodotrinitromethane [196]. Guanidinium dinitromethanide was also prepared in a metathetical reaction from guanidinium nitrate and sodium dinitromethanide [197]. Guanidinium, triazolium, and tetrazolium dinitromethanide salts are thermally stable and can be relatively insensitive to impact [198].

#### 11.4.3 Guanidinium Salts of Other Nitrogen-Rich Acids

As a general rule in organizing the overwhelming amount of information on nitrogen-rich salts derived from guanidine, aminoguanidine, diaminoguanidine, and triaminoguanidine, we have attempted to sort the salts by the cation first, followed by a list of the anions. There are several exceptions to this rule, e.g., if the common denominator of a publication is the evaluation of one anion paired with several cations. Properties that make salts useful as propellant ingredients may come from either cation or anion or both. There is a substantial amount of overlap between the current sections on guanidinium salts and salts formed with heterocyclic anions. For instance, information on triaminoguanidinium 5,5'-azotetrazolate (TAGZT) can be found here and in *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic and Heterocycloaliphatic Amines.”

#### 11.4.4 Guanidinium Salts of Aromatic Nitrogen-Rich Acids

Picric acid and styphnic acid are often used for the characterization of organic amines, including guanidine derivatives, because these salts are relatively insoluble and well crystallized. However, some of these salts are impact and friction sensitive to the point that some people have considered them as primary explosives. The sensitivity and thermal stability data of picrates and styphnates of guanidine and guanidine derivatives are summarized in Table 17, 18, and 19. For an organic energetic compound, the high melting point of guanidinium picrate is remarkable. It is not likely that any of these will find applications as ingredients in rocket propellants.

**Table 17:** Impact sensitivity of guanidinium styphnates and picrates.

| Compound                                                       | Impact sensitivity <sup>a</sup> , 50% height, mm |
|----------------------------------------------------------------|--------------------------------------------------|
| Hydrazinium(1+) styphnate                                      | 200                                              |
| Guanylurea styphnate                                           | 200                                              |
| <i>N</i> -Methylguanidinium styphnate                          | 275                                              |
| <i>N</i> -Ethylguanidinium styphnate                           | 400                                              |
| Guanidinium styphnate                                          | 400                                              |
| Aminoguanidinium styphnate                                     | 450                                              |
| Guanidinium picrate                                            | 600                                              |
| Hydrazinium(1+) picrate                                        | 600                                              |
| For comparison, reference compound results for this apparatus: |                                                  |
| Nitroglycerin                                                  | 100                                              |
| Tetryl                                                         | 250                                              |
| Trinitrotoluene                                                | 600 +                                            |

<sup>a</sup> 5-kg weight used for all tests

Data source: [199]

**Table 18:** Thermogravimetric data of guanidine derivatives.

| Compound                              | Temperature of initial weight loss |     | Behavior at highest temperature reached |
|---------------------------------------|------------------------------------|-----|-----------------------------------------|
|                                       | K                                  | °C  |                                         |
| <i>N</i> -Ethylguanidinium sulfate    | 383                                | 110 | Lost 12% up to 533 K (260 °C)           |
| Guanidinium sulfate                   | 543                                | 270 | Lost 2% up to 568 K (295 °C)            |
| Nitroguanidine                        | 493                                | 220 | Decomposed at 513 K (240 °C)            |
| Guanylurea styphnate                  | 403                                | 130 | Detonated at 455 K (182 °C)             |
| Aminoguanidinium styphnate            | 478                                | 205 | Detonated at 483 K (210 °C)             |
| Hydrazinium(1+) styphnate             | 378                                | 105 | Detonated at 378 K (105 °C)             |
| <i>N</i> -Ethylguanidinium styphnate  | 393                                | 120 | Detonated at 398 K (125 °C)             |
| <i>N</i> -Methylguanidinium styphnate | 373                                | 100 | Detonated at 378 K (105 °C)             |
| Guanidinium styphnate                 | 403                                | 130 | Detonated at 453 K (180 °C)             |
| Hydrazinium(1+) picrate               | 373                                | 100 | Decomposed at 398 K (125 °C)            |
| <i>N</i> -Methylguanidinium picrate   | 423                                | 150 | Decomposed at 463 K (190 °C)            |
| <i>N</i> -Ethylguanidinium picrate    | 468                                | 195 | Decomposed at 483 K (210 °C)            |
| Guanidinium picrate                   | 493                                | 220 | Decomposed at 495 K (222 °C)            |
| Aminoguanidinium picrate              | 433                                | 160 | Decomposed at 448 K (175 °C)            |
| Guanylurea picrate                    | 423                                | 150 | Lost 72% up to 553 K (280 °C)           |
| Guanidinium nitrate                   | 373                                | 100 | Lost 95% up to 523 K (250 °C)           |

Data source: [199]

**Table 19:** Thermal stability of guanidinium picrates.

| Compound                            | Temperature of maximum decomposition rate |     | Melting point (lit.) |     |
|-------------------------------------|-------------------------------------------|-----|----------------------|-----|
|                                     | K                                         | °C  | K                    | °C  |
| Hydrazinium picrate                 | 388                                       | 115 | 474                  | 201 |
| <i>N</i> -Methylguanidinium picrate | 453                                       | 180 | 474                  | 201 |
| <i>N</i> -Ethylguanidinium picrate  | 468                                       | 195 | 453                  | 180 |
| Guanidinium picrate                 | 495                                       | 222 | 606                  | 333 |
| Guanylurea picrate                  | 463                                       | 190 | 558                  | 285 |

Data source: [199]

#### 11.4.5 Guanidinium Salts of Aliphatic Nitrogen-Rich Acids

Two modifications of guanidinium dicyanamide  $[\text{C}(\text{NH}_2)_3][\text{N}(\text{CN})_2]$  were obtained by ion-exchange reactions in aqueous or methanolic solutions [200]. The hygroscopic compounds were characterized by NMR, MS, and vibrational spectroscopy. The single-crystal XRD crystal structures were  $\beta$ - $[\text{C}(\text{NH}_2)_3][\text{N}(\text{CN})_2]$ :  $Pna2_1$ ,  $Z = 8$ ,  $a = 1373.1(3)$ ,  $b = 495.5(1)$ ,  $c = 1802.9(4)\text{pm}$ ,  $V = 1226.7(4)\text{pm}^3$ ;  $\alpha$ - $[\text{C}(\text{NH}_2)_3][\text{N}(\text{CN})_2]$ :  $P2_1/c$ ,  $Z = 8$ ,  $a = 1924.9(4)$ ,  $b = 496.0(1)$ ,  $c = 1372.4(3)\text{pm}$ ,  $\beta = 110.46(3)^\circ$ ,  $V = 1227.5(4)\text{pm}^3$ . The structures were largely equivalent in terms of the overall assembly of the molecular ions. The polymorphs showed a succession of thermal events in the temperature region between 240 and 440 K when examined by temperature-dependent XRD and TGA. Due to the chemical composition of guanidinium dicyanamide ( $\text{C}_3\text{N}_6\text{H}_6$ ), which is formally identical to that of melamine  $\text{C}_3\text{N}_3(\text{NH}_2)_3$ , and its thermal reactivity, which leads to melamine at around 400 K, guanidinium dicyanamide may be suited as a molecular precursor for synthesis of graphitic carbon nitride.

Guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium dicyanamides have been evaluated as ionic liquids and hypergolic fuels. Ionic liquids derived from combinations of alkylammonium, hydrazinium, guanidinium, and hydrazidinium cations with dicyanamide anions were tested for their reactivity toward hypergolic oxidizers [201]. Table 20 is a summary of properties of guanidinium dicyanamides.

**Table 20:** Properties of guanidinium dicyanamides.

| Compound                        | Melting point |     | Decomp. onset |     | Density<br>g/cm <sup>3</sup> |
|---------------------------------|---------------|-----|---------------|-----|------------------------------|
|                                 | K             | °C  | K             | °C  |                              |
| Guanidinium dicyanamide         | 330           | 57  | 418           | 145 | 1.38                         |
| Aminoguanidinium dicyanamide    | 328           | 55  | 393           | 120 | 1.41                         |
| Diaminoguanidinium dicyanamide  | 334           | 61  | 385           | 112 | 1.36                         |
| Triaminoguanidinium dicyanamide | 397           | 124 | 423           | 150 | 1.42                         |

Data source: [201]

#### 11.4.6 Guanidinium Salts of Heterocyclic Nitrogen-Rich Acids

Guanidinium salts of heterocyclic acidic compounds are promising propellant and gas generant ingredients because they are often the thermally most stable in a group of salts tested for thermal stability. Guanidine is a strong base and forms stable salts with many proton donors, even with weak proton donors. The following heterocyclic guanidinium salts are arranged in order of increasing nitrogen atoms in the ring, starting with triazoles and continuing with tetrazoles.

##### 11.4.6.1 Guanidinium 4,5-Dicyano-2*H*-1,2,3-Triazoles

The ammonium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium salts of the 4,5-dicyano-1,2,3-triazolate anion were prepared by metathetical reactions from the corresponding ammonium and guanidinium halides with the silver salt of 4,5-dicyano-1,2,3-triazole and spectroscopically characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, and Raman, and the thermal stabilities investigated using DSC [202]. The solid-state crystal structures determined using single-crystal XRD are summarized in Table 21. The impact and friction sensitivities of these compounds were investigated, and all compounds were found to be neither impact (30 J) nor friction sensitive (360 N).

##### 11.4.6.2 Guanidinium 5-Aminotetrazolate

Guanidinium 5-aminotetrazolate (GA, GAT, GZT) has been evaluated as a gun propellant additive that reduces barrel wear and muzzle flash. Guanidinium 5-aminotetrazolate (GA) can be prepared by the simple reaction of guanidinium carbonate and 5-amino-1*H*-tetrazole monohydrate in ethanol. The basicity of guanidinium carbonate suffices for the abstraction of a proton in the 5-aminotetrazole ring. After only 30 min reaction time, the final product can be obtained with a yield of 95% after one reaction step [203]. The standard enthalpy of formation, measured by combustion calorimetry, is +85.9 kJ/mol. The IR spectrum of GA in Figure 14 is dominated by the N–H stretch and deformation vibrations of the amine groups ( $\nu = 3426, 3337, 3184, 1662, 1519 \text{ cm}^{-1}$ ) and the absorption bands of the tetrazole fragment ( $\nu = 1561, 1136, 1105, 1001 \text{ cm}^{-1}$ ).

In the DSC thermogram of GA with a heating rate of 0.5 K/min under argon atmosphere, one can see a melting point at 397.2 K and the peak area translates into a melting enthalpy of 26.5 kJ/mol (Figure 15).

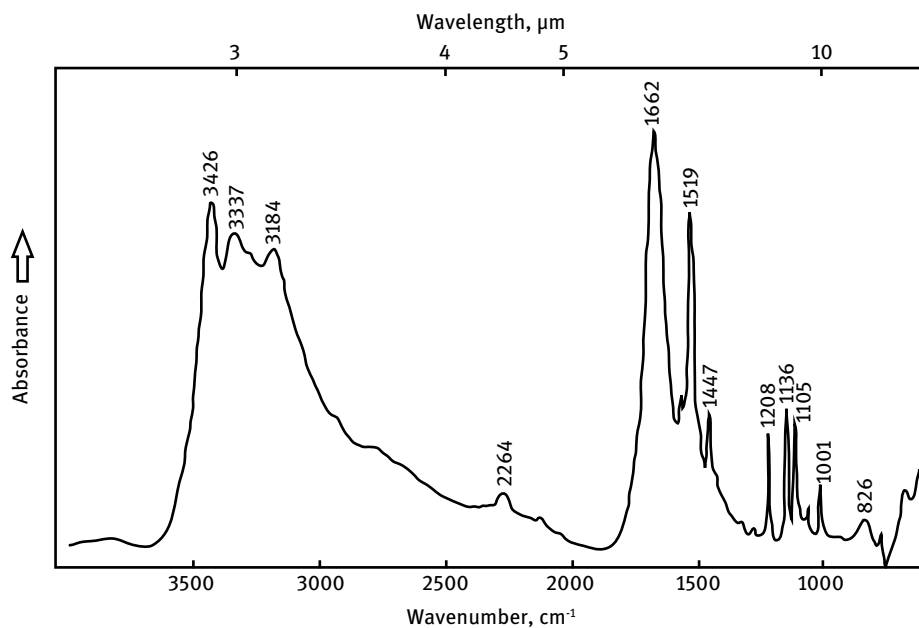
The thermal decomposition of guanidinium 5-aminotetrazolate was evaluated in comparison to GuN, TAGN, and five other nitrogen-rich additives [203, 204]. The TGA-DTA curve for guanidinium 5-aminotetrazolate showed an endothermic melting at 397 K (124 °C), followed by a four-stage, stepwise weight-loss sequence (Figure 16). The first stage corresponded to weak exothermic decomposition observed in the simultaneous DTA between 423 and 505 K (150 and 232 °C); the second and third stages also corresponded to weak exothermic decomposition within the temperature range of 505 to 631 K (232 to 358 °C), accompanied by 15 and 11.6% weight loss, respectively; and the fourth stage corresponded to an endothermic decomposition between 631 and 833 K



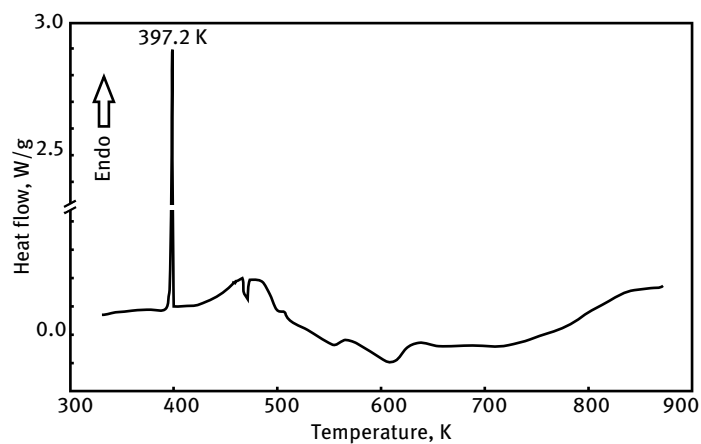
Table 21: Crystal structures of 4,5-dicyano-1,2,3-triazolate salts of several nitrogen bases.

| Compound                                         | Family       | Space group           | Cell structure parameters |             |             |             |                     | Z  |
|--------------------------------------------------|--------------|-----------------------|---------------------------|-------------|-------------|-------------|---------------------|----|
|                                                  |              |                       | a<br>Å                    | b<br>Å      | c<br>Å      | β<br>°      | V<br>Å <sup>3</sup> |    |
| Ammonium 4,5-dicyano-1,2,3-triazolate            | orthorhombic | <i>Pnma</i>           | 6.5646(13)                | 7.5707(16)  | 13.303(3)   |             | 661.1(2)            | 4  |
| Guanidinium 4,5-dicyano-1,2,3-triazolate         | monoclinic   | <i>Cc</i>             | 12.6000(11)               | 17.1138(15) | 12.0952(9)  | 106.098(7)  | 2505.9(4)           | 12 |
| Aminoguanidinium 4,5-dicyano-1,2,3-triazolate    | monoclinic   | <i>Pg</i>             | 7.0921(9)                 | 7.2893(9)   | 8.8671(11)  | 105.141(11) | 442.48(10)          | 2  |
| Diaminoguanidinium 4,5-dicyano-1,2,3-triazolate  | monoclinic   | <i>P2<sub>1</sub></i> | 3.7727(4)                 | 15.6832(17) | 8.3416(10)  | 101.797(10) | 483.13(9)           | 2  |
| Triaminoguanidinium 4,5-dicyano-1,2,3-triazolate | monoclinic   | <i>C2/c</i>           | 14.0789(14)               | 11.5790(11) | 13.5840(14) | 115.239(10) | 2003.1(3)           | 8  |

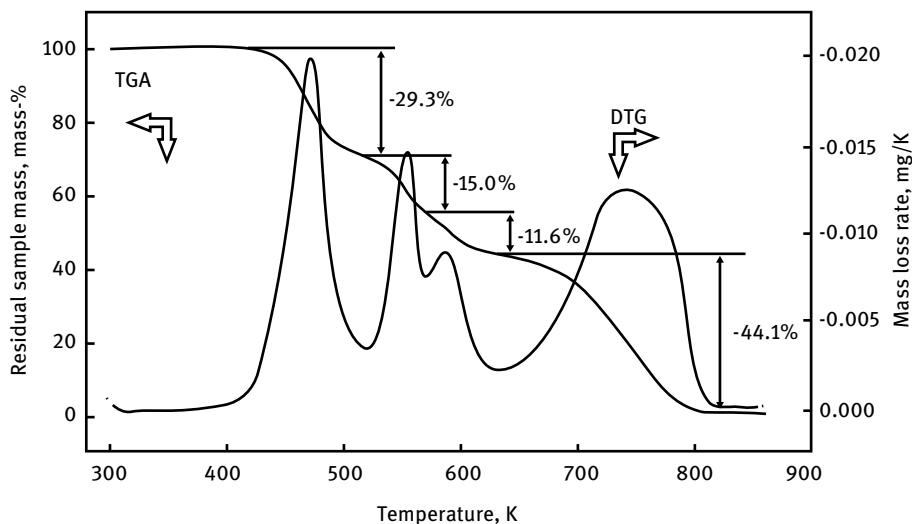
Data source: [197]



**Figure 14:** IR spectrum of guanidinium-5-aminotetrazolate. (Republished and modified from [203], with permission of ©2003 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)



**Figure 15:** DSC thermogram of guanidinium-5-aminotetrazolate. (Republished and modified from [203], with permission of ©2003 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)



**Figure 16:** TGA-DTA thermogram of guanidinium-5-aminotetrazolate decomposition. (Republished and modified from [203], with permission of ©2003 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

(358 and 560 °C), corresponding to 44.1% weight loss. The identification of the decomposition gases by FTIR and GC-MS allowed evaluation of the chemical processes during the thermal degradation of guanidinium 5-aminotetrazolate, and identified  $\text{HN}_3$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{N}-\text{CN}$  as the decomposition gases evolved in the first, second, and third stages of the decomposition process, respectively.

Decomposition products identified by IR were hydrogen azide  $\text{HN}_3$ , ammonia  $\text{NH}_3$ , and cyanamide  $\text{H}_2\text{N}-\text{CN}$  at higher temperatures. The thermal decomposition of GA is initiated by the ring opening of the heterocyclic tetrazole structure. The release of hydrogen azide is typical for the thermolysis of substituted 5-aminotetrazole.

An investigation of the molecular and electronic structures of GA showed that the ion pair  $[\text{C}(\text{NH}_2)_3]^+ \cdots [\text{CN}_5\text{H}_2]^-$  forms two planes with the planar ions parallel at a distance of 1.8 Å [205]. A CNDO/2 approximation of the MO method was used for calculating the equilibrium distance, the charge separation, and the electron distribution, and for examining the possible role of hydrogen bonding in the crystal lattice.

Physical properties of GA and several other 5-aminotetrazolate salts as reported by Tao et al. [206] are summarized in the chapter “Heterocyclic and Heterocycloaliphatic Amines.”

A detailed reaction mechanism for the decomposition of GA consisting of 55 species and 85 elementary chemical reactions was formulated based on quantum chemical calculations with insight from experiments [207, 208].

Numerical simulation of the GA and GA/RDX decomposition process was carried out by solving a system of ordinary differential equations representing the mass loss, reversible reactions, and evaporation of stable species. Simulation results were found to satisfactorily match the experimental data of Neutz et al. [203]. Within the present modeling framework and assumptions, the following major conclusions were obtained:

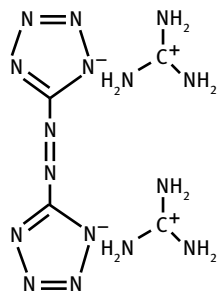
1. Decomposition of GA begins with chemical interaction within the ion pair  $\text{Gu}^+$  and  $5\text{ATz}^-$ , where the carbon in  $\text{Gu}^+$  bonds to a ring nitrogen adjacent to the carbon in  $5\text{ATz}^-$ , forming an intermediate INT5.
2. The pathway in which the intermediate species INT5 is formed is the most critical step.
3. The first step observed in mass loss is caused by formation and evaporation of  $\text{NH}_3$ ,  $\text{HN}_3$ ,  $\text{N}_2$ , and  $\text{H}_2\text{NCN}$ , whereas melamine evaporation results in the second step.
4. Decomposition at first proceeds through endothermic reactions, but is later replaced by exothermic reactions producing  $\text{N}_2$ ,  $\text{NH}_3$ , and  $\text{HN}_3$ .
5. Proton transfer between  $\text{Gu}^+$  and  $5\text{ATz}^-$  is not predicted to occur by the quantum mechanics calculations for the liquid phase.

#### 11.4.6.3 Guanidinium 1,5'-bis-1*H*-Tetrazolates

The thermal decomposition behavior of the guanidinium salt of 1,5-bis-1*H*-tetrazole was analyzed by TG-DTA-MS [209]. The combustion behavior of  $\text{CuO}$ /guanidinium 1,5'-bis-1*H*-tetrazolate mixtures was examined for varying O/F mixture ratios [210–213].

#### 11.4.6.4 Guanidinium Azotetrazolate

Guanidinium azotetrazolate, GAT, GZT,  $\text{GAzT}$ ,  $\text{GUZT}$ ,  $\text{C}_4\text{H}_{12}\text{N}_{16}$ , is a unique energetic material with good thermal stability and an exceptionally high nitrogen content (79 mass-% nitrogen).



Ammonium, guanidinium, and triaminoguanidinium azotetrazolate (AAZ, GAZ, and TAGAZ) were synthesized starting with sodium azotetrazolate pentahydrate [214].

For comparison, the reported heats of formation for ammonium (AAZ), guanidinium (GAZ), and triaminoguanidinium azotetrazolate (TAGAZ) salts are +410, +443, and +1075 kJ/mol (+98, +106, and +257 kcal/mol), respectively. The density of GAZ is 1.54 g/cm<sup>3</sup> and the enthalpy of formation is +410 kJ/mol (+98 kcal/mol).

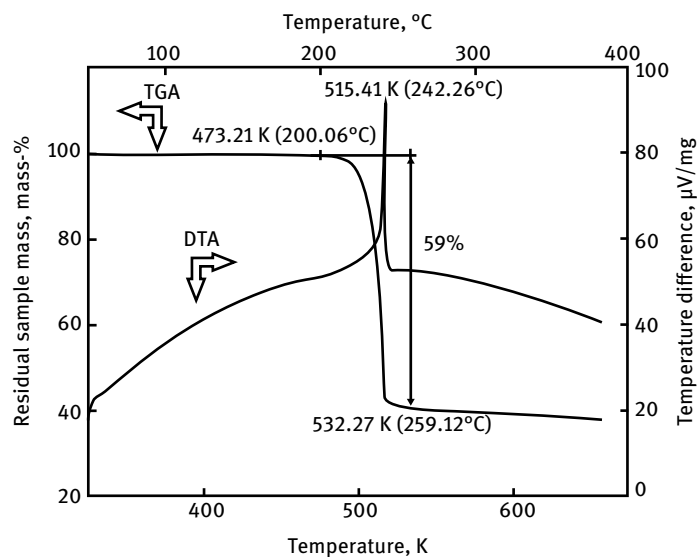
The maxima of the melting endotherm for AAZ, GAZT, and TAGAZ in the DSC were at 485, 477, and 532 K (212, 204, and 259 °C), respectively [215]. The onsets of thermal decomposition in the TGA were at 453, 473, and 523 K (180, 200, and 250 °C), respectively. TAGAZ has the highest positive heat of formation of the three salts investigated, +1075 kJ/mol (+257 kcal/mol). Triaminoguanidinium azotetrazolate (TAGAZ) was incorporated into solid propellant formulations and DSC results indicated that it does not have any adverse effect on thermal stability of a double-base matrix. The burning rate data indicated that TAGAZ acts as an efficient energetic additive in composite-modified double-base (CMDB) propellant formulations in the high-pressure region. Guanidinium azotetrazolate has been evaluated as an additive to gun propellants to reduce barrel wear.

Guanidinium azotetrazolate (GAzT) was evaluated as an additive for a high-regression-rate fuel mixture with hydroxyl-terminated polybutadiene (HTPB) [216]. GAzT was found to react with N100, a common curative for HTPB, and a test grain made with N100, HTPB, and GAzT formed a foam about one and a half times its original volume. An alternative isocyanate curative was found, polyisocyanate (PAPI), with which it did not react.

As shown in Figure 17, the TGA curve of guanidinium azotetrazolate (GAzT) at a heating rate of 2°/min consisted of a two-stage weight-loss process [204]. The first stage indicated the exothermic rapid reaction also observed in the parallel DTA between 473 and 532 K (200 and 259 °C), resulting in a 59% weight loss, and the second stage corresponded to a slow endothermic reaction observed beyond 532 K (259 °C). The first stage is the result of the heterocyclic ring opening, which involved abstraction of the acidic protons available in the guanidinium cation by the azotetrazolate anion, which leads to the formation of a highly unstable azotetrazolate cation and subsequent opening of the azotetrazolate ring with the release of molecular nitrogen and cyanamide.

The thermal decomposition of guanidinium azotetrazolate (GAzT) was studied by TGA and DSC [217]. Based on the *in situ* analysis of products in condensed and gas phases by a combination of hot-stage with rapid-scan FTIR spectroscopy and pyrolysis gas chromatography mass spectrometry (Py-GC-MS), a thermal decomposition mechanism of GAzT was proposed. Results showed that the first mass loss is caused by an exothermic decomposition reaction of azotetrazolate and the endothermic decomposition reaction of guanidinium. An intermediate product, tetrazole azide (CHN<sub>7</sub>), may form through a ring-opening reaction of one tetrazole on the azotetrazolate molecule.

Additional work analyzed the decomposition of guanidinium azotetrazolate (GAzT) in the liquid phase by a combined experimental and computational approach



**Figure 17:** DTA-TGA Thermogram of guanidinium azotetrazolate decomposition. (Republished and modified from [204], with permission of ©2009 American Institute of Aeronautics Astronautics; permission conveyed through Copyright Clearance Center Inc.)

using FTIR spectroscopy to acquire the spectral transmittance of the evolved gas-phase species from rapid thermolysis as well as time-of-flight mass spectrometry (ToFMS) to acquire mass spectra of the evolved gas-phase species [218]. Sub-milligram samples of GAzT were heated at rates of about 2000 K/s to a pre-set temperature (553–573 K), at which decomposition occurred under isothermal conditions.  $N_2$ ,  $NH_3$ , HCN, guanidine, and melamine were identified as products of decomposition.

TGA analyses showed that GAzT loses about 62.2% mass between 522 and 531 K (249–258 °C) [219]. See also [220].

Guanidinium azotetrazolate was prepared by a replacement reaction using guanidinium nitrate and 5-amino-tetrazole as raw materials [221, 222]. The morphology and structure of GAzT were characterized by SEM, FTIR, and elemental analysis. Thermal decomposition of GAzT was investigated by TGA, DSC, condensed-phase thermolysis/rapid-scan FTIR, and pyrogenetic MS in a temperature-programmed mode. The thermal decomposition onset temperature was 529 K (256 °C).

A numerical simulation of the GuzT decomposition process was carried out by solving a system of ordinary differential equations representing the mass loss, reversible reactions, and evaporation of stable species [223, 224]. A detailed reaction mechanism for the decomposition of GuzT consisting of 76 species and 107 elemen-

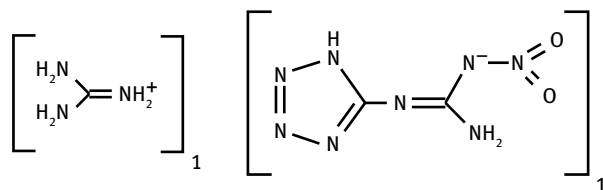
tary chemical reactions was validated. Simulation results were found to satisfactorily match the experimental data reported by An [221]. The major conclusions were:

1. Decomposition of GuZT begins with the ring opening of  $AzT^{2-}$  to release  $N_2$ , forming the intermediate INT4.
2. A pathway in which the intermediate species INT4a and guanidine are formed is the most critical step, as all the major product species are sensitive to this pathway.
3. The first step observed in mass loss is caused by formation and evaporation of  $NH_3$ ,  $N_2$ , and  $HCN$ , whereas melamine evaporation results in a second step.
4. Decomposition proceeds through exothermic reactions throughout the event, producing  $N_2$ ,  $NH_3$ , and  $HCN$ .

#### 11.4.6.5 Other Guanidinium Salts of Heterocyclic Acids

The guanidinium, ethylenediammonium(2+), ammonium, and hydrazinium(1+) salts of 3-nitro-1,2,4-triazol-5-one (NTO) were synthesized and characterized [225]. Small-scale sensitivity tests indicated that these compounds are thermally stable and only moderately insensitive to impact.

The guanidinium salt of *N*-nitro-*N'*-1*H*-tetrazol-5-yl-guanidine,  $C_3H_9N_8O_2$ ,  $M=189.16$  g/mol, has been prepared and patented as an additive to double-base propellants [226]. It melts at 509–513 K (236–240 °C).



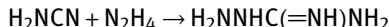
Guanidinium salt of *N*-nitro-*N'*-1*H*-tetrazol-5-yl-guanidine

#### 11.4.6.6 Other Guanidinium Salts with Substituents on the Guanidine Molecule

Energetic salts based on substituted guanidinium cations containing a picryl moiety, *N*-(2,4,6-trinitrobenzylideneamino)guanidinium cation, were synthesized and characterized by IR and multi-nuclear NMR spectroscopy, DSC, TGA, elemental analysis, and single-crystal XRD [227]. Most of the salts decomposed at temperatures above 180 °C, exhibited low impact sensitivities (20–40 J), low friction sensitivities (220–340 N), and were insensitive to electrostatic discharge (ESD). The predicted detonation velocities ranged from 7842 to 8394 m/s.

## 12 Aminoguanidine

Aminoguanidine,  $\text{H}_2\text{NNHC(=NH)NH}_2$ ,  $\text{C}_1\text{N}_4\text{H}_6$ , hydrazinecarboximidamide, guanylhypurazine, CAS RN [79-17-4], is prepared by reaction of cyanamide and hydrazine hydrate.



It is available in industrial quantities in the form of its bicarbonate salt, which is prepared by treating a cyanamide solution with hydrazine hydrate and simultaneously bubbling through an excess of carbon dioxide [228, 229]. Free aminoguanidine is rarely used as such. It is mostly used in the form of one of its salts. Several aminoguanidinium salts have already been discussed or will be discussed in sections where they were compared to similar salts derived from guanidine or triaminoguanidine. All of these salts are good sources of nitrogen in solid gas generants.

Aminoguanidine is a starting material in making tetracene, a primary explosive (see chapter “Heterocyclic and Heterocycloaliphatic Amines”). A method for analyzing trace amounts of aminoguanidine was necessary to characterize the conversion from aminoguanidine to tetracene and to detect any unreacted aminoguanidine in the waste solution from the preparation process of tetracene. Aminoguanidine is not an electroactive species in polarographic determinations. However, some compounds containing hydrazine groups can become an electroactive species by reacting them with sodium nitrate or acetone in acidic solution. An electroactive species was produced from aminoguanidine by reacting with sodium nitrite or acetone in acidic solution, and aminoguanidine in the solution could be analyzed by polarography [230].

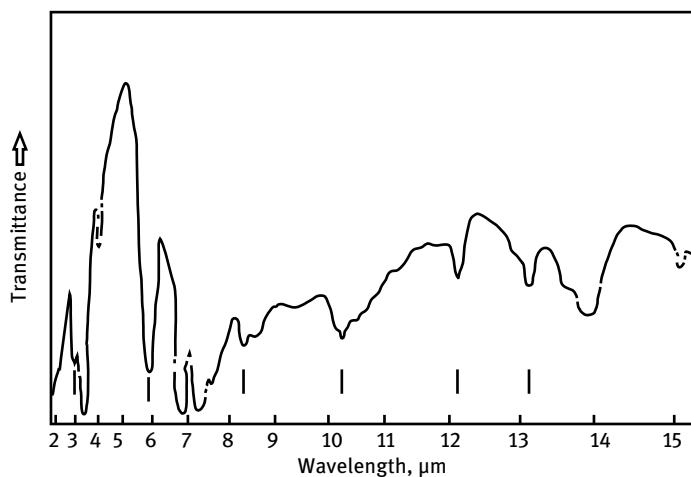
### 12.1 Aminoguanidinium Nitrate

Aminoguanidinium nitrate, monoaminoguanidinium nitrate; hydrazinecarboximidamide, nitrate (1:1); AGN, MAGN,  $\text{C}_1\text{H}_7\text{N}_5\text{O}_3$ , molecular mass 137.1 g/mol, nitrogen content 51.08% N, oxygen balance -29.2, CAS RN [10308-82-4], forms colorless crystals that melt at 417–419 K (144–146 °C) and are soluble in water or ethanol. For the heats of combustion, enthalpies of formation, and enthalpies of solution of (mono)aminoguanidinium nitrate, see Table 10. The IR spectrum of aminoguanidinium nitrate is shown in Figure 18.

Monoaminoguanidinium nitrate melts at 417.6–418.6 K (144.5–145.5 °C) and in the DTA the maxima of two exotherms are at 523 and 563 K (250 and 290 °C).

Aminoguanidinium nitrate crystallizes in triclinic crystals in space group  $P\bar{1}$ , and the cell parameters are  $a = 7.341 \text{ \AA}$ ,  $b = 7.722 \text{ \AA}$ ,  $c = 6.024 \text{ \AA}$ ,  $\alpha = 110.47^\circ$ ,  $\beta = 102.64^\circ$ ,  $\gamma = 104.87^\circ$ ,  $V = 290.7 \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{XRD}} = 1.566 \text{ g/cm}^3$  [231]. The oxygen atoms of the nitrate





**Figure 18:** IR Spectrum of aminoguanidinium nitrate. (Reproduced and modified from [125], with permission from Levering Estate.)

ions in aminoguanidinium nitrate are connected by hydrogen bonds to the hydrogen atoms in the aminoguanidinium ions.

Similar results were obtained with aminoguanidinium nitrate that was prepared through the reaction of aminoguanidinium bicarbonate and nitric acid solution. The crystal structure of MAGN was determined by single-crystal XRD [232]. The result showed that there is no double bond in the compound and that it is a typical nitrate. The crystal is triclinic with space group  $P\bar{1}$ ,  $a = 0.6028(1)\text{nm}$ ,  $b = 0.7344(1)\text{nm}$ ,  $c = 0.7723(1)\text{nm}$ ;  $\alpha = 104.850(10)^\circ$ ,  $\beta = 110.450(10)^\circ$ ,  $\gamma = 102.660(10)^\circ$ ;  $V = 0.2911(7)\text{nm}^3$ ,  $Z = 2$ ,  $\rho_{\text{XRD}} = 1.564\text{g/cm}^3$ .

The Cu-complex nitrate of aminoguanidine  $\text{Cu}[\text{HN}=\text{C}(\text{NH}_2)(\text{NHNH}_2)](\text{NO}_3)_2$  was synthesized as a potential new gas generant, and the thermal decomposition behavior was investigated [233]. During the isothermal decomposition reaction at 374–398 K (101–125 °C), the complex formed a stable intermediate. The activation energy of the reaction was 51 kJ/mol. Above 398 K (125 °C), the Cu-complex nitrate of aminoguanidine decomposed so rapidly that ignition occurred. The linear burning rate of a stoichiometric mixture with  $\text{Sr}(\text{NO}_3)_2$  as the oxidizer was 6.48 mm/s and the flame temperature was 1616 K (1343 °C).

The enthalpy of formation of monoaminoguanidinium nitrate in comparison to GuN and other nitrates is listed in Table 10. Additional data were published for the enthalpy of formation of monoaminoguanidinium nitrate:  $\Delta H_f^{298} = -278.7 \pm 0.7\text{kJ/mol} = -66.62 \pm 0.18\text{kcal/mol}$  [234, 235].

## 12.2 Aminoguanidinium Perchlorate

Aminoguanidinium perchlorate,  $\text{CH}_7\text{N}_4\text{ClO}_4$ ,  $\text{AGClO}_4$ , aminoguanidine perchlorate; CAS RN [41195-24-8]; hydrazinecarboximidamide, monoperchlorate; can be formed by the reaction of aminoguanidinium bicarbonate (which is readily available) with aqueous perchloric acid solution [5].  $\text{AGClO}_4$  (not to be confused with silver perchlorate,  $\text{AgClO}_4$ ) melts at 345 K (72°C) and is the most stable of three similar compounds and begins to decompose at 523 K (250°C). It is thermally more stable than  $\text{TAGClO}_4$ . The structure of  $\text{AGClO}_4$  in the crystalline state was determined using low-temperature single-crystal XRD, indicating a monoclinic structure. The crystallographic data of aminoguanidinium, triaminoguanidinium, and azidoformamidinium perchlorate are summarized in Table 22.

Further information regarding the crystal structure determinations have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers listed in Table 22. The enthalpy of formation of  $\text{AGClO}_4$  is  $-161 \pm 7$  kJ/mol. The impact sensitivity of  $\text{AGClO}_4$  as tested in the BAM fall hammer machine was 4 N m, and the friction sensitivity was 110 N. It is less sensitive than  $\text{TAGClO}_4$ .

Other data for the enthalpy of formation of monoaminoguanidinium perchlorate derived from the enthalpy of solution in infinitely diluted solution gave  $\Delta H_f^{298}(\text{S}) = -191.96 \pm 0.87$  kJ/mol =  $-45.88 \pm 0.21$  kcal/mol [234].

**Table 22:** Crystallographic data of aminoguanidinium, triaminoguanidinium, and azidoformamidinium perchlorate.

| Gross formula                             | $\text{CH}_7\text{N}_4\text{ClO}_4$ | $\text{CH}_9\text{N}_6\text{ClO}_4$ | $\text{CH}_4\text{N}_5\text{ClO}_4$ |
|-------------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| Abbreviated name                          | $\text{AGClO}_4$                    | $\text{TAGClO}_4$                   | $\text{AZClO}_4$                    |
| CAS RN                                    | 41195-24-8                          | 4104-85-2                           |                                     |
| Formula weight, g/mol                     | 174.56                              | 204.59                              | 185.54                              |
| Crystal system                            | monoclinic                          | monoclinic                          | orthorhombic                        |
| Space group                               | $P2_1/c$ (no. 14)                   | $P2_1/c$ (no. 14)                   | $Pbca$ (no. 61)                     |
| $a$ , Å                                   | 7.988(1)                            | 10.2506(3)                          | 8.5992(3)                           |
| $b$ , Å                                   | 8.498(1)                            | 15.0671(4)                          | 11.0586(4)                          |
| $c$ , Å                                   | 9.958(2)                            | 10.3572(3)                          | 14.1919(4)                          |
| $\alpha$ , °                              | 90.0                                | 90.0                                | 90.0                                |
| $\beta$ , °                               | 103.50(1)                           | 102.443(3)                          | 90.0                                |
| $\gamma$ , °                              | 90.0                                | 90.0                                | 90.0                                |
| $V$ , Å <sup>3</sup>                      | 657.3(2)                            | 1562.06(8)                          | 1349.58(8)                          |
| $Z$                                       | 4                                   | 8                                   | 8                                   |
| $\rho_{\text{calc.}}$ , g/cm <sup>3</sup> | 1.764                               | 1.740                               | 1.826                               |
| $T$ , K                                   | 200                                 | 100                                 | 200                                 |
| Cambridge No.                             | 664916                              | 664917                              | 664918                              |

Data source: [5]

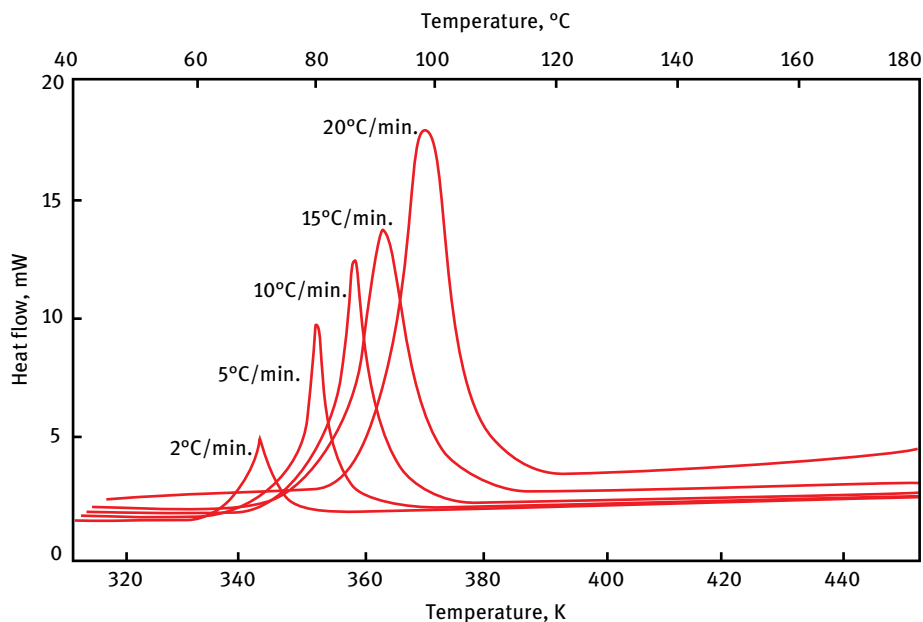
### 12.3 Aminoguanidinium Dinitramide

Aminoguanidinium dinitramide, aminoguanidinium dinitramide, aminoguanidine dinitramide,  $[\text{H}_2\text{NC}(=\text{NH})\text{NHNH}_3^+][\text{N}(\text{NO}_2)_2^-]$ , melts at 367 K (94 °C) [131]. Other sources give the same melting point of 367 K (94 °C) [116, 236].

For the heats of combustion, enthalpies of formation, and enthalpies of solution of (mono)aminoguanidinium dinitramide, see Table 13. Other sources gave an enthalpy of formation of aminoguanidinium dinitramide as  $-48 \text{ kJ/mol}$  ( $-11.5 \text{ kcal/mol}$ ) [44].

### 12.4 Aminoguanidinium Nitroformate

Aminoguanidinium nitroformate,  $[\text{H}_2\text{NC}(=\text{NH})\text{NHNH}_3^+][\text{C}(\text{NO}_2)_3^-]$  is one of four guanidine-derivative nitroformate compounds prepared and characterized by a group of researchers at the University of Munich in Germany [193, 195]. The properties are summarized in Tables 14 and 15 above. Here, one of the several images from the poster was selected as an example of the influence of heating rate on the shape of thermograms of energetic compounds (Figure 19). When describing thermograms of



**Figure 19:** DSC thermogram of the thermal decomposition of aminoguanidinium nitroformate. (Reproduced and modified from [193].)

other energetic compounds, we have attempted to always include information about the heating rate at which the data were obtained.

## 12.5 Other Aminoguanidinium Salts

Based on TG-DTA-MS measurements, aminoguanidinium 5,5'-azobis-1*H*-tetrazolate melted at 482 K, followed immediately by a rapid exothermic decomposition, leading to 50% weight loss [237]. The decomposition started with cleavage of the heterocyclic ring, which produced nitrogen and cyanamide with generation of heat.

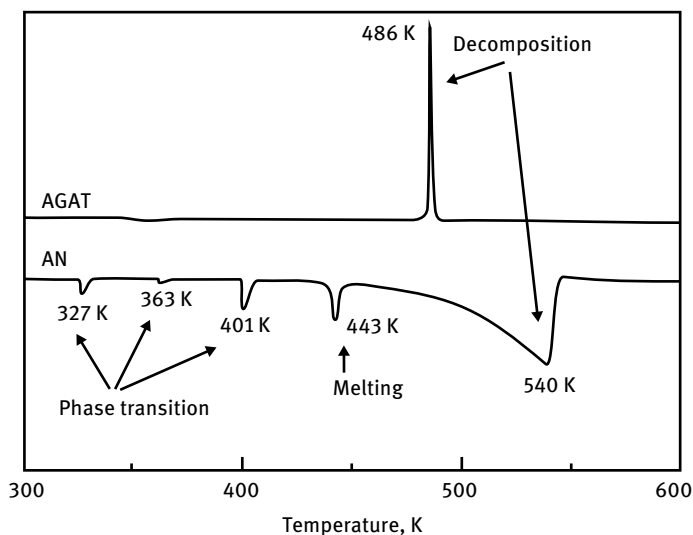
Mono-, di-, and triaminoguanidinium sulfate and azidoformamidinium sulfate are not used as rocket propellants, but they are useful intermediates in the synthesis of other nitrogen-rich compounds and their crystal structures were compared to those of salts with other anions [238].

The kinetics of the thermal decomposition of aminoguanidinium 5,5'-azobis-1*H*-tetrazolate (AGAT), which is a promising candidate for gas-generating agents in airbags, were investigated by MS [239]. The main path of decomposition of AGAT was a single elementary process. The activation energies for the main decomposition obtained under helium by non-isothermal analysis and isothermal analysis were 207 and 209 kJ/mol, respectively.

The effects of initial temperature, pressure, particle size, and composition ratio on the burning rate of aminoguanidinium 5,5'-azobis-1*H*-tetrazolate (AGAT)/ammonium nitrate (AN)-based gas generants were studied in a temperature-controlled chimney-type strand burner [240, 241]. More detailed AN/AGAT burning rate data are described in a future set of several volumes on solid propellants and gas generants to be published as part of *Encyclopedia of Rocket Propellants*. The thermal decomposition of AGAT in comparison to that of AN is shown in Figure 20.

The decomposition of AGAT occurs in one sharp exothermic peak, while the endothermic phase changes and decomposition of AN are spread over a wide temperature range. Physical properties of aminoguanidinium 5-aminotetrazolate and several other 5aminotetrazolate-salts are also summarized in the chapter "Heterocyclic Amines" [206].

Aminoguanidinium 1-methyl-5-nitriminotetrazolate can be prepared by reaction of aminoguanidinium bicarbonate with 1-methyl-5-nitriminotetrazole, which is made from 5-aminotetrazole through methylation and nitration [242]. Optimizing the nitration dosage, reaction temperature, and time resulted in a good yield of 81%. The products were characterized by means of <sup>1</sup>H NMR, IR, and MS.



**Figure 20:** DTA curves of AGAT and AN at heating rate of 5 K/min in helium. (Republished and modified from [241], with permission of ©2011 Taylor & Francis, [www.tandfonline.com](http://www.tandfonline.com))

## 13 Diaminoguanidine

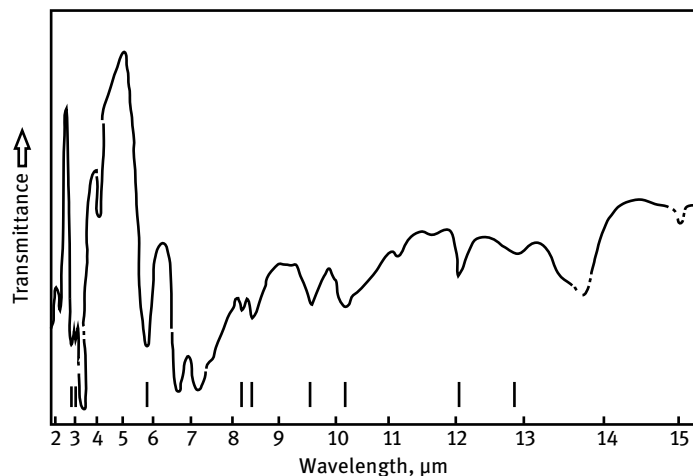
Diaminoguanidine,  $C_1H_7N_5$ ; carbonimidic dihydrazide; CAS RN [4364-78-7], is rarely used as an intermediate. When trying to prepare it by reaction of guanidine with hydrazine hydrate, it is difficult to stop the amido group replacement at exactly this intermediate step between aminoguanidine and triaminoguanidine. The reaction of diaminoguanidine with nitrous acid leads to a variety of tetrazole derivatives [125, 127].

### 13.1 Diaminoguanidinium Nitrate

Diaminoguanidinium nitrate, diaminoguanidine nitrate, DAGN; carbonimidic dihydrazide, nitrate (1:1);  $C_1H_8N_6O_3$ , CAS RN [37160-07-9], molecular mass 152.11, nitrogen content 55.25% N, is a good source of nitrogen for gas generants. Diaminoguanidinium nitrate and the corresponding picrate and perchlorate have been patented as explosives [243]. Its melting point is 415–417 K (142–144 °C) and it will explode when rapidly heated to 563 K (290 °C). Its impact sensitivity (50% point) is 40 cm with a 2-kg weight. With an excess of nitric acid, diaminoguanidine may form a dinitrate salt. Chemical Abstracts nomenclature called this salt “Carbonimidic dihydrazide, dinitrate” with a CAS RN [244639-25-6P].

Diaminoguanidinium nitrate melts at 417–418 K (144–145 °C) and the temperature at the maximum of the exotherm in the DTA is 533 K (260 °C), where it decomposes in

a violent reaction [172]. In a vacuum stability test at 393 K (120 °C) for 40 h comparing GuN, DAGN, and TAGN, DAGN was the least stable with a gas evolution of 1.92 versus 0.23 cm<sup>3</sup> for GuN and 1.06 cm<sup>3</sup> for TAGN [244]. The IR spectrum of diaminoguanidinium nitrate is shown in Figure 21.



**Figure 21:** IR spectrum of diaminoguanidinium(1+) nitrate. (Reproduced and modified from [125], with permission from Levering Estate.)

### 13.1.1 Toxicity of Diaminoguanidinium Nitrate

Diaminoguanidinium nitrate (DAGN) was among 13 other chemicals tested as ingredients for “non-toxic” propellants [245]. The results in hepatocytes showed a dose-dependent decrease in mitochondrial activity (MTT), an increase in lactate dehydrogenase (LDH) leakage, and depletion of glutathione (GSH) levels. Responses to hydrazine were used as reference values for ranking the other chemicals. According to the MTT assay, the hydrazine-containing compounds were the most toxic, but DAGN was at the lower end of that list where the salts were listed in the order hydrazinium nitrate (HN) diethylhydrazinium nitrate (DEHN) 1,4-dihydrazinotetrazinium nitrate (DHTN) methylhydrazinium nitrate (MMHN) 2-hydroxyethylhydrazinium nitrate (HEHN) DAGN nitroaminoguanidinium nitrate (NAGN).

### 13.2 Other Diaminoguanidinium Salts

Hypergolic liquid bipropellant fuels that are self-igniting with N<sub>2</sub>O<sub>4</sub> as the oxidizer can be made from guanidinium or mono-, di-, and triaminoguanidinium as the cation and

dicyanamidate or tricyanomethanide as the anion [246]. Properties of these salts are summarized in Table 23. See also [238].

**Table 23:** Properties of hydrazidinium dicyanamidates and tricyanomethanides.

| Compound name                        | Formula                                      | Melting point |                 | Decomposition onset |     | Density<br>g/cm <sup>3</sup> |
|--------------------------------------|----------------------------------------------|---------------|-----------------|---------------------|-----|------------------------------|
|                                      |                                              | K             | °C              | K                   | °C  |                              |
| Acethydrazidinium dicyanamidate      | C <sub>4</sub> H <sub>9</sub> N <sub>7</sub> | 324           | 51 °C (decomp.) | 324                 | 51  | 1.35                         |
| Acethydrazidinium tricyanomethanide  | C <sub>6</sub> H <sub>9</sub> N <sub>7</sub> | 344           | 71              | 373                 | 100 | 1.23                         |
| Butyryhydrazidinium dicyanamidate    | C <sub>6</sub> H <sub>9</sub> N <sub>7</sub> | 322           | 49              | 328                 | 55  | —                            |
| Diaminoguanidinium dicyanamidate     | C <sub>3</sub> H <sub>8</sub> N <sub>8</sub> | 334           | 61              | 385                 | 112 | 1.36                         |
| Diaminoguanidinium tricyanomethanide | C <sub>5</sub> H <sub>8</sub> N <sub>8</sub> | 363           | 90              | 462                 | 189 | —                            |

Data source: [246]

Diaminoguanidinium azide, [(H<sub>2</sub>NNH)<sub>2</sub>C=NH<sub>2</sub>]<sub>3</sub>N<sub>3</sub>, C<sub>1</sub>H<sub>8</sub>N<sub>8</sub>, with a molecular mass of 132.13 g/mol (7.568 mol/kg) and a density of 0.0513 lb/in<sup>3</sup> = 1.43 g/cm<sup>3</sup> has an enthalpy of formation of +741 cal/g = +97.908 kcal/mol = +409.6 kJ/mol [124]. It contains 84.8% nitrogen and is a good source of nitrogen for gas generators.

The diaminoguanidinium salt of 3-nitro-1,2,4-triazol-5-one, CH<sub>8</sub>N<sub>5</sub><sup>+</sup>•C<sub>2</sub>H<sub>1</sub>N<sub>4</sub>O<sub>3</sub><sup>−</sup>, molecular mass 219.16 g/mol, crystallized in triclinic crystals, space group *P* $\bar{1}$ , with the cell parameters of *a* = 6.735(2) Å, *b* = 6.753(2) Å, *c* = 9.844(2) Å,  $\alpha$  = 88.29(2)°,  $\beta$  = 77.17(2)°,  $\gamma$  = 86.50(2)°, *V* = 435.7 Å<sup>3</sup>, *Z* = 2, and  $\rho$  = 1.671 g/cm<sup>3</sup> [247].

## 14 Triaminoguanidine

The correct nomenclature name for triaminoguanidine, CH<sub>8</sub>N<sub>6</sub>, would be 1,2,3-triaminoguanidine, with the numbers indicating the nitrogen atoms to which the additional amino group has been attached.

Chemical Abstracts Service (CAS) nomenclature may also call triaminoguanidine by the unusual names carbonohydrazone dihydrazide or carbonohydrazonic dihydrazide.

Triaminoguanidine, TAG, CH<sub>8</sub>N<sub>6</sub>, CAS RN [2203-24-9], *M* = 104.12 g/mol, contains 80.7% nitrogen. Triaminoguanidine can be prepared by reaction of dicyandiamide with hydrazine hydrate. Triaminoguanidine free base exists in the form of colorless crystals that melt at 385–393 K (112–120 °C).

The reaction between hydrazine hydrate and carbon tetrachloride at reflux can form triaminoguanidinium chloride that can be converted to the free base or other TAG salts.

Free TAG base is not very stable. It can be prepared by passing a TAGN solution through a cation-exchange column. Once a solution of the free base is at hand, it can be neutralized with any of the oxygen-rich or energetic anion acids to obtain energetic high-nitrogen compounds, salts of the triaminoguanidinium ion. The free base can be used to synthesize a number of high-nitrogen compounds and all TAG salts, such as triaminoguanidinium 5-aminotetrazolate with 81.4 mass-% nitrogen. With strong nitric acid, triaminoguanidine can also form triaminoguanidinium(2+) dinitrate salts [74].

The structure of the free base was investigated in an effort to better understand the molecular structure of its salts [248–250]. 1,2,3-Triaminoguanidine free base crystals are monoclinic, space group  $P2_1/c$ , with the lattice parameters  $a = 7.460(3)$ ,  $b = 10.274(2)$ ,  $c = 6.343(3)$  Å,  $\beta = 110.8^\circ$ ,  $V = 454.5$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho = 1.52$  g/cm<sup>3</sup>.

The enthalpies of formation of triaminoguanidine free base vapor and other guanidine derivatives were calculated by quantum mechanical methods [111].

In 14 hydrazides, <sup>14</sup>N nuclear quadrupole resonance studies were performed at 77 K [251]. The results indicated extensive delocalization of the charge in the  $\pi$ -orbital of the substituted nitrogen atom. The charge lost to the acyl oxygen is of the order of 0.3 electrons. This loss of  $\pi$ -electrons is partially balanced by an increased polarization of the  $\sigma$ -bonds. In symmetrical hydrazides this amounts to an excess charge density in the order of 0.1 electrons. In hydrazides retaining an  $-\text{NH}_2$  group, the charge in the N–N bond is polarized towards the substituted nitrogen atom.

An excellent summary with 53 references on triaminoguanidinium compounds including information on molecular structure, preparation, physicochemical properties, explosion characteristics, and applications was published in 2008 [252] but could not be translated in time to be included in this book.

### 14.1 Triaminoguanidinium Nitrate

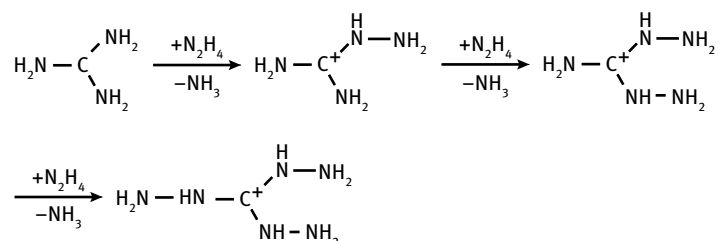
Triaminoguanidinium nitrate, also known as 1,2,3-triaminoguanidinium nitrate, TAGN,  $[(\text{H}_2\text{NNH})_3\text{C}^+]\text{NO}_3^-$ ,  $\text{CH}_9\text{N}_7\text{O}_3$ , triaminoguanidine nitrate; CAS RN [4000-16-2], is a valuable propellant and gas generant ingredient. It has a very high nitrogen content (58.67 mass-% N) and is relatively stable. It has been used in gas generants for airbag inflators, as a coolant in gun propellants to reduce barrel wear and muzzle flash, and in many other propellant formulations. With an excess of nitric acid, TAG may also form a dinitrate. Chemical Abstracts nomenclature called this compound “Carbonohydrazonic dihydrazide, dinitrate” with a CAS RN [60612-44-4P].



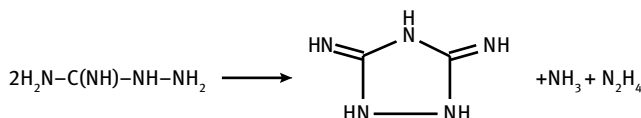
### 14.1.1 Preparation of Triaminoguanidinium Nitrate

Triaminoguanidinium nitrate can be prepared by reaction of hydrazinium(1+) nitrate with calcium cyanamide or dicyandiamide in presence of hydrazine hydrate. The other method starts with guanidinium nitrate, where gradual substitution of amino groups by hydrazino groups is possible by treating guanidinium nitrate with anhydrous hydrazine, and removal of the ammonia formed in the equilibrium.

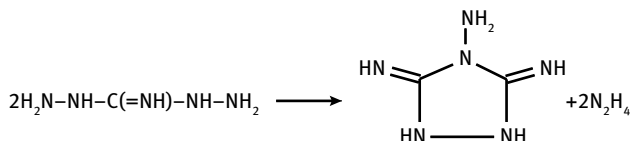
Initially, if guanidinium nitrate is dissolved in hydrazine without chemical reaction, a low-freezing, short-lived eutectic is observed at 30% guanidinium nitrate that freezes at 246 K (−27 °C) [253]. Then, within a few hours, a reaction takes place in which ammonia is liberated and an insoluble salt is formed that precipitates at room temperature. Reaction of hydrazine with guanidinium salts leads to progressive replacement of amino groups and the imino group by hydrazino groups:



It would be difficult to stop this reaction at exactly the mono- or disubstituted stage. On the other hand, an excess of hydrazine should be avoided because it will destabilize the TAGN product. Many of the guanidine–hydrazine reactions result in undesirable by-products as the result of ring-closure reactions. Aminoguanidine may close a ring to form guanazole:



Diaminoguanidine may close a ring structure to form guanazidine:



The formation of colored impurities in TAGN has been blamed for irregular ballistic behavior and incompatibility problems of propellants formulated with this material. Other unwanted ring-closure reactions may lead to pyrazoline derivatives [254].

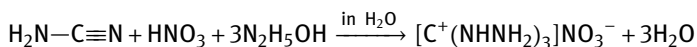
The sample purity affects the storability of TAGN even before it is processed into propellants [255]. Storage of recrystallized TAGN in IPA resulted in impurity formation.

One of the most easily obtained triaminoguanidinium compounds is triaminoguanidinium nitrate (TAGN) produced by reaction of guanidinium nitrate and hydrazine [256, 257] or hydrazine hydrate with an additional nitrate ion (from ammonium nitrate) as reaction catalysts [258]. Additional nitrate can be added to the starting mixture in the form of hydrazinium nitrate or ammonium nitrate [259] or some dilute nitric acid [260] to improve the yield. For instance, a solution of 74.5 parts by mass GuN in 400 parts by mass of 37.5% hydrazine in water and 12 parts by mass of AN was heated for 1 h at 355–275 K (82–102 °C) to expel the ammonia formed by the reaction. The TAGN crystallized in 68% yield on cooling to 283 K (10 °C). Doubling the amount of AN increased the TAGN yield to 75%; quadrupling the amount of AN increased the TAGN yield further to 83%.

Reacting a suspension of guanidinium nitrate in a C<sub>1</sub> to C<sub>5</sub> alcohol with 64% hydrazine in boiling alcohol gave TAGN in 94% yield with a minimum of melamine contamination [261]. A similar patent describes the synthesis of triaminoguanidinium salts by reacting guanidinium salts or cyanamide with hydrazine and/or hydrazine salts in an aliphatic C<sub>3</sub> to C<sub>5</sub> alcohol [262].

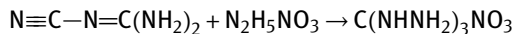
There are no color changes or other specific IR or UV absorption spectra that could be used to monitor the progressive replacement of one, two, and three amino groups by hydrazine and derive kinetics for the multi-step reaction. Instead, the kinetics of the guanidinium nitrate–hydrazine hydrate reaction were examined using the off-gas ammonia in a batch reactor at 366 K [263]. There are two reactions contributing ammonia to the off-gas, one the desirable TAGN-producing reaction and the other the metathetical reaction of AN with hydrazine. By measuring the ammonia formation rate of the AN–hydrazine reaction separately, the guanidinium nitrate–hydrazine reaction rate can be derived by the difference. The kinetics of the two reactions are different, so that the global rates measured by ammonia evolution can be used for sizing a continuous-flow stirred tank reactor, which would be more economical to operate than a batch process. Instead of obtaining coarse and irregular shaped crystals, it would be better to adjust process parameters so that the product is microcrystalline TAGN [264].

Another process for making TAGN starts out with cyanamide and reacts it with hydrazinium nitrate in aqueous solution



In one example, 4.2 g cyanamide, 9.5 g HN, 12.5 g 80% hydrazine hydrate, and 30 mL water were heated in a water bath for 4 h [265]. The TAGN crystals precipitated on cooling, were filtered, washed with methanol, and dried to give 14 g of TAGN in 83.7% yield. The salt melted at 479 K (206 °C) with decomposition. The low melting point indicates that the product may not have been very pure. The melting point should be at least 489 K (216 °C).

Instead of starting with cyanamide or calcium cyanamide, TAGN can be prepared from dicyandiamide, hydrazinium nitrate, and hydrazine hydrate [266]:



A typical reaction mixture was made up of 0.2 mol dicyandiamide, 0.25 mol hydrazinium nitrate, and 0.6 mol hydrazine hydrate. The TAGN yield was 87.7% and the melting point of the product was 215–216 °C. A similar method was used to make tris(dimethylamino)guanidinium nitrate by reaction of 0.2 mol dicyandiamide, 0.25 mol UDMH nitrate, and 0.6 mol UDMH.

Another method for preparation of TAG or TAGN starts with calcium cyanamide, a compound that was once used as a fertilizer and is readily available in industrial quantities. In order to prepare TAGN or TAG, a  $\text{CaCN}_2$  aqueous solution was treated at 363–403 K (90–130 °C) with a < 225% excess of a hydrazinium(I) nitrate solution [267]. The reaction mixture was treated with carbonates to precipitate  $\text{CaCO}_3$ , giving TAGN in at least 95% yield, along with 90% of the unreacted  $\text{N}_2\text{H}_4$ . Thus,  $\text{CaCN}_2$  of 68.94% purity was added to a 90% aqueous solution of hydrazinium(I) nitrate at 383 K (110 °C), stirred for 2.5 h,  $\text{H}_2\text{O}$  added, the temperature adjusted to 358 K (85 °C),  $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$  slowly added, filtered, the filtrate and washings cooled, and the precipitated TAGN removed to give a 94.8% yield. TAGN can be treated with an alkali and DMF is added to precipitate the free base TAG. In order to prepare the free base, a solution of 5 g TAGN and 1.2 g NaOH in 20 mL  $\text{H}_2\text{O}$  was treated with 40 mL DMF, chilled overnight, and the precipitate of TAG obtained in 66.5% yield. The base can be identified as its picrate which melts at 443–444 K (170–171 °C).

The use of a molar excess of hydrazine nitrate reactant relative to the amount of cyanamide reactant employed insures that all of the TAG will be neutralized to the nitrate salt rather than the more unstable TAG base, which is subject to decomposition to form undesirable by-products [268].

After a comparison of several candidate chemical synthesis methods for TAGN, such as the dicyandiamide method, calcium cyanamide method, cyanamide method, and the guanidinium nitrate method, the guanidinium nitrate method was selected for optimization, improvement, and scale-up [269]. The technology of TAGN synthesis by a one-step process from guanidinium nitrate using low-concentration hydrazine hydrate as raw material was scaled up to the kilogram scale. The yield was 94.8% and product purity based on characterization by melting point measurement, elemental analysis, IR, and XRD was very good.

#### 14.1.1.1 Identification and Removal of TAGN Contaminants

The problem associated with impurities in TAGN did not receive wide attention until a large shipment of TAGN desensitized with isopropanol (IPA) was delivered to Eglin AFB, Florida, from Rocketdyne in 1978 and stored for several years. Previously, TAGN was generally handled as a dry material or, if wet with a diluent, was used within

a few days. Examination of some of the TAGN shipment revealed that the IPA diluent exhibited various shades of yellow, brown, and pink.

Contaminants in TAGN can result in product discoloration and burning rate irregularities of propellants prepared with the discolored compound. It was therefore important to identify the source of discoloration and develop methods to avoid contamination during production and storage [270]. It was suggested that the culprit for discoloration is a small amount of the free base, triaminoguanidine, in the product. Triaminoguanidine is sensitive to oxygen in air and will form a variety of autoxidation products, including azo dyes and heterocyclic ring compounds. Trace metal cations will catalyze this oxidation reaction and subsequent ring-closure reactions. It is recommended to prepare and recrystallize TAGN only in non-metallic process vessels under an inert atmosphere and maintain slightly acidic conditions. Pink crystals can be washed with deionized water and the pink color removed. Other wash fluids tested were acetone-free IPA, IPA/hexane mixtures, and *n*-hexane. TAGN crystals appear as hollow cylinders when viewed under a microscope. It was believed that much of the pink color was due to liquid trapped in the hollow spaces of the cylinders. Discoloration was more likely to occur in polar fluids. TAGN wet with IPA also had a tendency to agglomerate (due to marginal solubility in IPA). TAGN processed in Freon-113 did not agglomerate, but had other ballistic irregularity problems, showing the worst irregularities of all solvents tested. Even doubly recrystallized TAGN again formed impurities after storage in IPA. TAGN should not be stored in IPA or any diluent in which TAGN has some solubility because of impurity formation. Impurities in solution can generally be removed by washing with IPA and presumably also with other polar solvents. Physically entrapped impurities can be removed by once again washing the TAGN after grinding it. The optimal conditions for synthesis of TAGN while avoiding colored impurities is to use an aqueous medium kept free of metal ions, in minimally alkaline conditions, with an absence of atmospheric oxygen.

As with most solid propellant oxidizers and additives, it is important not only to produce a pure ingredient, but also to produce it in the correct and reproducible particle size. In the case of TAGN (and many similar additives), it is possible to comminute a coarse product by wet-milling a suspension in an inert fluid [271]. In one example, 2 h of wet-milling of 3 kg coarse (av. 150  $\mu\text{m}$ ) TAGN in 20 L of 1,1,1-trichloroethane resulted in TAGN with an average particle size of 15  $\mu\text{m}$ , similar to that obtained with a colloid mill.

#### 14.1.2 Physical Properties of Triaminoguanidinium Nitrate

The molecular mass of TAGN,  $\text{CH}_8\text{N}_7\text{O}_3$ , is 166.12 g/mol = 6.020 mol/kg. The melting point of TAGN is 489 K = 216 °C = 420 °F (decomposition). The density of TAGN crystals is  $\rho = 1.594 \text{ g/cm}^3$  [272]. The oxygen balance of TAGN is -33.5% for combustion to  $\text{CO}_2$ . See also [273]. TAGN is not very soluble in water (Table 24).

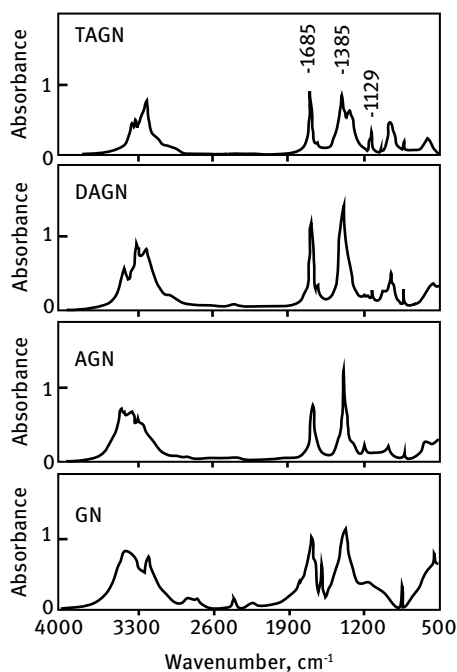
**Table 24:** Solubility of triaminoguanidinium nitrate in water.

| Temperature |     | Solubility       |
|-------------|-----|------------------|
| K           | °C  | g/100 g solution |
| 273         | 0   | 1.34             |
| 293         | 20  | 3.4              |
| 313         | 40  | 7.5              |
| 333         | 60  | 16.3             |
| 353         | 80  | 30               |
| 373         | 100 | 50               |

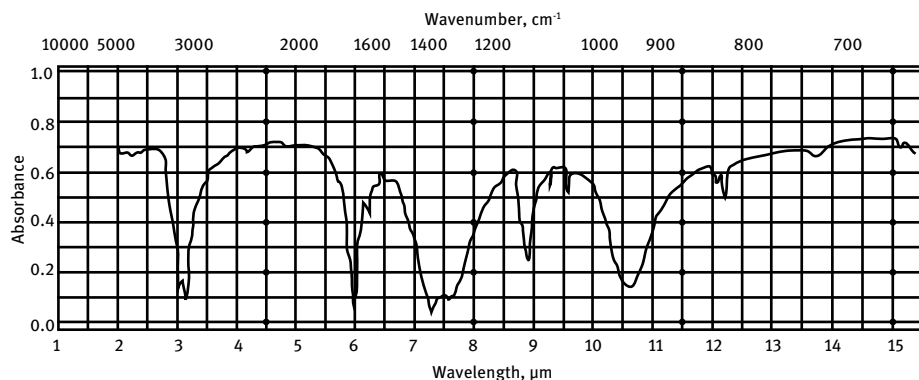
Data source: [274]

**Infrared Spectra of TAGN.**

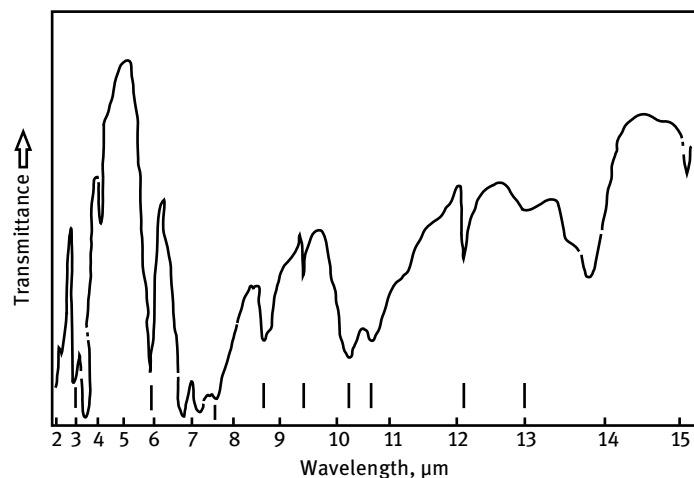
The IR spectra of TAGN are important for quality control and to study intermediates in the synthesis or thermal decomposition of this substance. In particular, it is of interest to observe the changes occurring in the spectra of guanidinium nitrate upon progressive substitution of amino groups by hydrazino groups (Figure 22).

**Figure 22:** Infrared spectra of the tri-, di-, monoamino and unsubstituted guanidinium nitrates. (Reproduced and modified from [275].)

Upon gradual and stepwise removal of the NH groups from TAGN, the bands due to N—H asymmetric stretch begin to broaden. The N—N band of medium intensity at  $1129\text{ cm}^{-1}$  in the TAGN spectrum has a significantly lower relative intensity in DAGN at  $1127\text{ cm}^{-1}$  and is barely discernable in MAGN at  $1120\text{ cm}^{-1}$ . The N—N band is fairly weak, even in TAGN which has three N—N bonds. DAGN has one N—N bond fewer and the band is weaker than in TAGN. In MAGN (AGN; only one N—N bond) the band is barely discernible. The other prominent bands in TAGN spectra are the nitrate bands, the strongest of which is at  $1384\text{ cm}^{-1}$ , and a small but sharp band at  $825\text{ cm}^{-1}$  (Figures 23 and 24). These  $\text{NO}_3^-$  bands can be identified by comparison to a pure sample of  $\text{KNO}_3$ . The infrared spectra and band assignments for TAGN have been reported previously



**Figure 23:** Infrared spectrum of triaminoguanidinium nitrate. (Reproduced and modified from [21].)



**Figure 24:** IR spectrum of triaminoguanidinium nitrate. (Reproduced and modified from [125], with permission from Levering Estate.)

[276]. The IR-active internal modes of polycrystalline TAGN below room temperature were unaffected by the transitions at 258 and 270 K, indicating that the relative atomic movements must be small. At 400 and 420 K, IR spectral changes with activation energy of 6.7 kJ/mol (1.6 kcal/mol) at 406 K occurred in the NO<sub>3</sub> sublattice. IR, XRD, and XPS spectra of TAGN are shown in [277].

#### 14.1.2.1 Thermodynamic Properties of Triaminoguanidinium Nitrate

The heat capacity of TAGN is listed in Table 25 and enthalpy data are listed in Table 26.

**Table 25:** Heat capacity of triaminoguanidinium nitrate.

| Temperature |    | Heat capacity                        |                                   |
|-------------|----|--------------------------------------|-----------------------------------|
| K           | °C | cal g <sup>-1</sup> °C <sup>-1</sup> | J g <sup>-1</sup> K <sup>-1</sup> |
| 293         | 20 | 0.391                                | 1.634                             |
| 303         | 30 | 0.403                                | 1.688                             |

Data source: [278]

**Table 26:** Thermodynamic properties of triaminoguanidinium nitrate.

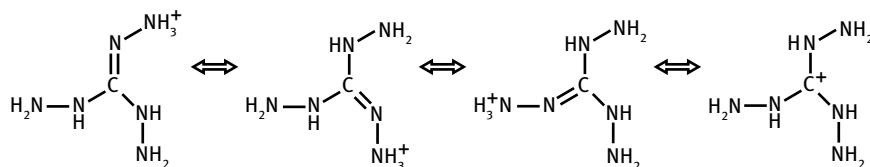
| Compound                                                   | SI units           |        | Other units   |       | References          |
|------------------------------------------------------------|--------------------|--------|---------------|-------|---------------------|
|                                                            | kJ/mol             | kJ/kg  | kcal/mol      | cal/g |                     |
| Enthalpy of formation                                      | -50.2              | -302.2 | -12.00        | -72.2 | [279, 280]          |
| $\Delta H_f^{298}$                                         | -50.2 ± 0.8        | -300.4 | -12.01 ± 0.19 | -71.8 | [131]               |
|                                                            | -48.1 ± 2.1        | -287.9 | -11.49 ± 0.5  | -68.8 | [18]                |
|                                                            | -46.68             | -281   | -11.16        | -67.2 | [281]               |
|                                                            | -58.4              | -351.5 | -13.95        | -84   | [124] #898          |
|                                                            | -47.96             | -288.7 | -11.46        | -69   | [124] #899 and #959 |
| Heat of fusion                                             | 12.6<br>(estimate) | 75.8   | 3.0           | 18.1  | [282]               |
| Heat of phase transition                                   | 3.26               | 19.6   | 0.78          | 4.69  | [276]               |
| For comparison, enthalpy of formation $\Delta H_f^{298}$ : |                    |        |               |       |                     |
| Triaminoguanidine free base                                | +240.9             | +2314  | +57.6         | +553  | [124] #958          |
| Triaminoguanidinium cation                                 | +210               | +2000  | +50.21        | +478  | [280]               |

TAGN Formula weight: 166.12 g/mol; TAG Formula weight: 104.12

For a comparison of the heats of combustion, enthalpies of formation, and enthalpies of solution of guanidinium nitrate with those of mono- and triaminoguanidinium nitrate, see Table 10.

### 14.1.2.2 Molecular Structure of Triaminoguanidinium Nitrate

Similar to the guanidinium ion, the triaminoguanidinium is also stabilized by the symmetry and multiplicity of resonance structures that can be written for the protonized compound. It should be pointed out that the positive charge on the TAG cation or on the guanidinium ion cannot be exactly located: one can write structures in which the proton attaches itself to any of the three hydrazino groups. The positive charge can also reside on the carbon, forming a symmetrical carbonium ion, the symmetry of which allows multiple resonance structures to which the thermal stability of this compound can be accredited.



Triaminoguanidinium nitrate (TAGN) is a frequently tested high-nitrogen compound and one of the thermally most stable organic hydrazine derivatives. The thermal stability can be explained by the highly symmetrical structure and resonance stabilization of the cation. The  $CN_6$  skeleton of the ion is planar. The ion is planar with the exception of the three pairs of terminal amino hydrogen atoms. The C—N bonds have partial double bond character. Hydrogen bonding between  $TAG^+$  cations and nitrate anions strengthens the stability of the crystals. The rotation of the nitrate ion (also a planar ion) is hindered by the forces of hydrogen bonding in a  $TAG^+$  environment. TAGN undergoes a phase change around 263 K. TAGN crystals occur in a low-temperature modification with a different crystal structure [283].

TAGN at room temperature crystallizes in orthorhombic crystals. Based on X-ray diffraction, the crystal structure is  $Pbcm$ ,  $a = 8.389(7)$ ,  $b = 12.684(8)$ ,  $c = 6.543(5)$  Å,  $z = 4$ ,  $\rho_{\text{measured}} = 1.60 \text{ g/cm}^3$ , X-ray density =  $1.594 \text{ g/cm}^3$  [284]. The crystal structure consists of layers of ions parallel to (001). Each nitrate ion is hydrogen bonded to two cations within each layer, and also to two cations in alternate layers. The structure consists of layers of planar triaminoguanidinium cations and nitrate anions located on mirror planes at  $\pm 1/4c$ . The cations are coplanar with the mirror planes (except for the amino H atoms), while each anion is bisected by the mirror plane with only the central N atom and one O atom on the mirror.

Neutron diffraction gave similar results [285]: orthorhombic crystals,  $Pbcm$ ,  $a = 8.389$ ,  $b = 12.684$ ,  $c = 6.543$  Å,  $Z = 4$ ,  $\rho_m = 1.60 \text{ g/cm}^3$ ,  $\rho$  (neutron diffraction) =  $1.594 \text{ g/cm}^3$ . According to the neutron diffraction results, the structure is made up of an infinite three-dimensional network of N—H...O hydrogen bonds linking the 1,2,3-triaminoguanidinium ions to the nitrate ions. The librational motions of the nitrate ion have a particularly large amplitude about an axis which is close



to the perpendicular to the plane of the ion. The differences between the atomic coordinates reported by Choi and Prince [285] and those reported by Bracuti [284] are closely correlated with the amount of thermal motion. Atoms near the centers of molecular groups agree within twice the estimated standard deviation, but atoms on the peripheries of the groups and all hydrogen atoms differ by four to five times the standard deviation. Neutron radiography is more accurate in locating hydrogen atom positions; therefore, the neutron hydrogen atom parameters should be more accurate.

The crystal and molecular structures of triaminoguanidinium nitrate were determined using single-crystal XRD to see if its unique burning rate behavior is structure related [272]. The TAGN structure consists of layers of ions parallel to the (001) plane, held together by van der Waals' forces and hydrogen bonding.

In trying to elucidate the TAGN structure by way of both experimental and theoretical study, MINDO/3 semi-empirical SCF-MO calculations of the triaminoguanidinium ion have provided information on the total energy, core-core repulsion energy, electronic energy, charge distribution, heat of formation, ionization potential, and dipole moment of the cation [286, 287]. The effect of rotation across the N–N bonds on the values of these parameters was studied. The configuration of the cation with the lowest total energy corresponds to the configuration determined by X-ray analysis on a crystal of TAGN. The energy barrier for the rotation of the three primary amino groups is of the order of 1.38 eV (133 kJ = 31.8 kcal).

In order to fully characterize nitrate ion motion/disorder in TAGN, the molecular structure of TAGN was redetermined on the basis of a positionally disordered nitrate ion model and compared with results from a model that assumed dynamic rigid-body motion in the nitrate ion [288]. It was concluded that at room temperature, the nitrate ion undergoes rigid-body motion.

A rigid-body motion study of TAGN was originally initiated to determine whether nitrate ion libration might be responsible for the fast burning rate of TAGN. A low-temperature polymorph of TAGN was discovered during the course of this rigid-body motion study [278, 283, 289, 290]. A single-crystal XRD structure determination of the low-temperature form was undertaken. The crystal structure was determined including space group, lattice parameters, atomic coordinates, extent of hydrogen bonding, and XRD density. At 169 K (–104 °C), TAGN exists in the orthorhombic space group *Pbca*, with  $a = 33.058$ ,  $b = 12.573$ , and  $c = 6.573$  Å. At 263 (–10 °C), TAGN transforms into the orthorhombic space group *Pbcm*, with unit cell dimensions at 296 K of  $a = 8.366$ ,  $b = 12.649$ , and  $c = 6.556$  Å. The density of the low-temperature form is 1.63 g/cm<sup>3</sup> and the density of the room-temperature form is 1.60 g/cm<sup>3</sup>. The densities of the two polymorphic forms of TAGN are very similar, such that phase changes should not cause grain delamination and grain swelling as observed with AN-based propellants. At room temperature, the crystal structure consists of layers of TAG cations and nitrate anions positioned in mirror planes normal to the *c*-axis. At 169 K (–104 °C), TAGN still

exists as a layered structure, but now the quasi-planes of the TAG cations are no longer coplanar with the layers and the nitrate ions are not normal to the layers.

The structure of TAGN and a similar TAG azide have been studied in an effort to explain the thermal stability behavior of these compounds.

### 14.1.3 Chemical Properties of Triaminoguanidinium Nitrate

#### 14.1.3.1 Analysis of TAGN

Polarographic determination of TAGN in a phosphate ion-buffered solution at pH 9 or in neutral or weakly acidic solutions revealed two peaks: the first is specific for TAGN and the second is observed with similar compounds (MAGN and DAGN) [291]. The first peak had characteristics for a catalyzed reaction, the second peak appeared to be diffusion controlled. The best medium for this analysis was a phosphate-buffered medium at pH 9.0 or a neutral or slightly alkaline medium with  $(\text{CH}_3)_4\text{N}^+\text{Br}^-$  as the supporting electrolyte. Both media exhibited good stability over time. This method can be used to determine TAGN content in propellant mixes or for quality control during TAGN production.

Ion chromatography can be used to monitor the progress of the stepwise replacement of amino groups with hydrazino groups in the reaction of guanidinium nitrate with hydrazine [292]. A direct, quantitative, chromatographic method has been developed for determination of AGN, DAGN, and TAGN as well as hydrazine in the reaction mixture. The ion chromatographic method has been used to monitor the synthesis of TAGN and to optimize reaction conditions.

#### 14.1.3.2 Thermal Stability of Triaminoguanidinium Nitrate

Triaminoguanidinium nitrate is one of the more stable high-nitrogen compounds, which is why it has been extensively investigated as a constituent in gun propellants and gas generants.

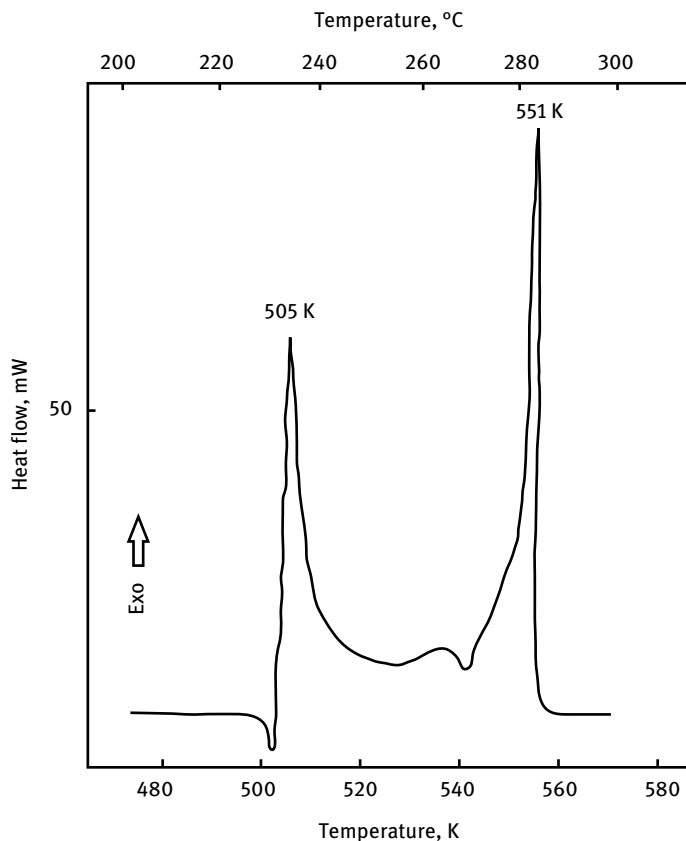
#### Rapid Pyrolysis

High-rate thermolysis of TAGN with simultaneous identification of the off-gassing products by FTIR has shown that the initial (first stage) decomposition products were ammonia  $\text{NH}_3$  and nitric acid  $\text{HNO}_3$  [276].  $\text{HNO}_3(\text{G})$  disappeared within 0.2s. The second stage of decomposition at higher temperatures produced  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{HCN}$ , followed by third-stage decomposition products of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}$ , and possibly  $\text{NO}_2$ . If the sample cell is pressurized to above 448 kPa (65 psia) with argon gas, a crossover takes place from decomposition products (dominance of nitrogen oxides) to those mostly characteristic of deflagration (dominance of carbon oxides). The thermolysis product distribution from TAGN pyrolysis was then compared to that from  $[\text{C}(\text{CH}_2\text{NH}_3)_4](\text{NO}_3)_4$ ,  $[\text{NH}_3\text{OH}]\text{NO}_3$  and  $\text{NH}_4\text{NO}_3$ .

### Differential Scanning Calorimetry Results

In the DSC at 10 °C/min, exothermic decomposition of TAGN began immediately after the melting point and reached its maximum at about 505 K = 232 °C [275] (Figure 25). A second, slightly sharper exotherm was observed at 551 K = 278 °C, with a smaller and more variable exotherm (538 K = 265 °C) occurring between the two larger exotherms. The first exotherm (just after the melting point) was the one associated with the reactions studied in the mass spectrometer (see next paragraph; mainly N<sub>2</sub> and NH<sub>3</sub> evolution). This was evidenced by the fact that when the residue from the MS experiments was run in the DSC, the first exotherm normally seen in TAGN was no longer observed.

The thermal decomposition of TAGN involved three stages with different rates of heat generation and mass loss. The first stage corresponded to an exothermic rapid reaction between 0 and 27% mass loss at up to 498 K = 225 °C, the second stage corresponded to a relatively slow endothermic reaction between 27 and 92% mass loss



**Figure 25:** Thermogram of TAGN decomposition in a DSC at 10 °C/min. (Reproduced and modified from [275].)

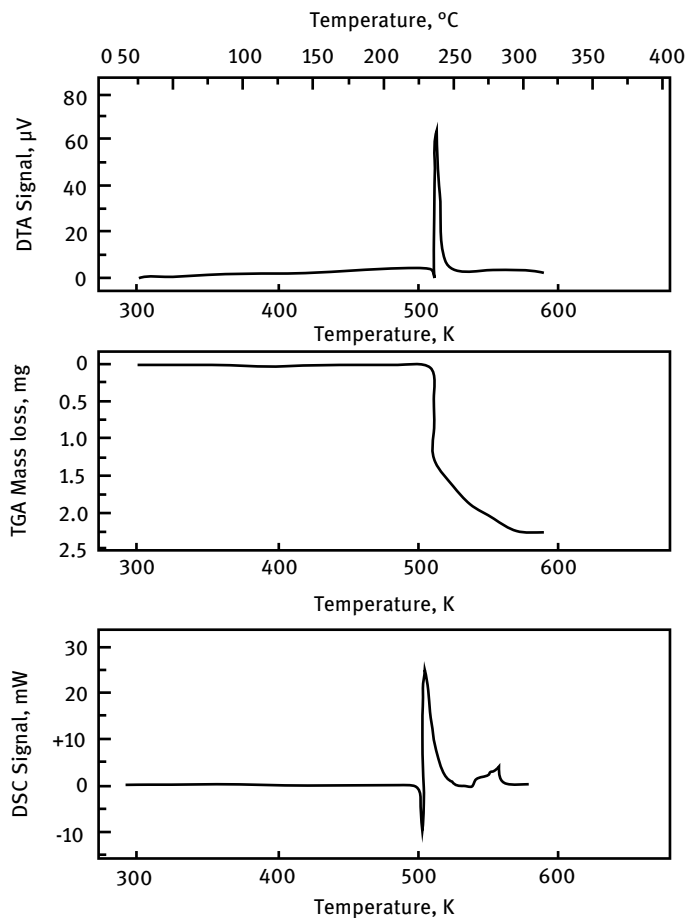
at up to 573 K = 300 °C, and the third stage was a very slow endothermic reaction between 92 and 100% mass loss, going to completion at 623 K [293]. The endotherm during the second stage was a melting-phase change process. The exothermic rapid reaction observed at the early stage of the decomposition occurred immediately after the endothermic phase change from solid to liquid. Since the weakest chemical bond in the TAGN molecule is the N–N bond (159 kJ/mol), the initial bond breakage should be in the hydrazino groups and three NH<sub>2</sub> radicals split off [294, 295]. The energy released by the dissociation of the NH<sub>2</sub> radicals (104.3 kJ/mol = 24.93 kcal/mol) is the heat produced at the early-stage decomposition of TAGN. The burning rate of TAGN is dominated by the release of the NH<sub>2</sub> radicals. It should be noted that the burning rate of TAGN is almost twice that of HMX, even though the energy contained in the unit mass of TAGN is less than that of HMX. The HNO<sub>3</sub> attached to the TAG cation is not the fragment to produce the exothermic rapid reaction observed at the early-stage decomposition process.

According to DSC analysis results, TAGN melts at 489–493 K (216–220 °C; the endothermic effect of 33.5–50.2 kJ/kg or 8–12 kcal/g) and decomposes in two stages (two exotherms with maxima at approximately 503 and 543 K = 230 and 270 °C). The heat release in the first stage (the first exotherm) is higher than in the second, and is equal to 837–1255 kJ/kg (200–300 kcal/g). Based on DTA and TGA analysis, it was shown that the fast exothermic reaction proceeded with the loss from 27 to 55% of mass [296]. In the second stage of decomposition, practically all substance (98%) was gasified (Table 27; Figure 26).

**Table 27:** DSC and DTA/TGA results with TAGN.

| DSC                  | Temperature, °C | DTA/TGA                  | Temperature, °C | Effect                           |
|----------------------|-----------------|--------------------------|-----------------|----------------------------------|
| $T_{\min}$           | 231/233         | $T_{\min}$               | 236/236         | Melting transition peak maximum  |
| $T_{\max}$           | 233/234         | $T_{\max}$               | 238/238         | Decomposition exotherm peak max. |
| $T_{\text{melting}}$ | 229/228         | $T_{\text{melting}}$     | 229/227         | Onset of melting                 |
| $T_{\text{onset}}$   | 231/233         | $T_{\text{onset}}$       | 232/232         | Decomposition exotherm onset     |
| $T_e$ onset          | 231/233         | $T_e$ onset              | —               | Extrapolated onset               |
|                      |                 | $T_{\text{mass loss 1}}$ | 226/228         | Start decomposition              |
|                      |                 | Mass loss 1              | 51/60           | Mass loss                        |
|                      |                 | $T_{\text{mass loss 2}}$ | 239/237         |                                  |
|                      |                 | Mass loss 2              | 45/36           |                                  |
|                      |                 | Total mass loss          | 96/96           |                                  |
| Endotherm enthalpy   | 35/48           | Endotherm enthalpy       | 31/31           | Melting enthalpy                 |
| Exotherm enthalpy    | 760/775         | Exotherm enthalpy        | 600/523         | Sublimation enthalpy, by DTA     |

Data source: [296]



**Figure 26:** DTA, TGA, and DSC thermograms of TAGN. (Reproduced and modified from [296].)

The exothermic reaction occurred immediately after the endothermic phase change from solid into liquid. The TGA curve consisted of two steps: The first step corresponded to a rapid reaction also observed in the DTA curve starting at a weight loss of 0% (499 K = 226 °C) and ending at a weight loss of ~55% (511 K = 238 °C). The second stage is a slow weight loss from ~55 to 96% at 623 K (350 °C). The measured DTA values were in good agreement with the literature values [294].

The kinetics of thermal decomposition of TAGN were studied by gas release under isothermal conditions in glass vessels with a Bourdon pressure gauge [297, 298]. The gaseous decomposition products that were not condensed after cooling to room temperature were analyzed chromatographically. The decomposition of crystalline powdered TAGN developed with drastic self-acceleration. The main cause of the acceleration is the progressive melting of the solid during its thermal decomposition. The cor-

responding activation energy is  $\sim 167 \text{ kJ/mol} = 40 \text{ kcal/mol}$ . The rate constant in the range 433–473 K (160–200 °C) can be expressed by the Arrhenius equation

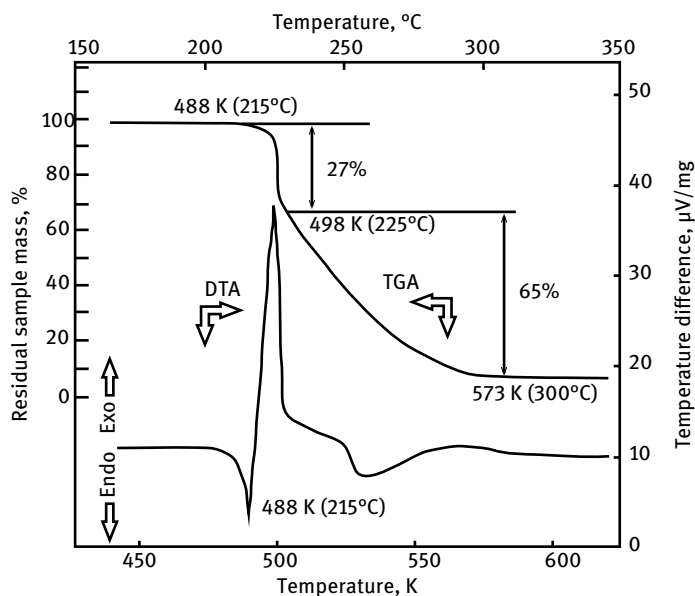
$$\log k = 14.67 - \frac{E_a}{RT}$$

where  $k$  is the reaction constant in  $\text{s}^{-1}$  and  $E_a$  is the activation energy  $E_a = 173000 \text{ J/mol}$ . The decomposition of TAGN in melt solution (a low-melting mixture of TAGN and AN) was 30 times faster than that in the solid state and proceeded at a rate decreasing with time. The main gaseous products of TAGN decomposition under those conditions were  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{H}_2\text{O}$  (but see section entitled “Analysis of Evolved Gases” below). While Lure and Smirnov [297, 298] reported the constants of TAGN thermal decomposition similar to those of AN, HAN, or HN in melt, Serushkin [282] measured that the rate of TAGN thermal decomposition was almost of three orders of magnitude higher than that of AN under the same conditions. See also [299].

The kinetics and mechanism of thermal decomposition of diaminoguanidinium nitrate (DAGN) and triaminoguanidinium nitrate (TAGN) have been studied using TGA, DTA, IR spectroscopy, and hot-stage microscopy [300]. The kinetics of thermolysis have been followed by isothermal TGA and IR. The activation energy,  $E_a$ , for the initial stage of thermolysis of DAGN was  $130 \text{ kJ/mol}$  and  $\log A = 11.4$ . The initial stage of thermolysis of TAGN was analyzed by isothermal TGA and the kinetic parameters were  $E_a = 160.0 \text{ kJ/mol}$  and  $\log A = 16.0$ . Spectroscopic and other results indicated a deamination reaction involving rupture of the N–N bond as the primary step in thermal decomposition.

The kinetics of TAGN thermal decomposition were studied by gas evolution under isothermal conditions in glass manometers in both the solid and the liquid state in a solution of AN or aromatic nitro compounds [301]. The decomposition of solid TAGN is self-accelerating. The main cause of the acceleration is progressive melting of the solid substance during its chemical transformation. TAGN decomposition rates in solution were 10–30 times higher than in the solid state. The main gaseous products of decomposition were  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{H}_2\text{O}$ , giving three mols of gas per mol of TAGN. Nitrous oxide appeared only at later stages of the process. The decomposition of TAGN is different from that of nitrate salts of other nitrogen bases like AN, HN, or HAN. Decomposition of the solid substance was investigated at 433–473 K (160–200 °C) at a loading density of the vessel by the substance ( $m/v$ ; ratio of weight to free volume of vessel) of  $0.04 \text{ g/cm}^3$ . Decomposition of TAGN in the liquid state in solution in molten AN was 30 times faster than in the crystalline state.

The TGA weight-loss curve of TAGN (Figure 27) consisted of a three-stage weight-loss process: the first stage corresponded to the rapid exothermic reaction observed in the DTA curve between 488 and 498 K (215 and 225 °C), corresponding to 27% weight loss [204]. The second stage corresponded to the slow endothermic reaction between 498 and 573 K (225 and 300 °C), corresponding to 65% weight loss. The third stage corresponded to the very slow endothermic reaction beyond 573 K (300 °C), with the



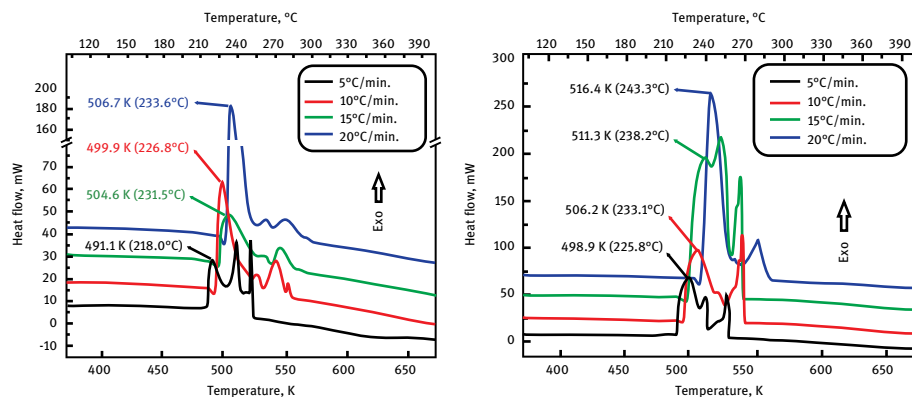
**Figure 27:** Combined TGA-DTA thermogram of TAGN. (Republished and modified from [204], with permission of ©2009 American Institute of Aeronautics Astronautics; permission conveyed through Copyright Clearance Center Inc.)

weight loss of 8% taking place at higher temperature ( $623\text{ K} = 350^\circ\text{C}$ ). The endothermic peak at  $488\text{ K}$  ( $215^\circ\text{C}$ ) in the DTA curve was recognized to be caused by melting.

### Analysis of Evolved Gases.

The gases evolved while heating TAGN in a hot bath from  $423$  to  $493\text{ K}$  ( $150$  to  $220^\circ\text{C}$ ) at a rate of approximately  $10^\circ\text{C}/\text{min}$  were analyzed by MS [275]. The results for TAGN over the temperature range  $463$ – $493\text{ K}$  ( $190$ – $220^\circ\text{C}$ ) were rather similar, with ammonia ( $35$ – $45\%$ ) and nitrogen ( $50$ – $65\%$ ) as the main gaseous products. Other gases found in small amounts included CO ( $2\%$ ), formaldehyde ( $4\%$ ), NO ( $1\%$ ), and possibly hydrazine ( $2\%$ ).  $\text{N}_2\text{O}$  was found in small amounts ( $1\%$ ), usually only at the higher temperatures ( $483$ – $493\text{ K} = 210$ – $220^\circ\text{C}$ ), or if prolonged ( $30$ – $60\text{ min}$ ) heating periods were used.

The gases evolved during TGA of TAGN, AP/TAGN, and AN/TAGN mixtures were analyzed by IR [277]. The DSC thermograms of bulk TAGN and nano-TAGN prepared by milling were very similar (Figure 28). Particle size does not seem to have a major effect on the thermal stability of TAGN. These thermograms are of a better quality than any of those shown above, because they illustrate the effect of different heating rates. While the heat evolution is resolved into several peaks at low heating rates, it merges into one major peak at high heating rates.



**Figure 28:** DSC thermograms of bulk (left) and nano-TAGN (right). (Republished and modified from [277], with permission from ©2019 American Chemical Society; permission conveyed through RightsLink.)

#### 14.1.3.3 Reactions of Triaminoguanidinium Nitrate

Many of the reactions of TAGN are undesirable and already occur during the preparation of TAGN, resulting in contaminants and by-products. On the other hand, TAGN and TAG are valuable building blocks for heterocyclic compounds because of the ease of heterocyclic ring formation. The easiest reactions to perform are those between TAG or TAG salts and carbonyl compounds, such as acetyl acetone. The reaction between acetyl acetone and TAGN gave 1,3,6-bis-(3,5-bismethyl-pyrazole-*N*-yl)-1,2-dihydro-s-tetrazine and 2,α,α'-bis(3,5-bismethyl-pyrazole-*N*-yl)-carbene-acetyl-isopropenyl hydrazine ( $C_{14}H_8Cl_4N_2$ ,  $M = 346.02$ ) [302].

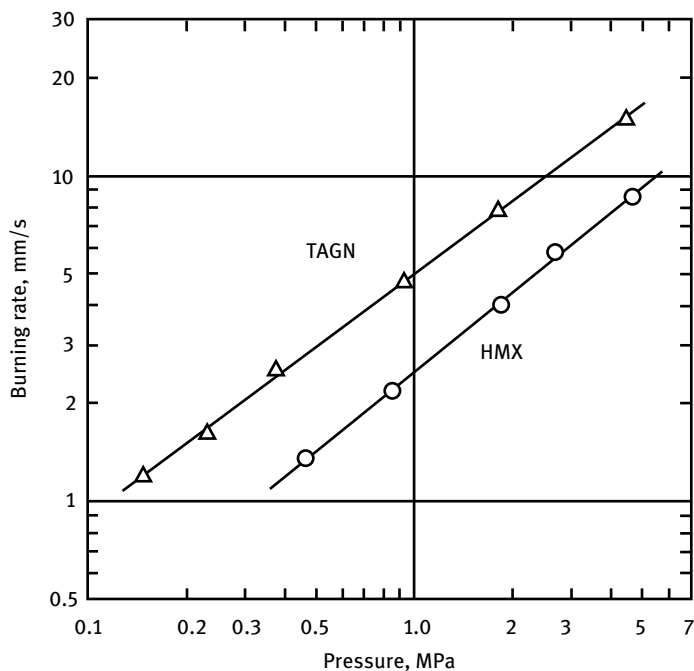
#### 14.1.4 Strand Burning of Triaminoguanidinium Nitrate

This chapter deals only with the strand burning rate of TAGN by itself or perhaps TAGN with burning rate catalysts. TAGN pellets were pressed to achieve a density of  $1.47 \text{ g/cm}^3$ , which is 98% of the theoretical maximum density, and the burning rates were measured in comparison to those of HMX pellets [281, 293]. The results are illustrated in Figure 29. TAGN burns faster than HMX.

The pressure exponent of TAGN is 0.78, which is very similar to that of HMX. The burning rate of TAGN is almost twice that of HMX, although the energy content of TAGN is lower than that of HMX and the adiabatic flame temperature of TAGN is much lower (1000 K lower) than that of HMX. The luminous flame of TAGN combustion stands some distance from the solid surface, with a dark zone in between. The luminous flame moves closer to the surface if the pressure is increased.

The combustion behavior and strand burning rates of TAGN were investigated over a wide pressure range and a detailed combustion mechanism has been proposed [282, 303]. Temperature profiles in the TAGN combustion wave were measured with





**Figure 29:** Strand burning rates of TAGN in comparison to HMX. (Republished and modified from [281], with permission of ©2002 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

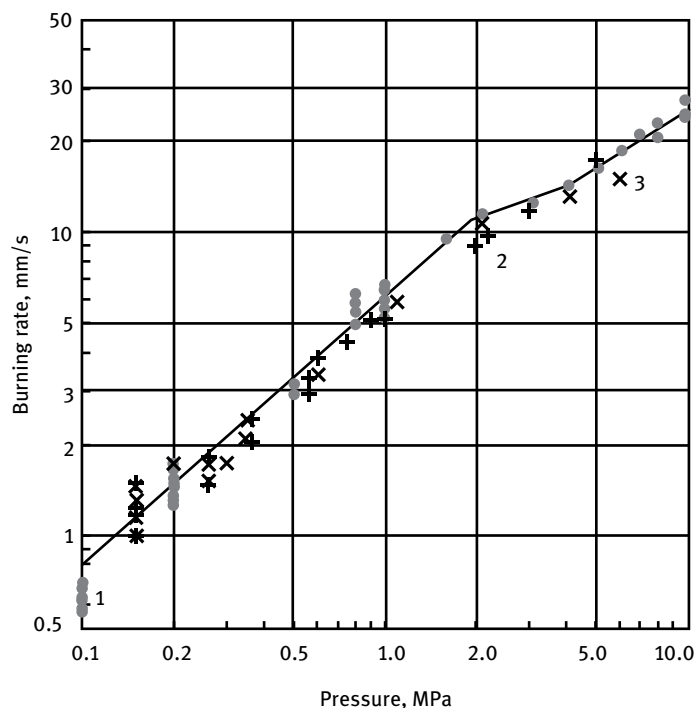
thin-wire tungsten/rhenium thermocouples. It was proposed that the burning rate of TAGN is governed by processes in the condensed phase. It was shown that the surface temperatures in combustion of TAGN as well as those of other onium salts are controlled by the process of dissociation into the free base and the acid:



A comparison of the most recent strand burning rates of TAGN determined in the form of pressed cylinders of 0.92–0.94 theoretical maximum density ( $1.594 \text{ g/cm}^3$ ) confined in transparent acrylic tubes of 7-mm inner diameter to burning rates determined at other laboratories showed a remarkably good agreement between the different sets of data (Figure 30).

TAGN in the form of samples pressed into 7-mm acrylic tubes can sustain stable burning at atmospheric pressure, although it was obvious that this is the lower pressure limit of TAGN combustion. The burning rate pressure dependence can be divided into three segments with different pressure exponents: in the interval 0.1–2 MPa

$$r_b = 6.11p^{0.88};$$



**Figure 30:** Comparison of TAGN burning rates measured in different laboratories. (Republished and modified from [282], with permission of ©2013 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center, Inc.) 1 – gray circles: Serushkin et al. [282]; 2 – + signs: Kubota, Hirata, and Sakamoto [294]; 3 – x signs: Kubota [304]

in the interval 2–4 MPa

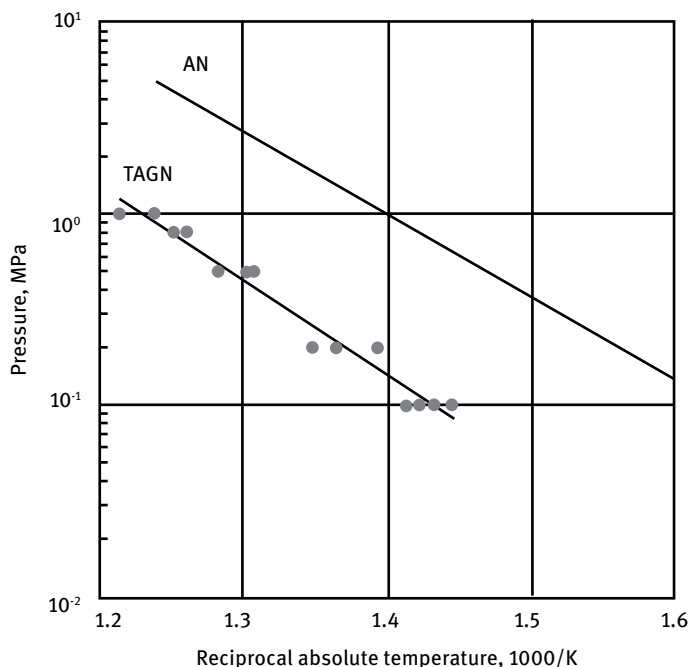
$$r_b = 8.76p^{0.34};$$

and in the interval 4–10 MPa

$$r_b = 5.97p^{0.63}$$

The surface temperature of burning TAGN increased with pressure. The surface temperature of burning TAGN was higher than that of burning AN (Figure 31), which can be explained by the fact that TAG is a stronger base than ammonia and it takes more energy to dissociate it.

It was concluded that the burning rate of TAGN is determined by processes in the condensed phase. The surface temperature in combustion of TAGN, as well as for AN and AP, is controlled by a dissociation process similar to those postulated for other onium salts [305]. It has been shown that the reaction that controls the burning rate of TAGN during combustion is decomposition at the surface temperature. For TAGN



**Figure 31:** Effect of pressure on surface temperatures of burning TAGN and AN. (Republished and modified from [282], with permission of ©2013 John Wiley Sons – Books; permission conveyed through Copyright Clearance Center, Inc.)

in pressure intervals of 0.1–2 MPa, the heat release in the condensed phase provided enough heat to warm up and melt the TAGN, and the heat flux coming from the gas phase to the surface was spent only for evaporation of non-decomposed TAGN and had no effect on the burning rate. Similar burning rate work was done in connection with an investigation on the flame structure of solid propellants [304].

The strand burning rates of TAGN and 3,6-diguanidino-1,2,4,5-tetrazine nitrate (DGTN), their combustion wave structure, and the location and chemical nature of the leading reaction on combustion were determined in a windowed 1.5-L constant pressure bomb with 7-mm diameter and 12–15-mm long samples pressed into acrylic tubes [306]. Temperature profiles in the combustion wave were measured using thin tungsten/rhenium thermocouples. Both compounds have the same structural fragment, i.e., the protonated guanidine moiety, which may result in similar combustion mechanisms. The burning rate of TAGN increased steadily as the pressure increased up to 2 MPa, showing a pressure exponent of 0.94. A kind of burning instability region set in at 2 MPa, characterized by a constant burning rate, which began to increase again at pressures higher than 4 MPa. Thermocouple measurements showed the similar surface temperatures for both salts. It was shown that combustion of both substances

obeyed the condensed-phase mechanism. The higher burning rate of TAGN connected with the higher decomposition rate in the melt layer.

#### 14.1.5 Toxicity of Triaminoguanidinium Nitrate

The LD<sub>50</sub>/14 d of TAGN in mice was 3.65 g/kg with 95% confidence limits of 3.54 to 3.76 g/kg [307]. Guanidine and derivatives of guanidine were reported to produce effects on the automatic nervous system and the neuromuscular junction. Therefore, a study was conducted to screen TAGN for effects on the physiological function of these peripheral nervous systems. Dogs were anesthetized and surgically instrumented to measure and record arterial blood pressure, lead II electrocardiogram (ECG), heart rate, contraction of the nictitating membrane upon vagus nerve stimulation, and contraction of the gastrocnemius muscle upon sciatic nerve stimulation. Intra-venous doses of 50–200 mg TAGN/kg given to anesthetized dogs caused a slightly decreased heart rate and a transient fall in arterial blood pressure followed by a slight increase. In these animals, TAGN did not alter the function of the peripheral autonomic nervous system or the neuromuscular junction. The duration of these effects was 20 to 25 minutes. TAGN belongs in the category of slightly toxic compounds.

The toxicologic and recalcitrant properties of TAGN were investigated by exposing pure cultures of microorganisms to TAGN [308]. The results indicated that while TAGN was generally bacteriostatic at concentrations of 100 ppm and above, the bacteria tested were not otherwise adversely affected by concentrations as high as 2000 ppm for contact periods up to 5 h. Under the experimental conditions of this study, TAGN was neither bactericidal nor did it appreciably affect the respiratory activity of the cells. Following exposure and subsequent removal of TAGN from solution, all bacteria tested were capable of normal growth resumption. Moreover, some bacteria were capable of degrading or at least removing TAGN from solution, thereby effectively reducing the aqueous concentration of this compound.

As a next step, a study was undertaken to examine the gaseous by-products generated from the deflagration of an experimental TAGN-based gun propellant and to compare the toxicity of these gases to those produced from standard gun propellants containing no TAGN [309]. Gas analysis results showed that TAGN-based propellants produced the same gaseous by-products as did four standard nitrocellulose (NC)-based propellants. However, quantitative differences in the response of bacteria were observed between the two groups.

The toxic effects of TAGN on the fruit fly *Drosophila melanogaster* were determined by administering the chemical via their growth medium [310]. Toxicological and reproductive effects were determined at concentrations up to 4000 ppm TAGN. Increasing the concentration of TAGN to 1000 ppm in the medium resulted in almost all cessation of pupae and larvae production, as well as approximately 50% death of adult *Drosophila*. Concentrations of 2000 ppm TAGN and above resulted in the death of almost all adult *Drosophila*. Concentrations of these levels are considered to be relatively

high, however, for practical use. Compared to other propellant ingredients, TAGN appeared to be relatively non-toxic to *Drosophila*.

TAGN was subjected to a matrix of *in vitro* assays employing microbial cells, mammalian cells in culture, and *in vivo* tests measuring potential germ cell effects in mice and rats [311]. TAGN was mutagenic and produced DNA damage in the *in vitro* assays. The response was obtained without the presence of an *in vitro* activation system, indicating that the TAGN molecule has genetic activity. No significant induction of dominant lethal effects was observed in either mice or rats. TAGN should be considered a suspect compound in terms of mutagenic and carcinogenic potential. The combined positive results from all *in vitro* assays indicated a high probability for carcinogenic activity.

Triaminoguanidinium nitrate was tested for teratogenicity in rats and administered by intra-peritoneal injections at doses of 0, 200, 400, and even 800 mg/kg during days 6–15 of gestation [312]. At the highest dose, most litters were entirely resorbed. In the highest dose group (800 mg/kg), three rats died during the dosing regimen and only one viable litter was obtained. The lower dose caused an increased incidence of runting and perinatal death. An increase in malformations due to TAGN was not observed.

#### 14.1.6 Environmental Fate of Triaminoguanidinium Nitrate Spills

The biodegradability of TAGN and wastewater from TAGN production was determined under a variety of environmental conditions [313, 314]. Supplemental carbon was required in order for biodegradation to occur under aerobic or anaerobic conditions. Although TAGN is biodegraded under both aerobic and anaerobic conditions, the nitrate portion of the salt will only degrade anaerobically (denitrification). The alternate carbon (e.g., sugar) is required for this process as well. TAGN was found to be unstable under alkaline conditions, resulting in the formation of carbohydrazide (diaminourea). No intermediates were identified during this process. No urea, guanidine cyanamide, cyanoguanidine, cyanoguanidine, or hydrazine were detected during the biodegradation of TAGN.

#### 14.1.7 Safety Properties of Triaminoguanidinium Nitrate

Triaminoguanidinium nitrate, when dry, is a class A or class 1.1 explosive with an impact sensitivity of approximately 45 kg-cm, and therefore presents a safety hazard for handling, transportation, and storage. TAGN is usually shipped and stored while wet with water or alcohol to reduce accidental ignition hazards. TAGN has been shipped wet with 20% water and some reports (Teledyne McCormick Selph MSDS) state that in two tests, the 20% water sample failed to initiate with a No. 6 blasting cap. However, there is concern that the water may evaporate and that the material could become more sensitive in transit. Other manufacturers have shipped TAGN wet with 2-propanol, but the material turned pink during storage.

The impact sensitivity of TAGN in the BAM machine is 4 N m. For comparison, the impact sensitivity of RDX in the same machine is 7.5 N m. The friction sensitivity of dry TAGN in the BAM machine is above a pistil load of 120 N, where crackling noises begin to be heard. For comparison, the friction sensitivity of RDX in the same machine is 120 N pistil load.

Table 28 gives a comparison of the increase in drop-weight sensitivity (decrease of the drop height resulting in ignition) of a series of guanidinium and guanidinium derivative salts with progressive replacement of amino groups with hydrazino groups. As can be seen from these data, the hydrazino compounds are more sensitive than the amino compounds.

**Table 28:** Drop-weight sensitivity of guanidinium and guanidine derivative salts.

| Compound name                   | Formula                                                                              | Drop-weight sensitivity, Bureau of Mines apparatus, 2 kg |
|---------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------|
| Guanidinium nitrate             | $[\text{C}(\text{NH}_2)_3]^+\text{NO}_3^-$                                           | 100                                                      |
| Diaminoguanidinium nitrate      | $[\text{H}_2\text{NC}(\text{NHNH}_2)_2]^+\text{NO}_3^-$                              | 40                                                       |
| Triaminoguanidinium nitrate     | $[\text{C}(\text{NHNH}_2)_3]^+\text{NO}_3^-$                                         | 28                                                       |
| Aminoguanidinium picrate        | $[\text{H}_2\text{NC}(\text{NHNH}_2)_2]^+\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$ | 100                                                      |
| Diaminoguanidinium picrate      | $[\text{H}_2\text{NC}(\text{NHNH}_2)_2]^+\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$ | 80                                                       |
| Triaminoguanidinium picrate     | $[\text{C}(\text{NHNH}_2)_3]^+\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$            | 80                                                       |
| Guanidinium perchlorate         | $[\text{C}(\text{NH}_2)_3]^+\text{ClO}_4^-$                                          | 40                                                       |
| Triaminoguanidinium perchlorate | $[\text{C}(\text{NHNH}_2)_3]^+\text{ClO}_4^-$                                        | 7                                                        |
| For comparison:                 |                                                                                      |                                                          |
| PETN                            | $\text{C}(\text{CH}_2\text{ONO}_2)_4$                                                | 17                                                       |
| Tetryl                          | $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{N}(\text{CH}_3)\text{NO}_2$                | 26                                                       |

Data source: [244]

#### 14.1.7.1 Explosive Properties of Triaminoguanidinium Nitrate

TAGN can be used as an explosive [274]. Confined TAGN had a detonation velocity of 5300 m/s at a packing density of 0.95 g/cm<sup>3</sup>, 7930 m/s at a packing density of 1.46 g/cm<sup>3</sup>, and of 5350 m/s at a packing density of 1.00 g/cm<sup>3</sup>. The corresponding triaminoguanidinium perchlorate has a detonation velocity of 7730 m/s at a packing density of 1.56 g/cm<sup>3</sup> and 5970 m/s at a packing density of 1.09 g/cm<sup>3</sup>. In the lead block test, explosion of TAGN caused an increase in the cavity volume by 350 cm<sup>3</sup>/10 g TAGN.

#### 14.1.8 Applications of Triaminoguanidinium Nitrate

The current chapter is limited to a summary of the physical, chemical, and safety properties of TAGN. There are many applications of TAGN that are discussed in other chapters of this book. Triaminoguanidinium nitrate is used in many propellant and gas

generant formulations because of its ability to lower the flame temperature and yet maintain high performance due to its high hydrogen and low carbon content. Applications of TAGN as a rocket propellant ingredient and in gas generants will be discussed in a future set consisting of several volumes on solid propellants and gas generants, to be published as part of the *Encyclopedia of Rocket Propellants*. Triaminoguanidinium nitrate is an essential ingredient in some gun propellants, gas generants, and pyrotechnic compositions, as well as in “green” double-base and composite rocket propellants. It enables lower molecular weight gases and reduced flame temperatures concomitant with increased impetus and muzzle velocity in guns. TAGN can also be used as an effective activator and burning rate modifier for AN-based propellants and cyclic nitramine (RDX) propellant formulations. The increased reactivity of TAGN in those propellant formulations limits the choice of binders, curing agents, and plasticizers.

There are hundreds of patents for propellant and gas generant compositions containing TAGN, which cannot all be cited here. It seems that some of the claims were farfetched and only rarely is experimental proof provided as part of the patent’s specifications.

Low-molecular-weight GAP oligomers have been used as energetic plasticizers, in particular for propellants with ingredients like TAGN that are not compatible with nitrate ester energetic plasticizers. One type of propellants used TAGN with a GAP plasticizer [315].

## 14.2 Triaminoguanidinium Perchlorate

### 14.2.1 Preparation of Triaminoguanidinium Perchlorate

Triaminoguanidinium perchlorate, also known as TAGP,  $\text{TAGClO}_4$ ,  $(\text{TAGH})\text{ClO}_4$ , 1,2,3-triaminoguanidinium perchlorate  $[(\text{H}_2\text{NNH})_3\text{C}^+]\text{ClO}_4^-$ ,  $\text{CH}_9\text{N}_6\text{O}_4\text{Cl}$ , triaminoguanidine perchlorate; carbonohydrazonic dihydrazide, perchlorate (1:1); carbonohydrazonic dihydrazide, monoperchlorate; guanidine, 1,2,3-triamino-, monoperchlorate; dihydrazinomethylenehydrazinium perchlorate, CAS RN [4104-85-2], can be prepared from aminoguanidinium bicarbonate with perchloric acid (first giving the aminoguanidinium perchlorate) followed by reaction with hydrazine hydrate. Another method is reaction of one mol of guanidinium perchlorate with three mols of hydrazine in isopropanol solution. Another method is the reaction of triaminoguanidine free base and perchloric acid in dilute solutions [316].

### 14.2.2 Physical Properties of Triaminoguanidinium Perchlorate

Triaminoguanidinium perchlorate was synthesized by nucleophilic attack of aqueous hydrazine solution on aminoguanidinium perchlorate under release of ammo-

nia [5]. TAGClO<sub>4</sub> has the highest melting point (398 K = 125 °C) among three similar compounds investigated, which can be explained by the many hydrogen bonds holding together its crystal structure. The onset of exotherm in the DSC is at 453 K (180 °C).

Other sources list the melting point of TAGP as 407–408 K (134–135 °C) and the maxima of the exotherm peaks in the DTA are at 516 and 590 K (243 and 317 °C), accompanied by violent decomposition [172].

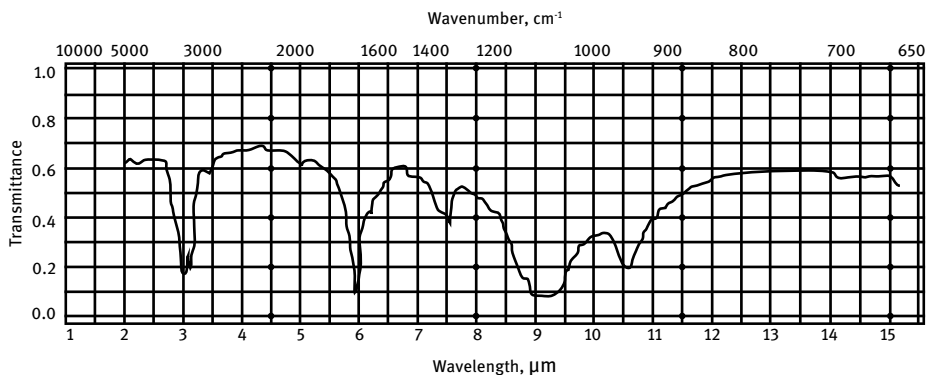
TAGClO<sub>4</sub> is less stable than AGClO<sub>4</sub>, which is more stable and decomposes at 523 K (250 °C). The structure of the perchlorate salt in the crystalline state was determined using low-temperature single-crystal XRD, indicating a monoclinic structure. The crystallographic data of aminoguanidinium, triaminoguanidinium, and azidoformamidinium perchlorate are summarized in Table 22 (in Section 12.2 “Aminoguanidinium Perchlorate”). Further information regarding the crystal structure determinations has been deposited with the Cambridge Crystallographic Data Centre [317]. The geometry of the cation is comparable to those reported for triaminoguanidinium chloride and nitrate in the literature. Again, the positive charge is delocalized, which can be seen by the similar C–N bond lengths building a planar fragment. The hydrazine N–N bonds have similar lengths between 1.40 and 1.42 Å. The layer packing is influenced by several N–H···O and N–H···N hydrogen bonds, resulting in a high density of 1.740 g/cm<sup>3</sup>. TAGClO<sub>4</sub> was characterized using multinuclear (<sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N) NMR spectroscopy. The <sup>15</sup>N NMR and <sup>13</sup>C NMR chemical shifts of TAGClO<sub>4</sub> (in ppm) are δ(N1)–289.1, δ(N2)–329.4, δ(N3)–289.1, δ(N4)–329.4, δ(N5)–289.1, δ(N6)–329.4, and δ(C1) 159.5. The IR (ATR, cm<sup>–1</sup>) wave numbers are ν = 3293(vs), 1680(s), 1359(w), 1218(w), 1056(s), 955(m), 936(m), 707(w), and 618(m), and the Raman (excited with 1064 nm) lines (in cm<sup>–1</sup>) are 3363 (8), 3305 (17), 1686 (4), 1638 (2), 1361 (2), 1146 (4), 937 (100), 890 (15), 626 (13), 461 (18), 414 (7), and 260 (7). The enthalpy of formation of crystalline TAGClO<sub>4</sub> is +121 ± 17 kJ/mol. The enthalpy of formation of TAGClO<sub>4</sub> in aqueous solution is +36.3 kJ/mol (+8.68 kcal/mol).

The IR spectrum of TAGP (from a different source) is shown in Figure 32.

The crystal structure of TAGP was determined by single-crystal XRD [316]. The results showed that TAGP crystals belong to the monoclinic system with space group *P*2<sub>1</sub>/*c* and cell parameters of *a* = 1.0213(11) nm, *b* = 1.4869(15) nm, *c* = 1.0936(11) nm, and β = 102.91(2)°. TAGP was characterized by elemental analysis, FTIR, DSC, and DTA/TGA. The TGA results showed that the title compound lost 99.7% mass at 730 K (457 °C) with a heating rate of 10 °C/min.

Triaminoguanidinium chloride may not be useful as a rocket propellant, but it may be used as an intermediate in the synthesis of other TAG salts; therefore, its crystal structure has been determined just to see how it differs from that of other TAG salts [318]. The hexagonal structure (*P*6<sub>3</sub>/*m*) has unit cell dimensions: *a* = *b* = 7.480(1) Å and *c* = 6.218(1) Å. The structure consists of layers of ions parallel to (001) located at + or –1/4 *c*, held together by van der Waals forces. The C–N bond length is 1.325(2) Å and the N–N bond length is 1.411(4) Å, which agrees quite well with the bond lengths found





**Figure 32:** Infrared spectrum of triaminoguanidinium perchlorate. (Reproduced and modified from [21].)

in TAGN. The heat of formation of triaminoguanidinium chloride in aqueous solution is +5.1 kJ/mol (+1.23 kcal/mol) [279, 280].

#### 14.2.3 Safety Properties of Triaminoguanidinium Perchlorate

Triaminoguanidinium perchlorate is a potential rocket propellant, gas generant, and explosive ingredient, but it is very hygroscopic and very sensitive to impact and friction [243]. The drop-weight impact sensitivity 50% point is at only 7 cm with a 2-kg weight (compared to 17 cm for PETN), which means it is very sensitive to accidental ignition and explosion by mechanical shock.

Similar applications in explosives have been suggested for diaminoguanidinium perchlorate and diaminoguanidinium picrate [243]. The impact sensitivity of triaminoguanidinium perchlorate can be reduced by addition of lithium perchlorate.

If triaminoguanidinium perchlorate were to be used as an oxidizer in solid composite propellants, its particle size would have to be reduced to achieve high burning rates. Grinding TAGP is virtually impossible due to the high friction and impact sensitivity of the dry material. It has therefore been suggested to convert TAGP to a solid solution by forming a low-melting eutectic with  $\text{LiClO}_4$ . The eutectic mixture containing 35% TAGP and 65%  $\text{LiClO}_4$  melts at 355 K (82 °C) and has an impact sensitivity of 20 cm with a 2-kg weight, thus it is less sensitive than pure TAGP. The eutectic containing 65% TAGP and 35%  $\text{LiClO}_4$  is a liquid at room temperature. Such low-melting oxidizers could be homogeneously mixed with the monomer binder prior to polymerization and would enable very uniform oxidizer distribution throughout the polymerized grain and high solids loading [319]. TAGP: $\text{LiClO}_4$  ratios of 65:35 to 35:65 were recommended for such solid solutions with polyacrylamide or polymethylacrylamide binders.

The impact sensitivity of  $\text{TAGClO}_4$  as tested in the BAM fall hammer machine is 3 N m and the friction sensitivity is 45 N. It is more sensitive than  $\text{AGClO}_4$ .

#### 14.2.4 Explosive Performance of Triaminoguanidinium Perchlorate

Triaminoguanidinium perchlorate has a detonation velocity of 7730 m/s at a packing density of  $1.56 \text{ g/cm}^3$  and of 5970 m/s at a packing density of  $1.09 \text{ g/cm}^3$  [274].

### 14.3 Triaminoguanidinium Dinitramide

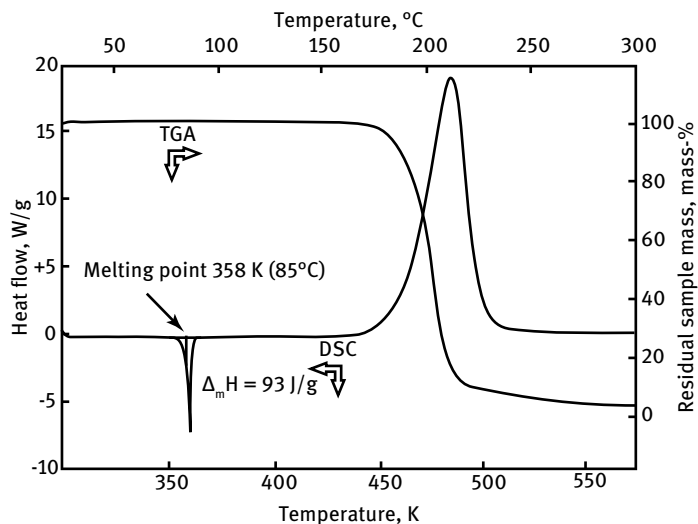
Triaminoguanidinium dinitramide, also known as triaminoguanidinium dinitramide, 1,3,5-triaminoguanidinium dinitramide; carbonohydrazone dihydrazide, compd. with *N*-nitronitramide (1:1);  $[(\text{H}_2\text{NNH})_3\text{C}^+][\text{N}^-(\text{NO}_2)_2]$ , TAGDN,  $\text{C}_1\text{H}_9\text{N}_9\text{O}_4$ , CAS RN [252062-65-0P], with a molecular mass of 211.14 g/mol and an oxygen balance of  $-18.94\%$  melts at 360 K (87 °C) [131].

The energetic compound 1,3,5-triaminoguanidinium dinitramide was prepared in good yield (82%) and fully characterized by single-crystal XRD, IR and Raman spectroscopy, multi-nuclear NMR spectroscopy, MS, and elemental analysis as well as thermal and mechanical sensitivity (DSC, thermal calorimetry, impact, friction, and ESD sensitivity tests) [320].

For the heats of combustion, enthalpies of formation, and enthalpies of solution of triaminoguanidinium dinitramide, see Table 13 in section “Guanidinium Dinitramide” and for the same data plus theoretical detonation performance data, see Table 29 in the “Other Triaminoguanidinium Salts” section.

Two dinitramide salts with a very high heat of formation, i.e., triaminoguanidine dinitramide (TAGDN, CAS RN [252062-65-0P]) and guanylazide dinitramide (GADN, CAS RN [639818-61-4P]), were evaluated as propellant ingredients [321]. The density of crystalline TAGDN is  $1.57 \text{ g/cm}^3$ , which is in the same range as the density of the free base itself ( $1.521 \text{ g/cm}^3$ ) and TAGN ( $1.594 \text{ g/cm}^3$ ). Thermochemical calculations showed that TAGDN propellants have a higher impetus than the corresponding GADN propellants at a given flame temperature. The melting point and enthalpy of melting of TAGDN was found to be 358 K (85 °C) and 93 J/g, respectively. At a heating rate of 10 K/min, TAGDN started to decompose at approximately 433 K (160 °C; Figure 33).

Preliminary sensitivity testing of crystalline TAGDN indicated that it was very sensitive to friction. Therefore, TAGDN was prilled by a melt-emulsion technique to form spherical particles. However, this procedure did not decrease the sensitivity. Due to its high sensitivity, TAGDN should be handled with care, and it is questionable whether it can ever be used in solid propellants. The solubility of TAGDN in water was measured to evaluate it as an energetic component in liquid monopropellants, but the solubility of TAGDN is low, and, therefore, TAGDN is less attractive than ADN for liquid monopropellants.



**Figure 33:** DSC and TGA curves for TAGDN. (Republished and modified from [321], with permission from ©2003 John Wiley Sons; permission conveyed through Copyright Clearance Center.)

If the heat of formation of a nitrate (XN) is known, it seems possible in many cases to calculate the heat of formation of the corresponding dinitramide (XDN) by the following equation:

$$\Delta H_f \text{XDN} = \Delta H_f \text{XN} + 230n \left( \frac{\text{kJ}}{\text{mol}} \right)$$

where  $n$  is the number of anions per cation. Applying this formula to TAGN and TAGDN gives a predicted standard enthalpy of formation for TAGDN of +184 kJ/mol.

Some of the most promising candidates for high-nitrogen compounds are triaminoguanidinium dinitramide and triaminoguanidinium 1-methyl-5-nitrimino-tetrazolate [322, 323]. They are even evaluated as potential replacements for RDX.

#### 14.4 Triaminoguanidinium Nitroformate

Triaminoguanidinium nitroformate, TAGNF, was one of four guanidine derivative nitroformate compounds prepared and characterized by a group of researchers at the University of Munich in Germany [193, 195]. The physical and sensitivity properties of TAGNF are summarized in Tables 14 and 16 above. As opposed to AGNF and DAGNF, which already decompose to the corresponding nitrate salts when standing in aqueous solution at room temperature, TAGNF is quite stable and can be stored indefinitely. The theoretically predicted values for the velocity of detonation and the detonation

pressure for ANF, HNF, MNF, GNF, AGNF, DAGNF, and TAGNF all lie within the range expected for high explosives such as RDX, and some are even superior to TNT, while at the same time releasing larger amounts of gaseous decomposition products and having a more favorable oxygen balance. Of all the compounds listed in Tables 10 and 13, HNF has the highest predicted values for detonation pressure (380 kbar) and the velocity of detonation (9286 m/s), whereas ANF shows the most positive oxygen balance with a value of +19%. Of the compounds listed in Tables 14 and 16, TAGNF is not only thermally more stable compared to AGNF and DAGNF (which decompose on standing at room temperature after several hours), but it also shows the highest predicted values for the detonation pressure (330 kbar) and the velocity of detonation (8982 m/s). TAGNF has the highest positive heat of formation (+59.1 kcal/mol) in this group.

Another salt similar to TAGNF which should be examined is the di-TAG salt of tetranitroethane (TAGTE). TAGTE has a high oxygen to carbon ratio (2 to 1) and good physical properties.

### 14.5 Triaminoguanidinium Azide

Triaminoguanidinium azide, also known as 1,2,3-triaminoguanidinium azide; hydrazoic acid, compound with 1,2,3-triaminoguanidine (1:1); TAG azide, TAZ, TAGZ, "TAGA,"  $[(\text{H}_2\text{NNH})_3\text{C}^+]\text{N}_3^-$ ,  $\text{CH}_9\text{N}_9$ , triaminoguanidine azide, CAS RN [15067-49-9], with a molecular mass of 147.15 g/mol (6.795 mol/kg), can be prepared in 70% yield by reaction of triaminoguanidinium sulfate with sodium azide in dilute alcohol and filtering out the insoluble sodium sulfate [324]. A product made by this method will contain some sodium sulfate as a contaminant. Triaminoguanidinium azide was tested as a rocket propellant at Atlantic Research Company under contract AF33(616)6623 as early as 1961. Propellants containing TAG azide, beryllium, and beryllium hydride were supposed to achieve specific impulse ( $I_{\text{sp}}$ ) values close to 300 s. One of the oxidizers considered was hydrazinium nitroformate (HNF). This is one of the first mentions of HNF as a rocket propellant. Only several decades later did HNF undergo renewed examination as a rocket propellant.

Using a cation-exchange technique in non-aqueous solvents, TAG azide can be prepared from TAG<sup>+</sup>-loaded ion-exchange resin and a methanolic solution of sodium azide [325, 326]. A lightly cross linked, strong acid cation resin was loaded with TAG ion by passing an excess aqueous solution of TAGN slowly through the column. After the TAGN feed solution was depleted, the column was rinsed with deionized water until the effluent had a pH of 7 (neutral). Water and dissolved oxygen were removed by displacement of the water by an excess of anhydrous methanol that had previously been deaerated by boiling and cooling under nitrogen gas. Triaminoguanidinium azide was then eluted from the column with an oxygen-free anhydrous methanolic solution of sodium azide. The effluent was protected from air oxidation by collection under a layer of iso-octane (or any inert non-polar liquid).

Overnight refrigeration of the protected effluent resulted in the precipitation of white TAGZ crystals which were filtered and dried under vacuum. The product initially obtained by this method was white and quite hygroscopic. The product did not rapidly discolor when exposed to dry air, but would rapidly change color in humid air. This suggests that pure TAGZ is relatively stable to dry air, but is highly reactive in moist air. This method works in non-aqueous solutions and facilitates removal of the solvent at the end of the process. The X-ray density of TAGZ is  $1.45 \text{ g/cm}^3$ . The enthalpy of formation is  $+414 \text{ kJ/mol}$  ( $+99 \text{ kcal/mol}$ ). The oxygen balance of TAGZ is  $-70.68\%$ . It has a positive heat of formation  $\Delta H_f = +464 \text{ kJ/mol} = +110.9 \text{ kcal/mol}$  and a high nitrogen content =  $85.70\% \text{ N}$ . The FTIR spectrum exhibited stretching frequencies at  $2100 \text{ cm}^{-1}$  ( $-\text{N}_3$ ) and at  $3400 \text{ cm}^{-1}$  ( $-\text{NH}_2$ ). TAGZ is less impact and friction sensitive than other conventional nitrogen-rich compounds. The drop-weight impact height for 50% explosion for TAGZ is 170 cm and the friction insensitivity is  $36 \text{ kg}_f$ .

A disadvantage of the reaction of TAGN with  $\text{NaN}_3$  is that it may leave some solid impurities like  $\text{NaN}_3$  unreacted and the by-product,  $\text{NaNO}_3$ , as contaminant in the final product. An alternate method to the reaction of TAGN with  $\text{NaN}_3$  with a cation-exchange resin is preparation of TAGZ in non-aqueous medium by reaction of triaminoguanidine free base with hydrazoic acid solution formed by ion-exchange resin and  $\text{NaN}_3$  [327]. The reaction of H-loaded sulfonate resin and  $\text{NaN}_3$  in methanol can produce  $\text{HN}_3$  in solution, which is easy to neutralize with a solution of triaminoguanidine free base and the salt then precipitates out. See also [328].

Triaminoguanidinium azide forms a double salt with hydrazinium azide, frequently abbreviated as THA. The THA salt is obtained in 58% yield from triaminoguanidinium sulfate, hydrazinium sulfate, and sodium azide in methanol solution [329]. This compound with a gross formula of  $\text{CH}_{14}\text{N}_{14}$  has a density of  $1.46 \text{ g/cm}^3$  and a heat of formation of  $665 \pm 4 \text{ kJ/mol}$  ( $158.9 \pm 1 \text{ kcal/mol}$ ). It is sensitive to impact (50% fire at 17.5 cm with a 2-kg weight) and decomposes at 423 K.

TAG azide forms another double salt with TAGN called TAZN, which crystallizes as orthorhombic (space group *Pbca*) crystals with  $a = 12.647(3) \text{ \AA}$ ,  $b = 6.573(2) \text{ \AA}$ , and  $c = 16.550(7) \text{ \AA}$  [330, 331]. Azide and nitrate ions are randomly distributed over eight general positions in the space group *Pbca* crystal lattice. This compound forms as a contaminant if nitrate ion is present during the preparation of TAG azide. The calculated X-ray density was  $1.52 \text{ g/cm}^3$ . Elemental analysis indicated that this compound contained 9.53% carbon, 78.17% nitrogen, 5.78% hydrogen, and, unexpectedly, 6.15% oxygen. In contrast, TAZ theoretically contains 8.16% carbon, 85.71% nitrogen, and no oxygen.

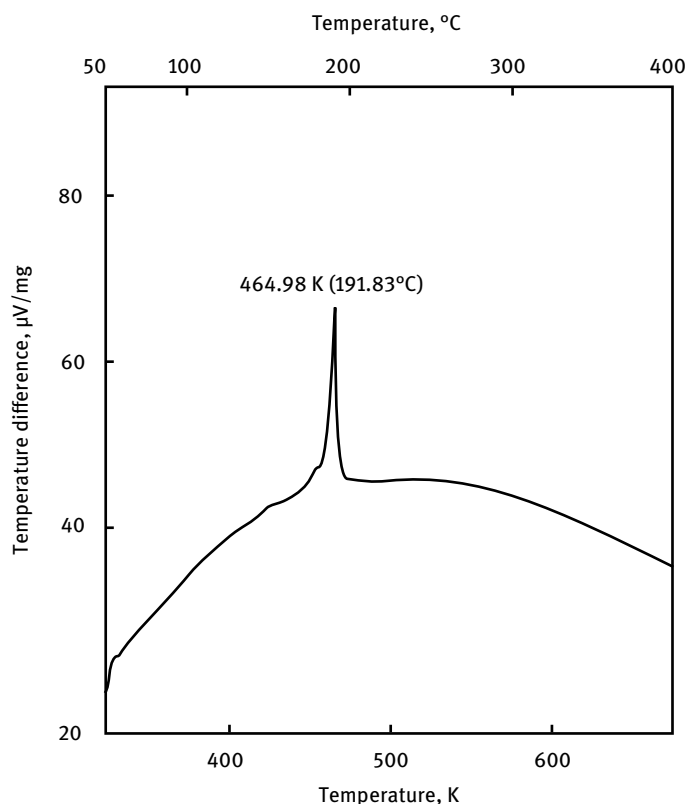
When making triaminoguanidinium azide by reaction of sodium azide with a cation-exchange resin, it was inevitable to leave some solid impurities like unreacted  $\text{NaN}_3$  and the by-product  $\text{NaNO}_3$  in the final product, and the yield of TAGZ was only 23% based on TAGN. In order to avoid this problem, TAGZ was synthesized

in non-aqueous medium by the reaction of free triaminoguanidine (TAG) with fresh  $\text{HN}_3$  solutions formed by ion-exchange resin and  $\text{NaN}_3$ , [332]. The neutralization of TAG with  $\text{HN}_3$  should be theoretically complete, but the yield of TAGZ was only 73.5% and 50% based on TAG and TAGN, respectively.

The enthalpy of formation of TAGZ is  $+718 \text{ cal/g} = +105.6 \text{ kcal/mol} = +442 \text{ kJ/mol}$  and the density is  $0.0520 \text{ lb/in.}^3 = 1.439 \text{ g/cm}^3$  [124].

#### 14.5.1 Thermal Decomposition of Triaminoguanidinium Azide

The thermal decomposition of TAGZ consisted of a four-stage heat-generation and mass-loss process when measured by DTA-TGA as shown in Figure 34 [134]. The first stage corresponded to the endothermic reaction observed in TGA between 363.6 and 416 K (90.45 and 143 °C), corresponding to 28.17% weight loss. The second stage corre-



**Figure 34:** DTA-TGA thermogram of triaminoguanidinium azide. (Republished and modified from [134], with permission of ©2009 Elsevier Science Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

sponded to an endothermic melting phase change from solid to liquid at 445 K (172 °C), followed by a rapid exothermic reaction between 445 and 450 K (172 and 177 °C) accompanied by a 30.70% weight loss. The third stage corresponded to endothermic decomposition between 450 and 587 K (177 and 314 °C), corresponding to 24.34% weight loss, and the fourth stage corresponded to a very slow endothermic reaction at the higher temperature (beyond 587 K [314 °C]) with 13% weight loss. DTA experiments indicate that TAGZ decomposed endothermically at the first stage, indicating the cleavage of  $\text{HN}_3$  at 388 K (115 °C). It underwent endothermic melting of the products at 445 K (172 °C) followed by rapid exothermic decomposition at up to 478 K (205 °C). Thereafter, it underwent a very slow endothermic decomposition. Similar data were obtained by DSC (Figure 34). The DSC thermogram showed that the decomposition of TAGZ took place with two endotherms and one exotherm. The first endotherm appeared between 363 and 416 K (90 and 143 °C), with a peak temperature at 388.3 K (115.2 °C). The second endotherm took place between 423 and 450 K (150 and 177 °C), with a peak temperature at 442.8 K (169.7 °C), whereas the exotherm appeared between 450 and 478 K (177 and 205 °C) with a peak temperature at 459 K (185.9 °C).

If TAGZ is heated to 453 K, it forms a polymer by auto-condensation and loss of hydrazine [333].

#### 14.5.2 Applications of Triaminoguanidinium Azide

The use of TAGZ in CMDB propellants has been patented [334]. Other applications are in pyrotechnic disseminating gas generators, where an excessively hot disseminating gas would damage the material (e.g., a chemical warfare agent) to be disseminated [335]. In other applications of TAGZ, it is advantageous that the exhaust of the rocket is so cool that it does not interfere with radio signal transmission [336].

### 14.6 Other Triaminoguanidinium Salts

The triaminoguanidinium cation is already a key component in high-nitrogen compounds. The nitrogen content can be increased further by combining it with nitrogen-rich anions.

Upon encountering a high-nitrogen compound containing a triaminoguanidinium cation and a tetrazolate anion, should we reference it here in Section 14 or in chapter “Heterocyclic and Heterocyaloaliphatic Amines” in Section 10 on tetrazole derivatives? In accordance with the rules established at the beginning of this chapter, salts are arranged by the cations first, and the compound is treated here as a triaminoguanidinium salt.

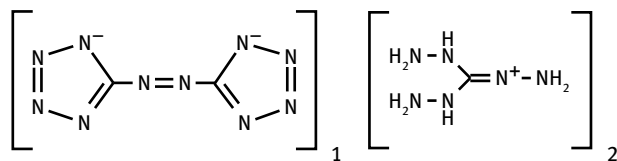
### 14.6.1 Triaminoguanidinium 5-Aminotetrazolate

A solution of the free triaminoguanidine base in methanol can be used to synthesize a number of high-nitrogen compounds, such as triaminoguanidinium 5-aminotetrazolate,  $C_2H_{11}N_{11}$ , by direct reaction of TAG with 5-AT [337]. The crystallized product first obtained is a hemihydrate that can be dehydrated by keeping it in a vacuum desiccator above  $P_2O_5$  at 353 K for 18 h. The dry product melts at 414–415 K (141–142 °C). Triaminoguanidinium 5-aminotetrazolate contains 81.5 mass-% nitrogen, is thermally stable below 403 K (130 °C), and is hygroscopic. The density of triaminoguanidinium 5-aminotetrazolate is  $\rho = 1.525 \text{ g/cm}^3$  and the heat of formation is  $\Delta H_f = +356 \text{ kJ/mol} = +85 \text{ kcal/mol}$ .

Bis(1,2,3-triaminoguanidinium) bis(5-aminotetrazolate) monohydrate,  $2[CH_9=N_6^+]\bullet 2[CH_2N_5^-]\bullet H_2O$ ,  $M = 396.4$ , is a high-nitrogen compound [338]. It crystallizes in monoclinic space group  $C2/c$  crystals with  $a = 10.448(2) \text{ \AA}$ ,  $b = 10.387(1) \text{ \AA}$ ,  $c = 15.544(3) \text{ \AA}$ ,  $\beta = 93.11(1)^\circ$ ,  $V = 1684.4(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 1.56 \text{ g/cm}^3$ .

### 14.6.2 Bis(triaminoguanidinium) 5,5'-Azotetrazolate

Bis(triaminoguanidinium) 5,5'-azotetrazolate, also known as di(triaminoguanidinium) 5,5'-azotetrazolate, TAGzT, TAGAT,  $C_4H_{18}N_{22}$ ,  $C_2H_2N_{10}\bullet 2CH_8N_6$ , CAS RN [2165-23-3], is a unique energetic high-nitrogen compound that has received a lot of attention during the past two decades. TAGzT is also described in CAS as “carbohydrazonic dihydrazide, compound with 5,5'-(1,2-diazenediyl)bis[2H-tetrazole] (2:1).”



Triaminoguanidinium azotetrazolate (TAGAT) is an energetic material with one of the highest nitrogen contents (82.3 mass-% N). The friction sensitivity in the Julius Peters apparatus is 230 N. The drop-weight sensitivity with a 2-kg mass is  $H_{50} = 25 \text{ cm}$ . The ESD sensitivity is 0.312 J.

Additional TAGzT properties are listed in Section 10 “Tetrazoles” of chapter “Heterocyclic and Heterocycloaliphatic Amines.” The density of TAGzT is  $1.6 \text{ g/cm}^3$  and the enthalpy of formation is  $+1076 \text{ kJ/mol}$  ( $+257 \text{ kcal/mol}$ ).

Bis-triaminoguanidinium azotetrazolate (TAGAT, TAGzT,  $C_4H_{18}N_{22}$ ) has been evaluated as an additive to gun propellants to reduce barrel wear. TAGzT has been evaluated as an additive to and/or as a replacement for RDX in nitramine propellants. The strand burning rates of mixtures of TAGzT and RDX showed a peculiar behavior which necessitated a more in-depth investigation. Because this compound is a salt of an amide cation with a heterocyclic amine anion, it is also described in more detail in



chapter “Heterocyclic Amines.” The burning rate and sensitivity depend on the particle size of the material, which is not very soluble in most common solvents. A variety of solvents were evaluated to find the best solvent for recrystallization of TAGzT to obtain crystals with a controlled crystal size [339].

The thermal decomposition of TAGzT was investigated by TGA, DSC, gas (solid) *in-situ* thermolysis, and rapid-scanning FTIR [340]. The results showed that thermal stability of TAGzT can reach up to 473 K (200 °C). The thermal decomposition of TAGzT was insensitive to pressure. The condensed-phase products at 738 K (465 °C) consisted of carbon black,  $\text{NH}_4\text{N}_3$ , and melem. The thermal decomposition kinetic parameters and kinetic rate equations of TAGzT were obtained from the DSC data, and a thermal decomposition mechanism for TAGzT was proposed.

The thermal decomposition characteristics of triaminoguanidinium azotetrazolate (TAGzT), 3,6-bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz), and 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112) were studied by DTA, DSC, high-pressure DSC, TGA-DTA, and T-jump/FTIR [341]. The thermal decomposition kinetic parameters, the  $E_a$  and  $\log A$  values, of TAGzT, BTATz, and LAX-112 were 231.87, 317.41, and 175.62 kJ/mol, and 25.01, 28.07, and 16.20 s<sup>-1</sup>, respectively.

The thermal decomposition products of three high-nitrogen compounds, triaminoguanidinium azotetrazolate (TAGzT or TAGAT), guanidinium azotetrazolate (GUzT), and 3,3'-diamino-4,4'-azoxyfurazan (DAAF), were analyzed on-line by MS to identify the weak links in the molecules so that in the future, new compounds could be synthesized that avoided these weak links [342]. The fragments allow one to backtrack to where they came from. The TAGzT decomposition showed a product distribution consisting of three temperature-correlated  $m/z$  groups: group I:  $\text{C}_2\text{H}_y\text{N}_z$  ( $z = 2, 3$ , or  $4$ ),  $\text{C}_3\text{H}_y\text{N}_z$  ( $z = 4$ , or  $5$ ), and  $\text{H}_y\text{N}_z$  ( $z = 1$ , or  $2$ ) evolving from 453–478 K (180–205 °C); group II:  $\text{C}_1\text{H}_y\text{N}_z$  ( $z = 3$ , or  $4$ ) and  $\text{C}_2\text{H}_y\text{N}_z$  ( $z = 4$ , or  $5$ ) evolving from 453–553 K (180–280 °C); and group III:  $\text{C}_3\text{H}_y\text{N}_z$  ( $z = 5$  or  $6$ ) evolving from 493–553 K (220–280 °C). Products from GUzT decomposition could be separated into three  $m/z$  groups which evolved in three stages from 485–528 K (212–255 °C), from 493–533 K (220–260 °C), and from 488–533 K (215–260 °C). The DAAF decomposition products showed a broad temperature range variation under low and high confinement in the overall range from 393 to 543 K (120 to 270 °C). For comparison, RDX was tested under the same conditions, and it decomposed between 483–533 K (210–260 °C).

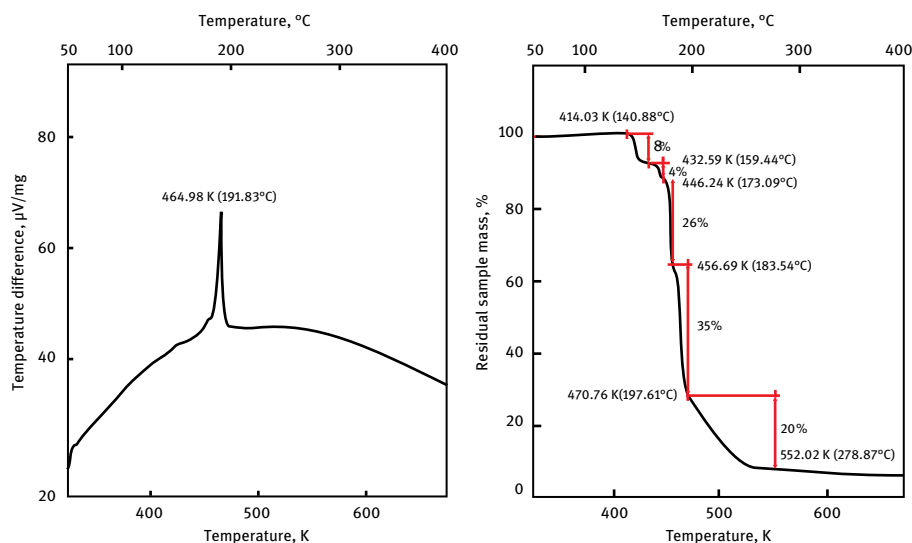
The thermal decomposition of TAG-based salts and their interaction with RDX were examined over a range of conditions that are relevant to performance, safety, and long-term aging behavior of gun propellants [343]. Four TAG-based salts (TAGzT, TAG-TATTz, TAG nitrate, and TAG chloride) have been examined to investigate the role of the anion in the reaction network. The reaction networks of TAG-TATTz and TAGN have features similar to those found in previous studies of TAGzT. The relative fraction of hydrazine observed in the four salts when examined by themselves has the following sequence: TAGzT TAG-TATTz TAGN TAGCl, indicating that the smaller inorganic anions,  $\text{Cl}^-$  and  $\text{NO}_3^-$ , are more reactive than the organic anions. Reactions of TAGzT,

TAG-TATTz, and TAGN with RDX showed that the extent of reaction of hydrazine with RDX is comparable for each salt. This suggested that even though the inorganic anions react more readily with hydrazine than the organic anions, the rate of reaction of hydrazine with RDX is faster than its rate of interaction with the anions. The reaction of hydrazine with RDX occurred primarily in the gas phase. The initial reaction for thermal decomposition of TAG salts is dissociation to TAG and an associated product from the anion. The observed onset temperature for decomposition was between 383 and 393 K (110 and 120 °C) for TAGzT and TAGN, and 438 K (165 °C) for TAG-TATTz.

Mixtures of 75, 50, 25, and 10% RDX with TAGzT were mixed with the non-solvent methanol, stirred, dried, and pressed into 6.6-mm pellets [344, 345]. TAGzT can significantly increase the burning rate of RDX in nitramine propellants. TAGzT and RDX have a synergistic interaction during combustion. A mixture of 10 RDX/90 TAGzT burned five times faster than pure RDX and about 1.2 times faster than pure TAGzT, while having a lower pressure sensitivity than that of both parent compounds. A graph showing the burning rate vs. pressure curve of TAGzT/RDX mixtures is shown in chapter “Heterocyclic and Heterocycloaliphatic Amines.”

TAGzT can significantly increase the burning rate of nitrate ester propellants [346].

The decomposition of TAGAT followed decomposition pathways with a decomposition mechanism entirely different from that of GAT [204]. The difference was attributed to the introduction of the triamino group. The TGA curve of TAGAT revealed a four-stage weight-loss process (Figure 35).



**Figure 35:** DTA (left) and TGA (right) thermograms of triaminoguanidinium azotetrazolate. (Republished and modified from [204], with permission of ©2009 American Institute of Aeronautics Astronautics; permission conveyed through Copyright Clearance Center Inc.)

The first stage corresponded to a rapid exothermic reaction simultaneously observed in the parallel DTA between 414 and 432 K (141 and 159 °C), resulting in an 8% weight loss; the second stage also corresponded to the rapid exothermic reaction between 446 and 456 K (173 and 183 °C), corresponding to a 26% weight loss; the third stage corresponded to the exothermic decomposition between 456 and 471 K (183 and 198 °C), corresponding to a 35% weight loss; and the fourth and final stage corresponded to a very slow endothermic reaction between 471 and 552 K (198 and 279 °C), corresponding to a 20% weight loss. The decomposition of TAGAT was initiated by the cleavage of the azo group rather than proton transfer initiation, as hypothesized in GAT.

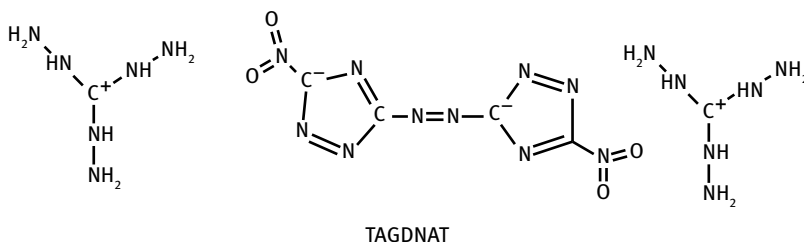
Premature, slow reaction of TAGzT with other propellant ingredients such as RDX may limit the useful life of composite propellants containing TAGzT [347].

Density functional theory and volume-based thermodynamics calculations have been performed to study the crystal densities, heats of formation, energetic properties, and thermodynamics of formation for a series of ionic salts composed of triaminoguanidinium or ammonium cations and tetrazole-based anions [348]. Substitution with  $-\text{NF}_2$ ,  $-\text{CH}_2\text{NF}_2$ ,  $-\text{CF}_2\text{NF}_2$ , or  $-\text{C}(\text{NO}_2)_2\text{NF}_2$  groups on the tetrazole ring increased the densities of the salts. The densities of the tetrazole-based salts were affected not only by different substituents but also by different cations. The triaminoguanidinium cation is more effective than the ammonium cation for increasing the heats of formation of the tetrazolate salts.

Similar density functional theory calculations were performed for energetic nitrogen-rich salts composed of the triaminoguanidinium cation and 5-nitroiminotetrazolate-based anions [349].

#### 14.6.3 Other Triaminoguanidinium Salts with Heterocyclic Anions

Bis-(triaminoguanidinium) 3,3-dinitro-5,5-azo-1,2,4-triazolate (TAGDNAT) is a high-nitrogen-content molecule that derives its energy release from both a high heat of formation and intra-molecular oxidation reactions.



TAGDNAT shows promise as a propellant or explosive ingredient not only due to its high nitrogen content (66.35 mass-% N) but also due to its high hydrogen content

(4.34 mass-% H). Strand burning rate studies showed that TAGDNAT had one of the fastest low-pressure burning rates (at 6.9 MPa) measured to date, i.e., 6.79 cm/s at 6.9 MPa (39% faster than bis-triaminoguanidinium azotetrazolate [TAGzT], a comparable high-nitrogen/high-hydrogen material) [350]. Furthermore, its pressure sensitivity coefficient was 0.507, a 33% reduction compared to TAGzT.

5,5'-Diamino-3,3'-azo-1*H*-1,2,4-triazole can be made by reaction of 5-acetyl-amino-3-amino-1*H*-1,2,4-triazole with potassium permanganate. Protection of one amino group in 3,5-diamino-1*H*-1,2,4-triazole by acetylation allows selective reactions of the remaining free amino group to form the azo functionality. Reactions of 5,5'-dinitrimino-3,3'-azo-1*H*-1,2,4-triazole with inorganic and organic bases (ammonia, hydrazine, guanidine, aminoguanidine, triaminoguanidine) formed the corresponding nitrogen-rich triazolate salts, which were characterized by IR, Raman, and multi-nuclear NMR spectroscopy, MS, DSC, and XRD [351].

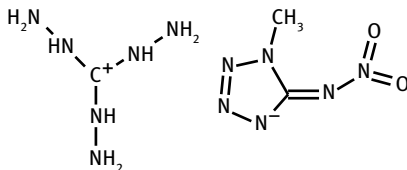
Density functional theory (DFT) and volume-based thermodynamics calculations were performed to study the crystal densities, heats of formation, and energetic properties of a series of ionic salts composed of triaminoguanidinium or ammonium cations and tetrazole-based anions [348]. Substitution of the tetrazole ring with  $-\text{NF}_2$ ,  $-\text{CH}_2\text{NF}_2$ ,  $-\text{CF}_2\text{NF}_2$ , or  $-\text{C}(\text{NO}_2)_2\text{NF}_2$  groups increased the densities of the salts. The densities of the tetrazolate-based salts were affected not only by different substituents but also by different cations. The  $-\text{CN}$  or  $-\text{N}_3$  groups were effective substituents for increasing the HOFs of the salts. The triaminoguanidinium cation is more effective than the ammonium cation for increasing the HOF of the tetrazole-based salts. Substitution of hydrogens with  $-\text{NO}_2$ ,  $-\text{NF}_2$ , or  $-\text{C}(\text{NO}_2)_2\text{NF}_2$  groups enhanced the predicted explosive performance of the salts. A study of the thermodynamics of formation of the salts revealed that all of the tetrazole-based salts with the triaminoguanidinium or ammonium cation could be synthesized using the proposed reactions.

Density functional theory and volume-based thermodynamics calculations were performed to study the effects of different substituents and linkages on the densities, heats of formation, energetic properties, and thermodynamics of a series of energetic nitrogen-rich salts composed of triaminoguanidinium cation and 5-nitroiminotetrazolate anions [349]. The results showed that the  $-\text{NO}_2$ ,  $-\text{NF}_2$  or  $-\text{N}_3$  group are effective substituents for increasing the densities of the 5-nitroiminotetrazolate salts, whereas the effects of the bridge groups on the density are coupled to those of the substituents. The substitution by  $-\text{NH}_2$ ,  $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{N}_3$ , or the nitrogen bridge is helpful for increasing the enthalpies of formation of these salts.

Triaminoguanidine also forms a salt with *N*-nitro-1*H*-tetrazol-5-amine:  $\text{CH}_9\text{N}_6 \bullet \text{CH}_3\text{N}_6\text{O}_2$ , CAS RN [1660-26-0].

Several high-nitrogen energetic materials based on the TAG ion with astonishing thermal behaviors and performances were synthesized by different metathesis reactions [352, 353]. Particularly the new compound triaminoguanidinium 1-methyl-5-ni-

triminotetrazolate (TAG-1 Me-AtNO<sub>2</sub>, TAG-MNT) showed powerful explosion performance and may be an alternative to RDX.



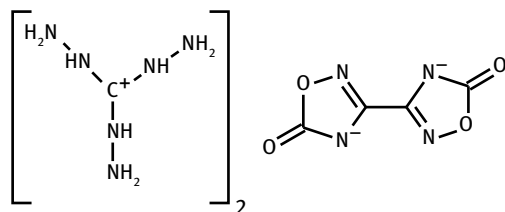
Triaminoguanidinium 1-methyl-5-nitriminotetrazolate

The structural and chemical properties of triaminoguanidinium 1-methyl-5-nitriminotetrazolate have been investigated at atmospheric pressure and under high-pressure isothermal compression using powder XRD, Raman, and IR spectroscopy [354, 355]. Beyond 15 GPa, pressure induces irreversible chemical reactions, culminating in the formation of a polymeric phase by 60 GPa.

The toxicity of triaminoguanidinium 1-methyl-5-nitriminotetrazolate (TAG-MNT) was evaluated in animal tests and *in vitro* assays [356]. In rats, TAG-MNT had no apparent adverse effect up to the limit dose of 2 g/kg. In the Ames assay, TAG-MNT was a weak mutagen only at the limit concentration of 2 g/L. TAG-MNT was not acutely toxic at the limit dose when administered to rats, but 14 d of daily oral exposure caused liver toxicity and death [357].

High-nitrogen compounds like TAG-MNT have the potential to stimulate algal growth at low concentrations in N-limited systems, like any good fertilizer would [358].

Triaminoguanidinium 3,3'-bis-1,2,4-oxadiazol-5-onate (TAG2-OD) with an N-content of 60% and a relatively low isobaric (20 bar) combustion temperature of 1420 K may be used in reduced-erosion gun propellants.



Triaminoguanidinium 3,3'-bis-1,2,4-oxadiazol-5-onate

The properties of these two compounds and several dinitramide salts are listed in Table 29 in comparison to the properties of RDX.

Aminoguanidinium, diaminoguanidinium, triaminoguanidinium, and aminonitroguanidinium salts of cyanuric acid are thermally stable, high-nitrogen compounds [359].

**Table 29:** Properties of TAG-based energetic compounds.

| Property                                                   | Units             | RDX (for comparison) | TAG 1-MeAtNO <sub>2</sub> | TAG OD | AF_DN <sup>a</sup> | TAG_DN | HAT_DN |
|------------------------------------------------------------|-------------------|----------------------|---------------------------|--------|--------------------|--------|--------|
| Molecular mass                                             | g/mol             | 222.1                | 248.25                    | 378.31 | 192.09             | 211.2  | 192.09 |
| Melting point                                              | °C                | 204                  | 158                       | 183    | 120                | 80     | 85     |
|                                                            |                   |                      |                           | dec.   | dec.               |        |        |
| Impact sensitivity                                         | J                 | 7                    | 6                         | 100    | 2                  | 3      | 2      |
| Friction sensitivity                                       | N                 | 120                  | 240                       | 218    | 7                  | 24     | 20     |
| ESD sensitivity                                            | J                 | 0.15–0.2             | —                         | 1.5    | 0.93               | 0.79   | 0.75   |
| Nitrogen content                                           | mass-%            | 37.8                 | 67.72                     | 59.2   | 58.33              | 59.7   | 58.33  |
| Oxygen balance                                             | %                 | –21.6                | –64.46                    | –71.9  | 0                  | –18.9  | 0      |
| <i>T</i> <sub>dec.</sub> , onset of exotherm               | °C                | ~213                 | 210                       | 197    | 120                | 180    | 117    |
| Density                                                    | g/cm <sup>3</sup> | 1.82                 | 1.57                      | 1.724  | 1.754              | 1.628  | 1.856  |
| Heat of combustion –Δ <i>H</i> <sub>c</sub>                | kJ/mol            | 2105                 | 3465                      |        |                    | 2027   |        |
| Enthalpy of formation Δ <i>H</i> <sub>f</sub> <sup>o</sup> | kJ/mol            | +66.5                | +569                      | +223   | +332               | +250   | +329   |
| <b>Calculated explosive performance values by EXPLO5</b>   |                   |                      |                           |        |                    |        |        |
| Explosion temperature                                      | K                 | 3986                 | 3210                      | 2673   | 4710               | 4231   | 4657   |
| Detonation pressure                                        | kbar              | 299                  | 273                       | 231    | 338                | 320    | 384    |
| Detonation velocity                                        | m/s               | 8796                 | 8770                      | 8104   | 9013               | 9039   | 9429   |

<sup>a</sup> Monohydrate

Abbreviation legend: triaminoguanidinium 1-methyl-5-nitriminetetrazolate = TAG 1-MeAtNO<sub>2</sub>; triaminoguanidinium 3,3'-bis-1,2,4-oxadiazol-5-onate = TAG OD; azidoformamidinium dinitramide = AF\_DN; 1,3,5-triaminoguanidinium dinitramide = TAG\_DN, 5-aminotetrazolium dinitramide = HAT\_DN

Data source: [352]

High-nitrogen-content energetic salts of ammonium, hydrazinium, guanidinium, aminoguanidinium, diamino-guanidinium, and triaminoguanidinium with 5-nitro-2*H*-tetrazolate anions were synthesized [360].

#### 14.6.4 Triaminoguanidinium Cyanoformate

Another high-nitrogen compound, triaminoguanidinium cyanoformate, C<sub>5</sub>H<sub>9</sub>N<sub>9</sub>, [(NH<sub>2</sub>NH)<sub>3</sub>C]<sup>+</sup> [C(CN)<sub>3</sub>]<sup>–</sup>, can be obtained from triaminoguanidinium sulfate and potassium cyanoformate in sulfuric acid solution [361].

Triaminoguanidinium dicyanamidate, C<sub>3</sub>H<sub>9</sub>N<sub>9</sub>, [(NH<sub>2</sub>NH)<sub>3</sub>C]<sup>+</sup> [N(CN)<sub>2</sub>]<sup>–</sup>, can be prepared by reaction of triaminoguanidinium sulfate with calcium cyanamidate, where the insoluble calcium sulfate precipitates and can easily be separated from the reaction mixture [362]. It melts at 396–397 K (123–124 °C), has a density of 1.415 g/cm<sup>3</sup> at 298 K and an enthalpy of formation of +400 ± 7 kJ/mol (+95.5 ± 1.8 kcal/mol), and

is non-hygroscopic. In the DTA it shows a sharp endotherm at 396 K = 123 °C (melting) and an exotherm at 423 K (150 °C).

#### 14.6.5 Bis-Triaminoguanidinium Decahydrodecaborate

Normally, nitrogen in energetic compounds converts to dinitrogen in the exhaust and does not contribute much to energy release. If the high-nitrogen compound is combined with a boron compound, the boron nitride formed in the exhaust contributes substantially to the overall energy release. One of the compounds in this category is bis-triaminoguanidinium decahydrodecaborate,  $[(\text{NHNH}_2)_3\text{C}]_2\text{B}_{10}\text{H}_{10}$  [363, 364].

#### 14.6.6 Triaminoguanidinium *N,N'*-Dinitro-1,2-Ethanediamine Salt

The salt formed from triaminoguanidine with *N,N'*-dinitro-1,2-ethanediamine,  $[(\text{NH}_2\text{NH})_3\text{C}]^+[\text{O}_2\text{NNHCH}_2\text{CH}_2\text{NNO}_2]^-$ ,  $\text{C}_3\text{H}_{14}\text{N}_{10}\text{O}_4$ , melts at 464–466 K (191–193 °C), and the maximum of the exotherm peak in the DTA is at 488 K (215 °C) [172].

#### 14.6.7 Other Triaminoguanidinium Salts

Triaminoguanidinium phosphate can be used to improve the performance and flammability characteristics of low-vulnerability propellants [365].

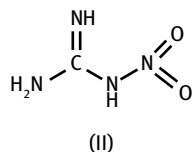
Polycondensation of triaminoguanidinium chloride with glyoxal results in a polymer (TAGP) which has a carbon-to-nitrogen ratio of 3:4, identical to the ratio found in carbon nitrides with a layered 2D network-type structure [366]. TAGP has a higher nitrogen content than all currently used energetic polymers, including glycidyl azide polymer (GAP); poly(3-nitrato-methyl-3-methyloxetane), poly-NIMMO; and poly(glycidyl nitrate), poly-GLYN. The properties of TAGP could be even further modified and tuned by coordination of transition metal ions.

## 15 Nitroguanidine and Dinitroguanidine

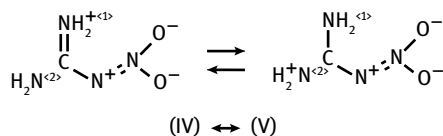
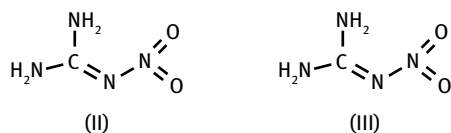
Nitroguanidine, also known as  $\text{CH}_4\text{N}_4\text{O}_2$ ,  $\text{C}_1\text{H}_4\text{N}_4\text{O}_2$ , NQ, NGu, NIGU, "picrite", CAS-RN [556-88-7], is prepared by dehydration of guanidinium nitrate by treating it with concentrated sulfuric acid. Nitroguanidine crystallizes in white, fiber-like crystals. Nitroguanidine is a very versatile energetic material additive for explosives, propellants, and gas generants. In gun propellants, it is the addition of NQ to reduce flame temperature and barrel wear that makes a triple-base propellant out of a double-base propellant. Nitroguanidine is a nitramine and should have been discussed in chapter "Nitramines" along with other nitramines, but somehow it was kept here with its parent imide, guanidine. The same rationale was applied for dinitroguanidine and nitroaminoguanidine, which are also discussed here in the following sections instead of in the "Nitramines" chapter.

Ordinarily, the abbreviation for **nitroguanidine** would be NG, but because NG was already in use as an abbreviation for **nitroglycerin**, the alternate acronym of NQ became generally accepted in the explosives lingo.

The structure commonly accepted for nitroguanidine was structure (II) shown below,



but other observations indicated a nitrimine structure (III) or even a partial zwitterion structure (IV)  $\leftrightarrow$  (V)



where the positive charge is not localized but can oscillate among the nitrogen atoms [367].

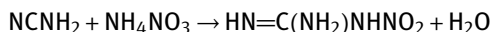
### 15.1 Production of Nitroguanidine

Nitroguanidine can be prepared from guanidinium nitrate, which is dehydrated by treatment with concentrated sulfuric acid.

Another method for preparation of NQ is by fusing urea with ammonium nitrate and then recrystallizing the product from boiling water (92% yield)



Another method is by enclosing an equimolar aqueous solution of cyanamide and ammonium nitrate in an autoclave, heating to 433 K (160 °C) under pressure (1.379 MPa = 200 psia), and recrystallizing the product from boiling water (88% yield)





## 15.2 Physical Properties of Nitroguanidine

Nitroguanidine is usually used as a component in mixed explosives and propellants. It has two crystal structures, namely  $\alpha$  and  $\beta$ , the former being more stable than the latter. The crystals are white needles that are neither hygroscopic nor volatilize at room temperature. The physical properties of NQ are summarized in Table 30. NQ is insoluble in cold water and diethyl ether, only somewhat soluble in ethanol, but soluble in aqueous alkaline solutions.

**Table 30:** Physical properties of nitroguanidine.

| Property                             | SI units                | Other units               | At temp. | References      |
|--------------------------------------|-------------------------|---------------------------|----------|-----------------|
| Molecular mass                       | 104.0681 g/mol          | 9.609 mol/kg              |          | [105]           |
| Density                              | 1.775 g/cm <sup>3</sup> | 0.064 lb/in. <sup>3</sup> | 298 K    | [368]           |
|                                      | 1.71 g/cm <sup>3</sup>  | 0.062 lb/in. <sup>3</sup> | 298 K    | [369] p. 244    |
| Melting point                        | 505 K                   | 232 °C                    |          | [368]           |
|                                      | 508 K                   | 235 °C                    |          | [370]           |
|                                      | 497.6                   | 224.5 °C                  |          | [371]           |
| Heat capacity                        | 0.33 J/g                | 0.076 cal/g               | 293 K    |                 |
| Enthalpy of formation                | −93.42 kJ/mol           | −22.33 kcal/mol           | 298 K    | [369] p. 244    |
| $\Delta H_f^{298}$                   | −92.96 kJ/mol           | −22.2 kcal/mol            | 298 K    | [18] p. 228–229 |
|                                      | −91.04 kJ/mol           | −21.76 kcal/mol           | 298 K    | [368]           |
|                                      | −91.00 kJ/mol           | −209 cal/g                | 298 K    | [124]           |
|                                      |                         | = −21.75 kcal/mol         |          |                 |
|                                      | −86.6 ± 2.5 kJ/mol      | −20.698                   | 298 K    | [105]           |
|                                      |                         | ± 0.6 kcal/mol            |          |                 |
|                                      | −97.9 ± 4.2 kJ/mol      | −23.399                   | 298 K    | [105]           |
|                                      |                         | ± 1.0 kcal/mol            |          |                 |
|                                      | −92.0 ± 2.5 kJ/mol      | −22 ± 0.59 kcal/mol       |          | [371]           |
| Isochoric upper heat of combustion   | 878.6 ± 2.5 kJ/mol      | 210 ± 0.59 kcal/mol       |          | [371]           |
| Heat of sublimation                  | 142.7 ± 2.0 kJ/mol      | 34.1 ± 0.5 kcal/mol       |          | [105]           |
| Oxygen balance (to CO <sub>2</sub> ) | −30.8%                  |                           |          |                 |

An older publication listed an NQ melting point of 329–331 K (56–58 °C), but that is most likely a mistake [172]. Additional information on the properties of nitroguanidine can be found in [372].

### 15.2.1 Mechanical Physical Properties of Nitroguanidine

Melting points of a eutectic mixture of hydrazinium(1+) nitrate (HN) and nitroguanidine (NQ) as well as fusion enthalpy of the pure components and the eutectic were determined using DSC [373]. The structure of the HN-NQ eutectic was characterized by IR, XRD, and SEM. Thermodynamic functions such as excess Gibb's energy, excess enthalpy, and excess entropy of the HN-NQ eutectic were calculated using activity coefficient data. The inter-molecular interactions of different molar ratios of the HN-NQ eutectic were determined by density functional theory (DFT) methods. The results of the excess thermodynamic functions and computer simulations indicated that the eutectic is not a mechanical mixture. IR spectroscopic and XRD studies confirmed that there is some interaction between the components during the formation of the eutectic mixture. In particular, the microstructure of the eutectic mixture at a molar ratio of 3 : 2 was more uniform than others. Similar eutectics were formed with methyl-nitroguanidine and hydrazinium(1+) nitrate [374].

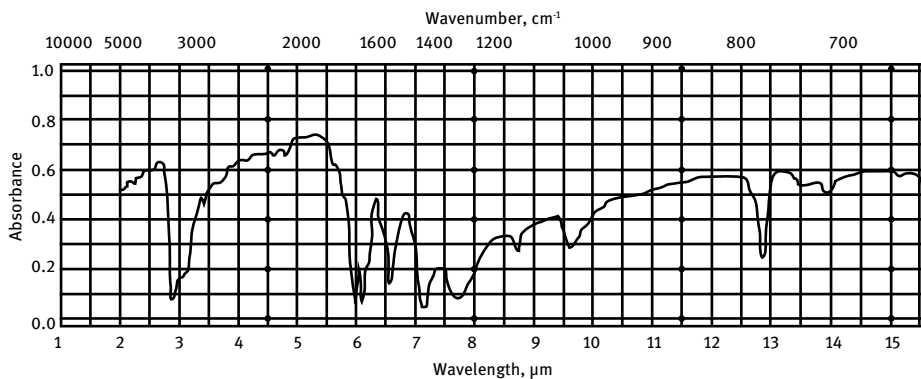
A study of eutectic and peritectic points in the binary systems HN/nitroguanidine (HN/NQ) and HN/methylnitroguanidine (HN/MeNQ) detected indications of double salt formation with a well-defined stoichiometric ratio. The HN/NQ binary system showed the presence of a new substance, which is probably a HN/NQ co-crystal. No new substance was detected in the MeNQ/HN binary system [375]. The HN/NQ system had two eutectics, one at an NQ mol fraction of 0.226, melting at 322 K (49 °C), and another at a mol fraction of 0.95, melting at 416 K (143 °C). In between was a peritectic melting at 500 K (227 °C), with a composition of three mols of NQ per mol HN. The HN/MeNQ had only one eutectic at a MeNQ mol fraction of 0.307 melting at 341.7 K (68.6 °C).

### 15.2.2 Optical Properties of Nitroguanidine

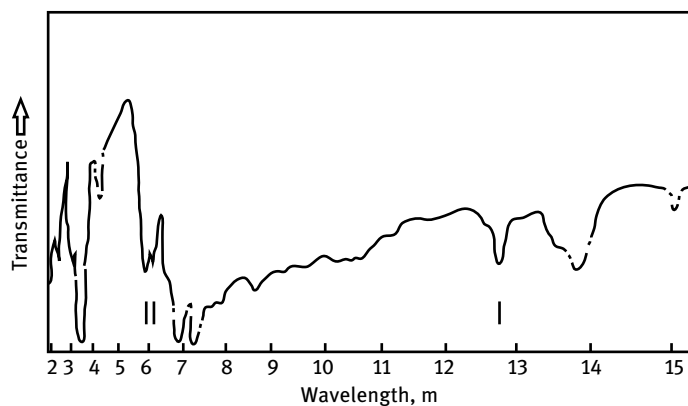
#### 15.2.2.1 Infrared Spectra of Nitroguanidine

The IR spectrum of nitroguanidine is shown in Figure 36 (from [21]). Unfortunately, most IR spectra of NQ found in the literature were of poor quality, which is surprising considering that this is an important chemical for formulating explosives and propellants. Many of the spectra were taken with the samples dispersed in nujol mulls, and the absorption of the dispersing fluid interfered with clean spectra.

An examination of the spectra of nitroguanidine (Figure 37), nitroaminoguanidine, and guanidinium nitrate showed that the region from 7.5 to 15  $\mu\text{m}$  was barren of any large peaks, except in the case of guanidinium nitrate, where the nitrate ion manifests at 12.1  $\mu\text{m}$ . The other nitrate salts also gave this band. However, mono-, di-, and triaminoguanidine in the form of their nitrate salts have absorption peaks at 10.35 and 13.0  $\mu\text{m}$ . These bands correspond to two of the strong bands in the hydrazinium(1+) chloride spectrum and can be attributed to the hydrazine-type NH—NH linkage. In



**Figure 36:** Infrared spectrum of nitroguanidine. (Reproduced and modified from [21].)



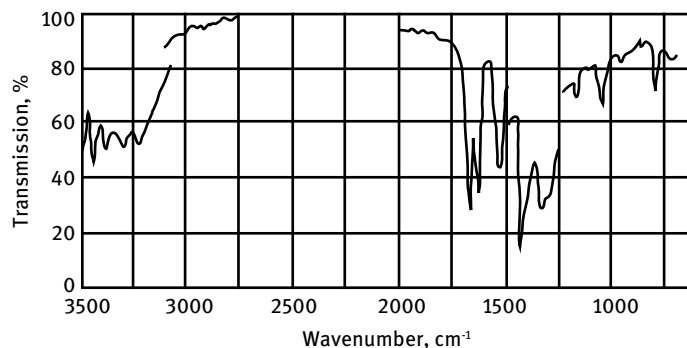
**Figure 37:** Infrared spectrum of nitroguanidine. (Reproduced and modified from [125], with permission from Levering Estate.)

Figure 37, absorption in the area with the dashed lines is due to the solvent in which the crystals were suspended. IR absorption bands in the IR spectrum of NQ were assigned as follows [376]:

|         |                    |
|---------|--------------------|
| 2.96 μm | N—H                |
| 3.01 μm | N—H                |
| 3.13 μm | N—H                |
| 3.20 μm | N—H                |
| 6.01 μm | C=N                |
| 6.11 μm | —NO <sub>2</sub> . |

In the C—H first combination region, the N—H first combination region (2300–1900 nm) of NQ was extraordinarily complex and the particular assignment of each band to the respective N—H stretching/bending combination mode was not feasible [377]. As a general assignment, the bands located at 1973, 2007, 2036, and 2083 nm were tentatively assigned to a combination of N—H stretching with N—H bending vibrations ( $\nu\text{NH} + \delta\text{NH}$ ), based on the available literature reported for amines. The bands above 2100 nm (2174, 2221, and 2262 nm) might be due to second overtones of N—H bending vibrations ( $3\delta\text{NH}$ ) and the combination of N—H stretching with N—N stretching/bending vibrations ( $\nu\text{NH} + \nu\text{NN}/\nu\text{NH} + \delta\text{NN}$ ).

Another IR spectrum of NQ found in the literature has been spliced together from several spectra of NQ suspended in different solvents, appears to be incomplete, and is not very useful [76] (Figure 38).



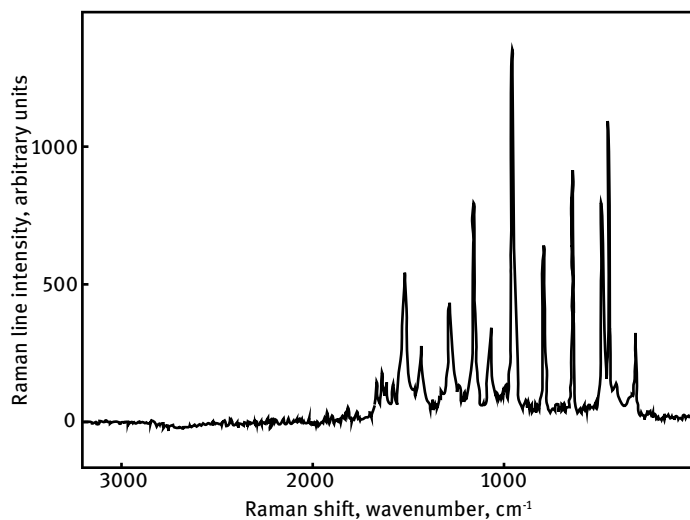
**Figure 38:** Infrared spectrum of nitroguanidine. (Reproduced and modified from [76].)

#### 15.2.2.2 Raman Spectra of Nitroguanidine

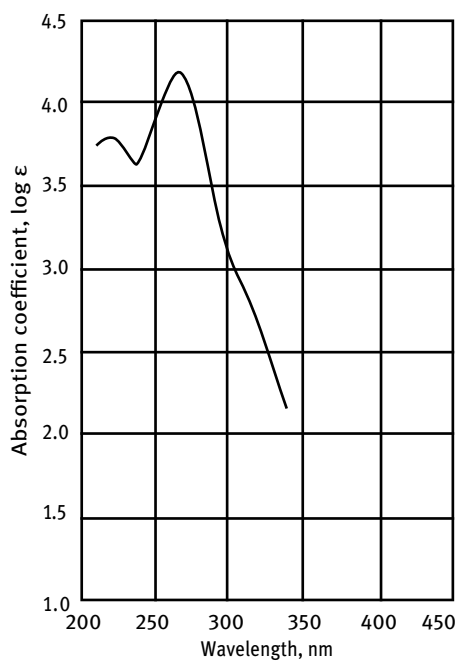
Fourier transform Raman (FTR) spectroscopy employing near-IR laser radiation at 1.06  $\mu\text{m}$  as the scattering source has been used to obtain Raman spectra of NQ and propellant formulations containing NQ [378, 379] (Figure 39).

#### 15.2.2.3 Ultraviolet Spectra of Nitroguanidine

The UV spectrum of a nitroguanidine solution in ethanol shows an absorption peak at 265 nm (Figure 40).



**Figure 39:** Raman spectrum of nitroguanidine. (Reproduced and modified from [378].)



**Figure 40:** Ultraviolet spectrum of nitroguanidine. (Reproduced and modified from [76].)

### 15.2.3 Thermodynamic Properties of Nitroguanidine

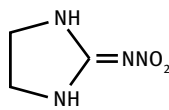
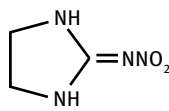
The molar heat capacity of NQ in the range 200–460 K (–73 to +187 °C) can be described by the following linear equation

$$C_p = (6 \pm 1) + (0.08 \pm 0.003)T$$

where  $C_p$  is the molar heat capacity in  $\text{cal mol}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin [371]. The molar heat capacity of NQ at 298 K is  $129.3 \text{ J mol}^{-1} \text{K}^{-1}$  ( $30.9 \text{ cal mol}^{-1} \text{°C}^{-1}$ ).

Energies of combustion of guanidine, nitroguanidine, and four nitroguanidine derivatives were measured by combustion calorimetry, and their enthalpies of formation were calculated and compared [380] (Table 31). A study of the influence of the effective energy of non-valency interactions of functional groups (EEI) on thermochemical properties of nitro derivatives of the guanidine will enable enthalpies of formation to be predicted just by looking at the structural formula of nitramines in the future.

**Table 31:** Thermochemical properties of guanidine, nitroguanidine, and derivatives of nitroguanidine.

| Compound                                                                                | Upper heat of combustion |                 | Standard enthalpy of formation |                 |
|-----------------------------------------------------------------------------------------|--------------------------|-----------------|--------------------------------|-----------------|
|                                                                                         | kJ/mol                   | kcal/mol        | kJ/mol                         | kcal/mol        |
| $\text{H}_2\text{N}-\text{C}(\text{NH})=\text{NH}_2$                                    | 1051.9                   | 251.4           | –56.1                          | –13.4           |
| $\text{H}_2\text{N}-\text{C}(\text{NH})=\text{NNO}_2$                                   | $875.3 \pm 0.8$          | $209.2 \pm 0.2$ | $-90.0 \pm 0.8$                | $-21.5 \pm 0.2$ |
| $\text{H}_2\text{N}-\text{C}(\text{NH})=\text{NH}-\text{C}(=\text{O})\text{NHNO}_2$     | $1179.5 \pm 0.8$         | $281.9 \pm 0.2$ | $-322.2 \pm 0.8$               | $-77.0 \pm 0.2$ |
|      | $2005.8 \pm 1.2$         | $479.4 \pm 0.3$ | $-32.2 \pm 1.2$                | $-7.7 \pm 0.3$  |
|      | $1963.6 \pm 1.2$         | $469.3 \pm 0.3$ | $+68.2 \pm 1.2$                | $+16.3 \pm 0.3$ |
| $\text{CH}_3-\text{N}(\text{NO}_2)-\text{C}(\text{NH})=\text{NH}_2$                     | $1509.2 \pm 1.2$         | $360.7 \pm 0.3$ | $+7.5 \pm 1.2$                 | $+1.8 \pm 0.3$  |
| $\text{H}_2\text{N}-\text{C}(\text{NNO}_2)=\text{N}-\text{C}(\text{NNO}_2)-\text{NH}_2$ | $1624.6 \pm 1.2$         | $388.3 \pm 0.3$ | $+266.1 \pm 1.2$               | $+63.6 \pm 0.3$ |

Data source: [380]

The heat capacity of NQ with a density of  $1.689 \text{ g/cm}^3$  in the range 310–440 K (37–167 °C) was

$$c_p = 0.269 + 0.00070t$$

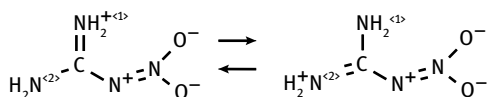
where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ °C}^{-1}$  and  $t$  is the temperature in °C [381]. The mid-range standard deviation was  $0.006 \text{ cal g}^{-1} \text{ °C}^{-1}$ . The thermal conductivity of the same sample of NQ at 314 K (41 °C) measured by a DSC comparative method was as follows:

$$\lambda = 9.85 \times 10^{-4} \text{ cal cm}^{-2} \text{ °C}^{-1} \left( \frac{\text{°C}}{\text{cm}} \right)^{-1} = 0.412 \text{ W m}^{-1} \text{ K}^{-1}$$

No complete vibrational assignments for NQ were available and, therefore, its thermodynamic functions in the vapor state could not be calculated by the statistical thermodynamic method. There are no experimental data on the enthalpy of formation of gaseous NQ. The calculated enthalpy of formation for NQ in the gas phase is  $-1 \pm 20 \text{ kJ/mol}$  and the calculated entropy is  $352 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$  [382].

#### 15.2.4 Molecular Structure of Nitroguanidine

The nitrimine structure



has been established for NQ  $(\text{NH}_2)_2\text{C}=\text{N}-\text{NO}_2$  by XRD [383], neutron diffraction [384], spectroscopic measurements [385], and theoretical investigations [386].

Crystalline nitroguanidine exists in at least two crystal modifications,  $\alpha$ -nitroguanidine and  $\beta$ -nitroguanidine. The  $\alpha$ -form may be prepared by dissolving guanidinium nitrate in concentrated sulfuric acid and drowning the solution with water. It crystallized from hot water in long, flexible needles, which are mechanically strong and difficult to pulverize. The  $\beta$ -nitroguanidine can be prepared by nitrating a mixture of guanidinium sulfate and ammonium sulfate. It crystallized from hot water in fern-shaped clusters of small, thin, elongated plates. The  $\beta$ -form can be converted to the  $\alpha$ -form by dissolving in concentrated sulfuric acid and drowning it with lots of water.

The two modifications of NQ have the same melting point, but their solubility in water differs somewhat except at 298 and 373 K (25 and 100 °C), where the solubilities are identical. Between 298 and 373 K (25 and 100 °C), the solubility is slightly lower for the  $\alpha$ -form.

$^{15}\text{N}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy spectra confirmed the nitroimine structure which had been suggested by other investigations in recent years and did not lend

any support to the commonly used nitroamine structure or to a tautomeric equilibrium with the nitroamine [387]. The  $^{15}\text{N}$  spin coupling constants to the neighboring  $^1\text{H}$  and  $^{13}\text{C}$  nuclei in the assigned structure confirmed this conclusion.

An investigation of the tautomeric properties of NQ using theoretical approaches for NQ in both the gas phase and in aqueous solution used a density functional method to estimate physical and chemical properties of NQ tautomers [388]. In order to analyze NQ behavior in aqueous solution, several properties were calculated. Deprotonating as well as protonating of NQ revealed positive energies, indicating that those processes are rather unfavorable and further characterized NQ as a compound with weak acid–base properties.

### 15.3 Chemical Properties of Nitroguanidine

Nitroguanidine is a powerful explosive, but its oxygen balance is still on the negative side with  $-30.7\%$ . It has excellent chemical stability. Nitroguanidine is soluble in hot water but practically insoluble in cold water. It is only very sparingly soluble in alcohol, insoluble in ether, but readily soluble in aqueous alkaline solutions.

Nitroguanidine derivatives, including *N*-methyl-*N'*-nitroguanidine (MeNQ), 3-amino-1-nitroguanidine (ANG), hydrazobis(nitroformamidine) (HABNF) 1-(2,2,2-trinitroethylamino)-2-nitroguanidine (TNEANG), 3,5-diamino-1-nitroamidino-1,2,4-triazole (DANAT), 2-nitroimino-5-nitrohexahydro-1,3,5-triazine (NNHT), and 1,2-dinitroguanidine (DNG) have been prepared in the hope of obtaining compounds with properties superior to those of NQ [389].

Reactions between *N*-nitroso-*N'*-alkylguanidines and the hydrazine derivatives of 1,3,5-triazine or 1,2,4,5-tetrazine resulted in a new class of nitroguanidyl-function-alized nitrogen-rich materials derived from 1,3,5-triazine and 1,2,4,5-tetrazine [390]. These compounds were characterized using NMR, IR, DSC, and elemental analysis, and detonation pressures and velocities were predicted from theoretical calculations.

#### 15.3.1 Reactions of Nitroguanidine

Nitroguanidine undergoes hydrazinolysis when reacted with hydrazine hydrate in a 1 : 1 molar ratio to form nitraminoguanidine, which is also an explosive and intermediate in the synthesis of other energetic compounds. Reaction of nitraminoguanidine with potassium nitrite in the presence of acetic acid gives the potassium salt of 5-nitraminotetrazole.

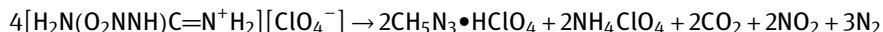
##### 15.3.1.1 Nitroguanidinium Salts

Nitroguanidine forms a monoperchlorate salt (NGP) and a diperchlorate salt with perchloric acid. Nitroguanidinium monoperchlorate forms when dissolving NQ in anhydrous perchloric acid. The diperchlorate forms from the monoperchlorate with even



more perchloric acid. The monoperoxchlorate salt melts and decomposes in reversal of its formation at 393 K (120 °C). The diperoxchlorate salt melts at 343 K (70 °C) and explodes at 366 K (93 °C). NGP has been reported to be less stable than GP.

The first step of the thermal decomposition of NGP begins in the solid phase and proceeds as follows, with guanidinium perchlorate as an intermediate product [115]:



Nitroguanidine is amphoteric and forms salts with strong alkalis as well as with strong acids. Nitroguanidinium nitrate forms by dissolving NQ in hot, concentrated nitric acid and allowing to cool, forming rhombohedral crystals. The crystals melt at 420 K (147 °C) under decomposition. The crystals are very sensitive to impact and will explode. The crystals lose nitric acid when standing in air at room temperature. Crystal structures of nitroguanidinium chloride and nitroguanidinium nitrate were examined by XRD [391]. The nitroguanidinium chloride crystal is triclinic, space group *P*1, with unit cell parameters  $a = 6.656(8) \text{ \AA}$ ,  $b = 6.719(9) \text{ \AA}$ ,  $c = 6.816(8) \text{ \AA}$ ,  $\alpha = 66.8(2)^\circ$ ,  $\beta = 75.4(2)^\circ$ ,  $\gamma = 84.5(2)^\circ$ ,  $DC = 1.7 \text{ g/cm}^3$ ,  $Z = 2$ . The nitroguanidine nitrate crystal is monoclinic, space group *P*2<sub>1</sub>/*c* with unit cell parameters  $a = 4.587(4) \text{ \AA}$ ,  $b = 6.377(6) \text{ \AA}$ ,  $c = 21.167(15) \text{ \AA}$ ,  $\beta = 94.7(1)^\circ$ ,  $DC = 1.8 \text{ g/cm}^3$ ,  $Z = 4$ .

#### 15.3.1.2 Nitroguanidinate Salts

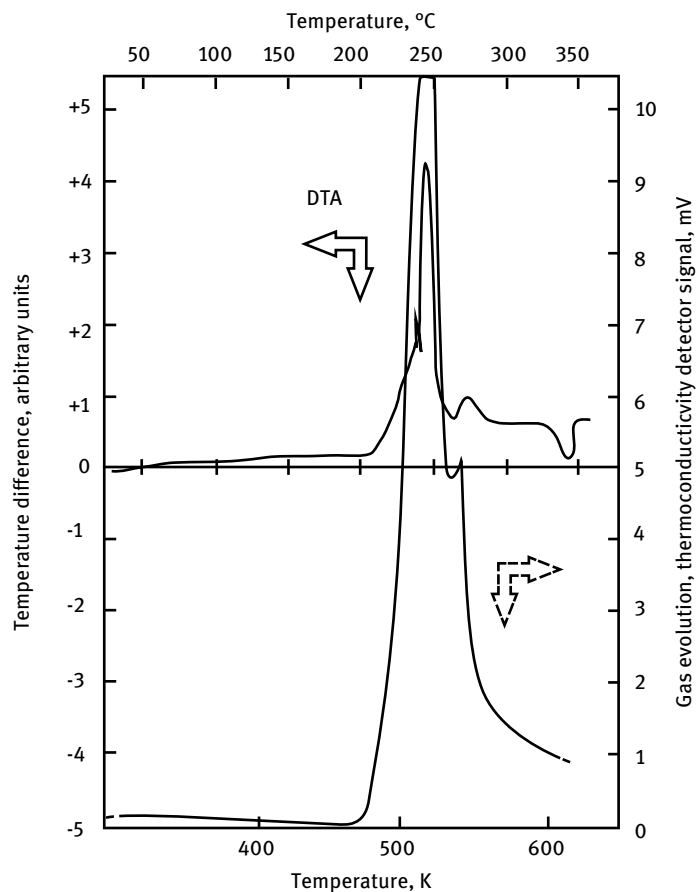
It is the general format of this book that salts are primarily listed under their cation and not under their anion. Thus there are several nitroguanidinate salts listed in other sections of this book, e.g., in chapter “Heterocyclic and Heterocycloaliphatic Amines.”

#### 15.3.2 Decomposition of Nitroguanidine

In the vacuum stability test at 373 K (100 °C), the gas evolved by a one-gram sample of NQ in 48 h was 0.37 cm<sup>3</sup>. The investigations of the decomposition of NQ have been performed mostly at temperatures between 463 and 513 K (190 and 240 °C). The aim of additional work was to study the decomposition behavior of NQ at temperatures as low as possible, namely at temperatures between 383 and 513 K (110 and 240 °C) [392]. In this temperature range, NQ with different grain sizes has been investigated by measuring the weight loss and analyzing the decomposition gases by MS. Solid residues, such as ammeline and melamine, remaining after the degradation tests were analyzed quantitatively by HPLC. The formation of melamine and ammeline was found to depend strongly on the extent of the weight loss of NQ. The better stability behavior of triple-base propellants in the presence of NQ is possibly due to the presence of NH<sub>3</sub>, which is formed in the decomposition of NQ. Ammonia reacts with and sequesters nitric oxides, and therefore acts similarly to a stabilizer. In the DTA, the maximum of exothermic decomposition of NQ was at 523 K (250 °C) [172].

The off-gassing of NQ decomposition products measured with a thermoconductivity GC detector (--- dashed line) was superimposed on the DTA trace (— solid line)

of NQ as shown in Figure 41 [393]. The off-gassing started simultaneously with the exotherm. The exotherm started before the melting. The melting endotherm is superimposed on the exotherm at ~500 K (~230 °C).



**Figure 41:** Off-gassing of NQ during decomposition superimposed on the DTA trace of NQ. (Reproduced and modified from [393].)

### 15.3.3 Specifications for Nitroguanidine

The procurement of NQ is governed by MIL SPEC MIL-N-494A (Mar 1963) superseding JAN-N-494 of Sep 1947, amended 11 Apr 1983 and 8 Aug 2013. The MIL SPEC contains several analysis methods for NQ.

## 15.4 Safety Properties of Nitroguanidine

Nitroguanidine is not very sensitive to shock or impact. In the USBM impact tester with the No. 12 tool and a 5-kg weight, the tests were negative at the maximum range of the machine (177 cm) [393].

### 15.4.1 Shock Sensitivity of Nitroguanidine

When testing the impact sensitivity at impact energies up to  $5 \text{ kJ} = 49 \text{ N m}$  there was no reaction. Impact sensitivity when measured in the Bureau of Mines Apparatus with a 2-kg mass was 47 cm, which was more sensitive than either TNT or PA. In the Picatinny Arsenal Apparatus with a 1-lb mass, the drop-weight sensitivity was 66 cm (26 in.).

In the NOL Large Scale Card-Gap Test, finely ground NQ at three different packing densities, 1.39, 1.44, or  $1.50 \text{ g/cm}^3$ , had card-gap sensitivities (50% positive) of 109, 98, or 81 cards, corresponding to attenuated shock pressures of 52, 56, or 63 kbar [394].

### 15.4.2 Friction Sensitivity of Nitroguanidine

When testing the friction sensitivity of NQ at pistil loads up to  $36 \text{ kp} = 353 \text{ N}$  there was no reaction.

### 15.4.3 Critical Diameter of Nitroguanidine Detonations

In studying the explosive behavior of NQ, a high-bulk density (NQ-h) and a low-bulk density (NQ-l) form of this material were examined [395]. Determination of failure limits in the charge diameter–density ( $\rho_0$ ) plane showed that both behave as a group 1 explosive (critical diameter decreasing with  $\rho_0$  increasing) at  $\rho_0 < 1.63 \text{ g/cm}^3$ , but that NQ-h exhibited “dead-pressing” and, thus, behaved as a group 2 explosive at higher densities. NQ-h had a large critical diameter, about three times that of NQ-l, in the range of their detonability.

## 15.5 Toxicity of Nitroguanidine

The toxicity of NQ was thoroughly re-examined in the late 1980s in parallel with measuring the toxicity of GuN from which it is made. However, only few military and contractor personnel ever get exposed to GuN, whereas exposure to NQ at LAP operations and in the field and during demilitarization operations is more likely. Consequently, a wider range of toxicity test protocols were applied to NQ than to GuN and performed in parallel [396].

### 15.5.1 Oral Toxicity of Nitroguanidine

Nitroguanidine was administered to rats in the diet at dose levels of 0, 100, 316, and 1000 mg kg<sup>-1</sup> d<sup>-1</sup> for 14 d [397]. The addition of NQ to the diet did not have an effect on food consumption, but there was a significant dose-response increase in water consumption. There were no observable clinical signs attributable to the NQ feeding. Microscopic examination of tissues from the control and 1000 mg kg<sup>-1</sup> d<sup>-1</sup> dose group animals revealed no lesions attributable to the administration of NQ. These findings indicated that NQ is non-toxic in rats when administered at doses as high as 1000 mg kg<sup>-1</sup> d<sup>-1</sup> for 14 d. Nitroguanidine is excreted unchanged in the rats' urine and may act as an osmotic diuretic. Essentially identical results were obtained in a 90-d feeding study using mice instead of rats [398].

The median lethal dose of NQ is greater than 5000 mg/kg body weight in both male and female rats [399, 400] or mice [401]. The predominant clinical signs associated with nitroguanidine administration were urinary excretion of a whitish precipitate (nitroguanidine) in the first 24 hours followed by excretion of a reddish urine for up to a week. Chemical analyses of a whitish crystalline material isolated from the urinary bladder of a rat indicated that the crystalline material was nitroguanidine.

The acute oral toxicity of NQ in mice was at or above the limit value of 5000 mg/kg which produced less than 50% mortality in male mice, while in female mice, the median lethal dose was 4345 mg/kg [402]. Similar toxicity tests were conducted with nitrosoguanidine, which is not used as a propellant or explosive, but may co-exist as a contaminant or degradation product of NQ.

### 15.5.2 Dermal Toxicity of Nitroguanidine

The dermal sensitization potential of nitroguanidine was tested in guinea pigs [403, 404] and rabbits [405, 406]. There was very little skin irritation.

### 15.5.3 Mutagenicity of Nitroguanidine

Nitroguanidine was not mutagenic under the conditions of the mouse lymphoma thymidine kinase forward-mutation assay either with or without prior metabolic activation by rat liver at concentrations ranging from 0.01 to 4 mg/mL [407]. Nitroguanidine was not mutagenic under conditions of the Ames *Salmonella*/mammalian microsome mutagenicity test at doses ranging from 2.8 to 0.0875 mg/plate [408]. Nitroguanidine was non-mutagenic in the *Drosophila melanogaster* sex-linked recessive lethal test following 72-h feeding exposures to concentrations of NQ ranging from 2.08 to 20.8 µg/mL [409].

The potential of NQ to induce sister-chromatid exchanges (SCEs) was assessed using Chinese hamster ovary cells both with and without exogenous metabolic acti-

vation achieved by addition of rat liver extract [410]. Nitroguanidine at concentrations of 4 to 0.01 mg/mL did not induce a statistically significant increase in SCEs either with or without exogenous metabolic activation.

#### 15.5.4 Teratogenicity of Nitroguanidine

Teratogenicity of NQ was evaluated by feeding NQ suspended in 1% carboxymethyl-cellulose at doses of 0, 100, 316, or 1000 mg kg<sup>-1</sup> d<sup>-1</sup> on days 6 through 15 of gestation to pregnant rats [411]. Fetuses were delivered by cesarean section on day 20, weighed, and examined externally. Fetuses from the 1000 mg kg<sup>-1</sup> d<sup>-1</sup> group were significantly smaller than controls with an increased incidence of retarded ossification of the sternbrae, caudal vertebrae, and pubis. Nitroguanidine caused maternal and fetal toxicity at the 1000 mg kg<sup>-1</sup> d<sup>-1</sup> dose level. The no-observed-effect level was 316 mg kg<sup>-1</sup> d<sup>-1</sup>.

In similar tests with rabbits instead of rats [412], fetuses in the 1000 mg kg<sup>-1</sup> d<sup>-1</sup> group were lighter in weight and had an increased incidence of retarded ossification of the sternbrae, olecranon, patellae, and phalanges. There were no dose-related malformations. It was concluded that NQ had no teratogenic potential but does have the potential to cause developmental toxicity.

In a three-generation study with rats, there were no dose-related effects on clinical signs, mating, fertility, gestation, litter size, pup weight, or survival [413]. Histopathological examination of the reproductive organs in adult animals and gross examination of weanlings showed no lesions attributable to NQ in any of the generations.

#### 15.6 Explosive Performance of Nitroguanidine

The cavity enlargement in the lead block test (Trauzl test) was 305 cm<sup>3</sup>/10 g, which is not a very large value. The detonation velocity of NQ confined and pressed into a steel tube at maximum density is 8200 m/s = 26900 ft/s. Other sources give the detonation velocity as 5360 m/s at a packing density of 1.0 g/cm<sup>3</sup> and 7650 m/s at a packing density of 1.5 g/cm<sup>3</sup>. Other sources give the detonation velocity as 7700 m/s and the C-J pressure (measured) as 253 kbar at a packing density of 1.6 g/cm<sup>3</sup> [393].

#### 15.7 Applications of Nitroguanidine

Nitroguanidine can be incorporated into single-base, nitrocellulose powder, and glycerol trinitrate or diethylene glycol dinitrate gelatinized double-base propellants. In these mixtures, it is not dissolved in the powder gel, but is embedded in it as a fine

dispersion. These “cold” (calorie-poor) powders erode gun barrels at a much slower rate than do the conventional “hot” powders. In addition, nitroguanidine has the advantage of quenching muzzle flash, but smoke formation is somewhat more intensive. NQ-NC gun propellants were already in use during World War II.

#### 15.7.1 Demilitarization and Recycling of Nitroguanidine

Laboratory-scale solubility and extraction studies were carried out to investigate the feasibility of recovery of NQ from M30 triple-base gun propellant [414]. The recovery process involved stripping nitroglycerine (NG) from M30 propellant using supercritical carbon dioxide, followed by aqueous extraction of NQ. The solubilities of NQ and NG in supercritical CO<sub>2</sub> were investigated. NQ was found to be relatively insoluble. NG was found to be up to six orders of magnitude more soluble than NQ in supercritical CO<sub>2</sub>. The solubility of NQ in water from 301 to 348 K (28 to 75 °C) was measured at atmospheric pressure. The solubility data were found to follow an exponential function of  $1/T$  over a range of 273 to 373 K (0 to 100 °C). The solubility of NQ varied by almost two orders of magnitude over this temperature range. NQ was readily extracted from NG-depleted M30 propellant using hot water. The bulk of the NQ was recovered by precipitation at 272 K (1 °C). A small amount of NQ remained unrecovered in the extraction solution.

#### 15.7.2 Environmental Degradation of Nitroguanidine

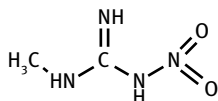
Nitroguanidine spilled on the ground and soaking into soil will eventually disappear by biodegradation [314, 415].

The stability of NQ was evaluated in three moist unsaturated soils under laboratory conditions [416]. The three soils were fortified using an aqueous spiking solution and the residual concentration of NQ was measured after storage for 0, 1, 2, 4, and 8 d at 273 K (20 °C) in the dark. The results yielded a range of half-life decay estimates for nitroguanidine from 7.5 to 56 d, depending on the soil type. No attempt was made to determine environmental transformation products of NQ in the soil or leachate.

### 15.8 Alkyl-Nitroguanidines

1-Methyl-3-nitroguanidine, *N*-methyl-*N'*-nitroguanidine, C<sub>2</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>, CAS RN [4245-76-5], can be prepared by heating nitroguanidine dissolved in water containing KOH to 313 K (40 °C) and adding methylammonium chloride gradually with stirring. This gave a viscous sludge, and some ammonia was evolved. The temperature was raised gradually to 332–334 K (59–61 °C) over a period of 8 min, and held there for 23 min while stirring the mixture. After the mixture was cooled to 279 K (6 °C), a white precipitate of methylnitroguanidine was filtered off, washed with cold water, and dried. The raw

product melted at 424–427 K (151–154 °C). Recrystallization first from hot water and then from ethanol gave the pure product with a melting point of 433 K (160 °C).



Methylnitroguanidine

The oxygen balance of methylnitroguanidine for combustion to CO<sub>2</sub> is –67.7%.

Methylnitroguanidine has been evaluated as an insensitive munitions explosive. Additional information on methylnitroguanidine can be found in [417].

Methylnitroguanidine forms a nitrate salt that melts at 360–364 K (87–91 °C) and a perchlorate salt that melts at 377 K (104 °C). The perchlorate was very sensitive to impact and detonated violently when hit with a hammer.

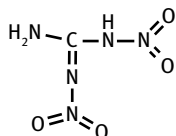
The melting point, crystal shape, structures, and interaction of different mixtures of 1-methyl-2-nitroguanidine and hydrazinium(1+) nitrate were tested by DSC, optical microscope, XRD, and density functional theory [374]. The experimental results showed that the lowest melting point was 340.2 K (67.06 °C); the most stable configuration, the needle-shape crystals, were different from methylnitroguanidine and hydrazinium nitrate, and appeared at a molar ratio of 3 : 2, and the structure was very uniform compared to other molar ratio eutectics. Quantum chemical calculation results showed that the eutectic is not a simply mechanical mixture but may be formed by some sort of loose molecular or atomic interaction, which may explain the observed enthalpy of fusion.

The crystal and molecular structure of *N*-methyl-*N'*-nitroguanidine, C<sub>2</sub>H<sub>6</sub>N<sub>4</sub>O<sub>2</sub>, molecular mass  $M = 118.096$  g/mol, have been determined by XRD at 115 K [418]. The space group is  $P2_1/n$ , with  $a = 4.6320$  Å,  $b = 10.1265(13)$ ,  $c = 11.2399(13)$  Å, and  $\beta = 100.164^\circ$ ,  $V = 518.94$  Å<sup>3</sup>,  $Z = 4$ , and  $\rho_{\text{calc}} = 1.511$  g/cm<sup>3</sup> at 115 K. The observed pycnometric density at 295 K was 1.50 g/cm<sup>3</sup>. The molecule is planar with an unusually long formal double C=N bond of 1.377 Å, and is interpreted as a zwitterionic structure.

1-Ethyl-2-nitroguanidine, C<sub>3</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub>,  $M = 132.13$  g/mol, is similar to other nitrimines [419]. The nitroguanyl group is planar and stabilized by an intra-molecular hydrogen bond. Inter-molecular hydrogen bonds hold the molecules together in the crystal. 1-Ethyl-2-nitroguanidine crystallized in transparent, colorless lumps, monoclinic crystals, space group  $P2_1/n$ , with the unit cell parameters of  $a = 8.9336(9)$  Å,  $b = 16.087(2)$  Å,  $c = 4.3173(4)$  Å,  $\beta = 96.119(8)^\circ$ ,  $V = 616.92(11)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{XRD}} = 1.423$  g/cm<sup>3</sup> at  $T = 293$  K.

## 15.9 Dinitroguanidine

1,2-Dinitroguanidine,  $\text{CH}_3\text{N}_5\text{O}_4$ , DNQ, CAS RN [666736-83-0],



is a product of nitroguanidine nitration with nitric acid and its mixtures with sulfuric acid and oleum [420]. It melts at  $442\text{ K} = 169^\circ\text{C}$ . It is moderately soluble in water and organic solvents. It is a diacid ( $\text{p}K_{\text{a}}1.11$ ,  $\sim 11.5$ ) and at the same time a weak base, undergoing protonation at the nitrogen of the amino group ( $\text{p}K_{\text{b}}\text{H}^+ - 5.81$ ). The decomposition kinetics of 1,2-dinitroguanidine were studied by spectrophotometry in both acid and alkaline media. In the media of high acidity ( $\text{H}_0 > -8$ ), 1,2-dinitroguanidine underwent reversible denitration to nitroguanidine. At lower acidity its conjugate acid or molecular form underwent hydrolysis yielding nitrourea. The monoanion of 1,2-dinitroguanidine in a weak acid or, in alkali, was hydrolyzed into  $N,N'$ -dinitrourea. The reaction of 1,2-dinitroguanidine with alkali in alcohol yielded its salts, and with nitrogen-containing bases one can synthesize both salts and derivatives of 2-nitroguanidine. The synthesis, reactivity, and thermal characteristics of 1,2-dinitroguanidine were summarized in [421–423].

The molecular structure of dinitroguanidine is almost planar, and the conformation is fixed by two intra-molecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds [424]. Due to the delocalization of  $\pi$ -electron density over the whole molecule, there is through-conjugation, with the  $\text{C}-\text{N}$ ,  $\text{N}-\text{N}$ , and  $\text{N}-\text{O}$  bond lengths having values intermediate between those typical for the corresponding single and double bonds. Methyl dinitroguanidine has a similar structure [425].

One of the salts described in the literature is the ammonium salt of dinitroguanidine [426, 427]. The salt crystallized in the monoclinic space group  $P2_1/c$  with a crystal density of  $\rho = 1.735\text{ g/cm}^3$ . The onset of exotherm during the decomposition of the ammonium salt of dinitroguanidine in a DSC is  $470\text{ K}$  ( $197^\circ\text{C}$ ), and its theoretical detonation velocity is  $9066\text{ m/s}$ , which somewhere between RDX and HMX. The impact sensitivity was  $10\text{ N}$ , and its friction sensitivity was  $252\text{ N}$ .

Nitrogen-rich salts of  $N,N'$ -dinitroguanidine, such as ammonium, hydrazinium, guanidinium, 1,3,5-triaminoguanidinium, urea, 5-aminotetrazolium, 1-methyl-5-aminotetrazolium, and 1,4-dimethyl-5-aminotetrazolium were synthesized by deprotonation or metathesis reactions and characterized by single-crystal XRD, IR and Raman spectroscopy, elemental analysis, and DSC [428]. The heats of formation were calculated as summarized in Table 32, along with density and thermal stability data. With these values and the experimental (X-ray) densities, predicted detonation



Table 32: Thermodynamic and thermal stability properties of dinitroguanidinate salts.

| Compound name                                      | Gross formula                                                 | Acronym                  | Density<br>g/cm <sup>3</sup> | $\Delta H_f^\circ(\text{S})$ |        | $\Delta n$ | $\Delta U_f^\circ(\text{S})$ |        | $\Delta U_c^\circ(\text{S})$ |     | Decomposition temp. |  |
|----------------------------------------------------|---------------------------------------------------------------|--------------------------|------------------------------|------------------------------|--------|------------|------------------------------|--------|------------------------------|-----|---------------------|--|
|                                                    |                                                               |                          |                              | kcal/mol                     | kJ/mol |            | kJ/mol                       | g/mol  | kJ/kg                        | K   | °C                  |  |
| Ammonium dinitroguanidinate                        | CH <sub>6</sub> N <sub>6</sub> O <sub>4</sub>                 | ADNQ                     | 1.735                        | -1.5                         | -6.4   | -8         | 13.5                         | 166.13 | 81.0                         | 468 | 195                 |  |
| Hydrazinium(1+) dinitroguanidinate                 | CH <sub>7</sub> N <sub>7</sub> O <sub>4</sub>                 | HyDNQ                    | 1.789                        | 33.4                         | 139.8  | -9         | 162.1                        | 181.15 | 894.9                        | 384 | 111                 |  |
| Guanidinium dinitroguanidinate                     | C <sub>2</sub> H <sub>8</sub> N <sub>8</sub> O <sub>4</sub>   | GDNQ                     | 1.683                        | -8.4                         | -35.1  | -10        | -10.3                        | 208.18 | -49.6                        | 446 | 173                 |  |
| Uronium dinitroguanidinate                         | C <sub>2</sub> H <sub>7</sub> N <sub>7</sub> O <sub>5</sub>   | UrDNQ                    | 1.769                        | -43.1                        | -180.4 | -9.5       | -156.9                       | 209.16 | -750.1                       | 437 | 164                 |  |
| Triaminoguanidinium dinitroguanidinate             | C <sub>2</sub> H <sub>11</sub> N <sub>11</sub> O <sub>4</sub> | TAGDNQ                   | 1.718                        | 69.3                         | 290.2  | -13        | 322.4                        | 253.24 | 1273.2                       | 410 | 137                 |  |
| 5-Aminotetrazolium dinitroguanidinate monohydrate  | + CH <sub>3</sub> N <sub>5</sub> O <sub>4</sub>               | 5-ATDNQ•H <sub>2</sub> O | 1.782                        | 130.4                        | 545.9  | -1.5       | 574.4                        | 252.15 | 2278.0                       | 450 | 177                 |  |
| 1-Methyl-5-aminotetrazolium dinitroguanidinate     |                                                               | 1-MATDNQ                 | 1.707                        | 83.3                         | 349.0  | -11        | 376.2                        | 248.21 | 1515.7                       | 470 | 197                 |  |
| 1,4-Dimethyl-5-aminotetrazolium dinitroguanidinate |                                                               | 1,4-DMATDNQ              | 1.627                        | 75.6                         | 316.7  | -12        | 346.4                        | 262.24 | 1320.9                       | 438 | 165                 |  |

Data source: [428]

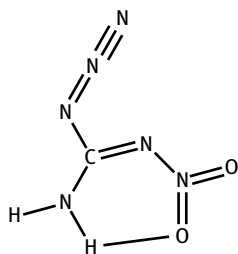
parameters such as the detonation pressure, velocity, energy, and temperature were computed using the EXPLO5 code. The sensitivities towards impact, friction, and electrostatic discharge were tested using a BAM drop hammer, a friction sensitivity tester, and a small-scale ESD test device. Impact sensitivities ranged from 2 J for the hydrazinium salt to 40 J for the guanidinium and urea salts. Friction sensitivity ranged from 60 N for the ammonium and hydrazinium salts to 240 N for the guanidinium and urea salts.

The 4-amino-1,2,4-triazolium salt of dinitroguanidine was synthesized and characterized by XRD, TGA-DTG-DSC, and the Kamlet–Jacobs equation for crystal structure, thermal stability, and detonation properties [429]. The critical temperature of thermal explosion was 459 K (186 °C), the predicted detonation pressure was 29.8 GPa, and the predicted detonation velocity was 8.28 km/s. The impact sensitivity was  $h_{50} = 135$  cm.

Dinitroguanidine (DNG) was synthesized from nitroguanidine and 100% nitric acid/20% oleum/ammonium nitrate as a nitrating system [430]. The structure of DNG was identified by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and MS. The thermal decomposition of DNG was studied using TGA and DSC. The peak temperature of the DSC thermogram for DNG was 456 K (183 °C), indicating that DNG has a very good thermal stability.

Dinitroguanidine has been extensively tested as an explosive [431, 432], and as a rocket propellant ingredient, replacing RDX or NQ [433]. The predicted detonation pressure and detonation velocity of DNG ranged from 24.8 to 30.3 GPa and 7665 to 8422 m/s, better than those of TNT [434].

The nitroguanyl azide, nitrocarbamidoyl azide,  $\text{CH}_2\text{N}_6\text{O}_2$ ,  $M = 130.09$  g/mol, crystal structure is stabilized by intra- and inter-molecular hydrogen bonds [435]. The molecule possesses a nitrimine structure.

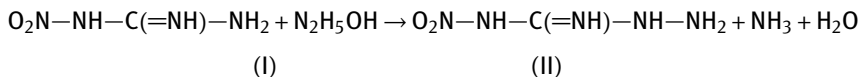


Nitroguanyl azide

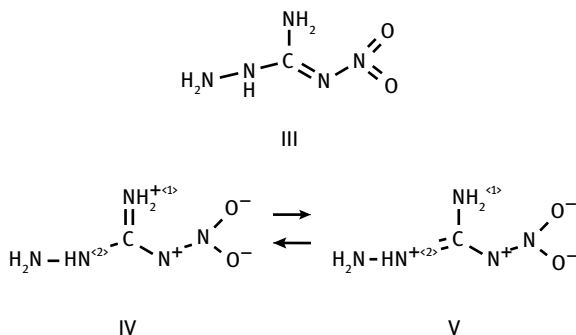
Nitroguanyl azide crystallized in colorless lumps, triclinic crystals, space group  $P\bar{1}$ , with the unit cell parameters of  $a = 9.9302(8)$  Å,  $b = 7.9433(9)$  Å,  $c = 7.1288(8)$  Å,  $\alpha = 98.31(1)^\circ$ ,  $\beta = 110.58(1)^\circ$ ,  $\gamma = 75.108(9)^\circ$ ,  $V = 507.83(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{XRD}} = 1.701$  g/cm<sup>3</sup> at  $T = 293$  K.

## 16 Nitroaminoguanidine

Nitroaminoguanidine,  $\text{CH}_5\text{N}_5\text{O}_2$ , nitraminoguanidine, 1-amino-3-nitroguanidine; hydrazinecarboximidamide, *N*-nitro-; *N*-nitrohydrazinecarboximidamide, CAS RN [18264-75-0], can be obtained by reacting nitroguanidine with hydrazine hydrate in aqueous solution [436, 437].



The structure commonly accepted for nitroaminoguanidine was structure (II) shown above, but other observations indicate a nitrimine (III) or even a partial zwitterion structure,



where the positive charge is not localized but can oscillate among the nitrogen atoms [367].

The crystal structure of nitroaminoguanidine has been investigated by XRD [438]. XRD studies showed that nitroaminoguanidine crystals belong to the tetragonal system. The crystal structure parameters were  $a = 17.063 \pm 0.005 \text{ \AA}$ ,  $b = 17.063 \pm 0.005 \text{ \AA}$ ,  $c = 5.155 \pm 0.005 \text{ \AA}$  and  $c/a$  axial ratio = 0.302.

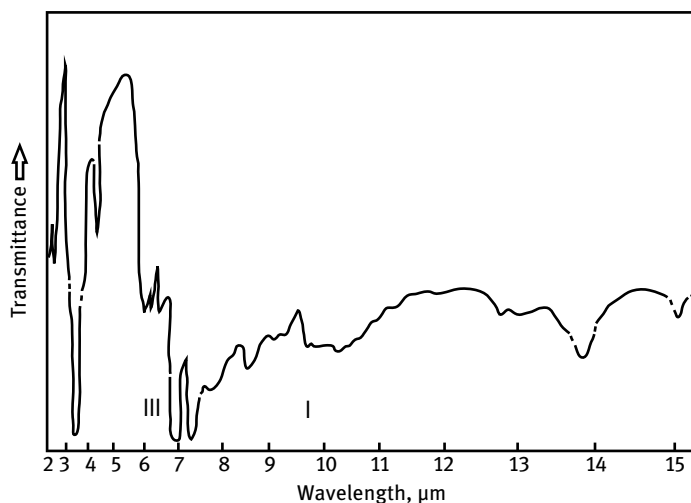
### 16.1 Physical Properties of Nitroaminoguanidine

Nitroaminoguanidine, 1-amino-2-nitroguanidine,  $\text{H}_2\text{N}-\text{NH}-\text{C}(=\text{NH})-\text{NH}-\text{NO}_2$ ,  $\text{CH}_5\text{N}_5\text{O}_2$ , CAS RN [18264-75-0], nitraminoguanidine, is an energetic compound that melts at 462 K (189 °C) and contains 58.8 mass-% nitrogen. Nitroaminoguanidine has an oxygen balance of -33.6%. The physical properties of nitroaminoguanidine are summarized in Table 33.

**Table 33:** Physical properties of nitroaminoguanidine.

| Property                                 | SI units                |               | Non-SI units              |             | Refer-<br>ences |
|------------------------------------------|-------------------------|---------------|---------------------------|-------------|-----------------|
| Molecular mass                           | 119.09 g/mol            | 8.3970 mol/kg | —                         | —           | [105]           |
| Melting point                            | 459–460 K (dec.)        | —             | 186–187 °C (dec.)         | —           | [436]           |
| Melting point                            | 462 K                   | —             | 189 °C                    | —           |                 |
| Density                                  | 1.710 g/cm <sup>3</sup> | —             | 0.062 lb/in. <sup>3</sup> | —           | [18]            |
| Enthalpy of formation $\Delta H_f^{298}$ | +22.1 kJ/mol            | +185.5 kJ/kg  | +5.27 kcal/mol            | +44.3 cal/g | [18]            |

The IR spectrum of nitroaminoguanidine shows bands typical for C–NH and N–NO<sub>2</sub> bonds (Figure 42).



**Figure 42:** IR Spectrum of nitroaminoguanidine (Reproduced and modified from [125], with permission from Levering Estate.)

## 16.2 Chemical Properties of Nitroaminoguanidine

1-Amino-3-nitroguanidine (nitroaminoguanidine) can be synthesized by hydrazinolysis of nitroguanidine. Due to its amphoteric character, it can form stable salts with strong acids and strong bases. Salts of nitroaminoguanidine with oxidizing acids are powerful explosives and attractive high-nitrogen compounds which burn without leaving residues.

Study of the thermal decomposition of nitroaminoguanidine under temperature-programmed conditions in a DSC and isothermal conditions in a TGA showed that

under non-isothermal conditions, nitroaminoguanidine apparently decomposed in one stage, with a loss in weight of 80% [438]. But the slow thermal decomposition of nitroaminoguanidine in the solid phase under isothermal conditions proceeded via three stages. The first and the second stages obeyed the Avrami–Erofeev equation. Gaseous decomposition products detected using IR were  $\text{NH}_3$ ,  $\text{NO}_2$ ,  $\text{HCN}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$ . High-temperature decomposition IR studies indicated preferential deamination reactions breaking the  $\text{N}-\text{NH}_2$  and  $\text{C}-\text{NH}_2$  bonds, leading to  $\cdot\text{NH}_2$  radical formation. Addition of diphenylamine, a known chain inhibitor, decelerated the thermal decomposition, supporting a radical chain reaction mechanism.

Although the molecular structure of 1-amino-2-nitroguanidine is very simple, its reactivity is surprisingly versatile. ANQ can undergo various reactions, including reduction reactions, acylation reactions, salification reactions, coordination reactions, aldimine condensation reactions, cyclization reactions, and azide reactions [439].

### 16.3 Safety Properties of Nitroaminoguanidine

Nitroaminoguanidine is sensitive to shock and friction. In the BAM impact test apparatus, the impact sensitivity was measured as 3 Nm. In the BAM friction test apparatus, the friction sensitivity was positive at 240 N pistil force. In the Picatinny tester, the impact sensitivity was 22 cm with a 2-kg weight. For comparison, the sensitivity of tetryl in the same machine was 30 cm.

### 16.4 Properties of Nitroaminoguanidinium Salts

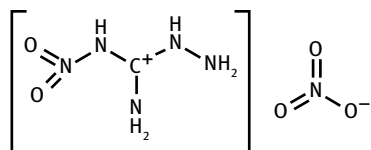
Due to its basicity, 1-amino-3-nitroguanidine can be protonated by strong mineral acids or acidic heterocyclic compounds. The nitrate and perchlorate salts of 1-amino-3-nitroguanidine (ANQ) were synthesized by protonation of ANQ with 40% nitric acid and 60% perchloric acid, respectively [440]. Another acid, 5-nitrimino-1,4*H*-tetrazole, was used to synthesize the 1-amino-3-nitroguanidinium nitriminotetrazolate salt. The dinitramide salt of 1-amino-3-nitroguanidine was synthesized by metathesis reaction of silver dinitramide and 1-amino-3-nitroguanidinium chloride. The dinitroguanidine salt was synthesized by protonation of ANQ with 1,3-dinitroguanidine. These salts were fully characterized by single-crystal XRD; IR, Raman, and NMR spectroscopy; MS; elemental analysis; and DSC. Barium, lead, silver, and copper salts of nitroaminoguanidine are sensitive to shock and were considered as primary explosives.

Nitroaminoguanidine forms complexes with nickel(II), cobalt(II), or copper(II) nitrate, where the metal ion is surrounded by two nitrate ions, two nitroaminoguanidine molecules, and two molecules of water of hydration.

Two energetic derivatives of 1-amino-3-nitroguanidine were synthesized by introducing the furoxan moiety and the 2,4,6-trinitrophenyl moiety into the nitroguanidine frame [441]. The resulting compounds,  $C_5H_7N_7O_4$  and  $C_8H_6N_8O_8$ , were characterized by IR spectroscopy, multi-nuclear NMR, DSC, TGA, and elemental analysis. Both compounds possess good thermal stability, with the decomposition onset temperature above 453 K (180 °C).

#### 16.4.1 Nitroaminoguanidinium Nitrate

1-Amino-2-nitroguanidinium nitrate (ANGN) was synthesized and fully characterized by NMR, IR spectroscopy, DSC, MS, and elemental analysis [442]. The calculated critical temperature of thermal explosion, entropy of activation, enthalpy of activation, free energy of activation, detonation pressure, and detonation velocity were 320 K, 130.2 J mol<sup>-1</sup> K<sup>-1</sup>, 155.4 kJ/mol, 106.4 kJ/mol, 43 GPa, and 9775 m/s, respectively.



##### 16.4.1.1 Toxicity of Nitroaminoguanidinium Nitrate

*In vitro* rat hepatocyte toxicity and bacterial (*Salmonella*) genotoxicity assays were performed on 13 high-energy chemicals that are candidates for potential replacement monopropellants for hydrazine [245]. The chemicals were mostly hydrazine derivatives and amino compounds in the form of their nitrate salts. The results in hepatocytes showed a dose-dependent decrease in mitochondrial activity (MTT), an increase in lactate dehydrogenase (LDH) leakage, and depletion of GSH levels. Nitroaminoguanidinium nitrate was the least toxic of the hydrazine derivatives tested.

#### 16.4.2 Nitroaminoguanidinium Perchlorate

The chloride and perchlorate salts of 1-amino-3-nitroguanidine were synthesized by protonation of 1-amino-3-nitroguanidine with diluted hydrochloric acid and perchloric acid, respectively [443]. 5-Nitrimino-1,4*H*-tetrazole was used to synthesize the nitriminotetrazolate salt. 5-Nitrimino-1,4*H*-tetrazole was obtained by reacting 5-amino-1*H*-tetrazole with 100%  $HNO_3$ . The dinitramide salt of 1-amino-3-nitroguanidine was synthesized by metathesis reaction of silver dinitramide and 1-amino-3-nitroguanidium chloride. The dinitroguanidinate salt was synthesized by protonation of 1-amino-3-nitroguanidine with dinitroguanidine. Prior to that, dinitroguanidine was prepared by nitration of nitroguanidine in anhydrous nitric acid/ $N_2O_5$ . All compounds were fully

characterized by single-crystal XRD, vibrational spectroscopy (IR and Raman), multi-nuclear NMR spectroscopy, elemental analysis, and DSC measurements. The heats of formation of several salts were calculated and, together with the experimental XRD densities, several detonation parameters such as the detonation pressure, velocity, energy, and temperature were computed using the EXPLO5 code. The sensitivities towards impact, friction, and electrostatic discharge were tested using the BAM drop hammer, friction tester, and a small-scale electrostatic discharge test device.

### 16.5 Applications of Nitroaminoguanidine

Gun propellants with nitroaminoguanidine have lower flame temperatures, minimum smoke signature, no muzzle flash, and reduced barrel erosion in artillery guns [444].

### 16.6 Other Nitroguanidine Derivatives

A more energetic derivative of NQ is *N*-nitro-*N*-(2,2,2-trinitroethyl)guanidine (TNENG), which is a burning-rate accelerator with an activity two to three times higher than that of HMX [445].

Propellants containing 1-nitro-1-(2,2,2-trinitroethyl)guanidine, TNENG, the glycidyl azide polymer, GAP, and several energetic plasticizers were shown to exhibit burn rates much higher than conventional oxidizers. The combustion efficiency of the selected propellant for 2-in motor tests was demonstrated to be quite good.

The crystal structure of TNENG was determined by XRD for comparison with NQ, and the crystal lattice parameters were orthorhombic, space group *Pbca*,  $a = 14.611(7) \text{ \AA}$ ,  $b = 11.973(5) \text{ \AA}$ ,  $c = 11.452(5) \text{ \AA}$ ,  $V = 2003(2) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{XRD}} = 1.758 \text{ g/cm}^3$  [446]. A hydrogen-bonded network like that present in NQ is largely responsible for the lattice cohesion of TNENG.

A series of nitroguanidine-fused bicyclic guanidinium energetic salts paired with inorganic energetic anions and mono- and ditetrazolate anions were synthesized through simple metathesis reactions of 2-iminium-5-nitriminoctahydroimidazo [4,5-d]imidazole chloride and sulfate with the corresponding silver and barium salts in aqueous solution [447]. Melting point, thermal stability, and density were measured. The structures of the nitrate salt 1 and the dinitrocyanomethanide salt 4 were confirmed by single-crystal XRD. Densities, heats of formation, predicted detonation pressures and velocities and specific impulses were calculated. All of the salts possess positive calculated heats of formation and most of them exhibited promising energetic performance that was comparable with that of TNT or RDX.

## 17 Dicyandiamide (2-Cyanoguanidine)

Dicyandiamide, also known as 2-cyanoguanidine, *N*-cyanoguanidine, DCD, CAS RN [461-58-5], is a nitrile derived from guanidine. It is a dimer of cyanamide, from which it can be prepared. Dicyandiamide is a useful intermediate in the synthesis of heterocyclic amines and energetic compounds. It can be used in gas generants as a source of nitrogen.

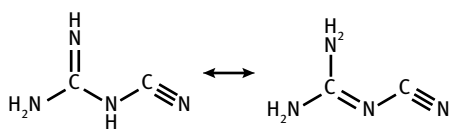
### 17.1 Physical Properties of Dicyandiamide (2-Cyanoguanidine)

The density of solid dicyandiamide is 1.400 g/cm<sup>3</sup>. The melting point is 482.6 K = 209.5 °C = 409.1 °F.

Adiabatic calorimetry, DSC, and TGA were used to measure thermochemical properties of dicyandiamide, such as the low-temperature heat capacity in the range 80–370 K [448]. A phase transition was found between 265 and 275 K, and the peak temperature, enthalpy, and entropy of transition were determined to be 269.5 K, 2.98 kJ/mol, and 11.07 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. The high-temperature heat capacity of DCD was measured with DSC in the range 330–500 K, showing that DCD melts at 487.6 K and the enthalpy and entropy of melting were 22.96 kJ/mol and 47.68 J K<sup>-1</sup> mol<sup>-1</sup>, respectively. The TGA analysis of DCD in the range 300–850 K showed that decomposition starts at 521 K and ends at 660 K in three steps.

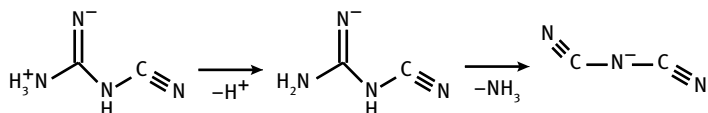
### 17.2 Chemical Properties of Dicyandiamide (2-Cyanoguanidine)

Dicyandiamide (2-cyanoguanidine) exists in two tautomeric forms:



Dicyandiamide (2-cyanoguanidine) can also exist in a zwitterionic form via a formal acid–base reaction among the nitrogens. Loss of ammonia from the zwitterionic form, followed by deprotonation of the remaining central nitrogen atom, gives the dicyanamide anion, [N(CN)<sub>2</sub>]<sup>-</sup>, which is widely used as the anion in ionic liquids:





2-Cyanoguanidine is a colorless solid that is soluble in water, acetone, and alcohol, but not in non-polar organic solvents. The solubility in water is 41.3 g/L. 2-Cyanoguanidine is a valuable intermediate in the synthesis of triaminoguanidinium salts and heterocyclic compounds.

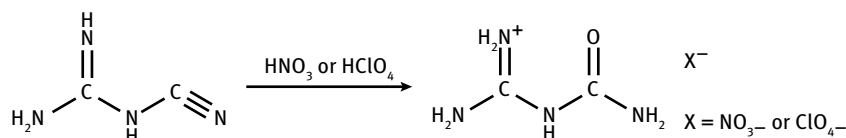
The gaseous decomposition products formed by rapidly (100°/s) heating dicyandiamide under an argon atmosphere at pressures up to 6.8 MPa (1000 psi) were analyzed and found to contain  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{HCN}$ , and  $\text{N}_2\text{O}$  [449]. The solid products were thermally stable cyclic azines (melamine and melone). It may be these cyclic azines that are responsible for lowering the burning rate and pressure coefficient of composite propellants when dicyandiamide is added to those propellants.

The kinetics of the potassium hydroxide-catalyzed formation of melamine from dicyandiamide in diethylene glycol monoethyl ether at 383–423 K (110–150 °C) is consistent with the rate of depolymerization of dicyandiamide to cyanamide [450]. The addition of cyanamide to the reaction system caused a marked increase in the rate. The rate of formation of melamine from a mixture of dicyandiamide and cyanamide (1:1 in molar ratio) was almost identical to that of cyanamide alone. These results suggested a mechanism involving a rate-determining depolymerization of dicyandiamide to cyanamide, followed by condensation of the cyanamide produced with dicyandiamide, leading to melamine by cyclization.

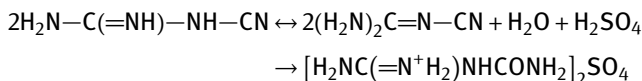
Cyanamide, dicyandiamide, and the related cyclic azines (melamine, ammeline, ammelide, and cyanuric acid) were reacted in water at 373–573 K (100–300 °C) in a sealed CRES-316 tube at 275 bar for the purpose of characterizing the hydrothermolysis chemistry of cyanamide [451]. The conversion of cyanamide to dicyandiamide dominated at 373–448 K (100–175 °C). At 448–523 K (175–250 °C), when the reaction times were shorter than 15 min, the major pathway was hydrolysis of the cyanamide–dicyandiamide mixture to  $\text{CO}_2$  and  $\text{NH}_3$ . A minor pathway was cyclization to higher azines (melamine, ammeline, ammelide, and cyanuric acid). Above about 498 K (225 °C), hydrolysis of these cyclic azines to aqueous  $\text{NH}_3$  and  $\text{CO}_2$  occurred in a relative ratio which depended on the particular cyclic azine, and which, to a certain extent, increased with temperature. At 573 K (300 °C), the conversion of all compounds to  $\text{CO}_2$  and  $\text{NH}_3$  was complete in 10 min.

## 18 Guanylurea (Dicyanodiamidine) and Biguanidine (Biguanide, Guanylguanidine)

Guanylurea salts, in particular those with oxidizing anions, can be formed from cyanoguanidine with strong mineral acids such as sulfuric acid, nitric acid, or perchloric acid, and are useful propellant ingredients:



The anion  $\text{X}^-$  can be exchanged for other anions, such as azide, or nitrogen-rich organic heterocyclic compound anions. The first step in the synthesis of energetic guanylurea salts is usually the preparation of the less energetic, but more readily accessible guanylurea sulfate. Guanylurea can be formed by hydrolysis of cyanoguanidine (dicyandiamide, dicyanodiamidine)



### 18.1 Preparation of Guanylurea Sulfate

To prepare guanylurea sulfate, 16.8 g (0.2 mol) of cyanoguanidine is treated with 50 mL (0.1 mol) of 2-N sulfuric acid and kept over a hot water bath for 3–4 h. Cyanoguanidine is not soluble in water and has to be added as a slurry. The resulting solution is kept in an ice bath for 1 h, and the formed white crystals are filtered off. The rest of the filtrate can be concentrated over a hot water bath and then cooled in ice for a second crop. The resulting crystals are filtered, combined with the first crop, washed with isopropanol, and then dried in a hot-air oven. The yield is 88–90% of theory.

### 18.2 Guanylurea Nitrate and Perchlorate

Guanylurea nitrate (GUUN) and guanylurea perchlorate (GUUP) were prepared from cyanoguanidine and concentrated nitric or perchloric acid, respectively [452]. Both compounds were characterized by analytical and spectroscopic methods. Crystals of GUUP were grown from water, and its crystal structure was determined by single-crystal XRD. GUUP crystallized in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell. The unit cell parameters were  $a = 8.0115(2) \text{ \AA}$ ,  $b = 9.7328(2) \text{ \AA}$ ,  $c = 9.5770(2) \text{ \AA}$ , and  $\beta = 105.89(1)^\circ$ . The heats of combustion of both com-

pounds were determined using oxygen bomb calorimetry. The predicted detonation velocity of GUUN was 5734 m/s, and the predicted detonation pressure was 10.6 GPa. Guanylurea nitrate (= dicyanodiamidinium nitrate) melts at 488 K (215 °C) with decomposition. Guanylurea nitrate,  $C_2H_7N_5O_4$ , with a nitrogen content of 42.4% N and an oxygen balance to  $CO_2$  of -33.91%, has a density of 1.54 g/cm<sup>3</sup> and is soluble in water. The salt is compatible with NC. It is non-hygroscopic and the weight gain at 30 and 90% RH was only 0.1%. GUUN had an impact sensitivity of 1.47 m (58 in) with a 2-kg weight. When heated to 373 K (100 °C) for 48 h, the weight loss was only 0.17%. In the 393 K (120 °C) vacuum stability test result, the gas evolution of a 5-g sample was only 1.54 mL of gas in 40 h.

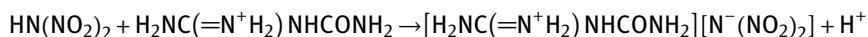
### 18.3 Guanylurea Dinitramide (Dicyanodiamidinium Dinitramide)

*N*-Guanylurea dinitramide, GUDN,  $[H_2NC(=N^+H_2)NHCONH_2][N^-(NO_2)_2]$ , FOX-12, CAS RN [217464-38-5], an energetic material developed in Sweden by FOI (Swedish Defense Research Agency), has low sensitivity and good potential for use as a propellant ingredient, gas generant, or insensitive explosive. It is already being used in gas generators for automotive airbags, which is the first full-scale application of any dinitramide outside of Russia. FOX-12 is a new energetic oxidizer with higher energy and lower sensitivity than similar compounds used in the past. GUDN has many advantages, such as low preparation cost, low sensitivity, excellent thermal stability, non-hygroscopic properties, and good compatibility with other ingredients. *N*-Guanylurea dinitramide is under-oxidized, with an oxygen balance of -19.1%, and contains 46.9% nitrogen.

*N*-Guanylurea dinitramide is neither soluble in cold water nor hygroscopic, and has a very low sensitivity. Its synthesis, physical properties, and sensitivity (friction and drop-weight), thermal stability, and explosion temperature have been described in several publications [453–455].

#### 18.3.1 Preparation of Guanylurea Dinitramide

Guanylurea dinitramide is not very soluble in water or acids. This property has been used with advantage to separate dinitramide salts from the mixture of reaction products, by-products, and unreacted starting materials. Synthesis methods of *N*-guanylurea dinitramide (GUDN) as a new insensitive high-energetic material have been improved since it was first reported. The guanylurea ion can be formed *in situ* in the process by cyanoguanidine, which reacts and hydrolyzes within the reaction mixture. The salt can be separated by filtration and later converted to other dinitramide salts.



A simple method for converting ADN or KDN into guanidinium dinitramide or guanylurea dinitramide (= dicyanodiamidinium dinitramide) by metathetical reaction is described in [456–460]. This is done by mixing a concentrated aqueous solution of ADN with a concentrated aqueous solution of an organic ammonium salt, whose anion is either  $\text{OH}^-$  or  $\text{CO}_3^{2-}$ , which is capable of taking up a proton from the ammonium ion of ADN and forming a substituted ammonium salt. Ammonia and possibly carbon dioxide are driven off from the solution, as well as a certain amount of water to maintain a concentrated solution. The organic dinitramide salt is then precipitated by cooling the solution, and recrystallized if needed. More specifically, for preparation of GUDN in small quantities, 30.2 g (0.1 mol) guanylurea sulfate is dissolved in 50 mL of water with slight warming and stirring and cooled to room temperature. 24.8 g ADN (0.2 mol) is dissolved in 10 mL of water and added to the above solution in portions, whereupon a precipitate of fine white crystals is formed. The precipitate is filtered, washed several times with cold water, and dried under vacuum for an hour. The yield is 90–95% of theory.

FOX-12, (*N*-guanylurea dinitramide), can be synthesized by reaction of ammonium dinitramide and dicyandiamide [461]. Its structure was identified by IR and UV spectra, and some properties such as friction sensitivity, impact sensitivity, and hygroscopicity were determined.

*N*-guanylurea dinitramide can be synthesized from *N*-guanylurea hydrochloride as a starting reactant by hydrolysis and double decomposition reaction, and the overall yield of GUDN can be as high as 79% [462]. The density of GUDN made by this method was  $1.755\text{ g/cm}^3$ . The friction sensitivity of GUDN was 2.45 MPa applied to a 20-mg sample at 66 °C. The drop-weight impact sensitivity  $H_{50}$  was 197 cm when impacted with a 2-kg mass. GUDN has low sensitivity, good thermal stability, and is non-hygroscopic. The results obtained by DSC showed that GUDN is compatible with common energetic materials such as HMX and RDX, and GUDN can be used in double-base propellants.

The production of GUDN has now been scaled up and FOX-12 is available in industrial quantities for evaluation purposes [463]. Performance was evaluated by detonation velocity and cylinder expansion measurements. The sensitivity was evaluated by large-scale gap tests. Three different explosives were tested: melt cast GUNTOL (50/50 mass-% FOX-12/TNT), GUNTONL1 (42.5/42.5/15 mass-% FOX-12/TNT/Al-H2), and GUNTONL2 (42.5/42.5/15 mass-% FOX-12/TNT/Al-A100).

The GUDN synthesis process involves nitration of the ammonium salt of sulfamic acid with concentrated  $\text{HNO}_3/\text{H}_2\text{SO}_4$  at 253 to 223 K (–20 to –50 °C) and further treatment with an aqueous suspension of guanylurea sulfate to obtain GUDN as a white crystalline solid in 50% yield [464]. A systematic study with variation of different parameters such as the molar ratio of the nitrating mixture, conditioning time, and temperature was carried out in order to optimize the process parameters and obtain products in higher yield and with improved purity.

*N*-Guanylurea dinitramide can be recrystallized from dimethyl sulfoxide or *N*-methyl pyrrolidone. The enthalpies of dissolution and the kinetics of dissolution were determined by microcalorimetry [465, 466].

### 18.3.2 Physical Properties of Guanylurea Dinitramide

*N*-Guanylurea dinitramide forms pale yellow crystals with a melting point of 487 K (214 °C dec.), but they usually decompose before melting. Its crystal density is 1.755 g/cm<sup>3</sup>. The molecular mass is 209.12 g/mol. The water solubility of GUDN is 5g/L (at 293 K = 20 °C).

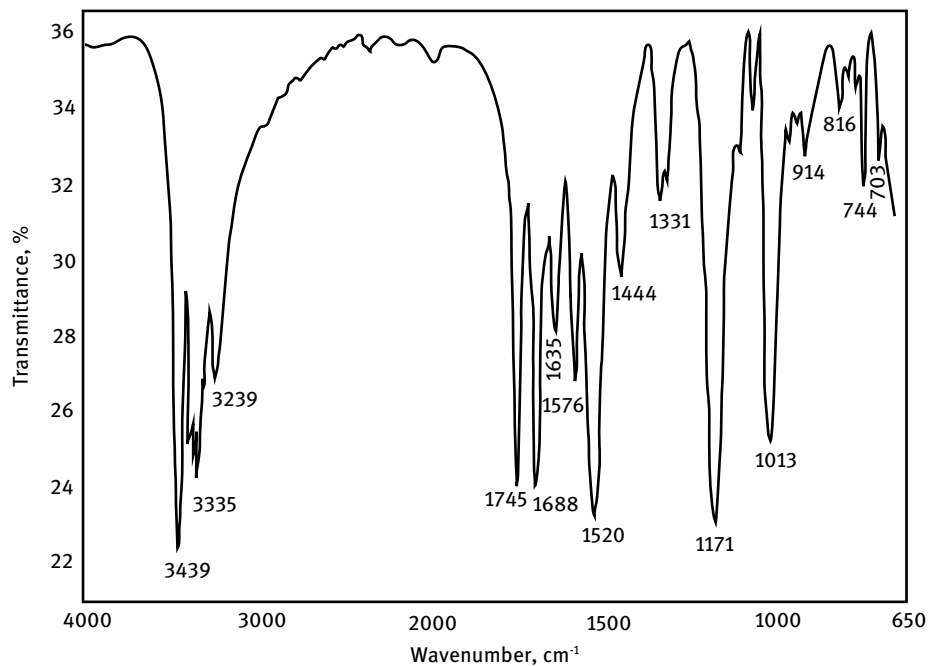
The properties of *N*-guanylurea dinitramide (FOX-12) have been studied [467]. FOX-12 is soluble in cold water. It has a crystal density of 1.755 g/cm<sup>3</sup>, a heat of combustion of 1484 kJ/mol, a temperature of decomposition of 491.56 K (218.41 °C), low sensitivity, and good thermal stability. FOX-12 can be mixed with common energetic materials, such as HMX, RDX, etc.

Physical and safety properties of *N*-guanylurea dinitramide are summarized in Table 34.

**Table 34:** Physical and safety properties of *N*-guanylurea dinitramide.

| Property                                   | Method                                          |                             | References |
|--------------------------------------------|-------------------------------------------------|-----------------------------|------------|
| Melting point                              | DSC                                             | 487 K dec.<br>(214 °C dec.) | [453]      |
| Crystal density                            | Powder X-ray                                    | 1.7545 g/cm <sup>3</sup>    | [453, 455] |
| Enthalpy of formation, $\Delta H_f^{298}$  | Bomb calorimetry                                | −355 kJ/mol                 | [453]      |
| Activation energy of thermal decomposition | DSC, ASTM E 698–79                              | 277 kJ/mol                  | [453, 455] |
| Ignition temperature                       | Wood's metal bath                               | $T_{\text{ign}} = 192$ °C   | [453]      |
| Drop weight sensitivity                    | BAM apparatus with a 2 kg drop weight           | 159 cm                      | [453]      |
|                                            | BAM, Maximum value according to the test method | 49 J                        | [468]      |
| Friction sensitivity                       | Julius–Petri friction apparatus                 | 350 Nm                      | [453]      |
|                                            | Maximum value according to the test method      | 353 Nm                      | [468]      |
| Electrostatic discharge                    | Maximum value according to the test method      | 3125 mJ                     | [468]      |

The IR spectrum of GUDN shows a multitude of peaks belonging to the cation and the anion Figure 43. The peak assignments for the IR spectrum above are listed in Table 35.



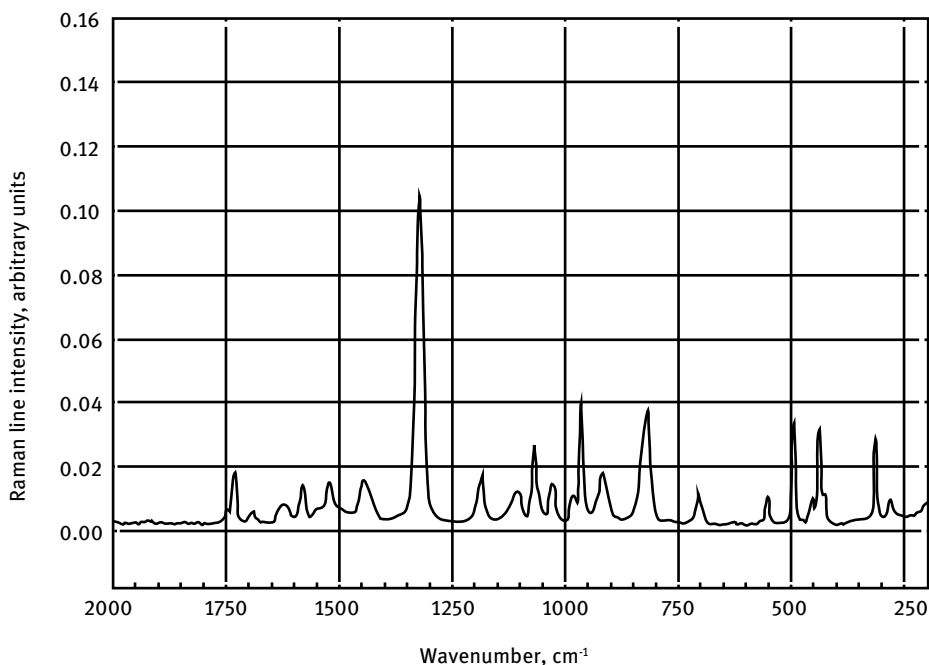
**Figure 43:** FTIR spectrum of guanylurea dinitramide. (Reprinted and modified from [459], with permission granted by Dr. Santhosh 8-Feb-2021.)

**Table 35:** Peak assignments for the IR spectrum of guanylurea dinitramide.

| Assignment                                    | Wave number, cm <sup>-1</sup> |
|-----------------------------------------------|-------------------------------|
| $\nu_{as}$ NO <sub>2</sub> in phase           | 1520                          |
| $\nu_s$ NO <sub>2</sub> in phase              | 1331                          |
| $\nu_s$ NO <sub>2</sub> out of phase          | 1171                          |
| $\delta_{sciss}$ NO <sub>2</sub> in phase     | 816                           |
| $\delta_{sciss}$ NO <sub>2</sub> out of phase | 744                           |
| $\delta_{rock}$ NO <sub>2</sub> out of phase  | 703                           |
| $\nu_{as}$ N3                                 | 1013                          |
| $\nu_s$ N3                                    | 914                           |
| N—H stretching                                | 3439, 3325, 3239              |
| C=O stretching                                | 1635                          |
| =C=NH stretching                              | 1688                          |

Data source: [459]

The Raman spectrum of *N*-guanylurea dinitramide shows the lines typical for both the organic cation and the dinitramide anions (Figure 44).



**Figure 44:** FT Raman spectrum of *N*-guanylurea dinitramide. (Republished and modified from [453], with permission from ©2002 Elsevier; permission conveyed through Copyright Clearance Center Inc.)

The FT-Raman spectrum presented here was measured with an excitation wavelength of 1064  $\mu\text{m}$  and the resolution was 4  $\text{cm}^{-1}$ . The conclusion from this FT-Raman spectrum is that FT-Raman gives sharper peaks and is easier to interpret than the corresponding IR spectra.

#### 18.3.2.1 Thermodynamic Properties of Guanylurea Dinitramide

The constant-volume combustion energy, enthalpy of solution in ethyl acetate, and kinetic behavior of the exothermic decomposition reaction of GUDN were determined by a precise rotating bomb calorimeter, a Calvet microcalorimeter, and DSC, respectively [469]. See Table 36.

**Table 36:** Thermodynamic properties of *N*-guanylurea dinitramide.

| Property                                       | SI units                   | Other units    | References |
|------------------------------------------------|----------------------------|----------------|------------|
| Constant-volume energy of combustion, 298.15 K | $-7068.64 \pm 2.37$ J/g    | -1689 cal/g    | [469]      |
| Heat of combustion                             | 1484 kJ/mol                | 355 kcal/mol   | [467]      |
| Standard enthalpy of formation                 | $-319.76 \pm 0.58$ kJ/mol  | -76.4 kcal/mol | [469]      |
|                                                | -356 kJ/mol                | -85.1          | [18]       |
|                                                | -355.6 kJ/mol              | -85 kcal/mol   | [463]      |
| Enthalpy of solution in ethyl acetate          | $165.737 \pm 0.013$ kJ/mol | 39.6 kcal/mol  | [469]      |

### 18.3.2.2 Molecular Structure of Guanylurea Dinitramide

The molecular structure of guanylurea dinitramide consists of two-dimensional planar sheets and the only interaction between the sheets is via van der Waals forces. Guanylurea dinitramide crystallizes in orthorhombic crystals, space group  $Pna2_1$ , with crystal structure parameters of  $a = 13.660(10)$  Å,  $b = 9.3320(10)$  Å,  $c = 6.1360(10)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 782.5$  Å<sup>3</sup>,  $Z = 4$  and  $\rho_{\text{XRD}} = 1.775$  g/cm<sup>3</sup>. See also [470, 471].

### 18.3.3 Chemical Properties of Guanylurea Dinitramide

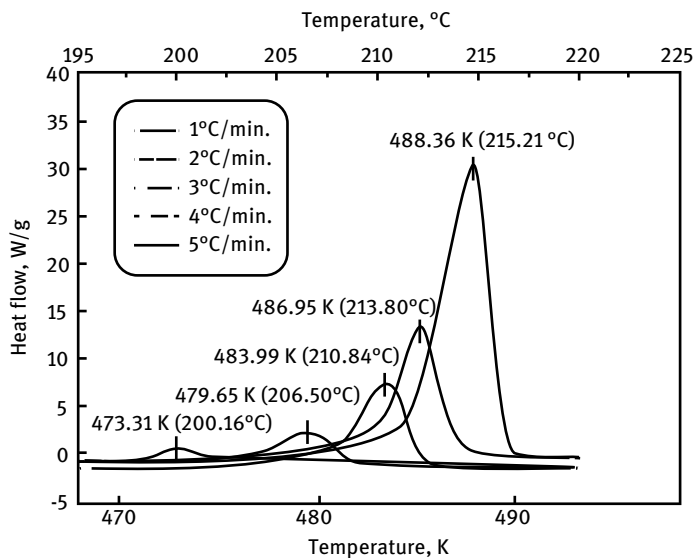
Guanylurea dinitramide is non-hygroscopic and compatible with most materials of construction and in contact with other energetic materials.

#### 18.3.3.1 Thermal Stability of GUDN

Samples of FOX-12 were heated from room temperature with heating rates ranging from 0.5 to 10 °C/min. [453]. FOX-12 has an onset of exotherm at 487.9 K (214.8 °C) with a heating rate of 10 °C/min. Using the ASTM method E 698–79, the activation energy was measured in a temperature interval from 473 to 498 K (200 to 225 °C). Compared to both RDX and ADN, FOX-12 has a higher activation energy (277 kJ/mol, compared to 201.5 kJ/mol for RDX), indicating a high degree of thermal stability. The increased thermal stability compared to ADN shows that the dinitramide ion can be stabilized by hydrogen bonding to appropriate cations and is not intrinsically unstable as was believed earlier. This is encouraging, as it seems likely that other low-sensitivity/high-thermal-stability dinitramide salts can be synthesized. The theoretical detonation properties were calculated, and the pressure dependence of the strand burning rate was measured.

An overlay of DSC curves of GUDN obtained with five different heating rates is shown in Figure 45. The peak maximum temperature ( $T_m$ ) for GUDN showed a regular increase as the heating rate was increased from 1 to 5 °C/min, which is in agreement with the general trend reported for similar compounds. Depending on which data reduction method is used, the activation energy for the decomposition of GUDN is 190 to 191.8 kJ/mol and the natural logarithm of the pre-exponential factor is 46 to 46.46.





**Figure 45:** Thermal decomposition of GUDN. (Reprinted and modified from [459], with permission granted by Dr. Santhosh 8-Feb-2021.)

The values of activation energy and pre-exponential factor of GUDN are higher than those for ADN or KDN and decrease in the order GUDN > KDN > ADN, which is also the trend of the decomposition temperatures of these three compounds.

The activation energy,  $E_a$ , and the pre-exponential factor,  $A$ , of the exothermic main decomposition reaction of GUDN were 220.2 kJ/mol and  $10^{21.18} \text{ s}^{-1}$ , respectively [469]. Other sources gave the temperature of decomposition of GUDN as 491.56 K (218.41 °C), but it was not specified whether that was the onset of the exotherm or the peak temperature of the exotherm peak [467].

The kinetics of the exothermic decomposition reaction and the specific heat capacity of *N*-guanylurea dinitramide (GUDN) were determined by DSC in a temperature-programmed mode and microcalorimeter [472]. The kinetic parameters of the major exothermic decomposition reaction, the apparent activation energy ( $E_a$ ), pre-exponential factor ( $A$ ), self-accelerating decomposition temperature, time to maximum rate, and time to ignition under adiabatic conditions were calculated. The self-accelerating decomposition temperature was 473.95 K. The time to ignition under adiabatic conditions was 3.51 s. The results showed that under non-isothermal DSC conditions, the thermal decomposition of GUDN could be described by the empiric-order autocatalytic equation

$$\frac{d\alpha}{dt} = 10^{18.49} \exp(-195500/RT)(1-\alpha)^{0.81} + 10^{18.00} \exp(-177000/RT)\alpha^{1.29}(1-\alpha)^{0.71}$$

and the value of the critical rate of temperature rise in GUDN was 0.1236 K/h when the decomposition reaction converted into thermal explosion. See also [473].

The decomposition of *N*-guanylurea dinitramide (FOX-12) and its reaction with RDX involves complex physiochemical processes that were investigated with DSC and rapid-scan FTIR of the decomposition products [474].

The thermal stability of ADN/ guanylurea dinitramide mixtures was already discussed in *Encyclopedia of Oxidizers*, chapter “Dinitramide Oxidizers.” Guanylurea dinitramide (GUDN) has excellent thermal stability and is non-hygroscopic. The thermal decomposition of guanylurea dinitramide has been studied by non-isothermal thermogravimetry (TGA) and thermogravimetry combined with mass spectrometry (TGA-MS) [475]. A strong dependence of the activation energy  $E_a$  on the degree of conversion,  $\alpha$ , was shown, where the  $E_a$  increases steadily up to an  $\alpha$  of ~0.6, followed by a marginal increase, and reaches ~435 kJ/mol at the end of the reaction.  $E_a$  has also been determined for GUDN using Kissinger’s method. A comparison of the results from the Kissinger and the isoconversional methods showed that the activation energies from these two methods are comparable. Using the model-free isoconversional method, the isothermal conversion as a function of time at two different temperatures was computed. The evolved gases during the decomposition of GUDN were analyzed by TG-MS, which revealed the formation of ions corresponding to  $N_2$ ,  $O_2$ ,  $NH_3$ ,  $H_2O$ ,  $N_2$ ,  $NO$ , methane diimine, isocyanic acid,  $N_2O$ ,  $NO_2$ , and urea.

The thermal decomposition of GUDN is a typical autocatalytic reaction [476]. Model-based kinetics were established by simultaneous fitting of a series of non-isothermal DSC data at different heating rates, which can be described as a generalized autocatalytic model and expressed by the following:

$$\frac{d\alpha}{dt} = 2.29 \times 10^{23} \exp(-225240/RT)(1 - \alpha)^{1.76} (\alpha^{1.47} + 0.59 \exp(-18300RT))$$

The reaction model matched the experimental results, with a high correlation coefficient,  $R^2$ , of 0.9994. Based on the established kinetic model, important thermal safety indicators such as the time to conversion limit, adiabatic time to maximum rate, and self-accelerating decomposition temperature were simulated, providing an important basis concerning the thermal hazard of GUDN in practical applications.

Thermal analysis revealed the compatibility of GUDN with benchmark explosives such as RDX and TNT, with which it was intended to be co-melted and co-cast in melt-cast explosive formulations [477]. GUDN was evaluated as a possible replacement for RDX/TNT-based aluminized and non-aluminized melt-cast explosive formulations. The thermal properties of the composition as well as its sensitivity to impact and friction were investigated and compared to a baseline composition based on RDX and TNT.

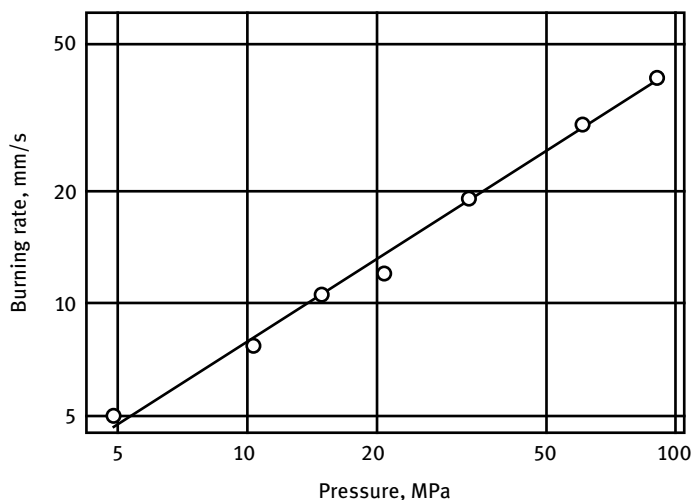
The isothermal decomposition of GUDN was studied by measuring gas-pressure versus time curves of the isothermal isochoric decomposition of GUDN at temperature intervals between 393 and 443 K (120 and 170 °C) [478]. An extremely long lag phase

and slow acceleration period were observed in the decomposition process of GUDN. The kinetic rate parameters of GUDN decomposition were obtained by the Arrhenius equation and a model-fitting method. An average  $E_a$  of 159.4 kJ/mol and  $\ln A$  of 34.74 s<sup>-1</sup> were obtained for the lag phase, whereas an average  $E_a$  of 125.6 kJ/mol and  $\ln A$  of 26.97 s<sup>-1</sup> were measured for the acceleration period. The time required for decomposition during long-term storage was estimated to be 9.8 years when the extent of reaction reached 0.1% at ambient temperature (298 K = 25 °C). The residue was analyzed by FTIR, gases were analyzed by GC, and a possible decomposition process equation was proposed.

The pyrolysis of GUDN was examined using DSC together with *in situ* microscopy and Raman spectroscopy, in order to determine the pyrolysis mechanism for this compound [479]. The experimental results showed that the thermal behavior of GUDN depended on the heating rate and on the presence of a condensed phase prior to a sharp exotherm at the highest heating rate. During pyrolysis of GUDN, guanidium nitrate (GN) and cyanuric acid were formed by solid-phase reactions that were associated with this exotherm, and molten GN formation promoted the exothermic reaction.

#### 18.3.4 Burning Rate of GUDN

The logarithm of the burning rate as a function of pressure showed a linear increase with pressure (Figure 46). The burning rate exponent,  $n$ , for FOX-12 was found to be



**Figure 46:** Burning rate of *N*-guanyllurea dinitramide as a function of pressure. (Reprinted and modified from [453], with permission of ©2002 Elsevier; permission conveyed through Copyright Clearance Center Inc.)

0.73, which is within the desirable range. The burning rate equation for FOX-12 is

$$r_b = 1.46p^{0.73}$$

where  $r_b$  is the burning rate in mm/s and  $p$  is the pressure in MPa. However, when mixed with inorganic oxidizers, such as perchlorates or nitrates, FOX-12 burns with a high rate and a pressure coefficient down to 0.3–0.4. See also [480].

### 18.3.5 Toxicity Hazards of GUDN

EURENCO Bofors has tested GUDN toxicity according to the European REACH regulations [481]. The test results are shown in Table 37. GUDN has received the ELINCS number 451-590-5.

**Table 37:** Toxicity and environmental effects testing of GUDN (CAS RN 217464-38-5).

| Test method                               | Test result                   |
|-------------------------------------------|-------------------------------|
| Toxicity LD50 (oral/dermal rat)           | 2000 mg/L                     |
| Toxicity to aquatic organisms LC50 (fish) | 100 mg/L                      |
| EC50 (daphnia, 48h)                       | 100 mg/L                      |
| EC50 (algae, 72h)                         | 39 mg/L                       |
| EC50                                      | 656 mg/L activated sludge, 3h |
| Acute inhalation                          | No effect                     |
| Sensitizing                               | Not sensitizing               |
| Effect on skin                            | No irritation                 |
| Effect on eyes                            | Not irritating                |
| Lipophilicity                             | Log $P_o/w$ –2.5              |
| Mutagenicity mammalian cell               | Negative                      |
| Mammalian bone marrow                     | Negative                      |
| Biodegradability COD                      | 0,1 g/g                       |
| BOD7/COD                                  | 0.5                           |

Data source: [481]

According to these tests, GUDN is considered non-carcinogenic and non-allergenic. It is not irritating, neither in contact with skin or eyes nor if inhaled.

In order to evaluate environmental pollution potential and persistence of FOX-12 if it were to be spilled accidentally in unexploded munitions, the photodegradability and biodegradability of FOX-12 were determined [482]. When dissolved in water, FOX-12 dissociated to produce the dinitramide ion moiety and guanylurea, as demonstrated by HPLC analysis. When an aqueous solution of FOX-12 was subjected to photolysis using a solar photoreactor, rapid removal of the dinitramide with concurrent formation of  $N_2O$ ,  $NO_2^-$ , and  $NO_3^-$  was observed, but the second component, guanylurea, was photostable. When FOX-12 was incubated aerobically with soil bacteria

and protected from light, the dinitramide component of FOX-12 was recalcitrant but guanylurea degraded effectively to ammonia, guanidine, and presumably  $\text{CO}_2$ . When FOX-12 was incubated with soil bacteria in the presence of light, both components of FOX-12 degraded simultaneously, giving products similar to those described above. It was recommended that FOX-12 can be effectively degraded by a joint photomicrobial process and, therefore, should not cause persistent contamination of surface waters.

### 18.3.6 Safety Properties of Guanylurea Dinitramide

The safety properties of guanylurea dinitramide have been described [468, 483]. The strand burning rate of GUDN as a pure substance is 5 mm/s at 5 MPa and 50 mm/s at 50 MPa. The pressure exponent is 0.6–0.7. The drop-weight impact sensitivity of GUDN is 49 J (maximum value according to the BAM test method). The friction sensitivity of GUDN is 353 N (maximum value according to the BAM test method). The electrostatic discharge sensitivity of GUDN is 3125 mJ (maximum value according to the test method). The critical temperature of thermal explosion of GUDN is 217.6 °C. In the large-scale gap test, GUDN had a 50% probability of detonation with 72–90 cards [463]. In the same test, Composition B required 234 cards.

Table 38 is a comparison of the sensitivity of FOX-12 to that of ADN and RDX. As can be seen, FOX-12 is less sensitive than ADN or RDX [455].

**Table 38:** Sensitivity data for GUDN in comparison to ADN and RDX.

| Compound | Explosive drop height, cm | Friction sensitivity, N m | Comments           |
|----------|---------------------------|---------------------------|--------------------|
| FOX-12   | 159                       | 350                       | Raw FOX-12         |
| ADN      | 31                        | 350                       | Unprilled material |
| RDX      | 38                        | 120                       |                    |

Data source: [453]

### 18.3.7 Applications of Guanylurea Dinitramide

The detonation velocity of GUDN is about 8210 m/s [469]. Its theoretical specific impulse when used as a rocket propellant by itself is 213.1 s. Mixtures of GUDN and HMX had a detonation velocity of 7500 m/s for a 50 : 50 mixture. In a 60-mm diameter copper tube with plane wave initiation and a 50-g Comp-B booster, the detonation velocity of FOX-12 was 7970 m/s [455].

GUDN has been evaluated as an ingredient in gas-generating compositions for airbags and seat belt tensioner systems [484, 485]. GUDN can be used in solid propellants, gas-generating agents, and as an insensitive explosive [486, 487].

### 18.4 Other Guanylurea Salts

The reaction of cyanoguanidine with hydrochloric, sulfuric, nitric, or perchloric acids yielded guanylurea chloride, sulfate, nitrate, and perchlorate. The chloride and sulfate serve as starting reactants for further syntheses to form energetic salts based on the guanylurea cation and azide, 5-nitrotetrazolate, 5-aminotetrazolate, picrate, and 5,5'-azotetrazolate anions [488]. The lower-molecular-weight salts are readily soluble in water and other polar solvents, whereas the picrate and azotetrazolate are only slightly soluble in boiling water. All materials were characterized by means of elemental analysis, MS, and vibrational (IR, Raman) and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14/15}\text{N}$ , and  $^{35}\text{Cl}$ ) spectroscopy. The crystal structures were determined by low-temperature XRD. The thermal decomposition of the nitrogen-rich salts was measured by DSC, and their enthalpies of formation were calculated on the basis of the electronic energies of the ions using the MP2 method. All compounds had high thermal stabilities, as suggested by their high decomposition points ranging from 453 K (180 °C; azide) to 526 K (253 °C; picrate). All salts showed sharp onsets of decomposition without melting. They showed two sharp decomposition steps in the case of the 5,5'-azotetrazolate salts, with the only exception of the 5-aminotetrazolate salt, which had a high melting point at 425 K (152 °C) and an even higher decomposition temperature at 513 K (240 °C). The 5,5'-azotetrazolate salt showed very good long-term thermal stability. The sensitivity to shock, friction, and electrostatic discharge of all materials in the standard BAM methods was 40 J for impact and 360 N for friction sensitivity. The detonation pressures and velocities of guanylurea salts were calculated from the energies of formation using the EXPLO5 code and the results are shown in Table 39. For comparison, the detonation pressure for guanylurea dinitramide (FOX-12) is 27.6 GPa and the detonation velocity is 8308 m/s.

Guanylurea dicyanamidate is a precursor for the synthesis of graphitic carbon nitride [489]. Similar reactions were observed with guanidinium dicyanamidate [200].

Table 39: Properties of guanylurea salts.

| No  | Compound name                              | Gross formula                                                   | Molecu-<br>lar mass | Nitrogen<br>content | Oxygen<br>balance |                           | Density <sup>a</sup><br>g/cm <sup>3</sup> | Decom-<br>position<br>temperature |       | Enthalpy of forma-<br>tion, theoretical<br>$\Delta H_f^{298}$ |        | Detonation<br>pressure,<br>GPa | Detonation<br>velocity,<br>m/s |
|-----|--------------------------------------------|-----------------------------------------------------------------|---------------------|---------------------|-------------------|---------------------------|-------------------------------------------|-----------------------------------|-------|---------------------------------------------------------------|--------|--------------------------------|--------------------------------|
|     |                                            |                                                                 |                     |                     | mass%             | %                         |                                           | K                                 | °C    | kJ/kg                                                         | kJ/mol |                                |                                |
| 6   | Guanylurea nitrate                         | C <sub>2</sub> H <sub>7</sub> N <sub>5</sub> O <sub>4</sub>     | 165.05              | 42.4                | -33.9             | <b>1.567</b> <sup>a</sup> | 476                                       | 203                               | -2512 | -414.6                                                        | 17.4   | 7004                           |                                |
| 7   | Guanylurea perchlorate                     | C <sub>2</sub> H <sub>7</sub> N <sub>4</sub> O <sub>5</sub> Cl  | 202.01              | 27.7                | -15.8             | 1.873                     | 477                                       | 204                               | -4    | -0.81                                                         | 23.3   | 8115                           |                                |
| 8a  | Guanylurea azide hydrate                   | C <sub>2</sub> H <sub>9</sub> N <sub>7</sub> O <sub>2</sub>     | 163.08              | 60.1                | -63.8             | 1.494                     | 453                                       | 180                               | 190   | 31.0                                                          | 20.6   | 7880                           |                                |
| 8b  | Guanylurea azide anhydrous                 | C <sub>2</sub> H <sub>7</sub> N <sub>7</sub> O                  | 145.07              | 67.6                | -71.7             | <b>1.499</b> <sup>a</sup> | 453                                       | 180                               | 213   | 30.9                                                          | 16.9   | 7289                           |                                |
| 9   | Guanylurea 5-nitrotetrazolate              | C <sub>3</sub> H <sub>7</sub> N <sub>9</sub> O <sub>3</sub>     | 217.07              | 58.1                | -47.9             | <b>1.615</b> <sup>a</sup> | 482                                       | 209                               | 174   | 37.8                                                          | 20.3   | 7439                           |                                |
| 10  | Guanylurea 5-aminotetrazolate              | C <sub>3</sub> H <sub>9</sub> N <sub>9</sub> O                  | 187.09              | 67.4                | -81.2             | 1.577                     | 513                                       | 240                               | 497   | 93.0                                                          | 18.4   | 7530                           |                                |
| 11  | Guanylurea picrate                         | C <sub>8</sub> H <sub>9</sub> N <sub>7</sub> O <sub>8</sub>     | 331.05              | 29.6                | -60.4             | <b>1.669</b> <sup>a</sup> | 526                                       | 253                               | -1136 | -376.1                                                        | 19.7   | 7152                           |                                |
| 12a | Guanylurea 5,5'-azotetrazolate hemihydrate | C <sub>6</sub> H <sub>15</sub> N <sub>18</sub> O <sub>2.5</sub> | 379.16              | 66.5                | -71.7             | <b>1.599</b> <sup>a</sup> | 486                                       | 213                               | 2157  | 817.8                                                         | 24.3   | 8222                           |                                |
| 12b | Guanylurea 5,5'-azotetrazolate anhydrous   | C <sub>6</sub> H <sub>14</sub> N <sub>18</sub> O <sub>2</sub>   | 370.15              | 68.1                | -73.5             | <b>1.588</b> <sup>a</sup> | 476                                       | 199                               | 2208  | 817.3                                                         | 23.3   | 8115                           |                                |

<sup>a</sup> Density determination method: pycnometric in **bold**, XRD calculated at 100K, in *italics*  
Data source: [488]

## 19 Other Guanidine Derivatives

### 19.1 Biguanidine (Biguanide, Guanylguanidine)

Biguanidine, also known as biguanide, guanylguanidine, imidodicarbonimidic diamide,  $C_2H_7N_5$ ,  $HN[C(=NH)NH_2]_2$ , CAS RN [56-03-1], is a diimide and a secondary amine. It is a colorless solid that dissolves in water to give highly basic solutions. These aqueous solutions of the free base slowly hydrolyze to ammonia and urea.

#### 19.1.1 Biguanidinium Salts

Biguanidine can accept one or two protons to form biguanidinium(1+) or biguanidinium(2+) salts. The salts are sometimes also called biguanidium salts. Dry biguanidinium salts are stable in solid form and make good high-nitrogen additives to gas generants.

##### 19.1.1.1 Biguanidinium Nitrates

Biguanidinium(1+) nitrate was prepared from aqueous solutions of biguanidinium sulfate and barium nitrate, removal of the precipitated barium sulfate by filtration, and slow evaporation of the filtrate. The structures of two energetic biguanidinium salts, biguanidinium(1+) nitrate,  $[H_2NC(N=H)NHC(=NH)NH_3]^+NO_3^-$ , and biguanidinium(2+) dinitrate,  $[H_3NC(N=H)NHC(=NH)NH_3]^{2+}(NO_3^-)_2$ , have been derived from XRD data collected at 193 K [490]. The mono- and diprotonated biguanidinium nitrates are dense organic materials with efficient packing of planar anions and biplanar (twisted) cations connected by multiple hydrogen bonds. The experimental densities were  $1.62\text{ g/cm}^3$  at 193 K and  $1.59\text{ g/cm}^3$  at 298 K for the biguanidinium(1+) nitrate and  $1.75\text{ g/cm}^3$  at 193 K and  $1.73\text{ g/cm}^3$  at 298 K for the biguanidinium(2+) dinitrate salt, which agreed well with theoretical predictions. Both salts are denser than the comparable DAGN and TAGN salts. The crystal structure of biguanidinium(1+) nitrate was monoclinic with space group  $P2_1/n$ , and the cell parameters were  $a = 6.959(1)\text{ \AA}$ ,  $b = 10.778(2)\text{ \AA}$ ,  $c = 9.489(2)\text{ \AA}$ ,  $\beta = 109.28(2)^\circ$ ,  $V = 671.8(4)\text{ \AA}^3$ ,  $Z = 4$ . The crystal structure of biguanidinium(2+) dinitrate was orthorhombic with space group  $Pca2_1$ , and cell parameters were  $a = 14.0232(8)\text{ \AA}$ ,  $b = 6.8842(5)\text{ \AA}$ ,  $c = 8.9541(5)\text{ \AA}$ ,  $V = 864.4\text{ \AA}^3$ ,  $Z = 4$ .

##### 19.1.1.2 Biguanidinium Perchlorates

Biguanidinium(1+) perchlorate can be prepared by reaction of biguanidinium sulfate with barium perchlorate. Biguanidinium(2+) diperchlorate can be prepared by treating biguanidinium(1+) perchlorate with an excess of perchloric acid. The structures of two energetic biguanidinium salts have been determined from low-temperature XRD data collected at 100 K. Biguanidinium perchlorate,  $[H_2NC(N=H)NHC(=NH)NH_3]^+ClO_4^-$ , and biguanidinium(2+) diperchlorate,  $[H_3NC(N=H)NHC(=NH)NH_3]^{2+}(ClO_4^-)_2$ , have structures characterized by twisted cations and extensive hydrogen bonding



[491]. Biguanidinium(1+) perchlorate crystallized in triclinic crystals with space group  $P\bar{1}$ , and the cell parameters were  $a = 7.409 \text{ \AA}$ ,  $b = 7.619 \text{ \AA}$ ,  $c = 9.843 \text{ \AA}$ ,  $\alpha = 82.02^\circ$ ,  $\beta = 83.20^\circ$ ,  $\gamma = 69.92^\circ$ ,  $V = 515.3 \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{XRD}} = 1.95 \text{ g/cm}^3$  at 100 K. Biguanidinium(2+) diperchlorate crystallized in triclinic crystals with space group  $P\bar{1}$ , and the cell parameters were  $a = 7.7421 \text{ \AA}$ ,  $b = 9.874 \text{ \AA}$ ,  $c = 12.267 \text{ \AA}$ ,  $\alpha = 112.75^\circ$ ,  $\beta = 91.89^\circ$ ,  $\gamma = 111.91^\circ$ ,  $V = 784.9 \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 1.71 \text{ g/cm}^3$  at 100 K.

In the DTA/DTG, biguanidinium(1+) perchlorate starts to lose mass at 597 K (324 °C) and the mass loss rate maxes at 611 K (338 °C) [492]. Time-/temperature-resolved mass spectra of the decomposition products showed similarity with the mass spectra of melamine, in particular with the peak at  $m/z = 126$  which corresponds to a melamine radical ion ( $[\text{C}_3\text{N}_6\text{H}_6]^+$ ). See also [199].

### 19.1.1.3 Biguanidinium Dinitramides

Biguanidinium(1+) mono-dinitramide crystallizes in triclinic crystals, space group  $P1$ , with  $a = 4.3686(4)$ ,  $b = 9.404(2)$ ,  $c = 10.742(1) \text{ \AA}$ ,  $\alpha = 83.54(1)^\circ$ ,  $\beta = 80.386(9)^\circ$ ,  $\gamma = 79.93(1)^\circ$ ,  $V = 426.8(1) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.62 \text{ g/cm}^3$  [493]. Biguanidinium(2+) bis-dinitramide forms monoclinic crystals with a space group  $C2/c$ ,  $a = 11.892(2) \text{ \AA}$ ,  $b = 8.131(1) \text{ \AA}$ ,  $c = 13.038(2) \text{ \AA}$ ,  $\beta = 115.79(1)^\circ$ ,  $V = 1135.1(3) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.84 \text{ g/cm}^3$ , m.p. 399–402 K. Biguanidinium(2+) bis-dinitramide also forms a monohydrate with a distinctly different crystal structure, forming orthorhombic crystals with space group  $P2_12_12_1$ ,  $a = 6.4201(6)$ ,  $b = 13.408(1)$ ,  $c = 14.584(2) \text{ \AA}$ ,  $V = 1255.4(4) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.76 \text{ g/cm}^3$ . All three structures are characterized by extensive hydrogen bonding. All the biguanidinium H atoms participate in hydrogen bonds, with an H–X (X = N, O) contact distance of less than 2.5 Å. The dinitramide anion has a surprisingly variable and asymmetric structure. The two halves of the anion are twisted with respect to each other; however, the twist varies from 5.1 to 28.9°, depending on the environment. Further, the two ends of the anion have significantly different geometries, e.g., the “equivalent” N–N bond lengths differ by up to 0.045 Å.

The electron density and hydrogen bonding in biguanidinium(1+) dinitramide and biguanidinium(2+) bis-dinitramide crystals (space groups  $P\bar{1}$  and  $C2/c$ ) have been determined from low-temperature (90 K) XRD experiments [494]. The kinetic, potential, and electronic energy distributions were calculated from the experimental electron density using DFT functionals for biguanidinium dinitramide and biguanidinium bis-dinitramide [495]. The spatial distribution of the electronic energy density was shown to be a useful descriptor of the chemical bonding and inter-molecular interactions in these molecules.

The crystal structures of biguanidinium(1+) dinitramide and biguanidinium(2+) bis-dinitramide crystals have been determined at several temperatures in the range of 85–298 K using single-crystal XRD techniques [496]. The thermal expansion was strongly anisotropic.

Single crystals of biguanidinium dinitramide undergo photolysis at low temperature, releasing free radicals which can be tracked by EPR [497].

## 19.2 Guanyl Azide

Guanyl azide nitrate was first prepared in 1892, so chemists should have had ample time to examine it, but it remains poorly characterized. Guanyl azide is formed by reaction of aminoguanidine with nitrous acid in strongly acidic solutions [228]:



Guanyl azide is a high-nitrogen compound that forms salts with strong mineral acids like nitric acid or dinitramidic acid. Guanyl azide itself is not very stable. When heated, guanyl azide decomposes to cyanamide and hydrazoic acid. Guanyl azide may exist in two tautomeric forms, but they are indistinguishable. Guanyl azide is presumed to be an intermediate in the synthesis of 5-aminotetrazole. Cyclization of guanyl azide leads to aminotetrazole. The enthalpy of formation of guanyl azide nitrate, GAzN,  $\text{C}_1\text{H}_4\text{N}_6\text{O}_3$ ,  $M = 148.08 \text{ g/mol}$ , is  $+35 \text{ cal/g} = +5.183 \text{ kcal/mol} = +21.68 \text{ kJ/mol}$ . The density is  $1.500 \text{ g/cm}^3$  [124].

Guanylazide nitrate reacts with amines to form the aminium salts of 5-aminotetrazole [498]. Amines used in this reaction included cyclohexylamine, dibutylamine, and pyrrolidine.

## 19.3 Cyanoguanyl Azide

Cyanoguanyl azide was first reported in 1928, but very little work has been done on it in the interim. Cyanoguanyl azides  $\text{NC—N=C(N}_3\text{)NHR}$  with  $\text{R} = \text{H, Me, Ar}$  can be used in the synthesis of substituted tetrazoles by reacting them with amines or hydrazines [499].

## 19.4 Nitroguanyl Azide

Nitroguanyl azide can be prepared by reaction of nitroaminoguanidine with nitrous acid in strongly acidic solutions [370]:



Nitroguanyl azide forms slightly yellowish crystals melting at  $351\text{--}352 \text{ K}$  ( $78\text{--}79^\circ\text{C}$ ) with decomposition [500]. Reactions of nitroguanyl azide with amines results in formation of heterocyclic compounds like 5-nitraminotetrazoles [501]. 5-Nitraminotetrazole forms a guanidinium salt containing 66.65% N that melts at  $498\text{--}499 \text{ K}$  ( $225\text{--}226^\circ\text{C}$ ).

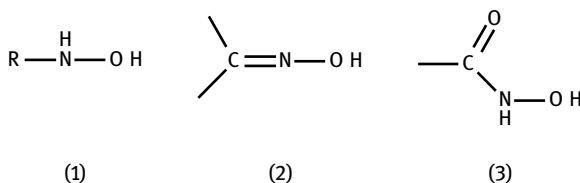
The IR spectra of nitroguanyl azide and numerous other high-nitrogen compounds were published in a very useful summary [126].

Nitroguanyl azide reacts with amines to form the aminium salts of 5-nitroaminotetrazole [498]. Amines used in this reaction included *n*-propylamine, aniline, cyclohexylamine, and piperidine.

## 20 Oximes

Aldoximes and ketoximes form readily by reaction of aldehydes or ketones with hydroxylamine or hydroxylammonium salts. Sometimes this reaction is used for the separation, purification, and identification of naturally occurring aldehydes and ketones. Some of the oximes are useful as solid propellant ingredients because of their high nitrogen content and favorable oxygen balance.

The structural common link between hydroxylamines (1), oximes (2), and hydroxamic acids (3) is the N—OH group:

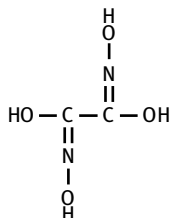


Formally, they can all be viewed as derivatives of hydroxylamine. A very wide-ranging survey of hydroxylamines, oximes, and hydroxamic acids was published in 2009, including chapters on intrinsic features of hydroxylamines, oximes, and hydroxamic acids [502], structural analysis of hydroxylamines, oximes, and hydroxamic acids [503], and the organic thermochemistry of hydroxylamines, oximes, hydroxamic acids, and their derivatives [504].

Oximes serve as intermediates in the synthesis of oxaza heterocyclic compounds [505].

### 20.1 Dihydroxyglyoxime

Dihydroxyglyoxime, also known as dihydroxyglyoxime, ethanedihydroxamic acid, *N,N'*-dihydroxyethane diamide, *N,N'*-dihydroxyoxamide, oxaldihydroxamic acid, oxalohydroxamic acid,  $\text{C}_2\text{H}_4\text{N}_2\text{O}_4$ , DHG, CAS RN [1687-60-1], molecular mass 120.864 g/mol, contains 23.33% nitrogen,



is a nitrogen-rich compound that has been used in a number of gas generants, and has an oxygen balance of −26.7% [506, 507]. The enthalpy of formation of

dihydroxyglyoxime is  $-542.7$  kJ/mol. Dihydroxyglyoxime can be prepared by reaction of hydroxylamine hydrochloride with diethyl oxalate in ethanol aqueous solution. An improved process prepares dihydroxyglyoxime by reaction of oxalate esters with a hydroxylammonium salt in an alkaline aqueous alcoholic solution [508]. In one example, a solution of diethyl oxalate in ethanol and an aqueous NaOH solution were added to an ethanol/water solution of hydroxylammonium chloride with stirring at 293–313 K (20–40 °C). Upon completion of the reaction, the mixture was filtered and the precipitate was dissolved in water at 353 K (80 °C) and acidified with acetic acid to give dihydroxyglyoxime in 58% yield.

The structure of oxalohydroxamic acid has been investigated by XRD and spectroscopic analyses [509]. It has been shown that oxalohydroxamic acid exists in the oxamic form in the solid as well as in solution. The variable-temperature NMR studies revealed an exchange of OH and NH protons, the exchange being faster at higher temperatures. The kinetic and thermodynamic parameters such as rate constant ( $K$ ), the free energy of activation, and the energy of activation ( $E_a$ ) for the proton exchange process have been obtained. The compound crystallized in the monoclinic shape, space group  $P2_1/c$ , with  $a = 5.208$  Å,  $b = 3.864$  Å,  $c = 11.482$  Å,  $\beta = 111.45^\circ$ , and  $Z = 2$ . There is strong hydrogen bonding between the molecules, which form dimers.

Dihydroxyglyoxime (DHG) can be prepared by reaction of hydroxylammonium chloride with diethyl oxalate in ethanol aqueous solution [510]. The molecular structure of DHG was characterized by elemental analysis, IR, and single-crystal XRD. The results showed that the crystal belongs to a monoclinic system, with  $Pn$  space group and cell parameters of  $a = 0.52219(15)$  nm,  $b = 0.38737(11)$  nm,  $c = 1.0750(3)$  nm,  $\beta = 115.396(5)^\circ$ ,  $V = 0.216(11)$  nm<sup>3</sup>,  $\rho_{\text{XRD}} = 1.873$  g/cm<sup>3</sup>, and  $Z = 2$ .

The assay of dihydroxyglyoxime in gas-generator propellants can be determined by a spectrophotometric analysis method based on the red complex formed from the reaction of dihydroxyglyoxime and iron(III) [511]. The maximum absorption wavelength of the complex was at 490 nm and the molar absorptivity was  $1.38 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>. The absorption was linear within the DHG content range of 0–5 mg/50 mL.

Microencapsulation of dihydroxyglyoxime can reduce its sensitivity to moisture and incompatibility with curing agents and improve bonding with a binder [512].

Just in case dihydroxyglyoxime should find more widespread distribution as an ingredient in gas generants for air bag inflation, the toxicity of dihydroxyglyoxime was investigated in animal tests with mice [513] and rats [514].

The ammonium salt of oxalohydroxamic acid,  $[\text{NH}_4^+][\text{C}_2\text{H}_3\text{N}_2\text{O}_4^-]$ ,  $M = 137.1$  g/mol, forms during decomposition of oxalohydroxamic acid [515]. The salt crystallized in the form of triclinic crystals, space group,  $P\bar{1}$ ,  $a = 3.952(1)$ ,  $b = 6.772(1)$ ,  $c = 9.993(1)$  Å,  $\alpha = 98.06(1)^\circ$ ,  $\beta = 89.96(1)^\circ$ ,  $\gamma = 106.96(1)^\circ$ ,  $V = 253.06$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_m = 1.805$  g/cm<sup>3</sup>,  $D_{\text{XRD}} = 1.798$  g/cm<sup>3</sup>. Only one hydroxyl hydrogen is associated with each molecule.

**Table 40:** Physico-chemical and thermodynamic properties of DGH and its onium salts.

| Substance abbreviated name | Gross formula                                               | Melting point |         | Density                    |         | Enthalpy of formation |         | Molecular mass | Oxygen balance |      | Nitrogen content | Adiabatic flame temperature <sup>a</sup> |   |
|----------------------------|-------------------------------------------------------------|---------------|---------|----------------------------|---------|-----------------------|---------|----------------|----------------|------|------------------|------------------------------------------|---|
|                            |                                                             | K             | °C      | $\rho$ , g/cm <sup>3</sup> | kJ/kg   | kJ/mol                | g/mol   |                | %              | %    |                  | K                                        | K |
| DGH                        | C <sub>2</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub> | 443           | 170     | 1.6                        | -4749.8 | -570                  | 120.064 | -26.7          | 23.33          | 1274 |                  |                                          |   |
| A-DGH                      | C <sub>2</sub> H <sub>7</sub> N <sub>3</sub> O <sub>4</sub> | 493           | 220     | 1.43                       | -5804   | -795                  | 137.095 | -40.8          | 30.65          | 791  |                  |                                          |   |
| H-DGH                      | C <sub>2</sub> H <sub>8</sub> N <sub>4</sub> O <sub>4</sub> | 478-483       | 205-210 | 1.35                       | -4266.8 | -649                  | 152.109 | -42.1          | 36.83          | 1094 |                  |                                          |   |
| Ha-DGH                     | C <sub>3</sub> H <sub>7</sub> N <sub>5</sub> O <sub>5</sub> | 431           | 158     | 1.27                       | -5346.2 | -818                  | 153.094 | -26.1          | 27.45          | 1142 |                  |                                          |   |

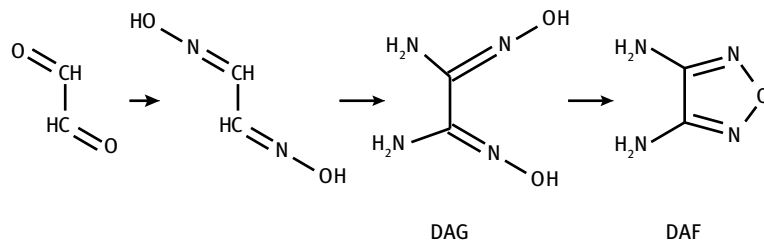
<sup>a</sup> Calculated for  $P = 10.13 \text{ MPa} = 100 \text{ atm}$ 

Data source: [516]

Salts of oxaldihydroxamic acid with ammonia (A-DGH), hydrazine (H-DGH), or hydroxylamine (Ha-DGH) are capable of self-sustained burning in a wide range of pressures, producing low-temperature gaseous products [516, 517]. Properties of oxaldihydroxamic acid and three salts of oxaldihydroxamic acid are summarized in Table 40. Burning rates and pressure exponents of DGH and the salts by themselves as well as of propellants formulated with these ingredients were measured, and are reported in this publication.

## 20.2 Diaminoglyoxime

Diaminoglyoxime; 2-amino-*N'*-hydroxy-prop-2-enamidine, hydroxylamine;  $C_2H_6O_2N_4$ , DAG, is an intermediate in the synthesis of diaminofurazan (DAF) and can be used as a ballistic modifier in solid propellants. Dehydration and ring closure of diaminoglyoxime leads to the formation of diaminofurazan:



The gaseous decomposition products formed by rapidly ( $100^\circ/\text{s}$ ) heating DAG or DAF under an argon atmosphere at pressures up to 6.8 MPa (1000 psi) were analyzed and found to contain  $NH_3$ ,  $CO_2$ ,  $HCN$ , and  $N_2O$  [449]. The solid products were thermally stable cyclic azines (melamine and melone). It may be these cyclic azines that are responsible for lowering the burning rate and pressure coefficient of composite propellants when DAG or DAF are added to those propellants. See also [518].

Differential scanning calorimetry (DSC) and simultaneous thermal analysis (DTA-TGA) revealed that DAG decomposed in two stages [519]. Kinetics of the initial stage of thermal decomposition of DAG evaluated from TG data gave an activation energy of 153 kJ/mol. The high-temperature FTIR spectra of DAG decomposition products suggested preferential cleavage of  $N-O$  and  $C-NH_2$  during decomposition. Mass spectral data also suggested the possibility of similar processes.

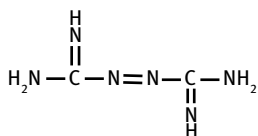
Diaminoglyoxime can be prepared by adding glyoxal and hydroxylamine hydrochloride into a cooled solution of sodium hydroxide in water [520]. The material was characterized by using single-crystal XRD, elemental analysis and FTIR. The crystal structure was monoclinic, space group  $P2_1$ , with the cell parameters:  $a = 0.6763(8)$  nm,  $b = 0.3578(4)$  nm,  $c = 0.9658(12)$  nm,  $\beta = 90.78(2)^\circ$ ,  $V = 0.2338(5)$  nm<sup>3</sup>,

$Z = 2$ ,  $\rho_{\text{XRD}} = 1.678 \text{ g/cm}^3$ . DSC techniques with a heating rate of  $10^\circ\text{C/min}$  showed that DAG melted at  $476.6 \text{ K}$  ( $203.5^\circ\text{C}$ ). The thermal decomposition occurred in two steps at  $482\text{--}485 \text{ K}$  ( $209\text{--}212^\circ\text{C}$ ) and  $485\text{--}513 \text{ K}$  ( $212\text{--}240^\circ\text{C}$ ), and decomposition was complete at  $513 \text{ K}$  ( $240^\circ\text{C}$ ).

The thermal stability of DAF and DAG was determined by DSC and TGA-DTA [521]. The thermal degradation of DAF and DAG occurred in the temperature ranges of  $503\text{--}548 \text{ K}$  ( $230\text{--}275^\circ\text{C}$ ) and  $453\text{--}503 \text{ K}$  ( $180\text{--}230^\circ\text{C}$ ), respectively. The thermal decomposition of DAG started simultaneously with its melting. The influence of heating rate ( $5, 10, 15$ , and  $20^\circ\text{C/min}$ ) on DSC behavior showed that as the heating rate was increased, decomposition temperatures of the compounds were also increased. Based on the values of activation energy, the thermal stability of DAF was better than that of DAG.

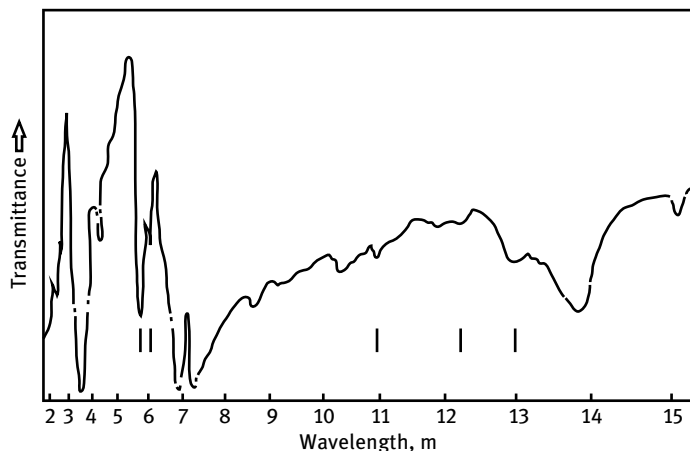
### 20.3 Azobisformamidine Derivatives

Azobisformamidine, azodicarboxamidine, E-1,2-diazenedicarboximidamide, 1,2-diazenedicarboximidamide, *N*-(carbamidimidoylimino)guanidine, 1-carbamimidoyliminoguanidine,  $\text{C}_2\text{H}_6\text{N}_6$ , CAS RN [2625-66-3], CAS RN [6272-66-8], and its salts with oxidizing acids are useful high-nitrogen compounds and have been proposed as ingredients in gas generants for airbag inflators.



With a molecular mass of  $114.12 \text{ g/mol}$ , the nitrogen content of the free base is  $73.65\% \text{ N}$ . When protonated (singly or doubly), the positive charge is not fixed in one location, but it can move among several tautomeric forms of the ion, which helps to stabilize the compound. Azo-bis-nitroformamidine exists as the nitrimino tautomer. In this configuration it undergoes Diels-Alder additions with dienes, yielding complex heterocycles.

Azobisformamidinium(2+) dinitrate (azodicarbamidine dinitrate,  $\text{C}_2\text{H}_8\text{N}_8\text{O}_6$ ) forms yellow platelets when recrystallized from warm water, but when heated to  $453\text{--}457 \text{ K}$  ( $180\text{--}184^\circ\text{C}$ ), it explodes without melting. It can be prepared by treating a nitric acid solution of aminoguanidinium nitrate with an aqueous  $\text{KMnO}_4$  solution. The picrate salt of this base is also explosive. The IR spectrum of azobisformamidinium(2+) dinitrate shows absorption bands typical for  $=\text{NH}$  bonds and nitrate ions (Figure 47). See also [74].



**Figure 47:** IR spectrum of azobisformamidinium(2+) dinitrate (Reproduced and modified from [125], with permission from Levering Estate.)

A clean method for the preparation of azobisformamidinium(2+) dinitrate by oxidation with nitric acid instead of potassium permanganate is described in the following patent: Azodiformamidine dinitrate can be prepared by placing 10 g of aminoguanidinium nitrate (AGN) into a 400-mL glass beaker with 25 mL water, forming a slurry of AGN/water. A dispersion was formed by slowly pouring 150 mL of reagent-grade nitric acid (70%) into the AGN/water slurry while stirring. A 10-degree temperature rise occurred as the acid was first added, but the temperature came back down with continued addition of acid. The dispersion was then heated to 328–338 K (55–65 °C), with moderate stirring on a hot plate. This caused any remaining AGN to go into solution. Heating was continued at 328–338 K (55–65 °C), during which time the solution went through a color transition from a white color to a straw color to an intensely bright yellow color. For safety reasons, the reaction temperature should be limited to below 338 K (65 °C). The beaker was then placed in an ice bath to cool down the contents. A yellow precipitate appeared as the temperature dropped below 285 K (+12 °C). After the reaction mixture was held in the ice bath at about 273–278 K (0–5 °C), the yellow precipitate was vacuum filtered and washed with several rinses of distilled water. The precipitate was then washed several times with ethanol and dried at 335 K (62 °C). The procedure can also be started with aminoguanidinium bicarbonate, but more nitric acid must be used. The use of this azodiformamidine dinitrate in airbag inflators has been patented [522].



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# Ammonia

## Hydronitrogen Compounds

*Encyclopedia of Liquid Fuels*, contains six chapters dealing with hydronitrogen compounds and four chapters dealing with hydrazines. “Ammonia” is the simplest hydronitrogen. The chapter “Hydrazine” deals with the parent inorganic compound hydrazine, while “Alkylhydrazines” deals with alkylhydrazines other than methylhydrazine and dimethylhydrazines, which are covered in the chapters “Methylhydrazine” and “Dimethylhydrazines,” respectively. Amines, amides, and imides are not counted as hydronitrogen compounds, although many of them contain N–H bonds.

### 1 Ammonia

Ammonia,  $\text{NH}_3$ , also known as nitrogen hydride, azane, CAS RN [7664-41-7], is a colorless gas at room temperature, with a pungent, lacrimatory odor. In an equestrian and agricultural setting, the ammonia concentration in horse stables resulting from the decomposition of urea in urine may be high enough to cause eyes to lacrimate and break out in tears. Ammonia dissolves quite rapidly in water. For laboratory and household use, ammonia is used as an aqueous solution. Reagent grade aqueous ammonia solutions (“*aqua ammonia*” in Latin) for chemical laboratory use usually contain 30 mass-%  $\text{NH}_3$  whereas household ammonia solutions, often used for window cleaning, contain only 10%  $\text{NH}_3$ . In either case, any ammonia solutions above 3%  $\text{NH}_3$  are hazardous and eye and skin contact must be avoided.

The most economic method to transport ammonia from production sites to end-use locations is in the anhydrous form as a liquid under its own vapor pressure. Anhydrous ammonia is evaporated and circulated in closed loops in commercial refrigeration units (cold-storage warehouses), where its high heat of evaporation results in efficient refrigeration cycles. Anhydrous ammonia was used as a rocket propellant fuel in the X-15 high-altitude-research rocket plane.

Ammonia intended for use as fertilizer is often transported through pipelines and by railroad cars and tanker trucks in the anhydrous liquid state under pressure and then diluted with water at the point of end use. Depending on soil and crop types, it can be used as a gas or dissolved in water. It can be injected into the soil in gaseous form (depending on the moisture content of the soil) or as an aqueous solution. Much ammonia is converted by the chemical industry into nitric acid, also often used in fertilizer production in the form of ammonium nitrate, an oxidizer which is based on ammonia as a feedstock [1].

Liquid and vaporized ammonia has been used in satellites as the working fluid for resistojets and arc jets.

Besides water and methane, ammonia may be the most abundant molecule in the universe with more than two atoms. Measurements of the atmosphere of Jupiter indicate that many of the clouds that we see are composed of frozen ammonia. Jupiter would be a good candidate for *in situ* propellant recovery if one could locate puddles, lakes, or glaciers of ammonia on other celestial bodies or scoop up ammonia on a flyby without dipping too deep into the atmosphere.

A major disadvantage of the use of anhydrous ammonia as a rocket propellant is its low density and the fact that it is not hypergolic with most oxidizers. Liquid ammonia was present on every Space Shuttle flight; it was used on the Space Shuttle orbiter as a dump (open-cycle) coolant to cool the fluorocarbon fluid that circulated through the heat exchangers in the crew compartment to provide air-conditioning and keep the computers at a safe operating temperature, in particular during re-entry and aerodynamic heating. The ammonia dump cooling was active only during the re-entry phase when much of the re-entry aerodynamic breaking heat had to be dissipated away from the crew compartment.

Liquid ammonia is pumped through several loops around the International Space Station (ISS) as a coolant and heat transfer fluid in the climate (temperature) control of the inhabited modules and to cool heat-producing computers and experiments. There have been several incidents of ammonia leaking from the ISS. Every once in a while, an ammonia pump has to be replaced. Ammonia leaks are a problem for astronauts performing extra-vehicular activity (EVA) during maintenance when ammonia crystals adhere to their space suits and get dragged into the air lock when they re-enter the ISS.

Liquid ammonia and ammonia mixtures have been considered as alternative automotive fuels [2–4]. When the supply of liquid and gaseous fossil fuels is exhausted a few centuries from now, there may be an economy based on hydrogen and ammonia as transportation fuels, although there is concern about  $\text{NO}_x$  formation during the combustion of ammonia (Section 10.1) [5].

At the same time, ammonia injection into stack gases of fossil fuel-burning stationary power plants is used as a method to **remove**  $\text{NO}_x$  before the stack gases are vented into the atmosphere in populated areas to minimize smog and air pollution. In the De $\text{NO}_x$  process, the gases with a carefully metered amount of ammonia are passed over a catalyst and the only products leaving the stack are nitrogen and water (besides the carbon dioxide, unchanged). Most likely, the first vehicle to be powered with liquid ammonia in an internal combustion engine or an air/ammonia/hydrogen fuel cell will be a farmer's tractor that plows the field and applies ammonia as a fertilizer since it has ammonia on board anyway and the driver is used to handling it. The delivery tanker from the ammonia production plant to the agricultural distribution center might also be powered by liquid ammonia instead of diesel fuel.

A widespread infrastructure for the supply of hydronitrogen fuels exists in the USA. For instance, there are ammonia pipelines such as the Magellan pipeline system which extends 1100 miles from Texas to Minnesota and serves 13 supply points along the route, and the Kaneb Pipeline Partners which extends 2090 miles from seaports on the Gulf of Mexico to North Dakota and Wyoming serving 17 supply points. Unfortunately, there have been several ammonia pipeline ruptures [6] with adverse effects similar to the other ammonia transportation spill events (see Section 7.7.1).

There have been logistics studies assuming that a military base in a hostile area, cut off from all supply routes but with an ample supply of electric power from a mobile nuclear reactor power plant, could use nitrogen from the air and hydrogen from water electrolysis to generate ammonia for use as a fuel for vehicles including internal combustion, fuel cell, and jet engine-driven vehicles [7–9]. Some of this mobile, modular ammonia plant technology, once it is developed for use on Earth, might even be useful for the production of ammonia on extraterrestrial bases, assuming that water and nitrogen will be available as *in situ* resource utilization (ISRU) feedstock locally.

Hydrogen is a clean form of energy but is difficult to store. Liquid ammonia is easy to store and would be an efficient method for storing hydrogen, provided there is sufficient energy available to catalytically dissociate ammonia into dinitrogen and dihydrogen at the point of end use [10]. The hydrogen content in liquid ammonia is 17.6 mass-% compared with only 12.5% in methanol. The volumetric storage density of hydrogen in liquid ammonia at room temperature is  $0.106 \text{ g/cm}^3$  whereas the density of cryogenic hydrogen at its normal boiling point is only  $0.085 \text{ g/cm}^3$ . Per unit volume, liquid ammonia has 1.3 times the heating value of liquid hydrogen. Ammonia could play a major role in a hydrogen economy in the future [11]. Ammonia and/or its hydronitrogen relative hydrazine can be used in fuel cells with oxygen or air as the oxidizer [12].

Ammonia evaporation and condensation is an efficient method for closed-loop heat pipes that can operate on the ground as well as in outer space. The condensed liquid returns to the evaporator by capillary action through a wick. Ammonia heat pipes are now widely used to cool the electronic compartments in large satellites.

Operating at much higher temperatures and much higher pressures than the physical heat pipes currently in use, a **chemical** heat pipe would dissociate ammonia into its elements at the hot end (typically in a nuclear reactor or solar thermal power plant), transport the dissociation products from point A to point B, and allow the gases to recombine over a catalyst at the cold end where the heat released could be used for residential heating or industry.

Standard chemical reference sources such as *Ullman's Encyclopedia of Industrial Chemistry* [13, 14] and the *Kirk-Othmer Encyclopedia of Chemical Technology* [15] contain detailed chapters with most of the information needed for the design of ammonia systems. We don't want to repeat this information, but rather collect and present here all information related to the use of liquid ammonia as a rocket propellant.

## 2 Production of Ammonia

Ammonia can be prepared from the elements nitrogen and hydrogen at high pressure in the presence of a catalyst. The Haber–Bosch process was developed in Germany in 1913 and has had a dramatic impact on the availability of fertilizers and other nitrogen chemicals worldwide. It has allowed high-intensity farming and has multiplied the number of crops that can be harvested on poor soil, thus feeding millions of people that would otherwise starve or depend on other types of nitrogen-rich fertilizers (manure and sewage).

Ammonia is currently produced by the Haber–Bosch process which is very energy- and capital-intensive. In search for more efficient and economical processes and in view of the potential use of ammonia as an energy carrier, a number of new processes are under development. Among these, electrochemical routes have the potential to substantially reduce the energy input (by more than 20%), simplify the reactor design, and reduce the complexity and cost of production facilities when compared to the high-pressure ammonia production route. Several electrochemical routes based on liquid, molten salt, or solid electrolytes are currently under investigation [16].

Prior to the invention of the Haber–Bosch process, the main route to synthetic production of ammonia by atmospheric nitrogen fixation was by means of cyanamide. The USA is the world's largest importer of ammonia, approximately 6.3 million metric tons during 2010 [17, 18]. The upward trend in US prices of natural gas from 2000 to 2006 led to a 17% decline in the national supply of ammonia. US ammonia production declined by more than 4%, while ammonia imports increased 115% in the same time frame and the shares from imports increased from 15 to 42%. The decline in production raised the price for farmers 130% from \$227 per ton in 2000 to \$521 per ton in 2006. Prices in 2011 were above \$800/metric ton. Department of Commerce figures showed a 36% increase in ammonia imports during the month of April 2011 alone.

An increasing amount of ammonia, although still small compared with other uses, is used as a concentrated solution in combating the discharge of polluting nitrogen oxides in the smoke stacks from fossil-fueled power stations.

Ammonia ranks second to sulfuric acid as the chemical with the largest tonnage. It is being increasingly produced in countries which have low-cost sources of natural gas and coal (China and Russia account for ca. 40%). The largest plants produce about 3000 tons a day, and there are plans to build plants that produce 4000–5000 tons a day, which would mean that the total world output could be managed with 100 such units. As of 2011, ammonia production was:

|               |                  |
|---------------|------------------|
| Global        | 140 million tons |
| Europe        | 16 million tons  |
| North America | 15 million tons  |
| USA           | 8 million tons   |

|                 |                   |
|-----------------|-------------------|
| Asia            | 74 million tons   |
| Russia          | 12.5 million tons |
| The Middle East | 13 million tons   |

Eighty-five percent of all ammonia produced is used as fertilizer and 5% is converted to nitric acid, and most of this goes into the production of nitrate fertilizers [19].

### 3 Physical Properties of Ammonia

Because ammonia has been known for a long time and because it is an important intermediate in many chemical processes, its physical properties are well documented. Some physical properties needed for designing the equipment for using ammonia under extreme conditions, such as those encountered in a rocket engine, have been determined specifically for this application.

Although this chapter deals with ammonia  $^{14}\text{NH}_3$  as a rocket propellant, the properties of its isotope analogs (isotopologs)  $\text{ND}_3$  and  $^{15}\text{NH}_3$  are sometimes listed here for comparison, in particular in the section on its spectroscopic properties. There is always some  $\text{NH}_2\text{D}$ ,  $\text{NHD}_2$ , and  $\text{ND}_3$  present in commercial  $^{14}\text{NH}_3$  due to the natural isotope distribution in nitrogen and hydrogen from which this chemical is made, and this small percentage may affect some of its physical properties. Although  $\text{ND}_3$  will never be used as a rocket propellant, some of its properties are nevertheless included here for reference; it may be of interest as a fuel for chemical lasers. Chemical D-F lasers depend on a source of deuterium. The other isotopologue,  $^{15}\text{NH}_3$ , is also present in small amounts in natural ammonia. It would be useful for kinetic reaction studies with isotope-labeled ammonia and hydrazine, for instance, to examine the effect of ammonia dissociation on the rocket performance of hydrazine monopropellant and compare the ammonia dissociation activity of different catalysts.

There are numerous physical property compilations for ammonia and other refrigerants assembled by the refrigeration industry. If physical or thermodynamic property data for ammonia cannot be found in the book at hand, it may be possible to find them in refrigeration system design handbooks. Oddly enough, ammonia and some of the other non-halocarbon refrigerants have been assigned numbers similar to the halocarbon refrigerants. Ammonia is sometimes listed as Refrigerant 717.

For quick and approximate calculations, the physical properties of ammonia can be read from a nomograph [20]. A frequently used summary of physical properties of ammonia appears in *Chemical Engineering* [21]. A chapter in *USAF Propellant Handbooks, Hydrazine Fuels*, AFRPL-TR-69-149, [22] gives a complete summary of the physical properties of ammonia and several images in this chapter have been derived from this source.



### 3.1 Freezing Point, Melting Point, Triple Point, and Phase Diagrams of Ammonia

Freezing point data for ammonia are summarized in Table 1.

**Table 1:** Freezing point of ammonia.

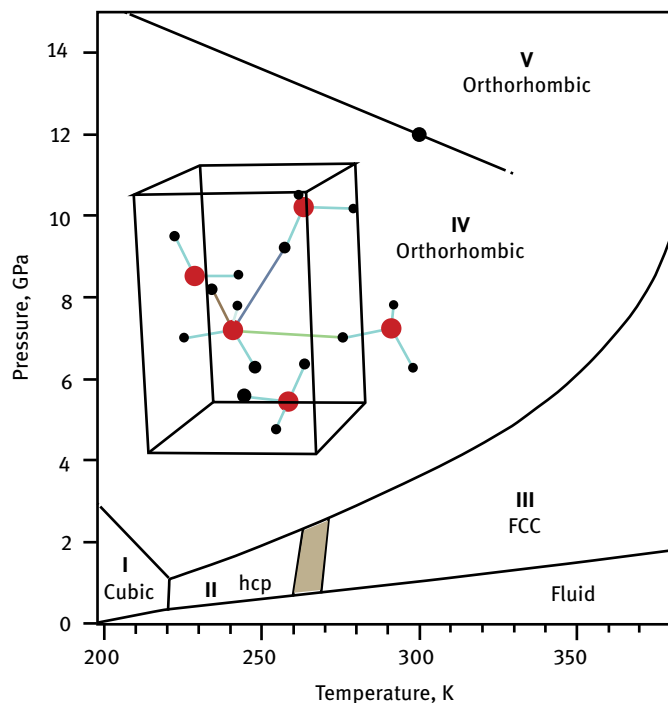
|                | K                    | °C                    | References |
|----------------|----------------------|-----------------------|------------|
| Freezing point | 195.41               | −77.74                | [23]       |
|                | 194.95               | −78.2                 | [24]       |
| Triple point   | 195.41 at 6.076 kPa  | −77.74 at 45.58 mm Hg | [23]       |
|                | 195.5 at 0.06060 bar | −77.6                 | [24]       |
|                | 195.4 at 6.0182 kPa  | −77.5                 | [25]       |

For a rocket propellant, ammonia will be kept in its liquid form, but frozen ammonia shows unusual multi-phase behavior which may affect other physical properties. It is highly unlikely that ammonia in a rocket engine will ever be exposed to conditions that cause it to undergo phase transitions like those described here, but ammonia that exists in the atmospheres, solid cores, and icy moons of the outer planets in our solar system may be under very high pressures; this totally changes its phase behavior from what we are used to at Earth's atmospheric pressure, also in combination with ice or in the presence of hydrogen which would complicate the phase diagram even further. We also need to know if ammonia under conditions of high pressure would convert to other previously unknown hydronitrogens like  $N_2H_6$  or  $NH_5$  which might be useful as rocket fuels.

The different phases of solid ammonia are usually represented by Roman numerals. They can be identified by X-ray diffraction (XRD), ultrasound attenuation, and Raman spectra. The molar volumes of ammonia solids I and II were measured from 0.5 to 14.0 kbar and from 185 to 320 K [26–28]. Over regions that extend 3 kbar and 20 K into the solid phases, variations in compressibility and thermal expansion could be described by power laws with exponents similar to those usually associated with critical transitions. It has been suggested that the breaking of hydrogen bonds may account for the extreme softening of solid ammonia.

The phase line equations were calculated using the mean field theory for the liquid–solid I/solid II phases in ammonia close to the melting point [29]. The calculated phase diagram agreed very well with the experimentally obtained  $P$ – $T$  phase diagram from the literature. Similar calculations were made for phases I, II, and III of solid ammonia [30].

A phase diagram of solid ammonia is shown in Figure 1. Above 4 GPa, three different phases may be stabilized depending on the temperature. In increasing order of temperature, these are the ordered, orthorhombic phase IV, the plastic (orientationally disordered) cubic phase III, and the fluid. The IV–III and III–fluid transition



**Figure 1:** Phase diagram of solid ammonia. (Reproduced and modified from [31], with permission of ©2008 AIP Publishing.)

lines have been determined up to 373 K. Experimental measurements of the phase diagram of NH<sub>3</sub> in the ranges 1–20 GPa and 300–900 K have been made and the III–IV transition line has been determined up to 20 GPa and 500 K in order to detect the influence of the isostructural phase transition [31]. The melting curve has been determined up to 9 GPa and 905 K. No evidence for the superionic phase has been observed in this  $P$ – $T$  range. No discontinuity is observed at the expected location for the III–IV–V triple point.

Temperature and pressure dependencies of the molar volume were studied along the transition curve between the solid I and solid II phases near the melting point in solid ammonia [32]. The molar volumes were calculated in the temperature range from 217 to 224 K and in the pressure range from 3 to 8 kbar with respect to the triple point ( $T_t = 217.34$  K and  $P_t = 3.070$  kbar), where the melting curves of solid I and solid II coincided with the transition curve in ammonia.

Raman spectroscopic and XRD measurements of ammonia in laser-heated diamond anvil cells at pressures of up to 60 GPa and temperatures of up to 2500 K revealed that the melting line exhibited a maximum near 37 GPa and intermolecular proton fluctuations substantially increased in the fluid with pressure [33]. It was found

that  $\text{NH}_3$  was chemically unstable at high pressures, partially dissociating into  $\text{N}_2$  and  $\text{H}_2$ . *Ab initio* calculations showed that this process is thermodynamically driven. The chemical reactivity dramatically increased at high temperatures (in the fluid phase at  $T > 1700\text{ K}$ ) almost independently of pressure. Quenched from these high-temperature conditions,  $\text{NH}_3$  exhibited structural differences from known solid phases.

It appears that solid molecular ammonia becomes unstable at room temperature and a high pressure, and transforms into an ionic crystalline form [34]. This material has been characterized in both  $\text{NH}_3$  and  $\text{ND}_3$  ammonia samples of up to about 180 and 200 GPa, respectively, by IR absorption, Raman spectroscopy, and XRD. The presence of a new, strong IR absorption band centered at  $2500\text{ cm}^{-1}$  in  $\text{NH}_3$  ( $1900\text{ cm}^{-1}$  in  $\text{ND}_3$ ) signals the start of the ionization of ammonia molecules into  $\text{NH}_2^-$  and  $\text{NH}_4^+$  ions, in line with previous theoretical predictions. There are two coexisting crystalline ionic forms, which *ab initio* calculations predict to be the most stable at the relevant pressures. The ionic crystalline form of ammonia is stable at low temperatures, which contrasts with the high-pressure behavior of water in which no equivalent crystalline ionic phase has been found.

### 3.2 Boiling Point of Ammonia

A collection of data for the boiling point of ammonia is presented in Table 2

**Table 2:** Boiling point of ammonia.

|                             | K       | °C     | References |
|-----------------------------|---------|--------|------------|
| Boiling point               | 239.73  | −33.42 | [35]       |
| Boiling point               | 239.823 | −33.3  | [24]       |
| Boiling point               | 239.82  | −33.3  | [24]       |
| Boiling point $\text{NH}_3$ | 239.79  | −33.36 | [25]       |
| Boiling point $\text{ND}_3$ | 242.20  | −30.95 | [25]       |

### 3.3 Density and Molar Volume of Ammonia

Data for the density of solid and liquid ammonia are summarized in Table 3.

The density data in Figure 2 for the low temperature range from the freezing point to 273 K can be represented by the equation

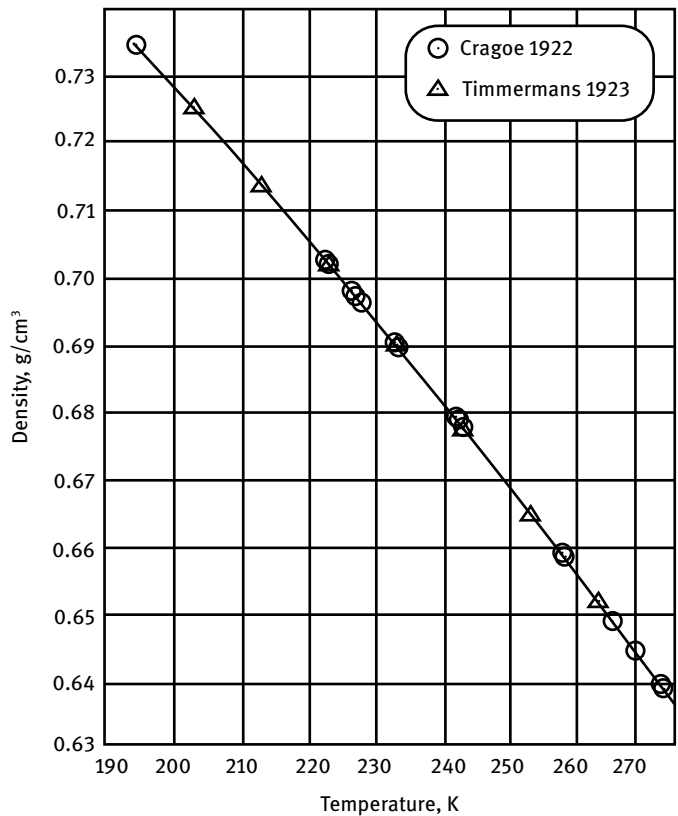
$$\rho = 0.88824 - 4.7742 \times 10^{-4} T - 1.5977 \times 10^{-6} T^2$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin.

**Table 3:** Density of ammonia.

| Physical state | Temperature |      | Density, g/cm <sup>3</sup> |
|----------------|-------------|------|----------------------------|
|                | K           | °C   |                            |
| solid          | 88          | −185 | 0.836                      |
| solid          | 194         | −79  | 0.817                      |
| liquid         | 203         | −70  | 0.7253                     |
| liquid         | 223         | −50  | 0.7020                     |
| liquid         | 243         | −30  | 0.6777                     |
| liquid         | 263         | −10  | 0.6520                     |
| liquid         | 273         | ±0   | 0.6386                     |
| liquid         | 293         | +20  | 0.6103                     |
| liquid         | 298         | +25  | 0.6029                     |
| liquid         | 323         | +50  | 0.5629                     |

Data source: [36]



**Figure 2:** Density of liquid ammonia, low temperature range. (Reproduced and modified from [22].)

The density data in Figure 3 for the high temperature range from 273 to 373 K can be represented by the equation

$$\rho = 0.54529 + 1.89323 \times 10^{-3}T - 5.69427 \times 10^{-6}T^2$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin.

Measurements of the density of liquid ammonia at elevated temperatures and pressures in the compressed liquid phase were carried out with a metal-bellows variable volumometer along 10 isotherms between 310 and 400 K at pressures from the vapor pressure to 17 MPa [37]. The results covered the high-density region from 343 to 601  $\text{kg/m}^3$  summarized in Table 4, and were used to calculate isothermal compressibility and the coefficient of thermal expansion.

Figure 4, which is essentially a combination of Figures 2 and 3 and covers a wider temperature range from 200 to 400 K, illustrates the steep dropoff of density as the liquid approaches the critical point.

Figure 5 gives a density phase diagram with the phase boundaries for ammonia.

The coefficient of thermal expansion of liquid ammonia at atmospheric pressure increases with increasing temperature (Table 5).

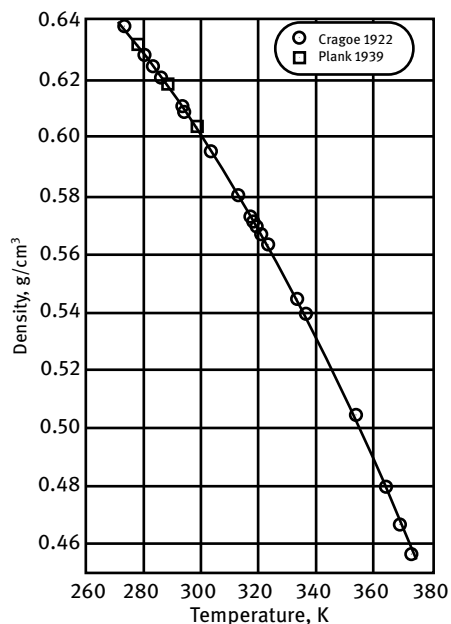
The orthobaric density of liquid  $\text{NH}_3$  has been measured from 200 to 287 K, and for liquid  $\text{ND}_3$  from 205 to 273 K [40]. The molar volume of liquid  $\text{NH}_3$  exceeds that of  $\text{ND}_3$  by between 0.8 and 0.9%. The molar volume of the two liquid ammonias can be expressed by the equation

$$V_m = V_{m \text{ ref}} + A(T - T_{\text{ref}}) + B(T - T_{\text{ref}})^2 + C(T - T_{\text{ref}})^3$$

where  $V_m$  is the molar volume in  $\text{cm}^3/\text{mol}$ ,  $V_{m \text{ ref}}$  is the reference molar volume at the triple point in  $\text{cm}^3/\text{mol}$ ,  $T$  is the temperature in kelvin,  $T_{\text{ref}}$  is the triple-point temperature, and A, B, and C are constants listed in Table 6 for both  $\text{NH}_3$  and  $\text{ND}_3$ .

Based on density measurements at pressures from 2 to 17 MPa at four different temperatures (317–398 K), the isothermal compressibility and the cubic expansion coefficient of liquid ammonia were calculated and are displayed in Figure 6a,b [37]. The Tillner-Roth et al. equation of state (EOS) agreed well with the Kasahara et al. results for the cubic expansion coefficient as shown in Figure 6b. The solid lines represent isotherms calculated using the EOS of Tillner-Roth et al. The dashed lines represent isotherms calculated using the EOS of Haar and Gallagher.

A very elegant method to represent the  $\rho VT$  phase diagram of ammonia in a 3-D graph is shown in Figure 7 [41]. To accommodate the full range of data, logarithmic scales were used for pressure and molar volume. Horizontal lines (constant  $\rho T$ ) are tie lines connecting phases (of differing volume) in mechanical and thermal equilibrium across the phase gaps. The label  $T_b$  is attached to the boiling point (100 kPa) tie line. The end dot of the liquid–vapor line in the  $\rho T$  projection represents its termination at the critical point. Volumes in the diagram (actually “space curves,” corresponding to areas in the projections) are labeled solid, liquid, vapor, and (above the critical point) gas. I, II, and III refer to the respective solid phases that can equilibrate with liquid

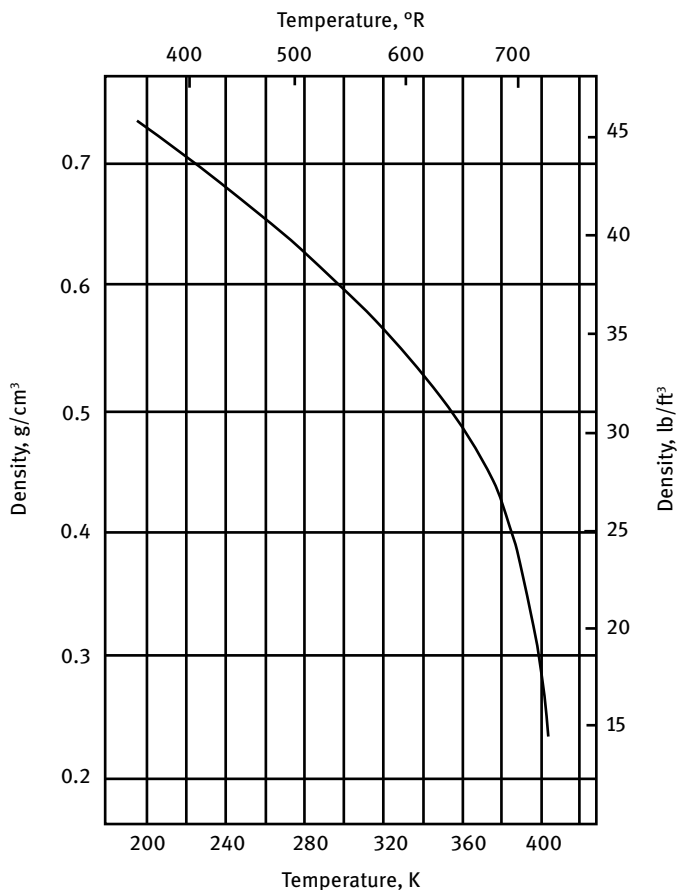


**Figure 3:** Density of liquid ammonia, high temperature range. (Reproduced and modified from [22].)

**Table 4:** Experimental results of the density of ammonia at elevated temperatures and pressures.

| P, MPa                     | T, K   |        |        |        |        |
|----------------------------|--------|--------|--------|--------|--------|
|                            | 310    | 320    | 330    | 340    | 350    |
| $\rho$ , kg/m <sup>3</sup> |        |        |        |        |        |
| 17.000                     | 601.08 | 586.09 | 570.60 | 554.45 | 536.96 |
| 16.000                     | 600.17 | 585.06 | 569.43 | 553.12 | 535.43 |
| 15.000                     | 599.22 | 584.02 | 568.21 | 551.72 | 533.79 |
| 14.000                     | 598.28 | 582.99 | 567.01 | 550.28 | 532.09 |
| 13.000                     | 597.30 | 581.92 | 565.78 | 548.82 | 530.39 |
| 12.000                     | 596.33 | 580.84 | 564.50 | 547.33 | 528.59 |
| 11.000                     | 595.34 | 579.69 | 563.19 | 545.79 | 526.77 |
| 10.000                     | 594.30 | 578.50 | 561.88 | 544.22 | 524.88 |
| 9.000                      | 593.37 | 577.40 | 560.52 | 542.70 | 522.92 |
| 8.000                      | 592.39 | 576.24 | 559.11 | 541.09 | 520.93 |
| 7.000                      | 591.32 | 575.02 | 557.71 | 539.41 | 518.83 |
| 6.000                      | 590.19 | 573.76 | 556.32 | 537.69 | 516.67 |
| 5.000                      | 589.09 | 572.53 | 554.89 | 535.90 | 514.38 |
| 4.000                      | 588.02 | 571.25 | 553.38 | 534.10 | 512.07 |
| 3.000                      | 586.92 |        | 551.86 |        |        |
| 2.990                      |        | 569.95 |        |        |        |
| 2.000                      | 585.76 | 568.62 |        |        |        |

Data source: [37]



**Figure 4:** Density of liquid ammonia in the proximity of the critical point. (Reproduced and modified from [38].)

ammonia. Interactive virtual 3-D versions of these phase diagrams, programmed in Jmol, an open-source Java viewer, are also available.

The space curves depicted in Figure 7 are

- A. Solid sublimation, in equilibrium with vapor (estimated)
- B. Vapor condensation, in equilibrium with solid (estimated)
- C. Liquid saturation, in equilibrium with vapor
- D. Vapor saturation, in equilibrium with liquid
- E. Solid–liquid melt equilibria, for solid phases I–III. The two separate curves, for solid and liquid in equilibrium, nearly overlay one another on the scale of the diagram.

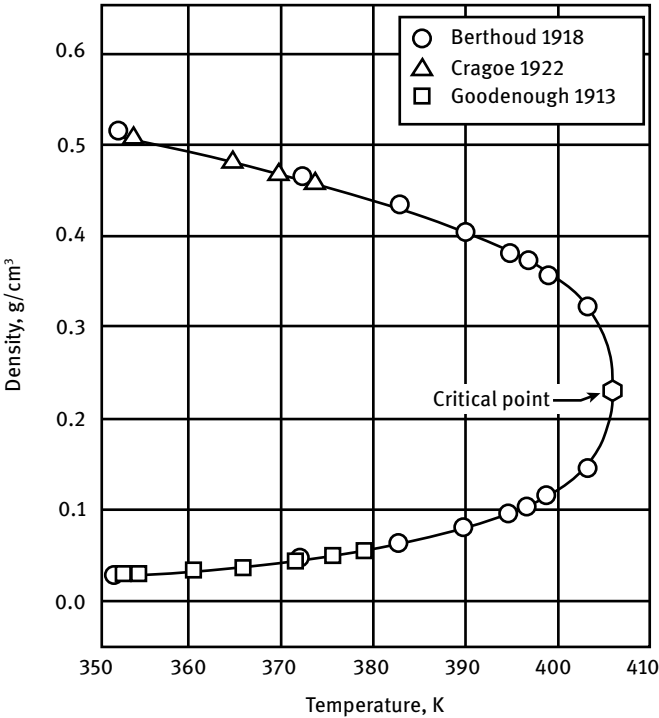


Figure 5: Phase diagram of liquid ammonia. (Reproduced and modified from [22].)

Table 5: Coefficient of thermal expansion of liquid ammonia at 101 kPa.

| Temperature range |            | Coefficient of thermal expansion, 1/K |
|-------------------|------------|---------------------------------------|
| K                 | °C         |                                       |
| 228 to 233        | −45 to −40 | 0.00174                               |
| 238 to 243        | −35 to −30 | 0.00180                               |
| 248 to 253        | −25 to −20 | 0.00185                               |
| 258 to 263        | −15 to −10 | 0.00194                               |

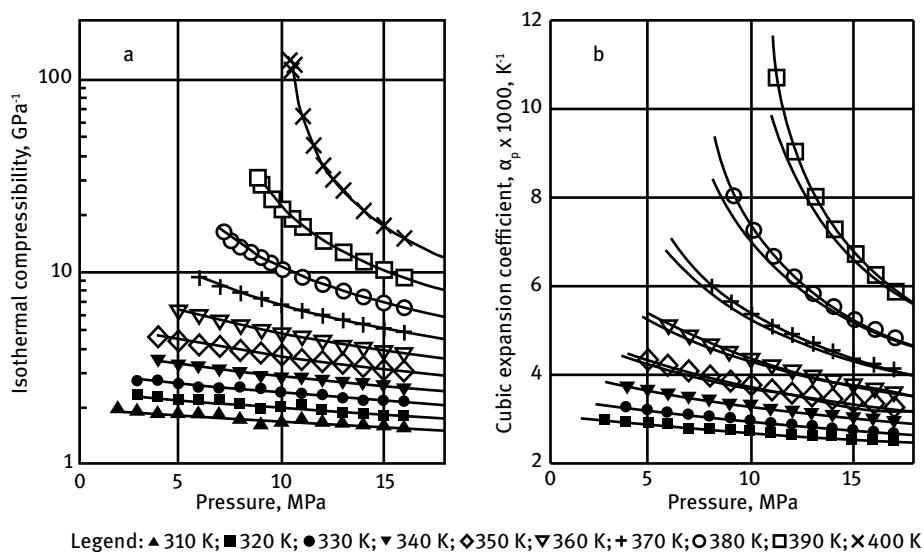
Data source: [39]

Table 6: Reference molar volume and equation constants for NH<sub>3</sub> and ND<sub>3</sub>.

| Compound        | V <sub>m ref</sub><br>cm <sup>3</sup> /mol | T <sub>ref</sub><br>K | A                         | B                         | C                         |
|-----------------|--------------------------------------------|-----------------------|---------------------------|---------------------------|---------------------------|
| NH <sub>3</sub> | 23.205                                     | 195.48                | 3.7445 × 10 <sup>−2</sup> | 0.0153 × 10 <sup>−4</sup> | 1.1524 × 10 <sup>−6</sup> |
| ND <sub>3</sub> | 23.121                                     | 198.84                | 3.5889 × 10 <sup>−2</sup> | 0.7231 × 10 <sup>−4</sup> | 0.6453 × 10 <sup>−6</sup> |

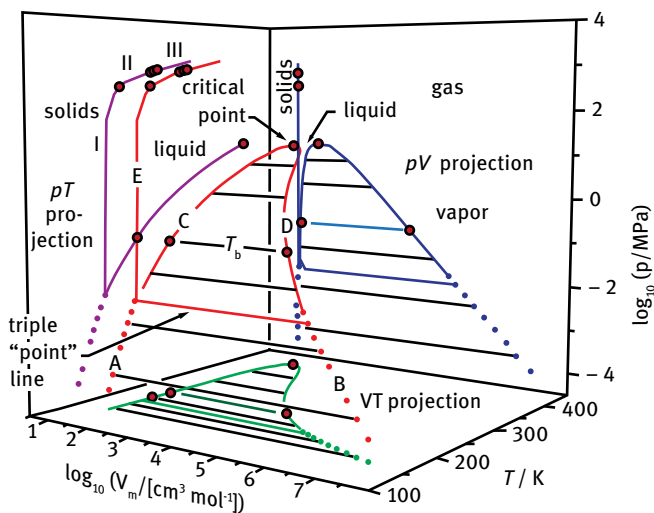
Data source: [40]





**Figure 6:** Isothermal compressibility and cubic expansion coefficient for liquid ammonia as a function of pressure  $p$ . (Reprinted and modified from [37], with permission from ©1999 Elsevier; permission conveyed through RightsLink.)

(a) Isothermal compressibility  $\kappa_T$ ; (b) cubic expansion coefficient  $\alpha_p$ .



**Figure 7:** Perspective 3-D  $pVT$  diagram for ammonia, with projections onto the  $pT$ ,  $pV$ , and  $VT$  planes. (Reprinted from [41], with permission from ©2009 American Chemical Society; permission conveyed through RightsLink.)

Data for ammonia are incomplete in that little information exists below the triple-point temperature ( $195.4\text{ K} = -77.75^\circ\text{C}$ ), and the lines had to be extrapolated. The  $\rho T$  properties of the high-pressure solid phases, I through V, and their relation to the liquid phase were already represented in Figure 1. The II–III–fluid triple point has not yet been determined because no corresponding discontinuity has been observed on the melting curve. Both phases II and III are plastic with large orientational disorder.

Acoustic velocity, refractive index, adiabatic bulk modulus and the EOS of liquid ammonia were determined at temperatures up to 410 K and at pressures up to the solidification point [42]. Sound velocity and refractive index increased smoothly with increasing pressure along isotherms but decreased slightly with the temperature increase. The bulk modulus increased linearly with pressure and its slope  $dB/dP$  decreased slightly with increasing temperature, from 6.67 at 297 K to 5.94 at 410 K.

Density measurements of the compressed-liquid phase for ammonia along four isotherms between 310 and 360 K at pressures from the vapor pressure up to 200 MPa and high densities from 492 to 693 g/cm<sup>3</sup> and vapor pressures at temperatures from 310 to 400 K created conditions of ammonia that would be rarely encountered in a rocket engine, but may exist in the core of icy planets and their moons [43]. The isothermal compressibility and the isobaric expansivity were derived and illustrated on the basis of those measurements.

Density, pressure–volume–temperature (PVT), and  $\rho VT$  data of ammonia, as shown in Figure 8, were also shown in log–log and rectilinear coordinates [44]. Additional data are available from other sources, but require critical examination [45–48].

### 3.4 Compressibility and Velocity of Sound of Ammonia

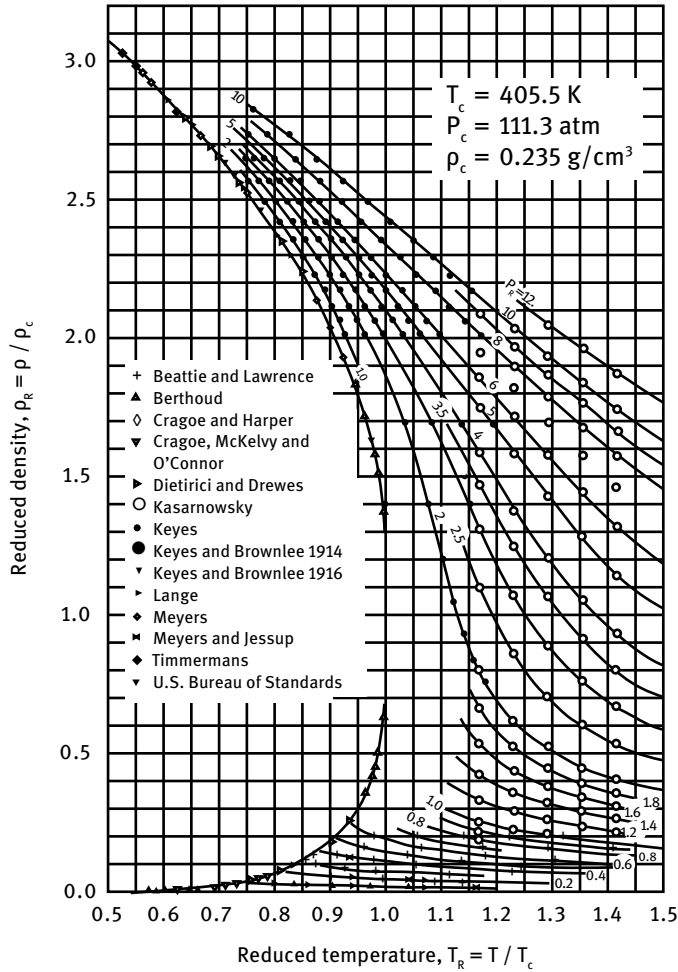
#### 3.4.1 Compressibility of Liquid Ammonia

Data for the compressibility of solid and liquid ammonia are listed in Table 7.

Figure 9 shows isothermal compressibility data calculated from sonic velocity data measured by Bowen and Thompson [49] and Blagoi et al. [50]. The temperature dependence of the adiabatic compressibility  $\beta$  of liquid ammonia can be expressed by the following equation:

$$\beta = -1.0098 \times 10^{-4} + 1.68095 \times 10^{-6} T - 8.0004 \times 10^{-9} T^2 + 1.5051 \times 10^{-11} T^3$$

where  $\beta$  is the adiabatic compressibility in atm<sup>-1</sup> and  $T$  is the temperature in kelvin.

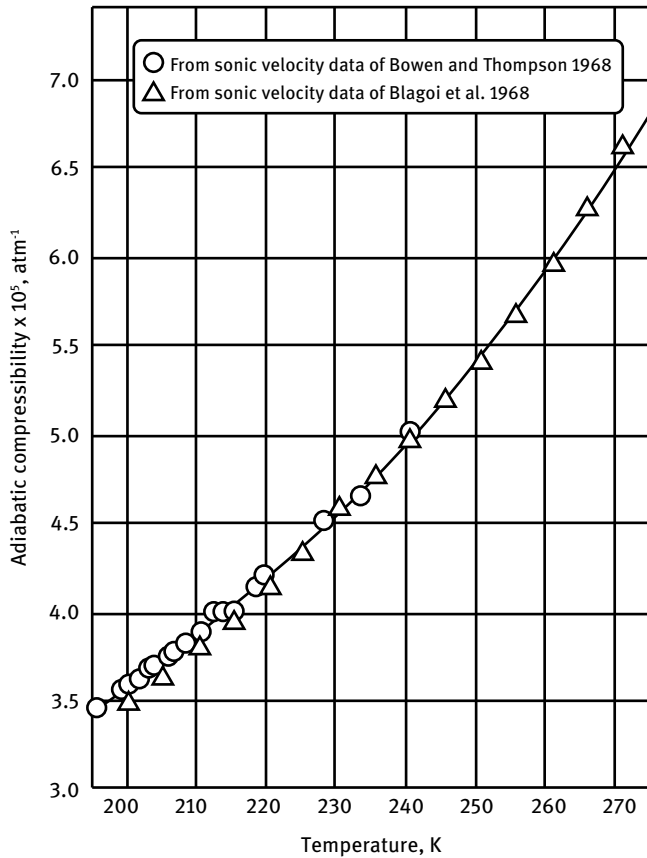


**Figure 8:** PVT data of ammonia. (Reprinted and adapted from [44], with permission from ©1960 American Chemical Society; permission conveyed through RightsLink.)

**Table 7:** Isothermal compressibility  $\beta$  of solid and liquid ammonia.

| Temperature |       | Compressibility $\beta$ |                        |
|-------------|-------|-------------------------|------------------------|
| K           | °C    | 1/Pa                    | 1/atm                  |
| 222.0       | −51.1 | $6.395 \times 10^{-10}$ | $0.648 \times 10^{-4}$ |
| 249.8       | −23.3 | $8.221 \times 10^{-10}$ | $0.833 \times 10^{-4}$ |
| 273.1       | ± 0   | $1.072 \times 10^{-9}$  | $1.086 \times 10^{-4}$ |

Data source: [39]



**Figure 9:** Adiabatic compressibility of liquid ammonia. (Reproduced and modified from [22].)

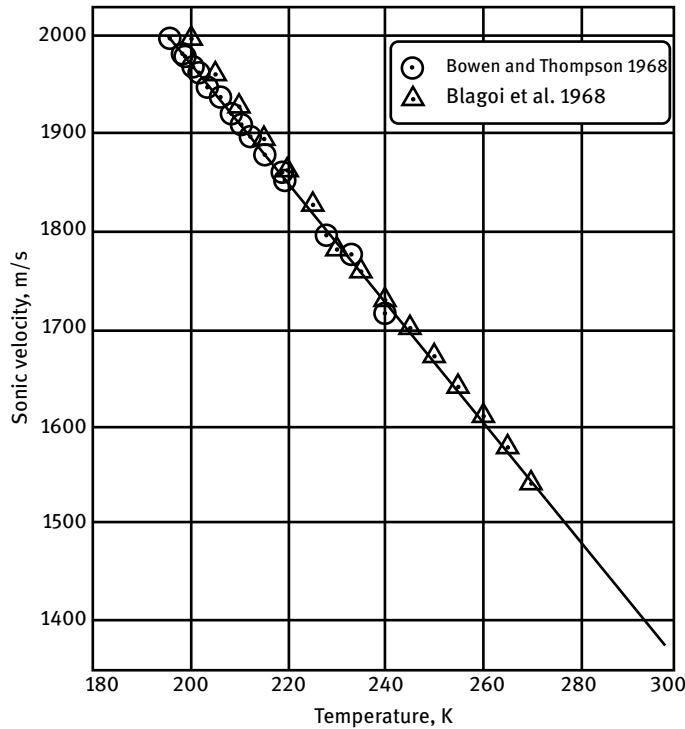
### 3.4.2 Velocity of Sound in Liquid Ammonia

The temperature dependence of sonic velocity in liquid ammonia can be expressed by the following equation:

$$c = 3202.49 - 6.1366T$$

where  $c$  is the velocity of sound in m/s and  $T$  is the temperature in kelvin (Figure 10).

Velocities of sound in fluid ammonia at high pressures were measured by Impulsive Stimulated Scattering, up to a pressure of 3.8 GPa and along isotherms of 297, 476, and 680 K [51]. For either liquids or highly compressed gases, plots of velocity of sound against density commonly yield straight lines. To the extent that the EOS of Tillner-Roth gives an adequate account of densities, this relation also holds true for ammonia, as shown in Figure 11. See also [28].



**Figure 10:** Sonic velocity in liquid ammonia at saturation pressure. (Reproduced and modified from [22].)

### 3.5 Vapor Pressure and Vapor Phase Composition of Ammonia

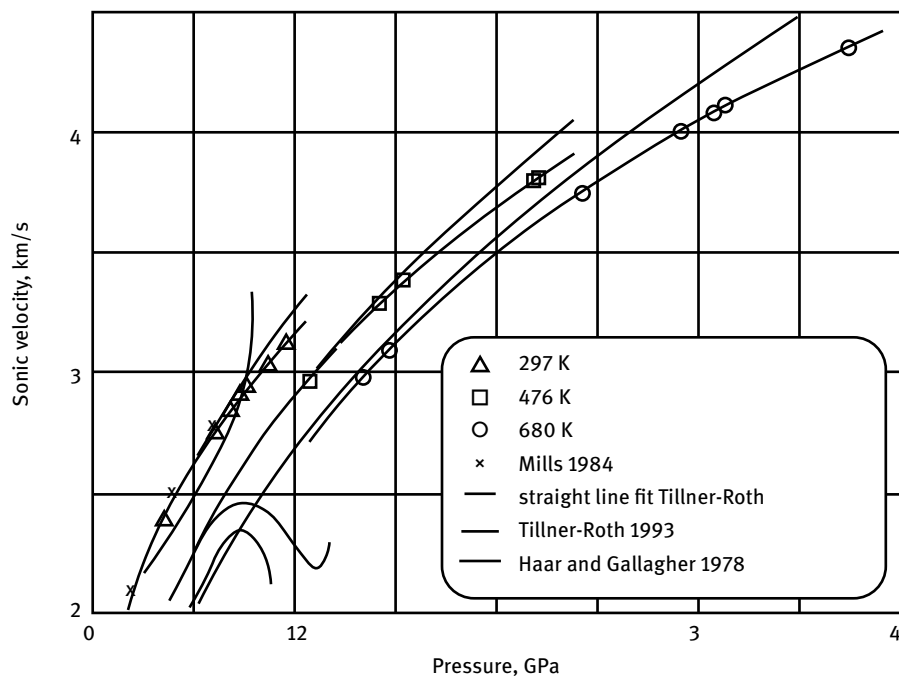
The vapor pressure of liquid ammonia can be calculated from the Antoine equation. The parameters A through C are available for two different temperature ranges and overlap (Table 8).

$$\log (P)_{10} = A - \left( \frac{B}{T + C} \right)$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

Measurements of the vapor pressure of ammonia in the temperature range 195.4–343 K, over which 150 data points were taken in the first of two experiments including 11 determinations for the normal boiling point, gave a historical, frequently quoted set of data [52] (Table 9). The data were taken at near uniform intervals except near the values of temperature associated with important fixed points, for which they were taken over very small intervals.

Vapor pressure measurements from 303.15 K to near the critical temperature were in excellent agreement at lower temperature with those of Cragoe, Meyers, and Taylor



**Figure 11:** Velocity of sound in liquid ammonia at high pressures. (Reprinted and adapted from [51], with permission from ©2008 American Chemical Society; permission conveyed through RightsLink.)

1920 within 0.03% at 303.15 K. However, the difference increased slightly with increasing values of temperature to just under 0.1% at 343.15 K, with an average deviation in this range of about 0.05% [53]. The agreement was within their reported uncertainty. Above 343.15 K, the data agreed with those of Keyes and Brownlee [54] to within 0.1% up to 383.15 K. Differences increased to about 0.2% at 393.15 K and then uniformly to 0.8% at 405.15 K, the highest value of temperature reported, with the values of Beattie and Lawrence being consistently higher throughout. Older measurements by Keyes and Brownlee [54] showed a considerable scatter and, at temperatures below 343 K, large deviations from the very accurate results obtained by Cragoe, Meyers, and Taylor 1920 [42].

**Table 8:** Parameters for Antoine vapor pressure equation for ammonia.

| Temperature range, K | A       | B        | C       |
|----------------------|---------|----------|---------|
| 164.0–239.6          | 3.18757 | 506.713  | –80.78  |
| 239.6–371.5          | 4.86886 | 1113.928 | –10.409 |

Data source: [24]

**Table 9:** Vapor pressure of solid and liquid ammonia.

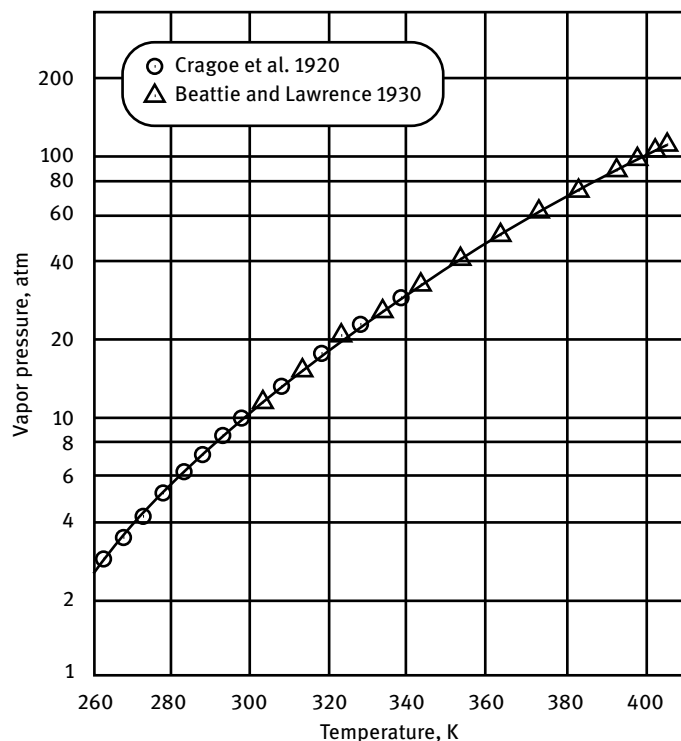
| Temperature |        | Vapor pressure |        |
|-------------|--------|----------------|--------|
| K           | °C     | kPa            | mm Hg  |
| 193         | −80    | 5.0            | 37.6   |
| 198         | −75    | 7.5            | 56.1   |
| 203         | −70    | 10.9           | 81.9   |
| 208         | −65    | 15.6           | 117.1  |
| 213         | −60    | 21.9           | 164.2  |
| 218         | −55    | 30.2           | 226.2  |
| 223         | −50    | 40.9           | 306.6  |
| 228         | −45    | 54.5           | 409.1  |
| 233         | −40    | 71.8           | 538.3  |
| 238         | −35    | 93.2           | 699.0  |
| 239.72      | −33.42 | 101.3          | 760    |
| K           | °C     | kPa            | atm    |
| 240         | −33    | 103            | 1.017  |
| 243         | −30    | 120            | 1.180  |
| 248         | −25    | 152            | 1.496  |
| 253         | −20    | 190            | 1.877  |
| 258         | −15    | 236            | 2.332  |
| 263         | −10    | 291            | 2.870  |
| 268         | −5     | 355            | 3.502  |
| 273         | ±0     | 429            | 4.238  |
| 278         | +5     | 516            | 5.089  |
| 283         | 10     | 615            | 6.068  |
| 288         | 15     | 728            | 7.187  |
| 293         | 20     | 857            | 8.458  |
| 298         | 25     | 1003           | 9.895  |
| 303         | 30     | 1166           | 11.512 |
| 308         | 35     | 1350           | 13.321 |
| 313         | 40     | 1554           | 15.339 |
| 318         | 45     | 1781           | 17.580 |
| 323         | 50     | 2032           | 20.059 |

Data source: [52]

Overstreet and Giauque [23] measured the vapor pressure of ammonia from the triple point to 241.6 K. Values of temperature were measured with a special gold resistance-thermometer-heater, but the primary standard was a thermocouple, which was calibrated with a hydrogen gas thermometer and compared from time to time with the gas thermometer.

The vapor pressure of liquid ammonia has been curve-fitted and can be calculated from the following polynomial equation:

$$\log p_v = 30.256818 - 1914.9569/T - 8.4598324 \log T + 2.3930 \times 10^{-3} T + 2.955214 \times 10^{-3} T^2$$



**Figure 12:** Vapor pressure of liquid ammonia. (Reproduced and modified from [22].)

where  $p_v$  is the vapor pressure in mm Hg, and  $T$  is the temperature in kelvin. The temperature dependence of the vapor pressure of liquid ammonia can be expressed by the equation

$$\log p_v = 8.42347 - 1565.85/T - 0.01036T + 1.0269 \times 10^{-5}T^2$$

where  $p_v$  is the vapor pressure in atm, and  $T$  is the temperature in kelvin (Figure 12).

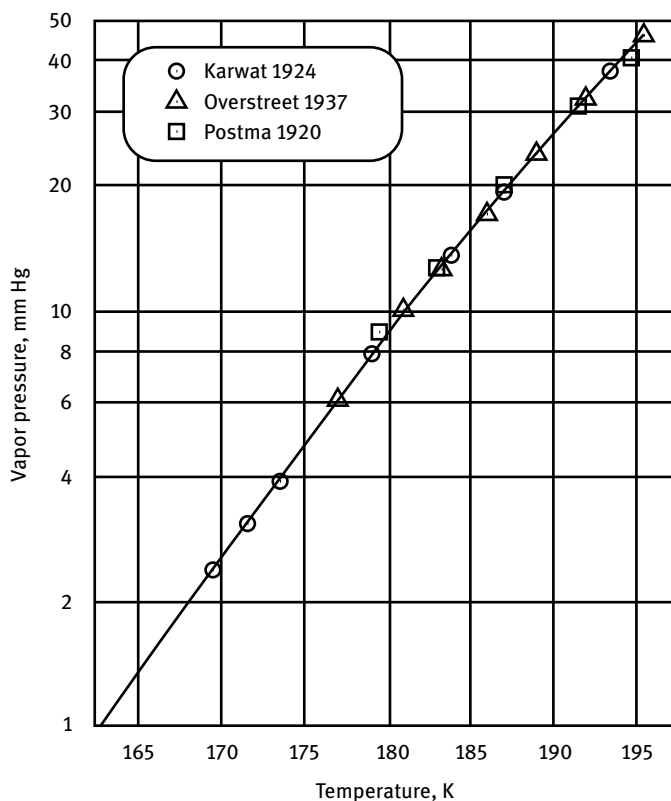
The temperature dependence of the vapor pressure of solid ammonia can be expressed by the equation

$$\log p_v = 1.00094 - 1631.54/T$$

where  $p_v$  is the vapor pressure in mm Hg, and  $T$  is the temperature in kelvin (Figure 13).

The differences in the vapor pressures of ammonia and trideuteroammonia are sufficiently large that one might consider using fractionated distillation of ammonia (instead of fractionated distillation of water) for isotope separation and deuterium production [55]. The differences in the vapor pressures of solid natural ammonia and





**Figure 13:** Vapor pressure of solid ammonia. (Reproduced and modified from [22].)

of isotopologue solid trideuteroammonia containing 98% deuterium were measured and found to be given by

$$\log\left(\frac{P_{\text{NH}_3}}{P_{\text{ND}_3}}\right) = (49.69/T) - 0.1305.$$

The ratio of the vapor pressures of the liquid ammonias were found to follow the equation

$$\log\left(\frac{P_{\text{NH}_3}}{P_{\text{ND}_3}}\right) = (46.25/T) - 0.14003.$$

These two equations agree at the triple point. The difference in the heats of sublimation was calculated to be 950 J (227 cal), while the difference in the heats of vaporization is 887 J (212 cal), the values for the trideuteroammonia being higher than those for ammonia. The triple-point pressures were found to be 45.57 mm Hg for ammonia and 48.22 mm Hg for the trideuteroammonia. This corresponded to triple-point tempera-

tures of 195.68 and 198.79 K, respectively. The boiling point of the  $^{14}\text{N}$  trideuteroammonia was found to be 2.37 K higher than that of the natural ammonia. The ratio of the vapor pressures and the difference in the heats of vaporization of the two pure isotopologues,  $^{14}\text{NH}_3$  and  $^{15}\text{NH}_3$ , were found to be

$$\log\left(\frac{P_{14}}{P_{15}}\right) = (0.7230/T) - 0.005822$$

and

$$\Delta H_{\text{vap } 15} - \Delta H_{\text{vap } 14} = 13.93 \text{ J } (3.33 \text{ cal}).$$

The triple point of the pure  $^{15}\text{NH}_3$  was found to be 0.058 K higher than that of  $^{14}\text{NH}_3$  and the boiling point was 0.052 K higher.

A simple extended corresponding-states principle that can be applied to highly non-spherical substances allows the interpolation and extrapolation of vapor pressures for ammonia and trideuteroammonia and similar polar fluids from the triple point to critical point and can be used to extrapolate the measurements beyond their ranges of available experimental data [25]. To represent experimental data over the entire range, i.e. from the triple point to the critical temperature, the vapor pressure curve was based upon an equation with known physical behavior that has only three substance-dependent parameters

$$\ln p_r = (a_0 + a_1 \tau^{n_1} + a_2 \tau^{n_2}) \ln T_r$$

where  $\tau = 1 - T_r$ , the reduced temperature  $T_r = T/T_c$  with  $T_c$  being the critical temperature, and  $p_r = p/p_c$  with  $p_c$  being the critical pressure. The value of  $n_1$  is 1.89 and the value of  $n_2$  is  $3n_1$  or 5.67. The parameters  $a_0$  and  $a_1$  and  $a_2$  are substance-dependent parameters listed in Table 24 in one of the next chapters on critical point data. The vapor pressures were described accurately by this equation within their scatter in the entire temperature range. Comparisons with the available data showed that the extended corresponding-states principle is capable of calculating the vapor pressure values with accuracies of 0.05–0.1%. The substance-dependent characteristic parameters, such as critical temperature, critical density, critical pressure, acentric factor, and aspherical factor were derived for  $\text{NH}_3$  and  $\text{ND}_3$ . The values of the pressures, along with their first and second derivatives as a function of temperature over the entire region from the triple point to the critical point were tabulated. Vapor pressure data for  $\text{NH}_3$  from 13 different sources in the literature and similar data for  $\text{ND}_3$  from 9 different sources were gathered, critically reviewed, and compared to numbers derived from the corresponding-states principle equation by putting them on a deviation plot with  $T_r$  as the independent variable.

The vapor pressure of liquid ammonia was measured with high accuracy and 16 values were obtained for temperatures between 328 K and the critical temperature ( $T_c$ ) 405.5 K [56]. The results, together with the very accurate measurements reported by Cragoe, Meyers, and Taylor 1920 [52] for temperatures below 343 K, formed the ba-

sis of a new vapor pressure equation. The vapor pressure expressed as the reduced pressure (vapor pressure divided by the critical pressure) can be calculated by the following equation:

$$\ln\left(\frac{p}{p_c}\right) = F(\tau) = \tau^{-1} \{a_1(1-\tau) + a_2(1-\tau)^{1.5} + a_3(1-\tau)^{2.5} + a_4(1-\tau)^5\}$$

$$= F(\tau) = \tau^{-1} [-7.28322(1-\tau) + 1.57160(1-\tau)^{1.5} - 1.85672(1-\tau)^{2.5} - 2.39312(1-\tau)^5]$$

where  $\tau = T/T_c$ ,  $p_c$  = critical pressure = 11.353 MPa, and  $T_c$  = critical temperature = 405.50 K. This equation, containing four terms only, correlated the measured vapor pressures within the limits of experimental accuracy. These data in their region of overlap were in excellent accord with the results of Cragoe, Meyers, and Taylor [52] to within the scatter of those data. They tended to be somewhat lower than the data of Beattie and Lawrence [53]. Near the critical point, the difference was about 0.1%. The uncertainty of the measured temperature was reported to be 0.008 K. The overall accuracy of these data was 0.05%. The differences between this equation and Haar and Gallagher's [57] equation were minor. Below 340 K, both equations correlated the data with the same accuracy. Larger deviations appeared at higher temperatures, where Baehr, Garnjost, and Pollak's equation closely followed the newer measurements which were not available to Haar and Gallagher.

Values of the vapor pressure of ammonia from 293.5 to 392.6 K obtained from triplicate static measurements in a constant-volume apparatus and summarized in Table 10 had a reported accuracy of the measured temperature and pressure of 0.01 K and 0.005%, respectively [47]. Four liquid-phase isochores were measured from 223 to 338 K (−50 to +65 °C), with pressures ranging from saturation pressure to 370 bar. The critical temperature was determined as  $T_c = 405.38 \text{ K} = 132.23 \text{ °C}$  by the visual observation of the disappearance of the meniscus. The deviations between the Zander and Thomas [47] experimental vapor pressures and those calculated according to the equation of Baehr [56] were within the range of experimental precision.

The difference of the vapor pressures of  $\text{NH}_3$  and  $\text{ND}_3$  has been measured as being from 200 to 266 K, and the vapor pressure of  $\text{NH}_3$  from the triple-point temperature up to 234 K [40]. Liquid  $\text{NH}_3$  has a higher vapor pressure than  $\text{ND}_3$ , the difference being relatively large for a pair of isotopic compounds. At 200 K, the ratio of the vapor pressure of  $\text{NH}_3$  to that of  $\text{ND}_3$  was about 1.2. The available vapor pressure data for  $\text{NH}_3$  have been fitted to a Wagner equation. By combining vapor pressures derived from this equation with the differential measurements, values for the vapor pressure of  $\text{ND}_3$  as a function of temperature have been obtained. These values have likewise been fitted to a Wagner equation:

$$\ln\left(\frac{p}{p_c}\right) = (A_0\tau + A_1\tau^{1.5} + A_2\tau^3 + A_3\tau^6)/T_R$$

where  $T_R = T/T_c$ ,  $\tau = (1 - T_R)$ , and  $p_c$  and  $T_c$  are the critical pressure and critical temperature ( $T_c = 405.5 \text{ K}$ ). The triple-point temperature chosen was 195.48 K and

**Table 10:** Vapor pressure of ammonia at temperatures above room temperature.

| Temperature |                    | Vapor pressure    |      |      |
|-------------|--------------------|-------------------|------|------|
| K           | °C                 | bar               | MPa  | psia |
| 293.56      | 20.41 <sup>a</sup> | 8.69 <sup>a</sup> | 0.87 | 126  |
| 303.33      | 30.18              | 11.73             | 1.17 | 170  |
| 313.37      | 40.22              | 15.64             | 1.56 | 227  |
| 323.33      | 50.18              | 20.43             | 2.04 | 296  |
| 333.24      | 60.09              | 26.20             | 2.62 | 380  |
| 343.16      | 70.01              | 33.11             | 3.31 | 480  |
| 353.10      | 79.95              | 41.34             | 4.13 | 600  |
| 362.98      | 89.83              | 50.96             | 5.10 | 739  |
| 372.88      | 99.73              | 62.16             | 6.22 | 901  |
| 382.73      | 109.58             | 75.10             | 7.51 | 1089 |
| 392.64      | 119.49             | 90.16             | 9.02 | 1308 |

Data source: [47]

<sup>a</sup> Note: Data from triplicate measurements in original publication were rounded off

the triple-point pressure was  $(6.079 \pm 0.003)$  kPa. For  $\text{NH}_3$ , the coefficients were  $\ln(p_c) = 9.33717$ ;  $A_0 = -7.20816$ ;  $A_1 = 1.23966$ ;  $A_2 = -2.3783$ , and  $A_3 = -1.528$ . The standard deviation of  $\ln p$  is  $+1.6 \times 10^{-3}$ , while  $p_c$  estimated in this way is  $(11352 \pm 3)$  kPa, virtually the same as the value of 11355 kPa proposed by Baehr et al. For  $\text{ND}_3$ , taking  $T_c \text{ND}_3 = 405.3$  K, the parameters obtained for the Wagner equation were:  $A_0 = -7.05354$ ;  $A_1 = 0.36799$ ;  $A_2 = -0.6903$ ;  $A_3 = -7.006$ , and  $\ln p_c = 9.34824$  (kPa). This corresponds to  $p_c = 11.48$  MPa, which is just an estimate.

The h-d vapor pressure isotope effect in liquid ammonia has been measured at 62 temperatures between 228 and 260 K [58]. The vapor pressures, corrected to 100% nuclidic purity, have been fitted to the equation:

$$T \ln r = A + \frac{B}{T} + CT,$$

where  $r$  is the vapor pressure ratio  $p(\text{NH}_3)/p(\text{ND}_3)$ . The least-squares fit yielded the parameters:

$$A = -(8.22508 \pm 0.03706) \text{ K}, \quad B = (12.3382 \pm 1.1833) \times 10^3 \text{ K}^2, \quad \text{and} \\ C = -(0.05544 \pm 0.02043).$$

Comparisons with the results of other authors were made in order to clarify some discrepancies found in the literature. The values were in accord with the previous results of King et al. and an extrapolation of the fitted equation down to the triple-point temperature gave good agreement with published results. The fitted equation was used in conjunction with the Clapeyron equation to calculate the difference in the molar

enthalpies of vaporization between  $\text{NH}_3$  and  $\text{ND}_3$ . At  $T = 230\text{ K}$ , the difference was  $-846\text{ J/mol}$ , decreasing to  $-747\text{ J/mol}$  at  $260\text{ K}$ .

Fourteen vapor pressure, eight near-saturation vapor ( $P, \rho, T$ ), and 28 near-saturation liquid ( $P, \rho, T$ ) data points of liquid ammonia were measured over a temperature range from  $279$  to  $392\text{ K}$  and are summarized in Table 11, see [59]. In addition to data for pure ammonia, liquid-phase isothermal ( $P, \rho, T$ ) and bubble-point-pressure measurements for two standard mixtures of  $\text{NH}_3 + \text{H}_2\text{O}$  ( $x_{\text{NH}_3} = 0.8360$  and  $0.9057$  mol fraction) (not suitable as rocket propellants) were taken over a temperature range from  $280$  to  $379\text{ K}$  and at pressures of up to  $7.7\text{ MPa}$ . These data were compared to literature data and correlations, and agreed within  $\pm 3\%$  for bubble-point pressures,  $\pm 0.005\text{ g/cm}^3$  for liquid densities, and  $\pm 0.0011\text{ g/cm}^3$  for vapor densities.

**Table 11:** Near-saturation liquid ( $P, \rho, T$ ) vapor pressure and density measurements for  $\text{NH}_3$ .

| Temperature, K | Pressure, MPa | Density, g/cm <sup>3</sup> |
|----------------|---------------|----------------------------|
| 279.37         | 0.558         | 0.6296                     |
| 279.68         | 0.558         | 0.6292                     |
| 280.60         | 0.577         | 0.6281                     |
| 282.53         | 0.613         | 0.6251                     |
| 297.39         | 1.021         | 0.6040                     |
| 299.07         | 1.055         | 0.6017                     |
| 299.40         | 1.071         | 0.6014                     |
| 300.74         | 1.115         | 0.5991                     |
| 316.94         | 1.764         | 0.5741                     |
| 319.48         | 1.855         | 0.5695                     |
| 319.85         | 1.866         | 0.5677                     |
| 319.90         | 1.900         | 0.5689                     |
| 320.89         | 1.931         | 0.5673                     |
| 323.28         | 2.047         | 0.5636                     |
| 336.17         | 2.915         | 0.5412                     |
| 339.54         | 3.069         | 0.5344                     |
| 339.62         | 3.066         | 0.5340                     |
| 342.99         | 3.315         | 0.5281                     |
| 356.33         | 4.583         | 0.5011                     |
| 358.31         | 4.665         | 0.4962                     |
| 362.17         | 5.103         | 0.4877                     |
| 362.17         | 5.105         | 0.4877                     |
| 377.03         | 6.876         | 0.4492                     |
| 379.25         | 7.257         | 0.4436                     |
| 379.28         | 7.256         | 0.4433                     |
| 388.05         | 8.597         | 0.4153                     |
| 388.16         | 8.532         | 0.4135                     |
| 388.16         | 8.542         | 0.4137                     |

Data source: [59]

Measurements of ( $P$ ,  $\rho$ ,  $T$ ) for  $\text{NH}_3$  at elevated temperatures and pressures in the compressed liquid phase were carried out with a metal-bellows variable volumometer along 10 isotherms between 310 and 400 K at pressures from the vapor pressure to 17 MPa at intervals of 10 K [37]. The experimental uncertainties in temperature  $T$ , pressure  $P$ , and density  $\rho$  were estimated to be less than  $\pm 4$  mK,  $\pm 1.0 \times 10^{-3} P$ , and  $\pm 1.0 \times 10^{-3} \rho$ , respectively. The vapor pressure measurements of Baehr, Garnjost, and Pollak [56] were lower than the Kasahara et al. [37] results, but the differences were within the uncertainty of the Kasahara et al. measurements.

Vapor pressures of ammonia were measured for three different temperatures as part of an effort to obtain more accurate critical point data and are summarized in Table 12.

**Table 12:** Vapor pressure of ammonia.

| Temperature |     | Vapor pressure |       |
|-------------|-----|----------------|-------|
| K           | °C  | MPa            | atm   |
| 310         | 37  | 1.423          | 14.04 |
| 350         | 77  | 3.867          | 38.16 |
| 400         | 127 | 10.302         | 101.7 |

Data source: [60]

### 3.6 Viscosity of Ammonia

One must differentiate between *dynamic* viscosity and *kinematic* viscosity. The SI physical unit of dynamic viscosity is the Pascal-second (Pa s), equivalent to  $(\text{Ns})/\text{m}^2$ , or  $\text{kg m}^{-1} \text{s}^{-1}$ . The cgs physical unit for dynamic viscosity is the *poise*, abbreviated as P or Ps.

$$1 \text{ Ps} = 0.1 \text{ Pa} \cdot \text{s}$$

$$1 \text{ cPs} = 1 \text{ mPa} \cdot \text{s} = 0.001 \text{ Pa} \cdot \text{s}.$$

The SI unit of kinematic viscosity is  $\text{m}^2/\text{s}$ . The cgs physical unit for kinematic viscosity is the *stokes*, abbreviated as St. It is sometimes expressed in terms of centistokes (cSt).

$$1 \text{ St} = 1 \frac{\text{cm}^2}{\text{s}} = 10^{-4} \frac{\text{m}^2}{\text{s}}$$

$$1 \text{ cSt} = 1 \frac{\text{mm}^2}{\text{s}} = 10^{-6} \frac{\text{m}^2}{\text{s}}.$$

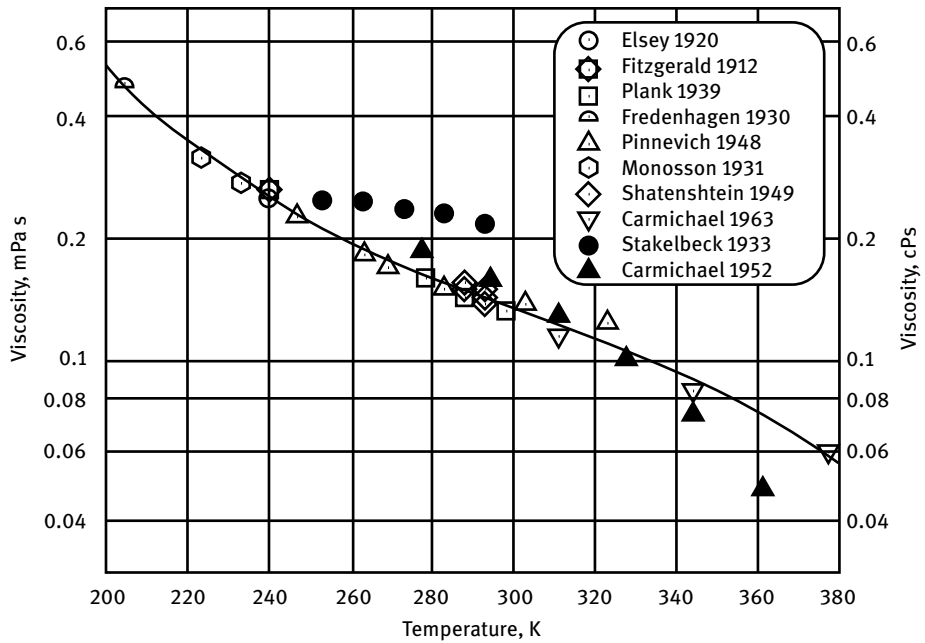
3.6.1 Viscosity of Liquid Ammonia

Data for the viscosity of liquid ammonia are listed in Table 13 and illustrated in Figure 14.

**Table 13:** Viscosity and density of liquid ammonia under pressure.

| Temperature |    | Density           | Viscosity |        |
|-------------|----|-------------------|-----------|--------|
| K           | °C | g/cm <sup>3</sup> | mPa s     | cPs    |
| 278         | 5  | 0.63197           | 0.1618    | 0.1618 |
| 288         | 15 | 0.61821           | 0.1457    | 0.1457 |
| 298         | 25 | 0.60427           | 0.1350    | 0.1350 |

Data source: [61]



**Figure 14:** Viscosity of saturated liquid ammonia. (Reproduced and modified from [22].)

When plotting viscosity data for liquid ammonia gathered from ten different sources, there was more scatter in the data than for most other physical properties. Two of the data sets (shown in solid symbols in Figure 14) had to be eliminated before calculat-

ing smoothed interpolated data represented by a polynomial equation. Carmichael, Reamer, and Sage [62] reviewed the available data and compared them to measurements they made in a rotating cylinder viscometer. All of these measurements were made in the temperature range 370–480 K and pressures below 345 bar. The solid triangles represent data from Carmichael and Sage [63]. The temperature dependence of the viscosity of liquid ammonia can be calculated by the following curve-fitted equation:

$$\log \mu = 5.7757 - 0.05837T + 1.7980 \times 10^{-4}T^2 - 1.9689 \times 10^{-7}T^3$$

where  $\mu$  is the viscosity in centipoise and  $T$  is the temperature in kelvin.

Viscosity data for ammonia and methylamine and several associated liquids have been obtained in the temperature ranges –65 to –35 °C and –65 to –10 °C, respectively, using an Ubbelohde viscometer [64] (Table 14). The results were compared with existing data, and all the data were fitted to the Fulcher (Tammann–Hesse) equation by the method of least squares. The significance of the values of  $T_0$  in this equation for these and other associated liquids was considered and it was attempted to give an interpretation to the significance of  $T_0$ . When comparing the different  $T_0$ , it can be noted that the quantity  $T_0$  (also written as -C by some authors) is largest for those liquids in which very extensive hydrogen bonding is possible.

**Table 14:** Viscosity of liquid ammonia and methylamine at various temperatures.

| Ammonia             |                    | Ammonia             |                    | For comparison: methylamine |                    |
|---------------------|--------------------|---------------------|--------------------|-----------------------------|--------------------|
| $T, ^\circ\text{C}$ | $\eta, \text{cPs}$ | $T, ^\circ\text{C}$ | $\eta, \text{cPs}$ | $T, ^\circ\text{C}$         | $\eta, \text{cPs}$ |
| –65.0               | 0.4314             | –41.8               | 0.290              | –70                         | 0.802              |
| –60.0               | 0.3906             | –40.6               | 0.2826             | –65                         | 0.681              |
| –55.0               | 0.3562             | –40.1               | 0.2817             | –60                         | 0.604              |
| –53.2               | 0.347              | –40.0               | 0.2823             | –55                         | 0.540              |
| –50.4               | 0.331              | –39.8               | 0.2794             | –50                         | 0.484              |
| –50.0               | 0.3285             | –39.5               | 0.280              | –45                         | 0.443              |
| –47.8               | 0.319              | –38.0               | 0.2714             | –40                         | 0.404              |
| –45.1               | 0.305              | –37.2               | 0.271              | –35                         | 0.374              |
| –45.0               | 0.3002             | –36.7               | 0.269              | –30                         | 0.348              |
| –42.2               | 0.290              | –35.0               | 0.2632             | –25                         | 0.323              |
|                     |                    |                     |                    | –20                         | 0.301              |
|                     |                    |                     |                    | –15                         | 0.280              |
|                     |                    |                     |                    | –10                         | 0.266              |

Data source: [64]



**Table 15:** Constants and valid ranges for the Fulcher viscosity equations.

|                    | A       | B        | $T_0$   | Viscosity at<br>298K, cPs | % Error | Valid range, °C |
|--------------------|---------|----------|---------|---------------------------|---------|-----------------|
| Ammonia            | -1.752  | 218.76   | 50.701  | 0.14                      | 0.76    | -69 to +40      |
| Methylamine        | -1.3634 | 126.389  | 102.886 | 0.19                      | 0.32    | -70 to -10      |
| 1,2-Diaminopropane | -1.0755 | 165.754  | 166.751 | 1.54                      | 1.1     | -35 to +50      |
| Methanol           | -1.6807 | 354.876  | 48.585  | 0.55                      | 2.05    | -98.3 to +50    |
| Water              | -1.5668 | 230.298  | 146.797 | 0.90                      | 0.51    | -10 to +160     |
| Ethanol            | -2.4401 | 774.414  | -15.249 | 1.08                      | 2.66    | -98.11 to +70   |
| Glycerin           | -2.8834 | 997.586  | 128.481 | 1003                      | 4.5     | -42 to +30      |
| Ethylene glycol    | -1.5923 | 438.064  | 141.617 | 16.2                      | 0.18    | +20 to +100     |
| <i>n</i> -Propanol | -2.4907 | 725.903  | 37.474  | 1.98                      | 1.1     | 0 to +70        |
| <i>n</i> -Butanol  | -3.0037 | 1033.306 | -4.3828 | 2.59                      | 0.8     | -50.9 to +100   |

Data source: [64]

The viscosity data in Table 14 can be expressed by a Fulcher-type equation

$$\log \eta = A + B/(T - T_0)$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The constants A, B, and  $T_0$  for ammonia are summarized in Table 15 below in comparison to other associated (hydrogen bonded) liquids.

Viscosity of ammonia measurements on five isotherms in the temperature range 448–598 K and pressures of up to 121 bar were made in a steady-state, capillary-flow viscometer [65]. The measurements were estimated to be accurate to better than 0.4% over the full range.

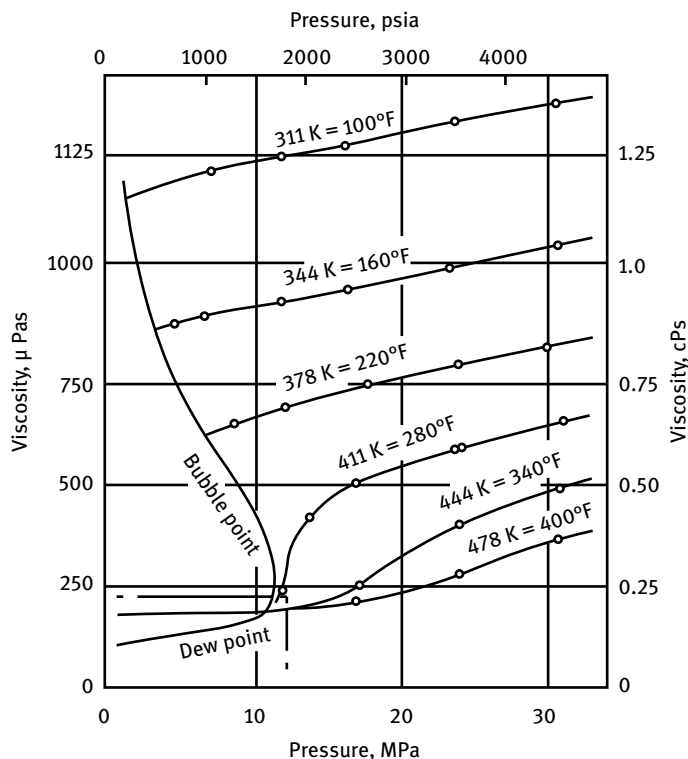
It was no easy task to bring together viscosity data for liquid and gaseous ammonia from over 40 different sources, spanning a time frame from 1846(!) to 1993 and temperatures from 196 K to beyond the critical point, and arrive at a consensus as to which data are reliable and should be used for a statistical averaging of results [66]. The majority of the primary set of experimental data was obtained from methods using either an oscillating disk or a capillary-flow apparatus. For the liquid phase, there is a paucity of reliable data. Only the later data from Carmichael, Reamer, and Sage [62] and Makhija and Stairs [64] were judged to be sufficiently accurate to be included in the primary set. The viscosity of ammonia in the liquid and gas phases was measured at pressures up to 34.5 MPa (5000 psia) in the temperature interval between 277.6 and 477 K (40 and 400 °F) by Carmichael, Reamer, and Sage [62]. The measurements were obtained with a rotating-cylinder viscometer, and results were presented in tabular and graphical form. Comparison with earlier measurements indicated fair agreement. The viscosity excess appeared to be a single-valued function of the specific weight. The

earlier data of Carmichael and Sage [63] tend towards low values at higher temperatures (343–373 K = 70–100 °C), but this seems to be a real effect due to the increasing specific volume of ammonia under its own vapor pressure at these temperatures. Raw (unsmoothed) viscosity data for liquid ammonia are summarized in Table 16. Deviation plot graphs were used to illustrate the deviation of data reported by individual investigators from the best correlation of Fenghour et al. [66], as a function of temperature. The best correlation for the viscosity of liquid ammonia and gaseous ammonia along the saturation line is summarized in Table 16. The effect of high pressures on the viscosity of liquid ammonia is illustrated in Figure 15.

**Table 16:** Viscosity and density of liquid and gaseous ammonia along the saturation boundary.

| $T, \text{ K}$ | $P, \text{ MPa}$ | $\rho_{\text{vap}}, \text{ mol/L}$ | $\eta_{\text{vap}}, \mu\text{Pa s}$ | $\rho_{\text{liq}}, \text{ mol/L}$ | $\eta_{\text{liq}}, \mu\text{Pa s}$ |
|----------------|------------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|
| 196            | 0.0063           | 0.0039                             | 6.85                                | 43.0041                            | 353.11                              |
| 200            | 0.0087           | 0.0052                             | 6.95                                | 42.7544                            | 507.28                              |
| 230            | 0.0177           | 0.0102                             | 7.21                                | 42.1111                            | 414.98                              |
| 220            | 0.0338           | 0.0187                             | 7.48                                | 41.4417                            | 346.68                              |
| 230            | 0.0604           | 0.0322                             | 7.77                                | 40.7482                            | 294.95                              |
| 240            | 0.1022           | 0.0527                             | 8.06                                | 40.0318                            | 254.85                              |
| 250            | 0.1649           | 0.0824                             | 8.36                                | 39.2933                            | 223.08                              |
| 260            | 0.2553           | 0.1242                             | 8.66                                | 38.5326                            | 197.34                              |
| 270            | 0.3811           | 0.1811                             | 8.06                                | 37.7485                            | 176.06                              |
| 280            | 0.5509           | 0.2573                             | 9.27                                | 36.9389                            | 158.12                              |
| 290            | 0.7744           | 0.3566                             | 9.58                                | 36.1008                            | 142.74                              |
| 300            | 1.0617           | 0.4845                             | 9.89                                | 35.2298                            | 129.33                              |
| 310            | 1.4240           | 0.6470                             | 10.22                               | 34.3199                            | 117.49                              |
| 320            | 1.8728           | 0.8520                             | 10.56                               | 33.3634                            | 106.91                              |
| 330            | 2.4205           | 1.1094                             | 10.93                               | 32.3495                            | 97.32                               |
| 340            | 3.0803           | 1.4325                             | 11.33                               | 31.2641                            | 88.55                               |
| 350            | 3.8660           | 1.8399                             | 11.79                               | 30.0867                            | 80.43                               |
| 360            | 4.7929           | 2.3598                             | 12.35                               | 28.7879                            | 65.49                               |
| 370            | 5.8778           | 3.0375                             | 13.05                               | 27.3212                            | 65.49                               |
| 380            | 7.1403           | 3.9558                             | 14.02                               | 25.6059                            | 58.31                               |
| 300            | 8.6045           | 5.2979                             | 15.53                               | 23.4655                            | 50.88                               |
| 394            | 9.2538           | 6.0518                             | 16.43                               | 22.3912                            | 47.62                               |
| 398            | 9.9436           | 7.0447                             | 17.67                               | 21.0667                            | 43.95                               |
| 402            | 10.6777          | 8.5479                             | 19.69                               | 19.1642                            | 39.20                               |

Data source: [66]

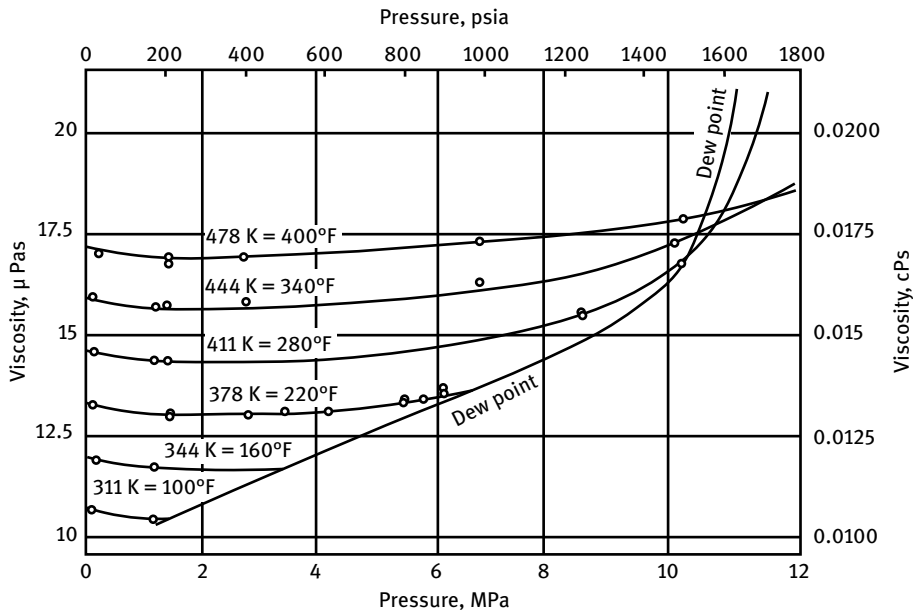


**Figure 15:** Viscosity of liquid ammonia at high pressures. (Reprinted and adapted from [62], with permission from ©1963 American Chemical Society; permission conveyed through RightsLink.)

### 3.6.2 Viscosity of Gaseous Ammonia

Below 5 bar, the viscosity and thermal conductivity of gaseous ammonia do not show much dependence on pressure (Figure 16).

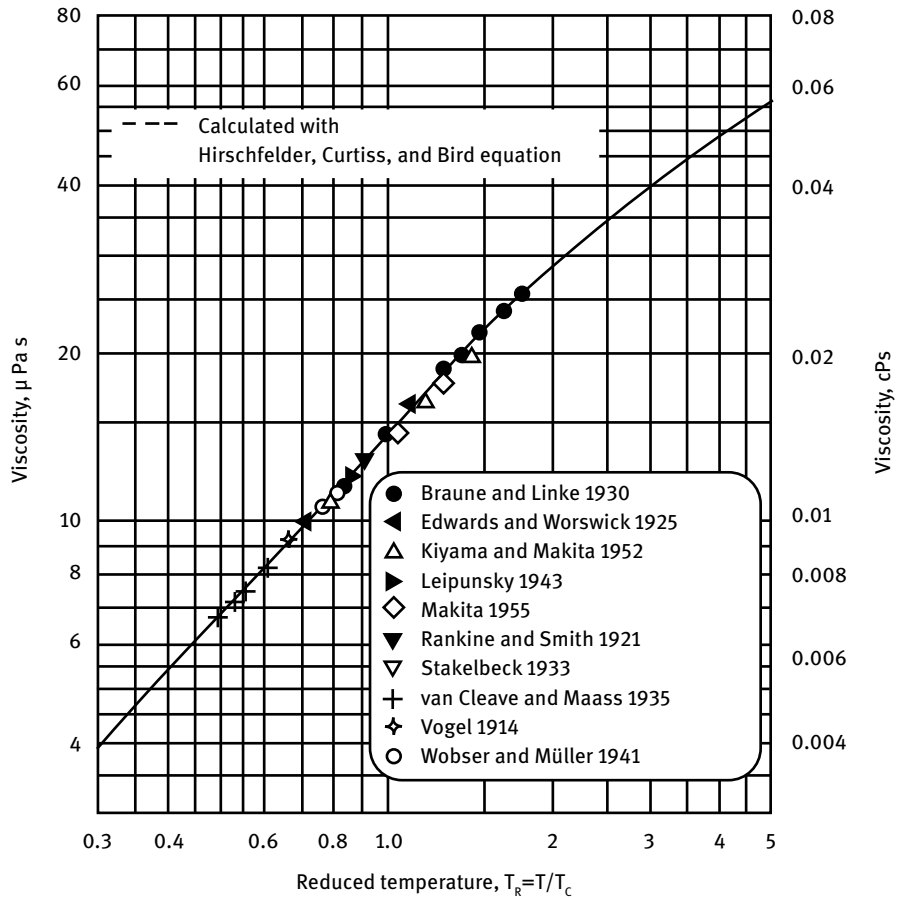
At higher pressures, the association of polar molecules causes a non-linear behavior of these properties with pressure. Measured viscosity data, a composite from ten different sources, of gaseous ammonia were fitted to an equation based on molecular collision theory containing terms for polarity parameter, dipole moment, collision diameter, and the maximum energy of attraction [67]. This equation would allow us to extrapolate (dashed lines in Figure 17) beyond the range of measured data (solid lines in Figure 17) both in the direction of higher and lower temperatures. The critical temperature used for this graph was 405.5 K.



**Figure 16:** Viscosity of gaseous ammonia. (Reprinted and adapted from [62], with permission from ©1963 American Chemical Society; permission conveyed through RightsLink.)

### 3.6.3 Viscosity of Supercritical Ammonia

Viscosity values at high, supercritical pressures and for the liquid state are difficult to obtain. High pressure viscosity data for ammonia are often scattered with wide error margins. Limited experimental data on ammonia for both viscosity and thermal conductivity necessitated the use of the theory of Enskog for the calculation of these transport properties at elevated pressures [67]. The residual viscosity  $\mu - \mu^*$  can be related directly to the reduced density  $\rho/\rho_c$  of ammonia as shown in Figure 18, where  $\mu^*$  is the thermal conductivity at moderate pressures and  $\rho/\rho_c$  is the density divided by the critical density. The critical density used for this graph was  $0.235 \text{ g/cm}^3$ .

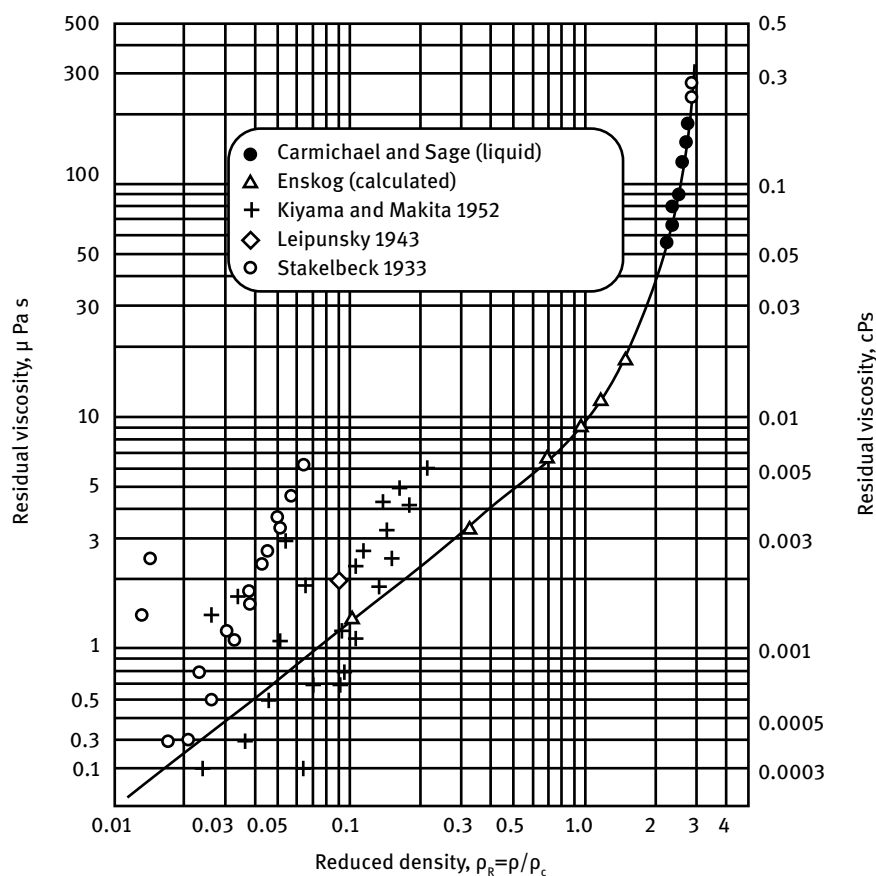


**Figure 17:** Viscosity of gaseous ammonia versus reduced temperature. (Reprinted and adapted from [67], with permission from ©1961 American Chemical Society; permission conveyed through RightsLink.)

### 3.7 Surface Tension of Ammonia

Measured data for the surface tension of liquid ammonia are tabulated in Table 17. The surface tension of liquid ammonia from 198 to 229 K (−75 to −44 °C) and of salt solutions in ammonia of sodium chloride and bromide and potassium bromide and iodide at 229 K (−44 °C) were measured by the method of maximum bubble pressure and checked by a few measurements by the capillary rise method [68]. The surface tension of ammonia may be represented by the equation

$$\sigma = 23.41 - 0.3371t - 0.000943t^2$$



**Figure 18:** Residual viscosity as a function of reduced density of ammonia in the dense phase/supercritical region. (Reprinted and adapted from [67], with permission from ©1961 American Chemical Society; permission conveyed through RightsLink.)

**Table 17:** Surface tension of ammonia

| Temperature |       | Surface tension $\sigma$ |        |
|-------------|-------|--------------------------|--------|
| K           | °C    | N/m                      | dyn/cm |
| 217         | −56   | 0.039                    | 39.15  |
| 221.4       | −51.7 | 0.038                    | 38.30  |
| 234         | −39   | 0.036                    | 35.56  |
| 239         | −34   | 0.034                    | 34.39  |
| 240         | −33   | 0.034                    | 34.06  |
| 284.2       | 11.1  | 0.023                    | 23.38  |
| 307.2       | 34.05 | 0.018                    | 18.00  |
| 332.13      | 58.98 | 0.013                    | 12.95  |

Data source: [39]

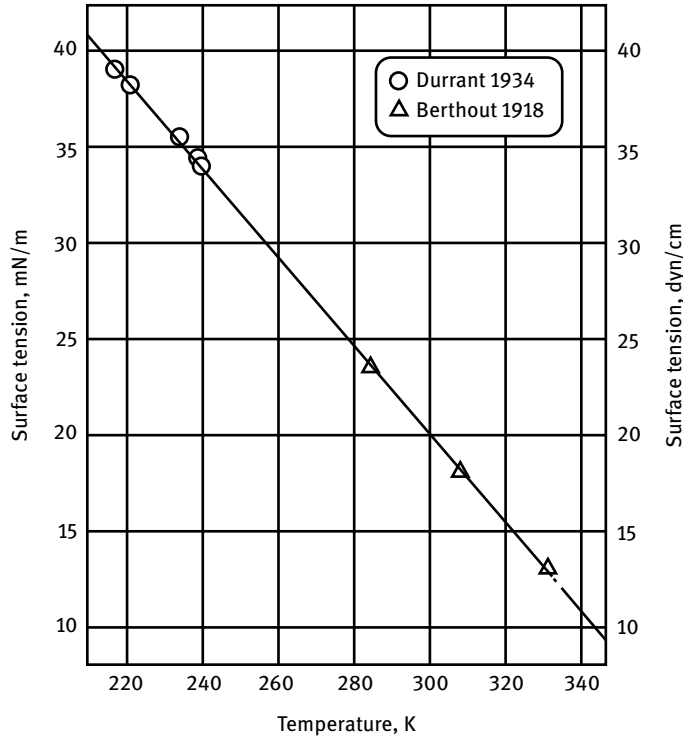
Conversion factors  $1 \text{ dyn} = 10^{-5} \text{ N}$ ;  $1 \text{ dyn/cm} = 10^{-3} \text{ N/m} = 1 \text{ mN/m}$

with a standard error of  $\pm 0.15$  dyn/cm where  $\sigma$  is the surface tension in dyn/cm and  $t$  is the temperature in  $^{\circ}\text{C}$ .

The temperature dependence of the surface tension of liquid ammonia can be calculated by the following curve-fitted equation:

$$\sigma = 89.8093 - 0.23252T$$

where  $\sigma$  is the surface tension in dyn/cm and  $T$  is the temperature in kelvin as shown in Figure 19.



**Figure 19:** Surface tension of liquid ammonia. (Reproduced and modified from [22].)

### 3.8 Thermal Conductivity of Ammonia

The thermal conductivity (also called *thermal conductance*) of ammonia is an important physical property needed in the design of commercial refrigeration machinery and regenerative cooling jackets in rocket engines that operate with liquid ammonia as a fuel. Temperature conditioning circuits on board the ISS are operating with liquid ammonia, and, every once in a while, an ammonia pump has to be replaced. The Space Shuttle orbiter had an ammonia evaporation dump coolant circuit with a heat

exchanger to a fluorocarbon coolant circuit to keep the crew compartment and electronics bays cool during re-entry. All these circuits were designed based on knowing the thermal conductivity and heat transfer characteristics of liquid ammonia. Considering the wide use of ammonia as a heat transfer fluid, it is surprising to discover the wide spread of data reported in the literature on the thermal conductivity of liquid ammonia at sea level pressure, ammonia at the saturation line, and gaseous ammonia. In many instances, the interference caused by convection resulted in high numbers. Some of the discrepancies carry over into this chapter and have not yet been resolved. Because so many different units of measurement are used for thermal conductivity, it is difficult to bring data from different sources to a common denominator for comparison.

### 3.8.1 Thermal Conductivity of Liquid Ammonia

Liquid ammonia as a refrigerant and heat transfer fluid is used in huge quantities in industrial refrigeration installations and even on board the ISS. It is surprising that it is very difficult to obtain consistent quality data for the thermal conductivity of liquid ammonia from the literature. Various investigators contradict each other about the dependence of the thermal conductivity of liquid ammonia on temperature. Some sources predict that the thermal conductivity increases with temperature, while other, more reliable data indicate that the thermal conductivity will decrease with temperature. Some of the older data for the thermal conductivity of liquid ammonia which showed an increase are summarized in Table 18.

**Table 18:** Thermal conductivity of liquid ammonia.

| Temperature |         | Thermal conductivity, $\lambda$ |                                                   |                                                   |
|-------------|---------|---------------------------------|---------------------------------------------------|---------------------------------------------------|
| K           | °C      | $\text{W m}^{-1} \text{K}^{-1}$ | $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$ | $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$ |
| 215.5       | -57.6   | 0.01597                         | $382 \times 10^{-7}$                              | $3.82 \times 10^{-5}$                             |
| 237.0       | -36.1   | 0.01843                         | $441 \times 10^{-7}$                              | $4.41 \times 10^{-5}$                             |
| 273.1       | $\pm 0$ | 0.02146                         | $513.5 \times 10^{-7}$                            | $5.135 \times 10^{-5}$                            |
| 285.0       | 11.9    | 0.02307                         | $551.9 \times 10^{-7}$                            | $5.519 \times 10^{-5}$                            |

Data source: [39]

Figure 15 on page 11 of Noel 1961, which the accompanying text described as representing liquid thermal conductivity data, showed an increase of thermal conductivity with temperature, supposedly based on data from Perry and Kordos (see [69]). Based on the increasing slope, the data used were most likely for gaseous ammonia and not liquid ammonia. This error was unfortunately not detected or corrected when the figure was used without further verification in a 1968 edition of this book on rocket propellants. The mislabeled figure has since been removed from the manuscript



for a revised edition. Figures 24 and 25 also show that the thermal conductivity of gaseous ammonia increases with temperature, similar to what appeared in the Noel 1961 report, Figure 15 [69]. *Perry's Chemical Engineers' Handbook*, 5<sup>th</sup> ed., on pages 3–214, cites a single number for Kardos 1933, 1934 data from 5 to 86 °F as  $0.29 \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1} = 0.00120 \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1} = 0.501 \text{ W m}^{-1} \text{ K}^{-1}$  for liquid ammonia. Yaws in *Chemical Engineering*, vol. 81, Issue No. 25, page 97, Unit 6, Figure 6–10 shows a decrease in the thermal conductivity of liquid ammonia with temperature. Interpolating from the graph, the thermal conductivity of saturated liquid ammonia at 298 K would be  $11 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ °C}^{-1} = 0.46 \text{ W m}^{-1} \text{ K}^{-1}$ , similar to the Perry/Kardos number.

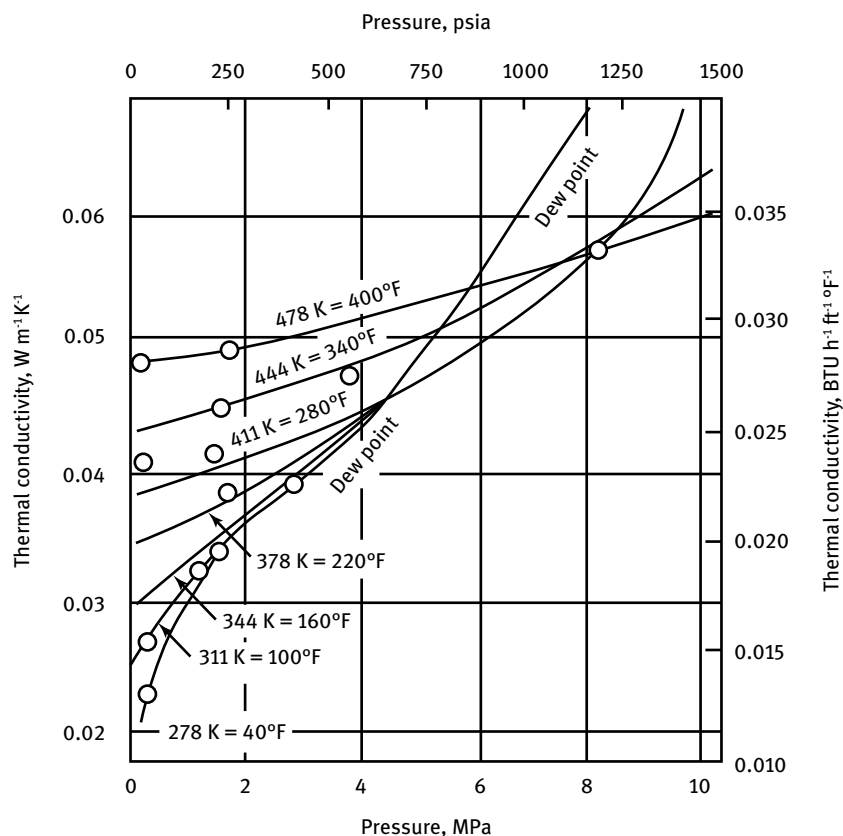
Sellschopp [70] determined the thermal conductivity of saturated liquid ammonia under pressure between 303 and 373 K (30 and 100 °C) and expressed the data by means of the equation

$$\lambda = 12.889(1 - 0.0042t) \times 10^{-4}$$

where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$  and  $t$  is the temperature in °C. This equation gives a thermal conductivity of  $11.5 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1} = 0.48 \text{ W m}^{-1} \text{ K}^{-1}$  for a temperature of 298 K = 25 °C, similar to the numbers discussed in the previous paragraph.

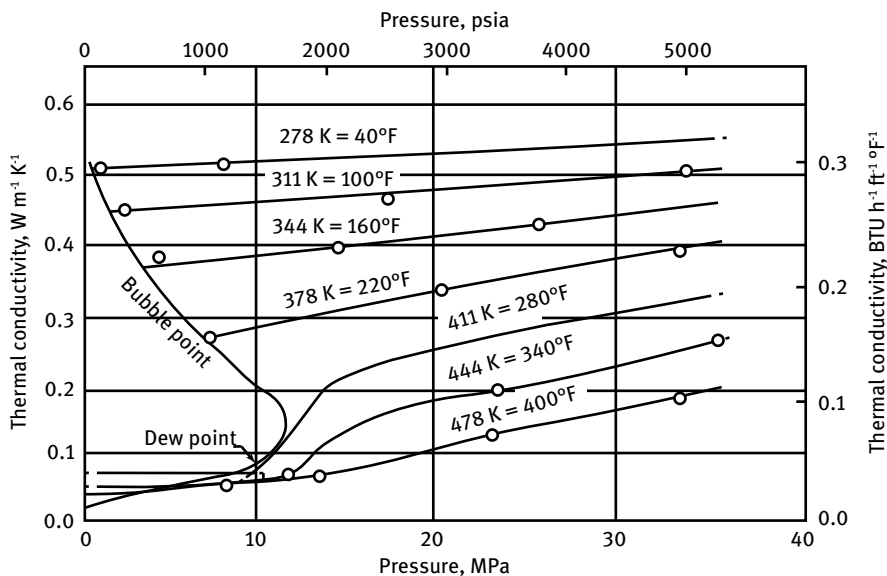
The unique relationship between the thermal conductivity and density, which was shown to exist for some monatomic and diatomic gases in their liquid and liquid-like fluid states, appears to also hold for ammonia. With the aid of this correlation, a value of  $3.65 \pm 0.06 \times 10^{-4} \text{ cal cm}^{-1} \text{ °C}^{-1} \text{ s}^{-1} = 0.153 \text{ W m}^{-1} \text{ K}^{-1}$  was found for the apparent thermal conductivity at the critical point [71].

The thermal conductivity of liquid and gaseous ammonia was measured in a spherical conductivity cell at pressures of up to 34.5 MPa (5000 psia) in the temperature interval between 278 and 478 K (40 and 400 °F) [72]. The results at atmospheric pressure agreed satisfactorily with earlier measurements. The residual thermal conductivity was a single-valued function of density for both the liquid and gas phases. This investigation did not include the critical region. Figures 20 and 21 show the experimental values of the thermal conductivity of gaseous and liquid ammonia at zero thermal flux as a function of pressure for each of the several temperatures investigated. A linear relationship between the apparent thermal conductivity and the thermal flux was assumed in this range of flux. Obviously, this was not strictly true. The standard error of estimate of these values of thermal conductivity from the smooth data was  $0.00277 \text{ W m}^{-1} \text{ K}^{-1}$  ( $0.0016 \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ °F}^{-1}$ ). The behavior at 411 K (280 °F), which was similar to that encountered with other fluids in the critical region, has been indicated by a dashed curve, since insufficient measurements were obtained to establish the behavior in this region with an accuracy equivalent to that at other states more distant from the critical region. The behavior in the gaseous region at lower pressures is shown in Figure 20.



**Figure 20:** Effect of low pressure on thermal conductivity of liquid and gaseous ammonia. (Reprinted and adapted from [72], with permission from ©1964 American Chemical Society; permission conveyed through RightsLink.)

The thermal conductivity of liquid and supercritical ammonia has been determined as being between 293 and 450 K (20 and 177°C) and at pressures from 0.1 to 50.7 MPa (1 to 500 atm), mapping the vicinity of the critical point ( $p_c = 11.3 \text{ MPa} = 111.5 \text{ atm}$ ,  $t_c = 132.4^\circ\text{C} = 405.5 \text{ K}$ ) along the reduced isotherms, 1.016 and 1.061, using a vertical, co-axial-cylinder apparatus [71, 73]. The measured thermal conductivity at 293 K was  $11.74 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^\circ\text{C}^{-1} = 0.49 \text{ W m}^{-1} \text{ K}^{-1}$ , in good agreement with literature data. An anomalous increase of thermal conductivity in the critical point regime has been found, similar to that for carbon dioxide. This anomaly becomes more visible if plotting the thermal conductivity versus the density in Amagat units. In Figure 22,  $k$  as a function of density is shown for three different temperatures. The solid straight line delineates normal behavior at 450 K = 176.9°C. The deviations from



**Figure 21:** Effect of high pressure on thermal conductivity of liquid and gaseous ammonia. (Reprinted and adapted from [72], with permission from ©1964 American Chemical Society; permission conveyed through RightsLink.)

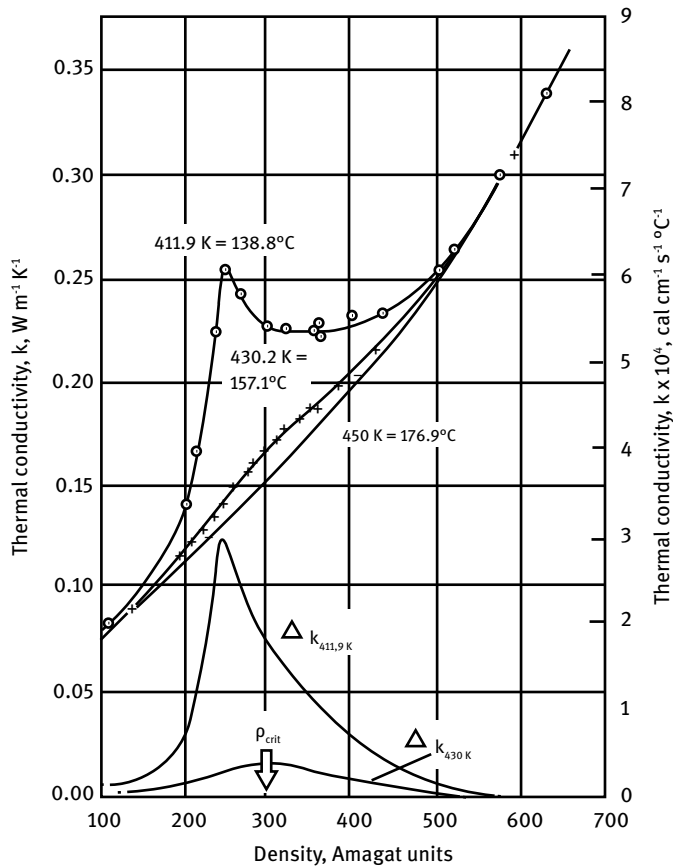
this line,  $\Delta k$ , are shown in the two dashed-line curves below. The  $\Delta k$  deviation curves max out at 250 and 314 Amagat, corresponding to pressures of 125 and 164 atm, respectively.

A tentative explanation of this phenomenon was given, based on the transport of energy by clusters of molecules. Experimental results for the liquid-like fluid state, both below and above the critical temperature, have been correlated by a quadratic equation between density and thermal conductivity. With the aid of this equation, values have been extrapolated for conditions outside those of the experimental range. Many investigators extrapolating thermal property data to higher temperatures have ignored the fact that ammonia begins to decompose at temperatures above 700 K.

The temperature dependence of the thermal conductivity of liquid ammonia can be calculated by the following curve-fitted equation which is based on data from three different sources:

$$\lambda = 1.4790 \times 10^{-3} + 2.2947 \times 10^{-6} T - 1.1726 \times 10^{-8} T^2$$

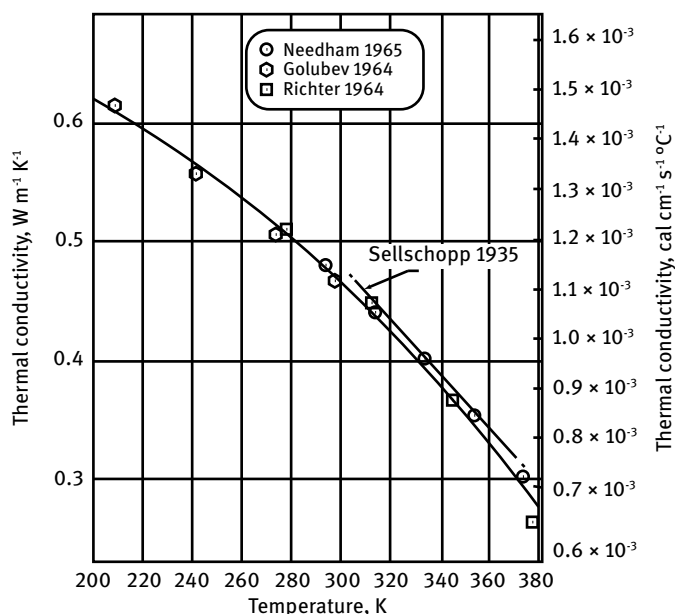
where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. A curve calculated from this equation is shown in Figure 23, also in comparison to the Sellschopp equation which gives slightly higher numbers.



**Figure 22:** Anomaly of thermal conductivity of ammonia in the vicinity of the critical point (Reprinted and modified from [73], with permission from ©1965 Elsevier; permission conveyed through RightsLink)

This equation and the illustration in Figure 23 show a decrease of thermal conductivity with increasing temperature, whereas older literature data reported an increase of the thermal conductivity of liquid ammonia with temperature. For comparison, the thermal conductivity of liquid hydrazine also decreases with temperature. There is a wide discrepancy with up to 20% spread between the data from Needham and Ziebland [73], Golubev and Sokolova [74] and Richter and Sage [72]. Additional uncorrected thermal conductivity data are widely scattered and are not considered reliable [75].

The thermal conductivity of gaseous and liquid ammonia was measured in the range 297–387 K and at pressures of up to 50 MPa [76]. The measurements were necessary for a fitting of the thermal conductivity surface in the density–temperature plane.



**Figure 23:** Thermal conductivity of saturated liquid ammonia. (Reproduced and modified from [22].)

Results were believed to be accurate to  $\pm 2\%$ . It was difficult to make a good comparison of these results with previous data because no full correlation of the thermal conductivity of ammonia has been completed. A preliminary assessment for the liquid phase indicated that agreement was reasonable over much of the range, with differences up to around 5% under certain conditions. Results from an earlier 1984 publication had to be revoked due to a systematic error in the measurements [77]. For the gas phase, an approximate extrapolation to atmospheric pressure can be made, and the results compared with recommended values where differences of  $\pm 3\%$  were observed.

A correlation of selected literature data on the EOS and thermal conductivity of ammonia provided a set of recommended data for the vapor pressure, density, and thermal conductivity of liquid and gaseous ammonia along the saturation line for a temperature range from 200 to 400 K as shown in Table 19.

In an effort to minimize interference by convection, a transient short-hot-wire method was used to measure the thermal conductivity of liquid ammonia at 284–354 K and 2–10 MPa [79]. The measured data are shown in Table 20. Compared with the calculated values from REFPROP 10.0, the average absolute deviation was  $-5.6\%$  and all the newly measured values were lower than those from REFPROP 10.0 which are based on old data from prior to 1988. See also [80] and [81].

**Table 19:** Recommended data for thermal conductivity of liquid and gaseous ammonia along the saturation line.

| Temperature |     | Vapor pressure |       | Density                                  |                                          | Thermal conductivity                                        |                                                             |
|-------------|-----|----------------|-------|------------------------------------------|------------------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| K           | °C  | MPa            | atm   | $\rho_{\text{liq}}$<br>g/cm <sup>3</sup> | $\rho_{\text{vap}}$<br>g/cm <sup>3</sup> | $\lambda_{\text{liq}}$<br>W m <sup>-1</sup> K <sup>-1</sup> | $\lambda_{\text{vap}}$<br>W m <sup>-1</sup> K <sup>-1</sup> |
| 200         | -73 | 0.00861        | 0.085 | 0.729                                    | 0.0001                                   | 0.610                                                       | 0.016                                                       |
| 225         | -48 | 0.04545        | 0.450 | 0.700                                    | 0.0004                                   | 0.596                                                       | 0.018                                                       |
| 250         | -23 | 0.16489        | 1.633 | 0.669                                    | 0.0014                                   | 0.564                                                       | 0.021                                                       |
| 275         | 2   | 0.45975        | 4.552 | 0.636                                    | 0.0037                                   | 0.519                                                       | 0.024                                                       |
| 300         | 27  | 1.0611         | 10.51 | 0.600                                    | 0.0082                                   | 0.466                                                       | 0.028                                                       |
| 325         | 52  | 2.1324         | 21.11 | 0.560                                    | 0.0166                                   | 0.409                                                       | 0.034                                                       |
| 350         | 77  | 3.8652         | 38.27 | 0.512                                    | 0.0313                                   | 0.350                                                       | 0.043                                                       |
| 375         | 102 | 6.4853         | 64.2  | 0.452                                    | 0.0589                                   | 0.292                                                       | 0.060                                                       |
| 400         | 127 | 10.297         | 102.0 | 0.344                                    | 0.1309                                   | 0.238                                                       | 0.142                                                       |

Data source: [78]

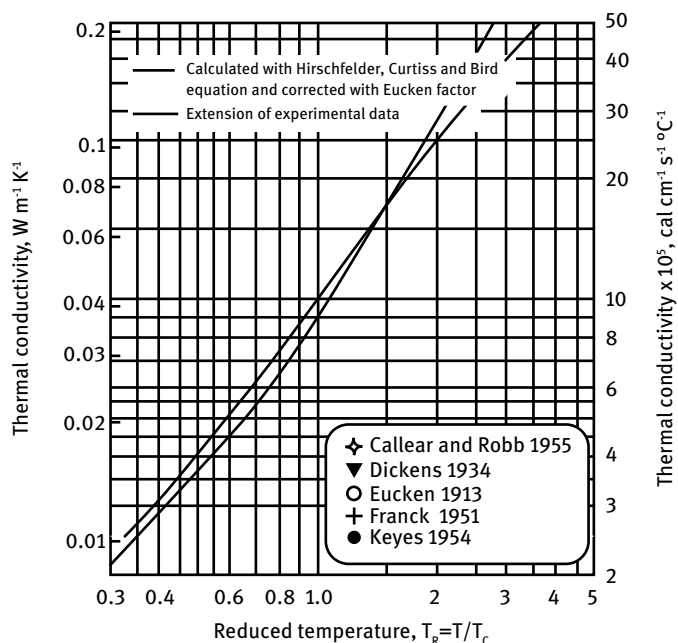
**Table 20:** Thermal conductivity of liquid ammonia.

| Temperature, K                                          | Pressure, MPa |        |        |        |        |
|---------------------------------------------------------|---------------|--------|--------|--------|--------|
|                                                         | 2             | 4      | 6      | 8      | 10     |
| Thermal conductivity, W m <sup>-1</sup> K <sup>-1</sup> |               |        |        |        |        |
| 284.1                                                   | 0.4719        | 0.4735 | 0.4780 | 0.4833 | 0.4864 |
| 294.1                                                   | 0.4495        | 0.4548 | 0.4594 | 0.4610 | 0.4633 |
| 304.2                                                   | 0.4290        | 0.4336 | 0.4406 | 0.4459 | 0.4496 |
| 314.2                                                   | 0.4115        | 0.4174 | 0.4218 | 0.4270 | 0.4300 |
| 324.1                                                   | —             | 0.3947 | 0.3968 | 0.4011 | 0.4037 |
| 334.1                                                   | —             | 0.3748 | 0.3771 | 0.3804 | 0.3833 |
| 344.2                                                   | —             | 0.3337 | 0.3459 | 0.3514 | 0.3558 |
| 354.3                                                   | —             | —      | 0.3346 | 0.3412 | 0.3472 |

Data source: [79]

### 3.8.2 Thermal Conductivity of Gaseous Ammonia

It has long been known that the transfer of energy by polyatomic and polar molecules like ammonia is quite complex because of the presence of internal degrees of freedom and the possibility of resonant energy transfer in the latter. Available thermal conductivity values for ammonia at essentially atmospheric pressure can be presented as a function of reduced temperature as shown in Figure 24. The critical temperature used for creating this graph was  $T_c = 405.5$  K. The compressibility factor was  $z_c = 0.242$ . Results of five available sources from the literature have been used to produce a relationship that is opposite in curvature to that found to exist for monatomic and



**Figure 24:** Thermal conductivity of gaseous ammonia. (Reprinted and adapted from [67], with permission from ©1961 American Chemical Society; permission conveyed through RightsLink.)

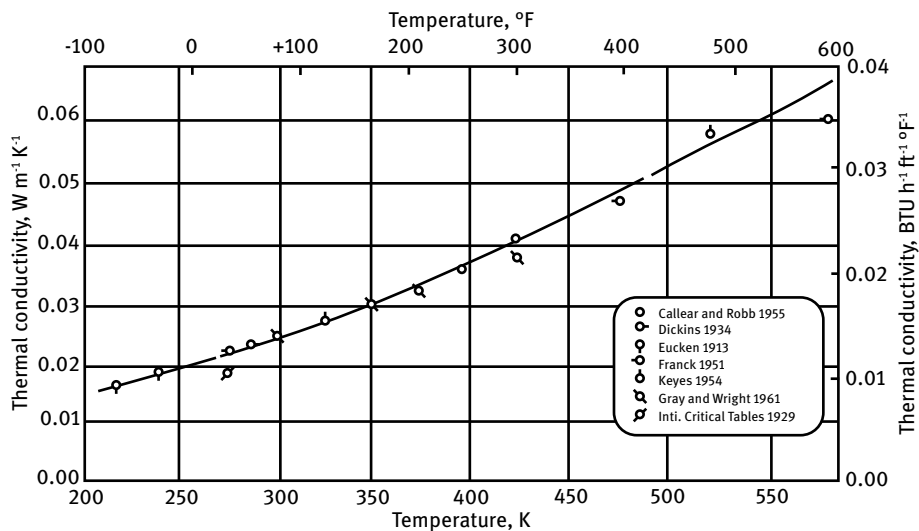
diatomic gases when plotted on log–log coordinates [67]. This type of behavior has been exhibited in a similar study for the thermal conductivity of methane.

The thermal conductivity of gaseous ammonia as a function of temperature at atmospheric pressure is shown as a function of temperature in Figure 25. The smooth curve represents values corrected for convection. The values in the literature have been included for comparison.

Thermal conductivity of gaseous ammonia at a sub-atmospheric pressure of 24 kPa (180 mm Hg) has been measured over the temperature range 311–473 K (38–200 °C) by a hot-wire method [82]. The collision numbers for rotational relaxation  $Z_{\text{rot}}$  have been determined from the experimental data and were found to increase with a rise of temperatures.

The thermal conductivity of ammonia gas has been measured by a column method at low pressures of 12.9, 26.5, and 45.0 kPa over the temperature range from 358 to 925 K [83]. The experimental data were correlated by a polynomial equation:

$$\lambda = 5.237 \times 10^{-3} + 5.179 \times 10^{-4} T + 8.404 \times 10^{-7} T^2 + 1.557 \times 10^{-10} T^3$$



**Figure 25:** Thermal conductivity of gaseous ammonia at atmospheric pressure. (Reprinted and adapted from [72], with permission from ©1964 American Chemical Society; permission conveyed through RightsLink.)

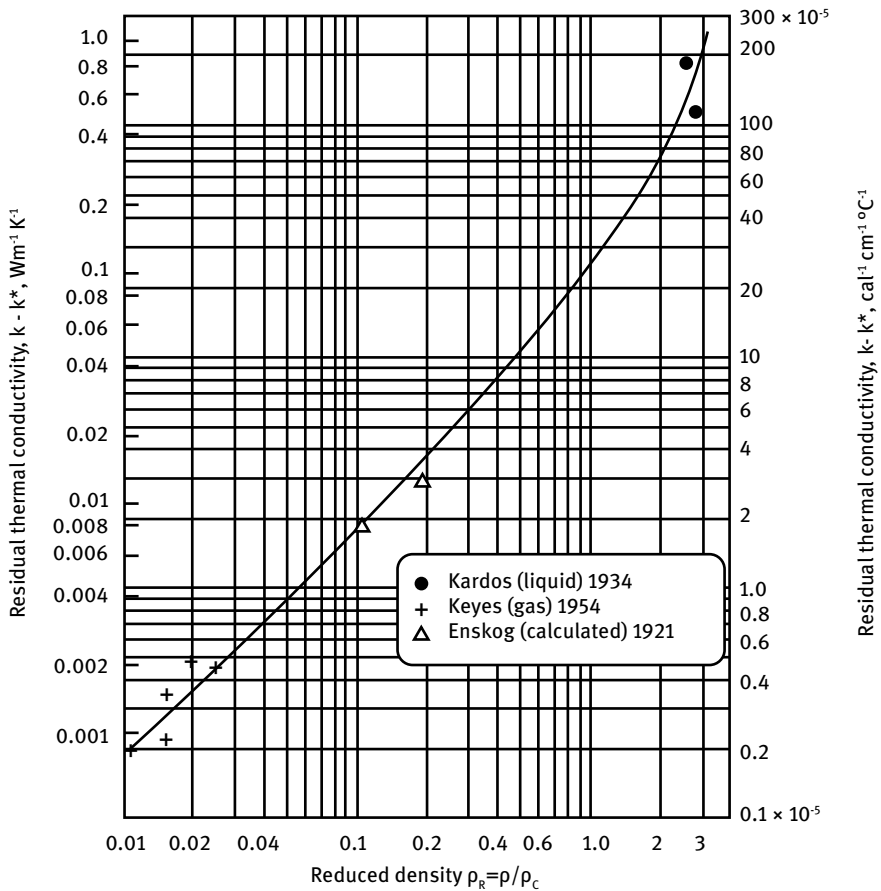
where  $\lambda$  is thermal conductivity in  $\text{mW cm}^{-1} \text{K}^{-1}$  and  $T$  is in kelvin. For example, this equation at 373K gives a thermal conductivity of  $0.323 \text{ mW cm}^{-1} \text{K}^{-1} = 3.234 \text{E-06 W m}^{-1} \text{K}^{-1}$ . See also [74, 78].

### 3.8.3 Thermal Conductivity of Supercritical Ammonia

Thermal conductivity values at high, supercritical pressures and for the liquid state are difficult to obtain. High-pressure thermal conductivity data for ammonia are not plentiful. Limited experimental data on ammonia for both viscosity and thermal conductivity necessitated the use of the theory of Enskog for the calculation of these transport properties at elevated pressures [67]. The residual thermal conductivity  $k - k^*$  can be related directly to the reduced density  $\rho/\rho_c$  of ammonia as shown in Figure 26, where  $k^*$  is the thermal conductivity at moderate pressures and  $\rho/\rho_c$  is the density divided by the critical density.

Using a coaxial-cylinder apparatus, the thermal conductivity of ammonia was measured at pressures of up to 80 MPa along nine quasi-isotherms in the supercritical regime and one quasi isotherm below the critical temperature, and the results were compared to previous data [77]. A semi-empirical equation was proposed to correlate the data in the supercritical regime.





**Figure 26:** Relationship of residual thermal conductivity and reduced density of ammonia in the dense-phase region. (Reprinted and adapted from [67], with permission from ©1961 American Chemical Society; permission conveyed through RightsLink.)

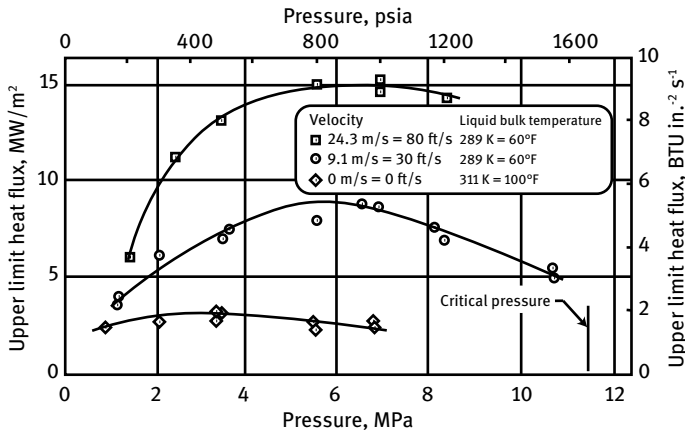
### 3.9 Heat Transfer Properties of Liquid Ammonia

Heat transfer properties of liquid ammonia are important not only for the design of commercial refrigeration machinery, but also for that of regeneratively cooled rocket engines such as the ones flown in the high-altitude research plane X-15 [69].

As with many other coolants in regeneratively cooled rocket engines, it is important to know the upper limit of nucleate boiling. At the transition from nucleate boiling to film boiling, a cushion of vapor forms between the wall and the liquid, causing high temperature gradients and hot spots in the wall which may lead to burnout of the

chamber or the nozzle. During nucleate boiling, the wall temperature rarely exceeds 30 degrees (C or K) above the boiling temperature at the prevailing pressure. The wall temperature and the heat transfer are a function of liquid temperature, flow velocity, and pressure. The upper limit of the heat flux is often abbreviated with the symbol  $q_{ul}$ .

Numbers reported in the literature for  $q_{ul}$  without stating the inlet temperature of the liquid are suspect. One cannot always assume that the liquid is entering the system at room temperature [84]. The results illustrated in Figure 27, which does have the inlet temperatures listed properly, mean it is possible to use its data for comparison.



**Figure 27:** Heat transfer to liquid ammonia at the upper limit of nucleate boiling, as a function of pressure and flow velocity. (Reproduced and modified from [69].)

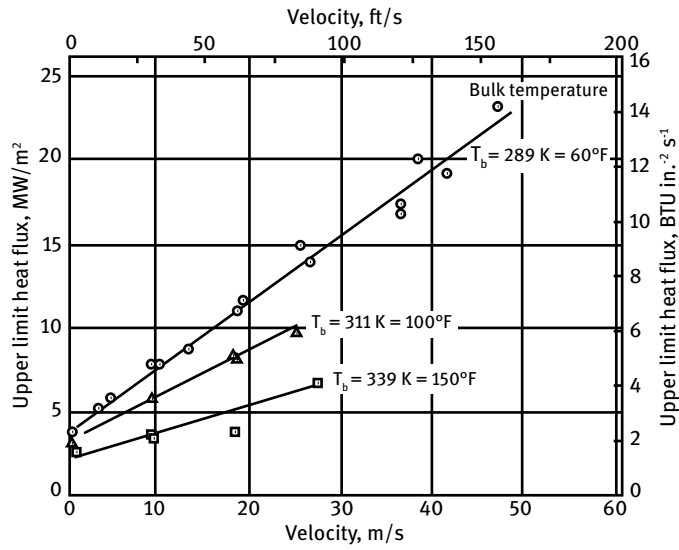
Figure 27 shows the heat transfer at the upper limit of nucleate boiling as a function of pressure, with three different curves for three different flow velocities. A maximum of heat flux was achieved at 6.18 MPa = 61 atm, which is 55% of the critical pressure. Above the critical point, one cannot establish an upper limit of nucleate boiling because the difference between the liquid phase and vapor phase ceases to exist.

Figure 28 shows that the heat transfer at different inlet temperatures increases linearly with the flow velocity.

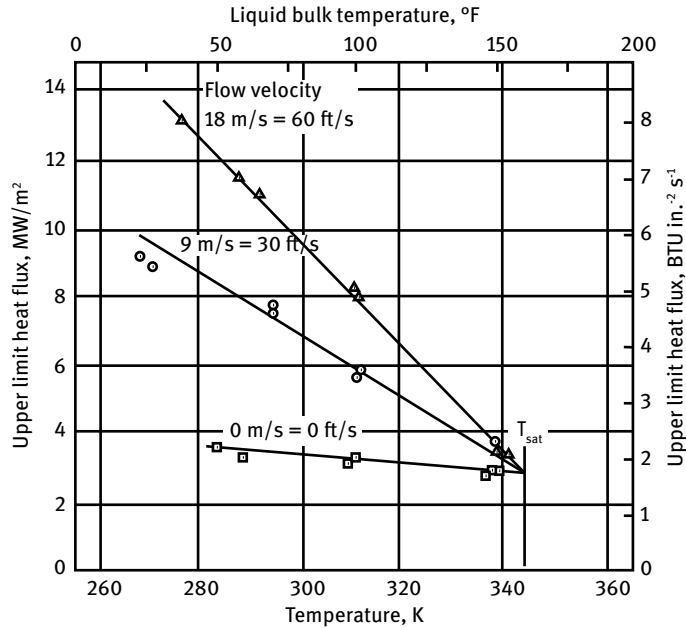
The upper limit of nucleate boiling heat transfer is a linear function of the initial inlet temperature of the liquid ammonia in the supply tank, as shown in Figure 29.

The slope of the linear function is dependent on the initial temperature of liquid ammonia in the reservoir. Figure 29 shows the upper limit of nucleate boiling of ammonia for various flow velocities as a function of the initial fluid temperature.

The heat transfer coefficient of liquid ammonia at the upper limit to nucleate boiling is low in comparison to other rocket propellants which might also be used as coolants in regenerative rocket engines (Table 21).



**Figure 28:** Heat transfer to liquid ammonia at 3.43 MPa = 34 atm as a function of flow velocities at different inlet temperatures. (Reproduced and modified from [69].)



**Figure 29:** Heat transfer to liquid ammonia at the upper limit of nucleate boiling, as a function of inlet temperature and flow velocity at a pressure of 3.43 MPa = 34 atm. (Reproduced and modified from [69].)

**Table 21:** Heat transfer coefficient of ammonia in comparison to other rocket propellants.

| Coolant liquid                | Heat transfer coefficient $q_{ul}$ at 2.07 MPa = 20.4 atm,<br>9.1 m/s and 310.9 K = 37.8°C inlet temperature |                                       | Heat capacity at<br>310.9 K = 37.8°C |                                      |
|-------------------------------|--------------------------------------------------------------------------------------------------------------|---------------------------------------|--------------------------------------|--------------------------------------|
|                               | kW/cm <sup>2</sup>                                                                                           | BTU in. <sup>-2</sup> s <sup>-1</sup> | J g <sup>-1</sup> K <sup>-1</sup>    | cal g <sup>-1</sup> °C <sup>-1</sup> |
| NH <sub>3</sub>               | 15.95                                                                                                        | 97.6                                  | 4.89                                 | 1.17                                 |
| JP-3                          | 28.73                                                                                                        | 175.8                                 | 1.82                                 | 0.435                                |
| N <sub>2</sub> O <sub>4</sub> | 29.38                                                                                                        | 179.8                                 | 1.64                                 | 0.393                                |
| RFNA                          | 43.39                                                                                                        | 265.5                                 | 1.76                                 | 0.42                                 |
| Corporal fuel <sup>a</sup>    | 51.64                                                                                                        | 316                                   | 2.09                                 | 0.50                                 |
| N <sub>2</sub> H <sub>4</sub> | 79.10                                                                                                        | 484                                   | —                                    | —                                    |

<sup>a</sup> The fuel used in the Corporal ballistic missile consisted of 80 mass-% aniline and 20 mass-% furfuryl alcohol

Data source: [84]

Besides its dependence on heat transfer properties, the suitability of a rocket propellant as a coolant in a regeneratively cooled rocket engine depends also on its heat capacity, on the difference between inlet temperature and the boiling temperature under cooling-jacket (pressure) conditions, and on the mixture ratio and the heat of reaction of the propellant combination. Calculations showed that ammonia as a regenerative coolant is barely capable of accepting the heat flux through the engine chamber wall of a 22.5-ton-thrust rocket engine operating on liquid oxygen (LOX)/NH<sub>3</sub> or red-fuming nitric acid (RFNA)/NH<sub>3</sub> [84]. In this comparison, the component listed first is the one used for regenerative cooling. In a comparison of RFNA/unsymmetrical dimethylhydrazine (UDMH), RFNA/Corporal missile fuel, RFNA/ diethylene triamine (DETA) or N<sub>2</sub>O<sub>4</sub>/JP-3, liquid ammonia did not emerge as a promising coolant. This is in spite of its relatively high heat capacity in comparison to the other fluids listed in Table 21. Ammonia's relatively low boiling point cancels out some of its advantages. Additional information on heat transfer to ammonia appears in the older technical publications summarized in Table 22.

Heat transfer experiments with anhydrous ammonia were conducted in a forced-convection apparatus [85]. The heart of the apparatus was an electrically heated, stainless-steel tube 4.8 mm O.D. × 0.25 mm wall thickness (3/16 in. O.D. × 0.010 in. wall thickness), mounted concentrically with a 7.9 mm I.D. (5/16 in. I.D.) heavy-walled Pyrex tube. The fluid under investigation flowed in the annulus between the two tubes. The heated section of the stainless-steel tube was 5 cm (2 in.) long. Auxiliary equipment included high-pressure storage and receiver tanks; a heat exchanger to regulate the bulk temperature of the fluid; a 20-kW direct-current generator (synchronous motor-driven) to supply the heater current; a Potter flowmeter to measure the fluid flow rate; thermocouples to measure heater-tube and bulk fluid temperatures; Tabor pressure transducers to measure system pressure and pressure drop across the heater; strip chart recorders to make simultaneous records of heater

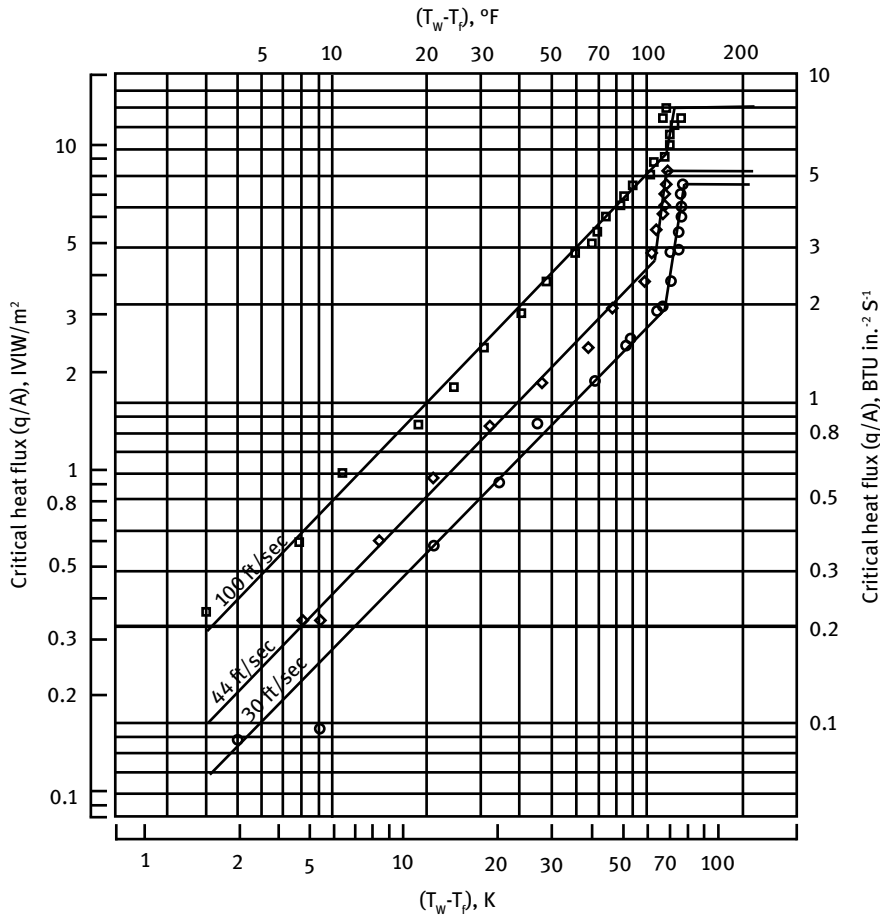
voltage and current, pressures, temperatures, and flow rate; and the necessary piping, valves, and controls. Gas pressure was applied to the storage tank to force the fluid through the test section. Current was applied to the heater tube in stepwise increments until tube burnout occurred, or until the maximum output of the generator had been reached. At maximum generator output, the heat flux from the heater tube was about  $19610954 \text{ W m}^{-2}$  at 1.8 MW ( $12 \text{ BTU in.}^{-2} \text{ s}^{-1}$  at  $6200000 \text{ BTU/h}$ ). A total of 36 test runs was made with anhydrous ammonia. During these tests, the system pressure was varied from 3.1 to 4.14 MPa (from 450 to 600 psia), the bulk temperature from 275 to 326 K (from 35 to 127 °F), and the velocity from 6.7 to 38 m/s (from 22 to 125 ft/s). The annulus width was 1.57 mm (0.0618 in.) in all tests, giving a flow area of  $0.313 \text{ cm}^2$  ( $0.0486 \text{ in.}^2 = 0.000338 \text{ ft}^2$ ) and an equivalent hydraulic diameter of 3.137 mm (0.1235 in. = 0.01029 ft). Burnout always occurred suddenly, without any visual or instrumented warning. There was no stable film-boiling region. The Dittus-Boelter equation used for data correlation is:  $\text{Nu} = 0.027 \text{ Re}^{0.8} \text{ Pr}^{0.4}$ . Figure 30 presents typical uncorrelated results of test runs, with the heat flux ( $q/A$ ) plotted versus the temperature difference ( $T_w - T_f$ ) on log-log paper. The slopes of the lines in the non-boiling region should all be equal to unity. The zero intercepts of these lines should give values of the heat transfer coefficient,  $h$ , which is a function of velocity. The curves showed a sharp upward break at the inception of nucleate boiling, and, at higher values of  $q/A$ , the wall temperature remains nearly constant. This break occurred at a temperature of only 2–10 °F above the boiling point of ammonia at the system pressure.

Figure 31 shows a plot of the burnout heat flux versus  $\Delta T_{\text{sub}}$ , with fluid velocity as the parameter. These data have been compared with data published by the Jet Propulsion Laboratory (JPL). The JPL data show a lower dependence of ( $q/A$ ) burnout on  $\Delta T_{\text{sub}}$  than is shown on these results.

Forced-convection heat transfer in liquid ammonia in a smooth Inconel tube of 3-mm I.D and 3.5-mm O.D., a 300-mm length was measured at 0.5–10 MPa (5–100 bar), flow rates of 40–500  $\text{g s}^{-1} \text{ cm}^{-2}$ , inlet temperatures of 306–368 K (33–95 °C), heat fluxes of up to 315  $\text{W/cm}^2$ , and maximum wall temperatures of 1123 K (850 °C) [86]. The correlation

$$\text{Nu} = C \text{ Re}^{0.8} \text{ Pr}^{0.4}$$

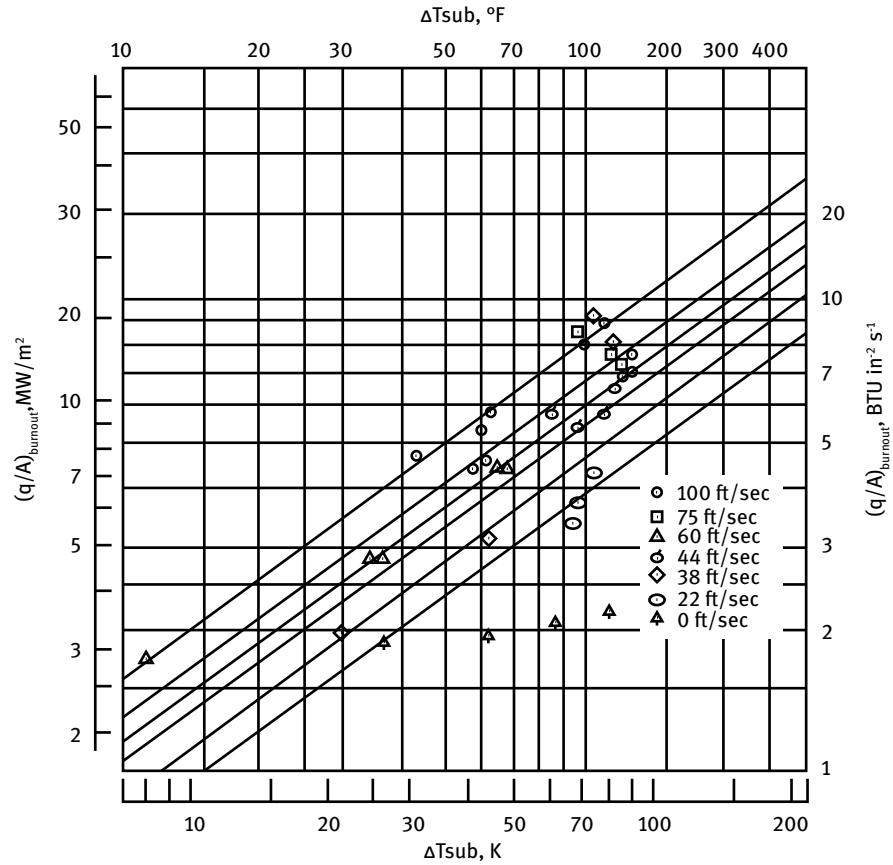
was found to be applicable with a constant  $C$  of 0.021. Table 22 gives a summary of additional publications on the heat transfer to liquid ammonia. This is a starting point for future in-depth study of this topic.



**Figure 30:** Heat transfer to flowing liquid ammonia. (Reproduced and modified from [85].)

**Table 22:** Summary of publications on the heat transfer to liquid ammonia.

| Author                       | Year | References |
|------------------------------|------|------------|
| Reinhardt, Potter, and Moore | 1957 | [85]       |
| Dimmock                      | 1957 | [87]       |
| Mascolo                      | 1958 | [88]       |
| McCarthy                     | 1963 | [89]       |
| Seader and Wagner            | 1964 | [90]       |
| Perroud, Rebiere, and Rowe   | 1966 | [86]       |



**Figure 31:** Critical heat flux at burnout for liquid ammonia. (Reproduced and modified from [85].)

The rate of evaporation of liquid ammonia sprays in a combustion chamber has been analyzed in comparison to several other evaporating liquids [91].

### 3.10 Critical Constants of Ammonia

The critical constants of ammonia are summarized in Table 23. Similar data for tri-deuteroammonia obtained from an extended corresponding-states principle for vapor pressure appear in Table 24.

**Table 23:** Critical constants of ammonia.

| Critical pressure |             | Critical temperature |        | Critical specific volume | Critical density  | Year | References |
|-------------------|-------------|----------------------|--------|--------------------------|-------------------|------|------------|
| MPa               | Other units | K                    | °C     | m <sup>3</sup> /kmol     | g/cm <sup>3</sup> |      |            |
| 11.298            | 111.5 atm   | 405.5                | 132.4  | —                        | 0.235             | 1935 | [39]       |
| 11.353            | 1647 psia   | 405.50               | 132.4  | —                        | —                 | 1976 | [56]       |
| —                 | —           | 405.38               | 132.23 | —                        | —                 | 1979 | [47]       |
| 11.15             | 1617 psia   | 405.5                | 132.4  | —                        | —                 | 1987 | [92]       |
| 11.300            | 1639 psia   | 405.40               | 132.3  | —                        | —                 | 1988 | [93]       |
| 11.34             | 1645 psia   | 405.4                | 132.3  | —                        | —                 | 1990 | [94]       |
| 11.3              | 1639 psia   | 405.2                | 132.1  | —                        | 0.276             | 2004 | [25]       |
| 11.357            | 1647 psia   | 405.56               | 132.41 | —                        | 0.244             | 2005 | [60]       |
| 11.333            | 1644 psia   | —                    | —      | 0.07569                  | —                 | 2012 | [24]       |

**Table 24:** Critical parameters, acentric factor, and aspherical factor for ammonia and trideuteroammonia.

|                               | Ammonia | Trideutero-ammonia |                           | Ammonia     | Trideutero-ammonia |
|-------------------------------|---------|--------------------|---------------------------|-------------|--------------------|
| $T_c$ , K                     | 405.37  | 405.2              | $a_0$                     | 7.115168    | 7.265948           |
| $p_c$ , kPa                   | 11345   | 11300              | $a_1$                     | 9.478726    | 9.904991           |
| $\rho_c$ , g cm <sup>-3</sup> | 234.3   | 276                | $a_2$                     | 20.236840   | 21.49400           |
| $\omega$                      | 0.2568  | 0.287              | $\theta$                  | 2.054531023 | 2.147631023        |
| $T_{\text{triple}}$ , K       | 195.4   | 199.0              | $p_{\text{triple}}$ , kPa | 6.0182      | 6.4855             |
| $T_{\text{boil}}$ , K         | 239.79  | 242.20             | $M$                       | 17.013      | 20.05              |

Data source: [25]

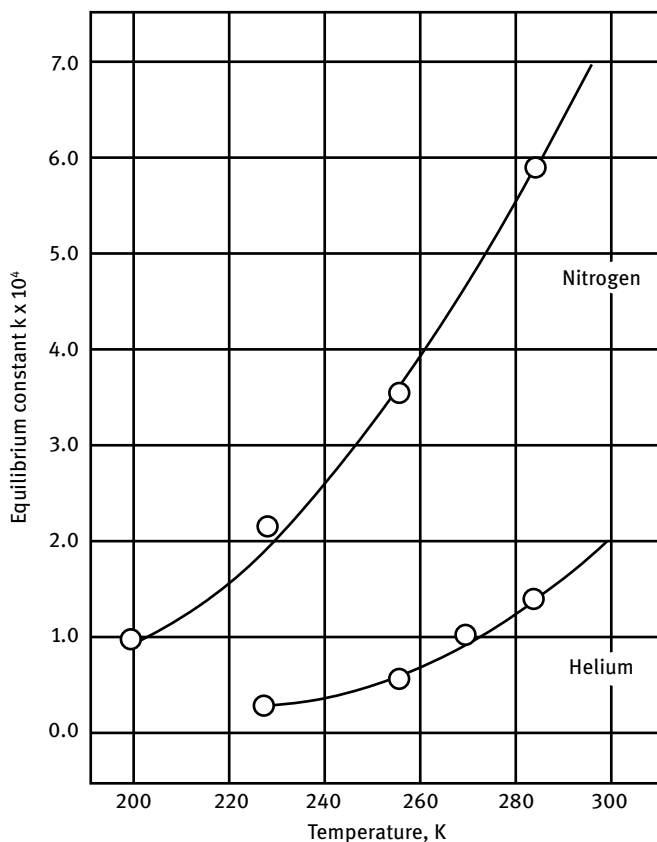
A theoretically based crossover model, which incorporated a crossover from singular thermodynamic behavior at the critical point to regular thermodynamic behavior far away from the critical point, was derived for the thermodynamic properties of ammonia [95]. The equation was capable of representing the thermodynamic properties of ammonia between 398 and 500 K in an appreciable range of densities around the critical density. The crossover EOS was constructed so that it could be used in conjunction with the classical EOS developed by Tillner-Roth et al., which worked well outside the critical region. The new crossover EOS was compared with the widely used EOS for ammonia developed earlier by Haar and Gallagher.



### 3.11 Solubility, Miscibility, Mixtures, and Solutions of Ammonia

#### 3.11.1 Solubility of Pressurant Gases in Liquid Ammonia

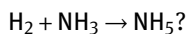
The solubility of the pressurant gases nitrogen and helium in liquid ammonia is illustrated in Figure 32, based on data from Cannon 1968.



**Figure 32:** Solubility of pressurant gases in liquid ammonia. (Reproduced and modified from [22].)

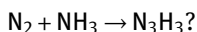
Solubilities and Henry's coefficients of hydrogen, nitrogen, and oxygen in liquid ammonia at 293 K decrease in the given order [96]. Enthalpies of solution are slightly positive.

At very high pressures, would reactions between dihydrogen and ammonia lead to a new compound



A study of the composition of the gas phase in heterogeneous mixtures of hydrogen and ammonia at pressures of up to 41 MPa (6000 psia) in the temperature interval between 278 and 394 K (40 and 250 °F) indicated that the hydrogen/ammonia system behaved according to the conventional pattern of inert binary systems, in which there is no significant chemical reaction between the components [97, 98].

With nitrogen instead of hydrogen, at very high pressures, would reactions between dinitrogen and ammonia lead to a new compound



A similar study of the composition of the gas phase in heterogeneous mixtures of nitrogen and ammonia at pressures of up to 31 MPa (4500 psia) in the temperature interval between 278 and 394 K (40 and 250 °F) indicated that the nitrogen/ammonia system behaved according to the conventional pattern of binary systems, in which there is no significant chemical reaction between the components [99, 100].

### 3.11.2 Solubility of Ammonia in Water

The solubility of ammonia in water must be known for the design of scrubbers that must absorb ammonia when venting pressurized tanks, or absorbing excess ammonia in the exhaust of rocket engines working with hydrazine, or resistojets and arc jets operating on ammonia as a working fluid. In the latter case, ammonia should theoretically be completely decomposed after passing through the arc discharge, but some ammonia may escape during startup and shutdown.

At room temperature and atmospheric pressure, the saturation concentration of ammonia in water is approximately 30 mass-%  $\text{NH}_3$ .

The solubility of ammonia in water also enters the equations for the diffusion of ammonia spills in moist atmospheres, where some of the released ammonia may precipitate from the high-humidity atmosphere in the form of water/ammonia droplets.

Ammonia/water chillers take advantage of the solubility of ammonia in water and the heat released upon condensation (on the radiator) or heat absorbed (on the evaporator inside the refrigerator). See also [101–106].

### 3.11.3 Solubility of Salts in Liquid Ammonia

Ammonia is a frequently used non-aqueous solvent and a lot of chemistry has been conducted with ammonia as the solvent. The high solubility of ammonium thiocyanate or ammonium nitrate in liquid ammonia is well known, and the solutions, stable at room temperature and atmospheric pressure, are commonly referred to as Divers' solution R ("R" from the German *rhodanide*, the name for thiocyanate) and Divers' solution N. The vapor pressure of ammonia is reduced by dissolving these ammonium salts to a point where the liquids can be handled at atmospheric pressure at room temperature, but the loss of ammonia under these conditions is very fast.

The solubility of other nitrates in liquid ammonia has been tested in an effort to develop lower-vapor-pressure fuels or even monopropellants. The solubility of tetramethylammonium nitrate in liquid ammonia at 243 K ( $-30^{\circ}\text{C}$ ) is very low, only 0.4 g/100 mL solution, not sufficient for a monopropellant. In the same series, it was found that sodium acetylide had a surprisingly high solubility in liquid ammonia, 5.12 g/100 mL solution [107].

Solutions of lithium boranate,  $\text{LiBH}_4$ , in liquid ammonia have been patented as rocket propellants [108]. Lithium boranate forms adducts with ammonia in stoichiometric compositions, containing one or two ammonia molecules:  $\text{LiBH}_4 \bullet \text{NH}_3$  or  $\text{LiBH}_4 \bullet 2\text{NH}_3$ . The addition of  $\text{LiBH}_4$  would make liquid ammonia hypergolic with dinitrogen tetroxide (NTO), white-fuming nitric acid (WFNA), or RFNA.

### 3.12 Thermodynamic Properties of Ammonia

With the extensive use of ammonia as a refrigerant and heat transfer fluid, the thermodynamic properties have been thoroughly investigated and are widely published. One can find elaborate tabulated and graphed data of enthalpy–entropy charts, also known as  $h$ – $s$  charts or Mollier diagram in the literature.

Additional summaries of the thermodynamic properties of ammonia are compiled in the publications listed in Table 25.

**Table 25:** Publications on thermodynamic properties of ammonia.

| Author                  | Year | Type of data                     | References |
|-------------------------|------|----------------------------------|------------|
| NBS                     | 1923 | Thermodynamic properties         | [109]      |
| Din (Ed.)               | 1956 | Thermodynamic functions of gases | [110]      |
| Stull                   | 1964 | JANAF thermochemical tables      | [111]      |
| Muraca (Ed.)            | 1963 | Pressurized gas systems          | [38]       |
| Illinois Inst. Technol. | 1966 | Pressurized gas systems          | [112]      |
| Haar                    | 1968 | Thermodynamic properties         | [113]      |
| Haar and Gallagher      | 1978 | Thermodynamic properties         | [57]       |
| Edison and Sengers      | 1999 | Critical point properties        | [95]       |

The Helmholtz function of ammonia in the fluid state was represented by an analytic model function [114]. The model function has been fitted to experimental data as well as to specific heat capacities, vapor pressures, saturated-liquid densities, enthalpies of vaporization, and an experimental value of the critical temperature. The best values of the model parameters were found from the minimum of the sum of squared residuals by a non-linear regression procedure using a modified Marquardt sub-routine.

### 3.12.1 Heat Capacity of Ammonia

The heat capacity of gaseous ammonia can be calculated from the Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$ , A, B, C, D, and E are constants, and  $\tau$  is the absolute temperature in kelvin divided by 1000. The coefficients are listed in Table 26. The same coefficients (and others) are used for formulas expressing the standard enthalpy of formation and the standard entropy of the vapor (see Sections 3.12.2 and 3.12.6). These equations were curve-fitted from data covering ranges from 298 to 1400 K and from 1400 to 6000 K.

Table 27 is a summary of the specific heat of the two-phase equilibrium saturated liquid ammonia.

**Table 26:** Constants for vapor-phase thermodynamic properties of ammonia.

| Temperature range, K | 298–1400  | 1400–6000 |
|----------------------|-----------|-----------|
| A                    | 19.99563  | 52.02427  |
| B                    | 49.77119  | 18.48801  |
| C                    | −15.37599 | −3.765128 |
| D                    | 1.921168  | 0.248541  |
| E                    | 0.189174  | −12.45799 |
| F                    | −53.30667 | −85.53895 |
| G                    | 203.8591  | 223.8022  |
| H                    | −45.89806 | −45.89806 |

Data source: [24]

**Table 27:** Specific heat of two-phase equilibrium saturated liquid ammonia.

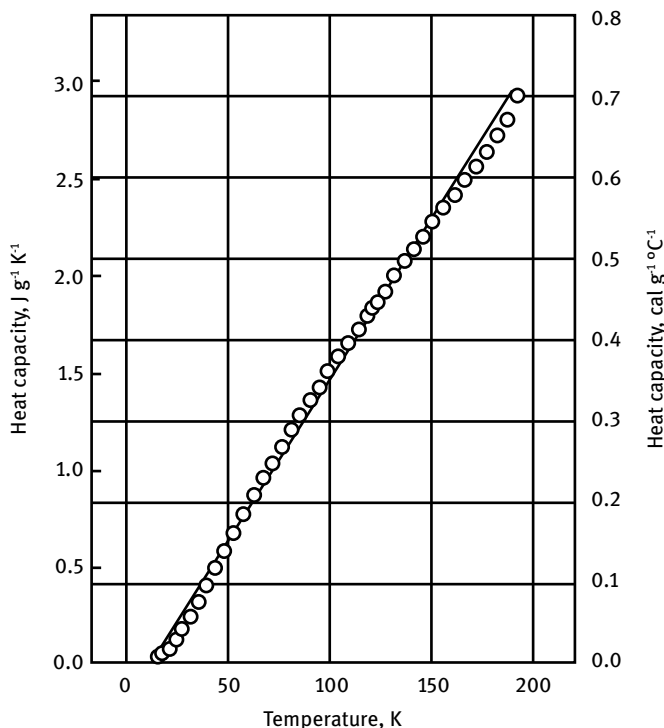
| Temperature |        | Heat capacity                   |                                    |
|-------------|--------|---------------------------------|------------------------------------|
| K           | °C     | $\text{J g}^{-1} \text{K}^{-1}$ | $\text{cal g}^{-1} \text{°C}^{-1}$ |
| 319.47      | −46.32 | 4.4049                          | 1.0528                             |
| 311.83      | −38.68 | 4.4409                          | 1.0614                             |
| 302.38      | −29.23 | 4.4760                          | 1.0698                             |
| 295.11      | −21.96 | 4.5007                          | 1.0757                             |
| 285.85      | −12.7  | 4.5388                          | 1.0848                             |
| 274.48      | −1.33  | 4.5878                          | 1.0965                             |
| 264.43      | 8.72   | 4.6380                          | 1.1085                             |
| 254.50      | 18.65  | 4.6957                          | 1.1223                             |
| 250.33      | 22.82  | 4.7275                          | 1.1299                             |
| 244.68      | 28.47  | 4.7681                          | 1.1396                             |
| 234.98      | 38.17  | 4.8480                          | 1.1587                             |
| 227.23      | 45.92  | 4.9258                          | 1.1773                             |

Data source: [39]

The temperature dependence of the specific heat of solid ammonia can be calculated from the polynomial equation [23]

$$c_p = -0.040675 + 3.9238 \times 10^{-3}T$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{K}^{-1}$  and  $T$  is the absolute temperature in kelvin. The data in Figure 33 are from Overstreet and Giauque [23].



**Figure 33:** Heat capacity of frozen ammonia. (Reproduced and modified from [22].)

The temperature dependence of the specific heat of liquid ammonia can be calculated from the polynomial equation based on data from Overstreet and Giauque [23] and [115, 116]:

$$c_p = 0.062839 + 0.011328T - 4.5591 \times 10^{-5}T^2 + 6.5877 \times 10^{-8}T^3$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{K}^{-1}$  and  $T$  is the absolute temperature in kelvin (Figure 34).

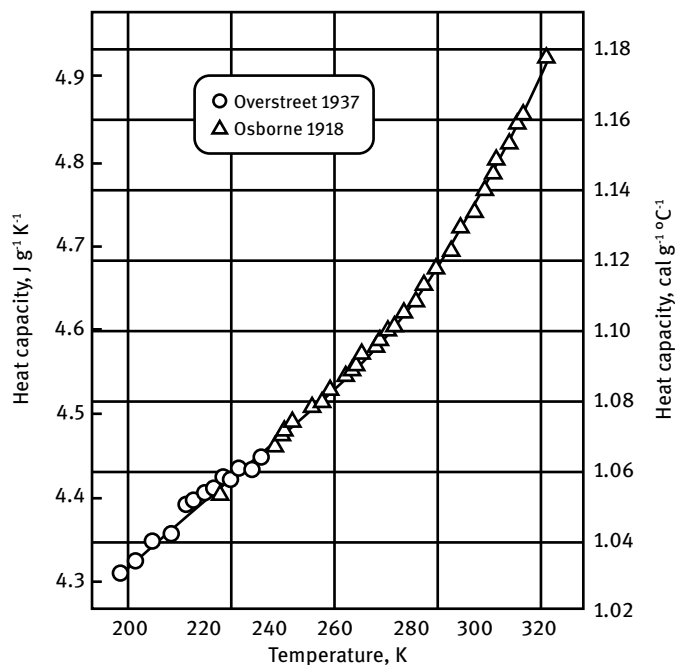


Figure 34: Heat capacity of liquid ammonia. (Reproduced and modified from [22].)

### 3.12.2 Enthalpy of Formation and Heat of Combustion of Ammonia

The vapor-phase excess enthalpy above the standard enthalpy of formation  $\Delta H_f^{\circ, 298}$  of  $\text{NH}_3$  can be calculated from the Shomate equation:

$$H^\circ - H_{298.15}^\circ = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - \Delta H_f^{\circ, 298}$$

where A, B, C, D, E, and F are constants and  $\tau$  is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 26. The same coefficients (and others) were used for a formula expressing the heat capacity of the vapor (see Section 3.12.1). These equations were curve-fitted from data covering a range from 298 to 6000 K.

Table 28 is a summary of literature data for the enthalpy of formation of solid, liquid, and gaseous ammonia.

**Table 28:** Enthalpy of formation ( $\Delta H_f^{298}$ ) of ammonia.

| Physical state | Enthalpy of formation |       |                   |       | References |
|----------------|-----------------------|-------|-------------------|-------|------------|
|                | SI units              |       | Other units       |       |            |
|                | kJ/mol                | J/g   | kcal/mol          | cal/g |            |
| Gas            | $-45.94 \pm 0.35$     | -2697 | $-10.97 \pm 0.08$ | -644  | [24]       |
|                | -46.19                | -2712 | -11.04            | -648  | [117]      |
| Liquid         | -69.45                | -4078 | -16.6             | -975  |            |
|                | -71.54                | -4201 | -17.098           | -1004 | [118]      |
|                | -68.64                | -4030 | -16.4             | -963  | [24]       |
| Solid          | -74.3                 | -4362 | -17.7             | -1043 | [24]       |

Molecular mass: 17.0305 g/mol; 58.718 mol/kg

### 3.12.3 Heat of Fusion and Solid-State Phase Transitions of Ammonia

Data for the heat of fusion ( $\Delta H_{\text{fusion}}$ ) of frozen ammonia are summarized in Table 29.

**Table 29:** Heat of fusion of frozen ammonia.

| Heat of fusion  |                  |       |         | References |
|-----------------|------------------|-------|---------|------------|
| kJ/mol          | kcal/mol         | kJ/kg | kcal/kg |            |
| 5.966           | 1.426            | 350.3 | 83.73   | [119]      |
| 5.774           | 1.380            | 339.0 | 81.03   | [120]      |
| $5.655 \pm 0.8$ | $1.3516 \pm 0.2$ | 332.1 | 79.36   | [23]       |

Molecular mass: 17.0305 g/mol; 58.718 mol/kg

Overstreet and Giauque [23] reported an average from three separate determinations for the heat of fusion of frozen ammonia and calculated it as  $5.655 \pm 0.8 \text{ kJ/mol} = 1351.6 \pm 0.2 \text{ cal/mol}$ , a value that was considered accurate enough to be included in [22].

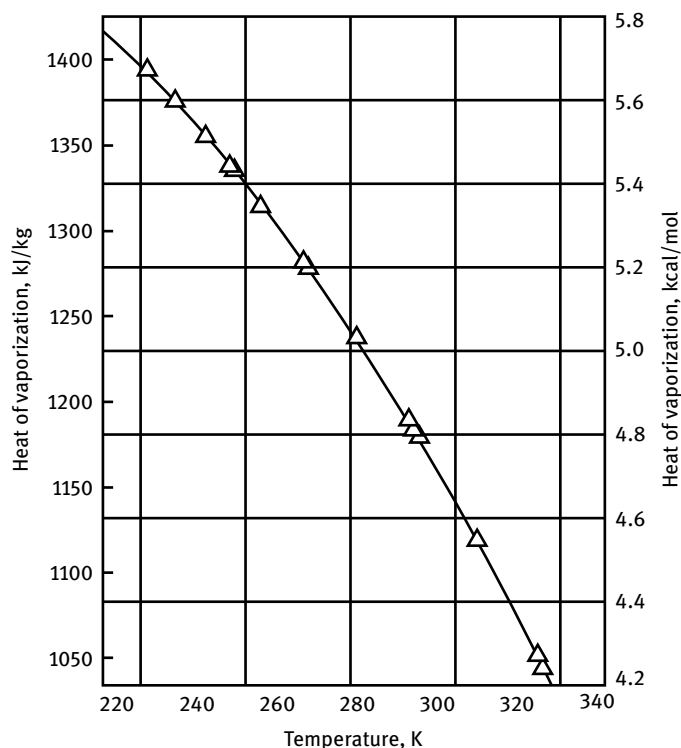
### 3.12.4 Heat of Vaporization of Ammonia

The heat of vaporization ( $\Delta H_{\text{vap}}$ ) of liquid ammonia at its normal boiling point of  $239.73 \text{ K} = -33.42^\circ\text{C}$  was measured and reported as  $23.35 \text{ kJ/mol} = 5.581 \text{ kcal/mol}$  [23].

The somewhat antiquated data on the heat of vaporization by Osborne and van Dusen 1918 were the most accurate data for many decades, and are still quoted in the literature today. The curve shown in Figure 35 is based on data from references [121] and [122]. The data can be curve-fitted by the polynomial equation

$$\Delta H_{\text{vap}} = 5.3115 + 0.013307T - 5.1012 \times 10^{-5}T^2$$

where  $\Delta H_{\text{vap}}$  is the heat of vaporization in kcal/mol and  $T$  is the temperature in kelvin.



**Figure 35:** Latent heat of vaporization of liquid ammonia. (Reproduced and modified from [22].)

The standard reference for the physical properties of ammonia and many other chemicals has been the National Bureau of Standards (NBS) circular *Tables of Thermodynamic Properties of Ammonia* (1923), in use for over 50 years until an update was published [57]. Nowadays, the best and most up-to-date data on the thermodynamic properties of ammonia and many other chemicals are available from the *NIST Chemistry WebBook* website [24] and the affiliated website listing properties of gases that are also used in semiconductor processing.

Haar and Gallagher correlated the vapor pressures obtained by Cragoe, Meyers, and Taylor [52], Beattie and Lawrence [53], and Keyes and Brownlee [54] by an equation containing five empirical constants. The differences between this equation and that of Baehr, Garnjost, and Pollak were minor [56]. Below 340 K, both equations correlated the data with the same accuracy. Larger deviations appeared at higher temperatures, where Baehr, Garnjost, and Pollak's equation closely followed the newer measurements which were not available to Haar and Gallagher.

The physical and thermodynamic properties of gaseous ammonia data in Table 30 were downloaded from the National Institute of Standards and Technology (NIST) website [123], where B and C are the 2<sup>nd</sup> and 3<sup>rd</sup> virial coefficients in the EOS.



**Table 30:** Physical and thermodynamic properties of gaseous ammonia.

| $T$ | $C_p(T)/R$ | Vapor pressure | $B(T)$                                                                   | $dB/dT \cdot T$               | $C(T)$                        | $\lambda$ | $\eta$           |
|-----|------------|----------------|--------------------------------------------------------------------------|-------------------------------|-------------------------------|-----------|------------------|
| K   |            | MPa            | $\text{cm}^3 \text{mol}^{-1}$                                            | $\text{cm}^3 \text{mol}^{-1}$ | $\text{cm}^6 \text{mol}^{-2}$ | mW/(m K)  | $\mu\text{Pa s}$ |
|     | 2%         | 0.2%           | densities calculated should be good to 0.5% away from coexistence curve. |                               |                               | 1%        | 3%               |
| 200 | 4.114      | 0.0087         | -1028.60                                                                 | 4285.60                       | -584290.0                     | 19.67     | 6.96             |
| 210 | 4.118      | 0.0177         | -843.29                                                                  | 3354.75                       | -439050.0                     | 19.83     | 7.23             |
| 220 | 4.127      | 0.338          | -703.65                                                                  | 2678.06                       | -301310.0                     | 20.08     | 7.52             |
| 230 | 4.139      | 0.604          | -596.21                                                                  | 2176.21                       | -197260.0                     | 20.41     | 7.82             |
| 240 | 4.153      | 0.1022         | -511.97                                                                  | 1796.88                       | -125070.0                     | 20.83     | 8.13             |
| 250 | 4.171      | 0.1649         | -444.79                                                                  | 1505.20                       | -76986.0                      | 21.33     | 8.45             |
| 260 | 4.191      | 0.2553         | -390.37                                                                  | 1277.43                       | -45675.0                      | 21.91     | 8.78             |
| 270 | 4.213      | 0.3811         | -345.67                                                                  | 1096.93                       | -25596.0                      | 22.57     | 9.12             |
| 280 | 4.238      | 0.5509         | -308.49                                                                  | 952.03                        | -12886.0                      | 23.30     | 9.47             |
| 290 | 4.264      | 0.7744         | -277.21                                                                  | 834.21                        | -4958.4                       | 24.11     | 9.83             |
| 300 | 4.292      | 1.0617         | -250.61                                                                  | 737.37                        | -111.8                        | 24.99     | 10.19            |
| 310 | 4.321      | 1.4240         | -227.78                                                                  | 656.92                        | 2761.2                        | 25.94     | 10.55            |
| 320 | 4.353      | 1.8728         | -208.02                                                                  | 589.44                        | 4377.9                        | 26.95     | 10.92            |
| 330 | 4.385      | 2.4205         | -190.78                                                                  | 532.32                        | 5201.9                        | 28.03     | 11.30            |
| 340 | 4.419      | 3.0802         | -175.63                                                                  | 483.58                        | 5532.2                        | 29.17     | 11.67            |
| 350 | 4.453      | 3.8660         | -162.23                                                                  | 441.67                        | 5561.4                        | 30.37     | 12.05            |
| 360 | 4.489      | 4.7929         | -150.31                                                                  | 405.32                        | 5412.9                        | 31.62     | 12.43            |
| 370 | 4.526      | 5.8778         | -139.65                                                                  | 373.66                        | 5165.5                        | 32.93     | 12.82            |
| 380 | 4.564      | 7.1402         | -130.06                                                                  | 345.86                        | 4869.1                        | 34.29     | 13.20            |
| 390 | 4.603      | 8.6045         | -121.40                                                                  | 321.32                        | 4554.7                        | 35.69     | 13.59            |
| 400 | 4.643      | 10.3050        | -113.55                                                                  | 299.54                        | 4241.1                        | 37.13     | 13.98            |
| 410 | 4.683      | —              | -106.39                                                                  | 280.11                        | 3939.6                        | 38.61     | 14.37            |
| 420 | 4.724      | —              | -99.86                                                                   | 262.70                        | 3656.0                        | 40.13     | 14.75            |
| 430 | 4.766      | —              | -93.86                                                                   | 247.02                        | 3393.4                        | 41.68     | 15.14            |
| 440 | 4.808      | —              | -88.35                                                                   | 232.85                        | 3152.6                        | 43.26     | 15.53            |
| 450 | 4.851      | —              | -83.26                                                                   | 220.00                        | 2933.3                        | 44.85     | 15.92            |
| 460 | 4.894      | —              | -78.56                                                                   | 208.28                        | 2734.5                        | 46.47     | 16.31            |
| 470 | 4.938      | —              | -74.19                                                                   | 197.58                        | 2554.9                        | 48.11     | 16.70            |
| 480 | 4.982      | —              | -70.14                                                                   | 187.77                        | 2393.0                        | 49.75     | 17.09            |
| 490 | 5.026      | —              | -66.36                                                                   | 178.74                        | 2247.1                        | 51.40     | 17.48            |
| 500 | 5.071      | —              | -62.83                                                                   | 170.42                        | 2115.8                        | 53.05     | 17.86            |
| 550 | 5.301      | —              | -48.25                                                                   | 137.02                        | 1631.4                        | 61.16     | 19.78            |
| 600 | 5.535      | —              | -37.41                                                                   | 113.18                        | 1341.7                        | 68.55     | 21.68            |
| 650 | 5.773      | —              | -29.08                                                                   | 95.39                         | 1165.0                        | 74.51     | 23.55            |
| 700 | 6.011      | —              | -22.54                                                                   | 81.68                         | 1055.7                        | 78.26     | 25.39            |
| 750 | 6.249      | —              | -17.29                                                                   | 70.81                         | 987.8                         | 78.96     | 27.20            |
| 800 | 6.484      | —              | -13.01                                                                   | 62.00                         | 946.3                         | 75.67     | 29.00            |
| 850 | 6.716      | —              | -9.47                                                                    | 54.74                         | 922.1                         | 67.41     | 30.79            |

Data source: [123,124]

The heat of vaporization based on data measured at 293–392 K was listed as 22.7 kJ/mol at 308 K [47]. New data for a fundamental EOS for ammonia were compiled [125].

Only few industrial processes, including rocket propulsion, would require thermodynamic data for ammonia for the temperature range extending from the triple point to 750 K, and for the pressure range extending from the dilute gas to 500 MPa (5000 bar). These conditions for the coexisting phases and even close to the liquid–vapor critical point might occur on the surface of Jupiter (if it has a surface), or on other large planets where ammonia prevails. Values for the thermodynamic and PVT properties reported in 189 references in the literature were correlated, curve-fitted, and tabulated at closely spaced intervals [57]. While this publication contains a lot of numerical data, it lacks a table with the best recommended data for the liquid and gaseous ammonia at the standard reference state of 101 kPa and 298 K. For the coexisting saturated liquid and gaseous phases at a pressure of 101 kPa, the following data in Table 31 can be read from the tables.

**Table 31:** Thermodynamic and PVT properties of liquid and gaseous ammonia at 101 and 1010 kPa.

| Pressure, bar                                       | 1         | 10        |
|-----------------------------------------------------|-----------|-----------|
| Temperature, K                                      | 239.5     | 297.9     |
| Temperature, °C                                     | –33.6     | 24.9      |
| Specific volume liquid, cm <sup>3</sup> /g          | 1.46636   | 1.65801   |
| Specific volume vapor, cm <sup>3</sup> /g           | 1137.99   | 128.51    |
| Free energy, G/RT                                   | –24.33    | –23.21    |
| Internal energy liquid J/g                          | –914.98   | –647      |
| Internal energy vapor J/g                           | 341.72    | 391.77    |
| Enthalpy liquid J/g                                 | –914.84   | –645.35   |
| Enthalpy vapor J/g                                  | 455.52    | 520.29    |
| Latent heat of evaporation J/g                      | 1370.3578 | 1165.6381 |
| Entropy liquid J g <sup>–1</sup> K <sup>–1</sup>    | 5.1043    | 6.1043    |
| Entropy vapor J g <sup>–1</sup> K <sup>–1</sup>     | 10.8249   | 10.0152   |
| $c_p$ liquid J g <sup>–1</sup> K <sup>–1</sup>      | 4.4286    | 4.7982    |
| $c_p$ vapor J g <sup>–1</sup> K <sup>–1</sup>       | 2.2325    | 3.1329    |
| $c_v$ liquid J g <sup>–1</sup> K <sup>–1</sup>      | 3.1237    | 2.8521    |
| $c_v$ vapor J g <sup>–1</sup> K <sup>–1</sup>       | 1.6457    | 2.1335    |
| $c_s$ liquid J g <sup>–1</sup> K <sup>–1</sup>      | 4.4254    | 4.7593    |
| $c_s$ vapor J g <sup>–1</sup> K <sup>–1</sup>       | –4.2192   | –3.3456   |
| Isothermal compressibility liquid bar <sup>–1</sup> | 0.000091  | 0.000167  |
| Isothermal compressibility vapor bar <sup>–1</sup>  | 1.042     | 0.117     |
| (dP/dt) <sub>p</sub> bar/K                          | 0.04964   | 0.30438   |
| Density, liquid g/cm <sup>3</sup>                   | 0.68196   | 0.60313   |
| Density, vapor g/cm <sup>3</sup>                    | 0.000879  | 0.007781  |

Data source: [57]

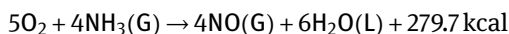
The vapor pressures of  $\text{NH}_3$  and  $\text{ND}_3$  have been used to estimate the molar enthalpies of vaporization of  $\text{NH}_3(\text{L})$  and of  $\text{ND}_3(\text{L})$  from the triple-point temperatures to 290 K via the Clapeyron equation, using the Wagner equation to give the required values of  $dp/dT$  [40]. The molar enthalpy of vaporization of  $\text{ND}_3$  exceeded that of  $\text{NH}_3$  throughout this range. The difference amounted to about 3.5% at the triple-point temperatures, and decreased with rising temperature. The estimate of 23375 J/mol for  $\Delta H_{\text{vap}}(\text{NH}_3)$  at its normal boiling temperature agreed with the value of  $(23351 \pm 38)$  J/mol obtained calorimetrically by Overstreet and Giauque. The difference in the enthalpies of vaporization of  $\text{NH}_3$  and  $\text{ND}_3$  decreased from -1313 to -602 J/mol while the temperature increased from 200 to 270 K. Streatfeild et al. used Wagner's equation:

$$\ln\left(\frac{p}{p_c}\right) = (a_0\tau + a_1\tau^{1.5} + a_2\tau^3 + a_3\tau^6)/T_r$$

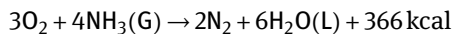
where  $T_r = T/T_c$ ,  $\tau = (1 - T_r)$  and  $p_c$  and  $T_c$  were the critical pressure and critical temperatures:  $\ln(p_c/\text{kPa}) = 9.33717$ , and  $T_c = 405.5$  K. The parameters had the values:  $a_0 = -7.20816$ ,  $a_1 = 1.23966$ ,  $a_2 = -2.3783$ , and  $a_3 = -1.528$ .

### 3.12.5 Heat of Combustion of Ammonia

When calculating the heat of combustion of ammonia, it is misleading to use the reaction



which results in a heat of combustion of gaseous ammonia of 292 kJ/mol = 69.9 kcal/mol. This reaction may take place on the surface of platinum catalysts. Instead, one must assume that the reaction goes to nitrogen and water



See Table 32.

**Table 32:** Heat of combustion of ammonia.

| Ammonia,<br>physical state                            | Combustion product |          |                       |                      |
|-------------------------------------------------------|--------------------|----------|-----------------------|----------------------|
|                                                       | kJ/mol             | kcal/mol | kcal/kg $\text{NH}_3$ | BTU/lb $\text{NH}_3$ |
| <b>Liquid water (upper heat of combustion)</b>        |                    |          |                       |                      |
| Liquid                                                | 357.2              | 85.386   | 5.014                 | 9024                 |
| Gaseous                                               | 382.8              | 91.505   | 5.373                 | 9671                 |
| <b>Water vapor (steam) (lower heat of combustion)</b> |                    |          |                       |                      |
| Liquid                                                | 291.2              | 69.607   | 4.087                 | 7357                 |
| Gaseous                                               | 316.8              | 75.73    | 4.446                 | 8004                 |

### 3.12.6 Entropy of Ammonia

The vapor-phase standard entropy of formation of  $\text{NH}_3$  can be calculated from the Shomate equation:

$$S^\circ = A \ln(\tau) + B\tau + \frac{C\tau^2}{2} + \frac{D\tau^3}{3} - E/(2\tau^2) + G$$

where  $S$  is the entropy in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ , and  $G$  are constants and  $\tau$  is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 26. Some of these coefficients (and others) were used earlier for a formula expressing the heat capacity or the enthalpy of formation of the vapor (see Section 3.12.1). These equations were curve-fitted from data covering a range from 298 to 1500 K. For comparison, the entropy of gaseous ammonia at 298 K is  $192.77 \pm 0.05 \text{ J mol}^{-1} \text{K}^{-1} = 46.07 \text{ cal mol}^{-1} \text{°C}^{-1}$ .

### 3.13 Molecular Structure and Molecular Orbital Calculations of Ammonia

Ammonia,  $\text{NH}_3$ , is the lowest member of the family of hydronitrogens. The next-higher member of the family of hydronitrogens, hydrazine,  $\text{N}_2\text{H}_4$ , is more widely used as a rocket propellant than ammonia; it will be discussed in *Encyclopedia of Liquid Fuels*, chapter “Hydrazine” in detail, along with other hydronitrogens.

The ammonia molecule forms a shallow trigonal pyramid, with bond angles of  $106.7^\circ$ , as opposed to the  $109.5^\circ$  of a methane tetrahedron (Figure 36). The lone electron pair repulses the other electrons, flattening the pyramid.

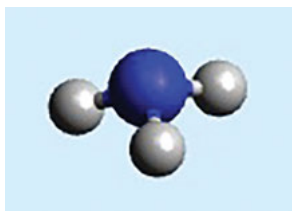


Figure 36: Molecular structure of ammonia

The nitrogen in the ammonia molecule can flip through the plane formed by the three hydrogen atoms and readily undergoes nitrogen inversion at room temperature. A popular analogy to this inversion is an umbrella turning itself inside out in a strong wind. The energy barrier to this inversion is  $24.7 \text{ kJ/mol}$ , and the resonance frequency is  $23.79 \text{ GHz}$ , corresponding to microwave radiation of a wavelength of  $1.260 \text{ cm}$ . The absorption at this frequency was the first microwave spectrum to be observed with radio telescopes. It is also observed in the interstellar gas.

### 3.13.1 Computational Chemistry of the Ammonia Molecular Structure

Because the ammonia molecule is symmetrical and relatively simple, there have been many studies predicting its vibrational energies using computational methods, but only a few will be referenced here as a starting point for further studies. Such calculations are useful to predict the spectral properties and enthalpies of formation of ammonia and other hydronitrogens. Linear Combination of Atomic Orbitals (LCAO) molecular orbitals have been calculated for the ground states of  $\text{NH}$ ,  $\text{NH}_2$ , and  $\text{NH}_3$  at various bond angles, using the LCAO self-consistent-field method [126]. Interactions between all electrons have been considered, and the orthogonality relationship between the  $1s$  orbitals of nitrogen and hydrogen was assumed.

*Ab initio* coupled cluster calculations have been carried out for the electronic ground state of ammonia [127].

Fourier transform infrared (IR) absorption and XRD experiments on equimolar mixtures of ammonia and water showed the formation of an ammonia monohydrate compound that spontaneously converted into an unusual crystalline state at high pressure in a diamond anvil cell at 25 GPa, where the standard molecular forms of water and ammonia coexisted with hydroxyl and ammonium ions [128]. The structure of the ammonia-ice compound was confirmed by *ab initio* molecular dynamics simulations. Such compounds are likely to exist in the interior of large gaseous planets like Jupiter.

### Bond Energies of Ammonia

The dissociation of  $\text{N-H}$  bonds in ammonia can be initiated by thermal, ultraviolet (UV) radiation, or X-ray radiation energy input or under electron bombardment in a glow discharge. The bond energies of  $\text{N-H}$  bonds decrease with increasing stepwise destruction (hydrogen abstraction and dehydrogenation) of the molecule, as shown in Table 33.

**Table 33:** Bond energies in ammonia.

| Bond            | Dissociation energy |             |              | References |
|-----------------|---------------------|-------------|--------------|------------|
|                 | kJ/mol              | kcal/mol    | eV           |            |
| $\text{H-NH}_2$ | $443 \pm 13$        | $106 \pm 3$ | $46 \pm 1.3$ | [129]      |
| $\text{H-NH}_2$ | $435 \pm 8$         | $104 \pm 2$ | $45 \pm 0.9$ | [130]      |
| $\text{H-NH}$   | $368 \pm 17$        | $88 \pm 4$  | $38 \pm 1.7$ | [130]      |
| $\text{H-N}$    | $368 \pm 25$        | $88 \pm 6$  | $38 \pm 2.6$ | [130]      |

### 3.13.2 Dipole Moment of Ammonia

Data for the dipole moment  $\mu$  of ammonia are summarized in Table 34.

**Table 34:** Dipole moment of ammonia.

| Dipole moment<br>Debye | References |
|------------------------|------------|
| 1.470                  | [24]       |
| 1.52                   | [8]        |
| 1.437                  | [131]      |
| 1.47149 and 1.47179    | [132]      |
| $1.468 \pm 0.009$      | [133]      |

### 3.13.3 Ammonia Dimers

Due to the intense intermolecular hydrogen bonding, ammonia molecules form dimers in the vapor phase. Dimers in the vapor phase and polymers in the liquid phase effectively reduce the vapor pressure of ammonia in comparison to non-associating fluids like liquid methane. The dimers can be detected by their IR spectrum which differs from that of the freely spinning molecule. Wherever ammonia exists on extraterrestrial bodies, part of it is likely to exist in the form of its dimer. Based on measurements of the quadrupole hyperfine structure, also in comparison to those of  $\text{ND}_3$  and its dimer, the structure of the dimer has been found to be asymmetric and quite different from what was previously assumed [134, 135]. It was previously thought that, in the dimer, one  $\text{NH}_3$  unit of hydrogen bonds to the other with a nearly linear  $\text{N}-\text{H}\cdots\text{N}$  arrangement, but the measured bond angles were quite different. The dissociation energy of the  $(\text{NH}_3)_2$  dimer has been estimated as less than 11.7 kJ/mol (2.8 kcal/mol).

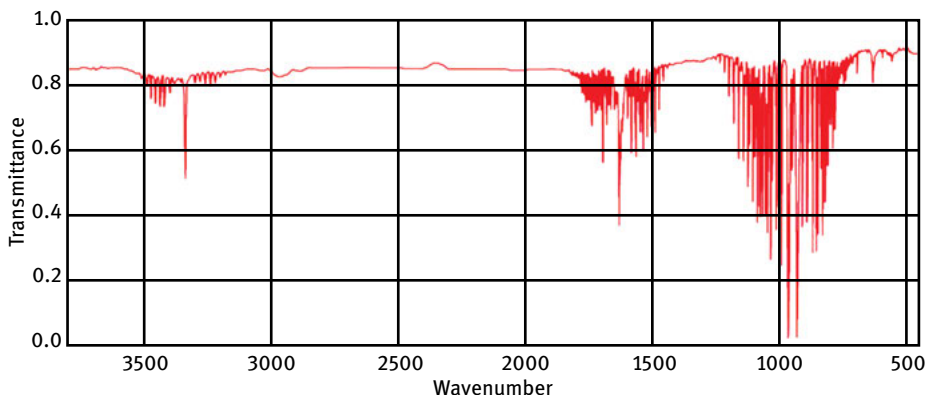
Ammonia in the vapor phase may form ion clusters  $(\text{NH}_3)_n$ , up to  $n = 5$ , see reference [136]. These clusters can be fragmented by electron impact ionization in molecular beams. In 1992, a debate evolved about the structure of ammonia dimers based on results obtained with far-IR vibration-rotation-tunneling (FIR-VRT) spectroscopy. Measurements indicate that two ammonia molecules can form a “cyclic” dimer structure instead of the traditionally assumed  $\text{N}\cdots\text{H}$  linear hydrogen bond.

VRT splittings have been computed for the dimer  $(\text{NH}_3)_2$  by the use of four different model potentials which have different barriers to internal rotations, the interchange of the donor, and the acceptor in the hydrogen bond [137]. Dipole moments, nuclear quadrupole splittings, and the amount of quenching of the monomer umbrella inversions were computed, and good agreement with the experimental data available for  $(\text{NH}_3)_2$  was obtained, also for the observed change in the dipole moment upon isotope substitution.

### 3.14 Optical Properties of Ammonia

#### 3.14.1 IR Absorption Spectra of Ammonia

The IR spectrum of ammonia (Figure 37) is one of the most thoroughly examined spectra of all small molecules. It has some unique features that help to explain intermolecular hydrogen bonding, inversion oscillations, and dimer formation.



**Figure 37:** IR spectrum of ammonia. (Reproduced and modified with permission from [138])

The ammonia molecule has four normal vibration frequencies, two of which are doubly degenerate:  $\nu_1 = 3335\text{ cm}^{-1}$  (single);  $\nu_3 = 948\text{ cm}^{-1}$  (single) and  $\nu_4 = 1631\text{ cm}^{-1}$  (double). The value of  $\nu_2$  is in some doubt since it has not been observed spectroscopically. It is known to be large, however, and therefore of least importance to the partition function. IR band assignments are listed in Table 35.

**Table 35:** Vibrational and/or electronic energy levels of ammonia.

| Sym.  | No. | Approximate type of mode | Selected IR frequency |                  |                     |
|-------|-----|--------------------------|-----------------------|------------------|---------------------|
|       |     |                          | $\text{cm}^{-1}$      | $\text{cm}^{-1}$ |                     |
| $a_1$ | 1   | Sym stretch              | 3337                  | 3336.2           | symmetric level     |
| $a_1$ | 1   | Sym stretch              | 3337                  | 3337.2           | antisymmetric level |
| $a_1$ | 2   | Sym deform               | 950                   | 932.5            | symmetric level     |
| $a_1$ | 2   | Sym deform               | 950                   | 968.3            | antisymmetric level |
| $e$   | 3   | Deg stretch              | 3444                  | 3443.6           | symmetric level     |
| $e$   | 3   | Deg stretch              | 3444                  | 3443.9           | antisymmetric level |
| $e$   | 4   | Deg deform               | 1627                  | 1626.1           | symmetric level     |
| $e$   | 4   | Deg deform               | 1627                  | 1627.4           | antisymmetric level |

Data source: [24]

Symmetry:  $C_{3v}$ ; Symmetry number  $\sigma = 3$

### 3.14.2 UV Absorption Spectra of Ammonia

The UV absorption of ammonia is an essential step in the photochemical synthesis of hydrazine from ammonia, a reaction that may also take place in the atmosphere of Jupiter. The discrete absorption spectrum of ammonia has been photographed from 2300 to 850 Å [139]. The bands down to 1665 Å are all diffuse because of predissociation. Below 1665 Å, all the bands are very sharp and show a rotational fine structure which is partly resolved. True continuous absorption (distinct from that produced by pressure broadening) does not begin until about 1200 Å. At 1150 Å and below, the continuous absorption is so strong that no more bands could be measured accurately. Sharp bands exist, however, at least as far down as 1085 Å. The UV absorption spectrum of ammonia starts absorbing only at wavelengths below 210 nm [140].

### 3.14.3 Index of Refraction of Liquid Ammonia

The index of refraction of liquid ammonia at 289.6 K (16.5 °C) is  $n_D^{16.5} 1.325$  [39].

## 3.15 Microwave Spectra of Ammonia

Ammonia gas is known to exhibit a strong microwave absorption in the region of  $1.25 \text{ cm} = 0.8 \text{ cm}^{-1}$ . The inversion of the flat  $\text{NH}_3$  prism where the nitrogen atom swings through the plane of the three hydrogen atoms like an umbrella inverted in a gust of wind is characterized by its microwave absorption at  $0.8 \text{ cm}^{-1} = 23.69448 \text{ GHz}$  (inversion,  $J = 1, K = 1$ ). This wavelength has been one of the main operating frequencies of radio astronomers looking for ammonia on other planetary bodies, comets, and in interstellar space. The lines shift when the pressure of ammonia is increased.

## 3.16 Electrical Properties of Liquid Ammonia

### 3.16.1 Electrical Conductivity of Liquid Ammonia

The electrical conductivity of liquid ammonia (at  $194 \text{ K} = -79^\circ\text{C}$ ) is  $1.3 \times 10^{-7} \text{ Ohm}^{-1} \text{ cm}^{-1}$  [39].

Ammonia has been considered as a non-aqueous electrolyte and fuel in batteries and fuel cells where thiocyanate or sulfide would be added to increase the conductivity [141–143].

The solution of metals like lithium in liquid ammonia drastically increases its electrical conductivity, approaching that of the metals themselves. The solutions are dark blue from the cloud of free electrons which are the prime carriers of electricity (see Section 9.1).



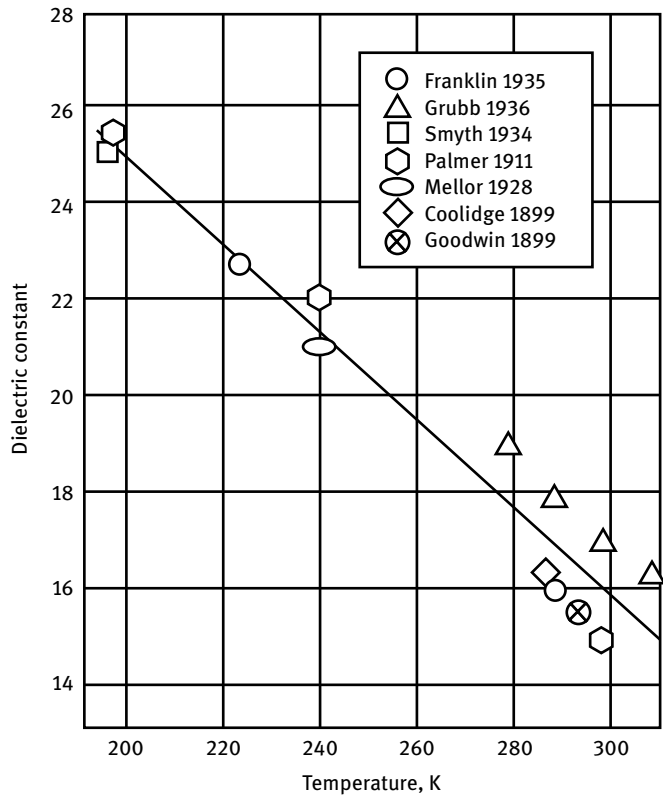
### 3.16.2 Dielectric Constant of Ammonia

Data for the dielectric constant of liquid ammonia are listed in Tables 36 and 37 and are illustrated in Figure 38.

**Table 36:** Dielectric constant of ammonia.

| Temperature |      | Dielectric constant <sup>a</sup> |
|-------------|------|----------------------------------|
| K           | °C   |                                  |
| 196         | -77  | 25.4                             |
| 223         | -50  | 22.7                             |
| 288         | +15  | 15.9                             |
| 293.6       | 20.5 | 15.55                            |
| 297.6       | 24.5 | 14.9                             |

<sup>a</sup> liquid,  $\nu = 4.2 \times 10^8$  Hz, from [39]



**Figure 38:** Dielectric constant of saturated liquid ammonia. (Reproduced and modified from [22].)

**Table 37:** Dielectric constant of ammonia.

| Temperature, K  | 278          | 288          | 298          | 308          | 213 ± 10 |
|-----------------|--------------|--------------|--------------|--------------|----------|
| Temperature, °C | 5            | 15           | 25           | 35           | −60 ± 10 |
|                 | 18.99        | 17.83        | 16.94        | 16.30        | —        |
|                 | 18.92        | 17.81        | 16.88        | 16.25        | 26.7     |
|                 | 18.91        | 17.81        | 16.87        | 16.24        | —        |
| Average         | 18.94 ± 0.05 | 17.82 ± 0.01 | 16.90 ± 0.04 | 16.26 ± 0.04 | —        |

Data source: [144]

An electric dipole moment function of  $\text{NH}_3$  was determined by fitting to experimental data (Stark splittings, absorption intensities) and to *ab initio* calculated dipole moment values using the non-rigid inverter Hamiltonian approximation [145]. The dipole moment function was used to calculate transition moments of some low-lying rovibrational states of symmetric isotopomers of  $\text{NH}_3$ . A close reproduction of the available experimental data was achieved which indicated that the predicted values were reliable.

### 3.17 Magnetic Properties of Ammonia

*Ab initio* calculations of the diamagnetic susceptibility of the ammonia molecule were performed by using gauge invariant atomic orbital methods [146, 147]. The results were  $\chi_{zz} = -14.64 \times 10^{-6}$  cgs units (along the molecular symmetry axis) and  $\chi_{xx} = \chi_{yy} = -14.94 \times 10^{-6}$  cgs units. The total predicted susceptibility was  $-14.84$  cgs units, which differed by 9% from experimental data  $-16.3 \pm 0.8$  cgs units [148].

The magnetic properties of ammonia change dramatically if alkali metals are dissolved in it, making it pseudo-metallic with good electrical conductivity.

## 4 Chemical Properties of Ammonia

Ammonia dissolves rapidly in water, forming alkaline solutions which contain a small fraction of ammonium hydroxide in equilibrium with physically dissolved, but chemically unreacted ammonia. Often bottles containing aqueous ammonia solutions are mislabeled “Ammonium Hydroxide.” Water saturated with ammonia at room temperature contains 30 mass-%  $\text{NH}_3$ , partially in the form of ammonia hydrate or ammonia dihydrate, but the concentration of undissociated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) is only very small.

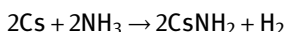
Ammonia gas in air forms a white smoke with acid fumes (e.g., HCl fumes); this is a frequently used primitive method to detect ammonia leaks in a plumbing system if no more sophisticated electronic leak detection equipment is available.

#### 4.1 Chemical Reactions of Ammonia

Neutralization of aqueous ammonia solutions with acids forms ammonium salts which crystallize out after the solvent is evaporated. For rocket and gas generator applications, the most important ammonium salts are ammonium perchlorate (see *Encyclopedia of Oxidizers*, chapter “Perchlorate Oxidizers”) and ammonium nitrate (see chapter “Nitrate Oxidizers”).

##### 4.1.1 Reactions of Ammonia with Alkali Metals

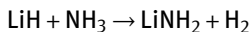
Alkali metals and earth alkaline metals dissolve in liquid ammonia to form an intensely blue-colored solution. Such solutions are not very stable. In particular, those formed by the higher atomic number metals (cesium and rubidium) decompose gradually, forming a metal amide and hydrogen gas:



This reaction is accelerated by traces of catalytically active contaminants, e.g. salts of transition metals, e.g.  $\text{Fe}(\text{NO}_3)_3$ . Solutions of small concentrations of lithium in liquid ammonia are dark blue. In this regime, the solutions are not sensitive to oxygen in the air. Higher concentrations of lithium in ammonia give the solutions a metallic sheen, and are more sensitive to oxygen, and when the solutions are poured out in air, they throw sparks but will not ignite the ammonia. Concentrated solutions of lithium in ammonia are not very stable. They decompose within one month, and it is best to use them soon after preparation. See Section 9.1.2.

##### 4.1.2 Reactions of Ammonia with Alkali Metal Hydrides

The reaction of lithium hydride with water is a convenient source of hydrogen, but the reaction is not reversible. On the other hand, the reversible reaction of ammonia with lithium hydride forms lithium amide and gaseous hydrogen



This reaction has been investigated as a convenient source of hydrogen gas that can then be used as a fuel for fuel cells or inflating a balloon or other applications. The reaction is reversible, such that a canister of  $\text{LiH}/\text{NH}_3$  could be used as a hydrogen storage tank. After  $\text{H}_2$  generation by the reaction of  $\text{LiH}$  and  $\text{NH}_3$ , the byproduct  $\text{LiNH}_2$  can be recycled back to  $\text{LiH}$  under  $\text{H}_2$  flow and pressure conditions at 500 K [149, 150]. Transition metal chlorides were examined as a potential catalyst to improve the kinet-

ics. For the hydrogen desorption reaction, the reaction with a  $\text{TiCl}_3$  catalyst was about 8 times faster than the raw  $\text{LiH}$  [151].

#### 4.1.3 Reactions of Ammonia Borane with Alkali Metal Hydrides

Another source of hydrogen involving ammonia is the dry solid-state reaction of lithium hydride with ammonia borane ( $\text{NH}_3\text{BH}_3$ ) [152]. This material possesses a hydrogen capacity of around 10 mass-%, and can rapidly release over 7 mass-% pure  $\text{H}_2$ .

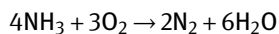
This reaction takes place during ball-milling at 293 K (20 °C), but can be suppressed when milling is conducted at the temperature of liquid nitrogen [153]. Cryomilling for 60 min reduced the reaction temperature from ~200 K (~70 °C) for unmilled powder to below room temperature, indicating that cryomilling can adjust the onset temperature for releasing hydrogen from solid materials that are thermodynamically unstable but with kinetic barriers. The reaction can be carried out in THF as a solvent/dispersant at 313 K (40 °C) [154].

#### 4.1.4 Reactions of Ammonia with Boron Hydrides

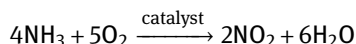
The reaction of ammonia with diborane forms an array of Lewis salt adducts. These compounds that may gain use as reversible storage media for dihydrogen gas will be discussed in the chapter “Boranes.”

#### 4.1.5 Reactions of Ammonia with Oxygen

There are two important reactions of ammonia with oxygen, one the simple combustion leading to nitrogen and water,



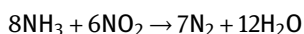
the other a catalyzed reaction leading to nitrogen dioxide



and, ultimately, nitric acid. The reaction of liquid ammonia with LOX was the main propellant in the X-15 hypersonic research plane.

#### 4.1.6 Reactions of Ammonia with Nitrogen Oxides

Reactions of ammonia with nitrogen oxides are used in the stack gas  $\text{DeNO}_x$  process for the removal of  $\text{NO}_x$  contaminants before the stack gases from fossil-fired powerplants are released into the atmosphere.



The combination of liquid dinitrogen tetroxide and liquid ammonia has been used in stationary rocket testing, producing a very clean, smokeless, transparent exhaust plume.

## 4.2 Thermal Stability of Ammonia

In the absence of catalysts, ammonia is thermally stable up to 673 K (400 °C). Above 673 K, it will decompose irreversibly into its elements nitrogen and hydrogen in a reversal of the industrial process by which it was made. This is an endothermic process and can be used to cool hot surfaces. When ammonia is used as a working fluid in electrothermal thrusters or arc jets, it will decompose, and the exhaust has a favorable low molecular mass due to the high content of hydrogen.

### 4.2.1 Decomposition Kinetics of Ammonia

The homogeneous gas-phase decomposition kinetics of ammonia over a wide range of pressures have been thoroughly investigated. This reaction limits the yield in commercial ammonia production. The rate of this reaction is a design parameter for electrothermal rocket engines operating on evaporated and dissociating gaseous ammonia. This reaction is part of the decomposition of hydrazine, an important monopropellant.

### 4.2.2 Homogeneous Gas-Phase Decomposition Kinetics of Ammonia

Homogeneous gas decomposition kinetics are studied mostly at low pressures and in shock tubes. The kinetics of ammonia decomposition (catalyzed or not) have been thoroughly studied for a variety of reasons. The main reason is that the decomposition of ammonia is a limiting factor in the synthesis of ammonia from its elements, a vital industrial process. If ammonia in the cooling jacket of a regeneratively cooled rocket engine overheats, it may decompose and form a two-phase gas/liquid mixture which would have different properties of heat transfer and pressure drop through an orifice.

The homogeneous rate of decomposition of  $\text{NH}_3$  in  $\text{NH}_3$ -Ar mixtures containing 1% and 8%  $\text{NH}_3$  in Ar was measured in a shock tube behind reflected waves [155]. The initial rate of decomposition of  $\text{NH}_3$  in Ar has been measured between 2000 and 3000 K by following the rate of decrease of emission intensity in the 2.7- to 3.2- $\mu\text{m}$  wavelength region. The measured activation energy of about 217.6 kJ/mol (52 kcal/mol) did not match the bond energy of breaking the first  $\text{H}_2\text{N}-\text{H}$  bond of 439 kJ/mol (105 kcal/mol). There must be more than one reaction occurring.

One of the ammonia dissociation products is imine ( $\text{NH}$ ). Mixtures of ammonia in xenon were shock-heated to temperatures in the range 2900–9600 K and the radiation from  $\text{NH}$  was monitored at 3360 Å [156]. It was found that the production of  $\text{NH}(\text{A}^3\Pi)$

was second-order in the initial ammonia concentration within experimental error, and could be described by a rate constant

$$k = 4 \times 10^{-14} \exp\left(\frac{-54000}{T}\right) \text{cm}^3 \text{mol}^{-1} \cdot \text{s}^{-1}.$$

It was found that NH normally decayed at two different rates, one being half of the other.

#### 4.2.3 Catalytic Decomposition Kinetics of Ammonia

The kinetics of catalytic ammonia decomposition have been thoroughly studied for a variety of reasons. The main reason is that the catalytic decomposition of ammonia is a limiting factor in the synthesis of ammonia from its elements, a vital industrial process.

Another industrial application of catalytic ammonia decomposition is in the creation of “furnace gas,” a mixture of nitrogen and ammonia often used as a reducing protective atmosphere in industrial furnaces where metal parts that are sensitive to oxygen in the air are annealed or melted under exclusion of oxygen. The catalytic decomposition of ammonia is the most convenient method for generating hydrogen gas for use in air/hydrogen fuel cells.

The catalytic decomposition of ammonia is also a step in the multi-step decomposition of hydrazine as a monopropellant, where it takes place mostly in the downstream end of the catalytic reactor.

Catalysts capable of decomposing ammonia include ruthenium, rhodium, and palladium [157], platinum [158], and ruthenium and platinum alloys [159]. There are many commercial catalysts available for the dissociation (“cracking”) of ammonia to generate furnace gas or hydrogen. Furnace gas is used as a protective atmosphere for heat treatment (annealing) of refractory metals that are sensitive to air. Some contain Rh, Ru or Ir supported on  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  [160].

If the hot dissociation products are passed through a palladium membrane tube, only hydrogen permeates through the membrane and exits in a very pure form suitable for use in fuel cells or other applications [161].

Ammonia decomposition catalysts are typically supported metal catalysts with alumina, ceria, or zirconia as the carrier material [162].

The catalytic decomposition of ammonia creates a gas mixture containing hydrogen gas that can immediately be used to convert energy in a fuel cell, most likely an air/hydrogen fuel cell. Waste heat from the fuel cell can be used to vaporize and pre-heat the ammonia before it enters the catalytic dissociation reactor. Nitrogen dilution reduces the electrode potential on the hydrogen side only moderately.

### 4.3 Photolysis of Ammonia

The UV absorption spectrum of ammonia starts absorbing only at wavelengths below 210 nm, with quantum yields of 0.25–0.45 [140]. The photolysis of ammonia is a process occurring on a cosmic scale in the atmosphere of Jupiter, potentially creating a small stationary concentration of hydrazine in a dynamic equilibrium. Photolysis of ammonia has been studied as a means of making quantities of hydrazine, avoiding the use of hypochlorite or hydrogen peroxide as the oxidant.

### 4.4 Radiolysis of Ammonia

Ammonia decomposes under the influence of ionizing radiation (X-rays, gamma rays, and electron beams) and forms amidogen free radicals  $\cdot\text{NH}_2$ . Amidogen radicals can either decompose to nitrogen and hydrogen, or recombine to form hydrazine. This has been studied as a potential route to produce anhydrous hydrazine in large quantities. Chapters 1.2.2 and 1.2.6 in the author's book *Hydrazine and Its Derivatives*, 2<sup>nd</sup> ed [163], contain a thorough summary of the radiolysis of ammonia leading to various products, mostly aiming for hydrazine.

Radiolysis of ammonia also occurs in the atmosphere of Jupiter where there appears to be an equilibrium of ammonia, with ammonia forming by a yet to be identified mechanism at the same rate as it is decomposed by ionizing radiation. Radiolysis of ammonia in the atmosphere may result in the formation of a small, stationary concentration of hydrazine which would decompose just as fast as it might have formed. It has been theorized that some of the white clouds of frozen ammonia in the atmosphere of Jupiter might contain frozen hydrazine.

There is concern that continued radiolysis of ammonia might not only produce hydrazine but also hydrazoic acid, which would immediately combine with ammonia to form ammonium azide; this would remain in solution in liquid ammonia and create a new hazard in the residue after all the ammonia has evaporated.

### 4.5 Storage Stability of Ammonia

Ammonia is stable at room temperature. Liquid or gaseous ammonia can be stored indefinitely at room temperature. Liquid ammonia at its boiling point at atmospheric surface-level pressure should not be allowed to stand open in the laboratory because it would quickly absorb carbon dioxide and water from the air and its boil-off causes a respiration hazard.

## 4.6 Analysis and Quality Control of Ammonia

### 4.6.1 Detection of Ammonia in Air

Ammonia leakage needs to be detected in the refrigeration compressor rooms of cold-storage warehouses and anywhere where liquid and aqueous ammonia are used as agricultural fertilizer. Ammonia is also an exhaust product of hydrazine monopropellant rocket engines and gas generators, for instance those used in F-16 fighter-plane emergency power units (EPUs) and Space Shuttle auxiliary power units (APUs), and would be detected downwind of these airplanes and spaceplanes while the gas generators are operating.

Nessler's reagent is used as an aqueous solution to detect free ammonia and ammonium ions in water. Nessler's reagent is  $\text{HgI}_2$  in KI solution, mixed with 6-N NaOH immediately prior to use. The reaction with ammonia causes a brown precipitate of the iodide of Millon's base ( $\text{Hg}_2\text{N}$ )I. The Nessler's reagent method is often used as a semi-quantitative method with a nephelometer.

The pungent odor of ammonia is noticeable already at concentrations of 17 ppm, which is 68% of the threshold limit value time-weighted average (TLV-TWA) (25 ppm), such that special warning installations are not required. There are several instruments which are capable of continuous analysis of ammonia content in air and which can be set to a threshold concentration where they will trigger an alarm.

For occasional spot checks of ammonia concentration in air, the easiest method is with gas detection tubes which contain an indicator supported on a granular material, which changes color when exposed to ammonia. Such tubes are available from Draeger, MSA, "Kitagawa" etc. Gas detection tubes are sensitive to as little as 0.25 ppm  $\text{NH}_3$  and can measure up to 10 vol %  $\text{NH}_3$  with ten strokes with the manual-bellows pump. A more accurate and automated sampler is the chip, which combines ten capillary tubes on one small board. Draeger ammonia gas detection tubes and chip boards are available for a wide range of concentrations (Table 38).

The Draeger chip-measuring-system (CMS) is a self-contained unit that has a pump and a digital readout. Each disposable chip contains ten measurement capillaries filled with a substance-specific reagent system. The reactive preparations necessary for detection are kept in hermetically sealed glass capillaries until needed. When the chip is inserted into the analyzer, all information required for detection is transferred to the analyzer by means of a bar code:

- type of gas
- measuring range
- measuring time
- parameters for the calibration function
- required flow rate.

The analyzer records the measurement effect optoelectronically, thereby eliminating human error in reading a color scale. In the CMS, miniaturization has resulted in



**Table 38:** Draeger ammonia gas detection tubes and chip boards.

| Type              | Tube designation | Concentration range | Draeger part no. |
|-------------------|------------------|---------------------|------------------|
| Single tube       | ammonia 0.25/a   | 0.25–3 ppm          | 81 01 711        |
| Single tube       | ammonia 2/a      | 2–30 ppm            | 67 33 231        |
| Single tube       | ammonia 5/b      | 2.5–100 ppm         | 81 01 941        |
| Single tube       | ammonia 5/a      | 5–700 ppm           | CH 20 501        |
| Single tube       | ammonia 0.5%/a   | 0.05–10 Vol.%       | CH 31 901        |
| 10-capillary chip |                  | 0.2–5 ppm           | 64 06 550        |
| 10-capillary chip |                  | 2–50 ppm            | 64 06 130        |
| 10-capillary chip |                  | 10–150 ppm          | 64 06 020        |
| 10-capillary chip |                  | 100–2000 ppm        | 64 06 570        |

Data source: [164]

a reduction in the sample volume necessary for a measurement (compared to the manual-bellows pump with 10 strokes). For a typical measurement, only 30 mL of air is needed for a measuring time of approximately two minutes and a flow of 15 mL/min. The power needed for operation of the analyzer is provided by four AA batteries. After inserting the chip, an optical system calculates the number of remaining measurements still available on the chip being used, and displays this together with the gas type and the measuring range. Up to 50 measurement results can be stored in the machine with the name of the measured substance, the concentration, the date and time of the measurement, and a code letter to help identify the measurement location.

Nessler's reagent has been employed for the analysis of ammonia in air or water, but this method lacks sensitivity and suffers from a variety of interferences and reagent instability.

A direct, one-step method for the determination of ammonia (and primary aliphatic amines) is so rapid that instantaneous determinations may be made of the ammonia concentrations being sampled. The method requires collection of ammonia in a suitable neutral solvent (e.g. dioxane) containing (benzenesulfonamido)-p-benzoquinone, and measuring the absorption of light at 480 nm [165].

Ammonia vapor concentrations from 1000 to less than 60 ppm were easily, reproducibly, and reversibly detected by a glass capillary coated with a thin solid film of oxazine perchlorate dye [166].

#### 4.6.2 Assay Analysis of Ammonia

One of the main contaminants in liquid ammonia is water. Analysis of water contamination in liquid ammonia can be performed by a colometric method [167, 168].

Another contaminant in liquid ammonia is carbon dioxide, most likely present in the form of dissolved ammonium carbamate. Carbon dioxide in anhydrous liquid ammonia can be determined by a titrimetric method [169]. The carbon dioxide, com-

bined as ammonium carbamate, is separated from the ammonia by evaporation at or below room temperature, and is determined by acidification and absorption in barium hydroxide. Analysis of known-concentration CO<sub>2</sub>-doped samples in the range of 0 to 50 ppm CO<sub>2</sub> showed a precision of  $\pm 1.5$  ppm.

#### 4.6.3 Military Specifications for Liquid Ammonia

MIL-P-27406 Military Specification: Propellant, Ammonia dated 9 May 1966 was canceled on 26 June 1984. Future procurements for this material were advised to refer to Federal Specification O-A-445, dated 25 February 1975. O-A-445 went through several revisions until Rev. C, O-A-445C, Federal Specification, Ammonia, Technical, 15 pp. (6 Aug 2003) was released, which covered one grade of compressed anhydrous ammonia for refrigeration and nitriding purposes, but was canceled without replacement by Notice 1 dated 16 July 2010.

The purity requirement of O-A-445C was purity (min.) 99.98 mass-%, oil (max.) 0.0005%, and moisture (max.) 0.02%. Purity is the mass percent of ammonia by difference, when the mass percent of the residue remaining after evaporation at no more than 86°F (30 °C) is adjusted for absorbed NH<sub>3</sub> and subtracted from 100%. The remaining residue is a mixture of water, oil, non-volatile impurities, and ammonia. The water content of the residue can be determined by dissolving it in methanol and titrating with Karl Fischer reagent. The oil content of the residue is determined gravimetrically after extraction with carbon tetrachloride and evaporation of the solvent. When the ammonia was produced with hydrogen from a source other than natural gas, it had to be tested for pyridine, naphthalene, and hydrogen sulfide. Analytical methods for these tests are described in the specification. A document contains detailed instructions for determining moisture content in liquid ammonia [168].

## 5 Compatibility with and Corrosion of Materials in Ammonia

Dry anhydrous ammonia is not very corrosive and can be used in contact with many metallic or non-metallic materials of construction.

### 5.1 Metallic Construction Materials for Ammonia

Most metals are compatible with dry, anhydrous ammonia. Stainless steel is resistant, even to moist ammonia, whereas copper, brass, zinc, magnesium, and their alloys must be avoided. Cast-iron components galvanized with zinc or cadmium should not be used because the coatings will peel off.

The preferred metals of construction for ammonia installations are the stainless steels of the 300 and 400 series. Storage tanks, pipes, pumps, valves, and pressure gauges are made from stainless steel. One must be careful that valves and pressure gauges do not have any copper-containing parts.

There are some contradictory recommendations about the contact of ammonia with mercury, as this would often occur in laboratory glass equipment in low-pressure apparatus with mercury U-gauge manometers. Some sources warn against contacting metallic mercury with ammonia because a reaction might lead to explosive and shock-sensitive mercuric azide [170] (but this has not been confirmed). Mercury diffusion pumps in high-vacuum systems should not be operated when ammonia is passed through the pump with hot mercury.

## 5.2 Non-Metallic Construction Materials for Ammonia

Gaskets, O-rings, and valve stem packings for ammonia service are made from Teflon, Kel-F, or asbestos-impregnated fluorocarbon polymers. Polyethylene is rarely used, but can be.

## 5.3 Lubricants for Ammonia Service

Common hydrocarbon-based lubricants are not suitable for liquid ammonia service because they are quite soluble in liquid ammonia. Perfluorinated greases, such as Kel-F Polymer Oil, Fluorolube, and silicon grease have been recommended. One must be aware that many chlorofluorocarbon refrigerants react with liquid ammonia. The author has observed a near-explosive delayed runaway reaction of a mixture of liquid ammonia and liquid FC-22 in a closed steel vessel. After venting the residual vapor, the tank was filled with a white solid, probably a mixture of ammonium chloride and ammonium fluoride. There are cooling circuits on spacecraft where heat is transferred between ammonia and chlorofluorocarbons. One must avoid any leakage and mixing between the two fluids.

# 6 Handling of Ammonia

Recommendations for the safe handling of liquid ammonia were published by several trade associations, including the Compressed Gas Association [171–173].

An excellent study was conducted in Denmark on the handling safety of ammonia as a fuel for general public automobiles as a replacement for gasoline and in comparison to other alternatives such as liquified natural gas (LNG), liquified petroleum gas (LPG), methanol, and compressed hydrogen [174]. The study addressed the safety of

operating an ammonia-powered vehicle under normal and accident (collision) conditions, of transporting ammonia to the refueling service stations, and of the activities at the refueling service station (bulk delivery unloading and refueling of consumers' cars). The conclusion was that the hazards associated with ammonia need to be controlled by a combination of technical and regulatory measures. The most important requirements are:

- Advanced safety systems in the vehicle
- Additional technical measures and regulations to avoid the release of ammonia in maintenance workshops and unauthorized maintenance of the fuel system.
- Road transport of ammonia to refueling stations in refrigerated form
- Sufficient safety zones between refueling stations and residential or otherwise public areas.

When these measures are applied, the use of ammonia as a transport fuel would not cause any more risks than currently used fuels (using current practice).

## 6.1 Storage of Ammonia

Ammonia is usually stored as a compressed liquid in steel containers at room temperature under its own vapor pressure. The vapor pressure of liquid ammonia at room temperature (298 K) is  $1003 \text{ kPa} = 9.895 \text{ atm} = 145 \text{ psig}$ .

Some ammonia storage cylinders for laboratory use have two valves, one to withdraw gas from the vapor space above the liquid and the other connected to a dip tube that allows one to withdraw liquid ammonia under pressure.

When transferring liquid ammonia from one container to another, e.g. a run tank at a rocket test site, one must be careful not to overfill the receiving tank. Because ammonia often cools during transfer due to evaporation, the liquid is dense and gradually expands as it warms up again after the transfer. If the ullage space is insufficient to accommodate the expansion of the liquid, the tank may overpressurize and burst.

If several liquid ammonia storage containers are placed together, and the tanks are not all at the same temperature (only rarely the case, e.g. if one side of the spacecraft is facing the sun), the liquid will flow from the warmest tank to the coldest tank. In a satellite, this would cause a shift in the center of gravity and the spinning satellite may become unstable. The other hazard would be overfilling one of the tanks and then closing a valve, causing the tank to overpressurize when the liquid expands upon warming.

Ammonia gas is lighter than air. It may accumulate under the roofline in closed buildings and become a flammability hazard.

## 6.2 Transfer of Ammonia

Liquid ammonia needs to be transferred between transportation tanks and stationary farm tanks. Transfer of liquid ammonia can be performed by three different methods: under its own vapor pressure, with a pressurant gas, or with a positive-displacement pump.

The first method is suitable only for small containers and small quantities. The vaporization of ammonia to fill the new vapor space above the liquid will cool the remaining liquid to a point where flow will soon cease due to a lack of differential pressure. A standing cylinder will form a ring of frost on the outside, which some people welcome as an unsophisticated means of liquid level indication. Users are advised not to attempt to speed the evaporation in tanks with frost rings by immersing them in hot water or heating them with open flames. Such one-sided heating might cause thermal stresses in the container and leaks or ruptures.

If high delivery rates of liquid ammonia are needed, it is better to pressurize the tank with an inert pressurization gas, typically nitrogen, and pressure-feed the contents from the source tank. One must not use compressed air for the pressurant gas because air and ammonia form combustible and explosive mixtures. If even higher delivery rates are needed, particularly in large installations, the liquid must be transferred with pumps. Pumps for liquid ammonia service are typically made from stainless steel.

Liquid ammonia was present on every Space Shuttle flight where it was used as dump coolant to provide cooling of the crew compartment during aerodynamic heating upon re-entry. Liquid ammonia is currently present on the ISS where it is used as a closed-loop heat transfer fluid. It remains in the liquid state (and is thus not a compressor/evaporator loop as in commercial refrigeration units).

The ISS contains two active thermal control sub-systems that function by using a liquid-ammonia cooling system to collect waste heat and dispose of it in space using radiator panels [175]. These sub-systems consist of a number of heat exchangers, cold plates, radiators, the pump flow control sub-assembly (PFCS), and the pump module, all of which are orbital replaceable units. The PFCS circulates the ammonia coolant in the photovoltaic thermal control sub-system (PVTCS), and has been in operation since December 2000. The pump module circulates liquid ammonia coolant within the external active thermal control sub-system (EATCS), cooling the ISS internal coolant (water) loops, collecting waste heat, and rejecting it through the ISS radiators. These pump module loops have been in operation since December 2006, but not without problems. Original reliability predictions of the PFCS and pump module were compared against the operational performance of the ISS external thermal control loops.

## 6.3 Components for Ammonia Service

### 6.3.1 Ground Support Equipment and Fueling Carts for Liquid Ammonia

Ground support equipment (GSE) included an ammonia fueling cart developed for the Electric Propulsion Space Experiment [176].

### 6.3.2 Flight Tanks

A liquid-ammonia propellant feed system for operating under zero-gravity conditions in a satellite with electrothermal resistojet thrusters contained a regulator/capillary tube assembly which controlled the propellant delivery pressure and assured that only vapor was delivered to the thruster [177]. The system demonstrated the capability of maintaining a pressure control dead band of  $\pm 6.9$  kPa ( $\pm 1$  psi) at a delivery pressure of 138 kPa (20 psia) with either liquid or vapor extracted from the tank. See also [178–180].

### 6.3.3 Couplings

A rotary shut-off ammonia fluid quick-disconnect coupling for ISS Alpha was a precursor to couplings later used on the ISS [181]. This is a dual-line coupling consisting of two halves, an active and a passive one, mounted on separate structures within the same system. Similar couplings could be used for ground servicing of reusable rockets (like the X-15) that use ammonia as a consumable fuel. These couplings on the ISS have caused repeated problems [182].

## 6.4 Accidental Ammonia Spills

### 6.4.1 Accidental Ammonia Spill Vapor Cloud Dispersion

A study of the behavior of ammonia which has escaped into the atmosphere as a result of accidental failure of a pressurized-liquid container showed that the formation of a cold ammonia/air mixture, which is denser than the surrounding air, is very likely [183]. As a result, gravity-driven phenomena must be taken into account, e.g. the cloud slumps and becomes very broad. It was shown that this slumping is insensitive to assumptions made about the rate of entrainment of the air and the rate at which the mixture is heated by the ground. It was also demonstrated that, unless the wind speed is very low, the dispersing ammonia may not become buoyant. This is another phenomenon that is insensitive to parameter variations. See also [184–187].

A large number of reports of incidents involving the accidental release of ammonia were studied and combined into a model that would allow one to predict the consequences of short-term exposure to high concentrations of gaseous ammonia [188].

Sixteen different source types were modeled including pressurized-liquid releases, flashing and aerosol formation, two-phase jet releases, explosive releases,

and releases of high-vapor-pressure liquids, cryogenic liquids, and gases [189]. Dispersion models took into account the differences in source strengths and higher-than-air density of clouds (due to aerosol presence, temperature, or molecular weight). The reactions of the chemicals with water vapor in the atmosphere were modeled and included in the dispersion model. The transition from heavy-gas dispersion to near-neutral density dispersion was modeled without abrupt changes in size or discontinuity in concentrations.

Potential atmospheric and human health impacts that may result from accidental releases of anhydrous ammonia were evaluated using a traditional Gaussian puff model [190]. Dense two-phase aerosol releases from a 68-m<sup>3</sup> (18000-gallon) liquefied-ammonia storage tank and a 22.7-m<sup>3</sup> (6000-gallon) tanker truck accident were evaluated by means of the refined vapor dispersion model, SLAB. The SLAB results were compared to those using the neutral-buoyancy puff model. A SLAB sensitivity analysis was presented which examined various combinations of ambient temperatures and wind speeds in order to determine worst-case downwind air concentrations. The results from the storage tank releases indicated that potentially serious ammonia concentrations (>1000 ppm) could result at downwind distances ranging from 150 m (relief-valve malfunction) to approximately 3 km (catastrophic tank failure). The tank failure scenario produced concentrations that could be rapidly fatal (>5000 ppm) to as far as 1.3 km. Under worst-case meteorological dispersion conditions, the recognized exposure limits, i.e. Immediately Dangerous to Life and Health (IDLH), TLV-short-exposure limit (STEL) were exceeded for very large distances (>15 km).

The US Air Force and the American Petroleum Institute, among others, have increased the emphasis on calculating toxic corridors due to releases of hazardous chemical into the air. Dozens of PC-based computer models were recently developed to calculate these toxic corridors. However, the uncertainties in these models have not been adequately determined, partly due to the lack of a standardized quantitative method that could be applied. Individual model developers generally present a limited evaluation of their own model, and the US Environmental Protection Agency (EPA) has published some partial evaluations, but no comprehensive study has yet been completed. A report provided examples of the application of air dispersion model software to 14 typical hazard response models and eight sets of field data [191].

#### **6.4.2 Controlled Ammonia Spill Tests**

Large-scale spill tests of ammonia and dinitrogen tetroxide were performed at the Nevada Test Site [192]. The tests were extensively instrumented, resulting in large amounts of data which can be used to quantitatively describe the observed atmospheric dispersion phenomena. Preliminary results from both test series indicated that aerosols play a very important role in the dispersion of dense gas. The test data were ideally suited for model validation, and several example model data comparisons were included. Gaussian model calculations were found to be

inadequate even at long distances downwind. Highly instrumented, controlled spill tests with large quantities of liquid ammonia were conducted at remote locations to better justify the limitations regarding liquid ammonia tanks being placed in the vicinity of residential areas [193].

## **6.5 Disposal and Ammonia Spill Neutralization**

### **6.5.1 Disposal of Surplus Ammonia**

As a result of replacing chlorofluorocarbons, that have ozone-depleting potential, as refrigerants with ammonia, many industrial installations have to consider the prospect of ammonia fires and have developed methods for the disposal of surplus ammonia in a flare burner in a controlled manner [194]. There may be new opportunities for catalytic reactors to clean up the exhaust gases from such burners, or to complete the ammonia destruction without  $\text{NO}_x$  formation and with a much lower consumption of natural gas in the flare stack.

### **6.5.2 Ammonia Spill Neutralization**

If liquid ammonia is spilled accidentally, it will initially evaporate quickly until the spill site has cooled to the boiling point of liquid ammonia ( $240\text{ K} = -33^\circ\text{C}$ ), and then more slowly depending on the spill area, the soil conditions, the ambient temperature, and the atmospheric conditions. The remaining puddle can be absorbed and diluted with water. Ammonia aerosol clouds can be absorbed by a fine spray of water mist. Ammonia absorbed into the soil at a spill site would gradually be consumed by natural processes (evaporation, leaching, mineralization, reacting with atmospheric carbon dioxide, and consumption by ammonia-oxidizing bacteria), similar to what happens in an ammonia-fertilized field.

## **6.6 Protective Clothing for Handling Ammonia**

Ammonia gas is very irritating to mucous membranes and will cause lacrimation. Liquid ammonia must be handled only by properly trained personnel wearing adequate protective clothing that consists of a face mask, goggles, a gas mask, and rubber gloves.

When handling liquid ammonia on a large scale, additional protective clothing includes aprons, helmets, and rubber boots. Gas mask filters are usually effective only against less than 3 vol.-% ammonia in air. At higher vapor concentrations, the operators must wear supplied-air ensembles.



## 7 Toxic Properties of Ammonia

The safety properties of ammonia are summarized in Table 39. The following information was taken from National Academies Press, Laboratory Chemical Safety Summaries [195].

**Table 39:** Safety properties of ammonia.

| Formula                  | NH <sub>3</sub>                                                   |
|--------------------------|-------------------------------------------------------------------|
| Physical properties      | colorless gas                                                     |
| Boiling point            | 240 K = -33 °C                                                    |
| Freezing point           | 195 K = -78 °C                                                    |
| Highly soluble in water  | 89.9 g/100 mL* at 0 °C                                            |
| Odor threshold           | intense pungent odor detectable at 17 ppm                         |
| Vapor density            | 0.59 (air = 1.0)                                                  |
| Vapor pressure           | 0.879 MPa at 294 K (8.71 atm at 21 °C)                            |
| Autoignition temperature | 963 K (690 °C)                                                    |
| Toxicity                 | LD50 oral (rat) 350 mg/kg<br>LC50 inhalation (rat) 2000 ppm (4 h) |
| PEL (OSHA)               | 35 ppm (27 mg/m <sup>3</sup> )                                    |
| TLV-TWA (ACGIH)          | 25 ppm (17 mg/m <sup>3</sup> )                                    |
| STEL (ACGIH)             | 35 ppm (27 mg/m <sup>3</sup> )                                    |

Ammonia gas is extremely corrosive and irritating to the skin, eyes, nose, and respiratory tract. Exposure by inhalation causes irritation of the nose, throat, and mucous membranes. Lacrimation and irritation begin at 130–200 ppm, and exposure at 3000 ppm is intolerable. Exposure to high concentrations (above approx. 2500 ppm) is life-threatening, causing severe damage to the respiratory tract and resulting in bronchitis, chemical pneumonitis, and pulmonary edema, which can be fatal. Eye contact with ammonia vapor is severely irritating, and exposure of the eyes to liquid ammonia or mists can cause serious damage, which may result in permanent eye injury and blindness. Skin contact with ammonia vapor, mists, and liquid can cause severe irritation and burns; contact with the liquid results in cryogenic burns as well. Ingestion of liquid ammonia burns the throat and pharyngeal tissues, causing severe abdominal pain, nausea, vomiting, and collapse, and can be fatal. Ammonia gas is regarded as having adequate warning properties. Ammonia has not been found to be carcinogenic or show reproductive or developmental toxicity in humans. Chronic exposure to ammonia can cause respiratory irritation and damage.

Ammonia inhalation toxicity is a matter of concern not only where ammonia is handled as such, but also downwind of testing rockets and gas generators with decomposing hydrazine operated on Earth, such as in F-16 EPUs. See also [196].

## 7.1 Symptoms of Ammonia Poisoning

The immediate response of mucous membranes of the nose and eyes to inhalation of ammonia gas in the air is lacrimation, increased saliva flow, and eye and nose irritation. At higher concentrations, the irritation causes reddening of the eyes, coughing fits, a feeling of suffocation, and vomiting. Even the sweat of a person suffering from acute ammonia poisoning and removed from the site of the accident will reek of ammonia. Most of the ammonia inhaled is retained in the lung; only 10% is exhaled again. Inhalation of a high concentration of ammonia may cause lung edema which can be fatal several days after the accident.

The body can gradually get used to higher and higher concentrations, such that even 200–300 ppm can be endured without lasting effects. The author once participated in a voluntary exposure experiment in a closed chamber with 500 ppm  $\text{NH}_3$  in air for 30 min. Lacrimation ceased 15 min after the start of the test.

Concentrations of 400–700 ppm cause immediate lacrimation and irritation of the respiratory tract, >1500 ppm causes strong coughing, >2000 ppm can cause permanent damage even after short exposure, and >5000 can be fatal after only a few breaths. Even if the subject is wearing respiratory protection, >10000 ppm will cause irritation of the skin, in particular in moist air and if the subject is sweating, and >30000 ppm can cause caustic burns and skin lesions.

## 7.2 Olfactory Threshold for Ammonia

The olfactory threshold for ammonia in air has been variously reported to be as low as 5 ppm and as high as 50 ppm. A frequently cited average is 20 ppm (0.015 mg/L).

Air monitoring data and human exposure reports were collected following a variety of accidental ammonia releases [197]. Of 65 readings between 1.1 and 1.5 ppm, odor was detected in 51 samples (78.5%). These data are consistent with an ammonia odor threshold within a concentration range of 1.1–1.5 ppm. This level is significantly lower than frequently cited historical data. Furthermore, a review of the ammonia literature demonstrated that the ammonia odor threshold is significantly lower than levels that produce eye, nose, or throat irritation.

## 7.3 Inhalation Toxicity of Ammonia

### 7.3.1 Inhalation Toxicity of Ammonia as Measured by Animal Exposure Tests

The acute inhalation toxicity of ammonia was examined in rats using various exposure concentrations and exposure periods [198]. Groups of male and female rats were exposed to dynamic atmospheres containing different concentrations of ammonia for 10, 20, 40, or 60 min. The aim of the study was to establish the relationship between

exposure concentration and exposure period on the one hand, and mortality on the other. The correlation between exposure concentration ( $c$ ), exposure period ( $t$ ) and mortality rate, expressed in probits was found to be  $\text{Probit} = 2.30 \ln [c^{2.02} \times t] - 47.8$ . The following  $\text{LC}_{50}$  values for ammonia were calculated: 10 min  $\text{LC}_{50}$  : 28130 mg/m<sup>3</sup> air (40300 ppm), 20 min  $\text{LC}_{50}$  : 19960 mg/m<sup>3</sup> air (28595 ppm), 40 min  $\text{LC}_{50}$  : 14170 mg/m<sup>3</sup> air (20300 ppm), 60 min  $\text{LC}_{50}$  : 11590 mg/m<sup>3</sup> air (16600 ppm). Experiments designed to determine an  $\text{LC}_{50}$  in mice from a 1-h exposure to  $\text{NH}_3$  followed by a 14-day observation period indicated that the  $\text{LC}_{50}$  was close to 18000 ppm [199].

### 7.3.2 Inhalation Toxicity of Ammonia as Measured by Human Volunteer Exposure Tests

Inhalation toxicity tests were conducted with healthy human volunteers under close medical surveillance. Sixteen subjects, eight experts (29–53 yr) and eight non-experts (students, 18–30 yr) were exposed for 2 h to ammonia in concentrations of 50, 80, 110, and 140 ppm [200]. No effect on vital capacity, forced exhaled volume 1 or forced inhaled volume 1 was found. Subjective responses (smell, irritation of eyes and throat, discomfort, etc.) were recorded every 15 min and appeared more pronounced in the non-expert group and 140 ppm was not tolerated by this group for 2 h.

Twelve healthy persons underwent sham or ammonia (5 and 25 ppm) exposure randomly in an exposure chamber on three occasions [201]. The exposure duration was 3 h, 1.5 h resting (seated), and 1.5 h exercising (50 W on a bicycle ergometer). Symptoms were registered repeatedly before, during, and after the exposure on visual analog scales. Bronchial responsiveness to methacholine, lung function, and exhaled nitric oxide (NO) were measured before and 7 h after the exposure. In addition, nasal lavage was performed, and peripheral blood samples were drawn before and 7 h after the exposure. All the symptom ratings increased significantly during 25-ppm ammonia exposure as compared with the control exposure. The ammonia exposure did not significantly influence lung function or the exhaled NO levels. Ammonia inhalation at the TLV did not cause detectable upper-airway inflammation or increased bronchial responsiveness to methacholine in healthy persons.

The author, in his younger years, once volunteered for a 500-ppm  $\text{NH}_3$  human volunteer exposure test of 30-min duration, and can report from his own experience that it was very uncomfortable.

## 7.4 Regulatory Exposure Limits for Ammonia

The governments of various countries have instituted different threshold limit values for exposure to ammonia at the workplace. The US Occupational Safety and Health Administration (OSHA) initially adopted an ammonia standard of 50 ppm as an 8-h TWA, based on the 1968 recommendation of the American Conference of Governmental Industrial Hygienists (ACGIH). In 1973, the ACGIH revised its recommended ammonia exposure limit to 25 ppm for 8-h TWA and added a 35-ppm, 15-min STEL to protect against irritant effects. In June 1988, OSHA proposed the adoption of these limits as legally enforceable standards, but concluded that the available evidence of chronic health effects was insufficient to support any 8-h TWA limit for ammonia.

In 1997, the National Advisory Committee on Acute Exposure Guideline Levels (NAC AEGL) proposed AEGL for ammonia as shown in Table 40 which were lower (more restrictive) than the levels recommended by the industry.

**Table 40:** Acute Exposure Guideline Levels (AEGL) for ammonia.

| AEGL                                      | Concentration (ppm-v) by exposure duration parameter |         |      |      |      |
|-------------------------------------------|------------------------------------------------------|---------|------|------|------|
|                                           | 5 min.                                               | 30 min. | 1 h  | 4 h  | 8 h  |
| NAC AEGL proposals                        |                                                      |         |      |      |      |
| 1                                         | 25                                                   | 25      | 25   | 25   | 25   |
| 2                                         | 380                                                  | 160     | 110  | 110  | 110  |
| 3                                         | 3800                                                 | 1600    | 1100 | 550  | 390  |
| RAM TRAC/Ammonia Industry recommendations |                                                      |         |      |      |      |
| 2                                         | 1704                                                 | 696     | 492  | 246  | 174  |
| 3                                         | 16869                                                | 6887    | 4870 | 2435 | 1722 |

Data source: [202]

The values were generally too low by a factor of approximately 4.5. An excellent summary of acute toxicity data of ammonia is given in [202]. Historical data suggesting that ammonia at 5000–10000 parts per million (volume/volume = ppm-v) might be lethal within 5–10 min were critically examined in view of more recent accident reconstructions that suggest that instant lethality requires higher ammonia concentrations. For example, 33737 ppm-vol. was a 5-min zero-mortality value in a major ammonia release accident in South Africa in 1973. Comparisons of secondary reports of ammonia lethality with original sources revealed discrepancies with contemporary sources. A survey revealed that contemporary accident reconstructions yield ammonia lethality levels comparable to those in dozens of reports of animal bioassays, after adjusting the concentrations to human-equivalent concentrations via US EPA procedures. Ammonia levels potentially causing irreversible injury or impairing the ability of ex-

posed people to escape from further exposure and concurrent perils have similarly been biased downwardly in contemporary sources. The EPA has identified ammonia as one of 366 extremely hazardous substances subject to community right-to-know provisions of the Superfund Act and emergency planning provisions of the Clean Air Act. The Clean Air Act defines emergency planning zones (EPZs) around industrial facilities that exceed a threshold quantity of ammonia on site. It was suggested that EPZs around ammonia facilities can be reduced, thereby also reducing emergency planning costs, which will vary roughly with the EPZ radius squared.

Criteria used in establishing acute AEGL were detailed in a National Research Council publication [203]. The 1987 National Research Council Emergency Exposure Guidance Levels (EEGLs) were: a 1-h EEGL of 100 ppm and a 24-h EEGL of 100 ppm. The original IDLH concentration (in standard cubic feet, SCF) for ammonia of 500 ppm was later (in 1994) revised to 300 ppm. The author has participated as a volunteer in a 500-ppm, 0.5-h exposure experiment with no lasting effects. See also [204, 205].

## 7.5 Liquid Ammonia Dermal Effects

Liquid ammonia spilled on the skin has a dual effect: a freezing frostbite effect and a caustic chemical burn effect.

In two cases of exposure to pressurized ammonia during an industrial accident, the skin conditions were quite different. One patient's symptoms were consistent with an ammonia alkali burn whereas the other patient's symptoms were more characteristic of a significant thermal injury caused by the rapid expansion and evaporation of a pressurized liquid [206].

As with any other alkali burns, early irrigation to remove the ammonia from the affected skin areas is crucial to limit tissue damage. Two cases of identical exposure to industrial-strength ammonia were presented and compared [207]. Each patient was exposed to ammonia liquid and vapors simultaneously when a tank containing this compound exploded. One patient showered at the scene immediately after exposure, but the other deferred irrigation until he arrived at the hospital. The first patient suffered minor burns with a 2-day, uncomplicated hospital stay. The second patient suffered 14% total body surface area burns and a significant inhalation injury. He required intubation, mechanical ventilation, and skin grafting during his 13-day hospitalization. Although much is written about the management of chemical burns, few articles address those caused by liquid ammonia. Aggressive initial management significantly reduces the morbidity of ammonia burns.

A 28-year-old patient suffered 45% total body surface area second- and third-degree burns as well as inhalational injury from an anhydrous ammonia explosion [208]. Along with fluid resuscitation, for the first 48 h, his body was scrubbed every 6 h with sterile water to decrease the skin pH, from 10 to 6–8. He subsequently underwent a total of seven wound debridements, initially with allograft and then

autograft. On post-burn day 45, he was discharged. The injuries associated with anhydrous ammonia burns are specific to the effects of ammonium hydroxide. Liquefactive necrosis results in superficial to full-thickness tissue loss. The affinity for mucous membranes of anhydrous ammonia and its byproducts can result in hemoptysis, pharyngitis, pulmonary edema, and bronchiectasis. Ocular sequelae include iritis, glaucoma, cataracts, and retinal atrophy. The desirability of treating anhydrous ammonia burns immediately cannot be overemphasized. Clothing must be removed quickly, and irrigation with water initiated at the scene and continued for the first 24 h. Resuscitative measures should be started as well as early debridement of non-viable skin. Patients with significant facial or pharyngeal burns should be intubated, and the eyes irrigated until a conjunctivae sac pH of <8.5 is achieved.

Severe ammonia injury is associated with high morbidity and mortality. One case report demonstrated the pathophysiology and treatment of both cutaneous burn wounds and inhalation injury caused by ammonia [209]. Frequent bronchoscopy was used to attempt to avoid intubation. The patient remained extubated, but later required skin grafts to close his wounds once his pulmonary injury had healed. Bronchoscopy can be a useful tool to avoid intubation.

Five patients with severe liquid ammonia injury after an explosion in a warehouse suffered severe inhalation and ophthalmic injuries, as well as cutaneous burns, representing the challenges inherent in simultaneously managing the dermal and pulmonary complications of this injury [210].

When treating ammonia accident victims, it is important to understand the influence of street clothing and environmental and other factors on the rate of ammonia absorption into the body. Ammonia was selected for *in vitro* human skin studies of absorption, penetration, and off-gassing at test concentrations of up to 2000 ppm, incorporating primary and secondary exposure combinations of up to 60 min [211]. Intact skin provided a good barrier to ammonia penetration from the gas phase. Human skin penetration was generally low for exposures up to 1000 ppm for 30 min. Heavy street clothing such as denim was found to act as an initial barrier to skin absorption but subsequently as a reservoir for secondary exposure, under variable temperature and humidity conditions. Rapid off-gassing was observed for lighter fabrics including polyester and cotton. In either case, contaminated clothing should be removed as soon as possible.

## 7.6 Ammonia Accident Statistics

In 2002, the US Poison Control Centers reported almost 6000 cases of toxic ammonia exposures: 93% of exposures were unintentional and 11% resulted in a moderate-to-severe outcome.

Unplanned releases of ammonia have led more often to evacuation and injury than releases of other chemicals, but few studies have systematically investigated

ammonia releases. A review of Hazardous Substances Emergency Events Surveillance system data for 1993–1998 revealed that 537 ammonia releases required the evacuation of a total of at least 40680 persons, and 248 ammonia releases led to the injury of 1434 persons [212]. Equipment failure and operator error were cited as factors contributing to ammonia releases 90% of the time. Eighty-seven percent of the releases occurred at fixed facilities. Risk factors for evacuation and injury differed between the food-manufacturing industry and other industries. Indoor release was a consistent risk factor, but the quantity of ammonia released was not always a risk factor. An ammonia leak in Crete, NE, USA, on 18 February 1969 caused 9 deaths and 53 injuries. In an accident on 11 May 1976 in Houston, TX, USA, a tanker truck crash released 17.2 tons of pressurized anhydrous ammonia. The chemical cloud extended 1500 m downwind and was 550 m wide. Five people were killed and 178 were injured, some with permanent disabling injuries. The fatalities and disabling injuries occurred within about 70 m of the accident. An ammonia leak in Lievin, France, on 21 August 1968 caused 5 deaths and 20 injuries. See also [213–216].

## 7.7 Other Ammonia Leakage Adverse Effects

Astronauts performing EVA to repair the ammonia cooling system on board the ISS may have spilled small amounts of ammonia on their suits and dragged the chemical into the air lock and the interior of the ISS when they returned from the EVA. In spite of the vacuum in outer space which would cause ammonia spills to evaporate quickly, some ammonia may adhere to the space suit. Another failure mode is an internal leak in the heat exchanger where heat from the low-pressure internal water loop is transferred to the high-pressure external ammonia loop [217].

### 7.7.1 Ammonia Accident History and Case Studies

Although ammonia is not currently used as a rocket propellant, the hazards of accidental release of ammonia are summarized in this section. This information may be useful in evaluating ammonia as a fuel for other applications. Individuals who are acutely exposed to high concentrations of ammonia and survive the immediate effects may die weeks to months later, probably due to the secondary effects of exposure. The lungs of an accident victim who died 2 months after exposure showed morphologic alterations [218]. Major pathologic findings included cylindrical bronchiectasis of the lower lobes and fibrous obliteration of the small airways.

A 25-year-old refrigeration technician died of obliterative bronchiolitis 85 days after an accidental massive ammonia inhalation [219]. Eighteen people died from accidental release of ammonia in South Africa [220]. The health status of a life-long non-smoker who was the victim of a massive accidental exposure to anhydrous ammonia gas was followed up for 10 years [221]. In the acute phase, the patient presented with

severe tracheobronchitis and respiratory failure caused by very severe burns of the respiratory mucosa. After some improvement, he was left with severe and fixed airways obstruction. Isotope studies of mucociliary clearance, computed tomography, and bronchography showed mild bronchiectasis. It was concluded that acute exposure to high concentrations of ammonia may lead to acute respiratory injury but also long-term impairment of respiratory function.

In a meat factory using liquid ammonia as a refrigerant, there was a breach in the refrigeration system caused by careless handling of the forklift truck by one of the factory workers. The penetrated pipe, part of the 2500-L refrigeration system, was located outdoors in the factory area and instantly started leaking. Factory personnel underwent immediate evacuation, except for a 20-year-old male worker who remained lying beside the broken pipe. He was not wearing protective gear. He had injuries to both eyes, second- and third-degree burns on his face, anterior neck, left axilla, left arm, part of the anterior and posterior chest wall, genitalia, and both lower limbs, i.e. covering a 50% total body surface area [222]. The initial chest radiograph showed congestion of both lung hiluses and perihilar vascular structures, with signs of swift development of acute respiratory distress syndrome seen on subsequent films. Severe inhalation injury was confirmed by bronchoscopy, revealing edema and reddish epithelium in the bronchial tree. The patient subsequently required a lung transplant; this is the first description of a case of successful lung transplantation after a massive anhydrous ammonia inhalation injury.

A tanker truck carrying anhydrous ammonia fell off a highway and released a dense cloud of ammonia aerosol. Fifty-four people were exposed to the gas. After 90 days, three people were still experiencing hoarseness and were examined, revealing laryngeal sequelae due to ammonia inhalation burn, one case of hyperemia and edema, one case of granuloma of the posterior third portion of the left vocal cord, and one case of vocal-cord adhesion [223].

Exposure to anhydrous ammonia can result in substantial injury to the respiratory system, eyes, and skin. Acute and chronic respiratory manifestations in 12 patients exposed to anhydrous ammonia as a result of the same accident were compared [224]. Survivors suffering significant ill effects were separated into two groups according to their history and clinical course. One group of patients sustained exposure to high concentrations of ammonia over a short period of time. They suffered upper airway obstruction and required early intubation or tracheostomy. These patients recovered with few pulmonary sequelae and regained good pulmonary health. The second group of patients were exposed to lower concentrations of gas over a prolonged period of time and did not manifest upper airway obstruction. In this group of patients, however, significant long-term pulmonary sequelae were observed.

A patient who had an accidental exposure to liquid ammonia over a prolonged period, manifesting in cutaneous, respiratory, and ocular damage, in addition to a severe cold thermal injury (frostbite), with a fatal outcome, had flaccid quadriplegia and



episodes of bradycardia [225]. These manifestations raise the possibility of the systemic toxicity in patients with prolonged exposure to ammonia.

Residents of Minot, ND, USA, were exposed to 200000 gallons of anhydrous ammonia after a train derailment caused the release of the chemical. The train derailment occurred just outside Minot on 18 January 2002, when a Canadian Pacific Railway freight train derailed in Harrison Township in Ward County, west of Minot, spilling hazardous materials [226]. All 15 tank cars carrying liquid ammonia derailed and five of these tank cars catastrophically ruptured, with an instantaneous release of about 146700 gallons of anhydrous ammonia and additional releases in the following days. Some of the breached tanks propelled themselves 1000 feet away from the railroad tracks. The liquid quickly turned into a gas and formed a toxic white aerosol cloud that engulfed most of the city, affecting more than 15000 people. One resident was fatally injured and 60–65 residents of the neighborhood nearest to the derailment site were rescued. As a result of the accident, 11 people sustained serious injuries and were hospitalized with respiratory, ocular, and burn injuries, and 322 people, including the two train crewmembers, sustained minor injuries. Local hospital and triage centers treated more than 300 people for respiratory and ocular injuries. See also [227].

#### **7.7.2 First-Aid Treatment of Ammonia Accident Victims**

Initial emergency response to ammonia accidents involves evacuation, decontamination, first aid, and alerting the appropriate authorities [228]. Decontamination must be complete and rescuers must avoid being overcome by fumes. Emergency department care is directed at respiratory, ocular, skin, and gastrointestinal treatment. Respiratory and ocular lesions tend to be the most severe and can be used as a triage guide. The need for a multi-disciplinary approach to hospital care is stressed. In severe exposures, adult respiratory distress syndrome is a common finding. In children who have ingested aqueous ammonia, early endoscopy, aggressive antibiotic therapy, and serial dilatations of strictures are recommended. Long-term complications occur predominantly to the eyes and respiratory tract.

In the case of accidental inhalation, the victim must be moved into the fresh air and a physician must be called to evaluate the case. In the case of respiratory failure, an oxygen mask should be kept at the ready to provide artificial respiration.

If liquid ammonia is spilled on the skin, the frostbite makes the caustic burns even worse, in particular after the tissue thaws out. First aid in the case of liquid ammonia spills on skin comprises flushing the affected area with copious amounts of water. Ammonia-soaked clothing must be removed. If ammonia has spilled into the eyes, they should be rinsed for at least 15 min in an eye-wash fountain and a physician must be consulted immediately. Some first aid instructors recommend a rinse with a dilute % boric acid solution.

## 8 Explosion and Fire Hazards of Ammonia

### 8.1 Flammable Range of Gaseous Air/Ammonia Mixtures

Ammonia forms flammable mixtures with air and other oxidants in a narrow range of concentrations, but is much less of a fire hazard than natural gas, propane, or gasoline. Ammonia fire hazards exist in lines and tanks that are being filled with ammonia without prior replacement of air by an inert gas like nitrogen. Ammonia fire hazards exist in buildings where an ammonia leak has occurred in the presence of ignition sources.

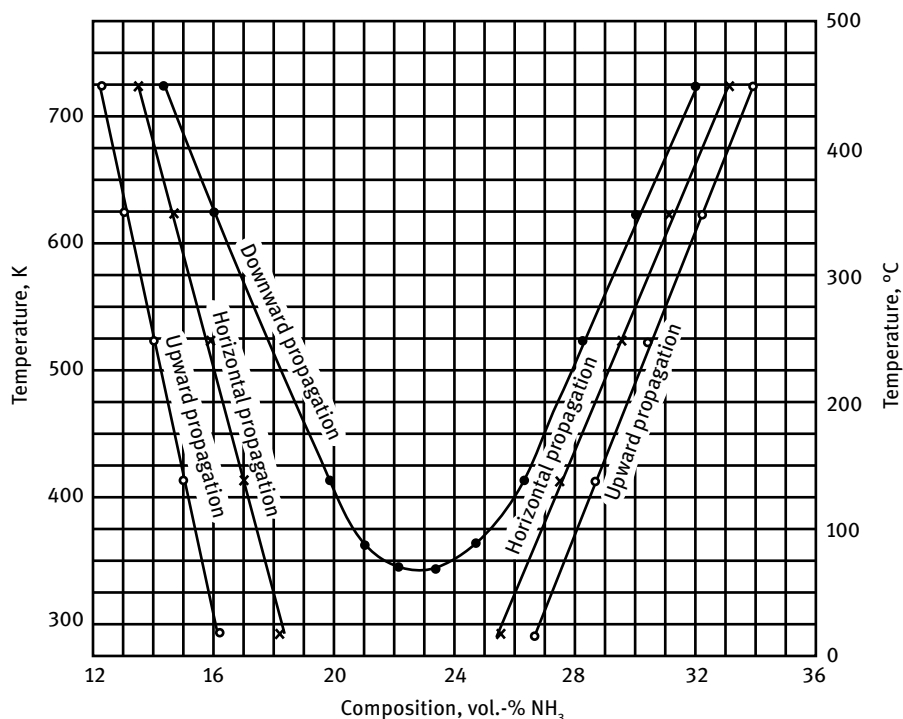
Air/ammonia mixtures are a potential hazard in refrigeration plants, where several accidents with ammonia explosions have been reported [229]. With the phasing out of fluorochlorohydrocarbons as the working fluids in refrigeration units, there will be an increase in the use of ammonia. The interest in accidental ammonia explosions and their prevention will continue for some time to come.

Non-flammable and non-detonable off-stoichiometric mixtures of oxygen and ammonia with or without inert diluent gases have been considered as propellants for catalytic microthrusters, but before such mixtures can be selected, the flammable range must be determined.

In flammable mixtures with borderline flammability, the convection as the result of the incipient combustion enhances flame propagation. These mixtures have a distinct difference in upward and downward propagation. Some (e.g. air/ammonia) burn upwards only. In Earth's orbit in a zero-gravity environment, these near-limit mixtures are self-extinguishing flames. This was demonstrated with air/ammonia and oxygen/hydrogen/nitrogen mixtures of borderline flammability under microgravity conditions [230].

Because ammonia in air has a very narrow flammable range, this mixture is well suited to demonstrate the dependence of flammable limits on the direction of propagation. In a gravity field, the buoyancy of the hot gases helps the upward propagation of the flame. Propagation of flames in a zero-gravity environment is a relatively new field of study. It appears that most flammable mixtures have very narrow ranges of flammability in a zero-gravity environment since the flame virtually suffocates in its own combustion products. Figure 39 illustrates the limits of flammability of ammonia in air as a function of the initial temperature and the direction of propagation of the flame in a 50-mm-diameter tube [231, 232]. It is interesting to note that ammonia in air cannot be made to burn downward until the mixture is pre-heated to 350 K.

The flammable range of air/fuel mixtures depends on the vessel geometry, direction of propagation, ignition energy, initial mixture temperature and pressure, and, most of all, on the oxidizer/fuel mixture ratio. Limits of flammability of flammable gases and vapors in air are generally reported for a 50-mm-diameter tube with upward propagation at 293 K = 20 °C and atmospheric pressure at sea level. The flame



**Figure 39:** Flammability of air/ammonia mixtures. Influence of temperature and direction of propagation of flame. (Reproduced and modified from [232].)

speed and critical diameters for air/ammonia flames such as those used in industrial combustors will be discussed in a future volume on non-hypergolic bipropellant combinations.

The limits of flammability of ammonia in dry air at 293 K = 20 °C with upward propagation are 16.1–26.8 vol.-% NH<sub>3</sub>. Other sources gave NH<sub>3</sub>/air at 293 K = 20 °C, 1 atm 15.5–28 vol.-% NH<sub>3</sub>, NH<sub>3</sub>/air at 373 K = 100 °C, 1 atm slightly widened limits from 14.5–29.5 vol.-% NH<sub>3</sub> and NH<sub>3</sub>/O<sub>2</sub> at 293 K = 20 °C, 1 atm distinctly widened limits from 13.5–82 vol.-% NH<sub>3</sub>.

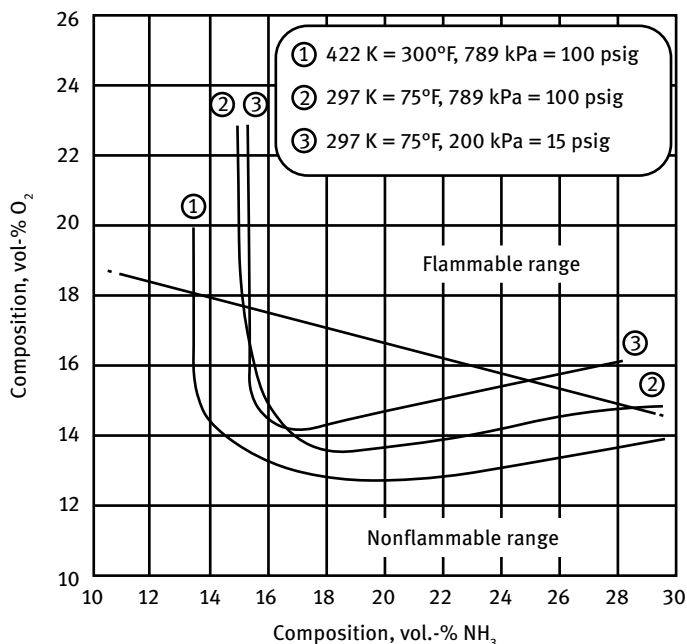
The fire hazard during handling of ammonia is relatively low, compared to hazards when handling other fuels such as propane or gasoline, or even liquid hydrogen. The flammable range of ammonia burning in air with upward propagation is from 15 to 28 vol.-% NH<sub>3</sub> [232, 233]. At room temperature, it cannot burn downwards. Additional information on ammonia flammability and critical diameters for flame propagation in air is now available [234, 235].

Experiments investigating the flammability of hydrogen and ammonia as well as mixtures of these two fuels in air were performed in a 12.6-L combustion vessel at an initial pressure of 101 kPa (1 atm) and initial temperatures of up to 873 K (600 °C) [236]. Flammability maps based on the limiting fuel concentration as a function of the initial temperature for the various mixtures were constructed. The flammability limit data obtained for both hydrogen and ammonia by themselves agreed well with the data in the literature. The flammability limits for both air/hydrogen and air/ammonia were found to widen linearly with increased initial temperature. The lower flammability limits of air/hydrogen/ammonia mixtures at various initial temperatures were found to follow closely the Le Chatelier flammability limit mixing rule. We know that ammonia readily dissociates to hydrogen and nitrogen. The flammability limits of ammonia dissociation products mixed with undissociated ammonia and air were also measured at initial temperatures of 673, 773, and 873 K (400, 500, and 600 °C). For experiments at 773 and 873 K (500 and 600 °C), it was found that mixtures with a large fraction of dissociated ammonia auto-ignited upon injection into the test vessel. The range of mixtures that autoignited was larger at 873 K (600 °C) than at 773 K (500 °C). For mixtures with a large fraction of dissociated ammonia, autoignition of the mixture prevented the measurement of the fuel-rich flammability limit. The knowledge of flammability limits of hydrogen/air mixtures in air is valuable for the assessment of explosion hazards of hydrazine decomposition products from a gas generator or rocket engine operating in air at sea level, as is often done prior to moving to testing in a vacuum chamber.

As with hydrocarbons, an increase in either temperature or pressure tends to widen the flammable range of ammonia in air. The lower-limit flame temperature remains essentially constant with the increase in initial temperature.

Data on the flammable range of  $O_2/N_2/NH_3$  mixtures at higher than atmospheric pre-combustion pressures, as shown in Figure 40 show three curves, one for atmospheric pressure and room temperature and two for 688 kPa (100 psia) and room temperature and elevated temperature (422 K = 300 °F) [237]. The dotted line is the stoichiometric composition.

Partial decomposition of ammonia, such as in ammonia decomposition products used as protective atmosphere (“furnace gas”) in heat treatment furnaces, will form air/ammonia/hydrogen mixtures which have a wider range of flammability than undissociated ammonia.



**Figure 40:** Flammability of ammonia-oxygen-nitrogen mixtures as a function of composition, temperature and pressure. (Republished and modified from [237], with permission from ©1962 American Institute of Chemical Engineers, permission conveyed through Copyright Clearance Center, Inc.)

## 8.2 The Flammable Range of Oxygen/Ammonia Mixtures

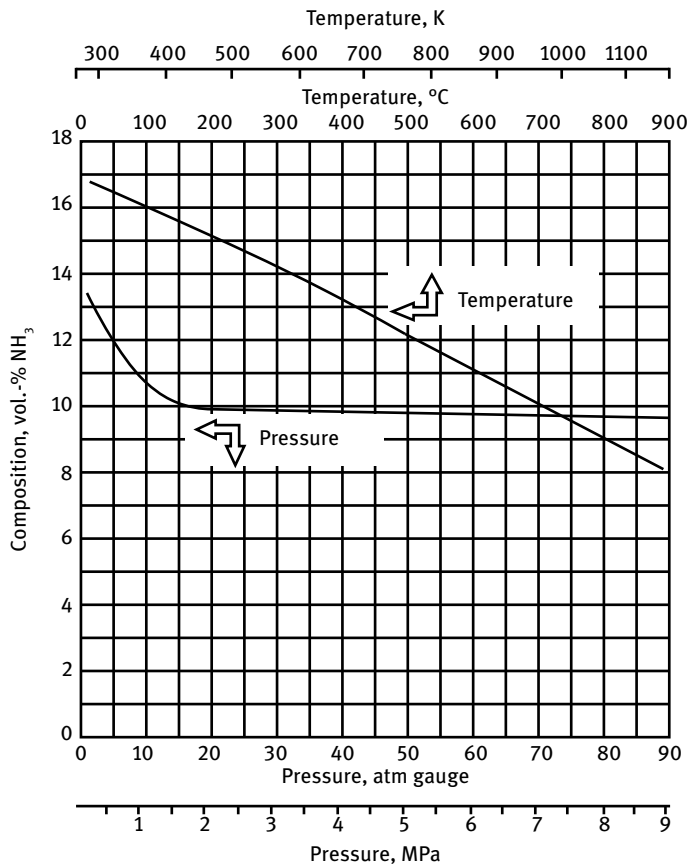
Other than using it as a fertilizer as is, one of the main industrial uses of ammonia is in the production of nitric acid which is then the main reactant in making fertilizers, explosives, and propellants. In the feed to the catalytic reactor, ammonia is mixed with oxygen or air, and the combustion may flash back into the mixing station and the feed system unless the pipes are protected by flashback arrestors in the form of stacks of narrow-mesh screens. The flammability limits of ammonia in oxygen are summarized in Table 41. In the 50-mm-diameter pipe at room temperature, the flammable range of ammonia in oxygen with upward propagation extended from 15.3 to 79 vol.-%.

Table 41 supplies several temperature-dependence data for oxygen/ammonia mixtures. Figure 41 gives the temperature dependence of the lower limit for higher temperatures approaching the ignition temperature [239].

**Table 41:** Flammability limits of ammonia in oxygen.

| Tube diameter<br>cm | Temperature<br>K | Direction of propagation |      |            |      |          |      |
|---------------------|------------------|--------------------------|------|------------|------|----------|------|
|                     |                  | upward                   |      | horizontal |      | downward |      |
|                     |                  | L.L.                     | U.L. | L.L.       | U.L. | L.L.     | U.L. |
| 7.5                 | 293              | 14.8                     | —    | 15.6       | —    | 17.3     | —    |
| 5.0                 | 293              | 15.3                     | 79   | 16.7       | 79   | 18.1     | 79   |
| 1.7                 | 293              | —                        | —    | —          | —    | 21       | 64.6 |
| 1.5                 | 293              | —                        | —    | —          | —    | 18.9     | 69.5 |
| 5.0                 | 291              | —                        | —    | 16.7       | —    | 18.1     | —    |
| 5.0                 | 298              | —                        | —    | 14.8       | —    | 15.8     | —    |
| 5.0                 | 318              | —                        | —    | 12.6       | —    | 13.5     | —    |

Note: Data in vol.-%  
Data source: [238]



**Figure 41:** Dependence of the lower limit of flammability of oxygen/ammonia mixtures on pre-combustion temperature and pressure. (Reproduced and modified from [239].)

### 8.2.1 Effect of Diluents on the Flammable Range of Air/Ammonia Mixtures

The inflammable limits of ammonia in air or oxygen-nitrogen mixtures, and particularly the effects of water vapor on these limits, were determined using a flame-quenching technique for determinations at atmospheric pressure and a dynamic bomb method at a pressure of ten atmospheres [240]. At atmospheric pressure, the flammability limits of ammonia in dry air were found to be 17.2 and 30.2 vol.-% ammonia, but these limits were found to narrow as the water vapor was increased until, at 10.8 vol.-%  $\text{H}_2\text{O}$  and 20.8 vol.-%  $\text{NH}_3$ , no flame could survive. With a dry oxygen-ammonia mixture, the lower limit was found to be 15.2 vol.-% ammonia. At ten atmospheres, the explosive limits of ammonia in dry air were found to be 16.9 and 28 vol.-%, and these limits were narrowed with addition of water vapor until, above 9 vol.-% water, no further explosion occurred. Nitrogen dilution in the flame gases of three rich  $\text{NH}_3/\text{O}_2/\text{N}_2$  flames had an effect on reaction kinetics [241].

### 8.2.2 Effect of Other Flammables on the Flammable Range of Air/Ammonia Mixtures

The Le Chatelier mixing rule can be applied to calculate the limits of flammability of mixtures of fuels with oxidizers such as oxygen or air. The predictive method gave only a rough approximation, deviating on either the safe side or the combustible side of the experimentally established limits when applying it to ammonia/fuel/air mixtures [242]. The flammable range of ammonia in oxygen or ammonia in air is widened substantially by the admixture of hydrogen [243] or methane [244]. Such mixtures may exist in the off-gas from ammonia production facilities. These flammable mixtures also once existed in the exhaust ducts from hydrazine-powered APUs on the STS Space Shuttle.

## 8.3 Autoignition Temperature of Air/Ammonia Combustion

The autoignition temperature of a stoichiometric mixture of ammonia with air is  $922\text{K} = 649^\circ\text{C}$ .

## 8.4 Electric-Spark Ignition Energy of Air/Ammonia Combustion

For the proposed use of ammonia as a fuel in internal combustion engines, the ignition energy required must be known. The ignition energy should also be known to evaluate the accidental ignition fire hazard in the vicinity of ammonia spills in air. Fortunately, the ignition energy, even for stoichiometric air/ammonia mixtures, is so high that it cannot be achieved by a typical electrostatic charge carried by a person that is not grounded. The ignition energy for air/ $\text{NH}_3$  mixtures is very high, at least 680 mJ for a stoichiometric mixture of air and  $\text{NH}_3$ . The hazard of accidental

ignition of air/ammonia mixtures by electrostatic charges is thus very low, much less than when working with hydrogen. However, air/ammonia/hydrogen mixtures such as those formed in the exhaust of hydrazine gas generators operating in air, are a potential explosion hazard.

The ignition energy required to ignite a stoichiometric GOX/ $\text{GNH}_3$  mixture is 680 mJ, much more than the 0.4 mJ required for igniting air/n-hexane vapor mixtures [237].

### 8.5 Fire Fighting of Air/Ammonia Fires

If for some odd reason a source of ammonia should have ignited, the fire is best fought with a strong water spray. Water spray will also be needed after the fire has been extinguished in order to absorb the unburnt ammonia and rinse the fire and spill site. Powder extinguishers are not suitable for ammonia fires because they are not as effective against unburnt ammonia as a strong water spray.

## 9 Properties of Ammonia Mixtures and Solutions

The unique properties of metal solutions in ammonia have attracted the interest of not only rocket propellant chemists, but scientists in general. There has even been an entire series of conferences devoted to free-electron and metal/ammonia solutions. The addition of lithium to ammonia has several purposes: it would make the solution hypergolic with nitric acid or dinitrogen tetroxide, increase the specific impulse, and lower the vapor pressure.

In 2014, searching the phrase “metal–ammonia solutions” in titles only in Google Scholar instantly produced 361 hits, and 51 of these were for lithium/ammonia solutions, obviously more than we can include in this book. See also [245, 246].

### 9.1 Lithium/Ammonia Solutions

In an early evaluation of ammonia, hydrazine, and hydrazine hydrate as rocket fuels, the potential use of lithium/ammonia solutions as fuels for WFNA or chlorine trifluoride was considered [247]. The vapor pressure of lithium/ammonia solutions is substantially lower than that of liquid ammonia.



### 9.1.1 Physical Properties of the Lithium/Ammonia System

Liquid ammonia has the unusual property that alkali metals dissolve in anhydrous ammonia and give up their free electron. The free electron imparts a deep blue color to the solution [248]. Physical chemical studies of dilute alkali metal/ammonia solutions indicated that the principal solution species are the ammoniated metal cation  $M^+$ , the ammoniated free electron  $e^-$ , the “monomer”  $M$ , the “dimer”  $M_2$ , and the “metal anion”  $M^-$ . The solution of alkali metals in liquid ammonia is reversible; if the ammonia is allowed to evaporate, alkali metals are left behind chemically unchanged in a highly reactive, finely dispersed form [249]. At higher concentrations, the surface of lithium solutions in ammonia assume a metallic copper-like sheen. Such solutions are potentially useful as rocket propellants, because the otherwise non-hypergolic liquid ammonia becomes hypergolic with a larger group of oxidizers and the specific impulse is increased due to the metal addition. Storage stability of these solutions may not be adequate for long-term missions [250].

In addition to theoretical interest in the nature of the solvated electron, these solutions also are unique reducing agents that have found applications in synthetic organic chemistry.

The physical properties of the lithium/ammonia system were investigated thoroughly by a group of investigators at the German Deutsche Versuchsanstalt für Luft- und Raumfahrt in Stuttgart [251].

In support of an investigation on the use of ammonia as a rocket propellant, the following properties of solutions of Li in  $NH_3$  have been studied [252]:

- the concentration of saturated solutions from 188 to 308 K (–85 to +35 °C);
- the variation of vapor pressure (up to 1500 mm Hg) with concentration and temperature;
- heats of vaporization, determined from vapor pressure versus temperature plots;
- densities from 203 to 278 K (–70 to +5 °C) and concentrations from 8.9 to 20.1 mol-% Li (the linear dependence of density on mol-% allowed extrapolation to higher and lower concentrations);
- corrosive action upon steel;
- variation of the rate of decomposition of saturated solutions with temperature.

#### Solubility of Lithium in Liquid Ammonia

The lithium concentration in a saturated solution decreases initially from about 21 mol-% at 188 K = –85 °C to 20.3 mol-% at 223 K = –50 °C, and then increases again to 21.5 mol-% at 308 K = +35 °C (Table 42).

#### Density of the Lithium/Ammonia System

The densities of lithium solutions in ammonia containing 8.9–20.1 mol-% Li at 203–278 K (–70 to +5 °C) are summarized in Table 43 and illustrated in Figure 42. While

**Table 42:** Solubility of lithium metal in liquid ammonia.

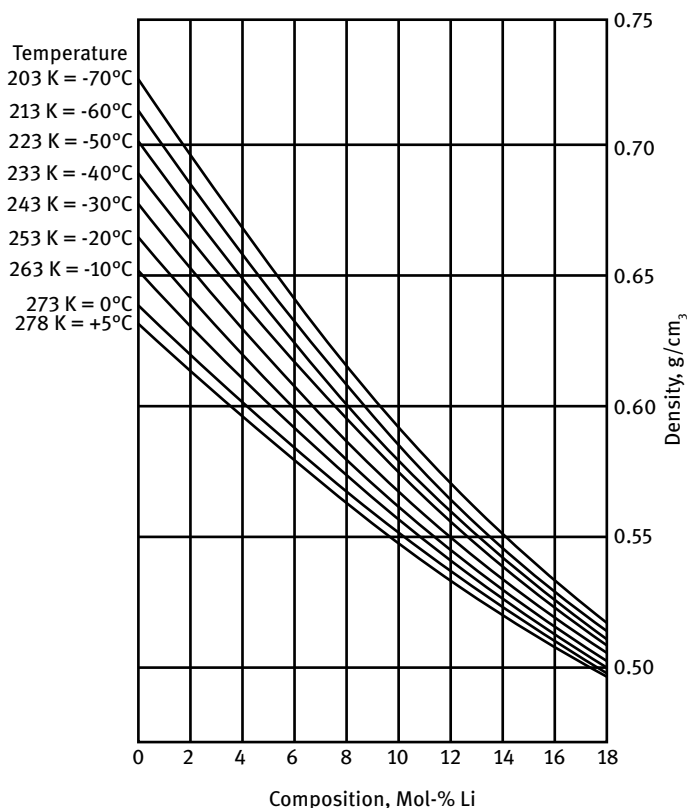
| Temperature |     | Saturation concentration of lithium |       |
|-------------|-----|-------------------------------------|-------|
| K           | °C  | Mass-%                              | Mol-% |
| 188         | -85 | 9.83                                | 21.10 |
| 193         | -80 | 9.72                                | 20.90 |
| 198         | -75 | 9.62                                | 20.72 |
| 203         | -70 | 9.56                                | 20.60 |
| 208         | -65 | 9.50                                | 20.49 |
| 213         | -60 | 9.47                                | 20.42 |
| 218         | -55 | 9.43                                | 20.36 |
| 223         | -50 | 9.42                                | 20.34 |
| 228         | -45 | 9.43                                | 20.36 |
| 233         | -40 | 9.46                                | 20.41 |
| 238         | -35 | 9.50                                | 20.49 |
| 243         | -30 | 9.56                                | 20.60 |
| 248         | -25 | 9.61                                | 20.69 |
| 253         | -20 | 9.64                                | 20.76 |
| 258         | -15 | 9.68                                | 20.83 |
| 263         | -10 | 9.72                                | 20.91 |
| 268         | -5  | 9.76                                | 20.98 |
| 273         | 0   | 9.79                                | 21.04 |
| 278         | 5   | 9.83                                | 21.10 |
| 283         | 10  | 9.86                                | 21.16 |
| 288         | 15  | 9.89                                | 21.22 |
| 293         | 20  | 9.93                                | 21.29 |
| 298         | 25  | 9.96                                | 21.35 |
| 303         | 30  | 10.00                               | 21.43 |
| 308         | 35  | 10.04                               | 21.50 |

Data source: [251,252]

**Table 43:** Density of solutions of lithium metal in liquid ammonia at 239.9 K (-33.2°C).

| Li, g  | NH <sub>3</sub> , g | Mol fraction Li | Density, g/cm <sup>3</sup> |
|--------|---------------------|-----------------|----------------------------|
| 0.2291 | 16.476              | 0.0331          | 0.639                      |
| 0.5545 | 22.452              | 0.0571          | 0.811                      |
| 0.5083 | 18.030              | 0.0713          | 0.597                      |
| 0.9170 | 18.813              | 0.1180          | 0.554                      |
| 0.9170 | 12.199              | 0.1557          | 0.523                      |
| 1.0697 | 13.821              | 0.1616          | 0.518                      |
| 0.9170 | 9.241               | 0.1958          | 0.498                      |
| 1.0697 | 8.895               | 0.2105          | 0.490                      |

Data source: [253].



**Figure 42:** Density isotherms of lithium/ammonia solutions as a function of lithium concentration. (Reproduced and modified from [251].)

most other slurries of metals in fuels will have higher densities than the fuel liquid, the opposite is the case with a solution of lithium in ammonia: the density of the solutions decreases with increasing lithium content.

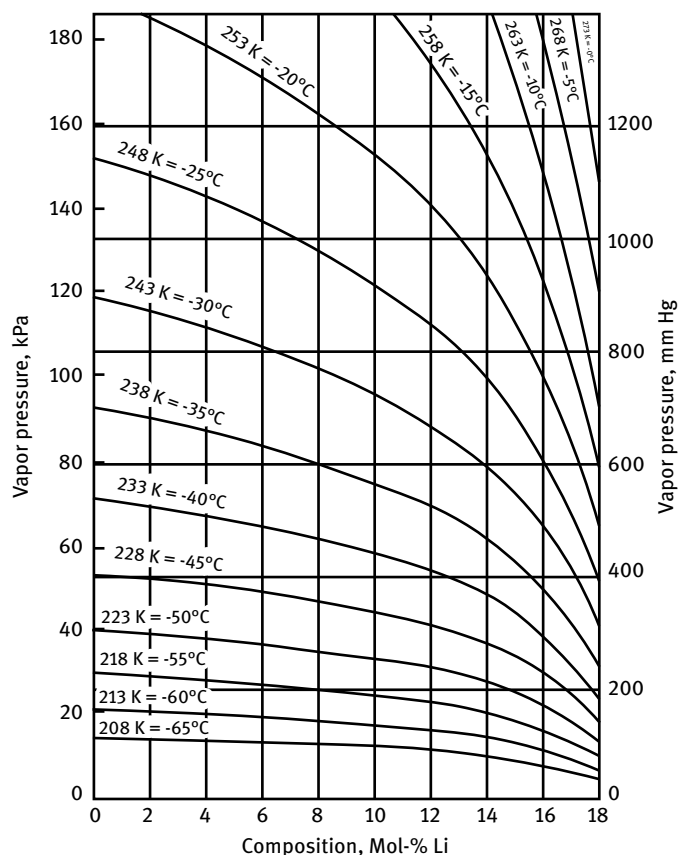
### Compressibility and Velocity of Sound of the Lithium/Ammonia System

The velocity of 10-MHz sound waves in lithium/ammonia solutions has been determined for 23 different metal concentrations in the temperature range 89–240 K [254]. By combining these data with the available density data, the adiabatic compressibility of these solutions could be determined. The compressibility was found to be a monotonic increasing function of the concentration. An analysis of the sound velocity revealed a change in the dependence on concentration at a concentration of 5 mol-%. This is the concentration at which the metal–non-metal transition occurs, and was interpreted as evidence for a “structure” change accompanying the Mott transition.

The compressibility of concentrated metal/ammonia solutions has been calculated by assuming the solutions to be binary alloys of solvated metal ions (including the first solvation layer as part of the ion) and ammonia [255]. The isothermal compressibility  $\kappa_T$  was computed from the structure factor, which was computed from the Ascroft adaptation of a model for hard spheres. In the absence of adequate data on  $\kappa_T$ , the results of the computation were compared to data on the adiabatic compressibility  $\kappa_S$ .

### Vapor Pressure of the Lithium/Ammonia System

The addition of lithium metal decreases the vapor pressure of ammonia significantly (Figure 43). The vapor pressure reduction with all solutions containing more than 3 mol-% Li is higher than what one would expect in accordance with Raoult's law.



**Figure 43:** Vapor pressure isotherms of lithium/ammonia solutions. (Reproduced and modified from [251])

Earlier investigators had found the vapor pressure of lithium/ammonia solutions as listed in Table 44.

**Table 44:** Vapor pressure of lithium/ammonia solutions.

| Lithium,<br>mass-% | Mol ratio<br>NH <sub>3</sub> : Li | Temperature |       | Vapor pressure |      |
|--------------------|-----------------------------------|-------------|-------|----------------|------|
|                    |                                   | K           | °C    | mm Hg          | kPa  |
| 11.32              | 3.60                              | 273.1       | 0     | 34.0           | 4.53 |
| 10.90              | 3.74                              | 240.4       | −32.7 | 3.4            | 0.45 |
| 10.89              | 3.75                              | 239.9       | −33.2 | 3.4            | 0.45 |
| 10.70              | 3.81                              | 209.6       | −63.5 | 1.1            | 0.15 |

Data source: [256]

Instead of vapor pressure, the boiling points of lithium/ammonia solutions at atmospheric pressure were measured as a function of lithium concentration, as summarized in Table 45. See also [257].

**Table 45:** Boiling points of lithium/ammonia solutions.

| Lithium concentration |        | Boiling point |       |
|-----------------------|--------|---------------|-------|
| Atom-%                | Mass-% | K             | °C    |
| 2.31                  | 0.95   | 240.0         | −33.1 |
| 3.17                  | 1.32   | 240.1         | −33.0 |
| 5.74                  | 2.42   | 240.4         | −32.7 |
| 8.72                  | 3.75   | 241.4         | −31.7 |
| 11.28                 | 4.93   | 243.3         | −29.8 |
| 16.04                 | 7.22   | 253.7         | −19.4 |
| 25.5 (saturated)      | 11.7   | 336           | +63   |

Data source: [258]

### Optical Properties of Lithium/Ammonia Solutions

Lithium dissolved in ammonia gives the solution a deep blue color. The absorption spectrum of lithium solutions in ammonia has a maximum of absorption at 6650–6700 cm<sup>−1</sup> (1492 nm). The spectra of all alkali metal solutions in ammonia are similar [259, 260].

### Thermal Conductivity of Lithium/Ammonia Solutions

Adding alkali metals to ammonia improves the thermal conductivity of the solution substantially, approaching the thermal conductivity of molten alkali metals.

The thermal conductivity of solutions of lithium, sodium, or potassium in liquid ammonia has been measured as a function of temperature and concentration [261]. The conductivity showed a strong dependence on concentration and rose with increasing concentration to values of 30–60 mW cm<sup>-1</sup> K<sup>-1</sup> at saturation. Pure ammonia has a conductivity of only 5 mW cm<sup>-1</sup> K<sup>-1</sup>. Two modes of heat transport, molecular and electronic, may have to be invoked to interpret the data. The molecular term followed a semi-empirical equation often used for insulating liquids. The electronic heat conductivity obeyed a Wiedemann–Franz law often used for solid metals, with a Lorenz number about 75% of the free-electron value.

### Electrical Conductivity of Lithium/Ammonia Solutions

With the solvated electron acting as a very fast carrier of electrical currents, it is of mostly theoretical interest to measure the electrical conductivity of lithium/ammonia solutions [262]. Measurements of electrical conductivities of Li/NH<sub>3</sub> and Cs/NH<sub>3</sub> solutions showed that temperature coefficients of conductivities became negative at higher concentrations and temperatures [238]. The electrical conductivity of solutions of lithium in liquid ammonia have been measured as a function of composition and temperature [263]. The transition from the semiconducting to the metallic state takes place in the intermediate concentration range, around 4.5 mol-% lithium.

Observations of the transport properties of several metallic metal/ammonia solutions indicated an electrical conductivity that rose sharply with increasing concentration of the metallic component [264]. It was attempted to explain this behavior by a model of independent scatterers, in this case dipolar scattering from ammonia molecules and scattering from solvated metal ion complexes. Numerical estimates of the cross-sections involved the details of the reduction of the corresponding potentials by the presence of electrons and dipoles. This required dielectric functions for a system of point dipoles and electrons.

### Thermodynamic Properties of the Lithium/Ammonia System

The heats of solution of Li, Na, and K metal in anhydrous ammonia at 298 K (25 °C) have been measured at concentrations down to 0.005 M [265, 266]. The solution of lithium in liquid ammonia is exothermic with 33.5 kJ/mol Li (8 kcal/mol). Dilution is endothermic, and the heat of dilution is greater in the presence of an added Na<sup>+</sup> ion.

### 9.1.2 Chemical Properties of the Lithium/Ammonia System

Ideally, ammonia should only serve as an inert solvent for the alkali metals, and all formation of metal amides is highly undesirable if the solutions are to be used as rocket propellants. However, alkali metals do slowly react with anhydrous ammonia even at room temperature [267].

The self-decomposition reaction of concentrated solutions of lithium in ammonia at atmospheric pressure was studied at various temperatures in polyethylene and in glass containers by observing the change in weight of the solution [268]. The reaction followed a first-order rate law and was apparently heterogeneous. An unusually large, negative value for the activation entropy and a relatively low activation energy were found for this reaction. Possible explanations for these results included the concepts that the solvated electron was involved in the decomposition reaction and that electron transfer occurred by a tunneling mechanism.

Isotopic substitution in neutron diffraction has been used to study the structure of saturated solutions of lithium and potassium in ammonia [269, 270]. Isotopic substitution of  $^*N$  by  $^{15}N$ , combined with difference analysis, showed that  $K^+$  acts as a “structure breaking” ion while  $Li^+$  acts as a “structure making” ion. It was found that lithium is tetrahedrally coordinated by ammonia molecules, at both 230 and 100 K. Potassium, on the other hand, is octahedrally coordinated at 160 K. A saturated metallic solution of lithium in ammonia contained 21 mol-% metal.

## 9.2 Ammonia/Hydrazine Mixtures

Ammonia and hydrazine are both hydronitrogens. Both are being used or have been used as rocket fuels. As close relatives of the same family of chemical compounds, they are totally miscible with each other over the entire range of compositions. Hydrazine can be added to ammonia to improve its hypergolic ignition with nitric acid or dinitrogen tetroxide as the oxidizer. Ammonia can be added to hydrazine to lower its freezing point and reduce its autodecomposition tendencies.

Mixtures of ammonia with hydrazine have unique features dominated by strong hydrogen bonding between the two (or several) molecules, although the interaction is not as strong as between ammonia and water or between hydrazine and water. Adding hydrazine to ammonia will lower the vapor pressure of ammonia and make it easier to handle. Adding ammonia to hydrazine will lower the exhaust temperature when hydrazine is used as a monopropellant, and will also lower the freezing point, thus requiring less heater power in a satellite to keep the hydrazine in the propellant tank from freezing. However, in a monopropellant application, adding ammonia to hydrazine will lengthen the ignition delay and shorten the catalyst life when many startups are needed. Ammonia/hydrazine mixtures have some attractive features but have not been used in flight applications up to now [271].

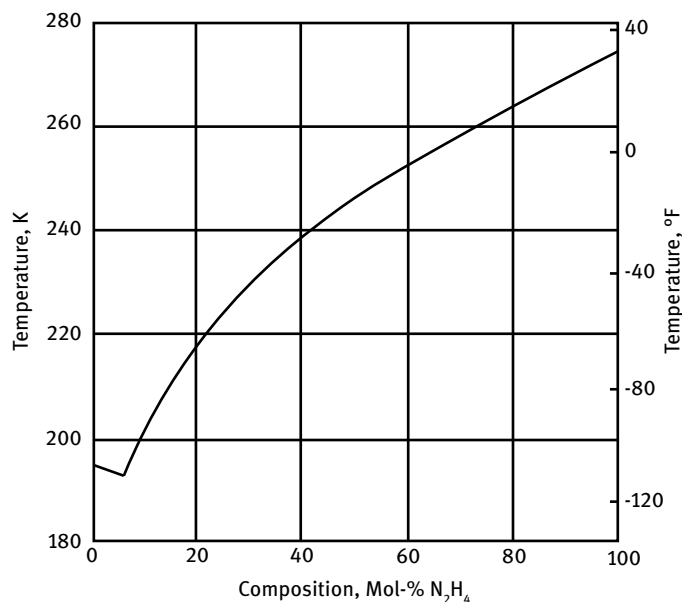
### 9.2.1 Physical Properties of the Ammonia/Hydrazine System

The physical properties of ammonia/hydrazine mixtures were measured thoroughly over a wide range of ratios and temperatures. These mixtures are of interest as hypergolic fuels with WFNA, RFNA, or NTO because they would be more hypergolic than ammonia alone and are more economical fuels and better regenerative coolants than pure hydrazine. They are also of interest as monopropellants when the temperature of hot gases from decomposing 100% hydrazine is too hot for turbine blades or expulsion bladders in gas generator applications.

Ammonia/hydrazine mixtures should be discussed only at one location in this book, either under ammonia or under hydrazine. It has been decided to discuss them at the first possible location, which is here under ammonia. A short reference in *Encyclopedia of Liquid Fuels*, chapter “Hydrazine,” will direct readers back to this location.

#### 9.2.1.1 Freezing Point of the Ammonia/Hydrazine System

The freezing point diagram of the binary hydrazine/ammonia system is illustrated in Figure 44. The lowest melting composition is a eutectic with 92.64 mol-% ammonia melting at approximately 193 K [272, 273].

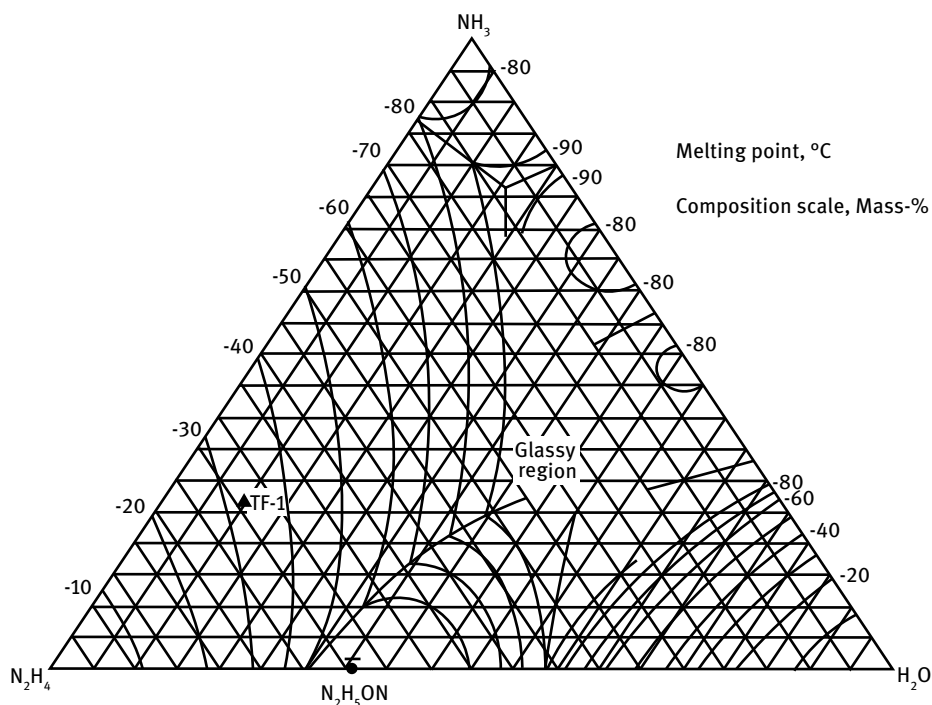


**Figure 44:** Freezing point diagram for the binary  $NH_3/N_2H_4$  system. (Reprinted and modified from [272], with permission from ©1957 American Chemical Society; permission conveyed through RightsLink.)



### 9.2.1.2 Freezing Point of the Ammonia/Hydrazine/Water System

The freezing points of the ternary ammonia/hydrazine/water system are illustrated in Figure 45. There is a range where the liquid does not crystallize, but turns into a viscous, glassy substance. It is not possible to determine freezing points in this area [22].



**Figure 45:** Melting point of the ternary  $\text{NH}_3$ - $\text{N}_2\text{H}_4$ - $\text{H}_2\text{O}$  system. (Reproduced and modified from [22].)

The ternary  $\text{N}_2\text{H}_4/\text{NH}_3/\text{H}_2\text{O}$  system has been investigated in the temperature range 183–233 K [274]. The isotherms at 233, 221, 190, and 182 K have been established over the entire range of compositions. Seven solid phases were identified:  $\text{N}_2\text{H}_4$ ,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ,  $\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $2\text{NH}_3 \cdot \text{H}_2\text{O}$ ,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , and  $\text{H}_2\text{O}$ . Below 193 K, anhydrous hydrazine precipitated from solutions starting out with hydrazine hydrate and ammonia. This is a possible method to make anhydrous hydrazine from hydrazine hydrate.

### 9.2.2 Density of Ammonia/Hydrazine Mixtures

The density of hydrazine/ammonia mixtures at  $229 \pm 1$  K is summarized in Table 46 and can be represented by

$$\rho\left(\frac{\text{g}}{\text{cm}^3}\right) = 0.6983 + 0.002837X$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $X$  is the hydrazine concentration in mass-%. The density at 293 K can be calculated from

$$\rho = 1.014557 - 5.5688 \times 10^{-3}X + 1.7735 \times 10^{-5}X^2 - 2.37 \times 10^{-8}X^3$$

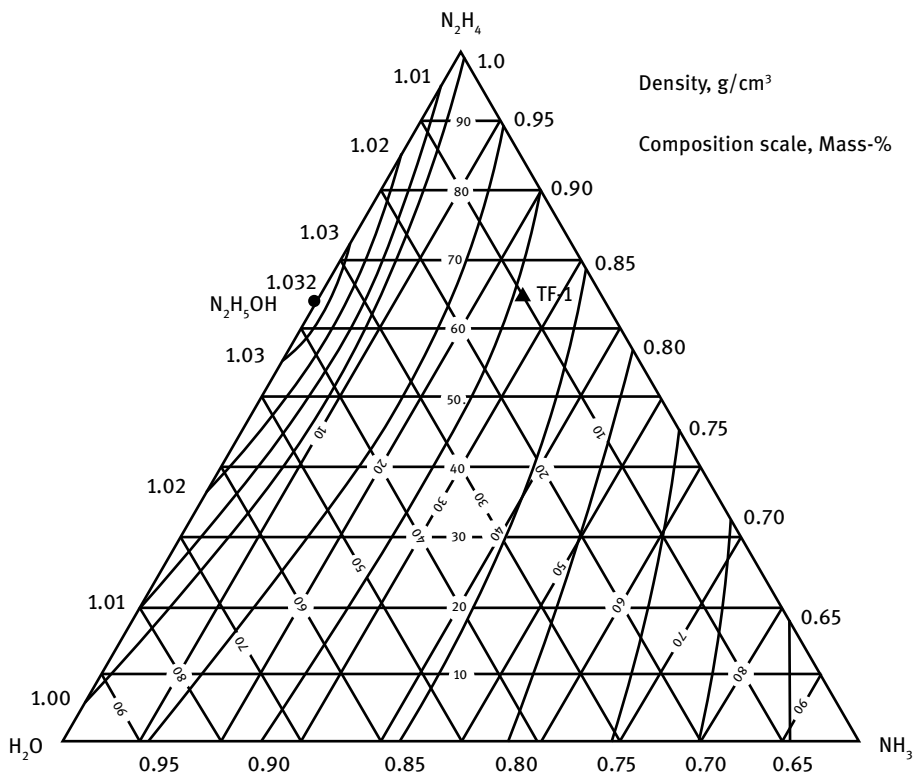
where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $X$  is the ammonia concentration in mass-%. Density data for ammonia/hydrazine mixtures are listed in Table 46.

**Table 46:** Density of ammonia/hydrazine mixtures.

| Ammonia | Hydrazine <sup>a</sup> | Temperature |       | Density                | References |
|---------|------------------------|-------------|-------|------------------------|------------|
| Mass-%  | Mass-%                 | K           | °C    | $\text{g}/\text{cm}^3$ |            |
| 100     | 0                      | 228.1       | -45   | 0.6986                 | [275]      |
| 92.6    | 7.4                    | 227.6       | -45.5 | 0.7200                 | [275]      |
| 89.1    | 10.9                   | 226.6       | -46.5 | 0.7280                 | [275]      |
| 87.0    | 13.0                   | 226.1       | -46.0 | 0.7346                 | [275]      |
| 84.1    | 15.9                   | 229.1       | -44.0 | 0.7442                 | [275]      |
| 77.8    | 22.2                   | 229.6       | -43.5 | 0.7596                 | [275]      |
| 73.5    | 26.5                   | 230.1       | -43.0 | 0.7749                 | [275]      |
| 40.1    | 59.9 <sup>a</sup>      | 235.2       | -37.9 | 0.9036                 | [276]      |
| 40.1    | 59.9 <sup>a</sup>      | 250.1       | -23   | 0.8877                 | [276]      |
| 40.1    | 59.9 <sup>a</sup>      | 265.3       | -7.8  | 0.8724                 | [276]      |
| 40.1    | 59.9 <sup>a</sup>      | 279.1       | 6.0   | 0.8562                 | [276]      |
| 40.1    | 59.9 <sup>a</sup>      | 292.9       | 19.8  | 0.8416                 | [276]      |
| 40.1    | 59.9 <sup>a</sup>      | 306.1       | 33    | 0.8284                 | [276]      |

<sup>a</sup> Hydrazine used for this test was not pure. It contained 4.5% water to start with.

The density of ternary hydrazine/ammonia/water mixtures increases fairly uniformly from the ammonia corner of the ternary diagram to the hydrazine-water side of the triangle (Figure 46).



**Figure 46:** Density of ternary hydrazine/ammonia/water mixtures at 298 K (77 °F). (Reproduced and modified from [163].)

### 9.2.2.1 Vapor/Liquid-Phase Composition of Ammonia/Hydrazine Mixtures

The liquid/vapor phase equilibrium compositions in the ammonia/hydrazine system have been extensively investigated over the course of several decades, but no applications of such mixtures as monopropellants have materialized [277–283].

Sometimes ammonia/hydrazine mixtures are obtained during the preparation of anhydrous hydrazine in the laboratory and have to be separated. This is one of the reasons why these mixtures are discussed in a little more detail here. The vapor-phase composition of  $\text{NH}_3/\text{N}_2\text{H}_4$  mixtures must be known in order to decide if complete separation by fractional distillation can be achieved. Unlike the  $\text{N}_2\text{H}_4/\text{H}_2\text{O}$  system, no azeotropes are formed in the  $\text{NH}_3/\text{N}_2\text{H}_4$  system, and separation is easy because of the disparate boiling points.

The earliest vapor pressure measurements were those listed in Table 47. The mixtures chosen were those that were in equilibrium with solid hydrazine at the temperature stated. The author also has an interesting method to represent vapor pressure data of binary systems and their dependence on temperature in the form of an isomet-

**Table 47:** Vapor pressure of equilibrium-melting ammonia/hydrazine mixtures.

| Temperature<br>K | Vapor pressure |       | Hydrazine<br>Mass-% |
|------------------|----------------|-------|---------------------|
|                  | kPa            | mm Hg |                     |
| 193              | 5.31           | 40    | 13                  |
| 203              | 10.36          | 78    | 19.5                |
| 213              | 19.27          | 145   | 29.1                |
| 223              | 33.5           | 252   | 39.7                |
| 233              | 52.5           | 395   | 51.0                |
| 243              | 74.7           | 562   | 63.8                |
| 248              | 83.7           | 630   | 69.8                |
| 253              | 89.7           | 675   | 76.0                |
| 258              | 90.0           | 677   | 81.6                |
| 263              | 82.4           | 620   | 87.6                |
| 268              | 62.5           | 470   | 92.6                |
| 273              | 23.25          | 175   | 98.0                |
| 274              | 13.95          | 105   | 98.6                |

Data source: [273]

ric view of a 3-D vapor pressure surface (instead of a vapor pressure curve in an X-Y graph).

Total vapor pressure, liquid-phase composition, and vapor-phase composition of ammonia/hydrazine mixtures were measured for molecular fractions of  $x_{\text{NH}_3}$  from 0.2 to 0.95 and temperatures from 361.6 to 398 K (from 88.5 to 124.9 °C) [279]. Data could not be obtained with liquid compositions greater than 80%  $\text{N}_2\text{H}_4$  because of considerable hydrazine decomposition in the steel autoclave used. Because of relatively small concentrations of hydrazine in the gas phase, it was assumed that the pressure–fugacity relationships for ammonia alone could be applied to the gas mixtures. The values reported for the total experimental vapor fugacity were calculated from the measured total vapor pressure by calculating a virial coefficient called  $B_{\text{mix}}$ :

$$B_{\text{mix}} = N_1^2 + 2N_1N_2 \frac{B_1 + B_2}{2} + N_2^2 B_2$$

where  $N_1$  and  $N_2$  are the mol fractions of the two compounds. Since  $B_{\text{mix}}$  and  $B(\text{NH}_3)$  are known,  $B(\text{N}_2\text{H}_4)$  was calculated from the above equation and an EOS

$$pV = nRT + Bp$$

The virial coefficients for hydrazine thus obtained are listed in Table 48.

Activities and activity coefficients for hydrazine in dilute hydrazine solutions in liquid ammonia could not be calculated because the vapor composition of dilute hydrazine solutions in ammonia could not be measured. Partial fugacities of hydrazine for solutions containing low hydrazine concentrations were not in accordance with Henry's law, although the partial fugacities of ammonia in these solutions were in ac-

**Table 48:** Virial coefficients for hydrazine in ammonia/hydrazine mixtures.

| Temperature, K | Virial coefficient, L/mol |
|----------------|---------------------------|
| 363            | 2.14                      |
| 368            | 3.49                      |
| 373            | 3.58                      |
| 383            | 4.32                      |
| 393            | 4.20                      |

Data source: [279]

cordance with Raoult's law. The activity coefficients for ammonia indicated that ammonia is behaving in accordance with Raoult's law up to 15 mol%  $\text{N}_2\text{H}_4$ . Accordingly, Henry's law should be obeyed in the same range. This trend is caused by association of hydrazine molecules in solution. At higher  $\text{N}_2\text{H}_4$  concentrations, the association in the liquid phase becomes more pronounced.

Since hydrazine is not associated in the vapor phase, the fugacity of hydrazine is directly proportional to the concentration of the monomer in the solution. The measurements by Drago and Sisler were eventually extended over the entire range of concentrations and also to lower temperatures (298 and 373 K) [281, 282].

Previous literature contained only hydrazine/ammonia vapor pressure data for the range from 361 to 398 K, but no data on the range of more practical interest were available prior to 1967. Additional measurement results obtained on seven mixtures with ammonia mol fractions from 0.1547 to 0.9162 can be represented by the following curve-fit equation [280]:

$$\log p_v = A + BT$$

where  $p$  is the vapor pressure in MPa and  $T$  is the absolute temperature in K. The coefficients  $A$  and  $B$  for this equation are listed in Table 49.

Vapor pressures of a 63.8% hydrazine (only 96.5% pure hydrazine was available at the time)/36.2% ammonia blend are summarized in Table 50.

**Table 49:** Vapor pressure coefficients for ammonia/hydrazine mixtures.

| Mol fraction $\text{NH}_3$ | A       | B         |
|----------------------------|---------|-----------|
| 0.1547                     | 3.49852 | -1296.960 |
| 0.3415                     | 3.62369 | -1198.108 |
| 0.4790                     | 4.08216 | -1293.257 |
| 0.6429                     | 3.91131 | -1215.820 |
| 0.7638                     | 3.97489 | -1214.671 |
| 0.8224                     | 3.92213 | -1187.159 |
| 0.9162                     | 4.04638 | -1210.375 |

Data source: [280]

**Table 50:** Vapor pressure of a 63.8% hydrazine (only 96.5% N<sub>2</sub>H<sub>4</sub>)/36.2% ammonia mixture.

| Temperature |       | Vapor pressure |       |
|-------------|-------|----------------|-------|
| °C          | K     | kPa            | mm Hg |
| 0.0         | 273.1 | 274            | 2053  |
| 14.0        | 287.1 | 432            | 3242  |
| 30.0        | 303.1 | 684            | 5129  |
| 50.0        | 323.1 | 1156           | 8670  |
| 70.0        | 343.1 | 1873           | 14050 |

Data source: [276]

These data can be expressed by

$$\log p = 7.413 - \frac{1120}{T}$$

where  $p$  is the pressure in mm Hg and  $T$  is the temperature in K. The solubility of ammonia in hydrazine was determined at 298, 303, 313, 323, 333, and 343 K [278]. When plotting the solubility against partial pressures of ammonia for the various temperatures, the otherwise straight lines showed a slight curvature as the pressures approached atmospheric pressure, indicating a slight deviation from Henry's law. At higher temperatures, this deviation became smaller until, at 343 K, the solubility almost obeyed Henry's law over the entire pressure range studied (4–95 kPa).

The solubility of ammonia in hydrazine could also be expressed in terms of the Bunsen absorption coefficient  $\alpha$  and the Ostwald coefficient for solubility  $L$ . The Bunsen coefficient is defined as the volume of gas reduced to 273 K and 1 atm (101 kPa = 14.686 psia), dissolved by unit volume of solvent at the temperature of the experiment at a partial pressure of the gas of 1 atm (101 kPa = 14.686 psia). The Ostwald coefficient of solubility is defined as the volume of gas, measured under the temperature and pressure at which the gas dissolves, taken up by unit volume of the liquid. It is related to the Bunsen coefficient by  $L = \alpha/273$ . Table 51 gives a summary of these two

**Table 51:** Solubility coefficients of ammonia in hydrazine.

| Temperature |     | Bunsen coefficient | Ostwald coefficient |
|-------------|-----|--------------------|---------------------|
| K           | °F  | $\alpha$           | $L$                 |
| 298         | 77  | 57.71              | 62.99               |
| 303         | 86  | 49.56              | —                   |
| 313         | 104 | 37.44              | —                   |
| 323         | 122 | 27.78              | —                   |
| 333         | 140 | 20.92              | 25.52               |
| 343         | 158 | 16.49              | 20.72               |

Data source: [280]

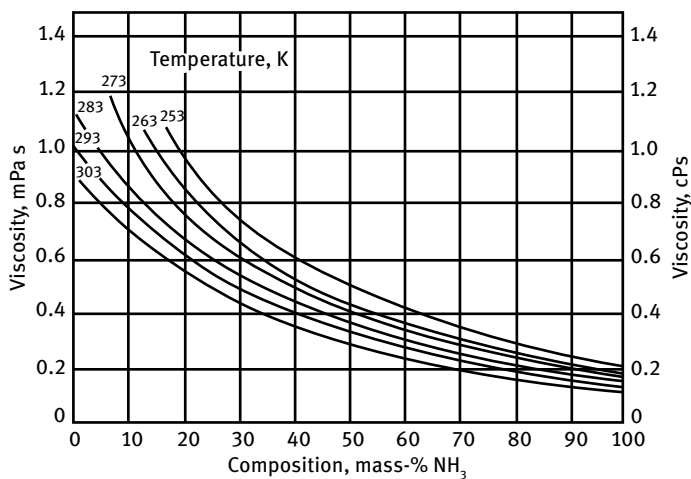
solubility coefficients. If one plots  $\log L$  versus  $1/T$  (reciprocal absolute temperature), one obtains a straight-line relationship. The heat of solution of ammonia in hydrazine can be derived from the slope of this curve. The straight line indicates that the heat of solution is not a function of the temperature in the range studied.

### 9.2.2.2 Vapor-Phase Composition of Monomethylhydrazine (MMH)/Ammonia and UDMH/Ammonia Mixtures

Deviations from Henry's law constants were listed for ammonia both above and in liquid hydrazine, MMH, and UDMH. These were eventually used to calculate the heat of solution of ammonia in these liquids. At 298 K and 1.2207 atm total pressure, the equilibrium mol fraction ammonia in the liquid is 0.0975 and Henry's constant  $K = X/f$  is 0.0808. Surprisingly, ammonia is less soluble in hydrazine than in UDMH or MMH. The relative solubility in the two methylhydrazines is as expected, with ammonia being more soluble in MMH than UDMH.

### 9.2.2.3 Viscosity of Ammonia/Hydrazine Mixtures

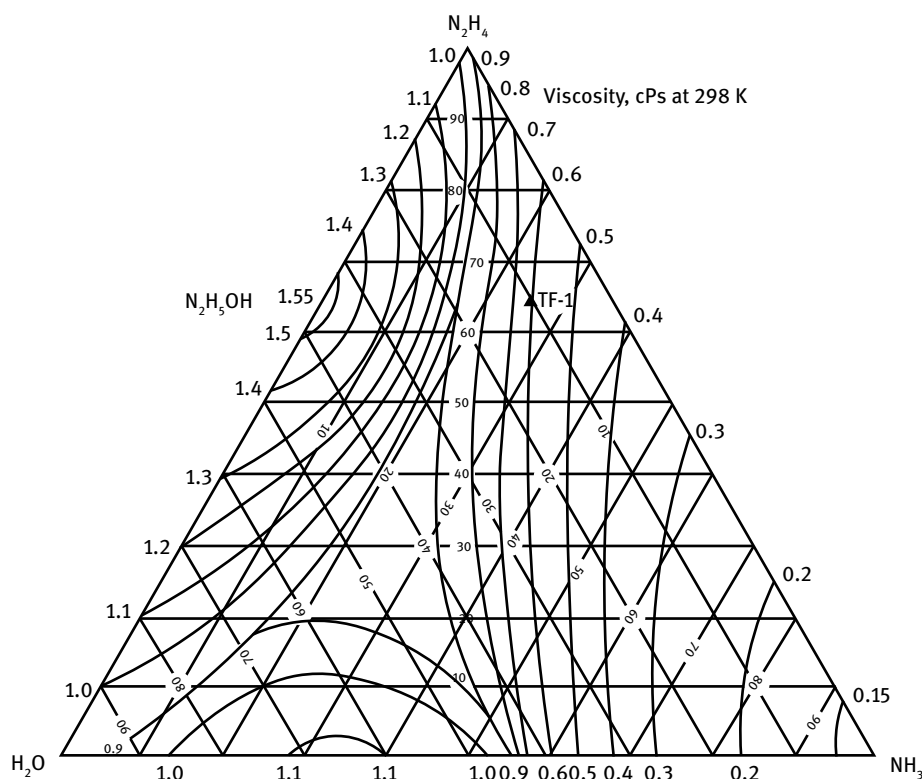
The viscosity of hydrazine/ammonia mixtures has been determined at six different temperatures over the entire range of compositions [280]. The data illustrated in Figure 47 were obtained using a falling sphere viscometer modified for operation at high fluid pressures.



**Figure 47:** Viscosity of ammonia/hydrazine mixtures. (Reproduced and modified from [280].)

### 9.2.2.4 Viscosity of Ammonia/Hydrazine/Water Solutions

Ternary ammonia/hydrazine/water solutions have been evaluated as monopropellants and as fuels for automobiles with reciprocating internal combustion engines. Viscosities of ternary ammonia/hydrazine/water solutions are illustrated in Figure 48.



**Figure 48:** Viscosity of ammonia/hydrazine/water ternary fuel blends. (Reproduced and modified from [163])

### 9.2.3 Chemical Properties of Ammonia/Hydrazine Mixtures

Ammonia/hydrazine mixtures can be analyzed by low-temperature thermogravimetry [275]. Gas mixtures of ammonia and hydrazine at low pressures were analyzed by first completely decomposing the hydronitrogens in an arc discharge and then analyzing the nitrogen/hydrogen mixture by mass spectrometry [284].



### 9.3 Other Fuel Mixtures with Ammonia

Because ammonia is a very cheap fuel with a chemical composition similar to that of hydrazine, a very desirable (but quite expensive) rocket propellant, there have been attempts to improve its hypergolic ignition with nitric acid or  $N_2O_4$  oxidizers by adding hypergolizing additives.

Other additives were aimed at improving the specific impulse, regardless of their ability to aid hypergolic ignition. One of the most promising additives is acetylene (ethyne).

#### 9.3.1 Ammonia/Acetylene Fuel Mixtures

In 2012, it was reported that the Russian rocket engine manufacturer Energomash had started development of a new rocket engine which could vastly reduce the cost of rocket launches and avoid the need to produce cryogenic hydrogen for fuel. Instead, the rocket was described as using “a completely novel fuel mixture of acetylene and ammonia (*atsetam*).” Officials expected to launch the new rocket in 2017 or 2018 “dependent on funding.” However, when the Internet and other sources were checked eight years later, there had been no additional announcements on eventual progress made in this development. The new rocket was expected to be around 30% more efficient than existing designs, working on a fuel mixture of acetylene and ammonia which is 20 times cheaper than hydrogen; a kilogram of hydrogen costs about 2000 rubles (\$67) and a kilo of *atsetam* can be made for 100 rubles (\$3.35), Energomash’s Director of Innovative Technology, Anatoly Likhvantsev, told the *Izvestiya* newspaper. The new *atsetam* engine will be assembled on the basis of the RD-161 oxygen and kerosene engine which has a successful history in hundreds of launches. Images of the engine shown with a news release reminds one of the bulbous design of the A-4 (V2) engine used in Germany in 1943.

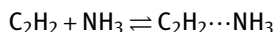
The exact parameters were to be determined during tests which began in 2012 and were supposed to last for about three years. Once the optimal ratio of acetylene and ammonia is found (in which fuel will be sufficiently powerful without exploding too easily), the designers plan to specify the parameters of the engine. According to preliminary calculations, the *atsetam* engine will not require major structural changes to be made to existing rocket motors since the physical properties of *atsetam* do not differ much from those of kerosene.

Ammonia and acetylene are miscible over the entire range of compositions. Ammonia is a protonophilic compound of average basicity, while acetylene is a proton-donor compound with a weak acid character. The hydrogen forming the hydrogen bond between the two molecules comes from the acetylene, not from the ammonia, and extends from the acetylene molecule to the free-electron pair on the nitrogen atom. The spectral analysis revealed that acetylene binds to ammonia through a  $C-H\cdots N$  weak hydrogen bond to form a  $C_{3v}$  symmetric top, consistent with

the previous microwave and IR spectroscopic studies at 3  $\mu\text{m}$ . Acetylene/ammonia system shows small negative deviations from Raoult's law. Such deviations, as foreseen, increase as the temperature decreases and have to be ascribed to ammonia/acetylene interactions of both the chemical and physical type.

Prior to considering them as a rocket fuel, ammonia/acetylene mixtures were used as a solvent for acetylene in organic synthesis reactions where the use of undiluted acetylene might constitute an undue explosion hazard [285].

The possibility of acid–base interactions between acetylene and ammonia lead to the formation of a complex by hydrogen bonding according to the equilibrium equation

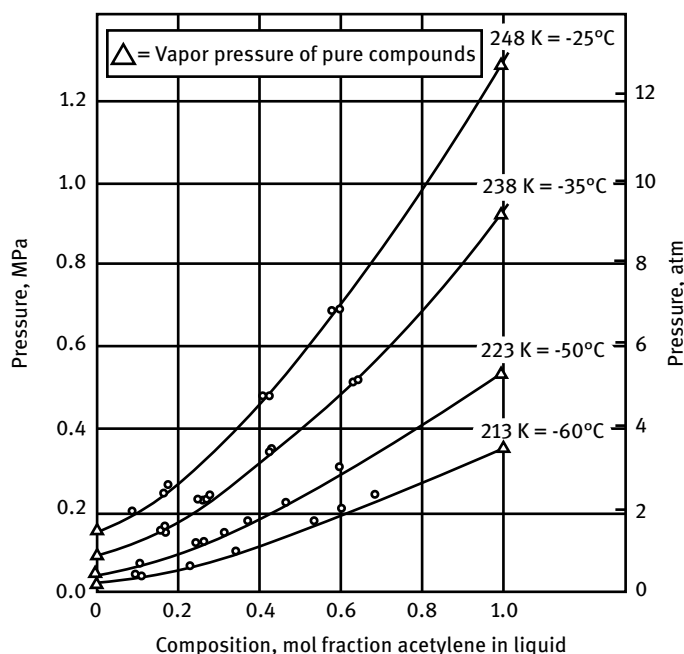


for which an equilibrium constant in the temperature range 323–423 K (50–150 °C) has been calculated.

Vapor–liquid equilibrium data of the acetylene/ammonia system for seven isotherms in the ranges 213–298 K (–60 to 25 °C) and 0.1–3.24 MPa (1–32 atm) were measured and interpreted according to the thermodynamics of associated systems [286]. It was shown that thermodynamic consistency could be observed by assuming a bimolecular complex formation between acetylene and ammonia. Equilibrium constants for this complex in the liquid phase have been derived and related to the corresponding gas phase values known from the literature. Figure 49 shows the vapor pressure isotherms in the ammonia/acetylene system in the 248–213 K (–25 to –60 °C) range. Vetere, Cojutti, and Scaramucci [286] include additional charts for higher temperature ranges. The curvature indicates a deviation from Raoult's law often observed with the formation of compounds or close associates. The acetylene/ammonia system shows small negative deviations from Raoult's law. Such deviations increase as the temperature decreases.

The Vetere, Cojutti, and Scaramucci publication also contains data on the equilibrium constant of the associate–product formation between ammonia and acetylene as a function of temperature, also in comparison to the dimerization of ammonia in the gas phase [286]. The equilibrium constant for  $\text{NH}_3\text{—C}_2\text{H}_2$  adduct formation is bigger than the equilibrium constant for ammonia dimerization. The enthalpy of reaction of adduct formation is  $\Delta H_0 = -9247 \pm 1255 \text{ J/mol}$  ( $-2210 \pm 300 \text{ cal/mol}$ ).

Volumetric data for gaseous ammonia/acetylene mixtures have been analyzed to obtain second virial coefficients as a function of temperature and composition [287]. From the pure-component virial coefficients of ammonia and acetylene, EOS parameters were obtained and used to calculate the physical contributions to the second cross-virial coefficients. The difference between the experimental coefficient and that calculated from the physical contribution can be attributed to chemical interaction, or complex formation, between the two molecules. Chemical equilibrium constants indicated a very weak hydrogen bond formation between the nitrogen atom in the ammonia and the hydrogen atom in acetylene. The concave curvature of the lines in



**Figure 49:** Vapor pressure isotherms of ammonia-acetylene mixtures. (Reprinted and modified from [286], with permission from ©1975 Elsevier; permission conveyed through RightsLink.)

a graph of second virial coefficients of ammonia/acetylene mixtures indicated strong compound formation in the middle of the mixture range, in particular at low temperatures. See also [288–291].

It was shown that thermodynamic consistency could be observed by assuming the formation of a bimolecular complex between acetylene and ammonia. Equilibrium constants for this complex in the liquid phase have been derived and related to the corresponding gas phase values known from the literature.

Interestingly, from a standpoint of theoretical chemistry, ammonia and acetylene form an adduct where the two molecules are linked together by hydrogen bonding [292]. At low temperatures, the two gases form co-crystals. Ammonia/acetylene fuel mixtures had been burned with oxygen in the laboratory, but no rocket engine tests were documented prior to the Russian studies.

The theoretical rocket performance of LOX/NH<sub>3</sub>-C<sub>2</sub>H<sub>2</sub> combinations was calculated [293]. We are looking forward to reports that this new propellant combination has actually flown.

### 9.3.2 Hypergolization of Ammonia by the Addition of Alkali- or Earth Alkaline Metals

Dilute solutions of alkali metals in ammonia electrons are localized in cavities in the solvent, and their thermodynamic and transport properties are very similar to those of dilute solutions of strong electrolytes. At higher concentrations, the properties deviate markedly from those of electrolyte solutions and approach those of a liquid metal.

Experiments at NASA have shown that even very small amounts of lithium or calcium dissolved in ammonia will hypergolize its reaction with  $\text{N}_2\text{O}_4$  (NTO) or  $\text{N}_2\text{O}_3/\text{N}_2\text{O}_4$  (MON) [294, 295]. Because the solutions are not storable, in many cases, it was sufficient to allow the propellant to flow over a chunk of lithium or calcium metal on its way into the rocket engine. This brief contact dissolved sufficient metal to make the ammonia hypergolic. The lithium or calcium content of the liquid ammonia will not only facilitate ignition, but also assures more stable combustion and avoids combustion pressure instabilities even after the engine has started. By adequately sizing the geometry of the metal grain in the cartridge (similar to a hybrid grain), the metal concentration in the ammonia leaving the cartridge can be kept fairly constant even as the grain surface recedes. Ammonia used for this purpose must be completely water-free because metal hydroxides are insoluble and will clog the injector orifices.

Based on the NASA tests, lithium is preferable to calcium for the hypergolization of ammonia. As far as performance is concerned, the type of metal makes little difference because only a small percentage of metal is dissolved in the fuel.

Other organizations have patented the application of metalized ammonia as a rocket propellant in combination with WFNA, RFNA, mixed acid, or hydrogen peroxide, using an alkaline earth metal (calcium or strontium) in concentrations ranging from 0.01 mass-% all the way to saturated solutions [296].

Metallic calcium dissolves in liquid ammonia, similar to the more widely investigated lithium/ammonia solutions. The viscosity of concentrated solutions of calcium in liquid ammonia was determined with solutions containing 3.4–8.9 mol-% calcium at temperatures from 233 to 213 K [297].

### 9.3.3 Hypergolization of Ammonia by Addition of Metal Hydrides

Some metal hydrides will react with ammonia forming hydrogen and metal amides, but some complex hydrides such as lithium borohydride instead will form ammoniates, some of which are solids at room temperatures. Lithium borohydride  $\text{LiBH}_4$  forms ammoniates that contain one, two or three molecules of ammonia in the solvate sphere, melting at 325, 284 or 312 K (52, 11 or 30 °C), respectively. Solutions of these ammoniates in liquid ammonia lower the vapor pressure of ammonia substantially, such that the vapor pressure of a solution containing >30%  $\text{LiBH}_4$  is <1 bar. Such solutions are hypergolic with either WFNA or  $\text{H}_2\text{O}_2$  [108].

### 9.3.4 Hypergolization of Ammonia by Addition of Hypergolic Fuels

In addition to lithium, a number of other additives have been tested to make ammonia hypergolic with common hypergolic oxidizers. Of all the mixtures, the mixture of ammonia with hydrazine has received the most attention and has been tested in several rocket engines with different oxidizers. Hydrazine and ammonia are chemically similar and are miscible over the entire range of compositions. Hydrazine/ammonia mixtures will be discussed in more detail in the hydrazine chapter (see volume 2, chapter “Hydrazine”).

Ammonia is completely miscible with UDMH, MMH, triethylamine, and methylamines. At least 25% UDMH is required to make ammonia hypergolic with WFNA.

### 9.3.5 Ammonia/Alkanol Fuel Mixtures

Ammonia and methanol are miscible over the entire range of mixture ratios. An ammonia/methanol mixture would be a very economical rocket fuel, with good regenerative cooling properties in bipropellant engines. The addition of methanol lowers the vapor pressure of ammonia [298], similar to the effect of adding water. The heat transfer properties of ammonia/methanol mixtures have been studied as an example of molecular simulation computational chemistry models [299]. Ammonia can also be absorbed in ethanol.

## 10 Applications of Ammonia as an Energy Carrier

Many applications of chemicals that were first developed for the space program later found applications in other sectors of the industry. The alternative energy and alternative energy carrier programs benefit from the information that is now available on energy sources and energy carriers and derived from the space program. Some of the prospective uses of ammonia are discussed here.

### 10.1 Ammonia for Internal Combustion Engines

There have been many attempts to use ammonia as a fuel in reciprocating internal combustion engines. Ammonia/air mixtures do not ignite very readily, at least not as readily as gasoline/air mixtures. Thus, many additives have been evaluated to improve the ignition characteristics of ammonia in combustion engines. These include hydrazine, alkylhydrazines, 2-hydroxyethylhydrazine, boranes, alkylboranes, and borane–amine complexes [300]. There is an organization that promotes the use of ammonia as automotive fuel, the  $\text{NH}_3$  Fuel Association [301]. The advantage of ammonia as an automotive fuel would be that it does not emit climate-changing carbon dioxide when it is burned. A ternary fuel, designated TF-1, consisting of

64% hydrazine, 10% ammonia, and 26% water, has been tested in a stationary internal combustion engine and proposed as an environmentally friendly (i.e. no CO<sub>2</sub> emissions) alternative to gasoline [2].

## 10.2 Ammonia as a Storage Medium for Excess Energy

Developers around the world are looking at using ammonia as a form of energy storage, essentially turning an ammonia storage tank into a very large chemical energy storage battery [302].

In the UK, Siemens is building an “all-electric ammonia synthesis and energy storage system.” [303]. In the Netherlands, Nuon’s is studying the feasibility of power to ammonia conversion “to convert high amounts of excess renewable power into ammonia, store it and burn it when renewable power supply is insufficient.” The design of installations like this may benefit from the experience gained with ammonia as a rocket propellant.

There are several studies on the design and performance of a grid-scale ammonia energy storage system. Ammonia is being examined as an energy storage system for integrating intermittent renewables on the utility scale [304].

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# Aromatic Amines

## Introduction

*Encyclopedia of Liquid Fuels* contains three chapters on amines, the current chapter on “Aromatic Amines,” a chapter on “Aliphatic Amines,” and a very large chapter on “Heterocyclic and Heterocycloaliphatic Amines.” Amines are used as rocket fuels and as raw materials for the synthesis of other fuels and energetic compounds. A different type of amine are the nitramines described in the chapter “Nitramines.”

## 1 Aromatic Amines

Aromatic amines, also called arylamines, contain a benzene ring with one or more amino and potentially other groups attached to the ring. The main member of this family of rocket fuels is aniline, aminobenzene, a primary amine, which was used as a rocket fuel either by itself or in a mixture with furfuryl alcohol in the early days of liquid rocket experimentation. Other compounds of interest for rocket propellant formulations are stabilizers for double-base solid propellants based on a secondary amine, diphenylamine. Most organic chemistry books and many encyclopedias, such as Ullmann's [1] or Kirk-Othmer's [2], contain chapters on aromatic amines.

### 1.1 Physical Properties of Aromatic Amines

An excellent 69-page summary of physical properties of primary arylamines was published as part of the National Bureau of Standards, National Standard Reference Data Series (NBS NSRDS) [3]. This summary includes data on thermodynamic and thermophysical properties of eight primary amines including benzeneamine and 2-, 3-, and 4-methylbenzeneamine, and recommended values are given for the normal boiling point, freezing point, and triple point temperatures, critical constants, thermodynamic properties in the solid and liquid phases, vapor pressure, enthalpy of vaporization, density, second virial coefficients, and enthalpy of combustion. Ideal gas thermodynamic properties were calculated by statistical mechanical methods. The boiling points were taken from a least-squares fit of the Cox equation (Table 1).

**Table 1:** Selected freezing, normal boiling, and critical temperatures of primary aromatic amines.

| Compound                  | Freezing point,<br>K        | Boiling point,<br>K | Critical point<br>temperature,<br>K | Critical point<br>pressure,<br>MPa | Critical<br>point<br>volume,<br>cm <sup>3</sup> /mol |
|---------------------------|-----------------------------|---------------------|-------------------------------------|------------------------------------|------------------------------------------------------|
| Benzeneamine<br>(aniline) | 267.133 ± 0.01 <sup>a</sup> | 457.32 ± 0.08       | 699 ± 2                             | 4.89 ± 0.12                        | 280 ± 14                                             |
| 2-Methyl-<br>benzeneamine | 256.8 ± 0.1                 | 473.49 ± 0.04       | 707 ± 2                             | 4.37 ± 0.12                        | 333 ± 17                                             |
| 3-Methyl-<br>benzeneamine | 241.9 ± 0.1                 | 476.52 ± 0.04       | 707 ± 2                             | 4.28 ± 0.12                        | 333 ± 17                                             |
| 4-Methyl-<br>benzeneamine | 316.9 ± 0.1                 | 473.57 ± 0.08       | 706 ± 2                             | 4.58 ± 0.14                        | 340 ± 17                                             |

<sup>a</sup> Triple point temperature

Data source: [3]

## 1.2 Thermodynamic Properties of Arylamines

Table 2 is a summary of experimentally obtained enthalpies of formation of primary arylamines.

**Table 2:** Thermodynamic data on primary aromatic amines.

| Property             | Enthalpy of formation, kJ/mol |               |                   |
|----------------------|-------------------------------|---------------|-------------------|
| Compound             | Ideal gas                     |               | Liquid            |
| Temperature          | 0 K                           | 298.15 K      | 298.15 K          |
| Benzeneamine         | −65.58 ± 0.81                 | +87.46 ± 0.81 | +31.63 ± 0.80     |
| 2-Methylbenzeneamine | −84.28 ± 2.1                  | +56.4 ± 2.0   | −6.3 ± 2.1        |
| 3-Methylbenzeneamine | −83.37 ± 2.1                  | +54.6 ± 2.0   | −8.1 ± 2.1        |
| 4-Methylbenzeneamine | −83.96 ± 2.1                  | +55.3 ± 2.0   | −23.5 ± 2.1 solid |

Data source: [3]

## 2 Aniline

Aniline, also known as benzeneamine, phenylamine, aminobenzene, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, CAS RN [62-53-3], is readily available and was used as a rocket fuel in the early years of rocketry but is no longer used for this purpose. It reacts hypergolically with all types of nitric acids, including white fuming nitric acid (WFNA), inhibited red fuming nitric acid (IRFNA), and mixed acid, but requires some additives to shorten the ignition delay.

The use of aniline as a rocket propellant is now mostly only of historical interest. Aniline played a role in the early days of liquid rocket experimentation and enabled the United States to achieve a few significant milestones, such as the first two-stage sounding rocket to reach a record altitude of 400 km. This milestone was achieved by the second stage of the V2/WAC Corporal combination (Operation Bumper) at White Sands Launch Complex 33 on 24 February 1949. Historically, a portion of the literature on amines as rocket propellants has always dealt with aniline, the simplest member of the family of aromatic amines, but this may no longer be necessary in the age of hydrazine fuels. We are listing aniline and its methyl derivatives here only as chemicals of historical interest.

Aniline is the simplest of the primary aromatic amines [4]. Aromatic amines can be produced by reduction of the corresponding nitro compounds, ammonolysis of an aromatic halide or phenol, and direct amination of the aromatic ring [4, 5]. At present, the catalytic reduction of nitrobenzene is the predominant process for manufacture of aniline. Aromatic amines are usually weaker bases than aliphatic amines. Important reactions of aniline include *N*-alkylation, ring alkylation, acylation, condensation, cyclization, reaction with nitrous acid, oxidation, halogenation, sulfonation, and nitration. Aniline is toxic and may be fatal if swallowed, inhaled, or absorbed through the skin.

The most important manufacturing processes for aniline and other bulk arylamines are based on the continuous catalytic hydrogenation of nitro compounds employing heterogeneous copper, nickel, or platinum-group catalysts [6]. To produce more complex amines on a smaller scale, homogeneous catalysis, with its greater possibilities for chemo- and regioselective hydrogenation, is increasingly the method of choice. An alternative process for production of aniline and phenylenediamines is the nucleophilic amination of phenols or the catalytic amination of haloarenes.

Aniline in the pure (freshly distilled) state is a colorless liquid with a characteristic odor that is not nearly as obnoxiously fishy smelling as aliphatic amines. It readily autoxidizes in air and quickly discolors as soon as air has gained entry into the storage flask.

Aniline is an important intermediate in the chemical industry for the production of dyes, pharmaceuticals, and other aromatic compounds. It is an intermediate in the production of centralites (stabilizers for double-base propellants) and tetryl. Aniline itself has been proposed as a stabilizer and  $\text{NO}_x$  scavenger for solid propellants, but it is too volatile for that application. Aniline was used as an auxiliary fluid in the production of anhydrous hydrazine by azeotropic distillation, and inevitably a small percentage of aniline was carried over into the hydrazine product, causing several types of operating problems for hydrazine monopropellant thrusters (see *Encyclopedia of Monopropellants*). At one time, the MIL SPEC for monopropellant-grade hydrazine allowed up to 0.5% aniline, but that was sufficient to render the hydrazine of very limited use for certain long-term, low-duty-cycle missions where hydrazine was used as

a monopropellant at certain duty cycles. In order to produce Viking grade or high-purity grade hydrazine, the aniline had to be removed (by fractionated crystallization) or the water from hydrazine hydrate had to be removed by alternate dehydration processes not involving any aniline as the auxiliary fluid to break the hydrazine-water azeotrope.

## 2.1 Physical Properties of Aniline

The physical properties of aniline are listed in Table 3.

**Table 3:** Physical properties of aniline.

| Property                                                    | SI units                                 | Other units                                                                   | References |
|-------------------------------------------------------------|------------------------------------------|-------------------------------------------------------------------------------|------------|
| Molecular mass                                              | 93.1265 g/mol                            | 10.738 mol/kg                                                                 | [7]        |
| Freezing point                                              | 267.1 K                                  | −6.0 °C                                                                       | [7]        |
|                                                             | 267.0 ± 0.3 K                            | −6.1 ± 0.3 °C                                                                 |            |
| Boiling point                                               | 457.3 K                                  | 184.2 °C                                                                      | [8]        |
|                                                             | 457.5 K                                  | 184.4 °C                                                                      |            |
|                                                             | 457 ± 2 K                                | 184.2 ± 2 °C                                                                  | [7]        |
| Density                                                     | 1021.6 kg/m <sup>3</sup> at 293 K        | 1.0216 g/cm <sup>3</sup> (at 20 °C)                                           | [9]        |
|                                                             | 1017.5 kg/m <sup>3</sup> at 298 K        | 1.0175 g/cm <sup>3</sup> (at 25 °C)                                           |            |
| Vapor pressure                                              | 345 Pa at 322 K                          | 2.59 mm Hg (at 48.9 °C)                                                       | [10]       |
|                                                             | 2.89 kPa at 355.3 K                      | 21.72 mm Hg (at 82.2 °C)                                                      |            |
|                                                             | 0.0867 kPa at 298 K                      | 0.65 mm Hg at 25 °C                                                           |            |
| Viscosity                                                   | 0.0102 Pa s at 273 K                     | 10.20 cPs (at 0 °C)                                                           | [9]        |
|                                                             | 0.00424 Pa s at 294.2 K                  | 4.24 cPs (at 21.1 °C)                                                         |            |
|                                                             | 0.000825 Pa s at 373 K                   | 0.825 cPs (at 100 °C)                                                         |            |
|                                                             | 0.0134 Pa s at 268 K                     | 13.4 cPs (at −5 °C)                                                           | [8]        |
|                                                             | 0.0044 Pa s at 293 K                     | 4.4 cPs (at 20 °C)                                                            |            |
| Surface tension                                             | 0.04267 N/m at 293 K                     | 42.67 dyn/cm (at 20 °C)                                                       | [8]        |
|                                                             | 0.0405 N/m at 313 K                      | 40.50 dyn/cm (at 40 °C)                                                       |            |
|                                                             | 0.03833 N/m at 333 K                     | 38.33 dyn/cm (at 60 °C)                                                       |            |
| Critical temperature                                        | 698.5 K                                  | 425.4 °C                                                                      | [11]       |
|                                                             | 698.7 K                                  | 798 °F                                                                        | [12]       |
|                                                             | 698.8 ± 0.4 K                            | 425.7 ± 0.4 °C                                                                | [7]        |
| Critical pressure                                           | 5.27 MPa                                 | 52.2 atm                                                                      | [11]       |
|                                                             | 5.29 MPa                                 | 755 psig                                                                      | [12]       |
|                                                             | 53.1 ± 0.2 bar                           | 770 psia                                                                      | [7]        |
| Thermal conductivity                                        | 0.1728 W m <sup>−1</sup> K <sup>−1</sup> | 4.13 × 10 <sup>−4</sup> cal cm <sup>−1</sup> s <sup>−1</sup> °C <sup>−1</sup> | [13]       |
|                                                             | 0.1774 W m <sup>−1</sup> K <sup>−1</sup> | 4.24 × 10 <sup>−4</sup> cal cm <sup>−1</sup> s <sup>−1</sup> °C <sup>−1</sup> | [8]        |
| Index of refraction ( <i>n</i> <sub>D</sub> <sup>20</sup> ) | 1.5863                                   | 1.5863                                                                        | [9]        |

The velocity of sound in aniline and mixtures of aniline and furfuryl alcohol was measured by a single-pulse technique at temperatures from 294 to 366 K (70–200 °F) and pressures of 0.1–4 MPa (1–40 atm) [14]. Values calculated for a mixture of aniline (80%) and furfuryl alcohol (20%) using the molar sound velocity concept of Rao agreed with the experimental values to within 10%.

### 2.1.1 Vapor Pressure of Aniline

The vapor pressure of aniline can be calculated from the Antoine equation

$$\ln p_{\text{sat}} = 6.2533 - 1590.91/(T - 82.81)$$

where  $p_{\text{sat}}$  is the saturation pressure in kPa and  $T$  is the temperature in kelvin. This is valid for the pressure range 20–200 kPa. A different Antoine equation for the vapor pressure of aniline in the range 304–457 K is

$$\log(P) = 4.34541 - [1661.858/(T - 74.048)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin [15].

Droplet evaporation experiments were performed with single drops of WFNA and of aniline on a hot surface in the temperature range from 573 to 1373 K (300–1100 °C) [16]. These drops showed initial evaporation periods, during which the diameters of the drops did not diminish. The influence of bubble inflation on the course of the evaporation, and in particular on the total evaporation time for a given initial diameter, was studied. The evaporation times were exponential functions of the temperature of the hot surface. It was demonstrated that, at constant temperature, the evaporation time per 1 mg of drops can be longer or shorter for nitric acid than for aniline depending on the actual value of the temperature.

### 2.1.2 Heat Transfer Coefficients of Aniline

The thermal conductivity of aniline is  $0.1774 \text{ W m}^{-1} \text{ K}^{-1}$  ( $4.24 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ) [8]. Other sources gave the thermal conductivity of liquid aniline at 293 K as  $0.1728 \text{ W m}^{-1} \text{ K}^{-1}$  ( $4.13 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ) [13].

The heat transfer from an electrically heated tube to aniline was measured at high heat flux to simulate conditions in the cooling channels of regeneratively cooled rocket engines [17].

### 2.1.3 Thermodynamic Properties of Aniline

The thermodynamic properties of aniline are listed in Table 4. The heat capacities of aniline and aniline/furfuryl alcohol mixtures in the range 300–422 K (80–300 °F) were determined by calorimetric measurements because they were needed to calculate the regenerative cooling capability of this fuel in a rocket engine [18].

**Table 4:** Thermodynamic properties of aniline.

| Property                                                               | SI units                                           | Other units                                            | References |
|------------------------------------------------------------------------|----------------------------------------------------|--------------------------------------------------------|------------|
| Molecular mass                                                         | 93.1265 g/mol                                      | 10.738 mol/kg                                          | [7]        |
| Heat capacity                                                          | 2.063 J g <sup>-1</sup> K <sup>-1</sup> (at 298 K) | 0.493 cal g <sup>-1</sup> °C <sup>-1</sup> (at 25 °C)  | [11]       |
|                                                                        | 2.167 J g <sup>-1</sup> K <sup>-1</sup>            | 0.518 cal g <sup>-1</sup> °C <sup>-1</sup>             | [19]       |
|                                                                        | (at 293–298 K)                                     | (at 20–25 °C)                                          |            |
|                                                                        | 192 J mol <sup>-1</sup> K <sup>-1</sup>            | 45.9 cal mol <sup>-1</sup> °C <sup>-1</sup> (at 25 °C) | [15]       |
| Standard enthalpy of formation, vapor ( $\Delta H_f$ ) <sup>298</sup>  | 87.03 ± 0.88 kJ/mol                                | 20.8 ± 0.2 kcal/mol                                    | [7]        |
| Standard enthalpy of formation, liquid ( $\Delta H_f$ ) <sup>298</sup> | +30.74 kJ/mol                                      | +7.347 kcal/mol                                        | [11]       |
|                                                                        | +31.63 ± 0.8 kJ/mol                                | +7.56 ± 0.2 kcal/mol                                   | [3]        |
|                                                                        | +31.2 ± 0.8 kJ/mol                                 | +7.47 ± 0.2 kcal/mol                                   | [15]       |
| Heat of fusion at 267.1 K                                              | 8.180 kJ/mol                                       | 1.955 kcal/mol                                         | [11]       |
|                                                                        | 10.54 kJ/mol                                       | 2.52 kcal/mol                                          | [7]        |
| Enthalpy of vaporization                                               | 40.4 kJ/mol                                        | 9.657 kcal/mol                                         | [11]       |
|                                                                        | 55.83 ± 0.1 kJ/mol                                 | 13.3 kcal/mol                                          | [3]        |
|                                                                        | 54 kJ/mol                                          | 12.9 kcal/mol                                          | [15]       |
| Heat of combustion, liquid                                             | 3397 kJ/mol                                        | 812 kcal/mol                                           | [11]       |

## 2.2 Molecular Structure of Aniline

Aniline (benzeneamine) has  $C_s$  ( $\sigma=1$ ) symmetry. From an investigation of the microwave spectra of  $C_6H_5NH_2$  and  $C_6H_5NHD$ , it was established that  $C_6H_5NH_2(G)$  has a non-planar structure in which the  $-NH_2$  plane (containing the nitrogen atom and its two attached hydrogens) makes an angle of about 40° with the plane of the phenyl ring. The molecular structure derived from microwave spectra of deuterated benzeneamine is such that the  $-NH_2$  group adopts an out-of-plane angle of  $37^\circ 29' \pm 2^\circ$ , with the  $\angle HNH$  angle being  $113^\circ 6' \pm 2^\circ$  [20].

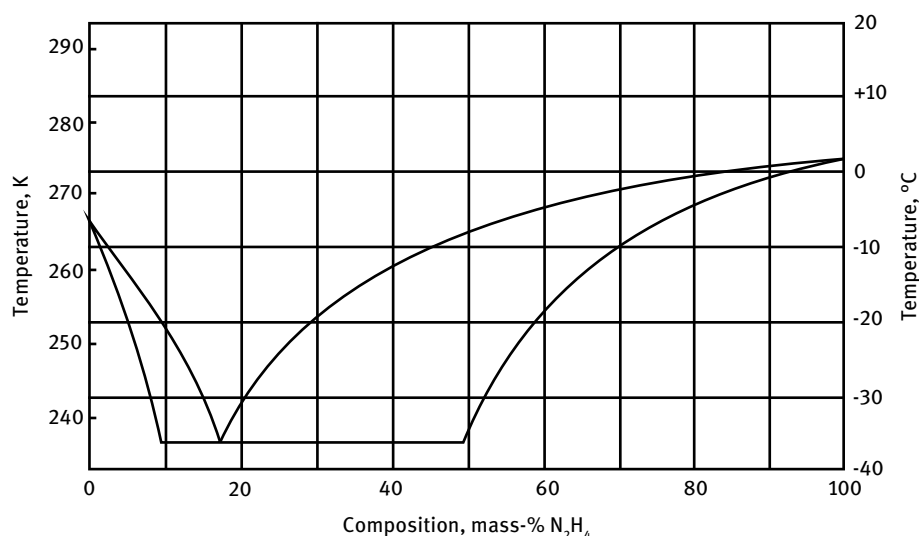
## 2.3 Fuel Mixtures with Aniline

Because aniline is readily available, many different mixtures of aniline with other fuels have been tested in the hope of improving its hypergolic ignition characteristics (see the future *Encyclopedia of Hypergolic Bipropellant Combinations*). A fuel mixture of aniline with methylamine and hydrazine has been evaluated as a hypergolic fuel for use with WFNA or RFNA.

A 50:50 mixture of aniline and furfuryl alcohol was used in one version of the first American liquid propellant ballistic missile, the MGM-5 Corporal, developed by Jet Propulsion Laboratory (JPL), Douglas Aircraft, and Firestone Rubber for the US

Army and deployed during the years 1954–1964. It was capable of carrying a payload of 680 kg, including nuclear warheads. An early version of Corporal E used a fuel consisting of 80% aniline and 20% furfuryl alcohol. The later type II Corporal used a 46.5 mass-% aniline, 46.5 mass-% furfuryl alcohol, and 7 mass-% hydrazine mixture as the fuel and stabilized IRFNA with 14%  $\text{NO}_2$ , 2.5%  $\text{H}_2\text{O}$ , and 0.6% HF as the oxidizer [21, 22]. The heat capacity of the aniline/furfuryl alcohol mixture in the range 300–422 K (80–300 °F) was determined by calorimetric measurements because it was needed to calculate the regenerative cooling capability of this fuel in a rocket engine [18].

Hydrazine and aniline form a eutectic mixture that freezes at 237 K (–36 °C) and has the composition 17.3 mass-% hydrazine and 82.7 mass-% aniline (Figure 1). The low freezing point of this mixture makes this hypergolic fuel suitable for small missile applications.



**Figure 1:** Freezing point diagram of aniline-hydrazine mixtures. (Reproduced and modified from [23].)

The freezing points of hydrazine-aniline mixtures can be depressed to 233 K (–40 °C) or below by the addition of small quantities of a third component. The freezing points and other physical properties of the ternary fuel mixtures hydrazine-aniline-methylamine, hydrazine-aniline-ethylamine, hydrazine-aniline-diethylamine, hydrazine-aniline-triethylamine, hydrazine-aniline-ethyleneimine, hydrazine-aniline-methanol, hydrazine-aniline-ethanol, hydrazine-aniline-ammonia, and hydrazine-aniline-acetylene were investigated [23]. Using ethylamine and diethylamine as third components with the hydrazine-aniline system was found to give solutions that



freeze below 233 K (−40 °C). The eutectic hydrazine-aniline mixture absorbs only 3.6 mass-% ammonia or 0.98 mass-% acetylene at ambient temperature and pressure, and the resulting modest effects on the freezing point and ignition properties of the mixture were too slight to warrant the use of these additives.

## 2.4 Chemical Properties of Aniline

Aniline is mildly alkaline [24]. It is a weak base and reacts with strong mineral acids to form solid salts that are soluble in water. Aniline (anilinium, anilino) salts with oxidizing acids ( $\text{HNO}_3$ ,  $\text{HClO}_4$ ) are potentially explosive. Aniline is hypergolic with concentrated nitric acid, which is the main reason why it is (still) listed in this book.

Aniline is soluble in ether, ethanol, and most organic solvents. It is only slightly soluble in water, which dissolves 3.2 vol.-% aniline at 293 K.

Aniline is indefinitely storable in the absence of air and will not decompose at its normal boiling point. Freshly distilled, clear aniline will slowly autoxidize and become discolored from dissolved autoxidation products.

Of the nitro-substituted aniline derivatives, only 2,4,6-trinitroaniline (2,4,6-TNA, picramide) is of practical interest as an explosive (but not as a propellant ingredient). As an explosive, picramide has some advantages over picric acid because it is less soluble in water and less corrosive. The remaining ring hydrogens can also be replaced by nitro groups, forming tetranitroaniline or pentanitroaniline, but these compounds are too sensitive for practical use. 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) can formally be considered an aniline derivative although it is not made from aniline. It is an energetic compound with exceptionally good thermal stability, and new methods for its large-scale production are still being developed.

### 2.4.1 Analysis of Aniline

Occasional instant spot checks of aniline vapor concentration in the air at the workplace are most easily performed with gas detection tubes, which contain an indicator (supported on a granular material) that changes color when exposed to ammonia. Such tubes are available from Draeger, MSA, Kitagawa and other commercial sources. Gas detection tubes are sensitive to as little as 5 ppm aniline and can measure up to 60 ppm  $(\text{C}_2\text{H}_5)_3\text{N}$  with ten strokes. Draeger aniline gas detection tubes are available for two ranges of concentrations (Table 5).

One of the first storable liquid hypergolic fuels used in the United States was a mixture of aniline, hydrazine, and furfuryl alcohol. This mixture had to be analyzed frequently to verify its storability [26].

**Table 5:** Draeger aniline gas detection tubes.

| Tube designation | Concentration range | Draeger part number |
|------------------|---------------------|---------------------|
| Aniline 0.5/a    | 0.5–10 ppm          | 67 33 171           |
| Aniline 5/a      | 1–20 ppm            | CH 20 401           |

Data source: [25]

## 2.5 Handling of Aniline

Aniline is a weak base and does not cause chemical burns when spilled on unprotected skin. However, aniline is a strong blood poison and will cause cyanosis and degenerative changes in red blood cells. Handling instructions emphasize the importance of preventing skin contact because aniline is readily absorbed through the skin [27, 28]. Aniline spilled on the skin should be washed with lots of water, neutralized with 5% acetic acid, and rinsed again.

One of the symptoms of aniline poisoning is a bluish tinge of the tissues, cyanosis, which results from inadequate oxygenation of the tissues. Other symptoms of aniline poisoning are headaches, weakness, difficulty breathing, convulsions, and psychologically unstable behavior.

The vapor pressure of aniline is very low, and the fire hazard it presents is very low (Table 6).

**Table 6:** Fire hazard properties of aniline.

| Property                 | Method     | SI units                         | Other units      | References |
|--------------------------|------------|----------------------------------|------------------|------------|
| Flammable range          | —          | 1.2–8.3 vol.-% at 413 K = 140 °C |                  | [29]       |
| Flash point              | —          | 348.6 K                          | 168 °F = 75.5 °C | [19]       |
| Flash point              | Open cup   | 364 K                            | 195 °F           | [12]       |
|                          | Closed cup | 344–349 K                        | 160–168 °F       | [12]       |
| Autoignition temperature | —          | 800–1044 K                       | 980–1420 °F      | [12]       |
|                          | I-8        | 890 K                            | 617 °C           | [30]       |

## 2.6 Toxicity of Aromatic Amines

The vapor pressure of aniline is very low, such that the inhalation hazard is not very high. However, all of the anhydrous hydrazine used for toxicity studies in various toxicological laboratories in the US in the 1970s and 1980s contained substantial amounts (~0.5%) of aniline, which could have contributed as a synergistic toxicant to the observed effects attributed to hydrazine – a circumstance that toxicologists did not recognize at the time. The Occupational Safety and Health Administration (OSHA) per-

missible exposure limit (PEL) Threshold Limit Value (TLV) Time Weighted Average (TWA) for aniline is 5 ppm. The immediately dangerous to life and health (IDLH) concentration of aniline is 100 ppm [31]. Acute Exposure Guideline Levels for Selected Airborne Chemicals (AEGL) values were initially developed for 30 min and 1, 4, and 8 h exposures [32]. Since that time, AEGL values have also been developed for 10 min exposures. The criteria used in establishing acute exposure guideline levels for aniline are outlined in [32].

The aromatic amine of the most concern regarding toxicity is benzidine, a relative of aniline. Toxicity studies of aromatic amines have often compared these two amines [33–36]. Benzidine has been evaluated as a hypergolic fuel grain for hybrid rockets.

## 2.7 Properties of Anilinium Salts

### 2.7.1 Anilinium Nitrate

Anilinium nitrate forms colorless crystals with a melting point of 455–457 K (182–184 °C) that yield nitraniline when heated to 463 K (190 °C). The crystal density is 1.356 g/cm<sup>3</sup> at 277 K (4 °C) and the crystals are very soluble in water or ethanol. The crystals belong to the *Pbca* (no. 61) space group of the orthorhombic system,  $a = 10.158(2) \text{ \AA}$ ,  $b = 9.277(2) \text{ \AA}$ ,  $c = 16.177(3) \text{ \AA}$ ,  $Z = 8$  [37].

### 2.7.2 Anilinium Perchlorate

Anilinium perchlorate decomposes slowly when heated to 453 K (180 °C) and explodes at 523 K (250 °C). Anilinium perchlorate is a molecular ionic solid [38].

### 2.7.3 Anilinium Dinitramide

Anilinium dinitramide,  $[\text{C}_6\text{H}_5\text{N}^+\text{H}_3][\text{N}^-(\text{NO}_2)_2]$ , CAS RN [165603-95-2], melts at 368–370 K (95–97 °C) [39].

## 3 Ring-Substituted Aniline Derivatives

Substitution of one or more hydrogens at the 2-, 3-, 4-, 5- or 6-position on the benzene ring of aniline by substituents leads to a variety of amines that have potentially better rocket fuel properties than aniline itself. The substituents could be one or more methyl groups or additional amino groups. Additional nitro groups improve the overall oxygen balance of the molecule, all the way up to triaminotrinitrobenzene, a powerful and thermally stable explosive. The most common substituents are methyl groups, leading to toluidines (*ortho*, *meta*, and *para*) for monomethyl-substituted anilines and xylidines for disubstituted anilines. These amines are described in their own sections below. Ring-substituted alkyanilines are isomers of *N*-substituted anilines but they

differ in their properties. Both types can potentially be used as hypergolic rocket fuels in place of aniline or in combination with aniline and triethylamine.

The effects of ring substitution on the basicity of the substituted aniline free base and the thermal stability of the substituted anilinium nitrates are tabulated in Table 7 [40, 41]. The electron-sucking  $\text{NO}_2$  group decreases the basicity and decreases the thermal stability of the nitrate salt. The electron-pushing  $-\text{CH}_3$  and  $-\text{NH}_2$  groups increase the basicity and increase the thermal stability of the nitrate salt. The thermal stability and impact sensitivity of the *meta*- and *para*-substituted anilinium nitrates were found to be linearly related to the Hammett substituent constant  $\sigma$ , the basicity constant  $\text{p}K_{\text{a}}$ , and the oxygen balance of the corresponding nitrate salt.

**Table 7:** Effects of ring substitution on the basicity of the substituted aniline free base and the thermal stability of substituted anilinium nitrates.

| Substituent R                   | $\text{p}K$ of base | $\sigma$ | DTA exotherm, $^{\circ}\text{C}$ |
|---------------------------------|---------------------|----------|----------------------------------|
| $-\text{NO}_2$                  | 13.01               | +0.78    | 166                              |
| $-\text{COOH}$                  | 11.62               | +0.40    | 185                              |
| $-\text{Cl}$                    | 10.01               | +0.23    | 190                              |
| $-\text{H}$ (aniline, baseline) | 9.4                 | 0        | 202                              |
| $-\text{CH}_3$                  | 8.9                 | -0.17    | 209                              |
| $-\text{NH}_2$                  | 7.9                 | -0.66    | 245                              |

Date source: [41]

If aniline is used as a hypergolic fuel, the aryl nucleus may be oxidized by  $\text{NO}_2$  or  $\text{HNO}_3$  prior to ignition, and gaseous products are formed.

Ring-substituted arylammonium nitrates have been prepared and characterized to see what influence substituents have on the reactivity of the amino group [42]. Thermal and ignition characteristics of these solid salts were studied via thermogravimetric analysis (TGA) and ignition delay measurements. The ignition temperatures (IT) and energies of activation (ignition) ( $E_{\text{i}}$ ) (21.3–39.3 kJ/mol) were found to be linearly related to the Hammett substituent constant  $\sigma$ , the  $\text{p}K_{\text{a}}$  of the amine, and the oxygen balance of the corresponding nitrate salt. The results suggested that the primary step in the slow and rapid thermolysis of these salts is a proton transfer (NH bond heterolysis) from the arylammonium ion to the nitrate ion.

Thermolysis of ring-substituted arylammonium nitrates has been carried out by TGA and differential thermal analysis (DTA) [43]. Although the thermal decomposition kinetics of these salts were evaluated by fitting TGA data with nine mechanism-based kinetic models, the contracting envelopes ( $n = 2, 3$ ) and Avrami-Erofeev ( $n = 2, 3$ ) methods gave the best fit. The activation energies for decomposition, exothermic decomposition temperatures (from DTA curves), and impact sensitivity data were shown to be linearly correlated to the Hammett substituent constant  $\sigma$  and the dissociation constant exponent  $\text{p}K_{\text{a}}$  of the corresponding arylamine. A proposed reaction scheme ac-

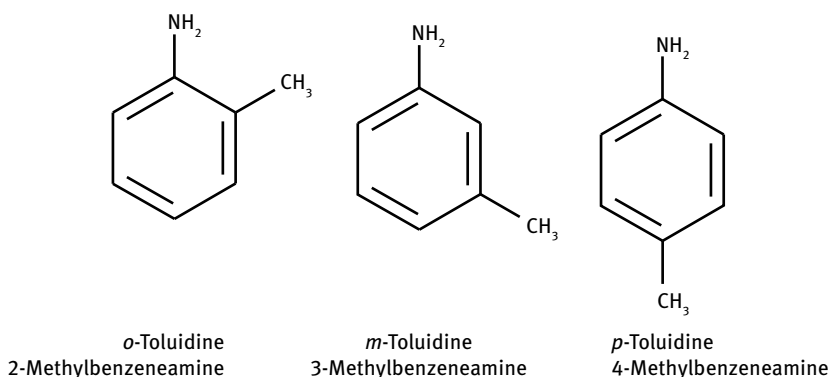
counting for the observed products involves proton transfer, leading to the formation of an arylamine and  $\text{HNO}_3$  and oxidation of the arylamine by decomposition products of  $\text{HNO}_3$ . The oxidation-reduction reactions near the surface of the thermolysing material are responsible for the decomposition.

In a similar way, thermolysis of dimethylanilinium nitrates was studied by TGA, DTA, ignition delay, impact sensitivity, and friction sensitivity measurements [44]. Again, the Avrami-Erofeev ( $n = 2, 3$ ) and contracting area ( $n = 2$ ) methods gave the best fits to the data. The most probable reaction scheme that can account for the decomposition products involves a proton transfer leading to the formation of free arylamine and  $\text{HNO}_3$ . Other probable routes (with the evolution of  $\text{NH}_3$ ) have also been suggested. The aryl nucleus seems to be oxidized by  $\text{NO}_2$ ,  $\text{HNO}_3$ , or its decomposition products prior to ignition, and gaseous products are then formed.

Similar experiments were performed with the perchlorates of ring-substituted arylamines [45–47]. The decomposition and dissociation temperatures, as well as the activation energy for explosion, increase with increasing basicity constant  $\text{p}K_a$  of the corresponding arylamine. These parameters, when plotted against the Hammett substituent constant  $\sigma$ , showed a linear relationship in the case of *meta*- and *para*-substituted derivatives. The results indicated that a proton transfer from arylammonium ion to perchlorate ion is involved in the decomposition and explosion processes of these arylammonium perchlorates. The explosion temperatures, explosion delay, and activation energy for explosion were substantially lower for the 3,4-dimethylanilinium perchlorate compared with the 2,5- and 2,4-substituted salts.

### 3.1 Toluidines

Of the three isomeric toluidines



only the *ortho* isomer is suitable as a rocket propellant. The *meta* isomer is difficult to obtain and the *para* isomer is a solid at room temperature.

*o*-Toluidine (2-methylbenzenamine) is an important intermediate in the production of dyes and pharmaceuticals by the chemical industry. It is produced by reduction of *o*-nitrotoluene. *o*-Toluidine in mixture with triethylamine has been used as a rocket fuel [48]. In all fuel blends, toluidine gave shorter ignition delays than aniline.

In the pure state, *o*-toluidine is a colorless oily liquid, but in the presence of air and in bright light it autoxidizes readily and discolors to form a dark brown liquid. The physical properties of *o*-toluidine are summarized in Table 8 [3]. Additional properties of toluidines are available in the literature [49].

**Table 8:** Physical properties of *o*-toluidine.

| Property                           | SI units                          | Non-SI units                       | References |
|------------------------------------|-----------------------------------|------------------------------------|------------|
| Freezing point                     | 248.7                             | −24.4 °C                           | [11]       |
|                                    | 256.8 K                           | −16.3 °C                           | [3]        |
| Boiling point                      | 472.9 K                           | 199.8 °C                           | [11]       |
|                                    | 473.5 K                           | 200.4 °C                           | [3]        |
| Density                            | 1004 kg/m <sup>3</sup> at 293 K   | 1.004 g/cm <sup>3</sup> at 20 °C   | [11]       |
|                                    | 994.69 kg/m <sup>3</sup> at 298 K | 0.99469 g/cm <sup>3</sup> at 25 °C | [3]        |
| Vapor pressure                     | 133 Pa at 317 K                   | 1 mm Hg at 44 °C                   |            |
|                                    | 0.0311 kPa at 298 K               | 0.233 mm Hg at 25 °C               | [3]        |
| Enthalpy of vaporization           | 42.68 kJ/mol                      | 10.2 kcal/mol                      | [11]       |
|                                    | 62.7 ± 0.5 kJ/mol                 | 14.98 ± 0.12 kcal/mol              | [3]        |
| Heat of combustion, liq.           | 4035 kJ/mol                       | 964.3 kcal/mol                     | [11]       |
| Index of refraction ( $n_D^{20}$ ) | 1.5727                            | 1.5727                             | [11]       |
| Standard enthalpy of formation     | −6.3 ± 2.1 kJ/mol                 | −1.51 ± 0.5 kcal/mol               | [3]        |

The precautions necessary for the safe handling of toluidine are the same as those for aniline. Similar to aniline, toluidine is a blood poison.

Toluidine forms salts with strong acids. *o*-Toluidine dinitramide melts at 343–344 K (70–71 °C) [39].

### 3.2 Xylidines

Xylidines, dimethylaminobenzenes, C<sub>8</sub>H<sub>11</sub>N, molecular mass 121.1796 g/mol, CAS RN [1300-73-8], are dimethyl anilines in which the two methyl groups can occupy different positions on the ring and create up to six possible isomers. They must not be confused with the isomeric *N,N*-dimethylaniline. Xylidines are produced by reduction of nitroxylenes, which are a mixture of different isomers. The composition of the mix-

ture depends on the conditions during the nitration of xylene and the xylenes that are used for the nitration to start with. The nitroxyls and xylidines are usually not separated but are used as a mixture of isomers. Xylidines can be used as hypergolic rocket propellants in combination with triethylamine. Additional information on properties of xylidines is available in the literature [50]. Most xylidines are suitable as hypergolic fuels, but some are solids. The effect of the molecular structure of the xylidine on the ignition delay when used in combination with nitric acid has been studied in detail.

During World War II (WW-II), xylidine/triethylamine mixtures were used as hypergolic fuels with WFNA and RFNA [51]. These mixtures had code names such as Tonka, followed by a number.

*Furaline*, a hypergolic fuel used extensively by the French company Société d'Études de la Propulsion par Reaction (SEPR) in its experimental anti-aircraft missile SEPR-2, was a mixture of 41% furfuryl alcohol, 41% xylidine, and 18% ethanol [52]. Another fuel blend was called TX-2, which consisted of triethylamine and xylidine.

A hypergolic fuel mixture with the code name of *Samin* (*Samine*) and consisting of 50 mass-% xylidine and 50 mass-% triethylamine was widely used for several types of missiles in Russia (USSR) [53]. At the end of the Cold War, large quantities of this material had to be demilitarized in compliance with the SALT disarmament agreements [54]. Unfortunately, the storage conditions were not always carefully controlled, and some of the Samin had already leaked into the ground. The abandoned and decaying storage magazines constituted a hazard to the surrounding communities [55]. Various weapon systems used the Samin fuel blend and had to be demilitarized [56].

At one time, 290 metric tons of Samin (TG-02) containing 50% xylidine were stored at the Mingchevir depot in Azerbaijan, waiting for disposal. Color pictures of the unsafe conditions at the neglected storage sites are shown on page 19 of the Winkelmann thesis [57]. Where the fuel had leaked into the ground, it had formed a red-brown layer of xylidine autoxidation products, and the discoloration was sometimes only revealed if the top layer of drift sand was scraped and moved to the side. Several different methods to not only dispose of but also to convert abandoned and unwanted rocket propellants, including Samin and Melanj, into commercially useful products such as fertilizer or plastics were evaluated [58–61].

Xylidines are sensitive to autoxidation by atmospheric oxygen, resulting in an increased ignition delay. *N*-Isopropyl-*N'*-phenyl-*p*-phenylenediamine, *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine, and *N,N'*-diphenyl-phenylenediamine were evaluated as antioxidants of amine-based fuel components [62]. They almost totally inhibited the consumption of xylidine while significantly retarding the autoxidation of triethylamine. *N*-Isopropyl-*N'*-phenyl-phenylenediamine was the most effective of all the antioxidants studied, and addition of only 0.5 mass-% was sufficient to give the required autoxidation protection.

### 3.3 Trimethylanilines

There are no known uses of trimethylaniline free bases as rocket propellants, but their oxyacid salts have been evaluated as propellant ingredients.

Several nitrate and perchlorate salts of 2,4,6-trimethylaniline have been prepared and characterized by X-ray diffraction (XRD), gravimetric analyses, TGA, TGA/DSC, and their ignition/explosion delays [63]. It was observed that proton transfer from a substituted anilinium ion to nitrate and perchlorate ions regenerates free amine,  $\text{HNO}_3$ , and  $\text{HClO}_4$  in the condensed phase at higher temperature, where oxidation-reduction between the amine and acids leads to ignition and explosion. The kinetics of thermal decomposition were evaluated by applying model fitting as well as isoconversional methods. The activation energies of the decomposition of the nitrate and perchlorate salts were 77.9 and 118.2 kJ/mol, respectively.

## 4 Phenylenediamines

Phenylenediamines form phenylenediammonium dinitrate salts, which are quite energetic. Four different phenylenediammonium dinitrate salts were prepared and characterized by elemental analysis, infrared (IR), and ultraviolet (UV) spectroscopy [64]. These dinitrates can potentially find applications in propellants, explosives, and pyrotechnics. Their thermal decomposition was studied by TGA and simultaneous TGA-DSC. The decomposition leads often to ignition. In a similar study, phenylenediammonium diperchlorate salts were prepared and characterized, which are also very energetic and potentially explosive [65].

## 5 *N*-Substituted Aniline Derivatives

In addition to substituting aniline on the ring, the two hydrogens on the amino group of aniline can also be substituted, leading to aniline derivatives with potential value as hypergolic fuels. *N*-Substituted anilines can be produced from aniline by reaction with methanol under high pressure.

### 5.1 *N*-Methylaniline and *N,N*-Dimethylaniline

The hypergolic ignition of *N*-methylaniline or *N,N*-dimethylaniline is no better than that of aniline itself. These aniline derivatives were evaluated back in WW-II by the Germans but were never practically utilized [51]. Physical properties of *N*-methylaniline and *N,N*-dimethylaniline are summarized in Table 9.



**Table 9:** Physical properties of *N*-methylaniline and *N,N*-dimethylaniline.

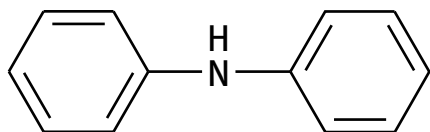
|                                    | SI units                                 | Other units                                                                 | References |
|------------------------------------|------------------------------------------|-----------------------------------------------------------------------------|------------|
| <b><i>N</i>-Methylaniline</b>      |                                          |                                                                             |            |
| Freezing point                     | 216 K                                    | −57 °C                                                                      |            |
| Boiling point                      | 469.3 K                                  | 196.2 °C                                                                    |            |
| Density                            | 990.2 kg/m <sup>3</sup> (at 288 K)       | 0.9902 g/cm <sup>3</sup> (at 15 °C)                                         |            |
| Index of refraction ( $n_D^{15}$ ) | 1.5736                                   | —                                                                           |            |
| Thermal conductivity               | 0.1849 W m <sup>−1</sup> K <sup>−1</sup> | $4.42 \times 10^{-4}$ cal cm <sup>−1</sup> s <sup>−1</sup> °C <sup>−1</sup> | [8]        |
| Standard enthalpy of formation     | +35.98 kJ/mol                            | +8.6 kcal/mol                                                               |            |
| Heat of combustion, liquid         | 4077 kJ/mol                              | 974.4 kcal/mol                                                              |            |
| <b><i>N,N</i>-Dimethylaniline</b>  |                                          |                                                                             |            |
| Freezing point                     | 275.5 K                                  | 2.4 °C                                                                      |            |
| Boiling point                      | 467.2 K                                  | 194.1 °C                                                                    |            |
| Density                            | 960.1 kg/m <sup>3</sup> (at 288 K)       | 0.9601 g/cm <sup>3</sup> (at 15 °C)                                         |            |
| Index of refraction ( $n_D^{15}$ ) | 1.5608                                   | —                                                                           |            |
| Standard enthalpy of formation     | +63.60 kJ/mol                            | +15.2 kcal/mol                                                              |            |
| Heat of combustion, liquid         | 4784 kJ/mol                              | 1143.4 kcal/mol                                                             |            |

For comparison, the thermal conductivity of aniline is  $4.24 \times 10^{-4}$  cal cm<sup>−1</sup> s<sup>−1</sup> °C<sup>−1</sup>. *N*-Ethylaniline has been tested as a hypergolic fuel, but has never found flight applications [66–68]. Substitution of hydrogens on the nitrogen atom of aniline by alkenyl groups instead of alkyl groups may lead to amines with better hypergolic ignition properties than the amines with saturated alkyl substituents. *N,N*-Diallylaniline is not readily available but was nevertheless tested as a hypergolic fuel by National Advisory Committee for Aeronautics (NACA) in the post-WW-II era in the US, both on its own and in mixtures with triethylamine. Its ignition found to be more reliable than that of *N,N*-diethylaniline.

The drop sensitivity, friction sensitivity, and thermal stability of dimethylanilinium nitrates have been tested by DTA and TGA, and a fairly complex mechanism for decomposition reactions was proposed [44]. A proposed reaction scheme accounting for the decomposition products involved proton transfer leading to the formation of an arylamine and HNO<sub>3</sub>. Other probable routes (evolution of NH<sub>3</sub>) have also been suggested. The aryl nucleus seems to be oxidized by NO<sub>2</sub>, HNO<sub>3</sub>, or its decomposition products prior to ignition, and gaseous products are formed.

## 6 Diphenylamine

Diphenylamine, *N,N*-diphenylamine,  $C_6H_5NHC_6H_5$ ,  $C_{12}H_{11}N$ , DPA, CAS RN [122-39-4], and diphenylamine derivatives are used as  $NO_x$  getters ( $NO_x$  scavengers) and stabilizers in double-base propellants. Diphenylamine is a relative of aniline, a secondary amine where one of the hydrogens on the amino group of aniline has been replaced by an additional phenyl group [69].



Diphenylamine can be made by heating a mixture of aniline and anilinium chloride in an autoclave. Diphenylamine is readily available. It is sparingly soluble in water, but readily soluble in acids and in ethanol or acetone.

Diphenylamine is very useful as a  $NO_x$  scavenger and stabilizer for solid double-base propellants. As the result of the slow decomposition of double-base propellants and release of nitrous fumes, diphenylamine is partially and irreversibly converted to a mix of dinitrodiphenylamine isomers. However, diphenylamine can not only stabilize nitrocellulose; it may also react with it.

A tertiary aromatic amine, triphenylamine (TPA) was used for the first time as a stabilizer for double-base propellants in France in 1937. The stability of those samples was described as good. Around 1950, an American group produced TPA-stabilized propellants and investigated the decomposition mechanism. Apart from a single experiment in the 1970s, no further attempts were made to use TPA as a stabilizer for propellants until 2007, when a study gave somewhat encouraging results [70]. One advantage of using tertiary amines over secondary amines is that they are less likely to form toxic and carcinogenic nitrosamines when they act as  $NO_x$  getters.

### 6.1 Physical Properties of Diphenylamine

Diphenylamine forms soft, colorless crystals. Physical and thermodynamic properties of diphenylamine are listed in Table 10. The *NIST Chemistry WebBook* [7] gives several numbers for the enthalpy of formation of solid DPA; we assume that the most recent is the most reliable source of data.

The volatility of DPA is undesirable because it may cause a loss of stabilizer from double-base propellants during storage. Therefore, it is important to know the vapor pressure of DPA. The vapor pressure of DPA in the range 381.5–575 K can be calculated

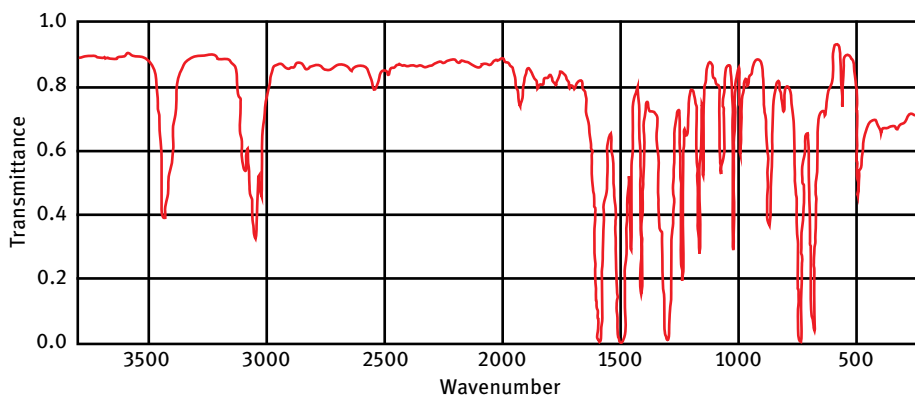
from the following equation:

$$\log_{10} P = 5.09811 - [2729.385 / (T - 39.207)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. The IR spectrum of a 10% DPA solution in  $\text{CCl}_4$  is shown in Figure 2.

**Table 10:** Physical and thermodynamic properties of diphenylamine.

| Property                              | SI units               | Non-SI units                   | References |
|---------------------------------------|------------------------|--------------------------------|------------|
| Molecular mass                        | 169.2224 g/mol         | 5.9094 mol/kg                  | [7]        |
| Melting point                         | 327 K                  | 54 °C = 129 °F                 | [71]       |
|                                       | 326 ± 2 K              | 53 ± 2 °C                      | [7]        |
| Boiling point at atmospheric pressure | 575 K                  | 302 °C = 576 °F                | [71]       |
|                                       | 575.2 K                | 302.1 °C                       | [7]        |
| Density at 293 K                      | 1160 kg/m <sup>3</sup> | 1.16 g/cm <sup>3</sup>         | [71]       |
| Oxygen balance                        | −278.9%                | —                              | [71]       |
| Enthalpy of formation, solid          | +130.0 ± 1.5 kJ/mol    | +183.6 cal/g                   | [7]        |
|                                       | +130 kJ/mol            | +31.07 kcal/mol = +183.6 cal/g | [72]       |
| Heat of sublimation                   | 110 kJ/mol             | 26.3 kcal/mol                  | [7]        |



**Figure 2:** IR spectrum of a 10% diphenylamine solution in  $\text{CCl}_4$ . (Reproduced and modified with permission from [73].)

## 6.2 Chemical Properties of Diphenylamine

The main use of diphenylamine in solid propellant formulations is as a  $\text{NO}_x$  getter ( $\text{NO}_x$  scavenger). By immobilizing the  $\text{NO}_x$ , premature decomposition and even (under extreme conditions) autoignition of aging and overheated double-base propellants can be avoided. However, stabilizer depletion has to be monitored. There are several analytical methods that allow the remaining unreacted diphenylamine in the propellant to be determined, making it possible to predict how many years the rocket can still be used before it needs to be retired. The reaction of diphenylamine with  $\text{NO}_x$  yields a mixture of 2,2'-, 2,4'-, and 4,4'-dinitrodiphenylamines.

## 6.3 Analysis of Diphenylamine

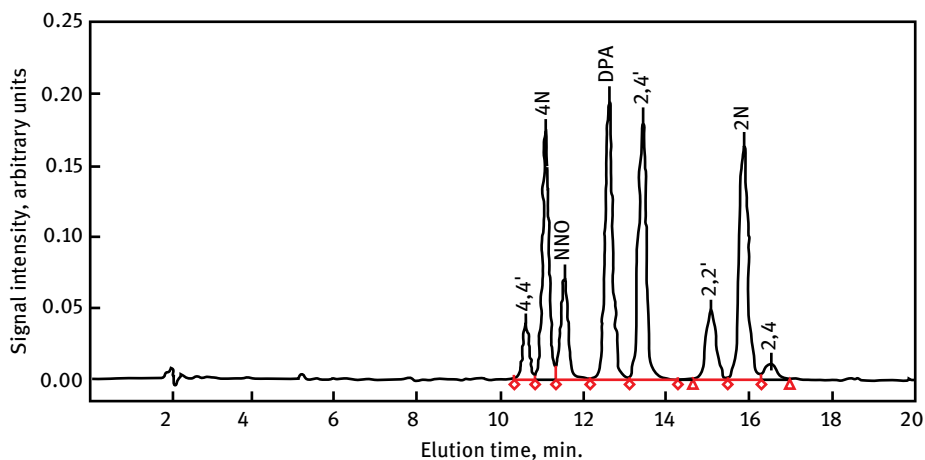
A variety of methods for analysis of diphenylamine in solid propellants are offered in MIL-STD 286C [74] (Table 11) and MIL-D-98A. Additional analysis methods are described in [75].

**Table 11:** Analytical methods for determination of diphenylamine in propellants.

| Title of analytical method                                                                                                 | No. of pages | Method number |
|----------------------------------------------------------------------------------------------------------------------------|--------------|---------------|
| <i>Diphenylamine (Gravimetric Method)</i>                                                                                  | 3            | 201.2.3       |
| <i>Diphenylamine (Solvent Extraction – Bromination Method)</i>                                                             | 2            | 201.1.4       |
| <i>Diphenylamine and Ethyl Centralite in Admixture or Separately (Steam Distillation Spectrophotometric Method)</i>        | 4            | 201.4.2       |
| <i>Diphenylamine or Ethyl Centralite (Steam Distillation Volumetric Bromination Method)</i>                                | 3            | 217.3.1       |
| <i>Diphenylamine and Ethyl Centrality in Admixture or Separately (Distillation Gravimetric and Volumetric Bromination)</i> | 4            | 217.4.1       |
| <i>Diphenylamine and Its Major Derivatives (HPLC Method)</i>                                                               | 5            | 217.5         |

Data source: [74]

High-performance liquid chromatography (HPLC) analysis with UV detection per Method 217.5 gives good separation of DPA and the reaction products of DPA with  $\text{NO}_x$  that may be found in aged propellant (Figure 3).



**Figure 3:** Typical HPLC fractogram of diphenylamine and its reaction products. (Reproduced and modified from [74].)

#### 6.4 Diphenylammonium Salts

The nitrate and perchlorate salts of diphenylamine have been prepared and characterized by elemental analysis, TGA, and DSC [76]. The proton transfer reaction plays a major role during thermolysis of these salts. On heating, the nitrate and perchlorate salts do not form ring-substituted nitro or perchloro derivatives; rather, they ignited and exploded, forming gaseous products along with some residual carbon.

### 7 *N*-Phenyl- $\beta$ -naphthylamine

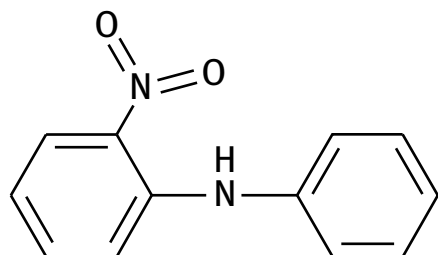
When used as a stabilizer, *N*-phenyl- $\beta$ -naphthylamine has the advantage over diphenylamine that it has lower volatility. It is also used as an antioxidant in polymers and lubricants. *N*-Phenyl- $\alpha$ -naphthylamine is a suspected carcinogen [77].

## 8 *N*- and Ring-Substituted Aniline Derivatives

### 8.1 2-Nitrodiphenylamine

2-Nitrodiphenylamine, also known as benzeneamine 2-nitro-*N*-phenyl-, 2-nitro-*N*-phenylaniline, mononitrodiphenylamine,  $C_{12}H_{10}N_2O_2$ , 2-NDPA, CAS RN [119-75-5], is a widely used stabilizer in double-base propellants. 2-Nitrodiphenylamine is a red

crystalline solid, usually in the form of flakes or powder, with a melting point of 347–349 K (74–76 °C).



Solid double-base rocket propellant formulations with 2-nitrodiphenylamine as the stabilizer will be discussed in a future volume of the *Encyclopedia of Rocket Propellants*. The current chapter contains only the physical and chemical properties of 2-nitrodiphenylamine by itself.

2-Nitrodiphenylamine is made from *o*-chloronitrobenzene (OCNB) and aniline, but some of the raw material is sometimes inadvertently carried over into the product and eventually ends up in double-base propellants where 2-NDPA is used as a stabilizer. The contaminant OCNB has been reported to cause tumors in male and female rats.

## 8.2 Physical Properties of 2-Nitrodiphenylamine

The physical and thermodynamic properties of 2-nitrodiphenylamine are summarized in Table 12. Additional properties of 2-nitrodiphenylamine are listed in [78].

**Table 12:** Physical and thermodynamic properties of 2-nitrodiphenylamine.

| Property                         | SI units               | Non-SI units      | References   |
|----------------------------------|------------------------|-------------------|--------------|
| Molecular mass                   | 214.220 g/mol          | 214.220           | [7]          |
| Melting point                    | 348.1 K                | 75 °C             | [7]          |
| Density                          | 1.48 g/cm <sup>3</sup> | 0.0535 lb/cu. in. | [79]         |
| Oxygen balance                   | −201.7%                | —                 |              |
| Enthalpy of formation            | +121.0 kJ/mol          | +135 cal/g        | [79]         |
|                                  |                        | = +28.92 kcal/mol |              |
|                                  | +79.0 kJ/mol           | +88.13 cal/g      | [72], p. 327 |
|                                  |                        | = +18.88 kcal/mol |              |
|                                  | +77 ± 2 kJ/mol         | +18.4 kcal/mol    | [80]         |
| Heat of sublimation at 335–346 K | 100.9 kJ/mol           | 24.1 kcal/mol     | [7]          |
| Heat of combustion               | 6228 ± 2 kJ/mol        | 1488 kcal/mol     | [80]         |

### 8.3 Chemical Properties of 2-Nitrodiphenylamine

The major role of a stabilizer is to eliminate the acidic nitrates and nitrogen oxides produced by the gradual decomposition of nitric acid esters, which would otherwise autocatalyze further decomposition. Typically, 1–2% stabilizer is added to the propellant mixture; higher amounts than 2% degrade the propellant's ballistic properties. The amount of stabilizer depletes gradually with time; when the content drops from 2% to less than 0.5% NDPA, increased surveillance of the munition is required, and a content of less than 0.2% warrants immediate disposal, as the depletion of the stabilizer may lead to autoignition of the propellant during storage at high temperatures or in confined spaces. Other stabilizers of a similar aromatic amine pedigree are 4-nitrodiphenylamine, *N*-nitrosodiphenylamine, *N*-methyl-*p*-nitroaniline, and the unsubstituted diphenylamine.

#### 8.3.1 Reactions of 2-Nitrodiphenylamine

The reaction of 2-nitrodiphenylamine with  $\text{NO}_x$ , which occurs in aging double-base propellants, yields a mixture of nitration and nitrosation products.

#### 8.3.2 Analysis of 2-Nitrodiphenylamine

2-Nitrodiphenylamine that is intended to be used as a stabilizer in solid or liquid monopropellants must meet the requirements of *Military Specification MIL-N-3399B – 2-Nitrodiphenylamine* [81]. The minimum melting point allowed per this specification is 346 K (73°C). The maximum insoluble residue allowed in 95% ethanol is 0.2 mass-%, and the maximum allowed ash content is 0.1 mass-%.

The amount of 2-nitrodiphenylamine in a propellant can be determined by a titanium(III) chloride buffer method or by reaction with an excess of bromide/bromate and back titration of the excess bromine with iodide and standard sodium thiosulfate per MIL-STD-286C [82], Table 13. The spectrophotometric method determines the amount of 2-NDPA by measuring the absorption at 420–430 nm. Additional analytical methods are described in [78].

The nitration and nitrosation products of 2-nitrodiphenylamine (2-NDPA) were synthesized *in vitro*, mimicking their production in aging propellants by exposing 2-NDPA to gaseous  $\text{N}_2\text{O}_4$  or nitrous acid in various solutions and by nitration and oxidation of NO/2-NDPA [83]. Reactants and products were analyzed by preparative-scale liquid chromatography using a short  $\text{SiO}_2$  column and by UV-VIS and IR spectra.

Reversed-phase high-performance liquid chromatographic methods can be used for the determination of stabilizers including diphenylamine, 2-nitrodiphenylamine, and *N*-methyl-4-nitroaniline in double-base solid propellants, even in the presence of RDX, DANPE, or TAGN [84].

**Table 13:** Analytical methods for determination of 2-nitrodiphenylamine.

| Title of analytical method                                              | No. of pages | Method number |
|-------------------------------------------------------------------------|--------------|---------------|
| <i>2-Nitrodiphenylamine (Spectrophotometric Method)</i>                 | 2            | 218.4.3       |
| <i>2-Nitrodiphenylamine (Titanous Chloride – Buffer Method)</i>         | 2            | 218.2.1       |
| <i>2-Nitrodiphenylamine (Volumetric Bromination Method)</i>             | 2            | 218.1.2       |
| <i>2-Nitrodiphenylamine (Resorcinol – Liquid Chromatography Method)</i> | 3            | 218.5.1       |

Data source: [82]

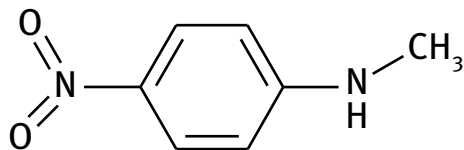
A reversed-phase isocratic HPLC technique was used to separate 2-nitrodiphenylamine and its major reaction products with nitrogen oxide in double- and triple-base rocket and artillery propellants [85]. These compounds were determined in a single-base gun propellant during a storage period of 168 h at 100 °C using a developed and successfully verified HPLC method. See also [86].

#### 8.4 Safety Properties of 2-Nitrodiphenylamine

2-Nitrodiphenylamine that is leached from spilled propellant into the soil is only slowly degraded by soil bacteria [87].

### 9 *N*-Methyl-*p*-nitroaniline

*N*-Methyl-*p*-nitroaniline, also known as *N*-methyl-4-nitroaniline, 4-nitro-*N*-methylaniline, benzeneamine *N*-methyl-4-nitro-,  $\text{O}_2\text{NC}_6\text{H}_4\text{NHCH}_3$ ,  $\text{C}_7\text{H}_8\text{N}_2\text{O}_2$ , MNA, CAS RN [100-15-2], is used as a stabilizer in double-base solid propellants.



Studies indicated that 4-nitro-*N*-methylaniline is superior to centralite, 2-nitrodiphenylamine, or Acardite in stabilizing NC. 4-Nitro-*N*-methylaniline forms brownish-yellow prisms with violet reflections. It decomposes soon after it starts melting. Physical properties of MNA are summarized in Table 14.

The toxicity of MNA, measured as the LD50, is 400–800 mg/kg (mice, intraperitoneal) and 800–1600 mg/kg (mice, oral). MNA caused slight skin irritation in guinea pigs after 24 h of skin contact.



**Table 14:** Physical properties of *N*-methyl-*p*-nitroaniline.

| Property              | SI units                | Other units                |
|-----------------------|-------------------------|----------------------------|
| Molecular mass        | 152.1506 g/mol          | 6.5724 mol/kg              |
| Oxygen balance        | −168.3%                 | —                          |
| Melting point         | 424.8 K                 | 151.7 °C = 305 °F          |
| Density               | 1.190 g/cm <sup>3</sup> | 0.0430 lb/in. <sup>3</sup> |
| Enthalpy of formation | −31.4 kJ/mol            | −7.5 kcal/mol = −49 cal/g  |
| Heat of combustion    | 3867 kJ/mol             | 924.3 kcal/mol             |

## 10 Aromatic Nitramines

2,4,6-Trinitrophenylmethylnitramine, also known as tetryl, tetranitromethylaniline, empirical formula  $C_7H_5N_5O_8$ , CAS RN [479-45-8], with a molecular mass of 287.1 g/mol and an oxygen balance of −47.4%, forms pale yellow crystals. Tetryl is used as a powerful explosive, often as the booster pellet for card gap tests. It is not used in rocket propellants. The lead block indentation of tetryl is 410 cm<sup>3</sup>/10 g, as compared to 300 cm<sup>3</sup>/10 g for TNT and 483 cm<sup>3</sup>/10 g for RDX.

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# Aromatic Hydrocarbons

## Introduction

*Encyclopedia of Liquid Fuels* contains eight chapters dealing with hydrocarbon fuels. The topic of hydrocarbon fuels had to be subdivided into several smaller sections that were easier to arrange in alphabetical order in five subvolumes of equal size. The titles of the eight hydrocarbon chapters are: “Alkanes,” “Alkenes and Alkynes,” “Aromatic Hydrocarbons,” “Cycloaliphatic Hydrocarbons,” “Hydrocarbons,” “Jet Fuels,” “Kerosenes,” and “Ramjet Fuels.”

## 1 Aromatic Hydrocarbons

Aromatic hydrocarbons are organic compounds with typically six-membered rings where carbon atoms sometimes drawn as alternating double bonds actually share their electron clouds, giving the ring structure increased stability compared to alicyclic saturated hydrocarbon compounds. This type of structure is also called a “resonance structure.” The parent member of the family of aromatic hydrocarbons is benzene.

## 2 Benzene

Properties of aromatic hydrocarbons such as benzene, toluene, [1] and the xylenes are already listed in most readily available handbooks [2]. These data are readily accessible from the literature, so we have not included them in our listing of the properties of rocket propellants.

## 3 Toluene

Toluene,  $C_6H_5CH_3$ , methylbenzene, phenylmethane, CAS RN [108-88-3], may be found as a trace constituent in some kerosene-type products from petroleum refineries. Toluene has not often been used as a rocket fuel. Toluene was used in a rocket engine and compared to methylcyclohexane and heptane as the fuels [3].

Toluene is of interest as it is the product of the thermolysis of endothermic fuels such as methylcyclohexane. Toluene is the parent compound of a very widely used explosive, trinitrotoluene (TNT).



### 3.1 Physical Properties of Toluene

Toluene boils at 384.7K (110.6 °C). The dependence of the vapor pressure of toluene on temperature can be expressed by a Cox equation,

$$\ln\left(\frac{P}{P_c}\right) = \left(1 - \frac{1}{T_r}\right) \exp(2.32973 - 1.10646T_r + 0.73531T_r^2)$$

where the reduced temperature  $T_r = T/T_c$ ,  $T$  is the temperature in kelvin,  $T_c$  is the critical temperature (593 K), and  $P_c$  is the critical pressure (4109 kPa) [4].

#### 3.1.1 Thermodynamic Properties of Toluene

The results of heat capacity measurements of subcritical toluene at saturation pressure between 300 and 580 K were only given in table format in [4]. It would have been more practical to give the parameters for a curve-fitted polynomial equation.

### 3.2 Safety Properties of Toluene

#### 3.2.1 Limits of Flammability of Toluene

The flammable range of toluene vapor in air at 373 K is from 1.2 to 7.1 vol.-%.

#### 3.2.2 Flash Point of Toluene

The flash point of toluene is 277.5 K (4.4 °C).

#### 3.2.3 Autoignition Temperature of Toluene

The autoignition temperature of toluene in air is 841 K (568 °C = 1054 °F), which is much higher than that of any alkane hydrocarbon. Other sources give an autoignition temperature of 753 K (480 °C).

## 4 Xylenes

Xylenes are dimethylbenzenes. There are three isomers: *o*-xylene, *m*-xylene, and *p*-xylene. Xylenes have not been used as rocket propellants. Xylenes may be found as trace constituents in some kerosenes, depending on the source of the crude and the processing history.

## 5 Ethylbenzene

Ethylbenzene,  $C_6H_5C_2H_5$ , a homologue of toluene, is found as a natural constituent of petroleum and in gasoline and kerosene. Ethylbenzene can be synthesized from benzene and ethene. Most of the ethylbenzene is used for the production of styrene, an important monomer for the production of polystyrene. Ethylbenzene is not used as a rocket propellant.

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# Azides and Azido Compounds

## Azides and Azido Compounds

This chapter contains information on inorganic and organic azides. The azide group carries extra energy that make these compounds useful as rocket propellant ingredients. In addition, many of these compounds contain a large amount of nitrogen, which makes them valuable as ingredients in nitrogen gas generators, such as in airbag inflators.

Azides contain three nitrogen atoms linked to each other in a very energetic, linear configuration. Theoretically the three nitrogen atoms could form a triangle, as in triaziridine, but that configuration is unstable. Most azides have a positive enthalpy of formation and decompose readily, liberating dinitrogen. The simplest azide, hydrogen azide, is a highly explosive and very toxic substance and has been the cause of many accidents. The following sections are subdivided into inorganic azides and organic azides. Both types of azides are being used in rocket propellant and gas generant formulations. Heavy metal azides are shock sensitive (stab sensitive) and are used as percussion primers in fire weapons. That application is not included in this book.

Early investigators assumed the shape of  $\text{N}_3^-$  azide ion to be a closed triangle, but other indications soon supported the linear structure of a chain of three nitrogen atoms. The open linear formula bore the perceived problem of a pentavalent middle nitrogen atom. This tripping point was later overcome by the resonance description of the azide ion: the nitrogen atom in the middle appears as iminium function, whereas the two terminal nitrogen atoms share the anionic charge. X-ray diffraction analyses and many other physical methods soon confirmed this open-chain structural formula of azides.

### 1 Inorganic Azides

The azide in solid inorganic azides exists as the  $\text{N}_3^-$  anion in a crystal lattice of anions and cations. In this configuration the azide ion is often grouped in the group of “pseudohalogenides” because it behaves like chloride or bromide or iodide, for instance in forming the insoluble silver salts. Inorganic azides, such as lead azide, are used as primary explosives (percussion initiators) and other azides, such as sodium azide, are used as sources of nitrogen in gas generants, predominantly those used for inflation of airbags in automobiles. We are not planning on providing a complete list of heavy metal azides like those used as primary explosives. Our inclination is to stay as far away from those as possible and take all necessary steps to prevent the inadvertent formation of shock-sensitive and friction-sensitive azides while preparing and using other azides.

The experimentally well-characterized covalent halogen azides ( $\text{XN}_3$ , where  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) are a group of energetic compounds that could potentially be used as oxidizers if only they were not so sensitive. There are also highly unstable N-bound azides such as  $\text{ON}-\text{N}_3$  and  $(\text{FSO}_2)_2\text{N}-\text{N}_3$ , but those are only of academic interest.

The primary purpose of this section on inorganic azides is to summarize the properties of solid azides that are useful sources of nitrogen in gas generants.

In addition to the most frequently used sodium azide, many other azides have been synthesized in an effort to obtain improved nitrogen output or higher energy content. The most interesting inorganic azides are those of ammonium and hydrazinium, compounds consisting only of nitrogen and hydrogen. Both have been evaluated as rocket propellants.

Ammonium azide, hydrazinium azide, and other inorganic azides are described in a comprehensive summary on inorganic azides [1]. Table 1 is a summary of the nitrogen content of inorganic azides.

**Table 1:** Nitrogen content of inorganic azides.

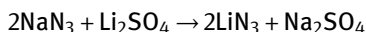
| Compound name     | Formula                          | CAS RN     | M<br>g/mol | Nitrogen content<br>Mass-% |
|-------------------|----------------------------------|------------|------------|----------------------------|
| Lithium azide     | $\text{LiN}_3$                   | 19597-69-4 | 48.96      | 85.83                      |
| Sodium azide      | $\text{NaN}_3$                   | 26628-22-8 | 65.01      | 64.64                      |
| Potassium azide   | $\text{KN}_3$                    | 20762-60-1 | 81.1184    | 51.80                      |
| Ammonium azide    | $\text{NH}_4\text{N}_3$          | 12164-94-2 | 60.059     | 93.29                      |
| Hydrazinium azide | $\text{N}_2\text{H}_5\text{N}_3$ | 14662-04-5 | 75.08      | 93.28                      |

## 1.1 Alkali Metal Azides

Alkali metal azides are useful as sources of nitrogen. All alkali metal azides are very toxic, comparable to potassium cyanide. Literature summaries on azides will provide the reader with additional information on these substances [1–3].

### 1.1.1 Lithium Azide

Lithium azide can be prepared by metathetical reactions starting with the readily available sodium azide



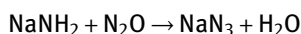
### 1.1.2 Sodium Azide

Sodium azide,  $\text{NaN}_3$ , CAS RN [12136-89-9] or [26628-22-8], is widely used as a source of nitrogen in airbag inflators. With a nitrogen content of 64.6 mass-% N it is a good

source of nitrogen in gas generants. Sodium azide is the most frequently produced and most used alkali metal azide. There would be much more information on sodium azide available from a wide variety of sources than can be presented here. The current section is only an incomplete sampling of some of the information, just a way to get started.

### 1.1.2.1 Production of Sodium Azide

Sodium azide is produced by reaction of sodium amide with nitrous oxide



### Coatings for Sodium Azide

Coatings were developed for various types of azides, to protect them from ambient moisture and carbon dioxide or to reduce their volatility, as was recommended for ammonium azide.

One would hesitate to mix sodium azide with an acid (any acid) for fear of releasing hydrogen azide. Thus, it is unclear what motivated some investigators to coat sodium azide with stearic acid. Although stearic acid is a good pelletizing aid if gas generants for airbag inflators need to be pelletized, it is still an **acid** [4]. Although stearic acid is a weak acid, there is always the potential of liberating free hydrogen azide and getting into trouble. The other coating material tested was nitrocellulose [5]. The results of these experiments showed that the decomposition temperature of nitrocellulose coated sodium azide was about 50 °C higher than that of the pure sample.

### 1.1.2.2 Physical Properties of Sodium Azide

Physical properties of sodium azide are summarized in Table 2.

**Table 2:** Physical properties of sodium azide.

| Property              | SI units                                   | Other units                                   | References |
|-----------------------|--------------------------------------------|-----------------------------------------------|------------|
| Molecular mass        | 65.0099 g/mol                              | 15.382 mol/kg                                 | [6]        |
| Melting point         | 548 K (dec.)                               | 275 °C = 527 °F (dec.)                        |            |
| Density               | 1.846 g/cm <sup>3</sup> (at 293 K = 20 °C) | —                                             |            |
|                       | 1.849 g/cm <sup>3</sup>                    | 0.0668 lb/in <sup>3</sup>                     | [7]        |
| Heat capacity         | 76.6 J mol <sup>-1</sup> K <sup>-1</sup>   | 18.31 kcal mol <sup>-1</sup> °C <sup>-1</sup> |            |
| Enthalpy of formation | +21.76 kJ/mol                              | +80 cal/g = +5.2 kcal/mol                     | [7]        |

### Solubility of Sodium Azide

The solubility of sodium azide in water is 38.9 g/100 mL (at 273 K = 0 °C), 40.8 g/100 mL (at 293 K = 20 °C), and 55.3 g/100 mL (at 373 K = 100 °C). Sodium azide is very solu-

ble in ammonia and somewhat soluble in methanol (2.48 g/100 mL at 298 K = 25 °C) or ethanol (0.22 g/100 mL at 273 K = 0 °C).

### Thermodynamic Properties of Sodium Azide

Standard enthalpies of formation of groups of inorganic and organic azides were calculated based on data for crystalline and aqueous ammonium azide and silver azide [8]. Data are presented for  $[\text{Me}_4\text{N}]\text{N}_3$  and  $[\text{Et}_4\text{N}]\text{N}_3$ , also in comparison to  $[\text{Me}_4\text{N}]\text{NO}_3$  and  $[\text{Et}_4\text{N}]\text{NO}_3$ .

### Molecular Properties, Crystal Structure, Dipole Moment of Sodium Azide

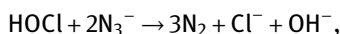
Sodium azide is an ionic solid. Two crystalline polymorphs are known, one rhombohedral and the other hexagonal. Both adopt layered structures [9].

Three pressure-induced phase transitions of sodium azide were observed by *in situ* synchrotron XRD measurements in a diamond anvil cell up to 52.0 GPa at room temperature [10]. The phase transition pressures were 0.3, 17.3, and 28.7 GPa. The first high pressure phase,  $\alpha\text{-NaN}_3$  (0.3 ~ 17.3 GPa), was identified to be monoclinic with a  $C_{2/m}$  space group. The  $\beta\text{-NaN}_3$  to  $\alpha\text{-NaN}_3$  transition is a second-order phase transition, accompanied by the shearing of the Na-layers and the tilting of the azide chains. The second high-pressure phase,  $\gamma\text{-NaN}_3$  (18.4 ~ 28.7 GPa), had a lower symmetry than  $\alpha\text{-NaN}_3$ . A further phase transition of  $\gamma\text{-NaN}_3$  to  $\delta\text{-NaN}_3$  at 28.7 GPa was observed.

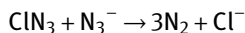
#### 1.1.2.3 Chemistry of Sodium Azide

##### Reactions of Sodium Azide with Other Compounds

The oxidation of azide by ozone has been studied as one method of azide disposal and clean-up if azide (e.g., from airbag inflators) is accidentally spilled into surface waters [11]. Another method for the disposal of azide is the reaction with sodium hypochlorite [12]. The reaction stoichiometry is:



and proceeds by a key intermediate chlorine azide,  $\text{ClN}_3$ , which subsequently decomposes by reaction with a second azide molecule in the rate determining step:



Another method for disposal of azide ions in aqueous solutions is by catalytic hydrogenation [13].

### Thermal Decomposition of Sodium Azide

Sodium azide is thermally more stable than any of the organic sources of nitrogen in nitrogen gas generants, such as the ones used in airbag inflators. A good summary of the thermal decomposition of sodium azide and other metal azides is provided in

[14]. The rate of decomposition of sodium azide was proportional to the surface area of the reacting crystals. Reaction commenced at the edge of thin crystals and proceeded inwards parallel to the azide ions.

A study of the kinetics of thermal decomposition of sodium azide crystals provided experimental results for the rates of decomposition, which fell into three temperature regions: **(1)** below 573 K (300 °C); **(2)** 573–618 K (300–345 °C); and **(3)** above 623 K (350 °C) [15, 16]. Below 573 K (300 °C) the rate followed a linear relation after a rapid initial stage, leaving a white residue in the shape of the original crystal. The reaction began on preferred crystallographic faces and moved along a two-dimensional path towards the center of the crystal. During the progress of decomposition, a sharp line of demarcation was observed at the undecomposed azide and white residue interface. Between 573–618 K (300–345 °C) the rate was of the sigmoid curve shape, leaving white residue enclosing a central cavity. Above 623 K (350 °C) two different linear rates were observed, the latter being 100 times faster than the former with no detectable residue. The enhanced rate was attributed to adsorbed elemental sodium which catalyzes the reaction.

There is evidence that the decomposition takes place over a surface or interface which moves into the crystal in a preferred crystallographic direction. It is the area of this surface which controls the rate of decomposition [17]. The kinetics of thermal decomposition of sodium azide were dependent on the specific surface area of crystals [18]. Decomposition commenced at the edges of crystal platelets and advanced inward in directions parallel to the alternating planes of sodium and azide ions. The acceleration and decay of the decomposition after an initial first stage was dependent on the development of a closed two-dimensional envelope at the crystal edges and a subsequent contraction of the envelope. The boundary between decomposed and undecomposed material was indicated by three colored zones of the sodium decomposition product in different states of aggregation. With crystals grown slowly from aqueous solutions a residue remained when crystals were decomposed at temperatures up to 643 K (370 °C). At temperatures higher than 643 K (370 °C), where NaOH is appreciably volatile, little residue remains.

The thermal decomposition of sodium azide has been investigated by monitoring changes in dielectric constant, dielectric loss, and pressure with time at a fixed frequency during decomposition at 535–578 K (262–305 °C), and by monitoring changes in dielectric properties with frequency in the range 100–300 kHz for samples cooled to 293 K (20 °C) after partial decomposition at 563 K (290 °C) [19]. Three stages of decomposition could be identified for  $\alpha < 0.02$ , and activation energies for the three stages and for two types of sodium azide varied between 117 and 307 kJ/mol (28.0 and 73.4 kcal/mol).

Sodium azide doped with 1 mol-% potassium azide or 1 mol-% cesium azide showed a significant shortening of the induction period for decomposition at above 573 K (300 °C), but a lengthening of the induction period at low temperatures [20].



The extent to which cations affect the decomposition of sodium azide depends on their ionic radii. A similar effect was noted as the result of doping with  $\text{Ba}^{++}$  or  $\text{Hg}^{++}$  ions [21].

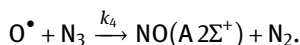
Differential thermal analysis and thermogravimetric analysis of sodium azide diluted with sodium chloride both showed one major peak followed by a second minor one [22]. This was interpreted as indicating the occurrence of two distinct decomposition processes. The activation energy of the first major process was 36 kcal/mol, which agreed with values reported previously from measurements of the rate of nitrogen evolution. Differential thermal analysis of sodium azide mixed with alumina was complicated by the presence of variable amounts of water adsorbed on the alumina. The presence of water was shown to have an inhibiting effect on the decomposition.

The thermal decomposition of sodium azide has been studied in the temperature range 513–633 K (240–360 °C) in vacuum and under pressure of an inert gas, argon [23]. The results showed that the decomposition is only partial at temperatures below 633 K (360 °C). It was found that: **(1)** the decomposition is incomplete both under vacuum and inert gas; **(2)** mass spectrometric studies did not reveal any decrease in the intensity of the background species,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{H}_2\text{O}^+$ , and **(3)** sodium metal remained in the “free state” as seen by the formation of a metallic mirror at temperatures above 573 K (300 °C). It has been argued that the partial nature of decomposition is due to the confinement of the decomposition to intermosaic regions within the crystal lattice.

The effects of dopants and pretreatment, mechanical and thermal pretreatment, on the thermal decomposition of sodium azide have been investigated with a view to understanding the role of crystal imperfections in the decomposition [24]. It was observed that aliovalent ions,  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions, as well as precompression, sensitized the decomposition while preheating lowered the decomposition rate. The effects were then discussed in terms of the dependence of the decomposition rate upon the concentration of gross imperfections in the sodium azide crystal lattice.

When the thermal decomposition of sodium azide was investigated in the temperature range 513–638 K (240–365 °C), 3 values for the activation energy, 155, 247, and 58 kJ/mol (37.0, 59.0, and 14 kcal/mol) were obtained, depending on the temperature range studied [25]. The mechanism of decomposition seems to involve excited azide ions (through internal conversion) and excitations. The activation energy of 58 kJ/mol (14 kcal/mol) appears to be associated with the promotion of electrons in the presence of sodium metal.

Gaseous azide radicals at concentrations up to  $10^{13}$  molecules  $\text{cm}^{-3}$  appear to have been generated in a flow system during the thermal decomposition of solid  $\text{NaN}_3$  at temperatures between 423 and 623 K (150 and 350 °C) [26]. Between 423 and 523 K (150 and 250 °C), the activation energy for the decomposition was  $0.80 \pm 0.15$  eV. The addition of small concentrations of oxygen atoms to the reactor excites NO  $\gamma$ -band chemiluminescence from the reaction



The  $\gamma$ -band emission may be used as a sensitive tracer for  $N_3$  in kinetic measurements;  $k_4$  was determined to be  $(10 \pm 4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Large concentrations of O atoms quantitatively convert the  $N_3$  to NO, and the resulting O/NO afterglow has been used to determine absolute concentrations of the  $N_3$  radicals. Several other chemiluminescent emissions are observed, most notably the nitrogen first-positive emission excited in azide-radical recombination.

The decomposition characteristics of  $\text{NaN}_3$  are variable and depend on parameters such as the particle size and shape, heating rate, defect concentration, and purity. The catalyzed thermal decomposition of  $\text{NaN}_3$  was found to be remarkably sensitive to metal oxides that may be present as contaminants. The effect of  $\text{Mn}^{2+}$  doping on the thermal decomposition of sodium azide has been studied [27]. It was found that  $\text{Mn}^{2+}$  is acting as an electron donor in compositions with some intermediate reaction occurring.

Evaluating another catalyst, a series of  $\text{NiO}/\text{Co}_3\text{O}_4$  mixed oxides in different ratios, 0.1–50 mol-%, were prepared by an impregnation method and tested for their activity in  $\text{NaN}_3$  decomposition [28].

The thermal decomposition of sodium azide was studied by thermal analysis to isolate effects caused by the gas atmosphere species, gas pressure, sample type (powdered or tablet), particle size, sample weight, surface heterogeneity, additives, and pre-aging [29]. Very complicated reaction mechanics arose if those effects were combined. It became evident that heat and mass transfer effects must also be considered when evaluating the thermal reactivity of sodium azide and its mixtures.

Manganese(IV) dioxide acts both as a catalyst and as an oxidizer in the decomposition of sodium azide, a reaction that is of interest for the use of sodium azide in airbag inflators [30]. Both  $\text{MnO}_2/\text{NaN}_3$  binary mixtures and  $\text{MnO}_2/\text{NaN}_3/\text{SiO}_2$  ternary mixtures were studied by thermal analysis, measurement of gas evolution, heat of reaction and burning rates. On heating, the thermal reaction for all mixtures started at 673 K (400 °C). The onset temperature was not sensitive to the mixture ratio of oxides and sodium azide.  $\text{MnO}_2$ -rich formulations produced some nitrogen oxides.

The effect of the surrounding gas atmosphere on the thermal decomposition of sodium azide was examined by thermal analysis, electrical conductivity measurement during heating and hot-stage microscopic observations [31]. Microscopic observations showed that the decomposition of  $\text{NaN}_3$  occurred regardless of the type of atmosphere surrounding it. The electrical conductivity increased with increasing temperature and suddenly became unmeasurably large (metallic sodium) when the temperature reached 653 K (380 °C).

The thermal decomposition of sodium azide with and without addition of metal oxide catalysts was studied by a combined differential thermal analysis-thermogravimetric analysis (DTA-TGA) method [32]. The onset of decomposition temperature was reduced by addition of metal oxides like  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$ . Similar reactions take place in airbag inflator gas generants.

The thermal decomposition of sodium azide and its mixtures was examined by DTA and the energy of activation,  $E_a$ , and pre-exponential factor,  $A$ , were calculated by the Kissinger and Ozawa equations [33].

#### 1.1.2.4 Handling of Sodium Azide

##### Transportation, Storage, and Disposal of Sodium Azide

Disposal of sodium azide in decommissioned airbag inflators has become a serious worldwide safety problem [34]. The primary approach was to activate the airbag inflators in the automobiles remotely from a safe distance before beginning to dismantle and shred the automobiles in the wrecking yards. It was assumed that the controlled activation and combustion consumes all azide contained in the gas generant and that there are no unburnt azide residues in the inflator and its filters. The section on reactions of azides (Section 1.1.2.3) contains several chemical reactions that are suitable for the disposal of azide.

#### 1.1.2.5 Toxicity of Sodium Azide

The literature on sodium azide toxicity was reviewed and summarized in several publications [35, 36]. Many of the toxic and environmental effects listed here for sodium azide would apply to other alkali metal azides as well. There is just more information on sodium azide than on the other azides. The active and toxic ingredient in all those cases is the azide ion, not the metal ion. The toxicity of sodium azide was a major concern during the development of gas generants for airbag inflators. Excessive concern about the toxicity of sodium azide may have forced the airbag inflator industry to switch to azide-free gas generants, some of which, in particular the ammonium nitrate-based gas generants, turned out to have other, more deadly side effects.

##### Acute Toxicity of Sodium Azide

The toxicity of azides is due to inhibition of cytochrome C oxidase in the blood. Azide inhibits cytochrome oxidase by binding irreversibly to the heme cofactor in a process like the action of carbon monoxide. Sodium azide particularly affects organs that need oxygen for high metabolism, such as the heart and the brain. Methods developed during medical surveillance of workers in sodium azide processing plants can also be applied to workers involved with other azide chemicals, e.g., glycidyl azide polymer (GAP).

The widespread use of sodium azide in airbag inflators has increased the risk of accidental exposures both during the manufacturing, active use, and eventually the disposal of airbag inflators [37].

The development of an occupational health surveillance and exposure control system for a chemical manufacturing plant making sodium azide has had to confront biological and hygienic difficulties related to the toxic nature of sodium azide. Sodium azide in pellet form was to be used as the nitrogen gas generant for automobile air

bags, but before it could be pelletized, it was manufactured as a very fine powder, liable to be carried away as dust, making exposure control more difficult. Sodium azide is a rapidly active, hypotensive agent that causes headaches and sudden drops in blood pressure. Occupational health assessment of the plant and its employees demonstrated the need for exposure control, based on inspection, interviews, health data, process review, and site review [38]. Engineering control and personal hygiene changes were developed in response to the evidence of worker exposure revealed by the studies.

Until 1996 there was no published literature describing occupational exposures to sodium azide in the rapidly growing automobile airbag inflator manufacturing industry. In 1994–1995, the National Institute for Occupational Safety and Health (NIOSH) conducted a cross-sectional study of health complaints reported by sodium azide production workers at the only continuous sodium azide production facility in the United States. The NIOSH evaluation consisted of a plant industrial hygiene survey, a symptom questionnaire, ambulatory blood pressure monitoring, and blood azide analysis [39]. Personal breathing zone air monitoring revealed exposures to sodium azide and hydrazoic acid at levels greater than the NIOSH recommended exposure limits (RELs). In some cases, exposures exceeded the REL despite the use of air-supplied respirators. The questionnaire revealed that most workers reported headache (10 of 11, 91%), episodes of low blood pressure (9 of 11, 82%), and palpitations (8 of 11, 73%) occurring in the production areas within the 6 months preceding the study. Mild headache (4 of 11, 36%) was the only symptom reported during a 24-h medical survey.

Despite its known toxicity and extensive current industrial use, the occupational neuropsychotoxicology of sodium azide had not yet been investigated until 2003. Neuropsychological and psychological tests, a symptom self-report questionnaire and hematological and cardiac measurements were gathered from 41 exposed workers and 42 unexposed workers in a chemical production plant annually for 3 years [40]. The exposed workers presented significantly more acute symptoms of exposure (headache, vertigo, nausea, fatigue, cardiac palpitations, irritated or red eyes) than did the unexposed workers; however, only one chronic symptom was repeatedly and more significantly reported, namely trembling of the hands. No psychological or neuropsychological tests (reaction time, psychomotor, cognitive, chromatopsia, profile of mood states) differentiated the two groups; however, acute effects of exposure on plasma creatinine and on systolic pressure were noted.

Table 3 is a summary of acute toxicity tests performed in test animals with hydrogen azide and sodium azide under various conditions of administration and with gradually increasing doses. The main objective of these tests was to determine the LD50 dosage or the LC50 concentration in air at which 50% of the test animals did not survive. This table is a summary compiled from nine different sources in the literature.

**Table 3:** Acute toxicity of hydrogen azide and sodium azide in animal tests.

| Test animal           | Mode of administration | Dose                 | Response, result        |
|-----------------------|------------------------|----------------------|-------------------------|
| <b>Hydrazoic acid</b> |                        |                      |                         |
| Mouse                 | Intraperitoneal        | 21.5 mg/kg           | Lethal dose             |
| Rat                   | Inhalation             | 849–967 ppm          | 0/14 died in 60 min.    |
| Rat                   | Inhalation             | 1024 ppm             | 3/8 died in 60 min.     |
| Rat                   | Inhalation             | 1081 ppm             | 3/4 died in 60 min.     |
| Rat                   | Inhalation             | 1138 ppm             | 17/18 died in 60 min.   |
| Rat                   | Inhalation             | 1162–1365 ppm        | 16/16 died in 60 min.   |
| Rat                   | Inhalation             | 1566 ppm             | 2/2 died in 30 min.     |
| Rat                   | Inhalation             | 1872 ppm             | 2/2 died in 19 min.     |
| Rat                   | Inhalation             | 2080 ppm             | 2/2 died in 10 min.     |
| <b>Sodium azide</b>   |                        |                      |                         |
| Rat                   | Oral                   | 40 mg/kg             | 0/3 died in 3 h         |
| Rat                   | Oral                   | 45 mg/kg             | 5/8 in 3 h              |
| Rat                   | Oral                   | 46 mg/kg             | 3/3 in 3 h              |
| Rat                   | Intraperitoneal        | 25 mg/kg             | 0/4 in 3 h              |
| Rat                   | Intraperitoneal        | 33 mg/kg             | 8/12 died in 3 h        |
| Rat                   | Intraperitoneal        | 37 mg/kg             | 5/5 died in 3 h         |
| Rat                   | Intraperitoneal        | 75 mg/kg             | LD75, 3/4 died in 3 h   |
| Rat                   | Subcutaneous           | 33 mg/kg             | 0/5 died in 3 h         |
| Rat                   | Subcutaneous           | 35 mg/kg             | 4/9 died in 3 h         |
| Rat                   | Subcutaneous           | 38 mg/kg             | 8/8 died in 3 h         |
| Mouse                 | Oral                   | 27 mg/kg             | LD50                    |
| Mouse                 | Oral                   | 37.4 mg/kg           | LD50                    |
| Mouse                 | Intravenous            | 19 mg/kg             | LD50                    |
| Mouse                 | Intraperitoneal        | 28–34 mg/kg          | LD50                    |
| Mouse                 | Intraperitoneal        | 18 mg/kg             | LD50                    |
| Mouse                 | Intraperitoneal        | 15–20 mg/kg          | LD50                    |
| Mouse                 | Intraperitoneal        | 23.7 mg/kg           | LD5                     |
| Mouse                 | Unspecified            | 27 mg/kg             | LD50                    |
| Mouse                 | Unspecified            | 23 mg/kg             | LD50                    |
| Monkey                | Intravenous            | 12 mg/kg             | LDLo <sup>a</sup>       |
| Monkey                | Intramuscular          | 20 mg/kg             | Sick but survived       |
| Monkey                | Intramuscular          | 10–12 mg/kg repeated | Death after 3–4 doses   |
| Monkey                | Intramuscular          | 5 mg/kg daily        | 5/6 died in 60–130 days |

<sup>a</sup>LDLo Lowest lethal dose

Data source: [41]

### Mutagenicity of Sodium Azide

Besides concern about acute and chronic toxicity effects of azides, there has been increased concern about possible mutagenic, teratogenic or carcinogenic effects of azides in mammals in general and in humans in particular; however, up to this time there are no indications that azides are mutagenic, teratogenic or carcinogenic in ei-

ther test animals or humans. During 1977, while certain members in US Congress actively opposed the introduction of airbags with azide inflators as a safety device in automobiles, a controversy evolved about mutagenic effects of azides on plants and bacteria and the implication of tests with plants and bacteria relative to the widespread use of azides in airbag inflators and potential exposure of automobile occupants to azides. The following information may assist in a critical evaluation of potential hazards in the use and disposal of azides in airbag inflators.

### Azide Mutagenicity in Bacteria

The test most commonly used to detect bacterial mutagens is the Ames test. This test is also used to screen materials for potential carcinogens. The mutagenesis test originated in a system developed by Dr. Bruce N. Ames and his co-workers at the University of California in Berkeley. Specially developed strains of *Salmonella typhimurium* which cannot grow without the essential amino acid histidine were selected for this test. The bacteria are placed onto a nutrient medium containing the suspected mutagen and all essential components except histidine. For growth to occur, the bacteria must mutate (revert). Mammalian liver enzymes can be added as a model for metabolic action. These enzymes convert potential mutagens into active forms. Sodium azide at  $10^{-4}$  M concentration was reported to cause a 30-fold increase in reversion rate in several strains of *S. typhimurium* and a similar increase in reversion rate for the histidine-requiring *Escherichia coli* strain WP2s. Azide treatment slightly increased the frequency of occurrence of penicillin-resistant and streptomycin-resistant mutants in *Staphylococcus aureus*. Results with several different types of *S. typhimurium* mutants have shown that azide is a base substitution mutagen [42–44]. The mutagenic action may not be due to azide, but to one of its metabolites. One mutagenic azide metabolite is L-azidoalanine,  $\text{N}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$  [45]. Treatment of DNA with hydrogen azide at pH 2.8 resulted in the release of the purines guanine and adenine from DNA [46]. The release of guanine and adenine was not observed at pH 7.0. In *E. coli*, azide is most effective as a mutagen in stocks defective for excision repair [47].

### Azide Mutagenicity in Plants

The mutagenic activity of sodium azide has been put to good use to develop new strains of grain (barley). Azide has been shown to be a potent mutagen in barley [48]. The mutation data suggested that azide may only act on replicating DNA. Azide has also been reported to be an effective mutagen in peas, rice, *Triticum monococcum* and soybeans. In barley, azide at pH 3 greatly increased mutation frequency but had no effect at pH 11. Studies of mutation frequency on germinating barley seeds suggest azide may act only on replicating DNA. These results, in connection with the experiments on bacteria suggest two things. First, hydrogen azide ( $\text{HN}_3$ ), rather than sodium azide is the mutagen. Further studies with plant tissue from tobacco leaves have shown that in plants, neutral compounds like sodium azide are not able to penetrate the epidermis, but hydrogen azide can penetrate this barrier. This may explain the pH dependence of

mutation frequency. The second result is that azide appears to induce a point mutation by removing a purine (especially adenine) from DNA. There is no gross change in the DNA or addition of extra bases to the DNA.

The mutagenic action of azide was studied in many different plant species, including oats [49], barley [50] and rice [51].

### **Azide Mutagenicity in Human Cell Cultures**

The mutagenicity of sodium azide in both higher plants and bacteria is well documented; however, in mammalian cells, research on the effects of azide on gene mutations has produced conflicting results. Sodium azide acted cytostatically to cytotoxicity on 2 lines of mammalian cells [52]. After application of the substance in an acidic environment the highest cytostatic effect was noted. The results of the DNA synthesis inhibition test suggested that sodium azide does not damage the DNA of the observed fibroblasts with any of the tested modes of application. In Chinese hamster cells, neither 20-h treatment in medium nor 60-min treatment in an acid environment gave rise to significantly increased occurrence of 6-TG-resistant mutations.

### **Carcinogenicity of Sodium Azide**

Based on animal tests, sodium azide is not a proven carcinogen.

### **Bacteriostatic Activity of Sodium Azide**

Sodium azide solutions are used to disinfect medical equipment (blood cell counters, dialysis equipment) and to sterilize aqueous fluids used in medical analytical and diagnostic methods where pathogens are killed without leaving any residue. Unfortunately, this use in medical laboratories has resulted in several fatal accidents. Azide destroys gram-negative bacteria, enabling the cultivation of streptococci in diagnostic tests [53].

Ammonia nitrogen remains in the soil longer than nitrate nitrogen that is readily leached from the soil by rain and irrigation water. Azides kill nitrifying soil bacteria that convert ammonia (ammonium) to nitrate and thus allow nitrogen fertilizer to remain in the soil longer so it can be absorbed by the roots of agricultural crop plants [54].

#### **1.1.2.6 Accident History of Sodium Azide**

In a review of accidental poisonings, most of the reported cases involved persons working in hematological laboratories with blood cell counters. The time between azide exposure and detection of hypotension can predict outcome. Fatal doses occurred with exposures of 700 mg (10 mg/kg). Non-lethal doses ranged from 0.3 to 150 mg (0.004 to 2 mg/kg) [35]. All victims with hypotension lasting for more than 1 h died.

The following is a collection of literature references and case histories in chronological order [55–60]. New approaches were sought for the treatment of this cause of

accidental human poisoning [61, 62]. Three fatal sodium azide poisonings were reported in 1989 [63]. Several patients in a dialysis center suffered hypotension when residual azide after sterilizing the equipment entered their bloodstream [64]. There has been a rare sodium azide poisoning by skin contact and dermal absorption of sodium azide [65].

#### 1.1.2.7 Environmental Effects of Sodium Azide in the Soil

The environmental fate of sodium azide is of considerable interest given the widespread distribution in automobile air bag inflators. Since the mid-1990s, demand for sodium azide has exceeded 5 million kg per year and most passenger vehicles sold in the United States between 2000 and 2010 contained approximately 300 g (~0.7 lb) of sodium azide [66]. This has greatly increased the potential for accidental environmental releases and for human exposure to sodium azide. This is because not only are millions of kilograms of sodium azide now transported to and processed at air bag inflator factories, but it is also widely distributed throughout the developed world in automobiles. Even if sodium azide were to be replaced by a more benign propellant in the future, the problem of safely disposing of large quantities of azide will remain as the vehicle fleet ages and is retired to scrap yards and shredders. Additional work is required to study the environmental fate of sodium azide at the end of its road trip.

Azides (mostly potassium azide) have been used for the control of nematodes in root crops (carrots, potatoes) by pre-planting application to the soil and covering the soil with plastic to contain the hydrazoic acid fumes until the seeds or tubers are planted [67, 68]. The decay of azides in the soil during this application has been studied extensively and it has been shown that there are no lasting adverse side effects to crops harvested after the azide has decayed.

Azides (sodium and potassium azide) have been widely promoted as nematocides in soils carrying agricultural crops. The advantage is that they perform their nematocidal duty (often while the soil is covered with plastic tarps to confine the vapors and extend their active period) but then decompose and dissipate before the crops are harvested. The theory was that all the azide would have decomposed by the time the root vegetables (carrots) are harvested.

#### 1.1.3 Potassium Azide

Potassium azide,  $\text{KN}_3$ , CAS RN [20762-60-1],  $M = 81.1184 \text{ g/mol}$ , is in many of its properties similar to sodium azide. It can be used as a source of nitrogen in gas generants, but its nitrogen content is less than that of sodium azide (51.8 mass-% nitrogen as opposed to 64.6% in  $\text{NaN}_3$ ).

The thermal decomposition of potassium azide leads to the elements from which it was formed [69, 70]. The rate of decomposition of potassium azide was increased by several orders of magnitude by addition of transition metal salts [71].



When freshly crystallized potassium azide is irradiated with UV light, color centers (F-centers) are developed and the salt simultaneously decomposes with evolution of nitrogen and deposition of potassium in the lattice.

Potassium azide has been used as a pre-harvest nematocide to control worm pests in agricultural beet and carrot crops.

## 1.2 Other Metal Azides

Most metal azides are explosive and shock sensitive. Lead azide is (was) used as a stab-sensitive primary explosive in percussion caps in munitions. The accidental formation of metal azides from sodium azide in contact with metals or metal oxides has caused accidents.

Aluminum azide,  $\text{Al}(\text{N}_3)_3$ , has a very high nitrogen content, but it is explosive and very sensitive and it has been the cause of laboratory accidents during attempts at its preparation. Aluminum azide can be prepared by reaction of aluminum chloride with sodium azide in tetrahydrofuran solution [72] or by reaction of trimethylaluminum with hydrogen azide at low pressures [73].

## 2 Azides of Nitrogen Bases

Azides of nitrogen bases are of interest as high-nitrogen compounds for gas generators. This involves mainly ammonium azide,  $\text{NH}_4\text{N}_3$ , and hydrazinium azide,  $\text{N}_2\text{H}_5\text{N}_3$ ,  $\text{N}_2\text{H}_5\text{N}_3$ . They have been tested in the solid and liquid (dissolved in water or hydrazine) forms. We opted to list inorganic azides here immediately preceding organic azides. Hydrazinium azide is the compound with the highest nitrogen content (93 mass-%) and has been discussed in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salt Oxidizers,” although it is not an oxidizer. Hydrazinium azide,  $\text{N}_2\text{H}_5\text{N}_3$ , is closely related to another hydronitrogen, ammonium azide,  $\text{NH}_4\text{N}_3$ , which is described here along with organic azides. This is not a very logical location for an ionic azide compound, such as ammonium azide, but it had to be either spliced in with ammonium salt oxidizers, such as ammonium nitrate (AN) or ammonium perchlorate (AP) or it could have been listed following the hydrazinium azide section.

The properties of azides of organic amines and amides are described in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines,” and chapter “Amides and Imides.” Guanidinium azide and triaminoguanidinium azide are relatively stable high-nitrogen compounds suitable as ingredients in gas generators.

## 2.1 Ammonium Azide

Ammonium azide, also known as ammonium trinitride, ammonium azoimide,  $\text{NH}_4\text{N}_3$ ,  $\text{N}_4\text{H}_4$ , CAS RN [12164-94-2],  $M = 60.059 \text{ g/mol}$ , is one of the few compounds that consists only of nitrogen and hydrogen. Thus, if it decomposes as constituents in gas generants, it does not leave a solid residue as the alkali metal azides would.

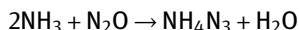
With a nitrogen content of 93.23 mass-%, ammonium azide is one of the best sources of nitrogen for gas generants. The exhaust of ammonium azide formulations with the proper oxidizer (e.g., AN) would be very clean since it contains only nitrogen and steam. Its oxygen balance is -53.28%, just enough oxygen is needed to combust the hydrogen in the ammonium ion to water. The main disadvantage of ammonium azide as a gas generant in any application is its high volatility and the toxicity of the ammonium azide vapors. Antiquated names at one time used for ammonium azide were ammonium trinitride or ammonium azoimide.

### 2.1.1 Preparation of Ammonium Azide

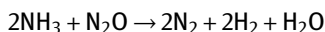
Ammonium azide can be prepared by mixing solutions of ammonium chloride and sodium azide in dimethylformamide at 373 K (100 °C). The solvent is then drawn off in a vacuum, but some of the volatile salt will be lost with the solvent. Owing to its high vapor pressure and toxicity, this compound has not yet found any practical applications.

Ammonium azide may be prepared by neutralization of hydrazoic acid in ether solution with gaseous ammonia or by metathetical reaction of dry sodium azide with ammonium nitrate at 473 K (a very hazardous operation) [74, 75].

Ammonium azide may be prepared by the reaction of ammonia and nitrous oxide over a hydrogenation catalyst at 783 K [76]



However, if the temperature conditions and the space velocity in the catalytic reactor are not chosen correctly, the ammonium azide formed would decompose and the reaction proceeds all the way to nitrogen and water, useless reaction products

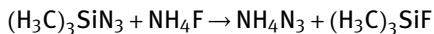


This reaction can proceed with explosive power.

Ammonium azide solutions were prepared by ion exchange by first loading an anion exchange resin with azide ions from sodium azide, and then eluting the column with aqueous ammonia [77].

Traces of ammonium azide may be formed during the slow decomposition or photolysis of hydrazoic acid  $\text{HN}_3$ . If the decomposition products of hydrazoic acid are quenched on a cold finger, blue imine  $(\text{NH})_3$  will freeze out, but eventually decompose forming ammonium azide.

Ammonium azide can be prepared by reaction of trimethylsilyl azide with ammonium fluoride in methanol [78]



The same method can also be used for preparation of hydrazinium(1+) azide or hydroxylammonium azide.

#### 2.1.1.1 Synthesis of Other Hydronitrogens

It has been attempted to synthesize new hydronitrogen compounds ( $\text{NH}_5$ ?  $\text{N}_2\text{H}_6$ ?) by subjecting ammonium azide to extremely high pressures. At first, density functional theory calculations were performed to develop a new equation of state and to see which polymorphs might form if the salt is compressed to 3.3 GPa [79]. Novel polymorphs of  $\text{NH}_4\text{N}_3$  were found using a simple structure search algorithm employing random atomic displacements upon static compression.

A combined theoretical and experimental study of the high-pressure behavior of ammonium azide using density functional theory considered the relative thermodynamic stability of the material with respect to two other crystal phases, *trans*-tetrazene and  $(\text{NH})_4$  [80, 81]. Raman spectra of  $\text{NH}_4\text{N}_3$  were measured at pressures up to 71 GPa at room temperature. There was no evidence of a phase transition to either tetrazene or tetrazetidine  $(\text{NH})_4$ .

*Ab initio* molecular dynamics simulations predicted that ammonium azide should be an effective precursor to form polynitrogen [82]. Simulations at 60 and 90 GPa showed that the critical temperatures for nitrogen polymerization were about 2200 and 1600 K, respectively. Compared with molecular nitrogen (110 GPa and 2000 K), the synthesis pressure of polymeric nitrogen starting with ammonium azide should be significantly lower.

Ammonium azide is the thermodynamic ground state of  $\text{N}_4\text{H}_4$  compounds in preference to *trans*-tetrazene or poly-hydro-nitrogen  $(\text{NH})_\infty$ . Calculations predicted that ammonium azide undergoes a phase transition to *trans*-tetrazene at around ~39–43 GPa followed by *trans*-tetrazene to  $(\text{NH})_\infty$  at around 80–90 GPa in the temperature range 0–650 K [83]. The calculated pressure dependent IR spectra predicted that the N–H stretching frequencies should undergo red and blue shifts corresponding to strengthening and weakening of hydrogen bonding, respectively, below and above 4 GPa.

#### 2.1.1.2 Encapsulation of Ammonium Azide

Because ammonium azide has a relatively high vapor pressure at room temperature and sublimates easily, it has been attempted to reduce its volatility by encapsulating it with an impermeable barrier coating [84, 85]. Viton and nitrocellulose (NC) have been tested as coating agents. The best stabilized coated ammonium azide was made by using 4.5% of NC as coating, which increased the maximum sublimation temperature

by about 30 °C with respect to an uncoated sample. Similar coating methods may also be useful for encapsulating hydrazinium azide.

### 2.1.2 Physical Properties of Ammonium Azide

Ammonium azide forms colorless, non-hygroscopic crystals with a density of 1.346 g/cm<sup>3</sup> which start to sublime at 406–407 K (133–134 °C) and explode when heated to 433 K (160 °C). The main disadvantage of ammonium azide as a potential propellant or gas generant ingredient is the high volatility and its tendency to sublime even at moderate temperatures.

#### 2.1.2.1 Density of Ammonium Azide

The density of ammonium azide derived from crystallographic XRD data is 1.365 g/cm<sup>3</sup> [78].

#### 2.1.2.2 Vapor Pressure of Ammonium Azide

The vapor pressure of ammonium azide is summarized in Table 4.

**Table 4:** Vapor pressure of ammonium azide.

| Temperature |       |       | Vapor pressure |       |        |
|-------------|-------|-------|----------------|-------|--------|
| K           | °C    | °F    | millibar       | mm Hg | Pa     |
| 302.3       | 29.2  | 84.6  | 1.3            | 0.98  | 130    |
| 322.5       | 49.4  | 121   | 7              | 5.25  | 700    |
| 332.3       | 59.2  | 138.6 | 13             | 9.75  | 1300   |
| 342.5       | 69.4  | 157   | 27             | 20.3  | 2700   |
| 353.2       | 80.1  | 176.2 | 54             | 40.5  | 5400   |
| 359.8       | 86.7  | 188.1 | 80             | 60.0  | 8000   |
| 368.3       | 95.2  | 203.4 | 135            | 101   | 13500  |
| 380.8       | 107.7 | 225.9 | 260            | 195   | 26000  |
| 393.5       | 120.4 | 248.7 | 530            | 398   | 53000  |
| 406.9       | 133.8 | 272.8 | 1010           | 758   | 101000 |

Data source: [86]

The vapor pressure of ammonium azide can be calculated from the equation

$$\log P = +11.325 - (3428.6/T)$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.

The kinetics of sublimation of ammonium azide have been investigated over the temperature range 360–389 K in a continuous flow of dry argon by TGA [87]. Sublimation follows zero-order kinetics with a corresponding activation energy of 93.3 kJ/mol,

which was slightly higher than its heat of sublimation (73.4 kJ/mol) determined from differential scanning calorimetric (DSC) cooling thermograms. It was suggested that ammonium azide undergoes molecular sublimation and that the vapor readily dissociates above 418 K into  $\text{NH}_3$  and  $\text{HN}_3$ . A heat of formation of 185.6 kJ/mol was deduced for gaseous  $\text{NH}_4\text{N}_3$ .

The solubility of ammonium azide in various solvents at 293 K is 20 g/100 mL water, 3.3 g/100 mL methanol, 1.06 g/100 mL ethanol and 0.006 g/100 mL ether.

### 2.1.2.3 Infrared Spectra of Ammonium Azide

Infrared spectra of solid ammonium azide at 68 K, prepared by sublimation onto a cold salt window, seem to indicate a disordered crystal which became ordered on warming above 150 K [88]. A band at  $1830\text{ cm}^{-1}$  was assigned as a combination involving a lattice torsional motion of the ammonium ion ( $420 \pm 20\text{ cm}^{-1}$ ). The vapor over ammonium azide at room temperature contained predominantly hydrazoic acid and ammonia.

The partial correlation field splitting of the symmetric stretching and bending  $\text{N}_3^-$  internal modes and the low frequency lattice modes in crystalline ammonium azide have been observed using far IR and laser Raman spectroscopy [89]. The vibrational modes were assigned by factor group analysis and compared with the neutron inelastic scattering spectrum of the salt.

High-pressure IR absorption and Raman scattering studies of ammonium azide at room temperature at pressures up to 20 and 22 GPa were done in search of a pressure-induced phase transition at 2.9 GPa [90]. All observed vibrational modes maintained their identities at the high-pressure phase, indicating that  $\text{NH}_4\text{N}_3$  was still present in the form of ammonium cations and azide anions linked by hydrogen bonds ( $\text{N}-\text{H}\cdots\text{N}$ ). Above 2.9 GPa, the relative magnitude of the torsional mode weakened, and the  $\text{N}-\text{H}$  symmetric stretch displayed a red shift, indicating strengthened hydrogen bonding energy. The opposite effects were observed above 12 GPa, where the relative magnitude of the torsional mode strengthened and the  $\text{N}-\text{H}$  symmetric stretch reverted to a blue shift, indicating weakened hydrogen bonding energy. The hydrogen bonding energy changes with an increase of pressure can be ascribed to a phase transition at 2.9 GPa and a rotational or bending behavior of azide ions at 12 GPa.

Absorptions in the IR spectrum of ammonium azide crystals in a KBr pellet were observed at 3144, 3012, 2834, 2036, 1818, 1418, 663, 651, and  $626\text{ cm}^{-1}$  [78].

### 2.1.2.4 Crystal Structure of Ammonium Azide

The unit cell dimensions of orthorhombic ammonium azide crystals with four molecules to the unit cell were determined from XRD data as  $a = 8.930 \pm 0.003\text{ \AA}$ ,  $b = 8.642 \pm 0.003\text{ \AA}$ ,  $c = 3.800 \pm 0.002\text{ \AA}$  with a space group assumed to be  $Pmna$  or  $D_{2h}^7$  [91]. The crystal density was  $1.352\text{ g/cm}^3$ .

Another XRD measurement of orthorhombic ammonium azide crystals with space group  $Pmna$ , gave  $a = 8.948\text{ \AA}$ ,  $b = 3.808(2)\text{ \AA}$ ,  $c = 8.659(3)\text{ \AA}$ ,  $Z = 4$ ,  $D_c = 1.352\text{ g/cm}^3$ , and

$D_m = 1.352 \text{ g/cm}^3$  [92]. The corrected N—N distance was  $1.186(4) \text{ \AA}$  in both azide groups. There were two strong hydrogen bonds, with N—N distances of  $2.975(4)$  and  $2.967(3) \text{ \AA}$ .

Pressure-dependent Raman spectroscopy studies revealed a polymorph phase transition in simple molecular ionic crystal  $\text{NH}_4\text{N}_3$  at a pressure of  $\approx 3 \text{ GPa}$  which had not been predicted by *ab initio* calculations [93]. Hydrogen bonding was spectroscopically evident in both low-pressure and high-pressure phases. The strength of hydrogen bonds appeared to change at the phase transition: in the low-pressure phase  $\text{NH}_4\text{N}_3$  behaved as a system with very strong hydrogen bonding whereas changes of spectra with pressure in the high-pressure phase were indicative of weak or medium-strength hydrogen bonds. The high-pressure phase is most likely thermodynamically stable up to pressures of  $\approx 55 \text{ GPa}$ , contradicting the *ab initio* studies predicting transformation of  $\text{NH}_4\text{N}_3$  to non-molecular hydronitrogen solid at  $36 \text{ GPa}$ . Polymorph phase transition was observed in  $\text{NH}_4\text{N}_3$  at  $\approx 3 \text{ GPa}$  by pressure-dependent Raman studies. The strength of hydrogen bonds appeared to change at the phase transition as illustrated by dependence of N—H stretching frequency on pressure.

A computational study of the structural, electronic, bonding and optical properties of orthorhombic ammonium azide has been performed using a plane wave pseudopotential method based on density functional theory (DFT) [94].

The peculiar behavior of the symmetric stretch of the  $\text{N}_3^-$  anion and the bending mode of the  $\text{NH}_4^+$  cation in the high-pressure phase II (above  $3 \text{ GPa}$ ) of the molecular ionic crystal  $\text{NH}_4\text{N}_3$  were studied by pressure-dependent Raman spectroscopy up to a pressure of  $20 \text{ GPa}$  [95]. The spectra in the pressure range above  $10 \text{ GPa}$  revealed a remarkable intensity transfer between bands and a level repulsion (characteristic of vibrational resonance coupling) that is mediated by hydrogen bonding between the  $\text{N}_3^-$  and  $\text{NH}_4^+$  ions.

The structural, elastic, mechanical, electronic properties, formation energy and cohesive energy of orthorhombic  $\text{NH}_4\text{N}_3$  and monoclinic  $\text{N}_2\text{H}_5\text{N}_3$  were studied by a plane wave method based on the first-principles density functional theory [96]. The orthorhombic  $\text{NH}_4\text{N}_3$  crystal is more energetically stable. The independent elastic constants, bulk modulus, shear modulus, Young's modulus and Poisson's ratio of two compounds were then investigated. The electronic band structures, density of states, and charge density distributions of orthorhombic  $\text{NH}_4\text{N}_3$  and monoclinic  $\text{N}_2\text{H}_5\text{N}_3$  were analyzed to better understand electronic properties and chemical bonding in these two molecules.

The crystal structure of ammonium azide has been studied by *in situ* high-pressure XRD and Raman scattering at room temperature [97]. Ammonium azide exhibits strong hydrogen bonding features with compression. The hydrogen bonds weaken with increasing pressure due to the bending of N—H $\cdots$ N bond, leading to an increase of N—H stretch frequency and rotation of azide anions up to  $2.9 \text{ GPa}$ . The orientation of azide anions influences the compressibility properties of ammonium azide. The phase tran-

sition involves rotation of azide anions and a proximity of *a* and *c*, preliminarily assigned as a reversible second-order orthorhombic to tetragonal transition.

The pressure-induced phase transitions in hydronitrogen compounds were investigated using first-principles density functional theory [98, 99]. The tetragonal structure with space group  $P4_2/n$  is mechanically stable and ductile. The thermodynamic stability decreased in the order  $Pmna > P\bar{1} > P4_2/n > P2_1/m$ . With increasing pressure, the phase transition pressures of transitions  $Pmna \rightarrow P4_2/n$ ,  $P4_2/n \rightarrow Pmna$ ,  $Pmna \rightarrow P\bar{1}$ , and  $P\bar{1} \rightarrow P2_1/m$  are 5.6, 15.0, 30.0, and 69.2 GPa, respectively, which are in agreement with the available data.

The structural parameters of orthorhombic ammonium azide crystals with a space group of  $Pmna$  obtained by crystallographic XRD measurements are  $a = 8.9331(10) \text{ \AA}$ ,  $b = 3.7824(4) \text{ \AA}$ ,  $c = 8.6519(10) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $Z = 2$  [78]. The calculated crystal density was  $1.365 \text{ g/cm}^3$ .

### 2.1.2.5 Thermodynamic Properties of Ammonium Azide

The literature gives several values of the enthalpy of formation of  $\text{NH}_4\text{N}_3$ , ranging from 20.2 to 27.6 kcal/mol. An analysis of the original sources showed that the values of the enthalpy of formation equal to 20.4 and 20.2 kcal/mol are erroneous, since uncorrected data were used. Values of 26.4–26.79 kcal/mol were regarded as the most reliable.

The standard enthalpy of formation of ammonium azide is  $+1922.8 \text{ kJ/kg} = +115.5 \text{ kJ/mol} = +459.6 \text{ kcal/kg} = +27.6 \text{ kcal/mol}$  [86]. The enthalpy of formation is a very high positive number, indicating that this is an energetic chemical that can be used as a solid propellant ingredient, nitrogen gas generant and clean exhaust explosive (if other detrimental properties do not prevent us from doing that).

The standard molar enthalpy of formation of ammonium azide at 298.15 K has been derived from measurements of the energy of combustion in oxygen as  $\Delta H_f(\text{cr}) = 114.14 \pm 0.94 \text{ kJ/mol} = +27.28 \pm 0.22 \text{ kcal/mol}$  [100].

### 2.1.3 Chemical Properties of Ammonium Azide

Ammonium azide is soluble in liquid ammonia and on evaporation of the solvent forms ammonates containing one or more molecules of ammonia as solvated ammonia of crystallization. The diammonate  $\text{NH}_4\text{N}_3 \cdot 2\text{NH}_3$  forms clear, colorless elongated plates stable at 240 K ( $-33^\circ\text{C}$ ) but decomposes at 273 K ( $0^\circ\text{C}$ ).

Another high-nitrogen azide, hydroxylammonium azide has not received much attention. It appears to be just as unstable as ammonium azide or hydrazinium azide.

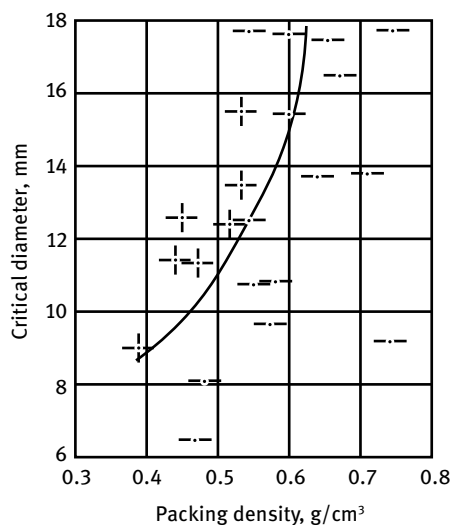
Ammonium azide sublimes below 523 K ( $250^\circ\text{C}$ ) at 1.3–20 kPa (10–150 mm Hg), and slowly decomposes between 523–583 K ( $250$ – $310^\circ\text{C}$ ) at 20 kPa (150 mm Hg). Ammonium azide vaporizes and dissociates into  $\text{NH}_3$  and  $\text{HN}_3$  and then the  $\text{HN}_3$  explodes.

### 2.1.4 Strand Burning of Ammonium Azide

The steady-state combustion of  $\text{NH}_4\text{N}_3$  and  $\text{N}_2\text{H}_5\text{N}_3$  was studied in a windowed constant-pressure bomb at 0.1–36 MPa [101]. The  $\text{N}_2\text{H}_5\text{N}_3$  burned 3–4 times faster than  $\text{NH}_4\text{N}_3$  over this pressure range. The combustion temperature of both compounds was 240–430 K higher than the temperature calculated for the thermodynamic equilibrium composition of the combustion products due to the presence of large amounts of undissociated  $\text{NH}_3$  (0.97 and 0.87 mol-% per mol of  $\text{NH}_4\text{N}_3$  and  $\text{N}_2\text{H}_5\text{N}_3$ , respectively). The reaction at the combustion surface was the dissociation of the salts into  $\text{HN}_3$  and the parent base. The increase in surface temperature with pressure was dependent on the dissociation enthalpy of the salts, and the combustion rate was dependent on the gas-phase heat release. The main energy release mechanism is the decomposition of  $\text{HN}_3$ . Kinetics of  $\text{HN}_3$  gas-phase decomposition can be expressed as  $k = 10^{16.26} \exp(-19350/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . For comparison, the combustion rate of liquid  $\text{HN}_3$  at 0.1 MPa is  $1.9 \text{ g cm}^{-2} \text{ s}^{-1}$ .

### 2.1.5 Safety Properties of Ammonium Azide

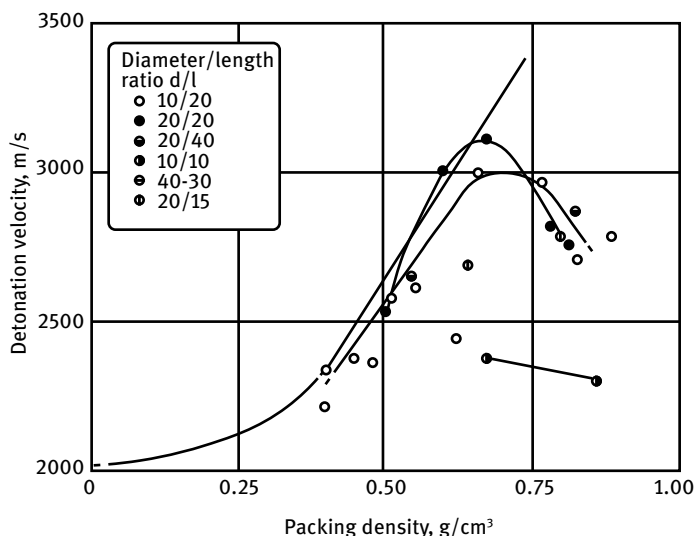
The critical diameter of  $\text{NH}_4\text{N}_3$  was determined in cellophane or thin-walled glass shells [102]. The critical diameter of  $\text{NH}_4\text{N}_3$  detonations as a function of packing density rises sharply with the bulk density (Figure 1).



**Figure 1:** Critical diameter of  $\text{NH}_4\text{N}_3$  detonations as a function of packing density (reprinted and modified from [102], by permission from ©1977 Springer Nature; permission conveyed through Copyright Clearance Center, Inc.)

The detonation velocity of  $\text{NH}_4\text{N}_3$  confined in steel tubes as a function of packing density and sample geometry goes through a maximum at  $0.7 \text{ g/cm}^3$  (Figure 2). The solid line is a linear curve fit for the range  $\rho = 0.4 - 0.7 \text{ g/cm}^3$  based on the equation  $D = 1.1 + 3.1 \times \rho \text{ km/s}$ .





**Figure 2:** Detonation velocity of  $\text{NH}_4\text{N}_3$  detonations as a function of packing density (reprinted and modified from [102], by permission from ©1977 Springer Nature; permission conveyed through Copyright Clearance Center, Inc.)

Theoretical calculations based on the enthalpy of formation predict a detonation velocity of 6.45 km/s and a detonation pressure about 15.16 GPa computed by Kamlet-Jacobs empirical equations [94].

### 2.1.6 Applications of Ammonium Azide

Ammonium azide has been proposed as the key ingredient for gas generant formulations where its advantage over sodium azide would be that it does not leave a solid residue, but its volatility prevents its actual use in practical systems [103].

Ammonium azide has been used as the starting material in the high-pressure synthesis of other hydronitrogens, subjecting it to very high pressures, where phase changes occur, and the atoms rearrange themselves [83].

## 2.2 Hydrazinium Azide

Hydrazinium azide (HA) is one of the compounds with the highest nitrogen content (93%) and has received considerable attention as a source of nitrogen gas in gas generators. Hydrazinium azide solutions in hydrazine have been evaluated as monopropellants (see *Encyclopedia of Monopropellants*, chapter “Hydrazine Monopropellants”).

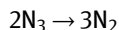
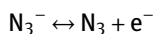
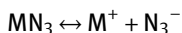
There are two Chemical Abstract Service Registry Numbers for hydrazinium azide: [38551-29-0] and [14662-04-5]. It is not known which is the correct (preferred) one.

There is a different CAS RN for hydrazinium(1+) azide hydrazinate which is [14546-45-3].

The preparation and physical properties of hydrazinium azide were already discussed in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salt Oxidizers,” along with other hydrazinium salts that are potential oxidizers. Hydrazinium azide is not an oxidizer, so it somewhat violated the ground rules for selecting chapter titles and contents in this book for oxidizers and fuels when hydrazinium azide was discussed under oxidizers instead of fuels. It would have made sense to discuss both ammonium azide and hydrazinium azide here in this chapter next to each other because the two salts are very similar in their chemical composition and behavior.

### 2.3 Decomposition of Inorganic Azides

In ionic inorganic azide compounds, the lengths of N—N bonds are the same (the polarization of azido group is not a consideration). N—N bonds are not broken in the decomposition, which follows equations like:



where M is an alkali metal.

## 3 Organic Azido Compounds

The azide group as a ligand in an organic compound is called the azido group. The “o” at the end of this term puts it in the same category with nitro, amino or nitramino groups. Sometimes it is also called the triazo group. Azido compounds are derivatives of hydrazoic acid (HN<sub>3</sub>) where the hydrogen is replaced by an alkyl or aryl group. The bond between the azido group and its organic skeleton is a covalent bond. The azido group attached to an organic carbon-carbon backbone makes fuels with higher enthalpy of formation and higher nitrogen content, both attractive for better rocket propellants and better gas generants. The azido group is an explosivesophoric group. So, if one lonely azido group attached to an organic compound does not yet give the desired specific impulse, one is inclined to try two, three or more azido groups attached to the same molecule. Unfortunately, there is a limit as to how many azido groups can be attached to a molecule before the compound becomes prohibitively unstable. Several compounds described in the current chapter may fall into that category. Nevertheless, these polyazido compounds were prepared and studied and described here in order to

find out where the limit of stability is. The other question is about the effect of neighboring groups like  $-\text{NO}_2$ ,  $-\text{CN}$  or  $-\text{NH}_2$  on the stability of alkyl azides.

Although liquid azides discussed here have not found the same wide range of applications in rocket propellants and gas generants as solid azides, they are discussed here in detail because some of the same synthesis methods can be used for solid, polymeric azides and some of the monomers are liquids before they are polymerized.

Polymeric azides as binders for solid propellants will be discussed in future volumes on solid propellants. Those discussions center around the use of glycidyl azide polymers (GAP) as binders in solid rocket propellants. Of all organic azido compounds, GAP is the only one that has found practical application and it is still actively being investigated in many new propellant formulations. Attaching allyl  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-$  groups to organic azides makes them suitable as monomers for polymerization and use as energetic binders [104].

Azides of heterocyclic ring structures, such as 3-azidooxetane or triazido-s-triazine, are discussed in *Encyclopedia of Liquid Fuels*, chapter "Heterocyclic Amines." Here we are summarizing only organic azido compounds that are neither polymers nor amines. The preceding section already described inorganic azides.

There are many publications on organic azides which may be useful as an introduction to this exciting group of chemicals [105–114]. Exciting because many of these compounds are thermally unstable or shock sensitive or both and may cause accidental explosions when they are least expected. The Patai book contains several chapters of interest for the synthesis and applications of azido compounds [105]. The book "Science of Synthesis: Houben-Weyl Methods of Molecular Transformations (former Methods in Organic Chemistry)" in volume 41 contains information on nitro, nitroso, azo, azoxy, and diazonium compounds, azides, triazenes, and tetrazenes [115].

A good, but now obsolete survey of alkyl and aryl azides was published in 1954 [116]. It should be updated. Another review covers decomposition and addition reactions of organic azides [117].

Other azido compounds have already been discussed under amines (CINCH, DMAZ) because the central skeleton of the molecule was an amine and the azido groups were only attached as explosophoric paraphernalia. Dimethylaminoethyl azide (DMAZ) has received much attention among all organic liquid azides both as a fuel (*Encyclopedia of Liquid Fuels*, chapter "Aliphatic Amines") and as a monopropellant. There is some overlap between these two sections. Compounds discussed here contain nitrogen only as part of the azido (or a nitro) group, but not as part of the skeleton of the molecule. The skeleton of the azido compounds discussed here is a carbon skeleton without any hetero-atoms. In many cases azido groups have been combined with other explosophoric groups, mostly nitro and nitroxy groups, in the quest for more energetic compounds.

There are hundreds of publications and patents on azide compounds in rocket propellants and a complete summary of all those references would fill an entire book in its own right. In the current section we can give only a superficial, introductory re-

view and include some typical applications. A new book on liquid explosives contains a chapter on azido compounds as liquid explosives [118]. Azides are physiologically active and have medicinal therapeutic uses, mainly for blood pressure lowering [119].

Organic azides have assumed an important position as building blocks for syntheses at the interface between chemistry, biology, medicine and materials science. They can be used in cycloadditions, aza ylide chemistry and the synthesis of a variety of heterocyclic compounds, as described in several summaries of the preparation and uses of organic azides [120, 121]. Another multi-author compendium on organic azides contains 16 chapters, including one on azides as energetic materials [122]. See also [123].

Azido compounds evaluated as energetic plasticizers include bis(1,3-diazo-2-propyl) formal,  $[(N_3CH_2)_2CHO]_2CH_2$ ,  $C_4H_7N_6O_2$ , BDPP [124], 1,5-diazo-3-nitrazapentane,  $N_3CH_2CH_2N(NO_2)CH_2CH_2N_3$ ,  $C_4H_8N_8O_2$ , DIANP [125], 1,1,1-tris-(azidomethyl)ethane,  $(N_3CH_2)_3CCH_3$  [126], and many others [127].

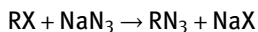
Various azido compounds, including azidonitramine, *N*-nitro-*N*-azidomethyl-gemdinitroethyl methylamine, *N,N*-bis(azidomethyl-*gem*-dinitroethyl)-ethylenedinitramine, azido nitro compounds, 2-nitro-2-methyl-1,3-diazidopropane, 2-nitro-2-azidomethyl-1,3-diazidopropane, and tetraazidomethyleneethane, pentaerythritol diazido dinitrate were evaluated as energetic additives for rocket propellants [128].

Azido compounds of high energy materials interest are bis(azidomethyl)oxetane, azidomethyl methyl oxetane, 1,3-diazo-2-nitrazapropane (DANP), 1,5-diazo-2,4-dinitrazapentane (DADZP), 1,7-diazo-2,4,6-trinitrazaheptane (DATH), and *n*-propyl azidoethyl nitramine [129].

Many organic azides have been tested as burning rate increasing additives for hydrocarbon fuels in turbojet or ramjet engines, where microexplosions cause fuel droplets to shatter into many small droplets that burn faster than the large droplets.

### 3.1 Preparation of Organic Azides

The simplest method for synthesis of alkyl azides is the reaction of alkyl halogenides with sodium azide:



where X = Cl, Br, or I. This can be done in aqueous solution or in aprotic solvents. An improved method for the synthesis of alkyl azides used 2-(2-ethoxyethoxy)ethanol, also known under the trade name Carbitol, as the solvent [130].

A series of monoazidoalkanes and diazidoalkanes were prepared to compare the molecular structure of these compounds with their impact sensitivity [131]. All monoazidoalkanes were insensitive to impact. The diazidoalkanes gave varying results, depending on the structure. See also [120, 132, 133].

Methyl azide has been found as an unwanted reaction product in the incomplete reaction of dinitrogen tetroxide and methylhydrazine, which ordinarily would lead to hypergolic ignition. Very short pulses of bipropellant thrusters may result in incomplete combustion and accumulation of intermediates, such as methylhydrazine (MMH) nitrate or methyl azide. Accumulation of methyl azide as a product of incomplete reaction of dinitrogen tetroxide (NTO) and MMH could lead to explosions.

A series of alkyl azides and diazides in quantities of 100–200 g were synthesized and characterized by IR and NMR spectra, including 1-azidobutane, CAS RN [7332-00-5P], 1-azidopentane, CAS RN [26330-06-3], 1-azidohexane, CAS RN [6926-45-0], 1-azidoheptane, CAS RN [44961-22-0], and 1-azidooctane, CAS RN [7438-05-3] [134]. The report gives some spectra but lacks physical properties of the prepared compounds. A new method for preparation of vicinal diazides starting with alkenes was developed and used for the synthesis of 1,2-diazidocyclopentane and 1,2-diazidocyclohexane.

### 3.2 Physical Properties of Organic Azides

The simplest alkyl azide, methyl azide, azidomethane,  $\text{CH}_3\text{N}_3$ , CAS RN [624-90-8] boils at near room temperature at 293–294 K. It is unstable and its vapor and liquid is detonable, in particular in the presence of mercury [135]. Ethyl azide, azidoethane,  $\text{C}_2\text{H}_5\text{N}_3$ , CAS RN [871-31-8] boils at 322 K (49 °C) and its vapors are also detonable.

#### 3.2.1 Melting Points of Organic Azides

It is difficult to determine the melting points of organic azides because they may decompose or explode before they melt. Three correlations for the prediction of melting point of different types of organic azides containing alkyl azides, alkenyl azides, aryl azides, acyl azides, and heteroazide compounds were based on the elemental composition as additive parameter and the contribution of some specific polar groups/structural moieties as non-additive functions [136]. These correlations have been used for 259 different organic azide compounds, including complex molecular structures. The models were validated by internal and external validation tests where their applicability domains were defined and analyzed.

A similar method was used for prediction of melting points of organic peroxides, organic azides, organic nitrates, polynitro arenes, polynitro heteroarenes, acyclic, and cyclic nitramines, nitrate esters, and nitroaliphatic compounds [137].

#### 3.2.2 Boiling Points of Organic Azides

Table 5 contains CAS RN numbers, normal boiling points and data for the ultraviolet spectra in 95% EtOH for several alkyl and cycloalkyl azides. A comparison of the normal boiling points of alkyl azides and cycloalkyl azides showed that the boiling points of cycloalkyl azides were slightly higher than those of straight chain alkyl azides with

same number of carbon atoms [138]. The mean molar refraction value of the azido group was calculated to be about 9.4 in alkyl azides and 10.2 in the case of aryl azides.

**Table 5:** Boiling points and UV absorption of alkyl and cycloalkyl azides.

| Compound name          | Formula                                       | CAS RN      | Boiling point      |                  | UV absorption         |                           |
|------------------------|-----------------------------------------------|-------------|--------------------|------------------|-----------------------|---------------------------|
|                        |                                               |             | K                  | °C               | $\lambda_{\max}$ , nm | $\epsilon \times 10^{-3}$ |
| Methyl azide           | CH <sub>3</sub> N <sub>3</sub>                | 624-90-8P   | 293–294            | 20–21            | —                     | —                         |
| Ethyl azide            | C <sub>2</sub> H <sub>5</sub> N <sub>3</sub>  | 871-31-8P   | 322                | 49               | 287                   | 0.02                      |
| <i>n</i> -Propyl azide | C <sub>3</sub> H <sub>7</sub> N <sub>3</sub>  | 22293-25-0P | 352                | 79               | —                     | —                         |
| <i>n</i> -Butyl azide  | C <sub>4</sub> H <sub>9</sub> N <sub>3</sub>  | 7332-00-5P  | 383                | 110              | 287                   | 0.025                     |
| <i>n</i> -Amyl azide   | C <sub>5</sub> H <sub>11</sub> N <sub>3</sub> | 26330-06-3P | 405                | 132              | —                     | —                         |
| <i>n</i> -Hexyl azide  | C <sub>6</sub> H <sub>13</sub> N <sub>3</sub> | 6926-45-0P  | 429                | 156              | 287                   | 0.021                     |
| <i>n</i> -Heptyl azide | C <sub>7</sub> H <sub>15</sub> N <sub>3</sub> | 44961-22-0P | 451                | 178              | —                     | —                         |
| <i>n</i> -Octyl azide  | C <sub>8</sub> H <sub>17</sub> N <sub>3</sub> | 7438-05-3P  | 471                | 198              | —                     | —                         |
| Cyclopentyl azide      | C <sub>5</sub> H <sub>9</sub> N <sub>3</sub>  | 33670-50-7P | 408                | 135              | 288                   | 0.024                     |
| Cyclohexyl azide       | C <sub>6</sub> H <sub>11</sub> N <sub>3</sub> | 19573-22-9P | 431                | 158              | —                     | —                         |
| Phenyl azide           | C <sub>6</sub> H <sub>5</sub> N <sub>3</sub>  | 622-37-7    | 346 at<br>0.67 kPa | 73 at<br>5 mm Hg | 285                   | 1.55                      |
|                        |                                               |             |                    |                  | 277                   | 2.27                      |
|                        |                                               |             |                    |                  | 248                   | 9.94                      |

Data source: [130,138]

### 3.2.3 Vapor Pressure of Organic Azides

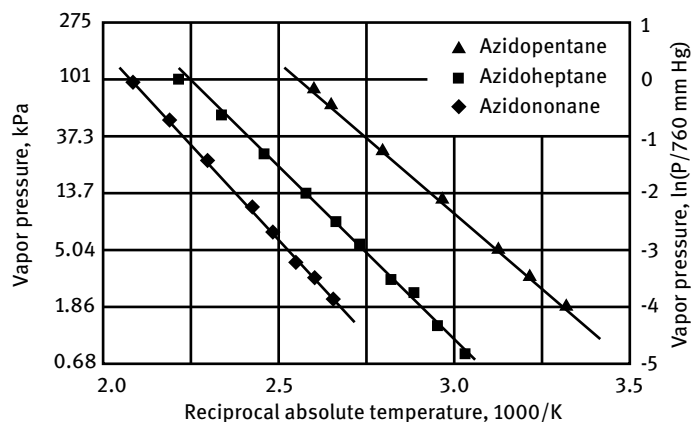
The vapor pressures of a group of alkyl azides have been experimentally determined by accurately measuring vapor pressure as a function of temperature and then correlating the data with the Clausius-Clapeyron relation [139]. The experimental procedure involved heating 10–15 mL of the test liquid in a two-neck, round-bottom flask immersed in a silicone oil bath that is stable to temperature variations and can be heated up to 573 K (300 °C). The test vapor-liquid temperature was measured with a thermocouple placed immediately above the liquid interface, where saturated conditions were best observed. To minimize evaporative loss and maintain saturation conditions within the system, a condenser was used to recover vaporized liquid. Magnetically driven stirring bars were used to circulate both the test liquid and silicone oil bath to ensure temperature uniformity. A typical datum point was collected by first fixing the system pressure and then slowly raising the system temperature until the state of steady boiling was attained. The boiling points and latent heats of vaporization for the monoazides and diazides are compiled in Table 6. Overall, the boiling points of alkyl azides were higher than those of their alkane parent compounds. It is not clear if all those azides were *n*-azides with the azide group(s) in the terminal position(s) of the carbon chain, but that is the most likely assumption.

Table 6: Physical and thermodynamic properties of alkyl azides.

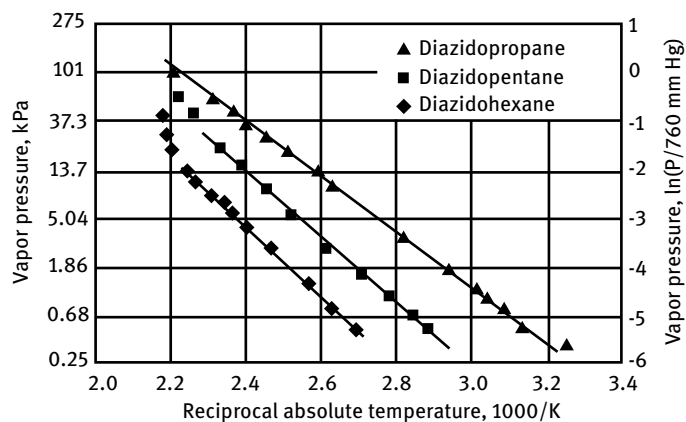
| Parent compound | Formula                                                       | Mol. mass | Density $\rho$    | Boiling point | Heat of evaporation |          | Enthalpy of formation, vapor, at 298 K |          | Heat of combustion at 298 K |          | Heat of decomposition |          |
|-----------------|---------------------------------------------------------------|-----------|-------------------|---------------|---------------------|----------|----------------------------------------|----------|-----------------------------|----------|-----------------------|----------|
|                 |                                                               |           |                   |               | at 298 K            | at 298 K | at 298 K                               | at 298 K | at 298 K                    | at 298 K | at 298 K              | at 298 K |
|                 |                                                               | g/mol     | g/cm <sup>3</sup> | K             | °C                  | kJ/mol   | kJ/mol                                 | kcal/mol | kJ/mol                      | kcal/mol | l/g                   | cal/g    |
| Monoazides      |                                                               |           |                   |               |                     |          |                                        |          |                             |          |                       |          |
| Butane          | C <sub>4</sub> H <sub>9</sub> N <sub>3</sub>                  | 99.14     | 0.883             | 377           | 104                 | 38.37    | 250.6                                  | 59.9     | 2912                        | 696.1    | -2168                 | -518.2   |
| Pentane         | C <sub>5</sub> H <sub>11</sub> N <sub>3</sub>                 | 113.24    | 0.873             | 403           | 130                 | 41.63    | 229.7                                  | 54.9     | 3529                        | 843.5    | -1898                 | -453.7   |
| Hexane          | C <sub>6</sub> H <sub>13</sub> N <sub>3</sub>                 | 127.15    | 0.869             | 427           | 154                 | 47.07    | 209.2                                  | 50       | 4139                        | 989.2    | -1690                 | -404     |
| Heptane         | C <sub>7</sub> H <sub>15</sub> N <sub>3</sub>                 | 141.21    | 0.867             | 451           | 178                 | 50.58    | 188.3                                  | 45       | 4755                        | 1136.5   | -1522                 | -363.8   |
| Octane          | C <sub>8</sub> H <sub>17</sub> N <sub>3</sub>                 | 155.24    | 0.866             | 468           | 195                 | 53.35    | 167.8                                  | 40.1     | 5370                        | 1283.5   | -1384                 | -330.9   |
| Nonane          | C <sub>9</sub> H <sub>19</sub> N <sub>3</sub>                 | 169.26    | 0.864             | 479           | 206                 | 55.65    | 146.9                                  | 35.1     | 5985                        | 1430.5   | -1270                 | -303.5   |
| Diazides        |                                                               |           |                   |               |                     |          |                                        |          |                             |          |                       |          |
| Propane         | N <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> N <sub>3</sub> | 126.1     | 1.113             | 453           | 180                 | 47.03    | 647.3                                  | 154.7    | 2553                        | 610.1    | -3399                 | -812.4   |
| Butane          | N <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> N <sub>3</sub> | 140.12    | 1.079             | 470           | 197                 | 52.01    | 626.8                                  | 149.8    | 3167                        | 756.9    | -3053                 | -729.8   |
| Pentane         | N <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> N <sub>3</sub> | 154.13    | 1.049             | 488           | 215                 | 56.74    | 605.8                                  | 144.8    | 3781                        | 903.7    | -2776                 | -663.5   |
| Hexane          | N <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> N <sub>3</sub> | 168.18    | 1.029             | 505           | 232                 | 61.21    | 585.3                                  | 139.9    | 4397                        | 1050.8   | -2544                 | -608     |
| Heptane         | N <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> N <sub>3</sub> | 182.2     | 1.011             | —             | —                   | —        | 564.4                                  | 134.9    | 5011                        | 1197.6   | -2348                 | -561.3   |
| Octane          | N <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> N <sub>3</sub> | 196.21    | 0.994             | —             | —                   | —        | 543.9                                  | 130      | 5625                        | 1344.3   | -2181                 | -521.2   |

Data source: [139]

Figures 3 and 4 show the vapor pressures of several alkyl azides and diazides. Vapor pressures of 23 organic azides have been determined by the transpiration method and the molar enthalpies of vaporization  $\Delta H_{\text{vap}}$  of these compounds were derived from the temperature dependencies of vapor pressures [140]. The results are summarized in Table 7.



**Figure 3:** Vapor pressures of several alkyl monoazides (reprinted and modified from [139], with permission from ©1989 Elsevier; permission conveyed through RightsLink.)



**Figure 4:** Vapor pressures of several alkyl diazides (reprinted and modified from [139], with permission from ©1989 Elsevier; permission conveyed through RightsLink.)



### 3.2.4 Infrared Spectra of Organic Azides

Not all compounds for which IR spectra are reported in this section are suitable as rocket propellants. The main reason these compounds were studied, and the results are discussed here in substantial detail, was to have a tool for characterizing the molecular structure of azides and develop correlations between molecular structure, thermal stability, and energy content. Thermal stability and energy content of these molecules are important properties when these compounds are to be used as rocket propellants. It was also important to identify resonance interaction of azide  $\text{N}=\text{N}$  with conjugated  $\text{C}=\text{C}$  bonds in the alkylene groups. Would it stabilize or destabilize the molecule? Of course, IR spectra can also be used for purity and quality control of azides that are used as propellant ingredients.

A number of organic monoazides, with the general formula  $\text{RN}_3$ , were synthesized in which  $R$  was: (1) a saturated alkyl group, e.g.  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n$ -propyl azide,  $n\text{-C}_3\text{H}_7$  CAS RN [22293-25-0P]; (2) an olefinic group, e.g., allyl, butadienyl; or (3) an acetylenic group, e.g. azidoacetonitrile,  $\text{N}\equiv\text{CCH}_2$ , CAS RN [57707-64-9P], 3-azidopropyne,  $\text{HC}\equiv\text{CCH}_2$ , CAS RN [14989-89-0P],  $\text{MeC}\equiv\text{CCH}_2$  and their IR spectra were measured [141]. In addition, two diazides with unsaturated alkenyl and alkynyl groups were made for comparison: 2,3-diazido-1,3-butadiene,  $\text{H}_2\text{C}=\text{C}(\text{N}_3)\text{C}(\text{N}_3)=\text{CH}_2$ , CAS RN [91686-86-1P], and 1,4-diazido-2-butyne,  $\text{N}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{N}_3$ , CAS RN [91686-83-8P]. The compounds (most of them very explosive) were studied by IR and Raman spectroscopy in liquid, in solution, and in the solid state, and by matrix isolation technique in IR. The spectra were interpreted in terms of one or in some cases two or more conformers and assigned with the aid of normal coordinate analysis. UV photolysis experiments in frozen nitrogen matrices at 12K were carried out and the reactions monitored by Fourier transform infrared (FTIR) spectroscopy. The intermediate products could in some cases be identified as imines. Six of the azides were investigated by gaseous electron diffraction and the molecular structures established.

Fully optimized geometries were calculated for hydrazoic acid, azidomethane, azidoethane, azidoethene, and azidomethanal and compared with existing experimental data [142]. Azidoethane exists in two conformations, *gauche* ( $71^\circ$ ) and *anti*, with an energy difference of 0.26 kJ/mol. Azidoethene and azidomethanal both prefer the *syn* orientation of the azide group with respect to the  $\text{C}=\text{C}$  or  $\text{C}=\text{O}$  bonds, the computed energy difference between the *anti* and *syn* conformation being 3.31 and 30.3 kJ/mol, respectively. The barrier to rotation around the  $\text{C}-\text{N}$  bond is 3.75 kJ/mol in azidomethane while in azidoethane it is 3.30 and 9.40 kJ/mol in the eclipsed anticlinal ( $120^\circ$ ) and *syn* positions, respectively. IR vapor phase absorption intensities were calculated, and theoretical spectra were presented for azidomethane and azidoethane.

Azidoacetonitrile, azidoethanenitrile,  $\text{N}\equiv\text{CCH}_2\text{N}_3$ , CAS RN [57707-64-9P] has been synthesized and the structure determined by electron diffraction from the vapor [143]. The substance slowly polymerized when kept at 243 K ( $-30^\circ\text{C}$ ) but appeared other-

wise to be considerably more stable than the isoelectronic 3-azidopropyne. IR spectra have been recorded of the vapor, liquid, solutions, solid at 90 K and of the molecule trapped in argon and nitrogen matrices at 15 K and absorption bands were assigned to molecular vibrations. Raman spectra of the cooled liquid and of the amorphous and crystalline solids were also obtained and assigned. The electron diffraction results showed the conformation to be *gauche* around the C—N bond with a dihedral angle of  $\alpha = 52^\circ(5)$  from *syn* and the NNN angle  $\alpha = 173^\circ(3)$  oriented *anti* to the C—N bond. The following bond distances ( $r_a$ ) between the heavy atoms were obtained:  $rC\equiv N = 115.4(5)\text{pm}$ ,  $rC-C = 146.5(15)\text{pm}$ ,  $rC-N = 147.5(6)\text{pm}$ ,  $rN=N = 124.5(5)\text{pm}$  and  $rN\equiv N = 113.5(4)\text{pm}$ . Note:  $1\text{pm} = 0.01\text{\AA}$ . Very large changes in both frequency and intensity have been observed in the vibrational spectra upon crystallization which may be due to intermolecular associations formed by the azido group but which can also be explained by a change of the molecular conformation from only *gauche* in the vapor and liquid phases to *anti* in the crystal phase.

3-Azidopropene, allyl azide,  $H_2C=CH-CH_2-N_3$ , CAS RN [821-13-6], was synthesized and its structure and conformational composition studied by electron diffraction from the vapor, IR spectra of the vapor, of the liquid and of the amorphous solid at 90 K, and Raman spectra of the cooled liquid and of the amorphous and crystalline solids at 90 K [144]. Analysis of the electron diffraction data revealed a multiplicity of indistinguishable solutions to the conformational composition consisting of variable amounts of the three conformers SG, GG, and GG', the letters referring to the *syn* or *gauche* conformation around the C—C and C—N bonds, respectively. The normal modes of vibration for the five distinct conformations of 3-azidopropene are calculated using transferred scaled quantum mechanical force fields for propene and azidoethane.

A safe method for the synthesis of azidoethane (ethyl azide,  $C_2H_5N_3$ ) starts with ethyl bromide [145].  $^1H$  and  $^{13}C$  nuclear magnetic resonance (NMR), IR, and Raman spectra of azidoethane in the region  $4000-40\text{cm}^{-1}$  have been recorded and interpreted in terms of two conformers, *anti* and *gauche*, present in the vapor and in the liquid, and of the *gauche* conformer in the crystalline solid (Figure 5). The enthalpy difference between the conformers, and the barrier to rotational isomerism in the nitrogen and argon matrixes were calculated. Raman studies of the liquid at 140–290 K revealed the *gauche* conformation to be the more stable in the liquid phase as well.

This series of spectroscopic work helped to understand the relationship between molecular structure and thermal stability of alkyl azides and in the future it would help in the synthesis of more stable azides that can be used as propellant ingredients.

### 3.2.5 Thermodynamic Properties of Organic Azides

Through either direct measurement or group additivity calculations, the densities, normal boiling points, latent heats of vaporization, limits of superheating, enthalpies of formation, combustion and decomposition, and adiabatic flame temperatures

have been approximately determined for the monosubstituted and disubstituted alkyl azides, which exhibit significantly enhanced droplet gasification rates and microexplosion events [139]. Similar determinations were also performed for some alkyl halides because their properties are like those of the organic azides.

The enthalpy of formation of  $\text{CH}_3\text{N}_3(\text{G})$  was predicted to be  $304.6 \pm 4 \text{ kJ/mol}$  ( $72.8 \pm 1 \text{ kcal/mol}$ ) at 298 K based on the agreement between the calculated and experimental values for  $\Delta H_f$  for  $\text{HN}_3$  [146].

The heats of vaporization of several azides determined by vapor pressure measurements by a transference method are summarized in Table 7. A correlation was sought between the heat of vaporization of alkyl monoazides and alkyl diazides and the number of carbon atoms in the alkyl chain [140].

**Table 7:** Heat of vaporization of organic azides.

| Compound name                | CAS RN      | Temp. range of measured data | $\Delta H_{\text{vap}}$ at 298.15 K, kJ/mol |
|------------------------------|-------------|------------------------------|---------------------------------------------|
| Azidocyclopentane(L)         | 33670-50-7  | 275–333                      | $41.3 \pm 0.4$                              |
| Azidocyclohexane(L)          | 19573-22-9  | 280–303                      | $49.2 \pm 0.5$                              |
| 2-Azidoethanol(L)            | 1517-05-01  | 285–316                      | $62.2 \pm 0.3$                              |
| 2-Azido-acetonitrile(L)      | 57707-64-9  | 290–325                      | $52.6 \pm 0.2$                              |
| Ethyl-(2-azido)-ethanoate(L) | 105-36-2    | 301–344                      | $56.3 \pm 0.4$                              |
| 2-Azido-ethoxy-methane       | 88511-17-5  | 274–301                      | $46.6 \pm 0.5$                              |
| Azidoethane(L)               | 871-31-8    | 253–298                      | 28.9                                        |
| 1-Azidobutane(L)             | 7332-00-5   | 290–350                      | 39.9                                        |
| 1-Azidopentane(L)            | 26330-06-3  | 290–380                      | 44.4                                        |
| 1,3-Diazidopropane(L)        | 100910-72-3 | 303–455                      | 53.7                                        |
| 1,4-Diazidobutane(L)         | 24345-72-0  | 320–425                      | 58.8                                        |
| 1,5-Diazidopentane(L)        | 17607-21-5  | 345–425                      | 65.4                                        |
| 1,6-Diazidohexane(L)         | 13028-54-1  | 370–453                      | 73.4                                        |
| Azidobenzene(L)              | 622-37-7    | 313–353                      | $47.1 \pm 0.8$                              |
| 1-Azido-1,1-dinitroethane(L) |             | 313–353                      | $59.6 \pm 0.8$                              |
| Azido-trinitromethane(L)     |             | 303–343                      | $48.2 \pm 2.2$                              |

Data source: [140]

Theoretical gas-phase enthalpies of formation of 29 azides were calculated by combining G4 theory calculations with an isodesmic reaction approach [147]. The internal consistency over a set of  $\Delta H_f^{\circ, 298}$  values was achieved by sequential adjustment of their values through the isodesmic reactions. Hydrogen azide,  $\text{HN}_3$ , was chosen as a key reference compound. Of the experimental data available for 16 compounds, predictive values agreed well with only 9 of them, while deviations of 25–55 kJ/mol were observed for 7 other compounds due to systematic errors in the experimental data for phenyl azide, 2-azidoethanol, azidocyclopentane, azidocyclohexane, 3-azido-

3-ethylpentane, 2-azido-2-phenylpropane and 1-azidoadamantane. The predicted gas-phase enthalpy of formation of 2-azidoethanol,  $\text{HOCH}_2\text{CH}_2\text{N}_3$ , ranged from +112.5 to +117.6 kJ/mol with an average of 114.7 kJ/mol.

1-Octyl azide,  $\text{C}_8\text{H}_{17}\text{N}_3$ , CAS RN [7438-05-3] and 1-decyl azide,  $\text{C}_{10}\text{H}_{21}\text{N}_3$ , CAS RN [62103-13-3] were prepared by reaction of the alkyl bromides with sodium azide and their heats of combustion measured in a combustion calorimeter [148]. The enthalpies of formation derived from the heats of combustion were  $+80.6 \pm 2.2$  kJ/mol for liquid octyl azide and  $+29.0 \pm 3.0$  kJ/mol for liquid decyl azide. The heats of vaporization of these compounds were measured by a vapor pressure method.

The measured enthalpy of formation of azidocyclohexane,  $\text{C}_6\text{H}_{11}\text{N}_3$ , CAS RN [19573-22-9] liquid was +108.4 kJ/mol while the predicted enthalpy of formation was +137.7 kJ/mol with a deviation of 29.3 kJ/mol [149]. The enthalpy of formation of azidocyclohexane vapor is +208 kJ/mol.

### 3.2.6 Molecular Structure of Organic Azides

*Ab initio* calculations of the structures of a group of organic  $\text{C}_1\text{--C}_4$  alkyl azides  $\text{RN}_3$  were carried out in comparison to hydrazoic acid  $\text{HN}_3$  [150]. Fully optimized geometries of all rotational conformers of these molecules were calculated. *Ab initio* MP2 analytical force fields were computed and the theoretical predicted vibrational wave numbers were compared to measured data. Good agreement was found between the theoretical and experimental IR/Raman and microwave spectra, and for structures obtained by electron diffraction. *Ab initio* calculations of organic alkyl azides revealed that they can exist as several rotational isomers. Raman spectroscopy and electron diffraction studies suggested that ethyl azide consists of two conformers: *gauche* with a dihedral angle of  $65^\circ$  and *anti* with a dihedral angle of  $180^\circ$  (Figure 5).

The calculated energy difference between the two conformers is only 0.59 kJ/mol, the *gauche* conformer being the more stable one. According to these studies, the following azides exist only as one conformer: 3-azidopropyne: *gauche*, azidoacetonitrile: *gauche*, 1-azido-2-butyne: *gauche*, 2-azido-1,3-butadiene: *trans*, *sym*. *Ab initio* calcu-

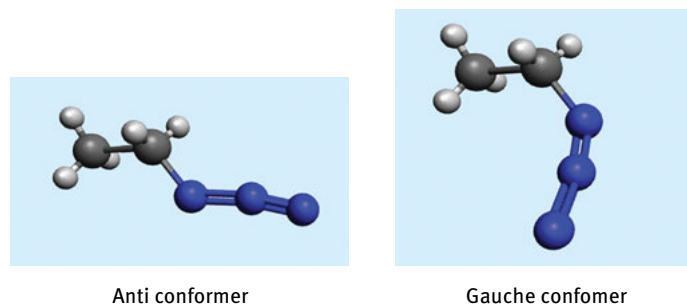


Figure 5: Molecular structures of ethyl azide.

lated relative stabilities were in full agreement with the experimental data, except for azidoacetonitrile. Allyl azide can exist as five distinct conformers.

The molecular structure of *tert*-butyl azide has been determined by gas-phase electron diffraction and quantum chemical calculations [151]. The calculations yielded near  $C_s$  symmetry for the *tert*-butyl group, *anti* conformation of the (C)N—N bond with respect to one of the (N)C—C(H3) bonds, and an essentially free rotation around the (C)N—N(N) bond with a 0.34 kcal/mol energy difference between *syn* and *anti* conformations of the CNNN moiety, the *anti* being the more stable form. The electron diffraction analysis yielded the following bond lengths ( $r_g$ ), bond angles, and torsional angles: C—H 1.111(5) Å, (N—N)<sub>terminal</sub> 1.143(4) Å, (N—N)<sub>central</sub> 1.240(5) Å, (C—C)<sub>mean</sub> 1.534(3) Å,  $\angle$ N—N—N 171.8°,  $\angle$ N—N—C 118.6°,  $\angle$ N—C—C 102.5° and 110.5°,  $\angle$ C—C—H 111.2°,  $\angle$ C—C—C 110.2° and 112.6°,  $\angle$ N—N—C—C 167.5°, 50.1° and -75.2°.

When calculating rotational barriers for methyl azide, and ethyl azide with *ab initio* methods, the results are very sensitive to the basis set quality and to the consideration of electron correlation [152]. For methyl azide a very good agreement between theory (2.9 kJ/mol) and experiment (2.98 kJ/mol) was observed for calculations. For ethyl azide, results suggested that a correct theoretical evaluation of the rotational barrier between the *anti* and *gauche* conformers cannot be carried out at the Hartree-Fock level for which the barriers were in the 0.8–1.4 kJ/mol range.

The geometries of the molecular structures of 55 organic azides were fully optimized by using semi-empirical molecular orbital (MO) methods of Austin Model 1 (AM1), Møller-Plesset (perturbation theory) (PM3), modified neglect of diatomic overlap (MNDO), and modified intermediate neglect of differential overlap (MINDO/3) [153]. Compared with the available experimental geometry parameters in gaseous phase, it was found that the calculation error from AM1 was the smallest and the next best ones are those from PM3 and MNDO. Among four MO methods used, the heat of formation computed with AM1 was the closest to the results obtained from the group additivity method. The results from MINDO/3 were the worst.

Geometries and electronic structures of methyl azide vapor and its dimers have been calculated by using *ab initio* methods at the Hartree-Fock (HF) level [154]. The intermolecular interaction energy was calculated with MP2 electron correlation correction, basis set superposition error (BSSE) correction and zero point energy (ZPE) correction. The most stable dimer with a binding energy of 9.49 kJ/mol has a six-membered ring structure with two C—H...N hydrogen bonds and belongs to the  $D_{2h}$  space group. The effect of methyl internal rotation on the interaction energy was investigated. A natural bond orbital analysis was performed to reveal the origin of the interaction.

The molecular structures of 30 azido compounds were optimized with the Becke, 3-parameter, Lee-Yang-Parr (B3LYP) method of density functional theory using six basis sets and semi-empirical PM3 and AM1 methods [155]. The molar volumes based on the isoelectron density contour were evaluated using a Monte Carlo integration scheme and the integral equation formalism polarized continuum model. The densi-

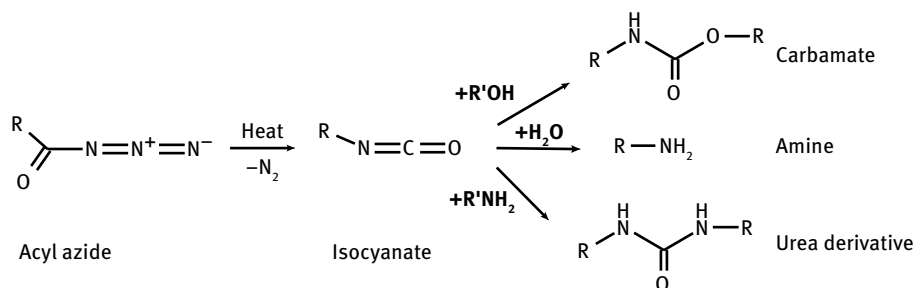
ties were subsequently predicted. Excellent linear correlations were found between the results obtained with the two models, and different methods had little effect on the densities. Quantitative relationships were established with the calculated and experimental densities of 25 azido compounds, and were used to predict the densities of five other azido compounds in the testing set. The predicted densities agreed well with the experimental data.

### 3.3 Chemical Properties of Organic Azides

The reactivity of organic azides is desirable on the one hand because it increases burning rates and specific impulse, but on the other hand it also increases sensitivity which may increase processing cost, or the propellant ends up in a higher hazard class (not low vulnerability ammunition – LOVA).

#### 3.3.1 Reactions of Organic Azides

Organic azides are quite reactive and can be used for the synthesis of many other organic compounds. The Curtius rearrangement is based on the intermediate formation of an acyl azide in the reaction. The Curtius rearrangement is the thermal decomposition of an acyl azide to an isocyanate with the loss of dinitrogen gas. The isocyanate can then undergo attack by a variety of nucleophiles such as water, alcohols or amines, to yield a primary amine, carbamate or a urea derivative, respectively:



Acyl azides can be obtained by treating acylhydrazines with nitrous acid. Some azido compounds are 1,3-dipoles, which are used in cycloadditions forming heterocyclic compounds.

The Schmidt reaction is an organic reaction involving alkyl migration over the carbon-nitrogen chemical bond in an azide with expulsion of nitrogen under the influence of a catalyst that can be a protic acid, usually sulfuric acid or a Lewis acid. The key reagent introducing this azide group is hydrazoic acid and the reaction product depends on the type of reactant: In this reaction, carboxylic acids form amines through an isocyanate intermediate and ketones form amides.

Trihalogenoamines, such as nitrogen trichloride or nitrogen triiodide are notoriously unstable and detonate even at the slightest stimulus. One would not expect triazidoamine  $N(N_3)_3$  to be any more stable, if it even exists. Calculations have shown it to contain much energy and it would leave pollution-free exhaust if it could be used in gas generants or rocket engines [156]. Maybe the molecule would be more stable if ethylene groups would be inserted between the central nitrogen atom and the three azido groups. The energy level of tris(2-azidoethyl)amine was also calculated and indicated that it should be stable. This compound was described in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines.”

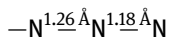
### 3.3.2 Decomposition of Organic Azides

This section contains only kinetic and thermochemical studies of the decomposition of organic azides. Combustion in flame reactions, with or without additional oxidizer, will be discussed in *Encyclopedia of Monopropellants*, chapter “Organic Monopropellants.” Strand burning of azido compounds in the absence of air is described in section “Strand Burning of Organic Azides” and section “Strand Burning of 2-Azidoethanol.”

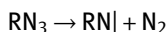
Simple alkyl azides, such as methyl azide, have been studied as model compounds in order to better understand the decomposition of more complex azido compounds which have more practical value than methyl azide. The decomposition of methyl azide is only of academic interest. The same is the case for decomposition studies of hydrogen azide, which of course nobody wants to use as a rocket propellant. The study of the decomposition of methyl azide and the other lower alkyl azides is being done for similar reasons like the study of methylnitramine. Like methyl azide, methylnitramine is not used as rocket propellant, but because it is a simple molecule it is easier to study its decomposition mechanism. It thus serves as a model compound for the decomposition of more complex organic azides.

An excellent summary of decomposition reactions of organic azides initiated by various stimuli like acid, heat, light or transition metal catalysts is available for further study of this topic [109].

The thermal decompositions of azido compounds can proceed by two different pathways, by way of ionic and covalent bonds. Most organic azido compounds are covalent azido compounds. The electromagnetivity of the  $-N_3$  group strengthens the C—N bond. So, the bond lengths of two N—N bonds in  $-N_3$  groups are different. The bond lengths of pairs of nitrogens in the azido groups are



The decomposition of azido compounds proceeds by the following equation:



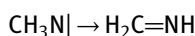
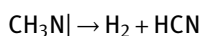
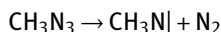
The nitrene with a free electron pair is unstable and undergoes further decomposition.

The simplest alkyl azide and easiest to investigate for its decomposition kinetics is methyl azide. The thermal decomposition of methyl azide or ethyl azide is a homogeneous unimolecular reaction [157].

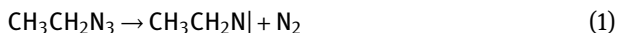
Alkyl azides tend to explode violently when ignited in the condensed phase but can be heated in low-pressure gas flow pyrolysis systems without much risk [158].

*Ab initio* MO calculations have been used to study the decomposition of methyl azide, methanimine  $\text{H}_2\text{C}=\text{NH}$ , and its isomers ( $\text{CH}_3\text{N}$ ) in order to explain the formation of HCN as a decomposition product [159]. The heat of formation of methyl azide vapor was estimated as  $305.8 \pm 12.5 \text{ kJ/mol}$  ( $73.1 \pm 3 \text{ kcal/mol}$ ). It appears that HCN is not directly formed upon fragmentation of methanimine but rather from rearrangement of HNC which is the primary product. The HCN formation from either methylnitrene or methanimine passes through successive losses of H atoms.

The thermal decomposition of methyl azide has been studied computationally and the reaction was predicted to occur in two steps via nitrene intermediate [160, 161]. The rate-limiting step is the  $\text{N}_2$  extrusion:



The potential energy surfaces of ethyl azide relevant to its thermal decomposition have been studied theoretically [162]. The reaction mechanism can be described by the following steps, like the methyl azide decomposition steps shown above:



The  $\text{CN}-\text{N}_2$  fission of ethyl azide is the rate limiting step (1), leading to ethylnitrene either along a spin-allowed path (2a) or along an alternative spin-forbidden one (2b). Both 1a and 1b channels show barriers of similar heights for  $\text{CN}-\text{N}_2$  bond fission,  $\Delta E = 42 \text{ kcal/mol}$ ,  $\Delta E$  being the energy difference between the minimum of the ground singlet state potential energy surface of ethyl azide and either the singlet transition state (TS1) or the lowest energy point of the intersystem crossing (ISC1), respectively. The decomposition of ethanimine formed in step (2b) has been studied as well and high energetic transition states have been identified for its decomposition.

Dinitrogen  $\text{N}_2$  extrusion from hydrazoic acid, methyl azide, and ethyl azide to yield the corresponding nitrene has been studied with high-level *ab initio* calculations [163]. The decomposition reaction is a competitive mechanism between a spin-allowed and a spin-forbidden channel, giving the nitrene either in the singlet or triplet states. The energy barrier height for  $\text{XN}-\text{N}_2$  bond fission is approximately the same in both channels for each azide.



The thermal decomposition of methyl azidoformate ( $\text{N}_3\text{COOMe}$ ), ethyl azidoformate ( $\text{N}_3\text{COOEt}$ ) and 2-azido-*N,N*-dimethylacetamide ( $\text{N}_3\text{CH}_2\text{CONMe}_2$ ) have been studied by matrix isolation IR spectroscopy and real-time UV photoelectron spectroscopy [164]. Dinitrogen  $\text{N}_2$  appeared as an initial pyrolysis product in all systems, and the next question is about the fate of the accompanying organic fragment. For methyl azidoformate, four accompanying products were observed:  $\text{HNCO}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_2\text{NH}$ , and  $\text{CO}_2$ , and these are believed to arise as a result of two competing decomposition routes of a four-membered cyclic intermediate. Ethyl azidoformate pyrolysis gave four corresponding products:  $\text{HNCO}$ ,  $\text{MeCHO}$ ,  $\text{MeCHNH}$ , and  $\text{CO}_2$ , together with the five-membered-ring compound 2-oxazolidone. Mechanisms were proposed for the formation and decomposition of all the products observed in these three systems, based on the experimental evidence and the results of supporting molecular orbital calculations.

The thermal decomposition of ethyl azide, *n*-propyl azide, and isopropyl azide was investigated by two different methods, a static method and a dynamic method [165]. Above a pressure of 25 mm Hg the kinetic rate was independent of pressure and typical for a homogeneous first order reaction. The kinetic rates can be expressed by the equations listed in Table 8.

**Table 8:** Kinetic rate equations for decomposition of alkyl azides.

| Compound               | Rate equation                                                  |
|------------------------|----------------------------------------------------------------|
| Ethyl azide            | $k_\infty = 3.30 \times 10^{14} \exp(40100/RT) \text{ s}^{-1}$ |
| <i>n</i> -Propyl azide | $k_\infty = 1.50 \times 10^{14} \exp(39400/RT) \text{ s}^{-1}$ |
| Isopropyl azide        | $k_\infty = 7.20 \times 10^{13} \exp(38500/RT) \text{ s}^{-1}$ |

Data source: [165]

Flash vacuum pyrolysis of azides is a very valuable method of generating nitrenes and studying their thermal rearrangements. The nitrenes can in many cases be isolated in low-temperature matrices and observed spectroscopically.  $\text{NH}$  and methyl, alkyl, aralkyl, vinyl, cyano, aryl and *N*-heteroaryl, acyl, carbamoyl, alkoxycarbonyl, imido, boryl, silyl, phosphonyl, and sulfonyl nitrenes can be made in this way [166]. Flash pyrolysis can be achieved under flow conditions or in solution or the solid state, and by photolysis.

### 3.4 Strand Burning of Organic Azides

Liquid organic azides have been evaluated as energetic plasticizers for solid propellants and as monopropellants. Linear strand burning rates have been measured as a quantitative measure of their reactivity and in preparation for their use as monopro-

pellants. Individual chapters in this book will discuss strand burning rates of GAP and 2-azidoethanol and their evaluation as monopropellants. Burning rates and critical diameters for flame propagation of several other alkyl azides have been investigated [167]. This study included 1,5-diazidopentane, 1,3-diazidopropan-2-ol, and two of its esters (Table 9).

**Table 9:** Properties of azido compounds.

| Compound name                                       | Formula                                                                                                        | Molec-<br>ular<br>mass | Density<br>at 293 K | Boiling<br>point at<br>reduced<br>pressure | Vis-<br>cosity<br>at<br>293 K | Nitro-<br>gen<br>content |
|-----------------------------------------------------|----------------------------------------------------------------------------------------------------------------|------------------------|---------------------|--------------------------------------------|-------------------------------|--------------------------|
|                                                     |                                                                                                                | g/mol                  | g/cm <sup>3</sup>   | °C at<br>(mm Hg)                           | cPs                           | mass-%                   |
| 1,3-Diazidopropan-2-ol                              | $\text{N}_3\text{CH}_2\text{CHOHCH}_2\text{N}_3$                                                               | 141.11                 | 1.2599              | 92 (3)                                     | 9.5                           | 59.6                     |
| 1,3-Diazidoglycerin (DAG)                           | $\text{C}_3\text{H}_5\text{N}_6\text{O}_1$                                                                     |                        |                     |                                            |                               |                          |
| 1,5-Diazidopentane<br>(DAPEN)                       | $\text{N}_3(\text{CH}_2)_5\text{N}_3$<br>$\text{C}_5\text{H}_{10}\text{N}_6$                                   | 154.18                 | 1.0600              | 75 (1)                                     | —                             | 54.5                     |
| 1,3-Diazidopropyl ester<br>of acetic acid (DAPA)    | $\text{H}_3\text{CCOOCH}(\text{CH}_2\text{N}_3)_2$<br>$\text{C}_5\text{H}_8\text{N}_6\text{O}_2$               | 184.16                 | 1.2226              | 89 (1)                                     | 5.5                           | 45.6                     |
| 1,3-Diazidopropyl ester<br>of propionic acid (DAPP) | $\text{H}_3\text{CCH}_2\text{COOCH}(\text{CH}_2\text{N}_3)_2$<br>$\text{C}_6\text{H}_{10}\text{N}_6\text{O}_2$ | 198.19                 | 1.1952              | 93 (2)                                     | 5.05                          | 42.4                     |

Data source: [167]

The azido derivatives were obtained and refined by methods described in the literature. The critical combustion diameters for the azido compounds under investigation were determined by a strand burning method. To diminish the possibility of heat transfer along the walls of the glass cones and tubes, these latter were placed in a vessel with a cooling fluid (water, glycerin). The following features were noted during determination of the critical combustion diameters: A flame was detected for DAG (fine, 2mm, blue-tinted luminous zone located on the fluid surface), for DAPEN (pale-blue-tinted flame and more extensive in height than for DAG), and also for DAPA (very pale, noticeable only in the dark). A flame was completely absent for DAPP.

### 3.5 Handling Precautions for Working with Organic Azides

An excellent summary of safe handling procedures for working with organic azides is given in [168]. It contains a detailed description of the sensitivity testing instruments used to characterize handling hazards of organic azides and compares it to the sensitivity of well-characterized explosives like glycerol trinitrate or TNT.

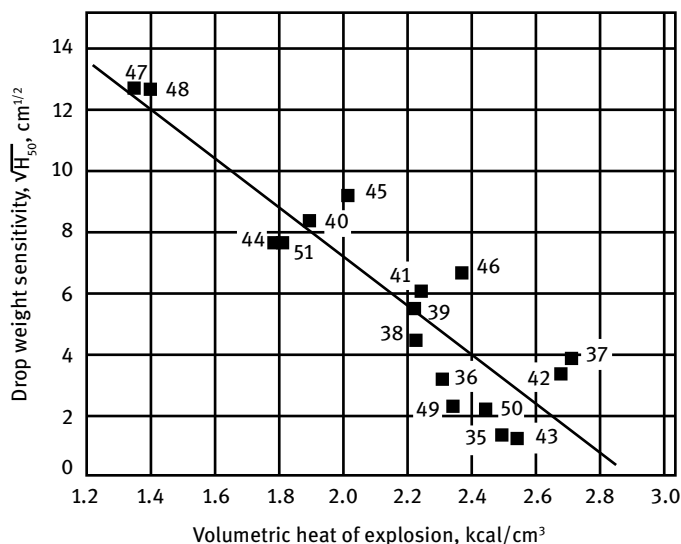
**Table 10:** Physical properties and impact sensitivity of nitroalkyl and heterocyclic azides.

| No. | Compound                                                                                                                                            | H50<br>cm | T<br>K | T<br>°C | $\Delta H_f^\circ$<br>kJ/mol | $\Delta H_f^\circ$<br>kcal/mol | $\rho$<br>g/cm <sup>3</sup> | $Q_{\max}$<br>kcal/g | $\rho Q_{\max}$<br>kcal/cm <sup>3</sup> |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------|-----------|--------|---------|------------------------------|--------------------------------|-----------------------------|----------------------|-----------------------------------------|
| 35  | (N <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> NNO <sub>2</sub>                                                                                     | 1.8       | 293    | 20      | 664                          | 158.6                          | 1.45                        | 1.716                | 2.49                                    |
| 36  | N <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N <sub>3</sub> | 10        | 293    | 20      | 615                          | 147                            | 1.48                        | 1.566                | 2.31                                    |
| 37  | O <sub>2</sub> NCNONCN <sub>3</sub>                                                                                                                 | 14.5      | 293    | 20      | 535                          | 127.8                          | 1.57                        | 1.724                | 2.71                                    |
| 38  | (N <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NNO <sub>2</sub>                                                                     | 20        | 293    | 20      | 632                          | 151                            | 1.36                        | 1.643                | 2.23                                    |
| 39  | CH <sub>3</sub> N(NO <sub>2</sub> )CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N <sub>3</sub>                                | 30        | 313    | 40      | 282                          | 67.4                           | 1.41                        | 1.578                | 2.22                                    |
| 40  | CH <sub>3</sub> N(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> N <sub>3</sub>                                                                   | 70        | 293    | 20      | 280                          | 67                             | 1.27                        | 1.497                | 1.9                                     |
| 41  | O <sub>2</sub> NCNONCCNOC(CH <sub>2</sub> N <sub>3</sub> )N                                                                                         | 37        | 293    | 20      | 556                          | 133                            | 1.56                        | 1.439                | 2.24                                    |
| 42  | N <sub>3</sub> C(O)CNONCC(NO <sub>2</sub> ) <sub>3</sub>                                                                                            | 11.5      | 293    | 20      | 610                          | 145.7                          | 1.63                        | 1.646                | 2.68                                    |
| 43  | N <sub>3</sub> C(O)CNON(→O)C(O)N <sub>3</sub>                                                                                                       | 1.5       | 293    | 20      | 615                          | 147                            | 1.7                         | 1.495                | 2.543                                   |
| 44  | (N <sub>3</sub> CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub>                                   | 59        | 305    | 32      | 523                          | 125                            | 1.32                        | 1.354                | 1.79                                    |
| 45  | N≡CN=N(→O)C=NON=CC=NOC(CH <sub>2</sub> N <sub>3</sub> )=N                                                                                           | 85        | 293    | 20      | 828                          | 198                            | 1.55                        | 1.443                | 2.02                                    |
| 46  | O <sub>2</sub> NC=N-O-N=CC=NC(CH <sub>2</sub> N <sub>3</sub> )=N-O                                                                                  | 45        | 293    | 20      | 631                          | 150.7                          | 1.57                        | 1.513                | 2.37                                    |
| 47  | CH <sub>3</sub> CNC(CH <sub>2</sub> N <sub>3</sub> )NO                                                                                              | 160       | 293    | 20      | 301                          | 71.83                          | 1.22                        | 1.105                | 1.35                                    |
| 48  | N <sub>3</sub> CH <sub>2</sub> CNC(CH <sub>3</sub> )NO                                                                                              | 160       | 293    | 20      | 327                          | 78.18                          | 1.22                        | 1.15                 | 1.4                                     |
| 49  | N <sub>3</sub> C=N-O-N=CN=NC(NO <sub>2</sub> )=CH                                                                                                   | 5         | 293    | 20      | 732                          | 175                            | 1.6                         | 1.465                | 2.34                                    |
| 50  | N <sub>3</sub> CH <sub>2</sub> N(NO <sub>2</sub> )CH <sub>3</sub>                                                                                   | 5         | 293    | 20      | 304                          | 72.6                           | 1.5                         | 1.631                | 2.45                                    |
| 51  | N <sub>3</sub> CH <sub>2</sub> N(NO <sub>2</sub> )(CH <sub>2</sub> ) <sub>6</sub> N(NO <sub>2</sub> )CH <sub>2</sub> N <sub>3</sub>                 | 59        | 293    | 20      | 523                          | 125                            | 1.32                        | 1.374                | 1.81                                    |

Data source: [169]

### 3.6 Impact Sensitivity of Alkyl Azides

Drop weight impact sensitivities of 58 liquid explosives and melts of high explosives were summarized in [169]. Compounds that were solids at room temperature were heated to just above their melting points. That publication contained data for eight azidonitro compounds. The data for individual alkyl azides were extracted from that table and shown here (Table 10). The compound numbers in the first column of the table are the same as those used in Figure 6 below. As shown in Figure 6, a linear correlation between impact sensitivity and their maximum volumetric heats of explosion could be established, like the one already shown for nitroalkanes and alkyl nitrates.



**Figure 6:** Correlation between the sensitivity of nitroalkyl azides and their maximum volumetric heats of explosion (republished and modified from [169], with permission of ©2010 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

### 3.7 Applications of Organic Azides

There are many applications of organic azides in addition to their uses in energetic binders, plasticizers, bipropellant fuels, and monopropellants. All these applications have been investigated in many other parts of the world [128, 170].

#### 3.7.1 Applications as Binders and Plasticizers

Many organic azides serve as energetic binders and plasticizers in various solid propellants. Most of the applications of azides are in solid propellants and only very few

(if any) are in liquid propellant fuels or monopropellants. For example, low-molecular-weight GAP oligomers have been used as energetic plasticizers.

### 3.7.2 Azide Additives to Fuels Enhance Droplet Dispersion by Microexplosions

Alkyl and aryl azides have been evaluated as additives to diesel engine fuels, jet engine fuels, and rocket fuels. The sudden decomposition of azides dissolved in jet engine fuel when heated in the flame zone would cause the hydrocarbon fuel droplets to break up under the influence of microexplosions sooner, scatter smaller droplets around, and burn faster in air in the combustor of jet engines, allowing more compact designs of combustion chambers. The rate of vaporization of fuel droplets can be increased by up to two orders of magnitude by addition of azides [139, 171–173]. The combustion characteristics of droplets of four energetic fuels, namely, 1) 1,4-dimethyl ester cubane (which is a solid and slightly soluble in conventional liquid fuels), 2) dihydrobenzvalene, 3) phenyl azide, and 4) carborane (which are all liquids), were examined experimentally [174]. The three liquid fuels all soot profusely, with the sooting propensity, when compared with other fuels, being in the following order: JP-10 < dihydrobenzvalene < phenyl azide < carborane; and that phenyl azide exhibits fast gasification rates and advanced microexplosion events. It was emphasized that a high energy density fuel does not automatically imply that it is fast burning, and that it must also possess desirable combustion characteristics, especially minimal sooting formation, before it can be considered for use as a jet fuel or jet fuel additive.

## 4 Organic Azides with One Azido Group

Organic azides are useful reactants in 1,3 dipolar cycloadditions to acetylenes (alkynes), which lead to five-membered heterocycles.

### 4.1 Methyl Azide

Methyl azide, azidomethane,  $\text{H}_3\text{CN}_3$ ,  $\text{CH}_3\text{N}_3$ , CAS RN [624-90-8],  $M = 57.0546 \text{ g/mol} = 17.527 \text{ mol/kg}$ , the lowest member of the family of alkyl azides, is often used as a model substance in kinetic studies on the thermal and photolytic decomposition of organic azides. Some of the properties of methyl azide were already listed in Table 5.

The molecular structure of methyl azide has been derived from Raman spectra and electron diffraction experiments and discussed in terms of the adjacent charge rule in comparison to methyl nitrate [175].

## 4.2 Ethyl Azide

Ethyl azide, azidoethane, 1-azidoethane,  $\text{H}_3\text{CCH}_2\text{N}_3$ ,  $\text{C}_2\text{H}_5\text{N}_3$ , CAS RN [871-31-8],  $M = 71.0812 \text{ g/mol} = 14.068 \text{ mol/kg}$ , is often used as a model substance in kinetic studies on the thermal and photolytic decomposition of organic azides. Some of the properties of ethyl azide were already listed in Tables 5 and 7. Ethyl azide is a liquid with a boiling point of 321.9–323.0 K at 102 kPa (48.8–50 °C at 766 mm Hg) and a density of  $0.8765 \text{ g/cm}^3$  at 298 K, and a refractive index  $n_D^{25}$  of 1.3928.

The standard enthalpy of formation of ethyl azide liquid is +266.872 kJ/mol. Ethyl azide is the parent compound of 2-dimethylaminoethyl azide (DMAZ), a thoroughly investigated compound intended as a less toxic hypergolic fuel replacement for MMH. The molecular structure of ethyl azide was illustrated in Figure 5. Ethyl azide detonates when stimulated with enough energy [176, 177].

## 4.3 2-Azidoethanol

2-Azidoethanol, also known as  $\beta$ -azidoethanol, 1-azido-2-hydroxyethane; ethanol, 2-triazo-;  $\text{N}_3\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{C}_2\text{H}_5\text{N}_3\text{O}$ , AZET, CAS RN [1517-05-1],  $M = 87.08 \text{ g/mol} = 11.48 \text{ mol/kg}$ , is discussed here under azido compounds, because its properties are dominated by the presence of the azido group and the presence of the hydroxyl group is only peripheral. The decision about its location in this chapter is counter to the decision to discuss DMAZ under amines instead of azides. DMAZ was assigned a section in the chapter on amines because the amine is the core of the molecule and the azido group is only an appendage. At one time we considered to move AZET to the alcohols in *Encyclopedia of Liquid Fuels*, chapter “Alcohols.” The current azide chapter was at one time reserved for alkyl azido compounds that did not carry other substituents in the alkyl group.

2-Azidoethanol can be made by azidation from ethylene chlorohydrin in water followed by distillation under vacuum. There has been an accidental explosion during the preparation of 2-azidoethanol [178]. 2-Azidoethanol can be made from a mixture of 2-chloroethanol (0.080 g) and sodium azide (0.072 g) with microwave irradiation [179]. The melting point given for 2-azidoethanol in [179], m.p. = 463 K (190 °C) is **incorrect**. Some literature describes the preparation of 2-azidoethanol without any warnings about its explosive properties [180].

### 4.3.1 Physical Properties of 2-Azidoethanol

2-Azidoethanol is a liquid with a boiling point of 333 K at 1.07 kPa and 346 K at 2.7 kPa (60 °C at 8 mm Hg and 73 °C at 20 mm Hg), a density of  $1.1435 \text{ g/cm}^3$  at 298 K and a refractive index of  $n_D^{20} = 1.4610$ . The oxygen balance of 2-azidoethanol for combustion to  $\text{CO}_2$  is –101%. The heat of evaporation of 2-azidoethanol at 298 K is

$62.21 \pm 0.28$  kJ/mol. The vapor pressure of 2-azidoethanol can be calculated from the equation [140]:

$$\ln P = 308.60/R - 81497.03/RT - \frac{64.7}{R} \ln(T/298.15)$$

where  $P$  is the vapor pressure in Pa and  $T$  is the temperature in kelvin, and  $R$  is the gas constant  $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ . This equation translates into a normal boiling point at atmospheric pressure of 432 K (159 °C), but that is not a safe temperature to heat AZET to. AZET can be safely distilled under a vacuum of 30 Pa where it boils at 344 K (71 °C). The refractive index of AZET is  $n_D^{20} = 1.4610$ .

The enthalpy of formation of liquid azidoethanol is +94.14 kJ/mol (+22.5 kcal/mol), which is substantially higher than the enthalpy of formation of ethanol, which is -278 kJ/mol (-66.3 kcal/mol). Substituting one hydrogen in the beta position with azide thus makes a difference of 88.8 kcal/mol thanks to the addition of azide.

The predicted computed gas phase enthalpy of formation of 2-azidoethanol,  $\text{HOCH}_2\text{CH}_2\text{N}_3$ , ranged from +112.5 to +117.6 kJ/mol with an average of +114.7 kJ/mol [147].

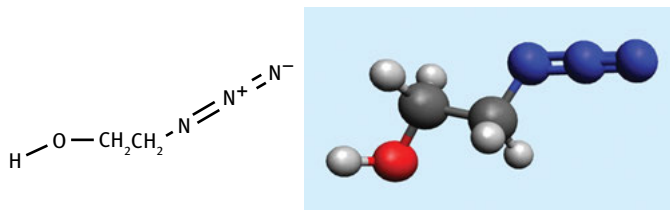
The PEPCODED.DAT data file has a similar enthalpy of formation of +258 cal/g = +22.47 kcal/mol = +94.0 kJ/mol for liquid AZET [7]. The density is listed there as  $0.0415 \text{ lb/in.}^3 = 1.149 \text{ g/cm}^3$ .

The addition of each azido groups to a molecule contributes a positive increase in the enthalpy of formation of 313–397 kJ/mol. This is evident from a comparison of enthalpy of formation of ethanol (-278.5 kJ/mol) and 2-azidoethanol,  $\text{N}_3\text{CH}_2\text{CH}_2\text{OH}$  (+104 kJ/mol).

A homologue of 2-azidoethanol is 3-azidopropanol, CAS RN [72320-38-8], refractive index  $n_D^{20} = 1.461$ , density  $\rho = 1.095 \text{ g/cm}^3$  at 298 K (25 °C), which is commercially available. Its isomer 3-azido-1-methyl-ethanol is also commercially available.

#### 4.3.1.1 Molecular Structure of 2-Azidoethanol

The molecular structure of 2-azidoethanol is illustrated in Figure 7.



**Figure 7:** Molecular structure of 2-azidoethanol.

### 4.3.2 Chemical Properties of 2-Azidoethanol

The hydroxyl group in 2-azidoethanol can be esterized with nitric acid, giving 2-azido-1-ethanol nitrate,  $\text{N}_3\text{CH}_2\text{CH}_2\text{ONO}_2$ , ethanol azido nitrate, which is a volatile liquid with a density of  $1.34 \text{ g/cm}^3$  and a freezing point of  $253 \text{ K}$  ( $-20^\circ\text{C}$ ).

#### 4.3.2.1 Reactions of 2-Azidoethanol

2-Azidoethanol ignites hypergolically with high concentration hydrogen peroxide [181, 182].

#### 4.3.2.2 Thermal Decomposition of 2-Azidoethanol

2-Azidoethanol has been considered as a monopropellant, thus its decomposition in reactors at high pressures will be discussed in *Encyclopedia of Monopropellants*. Here we are only looking at some academic studies of its decomposition mechanism, studies that can be carried out in glass apparatus at low pressure. A section on strand burning of 2-azidoethanol follows the current section in this chapter.

The thermal decomposition of 2-azidoethanol and 2-azidoethyl acetate was studied by matrix isolation IR spectroscopy and real-time UV photoelectron spectroscopy [183]. The products that were detected in a flow system at different temperatures ( $\text{CH}_2\text{NH}$ ,  $\text{H}_2\text{CO}$ ,  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{HCN}$ ) allowed mechanisms for decomposition to be proposed. The experimental evidence obtained is consistent with 2-azidoethanol decomposing via a stepwise decomposition mechanism as observed previously for azidoacetone.

The temperature dependence of the saturated vapor pressure of 2-azidoethanol was determined and the evaporation enthalpy, evaporation entropy and boiling point of this substance were  $33.9 \pm 1.2 \text{ kJ/mol}$  ( $8.1 \pm 0.3 \text{ kcal/mol}$ ),  $17.7 \pm 0.5 \text{ e.u.}$  and  $458 \text{ K}$  ( $185^\circ\text{C}$ ), respectively [184]. These numbers showed that 2-azidoethanol is a weakly associated liquid. Kinetics of the thermal decomposition of 2-azidoethanol in the gas phase can be described by an equation of the first order. Nitrogen and ethanolamine were found among the products of decomposition. The rate constant of the process did not depend on the initial gas pressure. The reaction has a partially heterogeneous character; however, the contribution of heterogeneous reaction to observable kinetics was negligible. It is assumed that the reaction proceeds with neighboring group participation (anchimeric assistance) by the hydroxyl group. The kinetic data were used for prediction of parameters of adiabatic explosion and combustion of 2-azidoethanol at higher pressure.

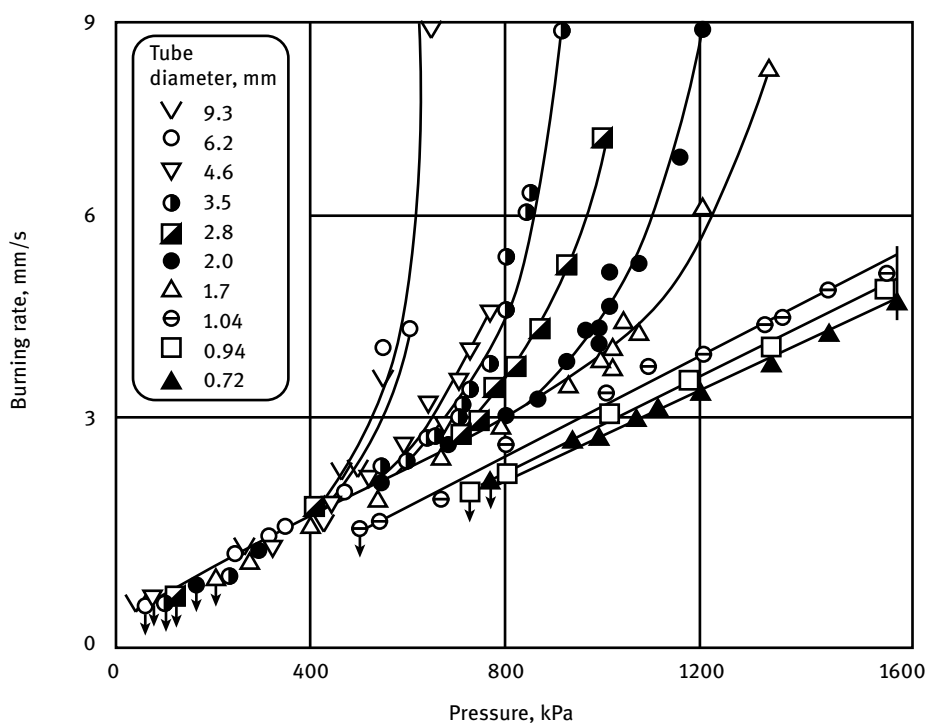
In a study of the pyrolysis of 2-azidoethanol it was found that a Curtius type rearrangement plays an important role in the pyrolysis reaction [185]. Two imine intermediates have been found in the pyrolysis reaction and the most likely pyrolysis products were  $\text{HCHO}$ ,  $\text{CH}_2=\text{NH}$ ,  $\text{HCN}$ , and  $\text{N}_2$ .



### 4.3.3 Strand Burning of 2-Azidoethanol

The strand burning and droplet burning of azidoethanol is of interest for its potential application as a monopropellant.

The strand burning rate and the critical diameter for propagation of combustion of 2-azidoethanol in capillary glass tubes were determined in a constant pressure bomb as a function of pressure [186]. The critical diameter when plotted against pressure showed two distinctly different regimes, a laminar steady combustion and a turbulent combustion. The critical diameter was below 1 mm when the pressure was increased beyond  $10^5$  Pa. This is a very small critical diameter, smaller than those observed with other monopropellants. The strand burning rate of 2-azidoethanol as a function of pressure is illustrated in Figure 8. The curves are for different capillary diameters. The diameters are identified in the legend to the figure. The smallest diameters are those shown with solid triangles (0.72 mm) and open squares symbols (0.94 mm).



**Figure 8:** Strand burning rate of 2-azidoethanol as a function of pressure (republished and modified from [186], with permission of ©1981 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

During the burning of 2-azidoethanol, pyrolysis with a rate constant

$$k = 0.794 \times 10^4 \exp(-37800/RT) \text{s}^{-1}$$

is the predominant reaction, where the combustion and the limiting conditions are closely described by the Zeldovich and Frank-Kamenetskii thermal theory [187, 188]. Measurements of the burning of 2-azidoethanol droplets in air were made by placing the droplets on a thin nichrome support and igniting them with a tungsten filament through which a current was passed. The external pressure effect on the burning rate was examined in a vacuum chamber fitted with two viewing windows. The surface area  $S$  decreased linearly with time at all pressures, so the rate can be characterized by the constant  $K = dS/dt$ ; however, at atmospheric pressure,  $K$  varied linearly with  $r^2$ . Above 0.2 kPa, there was a secondary flame, and the combustion rate increased to  $0.4 \text{ g cm}^{-2} \text{ s}^{-1}$  at atmospheric pressure.

During 2-azidoethanol combustion at lowered pressures in air in non-thermostatted tubes the heat supply along the tube walls from the decomposition zone to the condensed phase may lead to a transition of azidoethanol combustion to a pulsating regime [189].

A distinctive feature of the dependence of the combustion velocity of azidoethanol on the external pressure was that a density jump developed during the transition from normal combustion to a fluctuating regime. The periods of the fluctuations in the combustion velocity of azidoethanol were determined for different external pressures [190].

It was found that there are three regimes of ignition of individual drops that differ in kinetics of chemical reactions [191]. The first regime showed a temperature interval where oxidation and decomposition occurred simultaneously at ignition process of 2-azidoethanol. The burning rates of liquid 2-azidoethanol gelled with polymethyl methacrylate (PMMA) and placed into thin tubes with diameters of  $d = 2 - 10 \text{ mm}$  also had a pulsed character [192]. The burning rate of gelled 2-azidoethanol increased with pressures from 13 to 260 GPa in accordance with the linear law. The combustion of gelled 2-azidoethanol transitioned to turbulent regime at pressures above 260 GPa. Such transition was accompanied by an increase of burning rate by a factor of 5–6.

The flame of 2-azidoethanol burning in thin capillary tubes at atmospheric pressure has two combustion zones [193]. The first combustion front is near the surface where the reaction is a decomposition reaction of the azide group. The second combustion zone is above the upper edge of the capillary tube and has the form of a steady flame torch (secondary flame). The reaction in the secondary flame is an oxidizing reaction of decomposition reaction products with oxygen from ambient air.

The ignition delay of 2-azidoethanol in air dropped steeply from 17 s at 500 K to 1 s at 625 K and remained below 2 s between 625 and 725 K. When studying the behavior of a droplet of 2-azidoethanol in heated air, it was shown that droplet ignition

is a gas-phase process limited by heat release due to the vapor-phase oxidation of azidoethanol [194]. An increase in the ambient temperature with distance from the ignition limit leads to enhancement of the role of the thermal decomposition of azidoethanol molecules. In the range of ambient temperatures of 560–620 K, the droplet ignition is determined by the kinetics of the parallel reactions, the gas-phase oxidation and thermal decomposition of azidoethanol. The activation energy of the chemical reaction limiting the droplet ignition process was estimated to be  $E_a = 60.7 \pm 2.9$  kJ/mol ( $14.5 \pm 0.7$  kcal/mol). The value obtained is much lower than the activation energy for the thermal decomposition reaction of  $\beta$ -azidoethanol molecules, for which the reaction rate constant is  $k_2 = 8 \times 10^{13} \exp(-37800/RT) \text{ s}^{-1}$ . Thermocouples were used to study the oscillatory combustion of 2-azidoethanol [195].

#### 4.3.4 Safety Properties of 2-Azidoethanol

In view of accidental explosions that have occurred during the preparation of 2-azidoethanol, it is important to know the safety properties of this material [178]. An explosion with a force equivalent to 100–200 g TNT occurred during the preparation of 2-azidoethanol, CAS RN [1517-05-1] 1 h and 40 min. after 1.831 kg 2-bromoethanol had been added to 1.03 kg sodium azide. The homogeneous mixture was being maintained at steam bath temperature under stirring.

Limits of initiation of explosion of homogeneous liquid explosives can be determined by recording luminosity of shock waves during intersection at the contact interface of a non-explosive and an explosive liquid. The method was demonstrated by determining the limits of initiation of the detonation of azidoethanol [196].

Sensitivity tests of gelled non-Newtonian liquid propellants containing AZET, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), triaminoguanidinium nitrate (TAGN), and a gelling agent showed that these propellants were less sensitive than the pure ingredients from which they were made [197, 198].

#### 4.4 2-Azido-*N,N*-dimethylethanamine

2-Azido-*N,N*-dimethylethylamine, also known as *N,N*-dimethyl-2-azidoethylamine, 2-azidoethyl-*N,N*-dimethylamine, 2-azido-*N,N*-dimethylethanamine,  $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}_3$ ,  $\text{C}_4\text{H}_{10}\text{N}_4$ , DMAZ, CAS RN [86147-04-8] is a candidate fuel to replace hydrazine derivatives, especially MMH, in certain hypergolic fuel bipropellant applications. It can also decompose by itself in a monopropellant fashion and has been considered as a replacement for hydrazine as a monopropellant. Properties of DMAZ will be discussed in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines,” because the core of the molecule is an amine and the azide is only an attachment.

## 4.5 Propyl Azides

1-Azidopropane, *n*-propyl azide,  $C_3H_7N_3$ , can be made from a mixture of 1-bromopropane (0.122 g) and sodium azide (0.072 g) with microwave irradiation for 29 min. [179]. The melting point given in [179] (206 °C) is **incorrect**. A similar method starting with a mixture of 2-bromopropane (0.122 g) and sodium azide (0.072 g) gives 2-azidopropane. 3-Azidopropane-1,2-diol has been used as a chain extender for GAP solid propellant polyurethane binders.

## 4.6 Glycidyl Azide

Glycidyl azide,  $CH_2(O)CHCH_2N_3$ , GAP, CAS RN [80044-09-3], has been extensively investigated as the monomer that can be polymerized to form an energetic binder for solid propellant. Instead of allowing the polymerization to go to high molecular masses resulting in solid, flexible polymers, the polymerization can be interrupted after only a small number of monomer molecules have been linked to form liquid oligomers. Oligomers (telomers) of GAP can be used as energetic plasticizers. Oligomers can be formed with different end groups in the telomer. GAP has a low glass transition temperature (228 K = −45 °C). The functionality of linear GAP is nearly 2, and to achieve the desired level of crosslinking to produce a tough and elastomeric rubber it must be raised by the addition of triols or used with triisocyanate crosslinkers. Some of the methods described here in the chapter on plasticizers can also be applied to the synthesis of GAP products with higher molecular masses. Properties of GAP diol and GAP triol are summarized in Table 11. The precursor epichlorohydrin diol is commercially available. The synthesis of GAP triol starts with epichlorohydrin and glycerol.

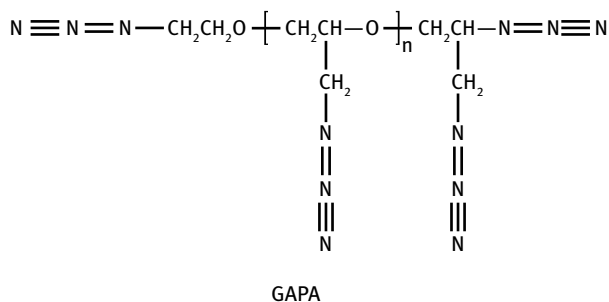
**Table 11:** Properties of GAP diol and GAP triol.

|                                                          | GAP diol            | GAP triol           |
|----------------------------------------------------------|---------------------|---------------------|
| $\Delta H_f$ , cal/g                                     | +280                | —                   |
| Density, g/cm <sup>3</sup>                               | 1.29                | 1.29                |
| Color                                                    | light yellow liquid | light yellow liquid |
| Molecular mass, $M_n$ , g/mol                            | 1700 ± 300          | ≥900                |
| Functionality                                            | 2.0                 | 2.5–3.0             |
| Thermal stability, cm <sup>3</sup> at 100 °C after 200 h | ≥3                  | ≥3                  |
| $T_g$ , K                                                | 228                 | 228                 |
| $T_g$ , °C                                               | −45                 | −45                 |

Data source: [199]

A convenient process for the preparation of low molecular weight hydroxyl-terminated glycidyl azide polymers involved the formation of glycidyl azide polymer in a single step [200]. The polymerization of epichlorohydrin was carried out in dipolar aprotic solvent *N,N*-dimethylformamide medium using diols as initiators in the presence of sodium azide. Various low molecular weight diols, such as ethylene glycol, propylene glycol, diethylene glycol, 2-methylpentane-2,4-diol and resorcinol were employed as initiators. The effect of different initiating diols on the polymer formation was confirmed by gel permeation chromatography (GPC) and vapor pressure osmometry (VPO). The GPC analysis indicated that the glycidyl azide polymers contained different-sized oligomers due to the multi-modal molecular weight distribution. The GAPs obtained in all the polymerizations by using different diols had a maximum of 5–7 glycidyl azide repeating units. The low-molecular weight GAPs obtained by using different diol units had a thermal decomposition pattern like that of GAP. Since the glycidyl azide polymers had low molecular weights, their glass transition temperatures were lower, between 203 and 201 K (between  $-70$  and  $-72^{\circ}\text{C}$ ).

In addition to poly(glycidyl azide) oligomers terminating in hydroxyl groups, oligomers with terminal azido groups (GAPA) have been synthesized. As a general rule, plasticizing effects will be lost if terminal hydroxyl groups on the plasticizer react with the isocyanate crosslinking agent, effectively tying the plasticizer into the cross-linked polymer matrix. An azide-terminated glycidyl azide plasticizer (GAPA) avoids this problem, being a plasticizer having no reactive terminal hydroxyl groups available for isocyanate reactions [201]. GAPA is produced by reacting polyepichlorohydrin with *p*-toluenesulfonyl chloride in pyridine and reacting the resulting tosylated polyepichlorohydrin with sodium azide in dimethylformamide. GAPA is a pale-yellow liquid with low molecular weight, low  $T_g$ , and good thermal stability (Table 12).



Low-molecular-weight GAP oligomers have been used as energetic plasticizers, in particular for propellants with ingredients that are not compatible with nitrate-ester energetic plasticizers. One of these propellants used TAGN with a GAP plasticizer [202].

The thermal stability of a special type of GAP plasticizer at one time available from 3M as L-12616 was studied at elevated temperatures [203]. Little change was observed

**Table 12:** Properties of azide terminated glycidyl azide plasticizer (GAPA).

|                                                          |                     |
|----------------------------------------------------------|---------------------|
| $\Delta H_f$ , J/g                                       | 2301                |
| $\Delta H_f$ , cal/g                                     | 550                 |
| Density, g/cm <sup>3</sup>                               | 1.27                |
| Color                                                    | light yellow liquid |
| Molecular mass, $M_n$ , g/mol                            | 700–900             |
| Thermal stability, cm <sup>3</sup> at 100 °C after 200 h | ≤3                  |
| $T_g$ , K                                                | 217                 |
| $T_g$ , °C                                               | –56                 |

Data source: [199]

at temperatures up to 383 K (110 °C) but aging at 423 K (150 °C) resulted in the formation of volatile, lower molecular weight species. Aging effects were less pronounced in air than in an inert atmosphere.

Low molecular mass hydroxyl-terminated glycidyl azide polymers can be made in a single step by polymerization of epichlorohydrin in dipolar aprotic solvent *N,N*-dimethylformamide (DMF) using diols as initiators in the presence of sodium azide [200]. Various low molecular mass diols, such as ethylene glycol, propylene glycol, diethylene glycol, 2-methylpentane-2,4-diol, and resorcinol were employed as initiators. The effect of initiating diols on the polymer formation was confirmed by GPC and VPO. The GPC analysis indicated that the glycidyl azide polymers contained different size oligomers, due to the multi-modal molecular weight distribution. Since the glycidyl azide polymers have low molecular mass, their glass transition temperatures are lower, between 203 and 201 K (–70 and –72 °C), due to variations in the structure of the polymers. Structural analysis of the GAPs using spectral methods revealed that the initiating diol units were present in the polyether backbone of GAP molecules.

Polyepichlorohydrin (PECH) precursor was synthesized by the ring-opening polymerization of epichlorohydrin using 1,4-butanediol as initiator and boron-trifluoride etherate as catalyst [204]. The second step of tosylation made tosylate-terminated epichlorohydrin polymer as intermediate by reaction of PECH and 4-toluenesulfonylchloride in pyridine. The third step yielded azido terminated glycidyl azide polymer (ATGAP) by the reaction of tosylate intermediate and sodium azide. The structure of ATGAP was characterized by IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. The glass transition temperature of ATGAP was 200 K (–73 °C). The onset of thermal decomposition temperature was 526 K (253 °C). ATGAP has a low viscosity and can be used as an energetic plasticizer.

There are two routes to the preparation of oligo (glycidyl azides): first, oligomerization of glycidyl azide and second, oligomerization of its halogen-containing precursors (oligoepichlorohydrin or oligoepibromohydrin) with simultaneous or subsequent substitution of azide groups for the halogen atoms. The first route is difficult to follow on account of the low reactivity of glycidyl azide. Instead

oligo(glycidyl azides) were prepared by the second route [205]. Prepolymers of different modifications were obtained by cationic polymerization of epichlorohydrin under the action of  $\text{BF}_3 \cdot \text{THF}$ . The synthesis of azide-substituted polymers, such as glycidyl azide and 3,3'-bis(azidomethyl)oxetane (azidopentone) polymers can be made by the azidation of their halogen-containing precursors with sodium azide in a dimethyl sulfoxide (DMSO) ( $353 \text{ K} = 80^\circ\text{C}$ , 10–100 h) or DMF medium ( $368 \text{ K} = 95^\circ\text{C}$ , 10–20 h). The synthesis of poly(glycidyl azides) by the simultaneous polymerization of ECH and displacement of its chlorine atoms in a  $\text{NaN}_3/\text{DMF}$ /ethylene glycol or propylene glycol medium ( $\sim 363 \text{ K} = \sim 90^\circ\text{C}$ , 15 h) has also been considered. A drawback of this method is the difficulty to completely remove the non-volatile solvent from the polymer.

The self-heating rate and thermal decomposition of octylazide, GAP-AA-2000 (normal GAP, but OH-end groups as esters of  $\alpha$ -azidoacetic acid), GAP-AA-500 (short chain GAP, but OH-end groups as esters of  $\alpha$ -azidoacetic acid), and GAPA were examined in an accelerating rate calorimeter (ARC) with 6-g samples contained in a titanium bomblet [206].

An acyl-terminated GAP was synthesized via the reaction between 2,4,6-trinitrobenzoyl (TNB) chloride and GAP [207]. The TNB-GAP structure was confirmed by FT-IR, UV-vis,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR. The glass transition temperature ( $T_g$ ) of TNB-GAP was evaluated by DSC, and the thermal stability of TNB-GAP was tested by TGA. DSC traces showed that TNB-GAP had a  $T_g$  of  $227 \text{ K} = -46^\circ\text{C}$ . TGA showed that the thermo-oxidative degradation of TNB-GAP in air was a two-step reaction, and the percentage of degraded TNB-GAP nearly reached 100% at  $923 \text{ K} = 650^\circ\text{C}$ . Non-isothermal DSC results indicated that the apparent activation energies of the two-step exothermic decomposition of TNB-GAP were 80.16 and 162.92 kJ/mol, and the values of the pre-exponential constant were  $1.75 \times 10^{10}$  and  $1.22 \times 10^{16}$ , respectively. Future volumes on solid propellants will contain detailed chapters on use of GAP polymers as energetic binders in solid propellants.

#### 4.7 Azidoacetic Acid

Azidoacetic acid,  $\text{N}_3\text{CH}_2\text{COOH}$ , contains only one azide group, but most of the esters formed with azidoacetic acid and polyols contain more than one azido group. This group of azido compounds that is actively evaluated as energetic plasticizers is discussed in the Section 13 “Polyol Esters of Azidoacetic Acid.”

Azidoacetic acid can be made by irradiating a mixture of 2-chloroacetic acid (0.094 g) and sodium azide (0.072 g) with microwaves for 30 min. [179]. Azidoacetic acid forms esters with alcohols and polyols that are suitable as energetic plasticizers.

## 4.8 Other Aliphatic Monoazides

There are many organic compounds that carry one azido group in addition to several other energetic groups, like nitrate or nitro groups. Azidotrifluoromethane,  $\text{CF}_3\text{N}_3$ , is thermally more stable than azidomethane, methyl azide  $\text{CH}_3\text{N}_3$  [208]. The structure of azidotrifluoromethane has been obtained by a combined analysis of electron diffraction intensities and ground-state rotational constants derived from the microwave spectrum  $\text{C}-\text{F}$  1.328 Å,  $\text{C}-\text{N}$  1.425 Å,  $\text{N}-\text{N}$  1.252 Å,  $\text{N}-\text{N}$  1.118 Å,  $\angle\text{CNN}$  112.4°,  $\angle\text{NNN}$  169.6°,  $\angle\text{FCF}$  108.7°. The  $\text{CF}_3$  group is in the staggered position with respect to the  $\text{N}_3$  group and tilted away from it by 5.8° [209].

Compounds with the general formula  $\text{F}(\text{NO}_2)_2\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{R}$  wherein  $\text{R}$  is  $-\text{CH}_2\text{N}_3$  or  $-\text{O}-\text{CH}(\text{CH}_2\text{N}_3)_2$ , such as 1,3-diazido-2-propyl fluorodinitroethyl formal, azidomethyl fluorodinitroethyl ether, 1,7-diazido-4,4-difluoraminoheptane, or *N*-(trinitroethyl)-*N*-(3-azidopropyl)nitramine can be used as energetic plasticizers for solid propellants [210]. Azidodinitroalkanes where the azido and two nitro groups are located on the same terminal carbon atom can be synthesized by reaction of 1,1,1-trinitroalkyl compounds with lithium azide [211, 212].

Azidodinitromethyl compounds can be prepared by electrooxidative coupling of azide ions to dinitromethyl carbanions. Thus, anodic coupling of sodium azide with ethyl 4,4-dinitrobutyrate produced ethyl 4-azido-4,4-dinitrobutyrate. Similarly, 4-azido-4,4-dinitrobutyl acetate was prepared from 4,4-dinitrobutyl acetate and converted by way of the corresponding alcohol to the nitrate ester, 4-azido-4,4-dinitrobutyl nitrate [213]. 1-Azido-1,1-dinitroethane may be prepared by reacting 1,1,1-trinitroethane with lithium azide and can be used as a monopropellant [214].

Several azidonitrazapropanes and azidonitrazapentanes are described in *Encyclopedia of Liquid Fuels*, chapter “Nitramines.” That chapter includes energetic azido eutectics which can be used as energetic plasticizers, e.g. [215].

2-Methyl-2-nitro-1-azidopropane was synthesized through a condensation reaction, substitution reaction and azidation [216]. The molecular structure of the product was determined by MS, IR, and  $^1\text{H}$  NMR. Thermochemical properties of  $\alpha$ -azidopolynitroalkanes and the energy of  $\text{C}-\text{N}_3$  bond-dissociation in organic azides were derived from experimental data [217].

$\alpha$ -Azidopolynitroalkanes can be prepared by reaction of polynitroalkanes or  $\alpha$ -(difluoroamino)polynitroalkanes with  $\text{NaN}_3$  [218]. In the case of tetranitromethane, one or two nitro groups can be substituted, depending on the reaction conditions. The reaction of 1,1,1-trinitroethane with  $\text{NaN}_3$  affords nitro-1,2,3-triazole, together with 1-azido-1,1-dinitroethane. 3-Azido-2,2-dinitropropanol can be made from a cyclic 2,2-dinitro 1,3-propanediol sulfite with azide, followed by hydrolysis of the sulfate [219].

Azidomethyl-dinitroxydimethyl-nitromethane,  $\text{N}_3\text{CH}_2(\text{O}_2\text{NOCH}_2)_2\text{CNO}_2$ , AMDN-NM, has been evaluated as a plasticizer for double-base propellants [220]. The small-scale explosive sensitivity of neat AMDNNM was determined to be slightly



more sensitive than pentaerythritol tetranitrate (PETN). Neat AMDNNM had thermal stabilities similar to that of PETN.

*n*-Butyl azide,  $C_4H_9N_3$ , CAS RN [7332-00-5], has a refractive index of  $n_D^{20} = 1.4102$  and boils at 344 K at 30 kPa (71 °C at 225 mm Hg) [221]. *n*-Amyl azide,  $C_5H_{11}N_3$ , CAS RN [26330-06-3], has a refractive index of  $n_D^{20} = 1.4266$  and boils at 336.6 K at 13.3 kPa (63.5 °C at 100 mm Hg). 4-Heptyl azide has a refractive index of  $n_D^{23} = 1.4370$  and boils at 351 K at 26.7 kPa (78 °C at 200 mm Hg).

1,3-Diazo-2-propyl trinitropropyl carbamate,  $(O_2N)_3CCH_2CH_2NHCOOCH(CH_2N_3)_2$ , DATC, can be prepared by reaction of 3,3,3-trinitropropyl isocyanate with 1,3-diazo-2-propanol. In a subsequent reaction, DATC can be reacted with nitric acid in acetic anhydride to make a nitramine, 1,3-diazo-2-propyl-*N*-nitro-*N*-trinitropropyl carbamate,  $(O_2N)_3CCH_2CH_2N(NO_2)COOCH(CH_2N_3)_2$ , DANTC which can be used as an energetic plasticizer [222]. The enthalpy of formation of DANTC is +163 kJ/mol (+39 kcal/mol) and its freezing point is 271 K (−2 °C).

#### 4.9 Alkenyl Azides

The structure of alkenyl azides is of interest if there is any interaction between the electron clouds in the C=C double bond and the adjacent N=N bonds. This was investigated by *ab initio* calculations of energy levels and vibrational frequencies of 3-azidopropene (allyl azide) and a comparison of calculated and measured data [223].

3-Azidopropene, allyl azide,  $H_2C=CH-CH_2-N_3$ , CAS RN [821-13-6], was synthesized and the structure and conformational composition studied by electron diffraction from the vapor, IR spectra of the vapor, of the liquid and of the amorphous solid at 90 K, Raman spectra of the cooled liquid and of the amorphous and crystalline solids at 90 K [144]. The normal modes of vibration for the five distinct conformations of 3-azidopropene were calculated using transferred scaled quantum mechanical force fields for propene and azidoethane. Vinyl azides can be incorporated in energetic binders for solid propellants [114].

#### 4.10 Alkynyl Azides

Like the case in alkenyl azides, the structure of alkynyl azides is of interest if there is any interaction between the electron clouds in the C≡C triple bond and the adjacent N=N bonds. Alkynyl azides are more energetic than comparable alkyl azides and can be used for the synthesis of heterocyclic compounds.

3-Azidopropyne was synthesized and the structure was determined by electron diffraction from the vapor and computed by *ab initio* Hartree-Fock self-consistent field (SCF) method calculations [224]. IR spectra of the vapor, of the cooled solid, of the matrix isolated species in argon and nitrogen at 13 K, and of the solid at 90 K were

recorded and Raman spectra of the cooled liquid and of the amorphous and crystalline solid were also obtained. From the spectroscopic investigation it was evident that the title compound exists as only one conformer in all states of aggregation. The electron diffraction results and the theoretical calculations showed unambiguously the conformation to the *gauche* around the C—N bond with a dihedral angle of  $37^\circ$  from *syn* and with the NNN angle of  $169^\circ$  oriented *anti* to the C—N bond.

The IR spectra and Raman of 4-azidobut-1-yne were recorded in the vapor and liquid state and as amorphous and crystalline solids at liquid nitrogen temperature [225, 226]. 4-Azidobut-1-yne can exist in five distinct conformations. IR spectra of the molecule were obtained in the vapor and liquid states at room temperature and as amorphous and crystalline solids at liquid nitrogen temperature [227]. Apparently, all five conformers were present in the liquid at room temperature and in the argon matrix at 12K, whereas only three conformers were observed in the nitrogen matrix. It was not possible to estimate the energy differences between conformers. An isomer of 4-azidobut-1-yne is 4-azidobut-2-yne and the vibrational spectra, molecular structures and conformations of these organic azides were measured and compared [228].

A polymeric polytriazole formed as an insoluble byproduct during the synthesis of propargyl azide from propargyl bromide and sodium azide [229]. It appeared to be a polymer of 4-methylene-1,2,3-triazole.

It has not been possible to isolate azidoethyne (acetylenyl azide),  $\text{HC}\equiv\text{C}-\text{N}_3$  in the pure state, only its reaction products with cyclooctyne, bicyclic compounds, could be found [230]. For instance, the reaction of sodium acetylide with tosyl azide gave only a mixture of two triazoles. The reaction of ethynyl chloride with sodium azide gave only mixtures of triazoles. Attempts to convert a C=C double bond in vinyl azide to a C $\equiv$ C triple bond failed.

#### 4.11 Cyanogen Azide

Cyanogen azide, consisting of only carbon and nitrogen, could be considered an organic or an inorganic compound. It is a very reactive compound and a useful intermediate in the synthesis of a range of other organic compounds. The reactive intermediate is cyanonitrene  $\text{N}\equiv\text{CN}^\cdot$  which readily adds to C=C double bonds or forms ring structures with C $\equiv$ C acetylenic bonds. Cyanogen azide is too sensitive to be used as a rocket propellant, but it is a useful intermediate in the synthesis of other energetic compounds.

Cyanogen azide can be synthesized in nearly quantitative yield by the reaction of sodium azide with cyanogen chloride in aprotic media [231, 232]. Cyanogen azide, a colorless oil, detonates with great violence when subjected to mechanical or thermal shock, and great care must be taken in any work with this compound. It can be handled relatively safely when diluted in solvents. The half-life of a 27% solution of the azide in acetonitrile is days at room temperature, but this solution can be stored

indefinitely without change at 0 to  $-20^{\circ}\text{C}$ . The pure, undiluted azide is too sensitive for combustion analysis or determination of its IR, Raman spectra [233] or microwave spectra [234] or electron diffraction spectra [235], or one must operate at very low pressures. Computer calculations predicted the enthalpy of cyanogen azide vapor to be  $+501.1\text{ kJ/mol}$  [149]. The reaction of cyanogen azide with olefinic hydrocarbons at 273–303 K ( $0$ – $30^{\circ}\text{C}$ ) gives *N*-cyanoaziridines and 1-alkylalkyldenecyanamides [236].

## 5 Aromatic Azides with One Azido Group

Phenyl azide, azidobenzene,  $\text{C}_6\text{H}_5\text{N}_3$ , CAS RN [622-37-7], has a density of  $1.088\text{ g/cm}^3$ , boils at 322 K at 0.67 kPa ( $49^{\circ}\text{C}$  at 5 mm Hg), freezes at 245.6 K ( $-27.5^{\circ}\text{C}$ ) and has an enthalpy of formation of  $+346\text{ kJ/mol}$  ( $+82.7\text{ kcal/mol}$ ) [221]. Phenyl azide is not sufficiently energetic to be used as a monopropellant but could potentially be used as a fuel. Phenyl azide is a yellow oil with a bitter almond-like odor and may explode on heating and the attempt to distil it. One would expect that the reaction of aniline with nitrous acid would give phenyl azide, but of course that reaction forms the phenyldiazonium salt. Phenyl azide can be prepared by reaction of phenylhydrazine with thionyl chloride. Phenyl azide has been prepared by the action of nitrous acid on phenylhydrazine hydrochloride, reaction of ammonia with diazobenzene perbromide and by the reaction between a diazo salt and sodium azide [237].

Photolysis of phenyl azide, a photo-initiated autocatalytic chain decomposition of phenyl azide, leads to ring widening and formation of dehydroazepines. The combustion characteristics of droplets of phenyl azide were examined experimentally [174].

4-Nitrophenyl azide would be more energetic than plain phenyl azide. The enthalpy of combustion of crystalline 4-nitrophenyl azide was determined by static oxygen bomb calorimetry at 298.15 K as  $3241.4 \pm 4.2\text{ kJ/mol}$  [238]. The corresponding enthalpies of formation using an estimated enthalpy of sublimation are  $\Delta H_f^0(\text{C}) = 308.7 \pm 4.3$  and  $\Delta H_f^0(\text{G}) = 389.7 \pm 5.2\text{ kJ/mol}$ .

## 6 Heterocyclic Azides with One Azido Group

There are numerous heterocyclic compounds with one azido group. Most of the heterocyclic compounds with azido and numerous other, potentially explosophoric groups, are described in *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic Amines.”

## 7 Aliphatic Azides with Two Azido Groups

There are numerous aliphatic linear azides with additional nitro or nitroxy groups in the molecule. These compounds may already have been covered in the nitro compound or alkyl nitrate chapters, but some of them are reported here in the azide chapter; however, linear aliphatic nitramines with azido groups in the alkyl group are all discussed in the chapter on alkylnitramines.

A series of terminal alkyl diazides in quantities of 200 g was synthesized and characterized by IR and NMR spectra, including 1,3-diazidopropane,  $C_3H_6N_6$ , CAS RN [100910-72-3], 1,4-diazidobutane,  $C_4H_8N_6$ , CAS RN [24345-72-0], 1,5-diazidopentane,  $C_5H_{10}N_6$ , CAS RN [17607-21-5], 1,6-diazidohexane,  $C_6H_{12}N_6$ , CAS RN [13028-54-1], 1,7-diazidoheptane,  $C_7H_{14}N_6$ , CAS RN [98428-99-0] and 1,8-diazidooctane,  $C_8H_{16}N_6$ , CAS RN [98560-17-9] [131]. The report gives some spectra but lacks physical properties of the prepared compounds. Mixtures of 2-azidoethanol or 1,3-diazidopropanol with 1-nitroso-3-nitrazapentane or 1-nitroso-3-nitrazabutane can be used as monopropellants [239].

2-Azidoethanol, 1,3-diazidopropanol, 2,3-diazidopropanol, 1,4-diazidobut-2-ene, dimethyl 2,2-diazidomalonate, 2,3-di(azidomethyl)oxirane, and 1,1,2,2-tetra(azidomethyl)ethane were evaluated as replacements for hydrazine in hypergolic combinations with hydrogen peroxide (HTP) or white fuming nitric acid (WFNA) [182]. The aliphatic azides with two azido groups in the molecule are discussed here in the sequence ordered by the number of carbon atoms in the molecule.

### 7.1 $C_1$ Aliphatic Azides with Two Azido Groups

#### 7.1.1 Methylene Azide

Methylene azide, diazidomethane,  $CH_2(N_3)_2$ , is unstable and it has not been fully characterized. Diazidomethane has been the likely cause of an accidental explosion in a laboratory [240]. A safer method is the use of azide-loaded ion exchange resins which allows the slow, but safe synthesis of diazidomethane and even triazidomethane [241]. When using dichloromethane as a solvent in the synthesis of organic azides, azide ion displaces chlorine from dichloromethane surprisingly rapidly to form diazidomethane, an explosive material [242].

#### 7.1.2 Carbonyl Diazide

Carbonyl diazide (formerly called azidophosgene, carbazoimide),  $OC(N_3)_2$ ,  $M = 112.06$  g/mol, nitrogen content 75.00% N, is a readily subliming solid, crystallizing in long needles that are very soluble in water, ethanol, and ether but insoluble in petroleum ether. In water it undergoes hydrolysis to yield  $CO_2$  and  $HN_3$ . It has a penetrating odor and like other carbonyl compounds (phosgene) is highly toxic

and dangerous. Carbonyl diazide can be prepared by the action of sodium nitrite on the hydrochloride of carbohydrazide, but this reaction did not always proceed homogeneously and hydrazinedicarboxyazide was always formed as a byproduct in ca. 20% yield. The two compounds could be separated by carrying out the diazotization under benzene. Carbonyl diazide may explode violently, even under water, on slightest friction or when exposed to light. Carbonyl diazide converts aromatic hydrocarbons into pyridine bases and into primary amines.

Carbonyl diazide was prepared by reacting  $\text{NaN}_3$  (0.5 mmol) with  $\text{FC(O)Cl}$  (1.4 mmol) in a flame-sealed glass ampule at room temperature for 4 days [243]. Volatile products from three batches were collected and separated by repeated trap-to-trap condensation. The product, ca. 60 mg  $\text{OC(N}_3)_2$ , was retained in the 213 K ( $-60^\circ\text{C}$ ) trap as a white solid. Carbonyl diazide crystallized in the orthorhombic space group  $Pnma$  with four molecules per unit cell. The pure substance showed remarkable kinetic stability at room temperature in the gaseous, liquid, and solid states. Gaseous and liquid  $\text{OC(N}_3)_2$  was found to be stable for 2 weeks at room temperature. A melting point of 289 K ( $16^\circ\text{C}$ ) and vapor pressure of 5.6 mbar at 273 K ( $0^\circ\text{C}$ ) were determined. Two planar conformers were found in the gas phase, and a composition of 12% *anti-syn* versus 88% *syn-syn* conformer in the gaseous equilibrium mixture at room temperature was estimated by matrix IR spectroscopy. In the crystal structure, only the more stable *syn-syn* conformer was observed. The partially reacted, more volatile product  $\text{FC(O)N}_3$  was found in the 173 K ( $-100^\circ\text{C}$ ) trap as confirmed by its IR spectrum.

The minimum energy structure, vibrational frequencies, and thermodynamic properties of carbonyl diazide,  $\text{OC(N}_3)_2$ , have been determined using Gaussian-X compound computational methods [244]. The calculations indicated that carbonyl diazide has a significantly high enthalpy of formation, and its enthalpy of decomposition is commensurate with high energy materials.

## 7.2 $\text{C}_2$ Aliphatic Azides with Two Azido Groups

1,2-Diazidoethane, ethylene azide,  $\text{N}_3\text{CH}_2\text{CH}_2\text{N}_3$ ,  $M = 112.07$  g/mol, nitrogen content 74.97%, can be prepared by reaction of 1,2-dichloroethane with sodium azide in DMF at 333 K ( $60^\circ\text{C}$ ) [245]. The formed diazidoethane can be extracted with ether from water and the extract dried over magnesium sulfate, and the ether evaporated to obtain the pure product.

1,2-Diazidoethane can be made from a mixture of 1,2-dibromoethane (0.187 g) and sodium azide (0.072 g) with microwave irradiation for 30 min. [179]. The melting point reported by these authors ( $198^\circ\text{C}$ ) is totally **in error**. 1,2-Diazidoethane is an oily liquid that has a density of  $1.178$  g/cm<sup>3</sup> and boils at 326 K under a vacuum pressure of 1.2 kPa ( $53^\circ\text{C}$  under a vacuum pressure of 9 mm Hg) [246].

### 7.3 C<sub>3</sub> Aliphatic Azides with Two Azido Groups

1,3-Diazidopropane,  $\text{N}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}_3$ ,  $\text{C}_3\text{H}_6\text{N}_6$ , CAS RN [100910-72-3],  $M = 126.12 \text{ g/mol} = 7.929 \text{ mol/kg}$ , is a colorless, clear, oily liquid. 1,3-Diazidopropane has a density of  $1.1042 \text{ g/cm}^3$ , a boiling point of 423 K (150 °C) at atmospheric pressure, a boiling point of 373 K at a reduced pressure of 1.2 kPa (100 °C at reduced pressure of 9 mm Hg), a boiling point of 321–323 K at a reduced pressure of 0.26 kPa (48–50 °C at reduced pressure of 2 mm Hg), and a refractive index  $n_D^{20}$  of 1.4788. Other sources list a refractive index of 1.4729 at 589.3 nm and 293 K (20 °C). It can be mixed with isopropyl nitrate and stored without any reactions. The saturation vapor pressure of 1,3-diazidopropane is 66.7 Pa at 293.5 K, 213 Pa at 313 K and 626 Pa at 333 K (0.5 mm Hg at 20.4 °C, 1.6 mm Hg at 40 °C and 4.7 mm Hg at 60 °C) [247].

1,3-Diazidopropan-2-ol has a density of  $1.2599 \text{ g/cm}^3$  at 293 K, a viscosity of 9.6 cPs at 293 K, and a boiling point of 365 K at 0.4 kPa (92 °C at 3 mm Hg). Its combustion in a strand burner is self-sustaining [248]. Esters of this energetic alcohol with acetic acid and propionic acid have been characterized for their physical properties and burning behavior (Table 9).

2-Nitro-1,3-diazidopropane derivatives were synthesized through a condensation reaction, substitution reaction, and azidation [249]. The molecular structures of the products were then determined by MS, IR, and  $^1\text{H-NMR}$ .

### 7.4 C<sub>4</sub> Aliphatic Azides with Two Azido Groups

High-energy azides containing gun propellants can be prepared using 1,5-diazido-3-nitrazapentane, 1,6-diazido-2,5-dinitrazahexane, 1,7-diazido-2,4,6-trinitrazahexane, or 1,9-diazido-2,4,6,8-tetranitrazanonane [250, 251]. While the compounds listed above are nitramines with  $\text{N-NO}_2$  linkages, similar azidoalkyl compounds with  $\text{C-NO}_2$  linkages, such as 2-methyl-2-nitro-1,3-diazido-propane, 1,3-diazido-2-methyl-2-nitropropane,  $\text{N}_3\text{CH}_2\text{C}(\text{CH}_3)(\text{NO}_2)\text{CH}_2\text{N}_3$ ,  $\text{C}_4\text{H}_7\text{N}_7\text{O}_2$ , NMPA, DAMNP, can also be used as energetic plasticizers [252, 253]. The density of NMPA is  $\rho = 1.28 \text{ g/cm}^3$ , the glass point as determined by DSC is  $T_g = 221.6 \text{ K}$  (−51.5 °C), the onset of thermal decomposition as determined by DSC is 507 K (234 °C), and its impact sensitivity is 34 cm with a 2-kg weight.

1-Azido-2,3-dihydroxy-2-azidomethylpropane, ADMP,  $\text{N}_3\text{CH}_2\text{C}(\text{OH})(\text{CH}_2\text{N}_3)\text{CH}_2\text{OH}$ ,  $\text{C}_4\text{H}_8\text{N}_6\text{O}_2$ , can be made by a five-step synthesis starting with mannitol, acetone, and formaldehyde [254]. ADMP is a colorless oil and has a molecular mass of  $172.15 \text{ g/mol} = 5.809 \text{ mol/kg}$ , an oxygen balance of −92%, a predicted velocity of detonation of 5.69 km/s, a density of  $1.40 \text{ g/cm}^3$ , and an enthalpy of formation of  $+317.1 \text{ kJ/mol} = +1842 \text{ kJ/kg} = +440.4 \text{ kcal/kg}$ . The molecular mass of 156 and oxygen balance of −70% shown in Table 1 of [254] is **incorrect**. DSC indicated that ADMP

undergoes exothermic decomposition in the temperature in the range of 464–533 K (191–260 °C) with heat release of the order of 1390 J/g. ADMP is a potential energetic plasticizer for solid propellants.

2-Methyl-2-nitro-1,3-diazidopropane (NMPA) can be used as a low-molecular weight plasticizer in solid propellants and as an ingredient in gas generants. NMPA was synthesized via a process that consisted of three steps, i.e. condensation, sulfonation and azido-substitution, using nitroethane and formaldehyde as starting materials [252]. The factors affecting the NMPA yield, including reaction temperature, time, and solvent for azido-substitution, were optimized. The optimal reaction conditions were:  $T = 366 - 368 \text{ K} = 93 - 95 \text{ °C}$ ,  $t = 30 \text{ h}$ , medium DMSO, which improved the NMPA yield up to 71.5% (based on nitroethane) with a purity of 99%. The structure of the resulting product was identified by IR, NMR, and elemental analysis. Some properties of NMPA were measured as follows:  $\rho$  1.28 g/cm<sup>3</sup>,  $T_g$ (DSC) 221.6 K = -51.5 °C,  $T_{\text{peak}}$ (DSC) 507 K = 234 °C, impact sensitivity 34 cm with a 2-kg weight.

## 7.5 C<sub>5</sub> Aliphatic Azides with Two Azido Groups

The simplest C<sub>5</sub> diazide is 1,5-diazidopentane, 1,5-pentanediazide, C<sub>5</sub>H<sub>10</sub>N<sub>6</sub>, CAS RN [17607-21-5]. 1,5-Diazidopentane has a density of 1.0600 g/cm<sup>3</sup> at 293 K and a boiling point of 348 K at 0.13 kPa (75 °C at 1 mm Hg) [167].

Property data on several diazides extracted from a summary on methods for preparation and physical properties of linear diazides of the general formula N<sub>3</sub>CHR<sup>1</sup>(CH<sub>2</sub>)<sub>n</sub>CHR<sup>2</sup>N<sub>3</sub> with 5 to 10 carbon atoms are listed in Table 13 [255].

Experimental research to improve the low density and oxygen balance of pure azido compounds has been directed at modified azido compounds, such as azido nitramines, azido nitrate esters, and azido nitro compounds. Experimental methods to obtain compounds with suitable performance can be supported by theoretical calculations. In a theoretical exercise, three azido compounds N<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>N<sub>3</sub> for  $n = 5, 7, 9$ , and their 27 modified derivatives were examined using density functional theory calculational methods [256]. Results showed that -NNO<sub>2</sub>, -NO<sub>2</sub>, and -ONO<sub>2</sub> all can improve the thermodynamic and energetic properties. The contribution to the thermodynamic properties is -ONO<sub>2</sub> > -NO<sub>2</sub> > -NNO<sub>2</sub> and that to the energetic properties is -NNO<sub>2</sub> > -ONO<sub>2</sub> > -NO<sub>2</sub>. The azido nitramines possess the best energetic properties and azido nitrate esters have the best thermodynamic properties. All these substituents slightly decrease the thermal stability and the azido nitrate esters possess the lowest thermal stability. 1,4-Diazidobut-2-ene was synthesized from 2-buten-1,4-diol via the chloro derivative, 1,4-dichlorobut-2-ene and evaluated as a hypergolic fuel [182].

**Table 13:** Properties of diazidoalkanes of the general formula  $N_3CHR^1(CH_2)_nCHR^2N_3$ .

| <i>n</i> | <i>R</i> <sup>1</sup> | <i>R</i> <sup>2</sup> | Gross Formula                                  | Yield<br>% | Boiling<br>point<br>K | at pressure<br>kPa | Boiling<br>point<br>°C | at pressure<br>mm Hg | <i>n</i> <sub>D</sub> <sup>25</sup> |
|----------|-----------------------|-----------------------|------------------------------------------------|------------|-----------------------|--------------------|------------------------|----------------------|-------------------------------------|
| 3        | H                     | H                     | C <sub>5</sub> H <sub>10</sub> N <sub>6</sub>  | 81         | 373                   | 1.2                | 100                    | 9                    | 1.4729                              |
| 4        | H                     | H                     | C <sub>6</sub> H <sub>12</sub> N <sub>6</sub>  | 80         | 392                   | 1.6                | 119                    | 12                   | 1.4707                              |
| 5        | H                     | H                     | C <sub>7</sub> H <sub>14</sub> N <sub>6</sub>  | 73         | 389                   | 0.7                | 116                    | 5                    | 1.4700                              |
| 6        | H                     | H                     | C <sub>8</sub> H <sub>16</sub> N <sub>6</sub>  | 75         | 402                   | 0.7                | 129                    | 5                    | 1.4698                              |
| 7        | H                     | H                     | C <sub>9</sub> H <sub>18</sub> N <sub>6</sub>  | 89         | 415                   | 0.8                | 142                    | 6                    | 1.4685                              |
| 8        | H                     | H                     | C <sub>10</sub> H <sub>20</sub> N <sub>6</sub> | 72         | 378                   | 0.0                | 105                    | 0.2                  | 1.4693                              |
| 2        | CH <sub>3</sub>       | H                     | C <sub>5</sub> H <sub>10</sub> N <sub>6</sub>  | 66         | 361                   | 1.1                | 88                     | 8                    | 1.469                               |
| 2        | CH <sub>3</sub>       | CH <sub>3</sub>       | C <sub>6</sub> H <sub>12</sub> N <sub>6</sub>  | 37         | 389                   | 3.5                | 116                    | 26                   | 1.4642                              |

Data source: [255]

## 7.6 Pentaerythritol Diazido Dinitrate

Pentaerythritol diazido dinitrate, 2,2-diazidomethyl-1,3-propyleneglycol dinitrate, 1,3-propanediol, 2,2-bis(azidomethyl)-, 1,3-dinitrate, PDADN,  $(N_3CH_2)_2C(CH_2ONO_2)_2$ , C<sub>5</sub>H<sub>8</sub>N<sub>8</sub>O<sub>6</sub>, CAS RN [96915-38-7], is an energetic azido nitrate plasticizer with two —N<sub>3</sub> groups and two —ONO<sub>2</sub> groups. In this book, this compound could also have been included in the chapter on nitrate esters in *Encyclopedia of Oxidizers*, chapter “Nitrate Esters,” somewhere close to PETN.

Pentaerythritol tetranitrate (PETN), monoazidopentaerythritol mononitrate (MAPEMN), diazidopentaerythritol dinitrate (PDADN), triazidopentaerythritol mononitrate (TAPEMN), and tetraazidopentaerythritol (TAPE) were prepared and analyzed for their chemical (XRD, NMR, EA, IR) and energetic properties (DTA/DSC, impact and friction sensitivity) and compared to each other [257]. An interesting trend of decreasing melting points from PETN to the triazide was observed.

### 7.6.1 Preparation of Pentaerythritol Diazido Dinitrate

Conversion of pentaerythritol to the chlorides and reaction with sodium azide is not a good method for synthesis of pentaerythritol azides, because the diazides and triazides are difficult to separate.

Diazido derivatives of pentaerythritol can be prepared by reacting 3,3-bis(azidomethyl) oxetane with inorganic acids such as hydrobromic or nitric acid [258]. The resulting diazido monobromide can be reacted with sodium azide to produce pentaerythritol triazide which can be subsequently nitrated to pentaerythritol triazido mononitrate. The pentaerythritol diazido mononitrate produced by the reaction of nitric acid with the above oxetane can be further nitrated with nitric acid



to produce pentaerythritol diazido dinitrate. This compound was described in the patent as a colorless oil,  $n_D^{22.5} = 1.5161$  but it was later shown that it is a solid at room temperature. These diazido and triazido derivatives of pentaerythritol can be utilized as energetic azido plasticizers per se or can serve as intermediates for the production of such plasticizers.

Pentaerythritol diazido dinitrate (PDADN) was synthesized and characterized [259]. The results showed that PDADN is a crystalline compound at room temperature and melts at 312.7–312.8 K (39.6–39.7 °C), which observation disagreed with the report by Frankel who reported that PDADN is a colorless oil with  $n_D^{22.5} = 1.5165$ .

A study was made of the synthesis, structure and physicochemical properties of pentaerythritol diazido dinitrate [260]. Thermal analysis results confirmed that this kind of plasticizer is beneficial to the thermal stability of double base composite propellants and hexogen, and its application in composite modified double base propellants could improve combustion properties.

The method described in US Pat. 4683086 is a four-step process and takes 40 h. A simplified three-step process used hydrogen bromide in acetic anhydride to make the dibromide instead of the dichloride [261]. The dibromide is then reacted with sodium azide to make the diazide, and the last step is the nitration. This process is not only faster, 6 h instead of 40 h, it also gives a better yield. The melting point of PDADN thus produced was 312–313 K (39–40 °C).

A new technique for preparing PDADN proceeds via bromination reaction of pentaerythritol as starting material, azidation reaction of 2,2-bromomethyl-1,3-propanediol and nitration reaction of 2,2-azido-1,3-propanediol [262]. The structure of PDADN was characterized by IR,  $^1\text{H-NMR}$ , and elemental analysis.

### 7.6.2 Molecular Structure of Pentaerythritol Diazido Dinitrate

The nitroxy and azido groups rotate around the C–N or C–O bond and can be in *trans* or *cis* configurations to each other. Their positions affect the energy and stability of the molecule.

Frankel reported that PDADN is a nearly colorless oil at room temperature, but Wang argued that this compound is a crystalline material with melting point 312.7–312.8 K (39.6–39.7 °C). To clarify this disagreement about liquid or solid state of PDADN at room temperature, the structure of PDADN was studied by means of FTIR, MS, and NMR [263]. The results showed that the structure of PDADN is that of a crystalline solid.

The molecular geometries and electronic structures of the four conformations of PDADN were optimized by using a semi-empirical AM1-MO method [264]. Among the four conformations, the structure with one  $-\text{ONO}_2$  group at *trans* conformation and another  $-\text{ONO}_2$  and two  $-\text{N}_3$  groups at *cis* conformations is the most stable.

The molecular geometries, electronic structures and IR spectra of the four conformations of PDADN were calculated by means of a DFT B3LYP method [265]. Among the

four conformations, the one with structure of one  $-\text{NO}_2$  group at *cis* position and another  $-\text{NO}_2$  group and two  $-\text{N}_3$  groups at *trans* position was predicted to be the most stable. The calculated IR absorption frequencies of  $-\text{NO}_2$  groups and  $-\text{N}_3$  groups were in good agreement with the experimental data.

One of the main applications of PDADN would be as an energetic plasticizer in double-base propellants. Density functional theory and molecular orbital dynamic calculations have attempted to predict interactions of nitrocellulose/nitroglycerin and PDADN during storage in propellants [266].

### 7.6.3 Thermal Decomposition of Pentaerythritol Diazido Dinitrate

Under non-isothermal conditions, the thermal behavior of PDADN was studied using TGA, DSC, pressure DSC and *in situ*/rapid scanning Fourier transform infrared (RSFT-IR) spectroscopy [267]. The results showed that **(1)** the extrapolated onset temperatures ( $T_e$ ), peak temperatures ( $T_p$ ) and enthalpy of decomposition ( $\Delta H_{\text{dec}}$ ) increase with the change of pressure from 0.1 to 2 MPa. Over the range of pressure from 2.0 to 6 MPa, the thermal behavior of PDADN does not seem to be obviously affected by the pressure; **(2)** the apparent activation energy, pre-exponential constant and the most probable integral mechanism function of thermal decomposition of PDADN at a pressure of 0.1 MPa were 134.9 kJ/mol,  $10^{12.7} \text{ s}^{-1}$  and  $1 - (1 - \alpha)^3$ , respectively; **(3)** the experimental values of pressure affected the magnitude of the apparent activation energy; **(4)** the critical temperature of thermal explosive for PDADN was predicted to be 424 K [268].

Pentaerythritol diazido dinitrate thermal decomposition was investigated by DSC-TGA-FTIR by measuring the thermo-infrared (TIR) curves of the change of the IR characteristics relative absorption intensity of decomposition gas products with temperature and time [269]. The non-isothermal kinetics, kinetic parameters and mechanism functions of PDADN decomposition gas products were obtained by using the Coats-Redfern and Ozawa equations. The mechanism of PDADN thermal decomposition was then analyzed based on isokinetic point of the formation rate among all the decomposition gas products.

The combustion and explosion characteristics, thermal stability and mechanical shock and friction sensitivities of PDADN were examined and the results indicated that PDADN has low friction sensitivity and good thermal stability, which would make it suitable as an energetic plasticizer in solid propellants [270].

### 7.6.4 Properties of Other Pentaerythritol Azides

Diazidopentaerythritol  $(\text{HOCH}_2)_2\text{C}(\text{CH}_2\text{N}_3)_2$  and triazidopentaerythritol  $\text{HOCH}_2\text{C}(\text{CH}_2\text{N}_3)_3$  can be used to make tris(2,2,2-triazidomethyl)ethyl esters of carboxylic acids [271]. Triazidopentaerythritol (pentaerythritol triazide) is a colorless oil,  $n_D^{22} 1.5319$ .

### 7.7 Other C<sub>5</sub> Aliphatic Azides with Two Azido Groups

An energetic plasticizer, 1,3-diazido-2-ethyl-2-nitropropane (DAENP), was synthesized by a three-step process **(1)** 1-nitropropane was condensed with formaldehyde to yield 2-ethyl-2-nitro-1,3-propane diol; **(2)** 2-ethyl-2-nitro-1,3-propane diol on tosylation gave 2-ethyl-2-nitro-1,3-bis(p-toluene sulfonyl) propyl ester; **(3)** azidation of the tosylated compound [272]. The product was characterized by elemental analysis, FTIR, and <sup>1</sup>H-NMR, and purity was tested by HPLC. Thermal studies revealed that DAENP is thermally stable up to 469 K (196 °C), has high energy output of the order 2056 J/g, and a very low glass transition temperature (176 K = -96.76 °C). DAENP was compatible with energetic binders like GAP, 3,3'-bis-azidomethyl oxetane-tetrahydrofuran (BAMO-THF) copolymer, and poly-3-nitratomethyl-3-methyl oxetane (NIMMO) or poly nitratomethyl oxetane (PLN).

### 7.8 C<sub>≥7</sub> Aliphatic Azides with Two Azido Groups

1,9-Diazido-2,2,8,8-tetranitro-4,6-dioxanonane, N<sub>3</sub>CH<sub>2</sub>C(NO<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>OCH<sub>2</sub>C(NO<sub>2</sub>)<sub>2</sub>=CH<sub>2</sub>N<sub>3</sub>, C<sub>7</sub>H<sub>10</sub>N<sub>6</sub>O<sub>10</sub>, has been synthesized from bis(trinitroethyl)formal [273].

An azido analog to [H<sub>3</sub>C-C(NO<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-O-]<sub>2</sub>CH<sub>2</sub>, bis-2,2-dinitropropyl formal (BDNPF), was synthesized that contained two azido groups instead of two nitro groups, although in different positions from where the vicinal nitro groups are in BDNPF [124]. The synthesis of [(N<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>CH-O-]<sub>2</sub>CH<sub>2</sub>, C<sub>7</sub>H<sub>12</sub>N<sub>12</sub>O<sub>2</sub>, BDPF, started with bis(1,3-dichloro-2-propyl)formal [(ClH<sub>2</sub>C)<sub>2</sub>-CH-O-]<sub>2</sub>CH<sub>2</sub> which was reacted with a metal azide in a solvent and resulted in a yield of 98% and purity of 98%. The optimum reaction conditions were: for condensation reaction, reaction temperature 273–278 K (0–5 °C), 4 mL sulfuric acid as catalyst, ethylene dichloride as solvent; for the azidizing reaction, reaction temperature 368–372 K (95–99 °C), dimethyl sulfoxide as solvent, reaction time 4 h.

Diazidoalkane fuel additives were investigated as a method to improve the performance of LOX/RP-1 booster engines by causing microexplosions of evaporating fuel droplets [274]. Compared with neat RP-1, the azide additives have a higher fuel density and allow an increase in theoretical specific impulse for mixture ratios below 2.6. 1,10-Diazidodecane (DAD) was used for the initial evaluation in four hot fire tests using subscale combustor hardware to determine the effect of diazidodecane on combustion performance. The density of DAD is 20% higher than that of neat RP-1. 1,10-Diazidodecane is a clear liquid and is completely miscible with RP-1.

## 8 Aliphatic Azides with Three Azido Groups

The simplest, and probably the most energetic alkyl azido compound with three azido groups is the triazidocarbenium ion,  $(\text{N}_3)_3\text{C}^+$ , which was synthesized in the form of salts combined with powerful oxidizing anions such as dinitramide, perchlorate, or tetrafluoroborate [275]. The enthalpies of formation of  $(\text{N}_3)_3\text{C}^+\text{N}(\text{NO}_2)_2^-$  and  $(\text{N}_3)_3\text{C}^+\text{ClO}_4^-$  were estimated to be +1054 and +912 kJ/mol (+252 and +218 kcal/mol, respectively), which explains the high explosive power of these salts.

1,1,1-Tris(azidomethyl)ethane (TMETA) can be synthesized from trimethylol-ethane by sulfonation and azide substitution [126]. It was evaluated as a plasticizer for double-base propellants. The structures of the intermediate and the product were confirmed by IR, NMR and elemental analysis. The factors influencing the azide substitution were investigated and under optimized conditions the yield of TMETA could be up to 92.25% and purity 99%. Recommended molar ratio of TMET/ $\text{NaN}_3$  is 4.5/1, temperature 378–383 K (105–110 °C), reaction time 48 h. Some properties of TMETA were measured as density  $\rho = 1.182 \text{ g/cm}^3$ , onset of exotherm in DSC 525.8 K = 252.7 °C, impact sensitivity 31.6 cm with a 2-kg weight.

## 9 Aromatic Azides with Three Azido Groups

Triazidotrinitrobenzene, 1,3,5- $(\text{N}_3)_3$ -2,4,6- $(\text{NO}_2)_3\text{C}_6$ , was synthesized by nitration of triazidodinitrobenzene with either a mixture of fuming nitric and concentrated sulfuric acid or with  $\text{N}_2\text{O}_5$  [276]. Crystals were characterized by single crystal XRD: monoclinic,  $P2_1/c$  (No. 14), with unit cell parameters of  $a = 0.54256(4) \text{ nm}$ ,  $b = 1.8552(1) \text{ nm}$ ,  $c = 1.2129(1) \text{ nm}$ ,  $\beta = 94.91(1)^\circ$ ,  $V = 1.2163(2) \text{ nm}^3$ ,  $Z = 4$ ,  $\rho = 1.836 \text{ g/cm}^3$ . Triazidotrinitrobenzene has a remarkably high density ( $1.84 \text{ g/cm}^3$ ). The standard heat of formation of triazidotrinitrobenzene was computed to be  $\Delta H_f^\circ = 765.8 \text{ kJ/mol} = 2278 \text{ kJ/kg}$ . The predicted detonation properties were  $P = 18.4 \text{ GPa}$  and  $D = 8100 \text{ m/s}$ . The drop weight sensitivity of triazidotrinitrobenzene was compared to that of other organic azides [277].

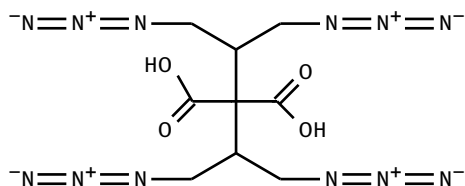
Triazidobenzenes can be synthesized by the diazotization and azidation reactions of the corresponding triamines. Triazides were considered as potential cross-coupling reagents for polymers, although they did not find wide practical use. Photolysis of triazides and polyazides gives aryl nitrenes which are highly reactive and either lead to ring widening or react with olefinic double bonds [278].

## 10 Organic Azides with Four Azido Groups

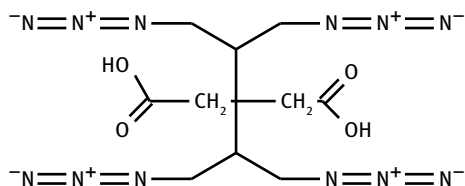
### 10.1 Aliphatic Azides with Four Azido Groups

Tetraazidomethane, perazidomethane,  $\text{CN}_{12}$ ,  $\text{C}(\text{N}_3)_4$  is the simplest organic azide with four azido groups in the molecule. Not surprisingly, this compound is extremely sensitive and would be difficult to synthesize.  $\text{CN}_{12}$  is a highly explosive liquid. With a nitrogen content of 93.3%, perazidomethane,  $\text{CN}_{12}$ , is highly explosive but nevertheless isolatable. Tetraazidomethane can be made from commercially available trichloroacetonitrile in one step and undergoes simple dissociation and trapping reactions as well as some more complex transformations [279]. The hydrolysis of tetraazidomethane leads to carbonyl diazide.

Two energetic azido esters derived from bis(1,3-diazido-prop-2-yl)malonic acid and bis(1,3-diazido-prop-2-yl)glutaric acid



Bis(diazidopropyl)malonic Acid



Bis(diazidopropyl)glutaric Acid

have been synthesized and characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS, thermal analysis, and compatibility tests [280, 281]. Both azido esters showed good thermal stability with onset of decomposition temperatures of 507 and 506 K (234 and 233 °C). Their densities were measured to be 1.25 and 1.27 g/cm<sup>3</sup>, respectively. Glass transition temperatures ( $T_g$ ) of the two compounds were 204 and 205 K (−69 and −68 °C). Thermal decomposition kinetics of both compounds was determined by TGA and DSC. The weight loss pattern of both compounds showed two-step decomposition. Both were compatible with energetic binders like GAP, BAMO-THF, and poly NIMMO or PLN. Density functional theory calculations on both compounds predicted positive heats of formations.

Three new  $\alpha,\alpha$ -diazidated azido esters derived from malonic acid were synthesized and characterized resulting in azido compounds which contain up to six azido moieties and are suitable as energetic plasticizers for solid propellants [282].

1,4-diazido-2,3-bis(azidomethyl)butane, 1,1,2,2-tetra(azidomethyl)ethane, 1,1,2,2-tetrakis(azidomethyl)ethane, has been synthesized and tested for its hypergolic ignition with hydrogen peroxide [182].

Three polyazido compounds based on pentaerythritol and its diether or triether have been prepared and characterized as potential energetic plasticizers [283]. The three compounds were:

Compound

|                                  |                                                             |
|----------------------------------|-------------------------------------------------------------|
| I pentaerythrityl tetraazide     | $C(CH_2N_3)_4$                                              |
| II dipentaerythrityl hexaazide   | $(N_3CH_2)_3C-CH_2-O-CH_2-C(CH_2N_3)_3$                     |
| III tripentaerythrityl octaazide | $(N_3CH_2)_3C-CH_2-O-CH_2-C(CH_2N_3)_2-O-CH_2-C(CH_2N_3)_3$ |

Their large positive enthalpies of formation, good thermal stability, low hydrolysis rates, low melting points and ease of preparation makes these azido compounds attractive as energetic plasticizers. Pentaerythrityl tetraazide (1,3-diazido-2,2-bis(azidomethyl)-propane) can be prepared from pentaerythritol in a two-step, one-pot procedure in 85% yield. Pentaerythrityl tetraazide is a solid that melts at 318 K (45 °C). When heated rapidly to 523 K (250 °C), it will detonate with a loud report and a bright flash. Compounds II and III are viscous, low-volatility oils that refused to crystallize even after being kept at dry ice temperature for a while. Compound III burned smoothly when ignited in an open vessel. No room temperature incompatibilities were noted with any of the three azides in contact with AP, AN, cellulose nitrate, trimethylolethane trinitrate (TMETN) or 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX).

Diethers with two oxygen atoms in ether linkages and alkyl groups with varying numbers of  $-CH_2-N_3$  groups can be prepared in a two-step reaction from 1,3-dichloropropan-2-ol, trioxane (polymeric formaldehyde) and sodium azide and can be used as energetic plasticizers [284, 285]. The simplest of these compounds, bis(1,3-diazido-2-propyl)formal,  $(N_3CH_2)_2CHOCH_2OCH(CH_2N_3)_2$ ,  $C_7H_{12}N_{12}O_2$ , is a yellow oil which has a density at 294 K (21 °C) of 1.28 g/cm<sup>3</sup> and a freezing point of 251 K (-22 °C). The predicted enthalpy of formation is +1002 kJ/mol (+239.4 kcal/mol).

A very thorough investigation of a variety of organic azides led to the synthesis and characterization of numerous polyazido compounds, including carbonyldiazide, 2,2-diazidomethyl-3-azido-propanol, a pentaerythritol where all four hydroxyl

groups were substituted by 2,2-diazidomethyl-3-azido-propyl groups in ether form, 1,3-diazido-2-amino-2-azidomethylpropane ("triazide"), triazidomethane, tetrazidomethane, azidomethyldimethylamine, and tris(azidomethyl)amine [286]. The reaction of trichloroacetonitrile with sodium azide gave triazidoacetonitrile and some tetraazidomethane. Tetraazidomethane is very unstable and contains 93.3% N, the highest possible nitrogen content for any organic compound. When trying to identify its structure by reaction with cyclooctyne, only three of the four azido groups reacted, forming tris(triazolooctane)azidomethane. The boiling point of tetraazidomethane was estimated at  $438\text{ K} = 165^\circ\text{C}$ . Adipic acid and *o*-phthalic acid esters of diazidoalkanol can be used as energetic plasticizers [287].

For the synthesis of tri(azidoethyl)amine, starting with triethanolamine, the hydroxyl groups were replaced with azide groups, giving tri(azidoethyl)amine, which can form an azide salt. It can be quaternized, forming tetrakis-(2-azidoethyl)ammonium ions. Many of the new azido compounds were identified by reaction with cyclooctyne.

## 10.2 Aromatic Azides with Four Azido Groups

The reaction of 1,2,4,5-tetrakis(dibromomethyl)benzene, obtained by photochemical bromination of 1,2,4,5-tetrakis(monobromomethyl)benzene, with  $\text{NaN}_3$  in DMF after 3 h at  $353\text{--}363\text{ K}$  ( $70\text{--}80^\circ\text{C}$ ) gave 1,2,4,5-tetrakis(diazidomethyl)benzene [288, 289]. The structure was confirmed by NMR. It detonated easily if struck with a hammer or by scraping with a spatula. Melting point was  $379\text{--}381\text{ K}$  ( $106\text{--}108^\circ\text{C}$ ). It was less stable than 1,2,4,5-hexakis(diazidomethyl)benzene

# 11 Organic Azides with Five or More Azido Groups

## 11.1 Aromatic Azides with Five or More Azido Groups

The most energetic aromatic azide would be hexaazidobenzene, but its synthesis is wrought with problems [290]. It is easier to look at it by computer [291]. A very detailed overview of aromatic and heterocyclic polyazides highlighted their photolysis, which leads to highly reactive nitrenes which were characterized by their ESR spectra [278].

## 12 Cycloaliphatic Azides

### 12.1 Single Ring Cycloaliphatic Azides

The vapor pressure of cyclopentyl azide, azidocyclopentane,  $C_5H_{11}N_3$ , CAS RN [33670-50-71], can be expressed by the equation [140]:

$$\ln P = 264.98/R - 61126.15/RT - \frac{66.6}{R} \times \ln(T/298.15)$$

where  $P$  is the vapor pressure in Pa,  $T$  is the temperature in kelvin, and  $R$  is the gas constant  $8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ . This equation translates into a normal boiling point of 416 K ( $143^\circ\text{C}$ ). The heat of vaporization of cyclopentyl azide at 298.15 K is 41.27 kJ/mol.

The heats of combustion of liquid cyclopentyl and cyclohexyl azides are 3433 kJ/mol (820.48 kcal/mol) and 4042 kJ/mol (965.96 kcal/mol), respectively [292]. This corresponds to standard enthalpies of formation of +179.1 kJ/mol (+42.81 kcal/mol) and +108.4 kJ/mol (+25.92 kcal/mol). The densities are 0.9789 and 0.9855 g/cm<sup>3</sup>, respectively.

The enthalpies of formation and densities of two cycloalkyl azides are listed in PEPCODED.DAT: Cyclohexyl azide,  $C_6H_{11}N_3$ ,  $M = 125.18 \text{ g/mol}$ ;  $\Delta H_f = +207 \text{ cal/g} = +25.9 \text{ kcal/mol} = +108.4 \text{ kJ/mol} = +866 \text{ J/g}$ ;  $\rho = 0.0356 \text{ lb/in.}^3 = 0.9854 \text{ g/cm}^3$ ; Cyclopentyl azide,  $C_5H_9N_3$ ,  $M = 111.15 \text{ g/mol}$ ,  $\Delta H_f = +385 \text{ cal/g} = +42.8 \text{ kcal/mol} = +179 \text{ kJ/mol} = +1611 \text{ J/g}$ ;  $\rho = 0.0353 \text{ lb/in.}^3 = 0.9771 \text{ g/cm}^3$ . Cyclohexyl azide has a refractive index of  $n_D^{20} = 1.4693$  and boils at 345 K at 4 kPa ( $72^\circ\text{C}$  at 30 mm Hg) [221].

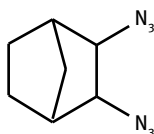
A new method for preparation of vicinal diazides starting with alkenes was developed and used for the synthesis of 1,2-diazidocyclopentane and 1,2-diazidocyclohexane. The following cycloaliphatic diazides were prepared and their IR and NMR spectra were measured [134]: cyclopentane, 1,2-diazo-, 1,2-diazidocyclopentane,  $C_5H_8N_6$ , CAS RN [141649-36-7]; cyclohexane, 1,2-diazo-, 1,2-diazidocyclohexane,  $C_6H_{10}N_6$ , CAS RN [26593-33-9], with a boiling point of 345–347 K at reduced pressure of 66.7 Pa ( $72\text{--}74^\circ\text{C}$  at reduced pressure of 0.5 mm Hg); and its isomer cyclohexane, 1,4-diazo-, 1,4-diazidocyclohexane,  $C_6H_{10}N_6$ , CAS RN [141649-37-8]. This report gives a few IR and NMR spectra of azides prepared, but no other physical properties.

In analogy to 2-azidoethanol and dimethylaminoethylazide (DMAZ), which have been extensively studied as potential rocket propellants, it would be more energetic to synthesize cycloaliphatic amino azides. In support of experimental efforts to make energetic azido compounds, quantum chemical calculations using a density functional theory method and charge density analysis of amine azide-based propellants (DMAZ, 2-azidoethylhydrazine, 2-azido-*N,N*-dimethylcyclopropanamine, 2-azido-*N*-methylcyclobutanamine, and 2-azidocyclopentanamine) were carried out to understand the geometry, bond topological, electrostatic, and energetic properties [293]. The electron density distribution of these molecules revealed the nature of chemical bonding in these molecules.

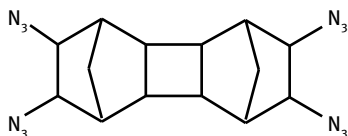


## 12.2 Bridged Polycyclic Cycloaliphatic Azides

Two of the more unusual aliphatic azides were prepared by the method referenced above, starting with norbornene. These were 2,3-diazido-bicyclo[2.2.1]heptane,  $C_7H_{10}N_6$ , CAS Registry Number [141649-38-9]

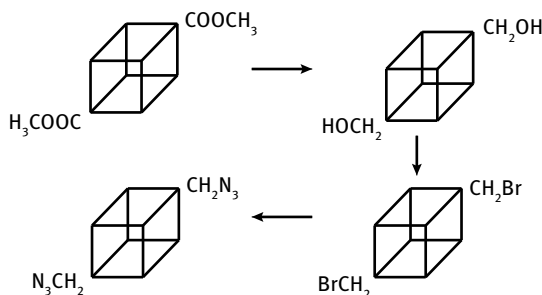


and its dimer, 2,3,6,7-tetraazido-dodecahydro-1,4:5,8-dimethanobiphenylene,  $C_{14}H_{16}N_{12}$ , CAS Registry Number [141649-40-3]



## 12.3 Caged Ring Cycloaliphatic Azides

1,4-Diazidomethylcubane was synthesized by a four-step procedure [221, 294]:



The enthalpies of formation for a series of polyazidocubanes were calculated by using density functional theory (DFT), Hartree-Fock and MP2 methods as well as semi-empirical methods [295]. There exists group additivity for the enthalpies of formation with respect to the azido group. It was found that the enthalpies of formation increased 330–360 kJ/mol for each additional increment of the number of azido groups being added to the cubane skeleton. The predicted detonation velocity of heptaazido and octaazido derivatives was over 9 km/s, and the detonation pressure was ca. 40 GPa.

## 12.4 Other Organic Azides

Azidoacetonitrile, azidoethanenitrile,  $\text{N}\equiv\text{C}-\text{CH}_2-\text{N}_3$ ,  $\text{N}_3\text{CH}_2\text{CN}$ ,  $\text{C}_2\text{H}_2\text{N}_4$ , CAS RN [57707-64-91],  $M = 82.07 \text{ g/mol}$ , contains two explosophoric energetic groups attached to a simple methane molecule. It boils at 326 K at 1.6 kPa (53 °C at 12 mmHg). The compound slowly polymerizes even when kept at 243 K (−30 °C), but it is more stable during storage than the isoelectronic 3-azidopropyne. The heat of evaporation of azidoacetonitrile at 298 K is  $52.58 \pm 0.19 \text{ kJ/mol}$ . The vapor pressure of azidoacetonitrile can be calculated from the equation [140]:

$$\ln P = 278.13/R - 68980.05/RT - \frac{55.0}{R} \ln(T/298.15)$$

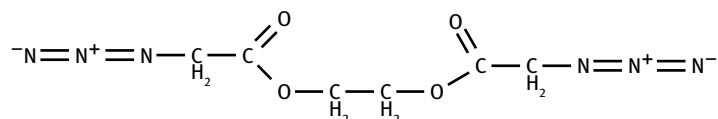
where  $P$  is the vapor pressure in Pa,  $T$  is the temperature in kelvin, and  $R$  is the gas constant  $R = 8.3143 \text{ J K}^{-1} \text{ mol}^{-1}$ . This equation translates into a normal boiling point of 423 K (150 °C), which is a very high boiling point for a molecule that contains only one carbon atom.

Matrix-isolation FTIR spectra of azidoacetonitrile and azidoacetone ( $\text{N}_3\text{CH}_2\text{COCH}_3$ ) in solid neon, argon, or nitrogen were recorded and compared to calculated IR spectra using a density-functional theoretical method [296].

## 13 Polyol Esters of Azidoacetic Acid

Azidoacetic acid,  $\text{N}_3\text{CH}_2\text{COOH}$ , can form esters with a wide range of polyols that have low vapor pressure and can serve as energetic plasticizers.

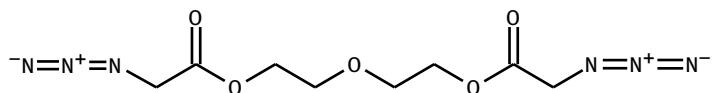
The simplest member of this group is ethylene glycol di(azidoacetate),  $\text{N}_3\text{CH}_2\text{COOCH}_2\text{CH}_2\text{OOCCH}_2\text{N}_3$ ,  $\text{C}_4\text{H}_8\text{N}_6\text{O}_4$ ,  $M = 204.15 \text{ g/mol} = 4.898 \text{ mol/kg}$ . It has a density of  $1.00 \text{ g/cm}^3$ , an oxygen balance of −100% and an enthalpy of formation of  $-80.0 \text{ kJ/mol} = -392 \text{ kJ/kg}$ . A17, an azidoacetic acid ester-based substance, is a product of ICT in Germany. It has the ability to significantly lower the glass transition temperature of other plasticizers.



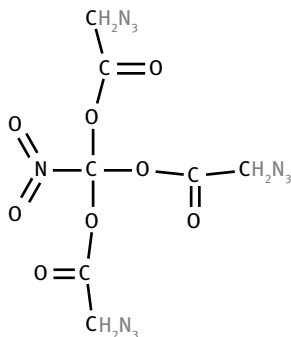
Ethylene glycol di(azidoacetate), EGBAA, A17

Prime candidates in this category of esters of azidoacetic acid are ethylene glycol bis(azidoacetate) (EGBAA), diethylene glycol bis(azidoacetate) (DEGBAA), trimethylolnitromethane(triazidoacetate) (TMNTA) and pentaerythritol tetrakis(azido-

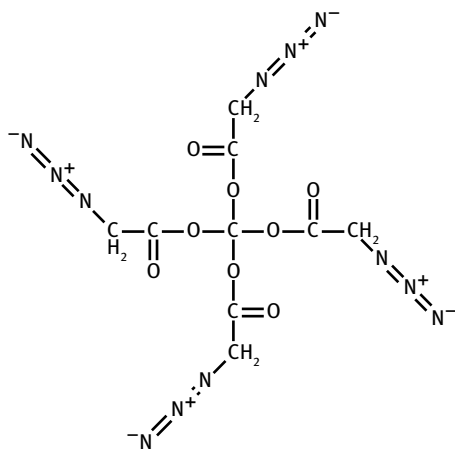
acetate) (PETKAA) [297]. They are liquid and the glass transition temperatures are between 202.3 and 239 K (−70.8 and −34.1 °C) and have an acceptable thermal stability for practical applications.



Diethylene glycol bis(azidoacetate), DEGBAA



Trimethylolnitromethane(triazidoacetate), TMNTA



Pentaerythritol tetrakis(azidoacetate), PETKAA

Physical properties of these low-volatility compounds suitable as energetic plasticizers are listed in Tables 14 and 15 below.

As two examples, azido esters 1,3-bis(azidoacetoxymethyl)-2-ethylpropane (I)  $\text{N}_3\text{CH}_2\text{COOCH}_2\text{C}(\text{N}_3\text{CH}_2\text{COOCH}_2)(\text{C}_2\text{H}_5)\text{CH}_2\text{OOCH}_2\text{N}_3$ ,  $\text{C}_{10}\text{H}_{17}\text{N}_9\text{O}_6$ , and 1,3-bis(azidoacetoxymethyl)-2,2-bis(azidomethyl)propane (II),  $\text{N}_3\text{CH}_2\text{COOCH}_2\text{C}(\text{N}_3\text{CH}_2)_2\text{CH}_2\text{OOCH}_2\text{N}_3$ ,  $\text{C}_8\text{H}_{12}\text{N}_{12}\text{O}_4$ , have been synthesized and characterized by IR, NMR, and elemental analysis [298]. Thermal studies revealed that both azido esters are thermally stable up to 453 K (180 °C) and their glass transition temperatures are 226 and 221 K (−47 and −52 °C), respectively.

Terminally azido functionalized dendritic esters have been synthesized from a commercially available dendritic polyol [299]. Structural features were confirmed by IR,  $^1\text{H}$  NMR, and elemental analysis. The DSC analysis showed an acceptable thermal stability for practical applications in high energy material formulations.

Azido-terminated dendritic esters have been synthesized by four step processes and the final products and the intermediates were characterized by IR,  $^1\text{H}$  NMR, and elemental analysis [300]. Thermal studies revealed that these dendritic esters were thermally stable up to ~463 K (190 °C) and the glass transition temperatures were found to be 219 and 241 K (−54 and −32 °C), respectively.

**Table 14:** Properties of azidoacetic acid esters.

|                                       | EGBAA   | DEGBAA  | TMNTA   | PETKAA |
|---------------------------------------|---------|---------|---------|--------|
| Density, g/cm <sup>3</sup>            | 1.34    | 1.00    | 1.45    | 1.39   |
| Oxygen balance, %                     | −84.15  | −99.92  | −71.95  | 88.82  |
| $\Delta H_f$ , kJ/mol                 | −167.36 | −328.86 | −230.54 | −215.2 |
| $\Delta H_f$ , kcal/mol               | −40     | −78.6   | −55.1   | −51.43 |
| Viscosity, mPa s                      | 23.4    | 29.2    | 1288    | 2880   |
| $T_g$ , K                             | 202.3   | 209.8   | 239     | 237.7  |
| $T_g$ , °C                            | −70.8   | −63.3   | −34.1   | −35.4  |
| Deflagration point, °C, (at 5 K/min)  | 232     | 235     | 214     | 234    |
| Weight loss (90 °C at ca. 80 days, %) | 0.9     | 0.48    | 0.25    | —      |
| Impact sensitivity, Nm                | 5.5     | >10     | 16      | 60     |
| Friction sensitivity, N               | 165     | 160     | 192     | 360    |

Data source: [199]

Table 15: Properties of azidoorganic plasticizers.

| Compound Name                                  | Acronym | Density<br>g/cm <sup>3</sup> | $\Delta H_f^{298}$<br>kJ/mol | $\Delta E_{\text{comb}}$ |          | Oxygen<br>balance | $T_g$<br>K |
|------------------------------------------------|---------|------------------------------|------------------------------|--------------------------|----------|-------------------|------------|
|                                                |         |                              |                              | kJ/mol                   | kcal/mol | %                 | °C         |
| Ethylene glycol bis(azidoacetate)              | EGBAA   | 1.34                         | -700                         | 3332                     | -167.36  | 796.26            | 202.3      |
| Diethylene glycol bis(azidoacetate)            | DEGBAA  | 1                            | -1377                        | 4523                     | -329     | 1081.07           | 209.8      |
| Trimethylolnitromethane(triazidoacetate)       | TMNTA   | 1.45                         | -962                         | 5414                     | -230     | 1294.04           | 239        |
| Pentaerythritol tetrakis(azidoacetate)         | PETKAA  | 1.39                         | -900                         | 7175                     | -215     | 1714.76           | 237.7      |
| Tris(azidoacetoxymethyl)propane                | TAAMP   | —                            | -157                         | -463                     | -37.5    | -114              | 226.1      |
| Bis(azidoacetoxymethyl)bis(azidomethyl)propane | BABAMP  | —                            | 603                          | —                        | 144.19   | -90.8             | 221.2      |

Data source: [280,281]

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# Boranes

## Introduction

Boranes share many properties, such as pyrophoricity, with their alkylated derivatives, the organic boranes described in *Encyclopedia of Liquid Fuels* chapter “Alkylboranes.” Their parent element, boron, is described in chapter “Boron.” Boranes, alkylboranes and elemental boron all share the common disadvantage of diboron trioxide deposition in the combustion products, possibly leading to clogged orifices and nozzle throats.

## 1 Boranes

For a brief period of about 10 years in the 1950s, the chemistry of boron compounds received a substantial amount of attention as a result of the proposed use of boranes and alkylboranes as fuels in air-breathing jet engines. This activity was often mistaken for a rocket propellant program, when actually it was intended primarily for air-breathing jet engines and ramjets. However, while the production base for boron chemicals was being expanded, the potential use of boranes and alkylboranes as rocket propellants was also examined at the same time. The closest alkylboranes have come to being actually used in rocket engines has been in mixtures with triethylaluminum for the hypergolic start and restart of bipropellant engines with LOX as the oxidizer. This practical and important use continues to this day and is a direct benefit of borane chemistry research done in the 1950s, which is reviewed in this chapter.

Other than this particular and only currently active application of alkylboranes, this chapter is not part of a book on modern rocket propellants, but a chapter on the history of rocket propellants. It is very unlikely that boranes will ever again be tested as rocket propellants. This chapter is mostly a *déjà vu* of what has been done in the past.

When it comes to writing a book about boron chemistry, the author has nostalgic memories about the time when, thrilled by the prospect of working with new pyrophoric rocket propellants, he worked as a summer intern student at the Max Planck Institut für Kohleforschung in Germany in 1959 under the direction of Nobel laureate Dr. Karl Ziegler and Dr. Roland Köster. During this time he enthusiastically (but very carefully) learned the safe handling of pyrophoric liquids such as triethylaluminum and the preparation of triethylborane and diethyldiborane in glass apparatus. Each time, when disassembling the apparatus after completion of a synthesis under a flow of inert argon blanketing gas, the disassembling was always a display of fireworks as soon as air was admitted to the few droplets of boranes still clinging to the glass tub-

ing pulled from the apparatus. This voluntary, unpaid summer work was done in the idealistic expectation of the author that some of these compounds could some day in the future be used as rocket propellants. At that time, Ziegler's research institute, close to the author's home town, had the world's largest triethylaluminum production facility to support the fledgling low-density polyethylene catalyst industry using the Ziegler-Natta process, a very lucrative undertaking for the institute and its director. On the loading dock of the institute there were rows and rows of metal drums filled with triethylaluminum waiting to be shipped to the polyethylene manufacturers. That was before the chemical industry assumed the role of supplying triethylaluminum to the polyethylene makers. The author walked in between these drums on the loading dock with mixed feelings, knowing what could happen if one of these drums accidentally started leaking and caught fire (you cannot extinguish burning triethylaluminum with water, it makes things worse).

A detailed write-up in book format of the US borane effort covering the years from 1950 to 1965 is the most comprehensive summary ever published on this exciting period of borane fuel development [1]. An anecdotal and historical account of the US boranes program, written by an insider old-timer, was published later and makes very entertaining reading [2]. We wished similar easy-to-read books had been written on the history of some of the other rocket propellants, such as the early years of hydrazines.

Half a century later, the chemistry of boron compounds still benefits from the boost it received when all of a sudden their potential as high-caloric-value fuels for air-breathing jet engines was realized. This book at hand is a book on rocket propellants, not a book on fuels for air-breathing engines, but we include some information on selected jet engine fuels that may also be of interest as rocket propellants or as fuels and ignition fluids in ramjets and scramjets. The high heat of combustion makes these boron compounds attractive as fuels in air-breathing engines. As we already know, a high heat of combustion alone is not necessarily a criterion for a good rocket propellant if the average molecular weight of the exhaust products is too high or if the exhaust products include condensed phases such as  $B_2O_3$ . In the case of air-breathing turbo jet engines with rotating parts, the deposition of boron oxide(s) as a condensed phase slag in the exhaust caused substantial problems with rotary machinery in turbojets and afterburners, and the project was eventually abandoned with substantial investments in facilities being idled and dismantled because the slag deposition problems could not be solved [3]. Some work on boranes as ramjet or afterburner fuels continued even after the work with turbojets was canceled. Ramjets and afterburners are less susceptible to clogging and erosion of sensitive moving parts by solid exhaust products than turbojets. Throughout this period of exuberant borane enthusiasm, several organizations studied the use of boranes and alkylboranes as rocket propellants (as opposed to jet engine fuels), but none of these studies lead to any practical flight applications of boranes as the main fuels for rockets.

The element boron itself has also been tested as a fuel in solid propellants, ram-air rockets, gelled liquid slurries, and hybrid fuel grains. Of course a large amount of elemental boron goes into making potassium nitrate/boron igniters, which are used in many solid propellant rockets, pyrotechnic devices and airbag inflators.

A long time after the interest in boranes as jet engine fuels and rocket propellants had subsided, the interest in boron hydrides has recently been revived because of their potential to serve as dihydrogen storage media. The hydrogen economy is dependent on efficient hydrogen storage methods, more efficient and compact than compressed hydrogen and easier to handle than liquid hydrogen. Hydrogen gas at high pressure will adsorb reversibly on certain boron hydrides, can then be released on demand, and in this way can be used as a light-weight portable source of energy for combustion machines or fuel cells (see Section 6.6.6). Some of the boron hydride hydrogen storage chemistry used now is based on the extensive borane work of the 1950s. The inorganic boranes are discussed here first, followed by organic borane adduct compounds.

There are at least 12 known boron hydrides, but of all these only three boranes are of interest as rocket propellants: diborane  $B_2H_6$ , pentaborane  $B_5H_9$ , and decaborane  $B_{10}H_{14}$ . Many other boron hydrides have been observed only as short-lived intermediates during transitions between the various boron hydrides, e.g., by pyrolysis.

Proposals for the use of these boranes as rocket fuels published in the 1950s and 1960s were overly optimistic and in the end the toxicity and the problems with boron oxide in the exhaust were insurmountable. In spite of these problems, many static tests with boranes in rocket engines have been conducted, but none of these engines has ever flown in a rocket. Boron oxide as a condensed phase in the two-phase exhaust causes a loss of exhaust velocity. Oxide slag deposits on the injectors and throats cause clogging and reduced heat transfer for cooling. The high heat of combustion of boranes would only be beneficial in the presence of a fuel with lots of hydrogen or possibly fluorine. Thus various fuel mixtures of boranes with other fuels have been tested as rocket propellants. However, boranes react with many of the other known fuels. The best compatibility and solubility would be with hydrocarbon fuels such as kerosene.

Boranes are well suited as fuels for fluorine or fluorine compounds as oxidizers because boron trifluoride is volatile and does not cause the same clogging and condensed exhaust particles problems as  $B_2O_3$ . But of course, boron trifluoride is more toxic than boron oxide.

The current section is an introduction to boranes as a family of chemical compounds. This section is followed by several sections on specific boranes, starting with diborane. This chapter concludes with sections on complex boron hydrides and borane Lewis salt adducts. Alkylboranes are now in a chapter by themselves and can be found in *Encyclopedia of Liquid Fuels*, chapter "Alkylboranes."

## 1.1 Literature Summaries on Boranes

Many chemists have made a lifelong career of studying mostly boranes, resulting in a flood of publications, and some have even received Nobel prizes for their work. There are many books dealing exclusively with boranes and other boron hydrides. Only a few are referenced here, not a complete list of what is available in the libraries, and probably many other books should be listed here, so our apologies to any of authors we may have missed [1, 4–8]. Other books on hydrides include chapters on boranes [9].

There are chapters on boranes in several encyclopedias, standard resources for chemical information where one would look first, such as those authored by Schubert [10], Brotherton et al. [11], and Fedoroff [12]. In addition to books, there are summary reports on the history of boranes that may also be very comprehensive, but not as formal as bound books [13–15]. These summary reports lost their actuality very quickly because progress in this field of high-calorie fuels was so quick during the 1950s and 1960s. In the periodical literature, several surveys on boranes have been compiled and updated at times [16–18]. The chemistry of the lower boron hydrides was reviewed in several publications [19, 20].

The nomenclature for hydrocarbons is fairly strict and well established and most chemists adhere to it. In comparison, unfortunately the nomenclature for boranes, being of a more recent origin, is less well known and many chemists ignore it and continue to use obsolete trivial names [21–24]. Additional prefixes were introduced to differentiate between closed and non-closed borane structures. Admittedly, this author has not checked his writings for consistency and compliance with the latest IUPAC nomenclature guidelines either.

## 1.2 Thermodynamic Properties of Boranes

In 1998, NIST published a compilation of published experimental and computational reports (containing 191 literature references) on the structures, vibrational frequencies, molar enthalpies of formation and standard entropies for 26 gas phase boranes and their fragments for the temperature range 0 to 1500 K [25]. The thermochemical properties were collated via standard programs and listed in tabular format (Table 1). The tabulated values were curve-fitted to standard seven-parameter (NASA CEA) polynomials to facilitate the computation of enthalpies of formation, entropies, and heat capacities for modeling purposes. The equilibrium compositions of the gas phase were calculated, constrained to constant temperature and volume, for several boron-hydrogen (B/H) ratios typical for existing boranes, at various temperatures and pressures. The results indicated that thermodynamic equilibrium was not attained in any of the reported gas-phase kinetics studies, even though the measured concentration profiles appeared to extrapolate to steady-state product distributions. The report lacks data for boranes in other than the gaseous state.

**Table 1:** Thermodynamic data of gaseous boranes and their fragments at 298.15 K and 1 bar.

| Compound                                       | Name            | CAS RN number | $\Delta H_f^{298}$ ,<br>kJ/mol | $S_0$ ,<br>JK <sup>-1</sup> mol <sup>-1</sup> | $C_p$ ,<br>JK <sup>-1</sup> mol <sup>-1</sup> |
|------------------------------------------------|-----------------|---------------|--------------------------------|-----------------------------------------------|-----------------------------------------------|
| BH                                             | borane(1)       | 13766-26-2    | 442.7                          | 171.85                                        | 29.18                                         |
| BH <sub>2</sub>                                | borane(2)       | 14452-64-3    | 318.0                          | 193.67                                        | 34.98                                         |
| BH <sub>3</sub>                                | borane(3)       | 13283-31-3    | 89.2                           | 188.23                                        | 36.02                                         |
| BH <sub>4</sub>                                | borane(4)       | 37365-60-9    | 236.4                          | 211.61                                        | 44.28                                         |
| BH <sub>5</sub>                                | borane(5)       | 35325-82-7    | 79.9                           | 230.55                                        | 54.12                                         |
| B <sub>2</sub> H                               | diborane(1)     | —             | 737.6                          | 214.29                                        | 42.33                                         |
| B <sub>2</sub> H <sub>2</sub>                  | diborane(2)     | 56125-74-7    | 396.5                          | 213.24                                        | 46.89                                         |
| single-bridge B <sub>2</sub> H <sub>3</sub>    | diborane(3)     | —             | 306.7                          | 236.07                                        | 52.53                                         |
| double-bridge B <sub>2</sub> H <sub>3</sub>    | diborane(3)     | —             | 315.9                          | 233.22                                        | 52.48                                         |
| single-bridge B <sub>2</sub> H <sub>4</sub>    | diborane(4)     | 18099-45-1    | 211.0                          | 236.15                                        | 57.12                                         |
| double-bridge B <sub>2</sub> H <sub>4</sub>    | diborane(4)     | 18099-45-1    | 209.7                          | 227.83                                        | 51.52                                         |
| single-bridge B <sub>2</sub> H <sub>5</sub>    | diborane(5)     | 124521-90-0   | 254.7                          | 243.47                                        | 58.27                                         |
| double-bridge B <sub>2</sub> H <sub>5</sub>    | diborane(5)     | 124521-90-0   | 275.1                          | 245.55                                        | 53.16                                         |
| B <sub>2</sub> H <sub>6</sub>                  | diborane(6)     | 19287-45-7    | 36.4                           | 232.05                                        | 56.65                                         |
| C <sub>s</sub> -B <sub>3</sub> H <sub>7</sub>  | triborane(7)    | 12429-70-8    | 128.4                          | 267.99                                        | 76.71                                         |
| C <sub>2s</sub> -B <sub>3</sub> H <sub>7</sub> | triborane(7)    | 12429-70-8    | 146.4                          | 265.96                                        | 81.62                                         |
| B <sub>3</sub> H <sub>9</sub>                  | triborane(9)    | 36350-66-0    | 138.9                          | 278.33                                        | 91.70                                         |
| B <sub>4</sub> H <sub>7</sub>                  | tetraborane(7)  | 158511-74-1   | 326.2                          | 277.61                                        | 80.38                                         |
| B <sub>4</sub> H <sub>10</sub>                 | tetraborane(10) | 18283-93-7    | 66.1                           | 280.27                                        | 93.17                                         |
| B <sub>4</sub> H <sub>12</sub>                 | tetraborane(12) | 60349-62.4    | 1883                           | 315.89                                        | 128.2                                         |
| B <sub>5</sub> H <sub>9</sub>                  | pentaborane(9)  | 19624-22-7    | 73.2                           | 280.62                                        | 99.59                                         |
| B <sub>5</sub> H <sub>11</sub>                 | pentaborane(11) | 18433-84-6    | 103.3                          | 320.96                                        | 130.31                                        |
| B <sub>6</sub> H <sub>10</sub>                 | hexaborane(10)  | 23777-80-2    | 94.6                           | 296.84                                        | 125.74                                        |
| B <sub>8</sub> H <sub>12</sub>                 | octaborane(12)  | 19469-16-0    | 147.3                          | 337.65                                        | 157.03                                        |
| B <sub>9</sub> H <sub>15</sub>                 | nonaborane(15)  | 19465-30-6    | 158.4                          | 364.91                                        | 187.02                                        |
| B <sub>10</sub> H <sub>14</sub>                | decaborane(14)  | 17702-41-9    | 47.0                           | 350.74                                        | 186.10                                        |

Data source: [25]

### 1.3 Chemistry of Boranes

Boranes are Lewis acids and ammonia, amines, and hydrazines are Lewis bases. Lewis acid-Lewis base reactions can be quite energetic, and the heat of reaction can lead to self-ignition. It is unusual to have a hypergolic rocket propellant combination such as pentaborane and hydrazine that consists of two fuels instead of an oxidizer and a fuel. The driving force behind this hypergolic reaction is the high enthalpy of formation of boron nitride, a solid reaction product.

Most boranes are pyrophoric in air and susceptible to hydrolysis, so working with boranes required exclusion of air and moisture, and use of a blanketing, inert gas atmosphere in all storage containers.

## 1.4 Toxicity of Boranes

All boranes are highly toxic [26, 27]. Clinical tests have been developed to detect toxic effects of borane exposure [28, 29]. Sections on toxicity dealing specifically with only one compound at a time are included in all of the following sections on specific boranes.

## 2 Diborane

Diborane, also known as diborane(6), diboron hexahydride,  $(\text{BH}_3)_2$ ,  $\text{B}_2\text{H}_6$ , CAS RN [19287-45-7], is the starting point for the synthesis of all other boranes. Diborane was produced in large quantities when the borane fuels project was in full swing in the US during the 1950s. Diborane is now consumed primarily by the electronics industry as a dopant in the production of silicon wafers for use in semiconductors.

A very comprehensive summary on all aspects of diborane was published in the form of a *Diborane Handbook* by Rocketdyne in 1970 [30]. This is the most detailed handbook on any rocket propellant available in the open literature. If similar handbooks were generally available on all other rocket propellants discussed in our book, then our book would no longer be necessary. We have allowed ourselves to extract a substantial amount of information from that handbook and reformat it for the book at hand.

### 2.1 Production of Diborane

#### 2.1.1 History of the Production of Diborane

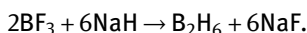
The production of diborane is possible using a variety of different methods [31]. Diborane was first isolated as a pyrolysis product of tetraborane, prepared by acid hydrolysis of magnesium boride. In 1931, Schlesinger and Burg prepared diborane by passing hydrogen and boron trichloride through an electric discharge. In about 1944, the first essentially quantitative process for preparing diborane was developed by Schlesinger and Brown. It used lithium hydride to reduce boron trifluoride in diethyl ether. This method was later used by Callery to prepare the first commercial quantities of diborane in the 1950s. In 1947, Hurd prepared diborane by passing a stream of boron halide and hydrogen through catalytic beds of active metals. Several methods using sodium borohydride were later developed. The method preferred involved the reaction of sodium borohydride with boron fluoride in the dimethyl ether of diethylene glycol.

The history of the first production of diborane on an industrial scale is described in the anecdotal book by Dequasie [2]. It is regrettable that there are only a few first-hand accounts of pioneering rocket or jet engine fuel development work during the period of the Cold War. This book is one and there is something to be learned from them. Dibo-

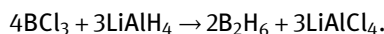
rane is the starting reactant for production of all other boranes. Diborane is the most important intermediate in the production of other boranes. Pentaborane and decaborane are produced by pyrolysis of diborane. When the US started the large-scale production of borane fuels in the 1950s, 90% of the installation costs were for the production of diborane. See also publications by Gould [32], Herrick et al. [33], and Major [34].

### 2.1.2 Reactions for the Production of Diborane

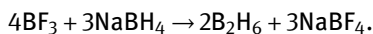
One of the methods used for the industrial synthesis involved the reduction of  $\text{BF}_3$  with sodium hydride [35]:



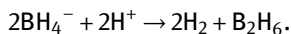
Either sodium hydride or lithium hydride can be used for the reduction. Lithium hydride as a fine powder suspended in ether reacts on heating with the ether adduct compound of boron trifluoride with the slow evolution of diborane. Two laboratory methods start from boron trichloride with lithium aluminum hydride or from boron trifluoride ether solution with sodium borohydride. Both methods yield only up to 30% of diborane:



It is more convenient to use the ether addition compound of boron trifluoride with ether  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , which may achieve a yield of diborane of 70–80%. Another convenient method for preparing diborane is the reaction of the addition complex of ether and boron trifluoride with lithium or sodium tetrahydroborate:



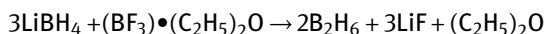
If sodium tetrahydroborate is used, the preferred solvent is diglyme (the methyl ether of diethylene glycol). Older methods entail the direct reaction of borohydride salts such as sodium borohydride with a non-oxidizing, non-volatile acid, such as phosphoric acid or dilute sulfuric acid, with the solid sodium borohydride suspended in an inert fluid to better control the heat release and achieve uniform mixing [36–38]:



Another small-scale synthesis method uses potassium tetrahydroborate and phosphoric acid as starting materials [39].

Diborane contaminated with  $\text{SO}_2$  is obtained by the action of sulfuric acid on sodium borohydride, but when the sulfuric acid is replaced by methanesulfonic acid, diborane is obtained in 76% yield free from  $\text{SO}_2$ .

A pilot plant consisting of three independent production units was constructed for the preparation of diborane according to the following equation [40]:

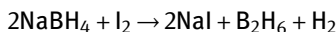


A total of 4.2 kg of diborane of about 95% purity was prepared in 47 runs with an overall yield of 90.9% based on the lithium borohydride. The production unit was built



essentially of all glass and consisted of a reactor connected to cold traps for purification and transfer of the product. The diborane is obtained in an ether solution and has to be fractionated to obtain the pure product. The vapor-phase equilibrium of the diborane-diethyl ether system must be known to achieve effective separation [41].

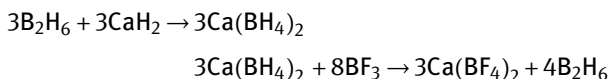
Oxidation of borohydride salts leads to diborane and that is a convenient method for small-scale preparations:



Passing a mixture of boron tribromide with an excess of hydrogen through an electric arc discharge forms diborane, which can be separated from unreacted boron tribromide and higher boranes by fractionated distillation [42]. Diborane may be purified from contaminants that do not react with pyridine by forming the solid, insoluble borane-pyridine adduct.

A process that starts out with cheap raw products and avoids the use of metal hydrides is the silver-catalyzed hydrogenation of boron trichloride and the disproportionation of the dichloroborane thus formed [43]. A pilot plant based on this process was operated for a while and experience was accumulated for the design of a large-scale plant.

Diborane can be prepared by reacting calcium borohydride with a boron halide in the presence of an inert solvent for calcium borohydride [44]. This reaction may be combined with the reaction of calcium hydride with  $\text{B}_2\text{H}_6$  in two-step cyclic processes for the production of further quantities of  $\text{B}_2\text{H}_6$  or  $\text{Ca}(\text{BH}_4)_2$ . To produce further quantities of  $\text{B}_2\text{H}_6$  the reactions are:



and this cycle may be repeated. Another method for the production of diborane is the high-pressure hydrogenation of alkyl boron compounds [45].

### 2.1.3 Purification of Diborane

Depending on the method how it was prepared, diborane may contain contaminants that interfere with its intended application. In particular, diborane intended for semiconductor processing must be of very high purity. Various methods for the purification of diborane have been recommended.

Diborane  $\text{B}_2\text{H}_6$  can be synthesized by the reaction of  $\text{BF}_3$  with  $\text{KBH}_4$ . Unreacted  $\text{BF}_3$  and/or  $\text{CO}_2$  contaminants can be removed from  $\text{B}_2\text{H}_6$  by contacting the mixture with an alkali metal hydroxide such as  $\text{LiOH}$  [46].

Diborane can be purified by low-temperature fractional distillation [47]. See also [48]. Diborane can be purified by adsorption of impurities and continuous distillation [49, 50].

## 2.2 Physical Properties of Diborane

At room temperature diborane  $B_2H_6$  is a colorless gas that can be liquefied and condensed below 180.6 K ( $-92.5^\circ\text{C}$ ).

The physical properties of diborane were measured repeatedly with great accuracy because this compound is important as an intermediate for the production of other boranes and for semiconductor processing. Summaries of physical properties of diborane were published in [51, 52] and are listed in Table 2.

**Table 2:** Physical properties of diborane.

|                                                             | SI units                                          | Other units                                                       | References |
|-------------------------------------------------------------|---------------------------------------------------|-------------------------------------------------------------------|------------|
| Molecular mass                                              | 27.670 g/mol                                      | 36.14 mol/kg                                                      | [53]       |
| Freezing point                                              | 108.29 K                                          | $-164.86^\circ\text{C}$                                           |            |
|                                                             | 108.30 K                                          | $-164.85^\circ\text{C}$                                           | [30]       |
| Boiling point                                               | 180.62 K                                          | $-92.53^\circ\text{C}$                                            |            |
|                                                             | 180.5                                             | $-92.6$                                                           | [30]       |
| Density, solid                                              | 0.577 g/cm <sup>3</sup> at 90 K                   | —                                                                 |            |
| Density, liquid                                             | 0.333 g/cm <sup>3</sup> (at 243 K)                | 0.333 g/cm <sup>3</sup> (at $-29.9^\circ\text{C}$ )               |            |
|                                                             | 0.210 g/cm <sup>3</sup> (at 288 K under pressure) | 0.210 g/cm <sup>3</sup> (at $+15.0^\circ\text{C}$ under pressure) |            |
| Critical temperature                                        | 289.8 K                                           | $16.7^\circ\text{C}$                                              | [54]       |
| Critical pressure                                           | 4.0 MPa                                           | 39.51 atm = 580 psia                                              | [54]       |
| Molar heat capacity $C_p$ (at 298 K)                        | 55.6 J mol <sup>-1</sup> K <sup>-1</sup>          | 13.30 cal mol <sup>-1</sup> °C <sup>-1</sup>                      |            |
| Standard enthalpy of formation, gas $(\Delta H)_f^{298}$    | $+41.0 \pm 16.7$ kJ/mol                           | $+9.8 \pm 4$ kcal/mol                                             |            |
| Standard free energy of formation, gas $(\Delta F)_f^{298}$ | +82.7 kJ/mol                                      | 19.78 kcal/mol                                                    |            |
| Heat of fusion $(\Delta H)_{\text{melt}}$                   | 4.47 kJ/mol                                       | 1.069 kcal/mol                                                    |            |
| Heat of vaporization $(\Delta H)_{\text{evap.}}$            | 14.4 kJ/mol                                       | 3.45 kcal/mol                                                     |            |
| Lower heat of combustion $(\Delta H)_{\text{comb.}}^{298}$  | 2016 kJ/mol                                       | 481.9 kcal/mol                                                    |            |
| Standard entropy $S_0^{298}$                                | 231.5 J mol <sup>-1</sup> K <sup>-1</sup>         | 55.34 cal mol <sup>-1</sup> °C <sup>-1</sup>                      |            |

Data Source: Unless otherwise identified, the data in this table were taken from a Callery product data sheet that is no longer available.

The effort in the US in the 1960s to develop high-energy space-storable bipropellant combinations for challenging deep space missions with high total impulse requirements, such as those to outer planets or comets, has resulted in a series of summary publications in support of the on-going experimental effort to bring diborane as a fuel closer to full-scale use, where it would have been used in upper stages and kick stages with fluorine oxidizers [55, 56].

### 2.2.1 Freezing Point and Phase Diagrams of Diborane

Although a data sheet from Callery gave a freezing point of diborane of 108.29 K = -164.86 °C, other sources listed it as 107.7 K = -165.5 °C [55].

### 2.2.2 Boiling Point of Diborane

Based on vapor pressure measurements, the normal boiling point of diborane is 180.59 ± 0.04 K [57]. The average of four literature boiling points of diborane was 180.65 K = -92.53 °C [55]. A very accurate measurement of the boiling point gave 180.32 K [58].

### 2.2.3 Vapor Pressure of Diborane

According to [58], the vapor pressure below normal boiling point can be calculated from:

$$\log P = 8.110 - \frac{870.95}{T} - 2.221 \times 10^{-3} T$$

and the vapor pressure between normal boiling point and critical point can be calculated from [59]:

$$\log P = 8.1251 - \frac{870.68}{T} - 2.339 \times 10^{-3} T$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. From the latter equation, the normal boiling point of diborane is predicted to be 180.6 ± 0.2 K.

Within the range 151 to 220 K, the vapor pressure data were fitted by the equation [57]:

$$\log P = 3.8262 - \frac{598.3}{T} - \frac{1.6733 \times 10^4}{T^2}$$

where  $P$  is the pressure in atm and  $T$  is the temperature in kelvin. Within the range 151–288 K, the data were fitted by the equation:

$$\log P = 4.8600 - \frac{1236.2}{T} + \frac{1.2215 \times 10^5}{T^2} - \frac{1.2247 \times 10^7}{T^3} + \frac{3.4141 \times 10^8}{T^4}$$

where  $P$  is the vapor pressure in atm and  $T$  is the temperature in kelvin. For the temperature range 108–150 K, the vapor pressure of diborane can be represented by the equation [60]:

$$\log P = 6.9881 - \frac{674.82}{T - 15.02}$$

and for the higher temperature range 150–181 K it can be represented by the equation:

$$\log p = 6.81885 - \frac{583.120}{T - 24.63}$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The boiling point of diborane derived from these equations would be  $180.63 \pm 0.02$  K, and the heat of vaporization at the normal boiling point would be 14.28 kJ/mol (3.413 kcal/mol). Two melting points were found for diborane:  $108.14 \pm 0.02$  K and  $108.30 \pm 0.02$  K. The first value is probably that of a metastable phase. No phase transitions were observed in the solid.

An older source obtained the following simple vapor pressure equation [52]:

$$\log p = 7.185 - \frac{782.8}{T}$$

where  $p$  is the pressure in mm Hg and  $T$  is the temperature in kelvin.

The vapor pressure of diborane within the range 118.3–180.8 K can be calculated from an Antoine equation [53]:

$$\log P = 3.78156 - \frac{598.39}{T - 22.175}$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. Several of the above referenced data sources were combined and least-square curve-fitted by the equation [30]:

$$\log P = 3.9426 - \frac{642.99}{T - 17.5}$$

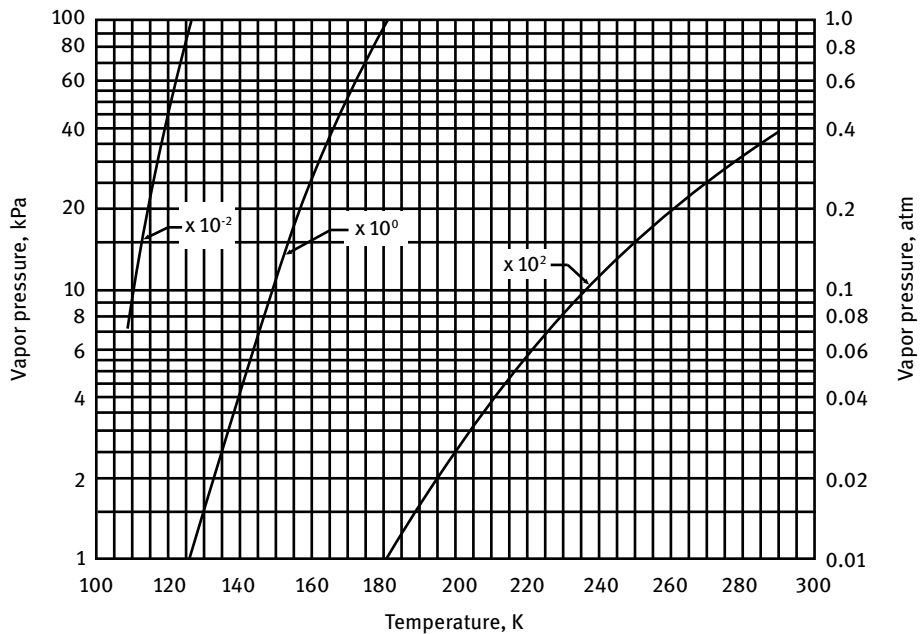
where  $P$  is the vapor pressure in atm and  $T$  is the temperature in kelvin. The curve in Figure 1 was calculated using this equation. Presumably, this averaging of results from different methods would give the most reliable data.

Deuterodiborane is useful to explain the nature of the hydrogen bridge bond and for kinetic and mass spectroscopic studies of diborane conversions. Perdeuterated diborane and lithium borodeuteride are useful sources of deuterium that is needed for chemical lasers. The vapor pressure of deuterodiborane differs substantially from that of the normal hydrogen diborane [61]:

$$\text{B}_2\text{H}_6 \quad \log P = -\frac{974.156}{T} - 0.00653809 T + 9.45290$$

$$\text{B}_2\text{D}_6 \quad \log P = -\frac{962.893}{T} - 0.00601480 T + 9.31798$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.



**Figure 1:** Vapor pressure of diborane. (Reproduced and modified from [30].)

### 2.2.4 Density and Partial Molar Volumina of Diborane

Density data of liquid diborane are listed in Table 3.

**Table 3:** Density of liquid diborane.

| Temperature |       | Density           |
|-------------|-------|-------------------|
| K           | °C    | g/cm <sup>3</sup> |
| 235.4       | −37.7 | 0.341             |
| 240.3       | −32.8 | 0.334             |
| 246.1       | −27.0 | 0.325             |
| 251.2       | −21.9 | 0.316             |
| 255.3       | −17.8 | 0.309             |
| 260.8       | −12.3 | 0.294             |
| 265.8       | −7.3  | 0.284             |
| 270.7       | −2.4  | 0.274             |
| 278.9       | +5.7  | 0.256             |
| 285.2       | +12.1 | 0.228             |
| 288.2       | +15.1 | 0.210             |

Data source: [52]

The density of liquid diborane as a function of temperature can be calculated from the equation:

$$\rho = 0.3140 - 0.001296t$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $t$  is the temperature in  $^{\circ}\text{C}$  [62].

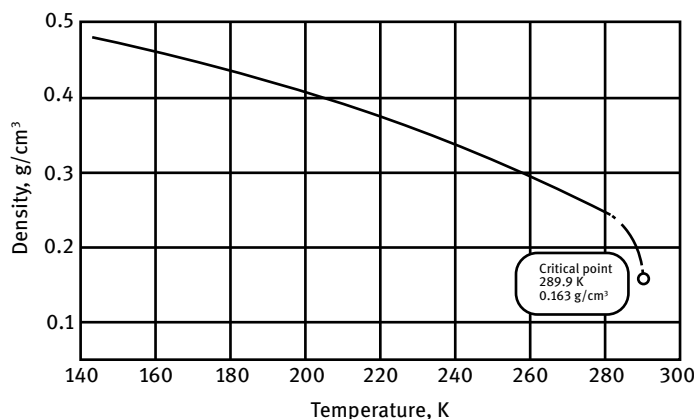
Density data from several sources for temperatures ranging from 144 to 285 K were combined and curve fitted to give the following equation:

$$\rho = 0.4857 + 7.618 \times 10^{-4} T - 5.747 \times 10^{-6} T^2$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin [30] (Figure 2). It was more difficult to obtain data for saturated liquid density at above normal boiling point temperatures from 181 to 285 K. The curve-fitted function was afflicted with an inaccuracy of at least 3%:

$$\log \rho = 10.6409 - \frac{6528.72}{T} + 1.19681 \times \frac{10^6}{T^2} - 8.18767 \times \frac{10^7}{T^3}$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin.

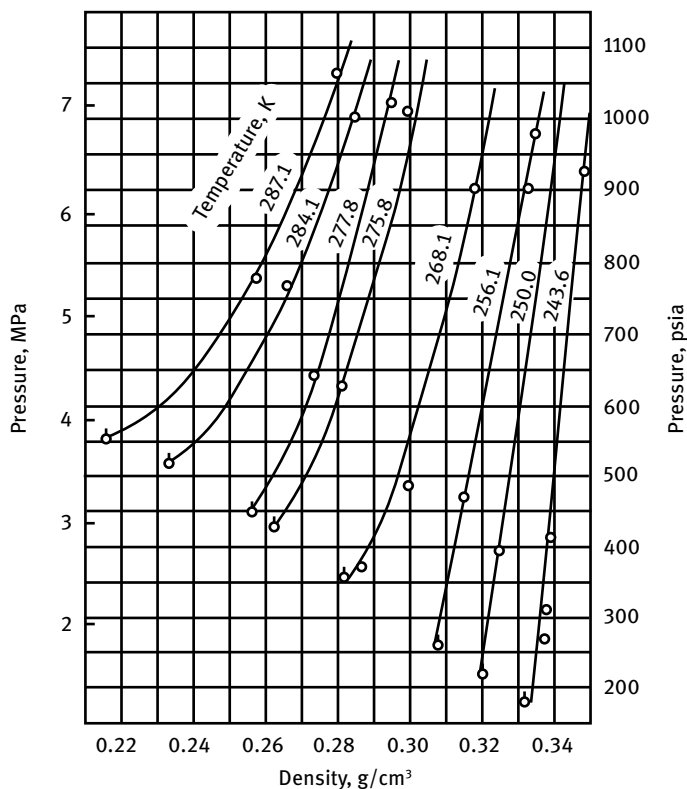


**Figure 2:** Density of liquid diborane. (Reproduced and modified from [30].)

### 2.2.5 Compressibility and Velocity of Sound of Diborane

Values of the molar volume, heat capacity ratio, adiabatic compressibility, sound velocity, molar compressibility, pseudo-Grüneisen parameter, Poisson's ratio, and the Debye temperature of liquid diborane were tabulated for a temperature range 108–180 K [63].

The compressibility of liquid diborane was measured for pressures up to 7.3 MPa (1060 psia) and temperatures up to 287 K [52]. The results are graphed in Figure 3.



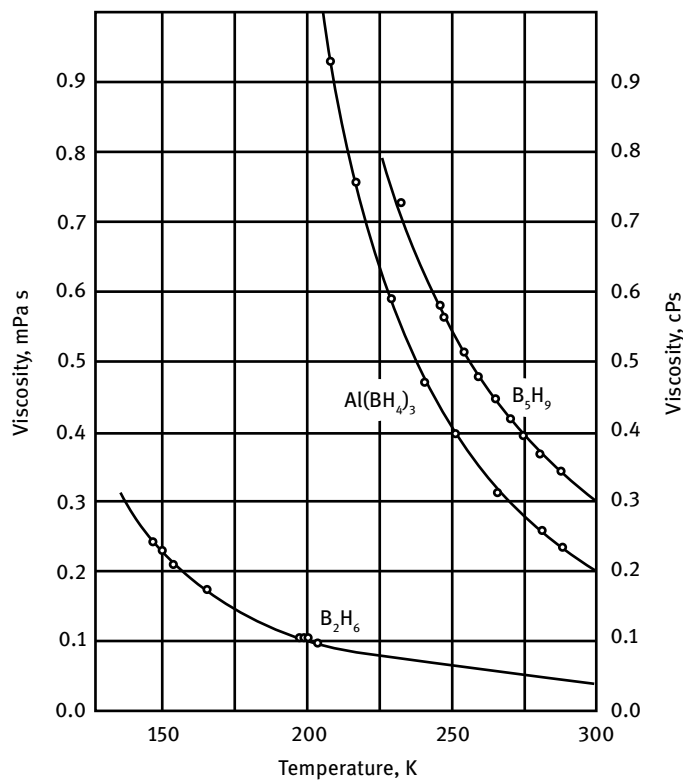
**Figure 3:** Diborane liquid compressibility isotherms. (Reprinted and adapted from [52], with permission from ©1950 American Chemical Society; permission conveyed through RightsLink.)

### 2.2.6 Viscosity of Diborane

The viscosity of liquid diborane is illustrated in Figure 4 in comparison with that of pentaborane and aluminum boranate. The viscosity of liquid diborane, the same data as shown in Figure 4, as a function of temperature can be expressed by the equation:

$$\eta = 36.86 \times 10^{-5} \rho^{\frac{1}{3}} e^{\left(\frac{551.8}{\rho T}\right)}$$

where  $\eta$  is the viscosity in Poise,  $\rho$  is the density in g/cm<sup>3</sup>, and  $T$  is the temperature in kelvin.



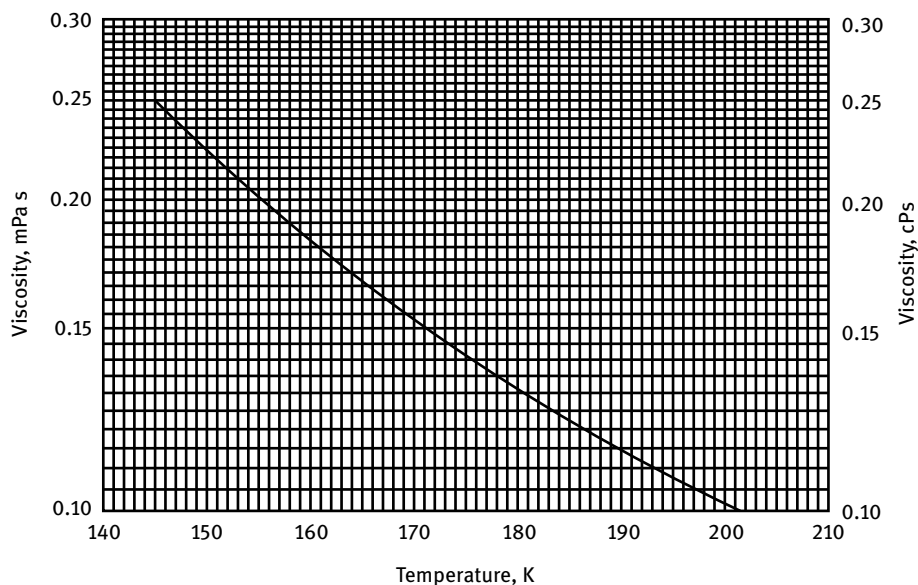
**Figure 4:** Viscosity of liquid diborane, pentaborane, and aluminum boranate. (Reprinted and adapted from [52], with permission from ©1950 American Chemical Society; permission conveyed through RightsLink.)

A different set of data within the temperature range 145–204 K was curve-fitted and resulted in the equation:

$$\log \eta = -2.027 + \frac{206.7}{T}$$

where  $\eta$  is the absolute viscosity in cPs and  $T$  is the temperature in kelvin. The data from this equation are illustrated in Figure 5.





**Figure 5:** Viscosity of liquid diborane. (Reproduced and modified from [30].)

### 2.2.7 Surface Tension of Diborane

At 203.4 K (−69.7°C) the surface tension of diborane was 10.9 dyn/cm and at 151.5 K (−121.6°C) the surface tension was measured as 18.6 dyn/cm. Surface tension data for diborane can be fitted to a linear equation:

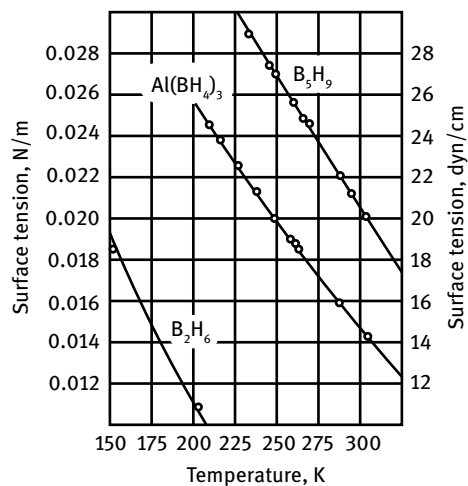
$$\sigma = (65.7 - 0.227T)\rho^{\frac{2}{3}}$$

where  $\sigma$  is the surface tension in dyn/cm,  $\rho$  is the density in g/cm<sup>3</sup> and  $T$  is the temperature in kelvin. Figure 6 shows the surface tension of diborane in comparison to that of pentaborane and aluminum boranate.

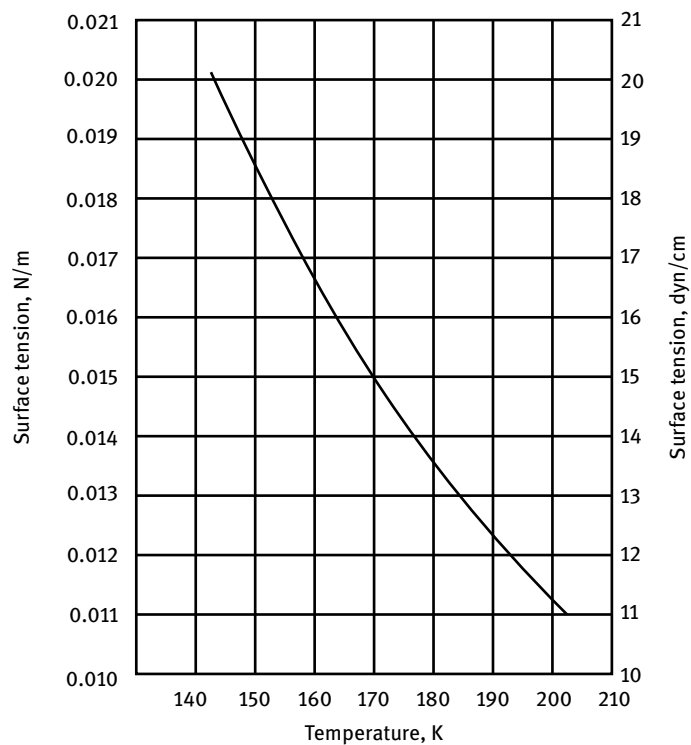
Another set of data for the temperature range 143–203 K was curve fitted and resulted in the equation:

$$\sigma = 72.07 - 0.5152T + 1.055 \times 10^{-3}T^2$$

where  $\sigma$  is the surface tension in dyn/cm and  $T$  is the temperature in kelvin. The curve generated from this equation is illustrated in Figure 7. See also [62].



**Figure 6:** Surface tension of diborane, pentaborane, and aluminum borane. (Reprinted and adapted from [52], with permission from ©1950 American Chemical Society; permission conveyed through RightsLink.)



**Figure 7:** Surface tension of saturated liquid diborane. (Reproduced and modified from [30].)

### 2.2.8 Thermal Conductivity and Heat Transfer Coefficient of Diborane

Diborane is not sufficiently thermally stable to serve as the cooling fluid in regeneratively cooled rocket engines. No thermal conductivity or heat transfer data were available. Attempts to use liquid diborane as a regenerative engine coolant were not successful and subsequent engine designs had to use both the fuel **and** the oxidizer for regenerative cooling of the thrust chamber and the nozzle. On the fuel side, the diborane decomposed under the coolant channel temperature conditions and solid residues coated the cooling channels and blocked heat transfer. On the oxidizer side, the OF<sub>2</sub> line burned out.

In an experimental program, heated-block heat transfer tests were conducted with both liquid and gaseous B<sub>2</sub>H<sub>6</sub> under conditions similar to those in a pressure-fed regeneratively cooled engine [64, 65]. Mass velocities were run in the range of 0.5 to 3.0 lb in<sup>-1</sup> s<sup>-1</sup> with coolant inlet pressures from 0.34 to 2.76 MPa (50 to 400 psia). A total test duration of 750 s was accumulated, with wall temperatures ranging from 294 to 589 K (70 to 600 °F). The results as Stanton Number and Nusselt Number correlations under bulk (B) conditions could be correlated by the relation:

$$N_{\text{NuB}} = 0.023 N_{\text{ReB}}^{0.8} N_{\text{PrB}}^{0.4}$$

where

$N_{\text{NuB}}$  = Nusselt Number =  $hD/T$

$N_{\text{ReB}}$  = Reynolds Number =  $DV\rho/\mu$

$N_{\text{PrB}}$  = Prandtl Number =  $C_p\mu/k$

$h$  = heat transfer coefficient

$D$  = characteristic length

$k$  = thermal conductivity

$V$  = velocity

$\rho$  = density

$C_p$  = heat capacity at constant pressure

$\mu$  = viscosity

### 2.2.9 Critical Constants of Diborane

The critical temperature and critical pressure of diborane were derived from PVT data [54]. The average critical temperature was  $289.8 \pm 0.2$  K ( $16.7 \pm 0.2$  °C). The average critical pressure was  $4.0 \pm 0.034$  MPa ( $581 \pm 5$  psia).

### 2.2.10 Solubility, Miscibility, Mixtures with Diborane:

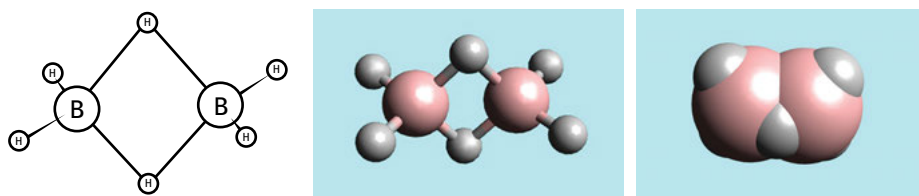
#### Miscibility with Other Solvents

Diborane dissolves in hydrocarbons, e.g., *n*-hexane, at room temperature at 258 kPa (2.55 atm) pressure with a solubility of 4.2 g B<sub>2</sub>H<sub>6</sub>/100 g *n*-hexane. Similarly, its solubility in 1,4-dioxane at 293 K (20 °C) and 241 kPa (2.38 atm) is ~3.4 g B<sub>2</sub>H<sub>6</sub>/100 g dioxane. However, dioxane may react with diborane or pentaborane, forming ether adducts.

When examining the solubility of pressurant gases between 144 and 228 K, it was surprising to see that the solubility of helium in liquid diborane increased with increasing temperature, whereas the solubility of nitrogen decreased with increasing temperature [30]. The solubility of hydrogen in liquid diborane increased with increasing temperature [66].

### 2.2.11 Molecular Structure, Dipole Moment, and Molecular Orbital Calculations of Diborane

Because boron hydrides have more valence orbitals than valence electrons, they have been called electron-deficient molecules. This electron deficiency gives boranes enhanced reactivity (compared with hydrocarbons) and unique molecular structures. The electrons that form the bonds that hold the diborane molecule together occupy the  $1s$  orbital of hydrogen and four  $2sp^3$  orbitals of boron. Diborane has four terminal and two bridging hydrogen atoms. Each of the boron atoms forms two covalent B—H bonds, both the boron atoms and four terminal hydrogen atoms are located in the same plane. The two remaining hydrogen atoms are situated at equal distances from this plane on a line perpendicular to it and bisecting the B—B line (Figure 8).



**Figure 8:** Hydrogen bridges in the diborane molecule.

Each of these two bridge hydrogen atoms is joined to both boron atoms by three-center bonds. Each  $B \cdots H \cdots B$  bridge is regarded as a filled three-center localized bonding orbital, which utilizes one hydrogen orbital and one hybrid orbital from each of the boron atoms. The hydrogen atom contributes one electron to this orbital, and each boron atom contributes half an electron. The length of a terminal B—H bond in diborane is  $1.19 \text{ \AA}$ , that of a bridge  $B \cdots H$  bond is  $1.33 \text{ \AA}$ , the distance between the boron atoms is  $1.77 \text{ \AA}$ , and the H—B—H angle is  $121.5^\circ$ . The frequencies of the stretching vibrations of the terminal B—H bonds lie in the range  $2500\text{--}2600 \text{ cm}^{-1}$  in the infrared (IR) and Raman spectra, whereas the vibrational frequencies of the  $B \cdots H$  bridge bonds are situated at  $\sim 1600 \text{ cm}^{-1}$  and  $\sim 1800\text{--}2000 \text{ cm}^{-1}$  in the IR absorption spectra, and  $\sim 2100 \text{ cm}^{-1}$  in the Raman spectra. The energy of dissociation of diborane into two borane  $BH_3$  molecules is  $119.2 \text{ kJ/mol}$  ( $28.5 \text{ kcal/mol}$ ).

Diborane possesses a  $D_{2h}$  structure containing four terminal and two bridging hydrogen atoms. The structure of this molecule can be modeled using molecular orbital theory. The model determined by molecular orbital theory indicated that the bonds

between boron and the terminal hydrogen atoms are conventional two-center, two-electron covalent bonds. The bonding between the boron atoms and the bridging hydrogen atoms is, however, quite different from that in molecules such as hydrocarbons. Having used two electrons in bonding to the terminal hydrogen atoms, each boron has only one valence electron remaining for additional bonding. The bridging hydrogen atoms each provide one electron each. Thus, the  $\text{BH}_2\text{B}$  ring is held together with four electrons, an example of three-center–two-electron bonding. This type of bond is sometimes called a “*banana bond*.” The lengths of the  $\text{B}\cdots\text{H}$  bridge bonds and the  $\text{B}-\text{H}$  terminal bonds are 1.33 and 1.19 Å, respectively, and the difference in the lengths of these bonds reflects the difference in their strengths, the  $\text{B}\cdots\text{H}$  bridge bonds being relatively weaker than the  $\text{B}-\text{H}$  covalent bonds. Diborane is one of many compounds with such unusual hydrogen bridging bonding. The higher boranes are held together by similar bonds.

The molecular structures of diborane and hydrazine are significantly different, yet similar methods can be used for calculating their significant structures in the liquid state and predicted heat of evaporation [67].

At very high pressures, several molecules of borane aggregate into new structures held together by hydrogen bonds. Molecular and crystalline structures of  $(\text{BH}_3)_n$  have been theoretically studied in the pressure regime from 101 kPa to 100 GPa [68]. At lower pressures, crystals of the familiar molecular dimer are the structure of choice. There are a number of metastable structures for oligomers of  $\text{BH}_3$ , including cyclic trimers, tetramers, and hexamers. Higher oligomers are stabilized, for reasons of molecular compactness, by application of external pressure. Based on density functional theory (DFT) calculations, near 4 GPa a molecular crystal constructed from discrete trimers was predicted to replace the  $\beta$  diborane structure as the most stable phase and remain as such until 36 GPa.

High-pressure ground-state phases of crystalline diborane and their stability against decomposition into B and H were investigated by DFT calculations. Although  $\text{B}_2\text{H}_6$  is thermodynamically unstable to phase separation into B and H in the intermediate pressure range, it is restabilized beyond 350 GPa by forming metallic (conductive) structures with quite high density of states at the Fermi energy [69].

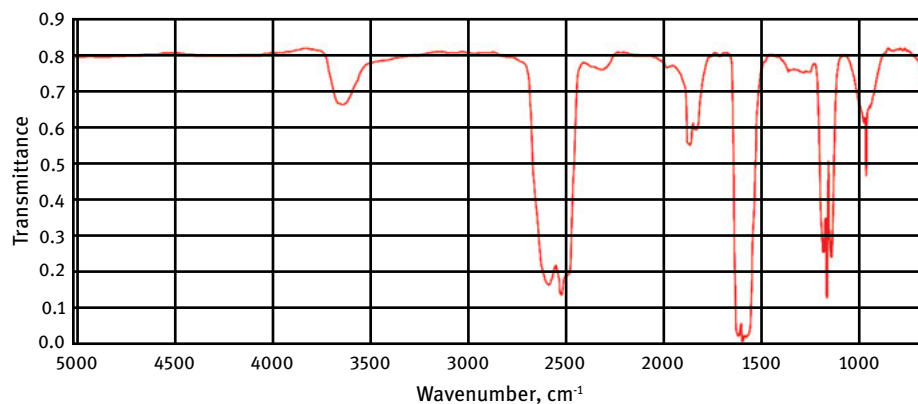
## 2.2.12 Absorption and Fluorescence Spectra of Diborane

### 2.2.12.1 Infrared Absorption Spectra of Diborane

The IR spectra of diborane are important for deriving thermodynamic properties and thermodynamic properties are important for calculating theoretical specific impulse of rocket engines with diborane. IR spectra of diborane are important for assuring the purity of the product and for identifying unwanted contaminants. The IR absorption spectrum of diborane was examined with high-resolution spectrometers from 3.7 to 30  $\mu\text{m}$  [70]. The rotational fine structure in two bands of each of the three types characteristic of asymmetric top molecules could be resolved. All results and observations were consistent with the conclusion that diborane has a bridge structure, and belongs

to the same symmetry point group,  $V_h$ , as ethylene. The observation and structure of the band with center at  $368.7\text{ cm}^{-1}$  provided spectroscopic evidence that the molecule is non-planar, and made the assignment of fundamental frequencies more definite. Data on all bands fit quite well the symmetric top approximation and predicted rotational constants. For the type A bands nearly every line obtained was accounted for, except those in or near the central maxima.

Another IR spectrum of liquid diborane was recorded within the range  $4500\text{--}10500\text{ cm}^{-1}$  and a complete assignment for the observed overtone and combination bands was possible [71]. The IR spectrum of  $\text{B}_2\text{H}_6$  gas at 50 mm Hg pressure is shown in Figure 9.



**Figure 9:** Infrared spectrum of diborane gas. (Reproduced and modified with permission from [72])

The IR spectrum of diborane showed only bands of lesser intensity indicating the absence of a first overtone and some uncertainty as to the presence of a second overtone [73]. Assuming  $D_{2h}$  point group symmetry, the bands observed have been assigned. The spectrum of diborane in the overtone region showed six weak bands between  $4800$  and  $5800\text{ cm}^{-1}$ . The gas was studied under greater pressure, longer path length and higher resolving power giving a spectrum in which the differences in intensity of the bands observed could be used as a guide in making assignments. By examining diborane under two atmospheres of pressure in a 40-cm cell, it was possible to observe the band at  $7580\text{ cm}^{-1}$ , which had not previously been reported.

The rotational structure of the bands in high-resolution IR spectra of  $\text{B}_2\text{H}_6$  vapor was analyzed for Coriolis perturbations owing to rotation about the axis of least moment of inertia (the B—B axis) [74]. Interactions between the Type A fundamental and inactive fundamentals confirmed the assignment of  $\nu_5$  at  $833\text{ cm}^{-1}$ . The assignment of unobserved fundamental vibrations of diborane was more difficult.

Polarized IR spectra of single crystals of diborane compared with spectra of the vapor and liquid showed evidence for the existence of three solid phases and the struc-

ture of a low-temperature form was partially elucidated [75]. This phase was found to be monoclinic with two or more molecules per primitive unit cell located on sites of symmetry no higher than  $C_i$ .

The two IR-active terminal B—H stretching bands,  $\nu_8$  and  $\nu_{16}$ , of  $^{10}\text{B}_2\text{H}_6$  and  $^{11}\text{B}_2\text{H}_6$  were studied with a resolution of  $0.04\text{--}0.05\text{ cm}^{-1}$ , and several ground-state rotational constants and moments of inertia were obtained [76]. These constants were then used to derive the following structural parameters:  $\text{B}\cdots\text{B} = 1.7628 \pm 0.0026\text{ \AA}$ ,  $\text{B—H}_{\text{terminal}} = 1.2005 \pm 0.0036\text{ \AA}$ ,  $\text{B}\cdots\text{H}_{\text{bridge}} = 1.3204 \pm 0.0010\text{ \AA}$ ,  $\angle\text{H}_{\text{terminal}}\text{BH}_{\text{terminal}} = 121.0 \pm 0.6^\circ$ , and  $\angle\text{H}_{\text{bridge}}\text{BH}_{\text{bridge}} = 96.2 \pm 0.2^\circ$ .

A thorough investigation of the IR spectra of diborane in the gas phase and polycrystalline films of normal and  $^{10}\text{B}$ -enriched samples of  $\text{B}_2\text{H}_6$  and  $\text{B}_2\text{D}_6$ , in conjunction with those from previous Raman studies, enabled a complete and unambiguous assignment of all 18 fundamental vibrations of  $\text{B}_2\text{H}_6$  and  $\text{B}_2\text{D}_6$  [77]. All previously uncertain or unassigned fundamentals were located by direct observation in the crystal phase and by means of one or more IR or Raman active combination bands. Boron isotopic vibration frequency shifts were used to analyze a number of Fermi resonances.

Four infrared active bands of  $^{10}\text{B}_2\text{H}_6$  were studied with a resolution of  $0.05\text{ cm}^{-1}$  [78]. From assignments in these bands, asymmetric-rotor ground-state parameters were determined from more than 500 possible combination differences. Upper-state parameters for all four vibrations were determined, and a few local perturbations were noted.

A total of 114 spectroscopic data accumulated from six isotopic species of diborane were used to determine the empirical harmonic potential functions [79]. Of the 33 independent force constants, 30 could be determined and agreed with scaled *ab initio* force constants. The potential function reproduced all known frequency, isotopic frequency shift, Coriolis, and centrifugal distortion with good accuracy.

An analysis of IR absorption bands near  $800\text{ cm}^{-1}$  of two isotopic species,  $^{10}\text{B}_2\text{H}_6$  and  $^{11}\text{B}_2\text{H}_6$ , of diborane has been carried out using IR spectra recorded with a resolution of approximately  $0.003\text{ cm}^{-1}$  [80]. It was possible to derive precise energy levels and Hamiltonian constants for the 41 vibrational states of both isotopic species.

As the simplest stable boron hydride in its condensed phase, diborane exhibits an interesting structural chemistry with uniquely bridging hydrogen bonds. Room-temperature IR absorption spectra of solid diborane compressed to pressures as high as 50 GPa using a diamond anvil cell displayed rich, sharply resolved fundamentals and overtones of the IR active bands, consistent with previous low-temperature IR measurements of condensed diborane at ambient pressure [81]. When compressed stepwise to 50 GPa, several structural transformations could be identified at pressures of 3.5, 6.9, and 14.7 GPa, as indicated by the changes in the band profile as well as the pressure dependence of the characteristic IR modes and bandwidths. These transformations can be interpreted as being enhanced intermolecular interactions resulting from compression. The geometry of the four-membered ring of  $\text{B}_2\text{H}_6\text{B}_2\text{H}_6$  did not seem

to be altered significantly during the transformations, and the  $\text{B}_2\text{H}_6\text{B}_2\text{H}_6$  molecule remained chemically stable up to 50 GPa.

Interpretation of some of the early period IR spectra was still based on the erroneous assumption that the molecule resembled that of ethane and that there was a potential barrier to internal rotation within the molecule (actually, the two halves do not rotate around the axis connecting the boron atoms) [82, 83]. Later IR spectra within the range 1–25  $\mu\text{m}$  ruled out the ethane-type structure but agreed very well with the interpretation of the electron diffraction results in terms of a bridge model [84].

Deuterated diborane was prepared by isotopic exchange and its IR absorption spectrum lent support to the assignment based on a hydrogen bridge model [85]. Redetermination of the Raman spectrum of normal diborane indicated several changes from previous assignments. The resulting vibrational assignment was used to calculate the thermodynamic properties of diborane within the range 100–1500 K.

#### 2.2.12.2 Raman Fluorescence Spectra of Diborane

High-resolution Raman spectra of the  $\nu_4$  bands of  $^{11}\text{B}_2\text{H}_6$  and  $^{11}\text{B}^{10}\text{BH}_6$  have been recorded using a high-resolution spectrometer based on the inverse Raman effect [86]. Q-branches have been observed, but P- and R-branches were too weak to be seen. A weak Coriolis resonance with the  $2\nu_{10}$  level was present in the  $^{11}\text{B}_2\text{H}_6$  spectrum. The band centers obtained were at 790.9829 and 804.76985  $\text{cm}^{-1}$  for  $^{11}\text{B}_2\text{H}_6$  and  $^{10}\text{B}^{11}\text{BH}_6$  respectively.

As an electron-deficient molecule with unique hydrogen bridge bonding, diborane has created considerable interest in structural chemistry. Pressure-induced structural transformations of diborane at pressures around 4 GPa, where diborane underwent a liquid-solid phase transformation to a new high-pressure phase I with a possible structure similar to the low-temperature phase, were probed by *in situ* Raman spectroscopy [87]. When compressed to above 6 GPa, the spectral features, such as doubling of the lattice modes, appearance of several new internal modes and emergence of a new ring stretch mode, indicated the structural transformation to another new high-pressure phase II. This phase had a possible extended network structure of higher hydrides of borane. At pressures above 14 GPa, diborane transformed to yet another high-pressure phase III. All of the observed pressure-induced structural transformations were completely reversible upon decompression.

#### 2.2.13 Dielectric Constant of Diborane

Diborane is a non-polar liquid (as opposed to  $\text{H}_2\text{O}$ ), and the dielectric constant of the liquid can be represented by the equation [60]:

$$\epsilon = 2.3721 - 0.002765 T$$

where  $\epsilon$  is the dielectric constant (dimensionless) and  $T$  is the temperature in kelvin.



### 2.2.14 Thermodynamic Properties and Thermal Properties of Diborane

There are four different types of bonds that hold the boranes together:

|           |                                                 |  | Bond energy |         |
|-----------|-------------------------------------------------|--|-------------|---------|
|           |                                                 |  | kcal/bond   | kJ/bond |
| B—H       | electron pair, two-center                       |  | 93.1        | 389.5   |
| B—B       | electron pair, two-center                       |  | 83.1        | 347.7   |
| B···H···B | one electron pair for two ligands, three-center |  | 107.2       | 448.5   |
| B···B···B | one electron pair for two ligands, three-center |  | 97.7        | 408.8   |

If one assumes that these bonds act independently of each other, the enthalpy of formation of boranes can be calculated assuming additive behavior [88, 89].

#### 2.2.14.1 Heat Capacity of Diborane

The heat capacity of gaseous diborane as a function of temperature can be calculated from the Shomate Equation:

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2},$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$ , A, B, C, D, and E are constants, and  $\tau$  is the absolute temperature in kelvin divided by 1000. The coefficients are listed in Table 4. The same coefficients (and others) are used for formulas expressing the standard enthalpy of formation and the standard entropy of the vapor (see Section 2.2.14.3). These equations were curve-fitted from data covering ranges from 298 to 1200 K and from 1200 to 6000 K, giving two overlapping sets of data. Of course, at those high temperatures diborane would long since have decomposed into the elements.

**Table 4:** Constants for vapor phase thermodynamic properties of diborane.

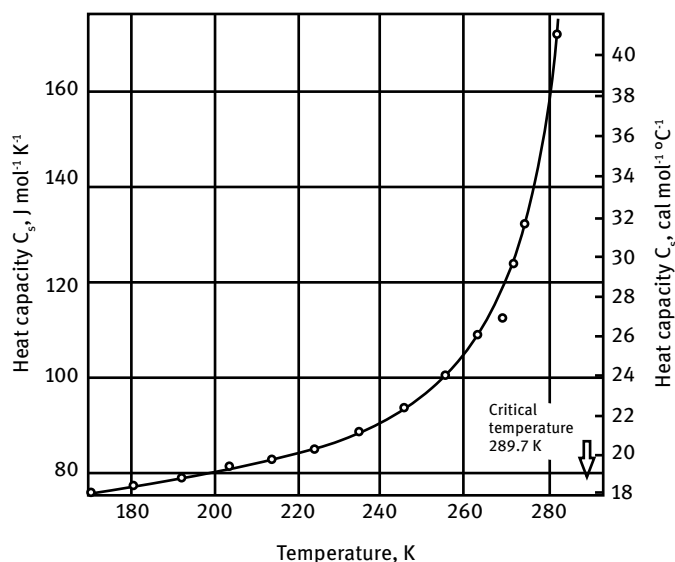
| Temperature range, K | 298–1200  | 1200–6000 |
|----------------------|-----------|-----------|
| A                    | −12.42167 | 161.6275  |
| B                    | 267.6112  | 11.23329  |
| C                    | −152.2612 | −2.178187 |
| D                    | 33.15879  | 0.146029  |
| E                    | 0.300489  | −36.76757 |
| F                    | 35.09886  | −89.40873 |
| G                    | 146.5115  | 320.5023  |
| H                    | 41.00303  | 41.00303  |

Data source: [53]

The heat capacity of solid diborane from 14 to 108 K was measured [58]. For temperatures below 21 K, the heat capacity followed the equation:

$$C_v = 1.486 \times 10^{-4} T^3 \text{ cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}.$$

At 89.54 K the heat capacity of solid diborane was  $48.9 \text{ kJ mol}^{-1} \text{ K}^{-1}$  ( $11.688 \text{ cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$ ). The heat capacity of liquid diborane was measured between 114 and 176 K. The average heat capacity was close to  $75 \text{ kJ mol}^{-1} \text{ K}^{-1}$  ( $18 \text{ cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$ ). The heat capacity of saturated liquid diborane at temperatures above the normal boiling point increased sharply as it approached the critical temperature [59] (Figure 10).



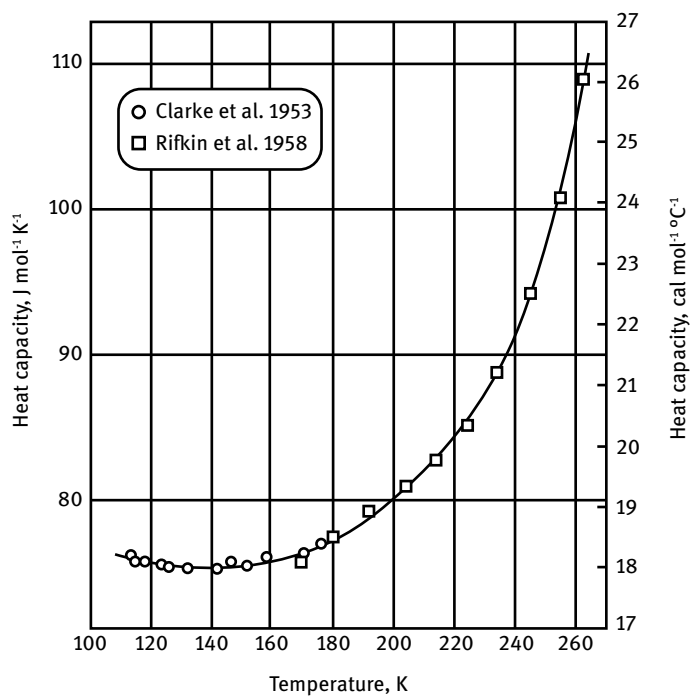
**Figure 10:** Heat capacity of saturated liquid diborane. (Reprinted and adapted from [59], with permission from ©1953 American Chemical Society; permission conveyed through RightsLink.)

Attempts to perform a curve fit of two sets of heat capacity data (from [58] and [59]) for liquid diborane between 112 and 282 K encountered difficulties, although the match in the overlap in the adjoining regions was good (as shown in Figure 11).

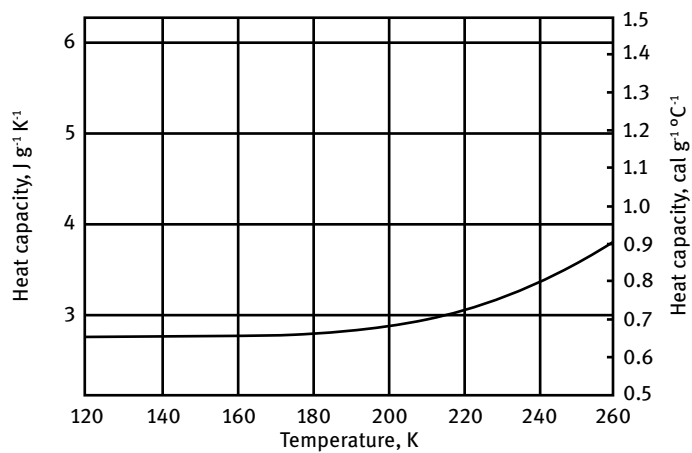
Only after the four highest data points with the worst scatter were eliminated was a reasonably good fit to the data achieved by the equation:

$$c_p = 0.4266 + 4.358 \times 10^{-3} T - 2.353 \times 10^{-5} T^2 + 2.05 \times 10^{-10} T^4$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ K}^{-1}$  and  $T$  is the temperature in kelvin [30]. The heat capacity curve generated from this equation is illustrated in Figure 12. It does not go through a minimum at 140 K, but remains fairly constant within that range.



**Figure 11:** Heat capacity of saturated liquid diborane. (Reproduced and modified from [55].)



**Figure 12:** Heat capacity of saturated liquid diborane. (Reproduced and modified from [30].)

### 2.2.14.2 Enthalpy of Formation and Heat of Combustion of Diborane

Accurate data for the heat of combustion of boranes and alkylboranes are important for their evaluation as jet engine fuels and rocket propellants. The presence of condensed phase reaction products such as  $B_2O_3$  and  $B(OH)_3$  made calorimetric measurements very difficult. In some cases the data needed to be corrected for incomplete reaction.

### 2.2.14.3 Enthalpy of Formation of Diborane

The enthalpies of formation of diborane and pentaborane were determined by measurements of the heat of decomposition into amorphous boron and hydrogen in a calorimeter [90]. The enthalpies of formation at 298 K (25 °C) from amorphous boron and hydrogen were  $+28.1 \pm 2.2$  kJ/mol ( $+6.73 \pm 0.52$  kcal/mol) for diborane (gas) and  $54.4 \pm 1.6$  kJ/mol ( $+12.99 \pm 0.39$  kcal/mol) for pentaborane (gas). The heats of decomposition are exothermic and therefore negative numbers. The enthalpies of formation are the opposite.

The vapor phase excess enthalpy above the standard enthalpy of formation  $\Delta H^\circ_{f,298}$  of diborane can be calculated from the Shomate Equation:

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - H$$

where A, B, C, D, E, and F are constants, and  $\tau$  is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 4 above. The same coefficients (and others) were used for a formula expressing the heat capacity of the vapor (see Section 2.2.14.1). These equations were curve-fitted from data covering a range from 298 to 6000 K.

The heat of formation of liquid diborane at its normal boiling point is  $+21 \pm 16$  kJ/mol ( $+5 \pm 4$  kcal/mol =  $325 \pm 260$  BTU/lb). Other sources gave the heat of formation of liquid diborane at 298 K (under pressure) as  $+4.97 \pm 4.0$  kcal/mol. The density under those conditions would be  $0.4371$  g/cm<sup>3</sup>. See also [91] and [92].

### 2.2.14.4 Heat of Combustion of Diborane

The heat of combustion of diborane is difficult to determine because the gas ignited as soon as oxygen is admitted. The combustion may not be complete because some of the diborane decomposes and forms higher boranes before it has a chance to burn to completion. Reported heats of combustion for diborane gas vary.

The net (lower) heat of combustion of diborane alone is 2018 kJ/mol = 72924 kJ/kg = 31373 BTU/lb [93]. Other sources quote the heat of combustion of diborane as 2082 kJ/mol = 75258 kJ/kg = 32377 BTU/lb [15].

### 2.2.14.5 Heat of Fusion of Diborane

The heat of fusion of diborane at the normal melting point was 4.473 kJ/mol = 1.0691 kcal/mol (average of four runs) [58].

#### 2.2.14.6 Heat of Vaporization of Diborane

The heat of vaporization of diborane at the normal boiling point is 14.28 kJ/mol ( $3.413 \pm 0.0015$  kcal/mol) [57]. The heat of vaporization as a function of temperature can be expressed by the equation:

$$\Delta H_{\text{vap}} = 546.2(T_c - T)^{0.39} = 546.2(289.7 - T)^{0.39}$$

where  $\Delta H_{\text{vap}}$  is the heat of evaporation in cal/mol,  $T_c$  is the critical temperature (289.7 K) and  $T$  is the temperature in kelvin [94]. For instance, the heat of evaporation at 179.4 K from this equation is 3.42 kcal/mol. Other experimenters reported a heat of vaporization of  $14.276 \pm 0.012$  kJ/mol =  $3.412 \pm 0.003$  kcal/mol [58].

### 2.3 Chemical Properties of Diborane

#### 2.3.1 Literature on Borane Chemistry

There exist many summary publications and monographs on borane chemistry. Only a few can be listed here [32, 95–97]. A very comprehensive summary of the chemistry of diborane and diborane derivatives with 238 references is a good source of information on the versatile reactions with diborane, leading to many other useful products [98].

#### 2.3.2 Pyrolysis of Diborane

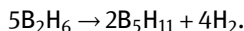
Diborane is unstable at room temperature. When heated, diborane will decompose with the formation of higher boron hydrides (mostly pentaborane  $B_5H_9$  and decaborane  $B_{10}H_{14}$ ) and an array of unstable intermediates [99, 100]. The first step in the decomposition of diborane would be its dissociation into two molecules of borine,  $BH_3$ , with which it is in equilibrium [101]. Splitting diborane into two borines would be an endothermic reaction and require 134 kJ/mol (32 kcal/mol) of diborane.

The kinetics of the pyrolysis of diborane between 358 and 436 K (85 and 163 °C) indicated a fractional order rate constant that appeared to be proportional to the square root of the initial pressure (indicating a free radical mechanism) times the 5/2 power of the fraction of unreacted diborane, and was depressed by the addition of dihydrogen but unaffected by an equivalent amount of dinitrogen or by an increase in surface [102]. The reaction is believed to be a radical-type polymerization process complicated by quasi-reversible dehydrogenation.

The rate of pyrolysis and the product ratio of desired higher boranes can be influenced by the choice of proper heterogeneous catalysts [103]. It was hoped that some catalyst might be found that would promote the selective formation of pentaborane(9) from diborane and avoid the formation of “yellow solids” [104].

At very high temperatures the only products are polymeric, non-volatile boron hydrides with very low hydrogen content. The pyrolysis of mixtures of diborane with other boron hydrides leads to the same undesirable results [105].

Pyrolysis of diborane was carried out in a borosilicate glass cell designed to freeze out products that would condense at 194.6 K (−78.5 °C) [106]. Between 373 and 403 K (100° and 130 °C) pentaborane(11) was the main condensable product. The stoichiometry of such a reaction should cause a decrease in total pressure, as pentaborane(11) exhibits little vapor pressure at the condensation temperature:



However, without exception, an initial increase in pressure was observed. This pressure increase was not due to fast initial decomposition of pentaborane(11) to polymer or pentaborane(9), nor to slow attainment of temperature equilibrium in the reaction vessel. An alternative explanation appeared to be a high initial concentration of unstable intermediates in the formation of pentaborane(11). See also [107].

The composition of diborane decomposition products in a flow reactor was measured in real time by mass spectrometry as a function of temperature, dwell time, pressure, and surface : volume ratio [108]. One of the intermediates is borine  $\text{BH}_3$ . The decomposition of diborane at low pressures is dominated by surface effects [109].

The mechanisms by which gaseous boron hydrides so readily interconvert and build up into larger clusters are based on a complex series of interconversion reactions that are still not quite understood. Initial reaction rates have been studied mass spectrometrically to obtain rate equations, orders of reaction and energies of activation [110, 111]. Detailed and continuous product analysis for evolved  $\text{H}_2$  and all the volatile boranes formed, coupled with a study of co-thermolysis reactions of selected pairs of boranes gave further insight into the processes occurring. The thermolysis of  $\text{B}_2\text{H}_6$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_{11}$ , and  $\text{B}_6\text{H}_{10}$  and the effects of added  $\text{H}_2$  and the co-thermolysis of  $\text{B}_6\text{H}_{10}$  with alkenes was also examined. Ultraviolet (UV) absorption spectra and photolytic stability of eight volatile boranes and the reaction kinetics of  $\text{B}_6\text{H}_{10}$  photolysis were measured to support the kinetic studies.

Among the decomposition products of diborane, the less common boron hydrides  $\text{B}_3\text{H}_7$  and  $\text{B}_3\text{H}_9$  were observed as trace species over the mass range 34–38 amu [112]. Additional reactions lead to formation of tetraborane and pentaborane. Kinetic rates for a proposed five-step reaction leading to the desired pentaborane were tabulated, along with forward rate and reverse rate constants.

The rate constants for the association of two boranes to form diborane were investigated by computational chemistry using several different methods [113]. Two variations of a multi-step mechanism for diborane pyrolysis were presented: one was initiated by the step  $\text{B}_2\text{H}_6 \rightleftharpoons 2\text{BH}_3$  whereas the other began with  $2\text{B}_2\text{H}_6 \rightleftharpoons \text{B}_3\text{H}_9 + \text{BH}_3$  as the initial elementary step. Both reactions were 3/2 order in diborane and had the same activation energy (120 kJ/mol = 28.65 kcal/mol at 420 K). The rate-limiting step in the initial stage of diborane pyrolysis is the concerted formation and decomposition of  $\text{B}_3\text{H}_9$ . Another mechanism involved a  $\text{C}_2$ -symmetry penta-coordinate  $\text{B}_3\text{H}_9$  structure that, although an electronic minimum, was not a stationary point on the free energy path between  $\text{B}_2\text{H}_6 + \text{BH}_3 \rightarrow \text{B}_3\text{H}_7 + \text{H}_2$ .

### 2.3.3 Photolysis of Diborane

The photolysis of diborane has been studied as a potential method for obtaining higher boranes by a more selective method than thermal pyrolysis, which forms many useless byproducts [114]. The photolysis of diborane at 1849Å has been studied with UV light from a mercury vapor lamp [115]. The products were  $H_2$ ,  $B_4H_{10}$ ,  $B_5H_{11}$ , and, at low pressures, a  $-BH-$  polymer. A mechanism consistent with the kinetic data and suggested by the kinetic results of thermal and photosensitized decomposition of diborane was postulated. The  $B_5H_{11}$  was assumed to be formed from a dissociation of  $B_2H_6$  into  $2BH_3$ , the latter arising from an excited molecule. The  $B_4H_{10}$  and polymer were assumed to be formed from a dissociation of  $B_2H_6$  into  $\cdot B_2H_5$  and  $H\cdot$ , followed by radical recombination. The primary quantum yield of the step forming  $\cdot B_2H_5$  and  $H\cdot$  was about 10 times higher than that of the one forming  $2BH_3$ . Borane  $BH_3$  is an intermediate in the UV-facilitated deuterium-hydrogen exchange in diborane [116].

### 2.3.4 Reactions with Diborane

Diborane is a mildly endothermic compound that is only on the verge of stability at room temperature, as it slowly decomposes during prolonged storage. Pure diborane does not ignite spontaneously in dry air, but in pure oxygen it will autoignite immediately. Once ignited in air or oxygen, it burns with a bright green flame. In moist air it will hydrolyze and form boric acid fumes. It has a repugnant odor and can be detected by this if a leak should occur (see Toxicity of Diborane, Section 2.8).

Because of the high reactivity of diborane, the types of reactions that it can undergo are unusually numerous and varied, as summarized in a review paper on the reactions of diborane [117]. Reactions that would be of interest here are those with hypergolic oxidizers that lead to immediate ignition with short ignition delays.

#### 2.3.4.1 Diborane Reactions with Lewis Bases

Diborane is a highly reactive and versatile reagent that has a large number of applications. Its dominating reaction pattern is the formation of Lewis adducts with Lewis bases. The complexes with tetrahydrofuran (THF) and dimethyl sulfide are notable; both are liquid compounds that are popular reducing agents in organic chemistry and they are more easy to handle than diborane itself. In these 1:1 complexes, boron atom assumes a tetrahedral geometry, being bound to three hydride hydrogens and the Lewis base (THF or  $Me_2S$ ). The THF adduct is usually prepared as a 1:5 solution in THF. The latter is indefinitely stable when stored under nitrogen at room temperature. Diborane reacts with ammonia to form ammonia borane or the diammoniate of diborane (DADB), depending on the conditions used.

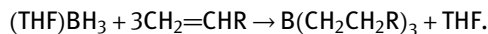
The reactions between diborane and Lewis bases are exothermic, like many other acid-base salt-forming reactions [118]. Part of the released energy goes into splitting diborane into two borine entities that then react with the amine that has a free electron pair. Depending on the affinity between borane and different amines, the amine com-

ponent of the adducts can be exchanged, forming new adducts. Section 7.4 contains detailed information on diborane-amine Lewis adducts.

The dissociation of diborane and the formation of adducts with trimethylamine or carbon monoxide imply the transitory existence of borine,  $\text{BH}_3$  [119].  $\text{H}_3\text{BCO}$  exists only in an equilibrium mixture with  $\text{B}_2\text{H}_6$  and  $\text{CO}$  in the presence of a large excess of  $\text{CO}$ . The carbon monoxide in  $\text{H}_3\text{BCO}$  is readily replaced by trimethylamine, which has a higher affinity to  $\text{BH}_3$  than  $\text{CO}$ .

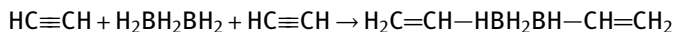
#### 2.3.4.2 Diborane Reactions with Alkenes and Alkynes

The addition of diborane in ether to alkenes is very rapid and almost quantitative. The addition of diborane to unsaturated compounds, is carried out by passing a current of diborane into an ether or THF solution of the alkene, the resulting trialkylborane being separated by distillation. The diborane-THF adduct is a useful organic synthesis reagent for *hydroboration*. *Hydroboration* is a widely used reaction where alkenes add across the B—H bonds to give trialkylboranes [120, 121]:



The reaction of diborane (diluted with hydrogen) and acetylene in a flow reactor gave a mixture of unidentified liquid alkylboranes [122]. The reaction of a diborane solution in THF with acetylene was exothermic and resulted in a white solid precipitate that was pyrophoric in air [123].

It was assumed that the reaction in the presence of an excess of acetylene would proceed as



The heat of combustion of the reaction product of diborane with acetylene, a yellow, viscous liquid with a gross formula of  $\text{B}_2\text{C}_4\text{H}_{10}$  and a molecular mass of 79.75 g/mol was 49511 kJ/kg = 3948 kJ/mol = 21300 BTU/lb [124].

Reactions of diborane with alkanes instead of alkenes take place only at higher temperatures and result in a medley of products of only limited commercial value [125].

#### 2.3.4.3 Diborane Reactions with Carboxylic Acids

Diborane can be used as a reducing agent comparable with the reactivity of lithium aluminum hydride. Diborane readily reduces carboxylic acids to the corresponding alcohols, whereas ketones react only sluggishly.

#### 2.3.4.4 Hydrolysis of Diborane

Diborane hydrolyzes with water to form hydrogen and boric acid [126]. This reaction with ubiquitous moisture in air can have very undesirable consequences.

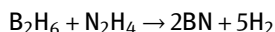
The heat of reaction of gaseous diborane with water to form gaseous hydrogen and a solution of boric acid has been measured by passing gaseous diborane through



two successive bubblers in a calorimeter [127]. The heat of reaction was  $-466.34 \pm 2.26$  kJ/mol ( $-111.46 \pm 0.54$  kcal/mol).

#### 2.3.4.5 Exothermic Reactions of Diborane

The reaction of diborane with hydrazine is strongly exothermic and results in spontaneous ignition, which would make it suitable as a hypergolic bipropellant reaction. The reaction is:



The molecular weight of the exhaust is very low, as it is mostly hydrogen gas with solid BN as a condensed phase. This allows a high specific impulse in a rocket. This combination can be used as a hypergolic rocket propellant. A similar reaction takes place between pentaborane and hydrazine.

These Lewis acid-Lewis base reactions are strongly exothermic and in the case of hydrazine can result in spontaneous ignition and a new type of bipropellant rocket propellant combination that does not involve traditional oxidizers [128].

#### 2.3.4.6 Reactions of Diborane with Oxygen

Diborane autoignites spontaneously in oxygen and occasionally in air. The kinetics of oxygen/diborane reactions will be discussed in a future volume on hypergolic propellants along with flame speeds and critical diameters.

### 2.3.5 Analysis of Diborane

#### 2.3.5.1 Assay of Diborane

The analysis of diborane in mixtures with other boranes and purity control of pure diborane can be done by gas chromatography [129, 130] or mass spectrometry [131]. For gas-liquid chromatography, Celite coated with paraffin oil or tricresyl phosphate was used as the stationary phase. Small amounts of ethane, which was present in diborane as an impurity, could be separated from diborane using this method.

Mixtures of boranes can be analyzed using IR spectroscopic methods. A method was developed for the determination of the four constituents, diborane, tetraborane, and dihydropentaborane in a relatively larger amount of pentaborane [132].

#### 2.3.5.2 Gas Detectors and Warning Monitors

Although diborane can be detected by its unpleasant odor at very low concentrations ( $2$  to  $4$  mg/m<sup>3</sup>), it is recommended to equip borane storage areas with recording gas detectors and monitors, which can trigger an audible alarm if the concentration exceeds a safe level. Gas detectors described in the literature respond to diborane as well as the higher boranes. A continuous, automatic coulometric titration system capable of determining diborane and decaborane in concentrations down to  $0.2$  ppm by volume was developed to monitor boranes in air. In this system, boranes scrubbed out of

air into a sodium bicarbonate/potassium iodide electrolyte were titrated with coulometrically generated iodine [133]. Spot tests may not be accurate enough to provide meaningful answers [134].

Instruments for monitoring atmospheres contaminated with boron hydrides used the non-specific reduction of triphenyl tetrazolium chloride by boron hydrides to form the red-colored formazan [135]. Metered air samples were drawn through filter paper or cloth tape impregnated with the reagent solution. The red color produced was measured by a differential reflectance photometer. The instruments were calibrated with diborane, pentaborane, and decaborane. The field model could detect 0.1 ppm of decaborane and 1.5 ppm of pentaborane, whereas the stationary, automatic instrument was capable of detecting 0.1 ppm of either compound.

## 2.4 Handling of Diborane

Equipment for the handling of diborane can be made from most common materials of construction, preferably stainless steel. The equipment has to be designed such that it can be evacuated and filled with inert gas before borane is admitted into the system. In particular, one must avoid intrusion of air into a system filled with diborane at sub-atmospheric pressure. Intrusion of air may cause explosions. It is therefore best practice to maintain a positive pressure at all times in diborane systems to prevent accidental intrusion of air.

Diborane is supplied as compressed gas in steel cylinders. However, it is recommended to store diborane at temperatures below 273 K (0 °C) to prevent decomposition. Remember that diborane has a positive enthalpy of formation, releasing energy when it decomposes. The rate of decomposition depends on the type of materials it is in contact with.

## 2.5 Materials of Construction for Diborane

The most comprehensive summary of recommended and compatible materials of construction for systems in contact with diborane is in the Diborane Handbook [30].

Radioactive tracer test methods that were successfully used to study metal corrosion in  $N_2H_4$  can possibly also be used for  $B_2H_6$  [136–138]. Materials compatibility tests with diborane were included in a series of tests that also tested hydrazine and oxygen difluoride. Metal bomblets of high pressure capability were fabricated from Ti-6Al-4V, Al-6061-T6, and CRES-304. Diborane was stored at 128 K (–230 °F) over a period of 3 months in these vessels. The measurement of minute amounts of hydrogen indicated that very little interaction between diborane and the metal containers was taking place. For instance, in the order of increasing hydrogen build-up over diborane were the metals 304 steel < 6061 aluminum < 6Al-4V titanium. Looking for leached

metals, no measurable quantity (less than 0.02 ppm) of titanium was taken up from a 6Al-4V titanium vessel by liquid diborane at 128 K (–230 °F), although a trace of aluminum was found.

Flow decay studies performed by TRW Systems Group examined clogging materials not only in diborane, but also in hydrazine, oxygen difluoride, and dinitrogen tetroxide, all in the category of space-storable propellants [139–141]. Approximately 100 flow tests were conducted flowing liquid diborane through two different size orifices. One was a 0.25 mm (0.010 in.) diameter and the other was a 0.51 mm (0.020-in.) diameter orifice, followed by a 2- $\mu$ m nominal to 10- $\mu$ m absolute rated filter and a 10- $\mu$ m absolute rated surface tension acquisition screen [142]. The diborane propellant used was both neat and doped and flowed under both isothermal and changing temperature (chilling) conditions. The dopants used were oxides of stainless steel, oxides of aluminum, low molecular weight hydrocarbons and finely divided Teflon. Temperature was varied from 222 to 122 K (–60 to –240 °F) for several experiments. No evidence for flow decay or blockage of any test section was found.

## 2.6 Fire-Fighting Equipment

Gaseous diborane that has leaked from a system and ignited accidentally cannot be extinguished with carbon dioxide fire extinguishers. It has been shown that diborane continues to burn in mixtures with carbon dioxide and air [143]. Tetrachloromethane, which was once used for fire extinguishers in electric installations, reacted vigorously with burning diborane under formation of soot and hydrogen chloride. If sand is poured on a diborane fire, the gas continues to burn on the top of the sand pile where it comes into contact with air. Bicarbonate powder, which is often used in dry chemical fire extinguishers, has a similar effect, i.e., it is ineffective against diborane fires. Somewhere it was recommended to fight gaseous diborane fires with water spray, but that was a bad choice. However, the hydrolysis of diborane is exothermic and develops hydrogen gas. If hydrogen gas mixes with air and reignites, it may explode, in particular in confined spaces. Burning liquid diborane should not be extinguished with water. A large amount of carbon dioxide snow may cool the puddle of burning liquid diborane to the point where the vapor pressure is lowered below the flammable limit in air.

## 2.7 Safety Properties of Diborane

Laboratories where diborane is handled must have adequate ventilation and work stations with well-drawing fume hoods. Diborane is both a toxicity and an explosion hazard [144]. A Hazard Ranking Score (HRS) was developed for hazardous chemicals, a composite index based on autoignition temperature, flammable range in air, the Na-

tional Fire Protection Association (NFPA) parameter, ionization potential parameter (for ease of detection), and trinitrotoluene (TNT) equivalency [145]. Chemicals were ranked on a scale from 0 (safe) to 100 (extremely hazardous). The NFPA diamond summarizes the hazard of chemicals through four characteristics: Health, Flammability, Instability or Reactivity, and Special Hazard. On a scale from 0 to 100, diborane received a HRS of 76.8, one of the highest of all chemicals evaluated. For comparison, pentaborane received an HRS of 64.4, and unsymmetrical dimethylhydrazine was ranked at 42.9. Triethylaluminum was ranked at 57.8. Safety procedures for the handling of diborane and the other boranes and alkylboranes have been established to prevent damage to personnel and facilities [146].

## 2.8 Toxicity of Diborane

All boranes are highly toxic and inhalation of borane vapors must be avoided. The toxic properties of all boron hydrides have been extensively investigated, in particular during the period in the past century when borane derivatives were actively proposed and evaluated as high-energy fuels for jet engines [147]. In the end, it was the toxicity of these compounds that prevented a more widespread application in military aviation. The mode of toxic action of diborane within the human body remained unknown for a long time. Primary effects of exposure involved the central nervous system. Prolonged exposure may also cause damage to both the liver and the kidneys. Skin contact with this compound caused severe chemical burns. The effects of ingestion are unknown. The most frequent cause of personnel exposure to boranes was accidental or negligent inhalation.

Within the human body the primary effect of exposure to diborane is pulmonary irritation. Prolonged exposure to diborane may also cause damage to both the kidney and the liver. Animal experimentation revealed that diborane compared with phosphene ranks below pentaborane and decaborane in its toxicological effects. A therapy of diborane poisoning must be aimed at the prevention of edema and assisting respiration until the lung tissue has healed. Additional animal studies revealed pulmonary edema (presence of serous fluid in lung tissues) and hemorrhage, tracheal and lung congestion, and liver and kidney damage. See also [27, 148–151].

### 2.8.1 Inhalation Toxicity of Diborane as Determined by Animal Exposure Tests

Diborane hydrolyzes in the respiratory tract and forms boric acid, which attacks the trachea and lung tissue. Higher boranes do not hydrolyze as rapidly as diborane and can penetrate deeper into the body. Higher boranes are predominantly toxic to the central nervous system. The acute inhalation toxicity LC<sub>50</sub> of diborane in rats for a 4-h inhalation period is about 50 ppm [152]. The necropsy revealed pulmonary edema and hemorrhaging. Tests with lower concentrations where rats were exposed repeatedly

6 h/day, 5 days/week to  $6 \text{ mg B}_2\text{H}_6/\text{m}^3$  resulted in lung damage after only 2–3 weeks of testing.

The acute toxicity of diborane by inhalation to dogs, rats, and guinea pigs was determined by exposing groups of six rats to diborane concentrations of 52 to  $492 \text{ mg}/\text{m}^3$  (47 to 446 ppm) for 1–4 h (Ct 10400 to  $37200 \text{ mg min}/\text{m}^3$ ) [153]. Animals were observed for 14 days after exposure, mortality was recorded, and pathological examination of animals dying as a result of gassing was performed. At the two highest concentrations, 317 and  $492 \text{ mg}/\text{m}^3$ , all animals died within 2 h after removal from gassing chamber. For chronic exposure (6 h/day, 5 days/week), two dogs and 18 rats were exposed to a diborane concentration of  $6 \text{ mg}/\text{m}^3$  (5 ppm) for periods of 3 weeks to 6 months. Pathological examination of exposed animals was performed. In another test with a lower concentration, 2 dogs, 20 rats, and 10 guinea pigs were exposed to diborane concentrations of  $0.8\text{--}1.7 \text{ mg}/\text{m}^3$  (1–2 ppm) for periods of 1–6 months. Exposure to  $6 \text{ mg}/\text{m}^3$  of diborane resulted in the death of two dogs after 10 and 25 exposures respectively. Seventeen out of 18 rats died during the course of 6 months' exposure.

The median LC50 lethal concentrations for 4-h exposure of rodents to diborane were 80 ppm for 5-month-old and 40 ppm for 2-month-old rats, and 29 ppm for mice [154]. Evidence from an additional experiment with the two different strains of rats suggested that the difference in LC50 values for the rats resulted in a greater measure from the age or weight difference than from the strain difference.

Diborane is rapidly hydrolyzed with release of heat and formation of boric acid in the tissue, but its toxic mechanism is more complex. Golden hamsters were exposed to 11 concentrations from 50 to 1000 ppm of diborane, which had been diluted with nitrogen, to diminish the explosive risk, and compressed air [155]. Each experiment continued until all animals in each group were dead and the time to death was recorded. The test animals quickly became inactive, then restless and increased activity was accompanied by loss of balance. Terminally, respiration decreased in depth and rate with prolonged periods of apnea. From exposures to concentrations up to 400 ppm, the lungs were bright red, and above this concentration dark reddish brown. Vascular congestion, edema, epithelial sloughing, alveolar blood cells and areas of atelectasis and emphysema were present in all animals, more markedly so above 400 ppm. The liver showed no microscopic changes, the kidneys, especially the glomeruli, showed some congestion. A time-concentration curve from 50 to 600 ppm showed progressive shortening of the mean exposure time for death, from 497 to 33 min, and also narrowing of the range around each mean. Above 600 ppm there were no further reductions in minimum, maximum or mean fatal exposure times.

The LC50 of diborane (and that of many other toxic chemicals) depends on the body weight and age of the test animals used [156].

A study of workers subjected to occupational, accidental exposure to diborane extended over a 5-year period (1956–1960) [157]. Among the total of 26 cases of acute diborane toxicity, 18 patients were seen primarily with respiratory involvement. Of

33 patients with subacute exposures, 8 became ill with chest pain. Acute diborane intoxication is associated predominantly with bronchopulmonary involvement, whereas acute decaborane and pentaborane toxicity is manifested primarily by neurological abnormalities. Two cases of acute diborane intoxication with pneumonitis were encountered. Chronic respiratory distress was present in two patients from recurrent diborane exposure and in one patient from repeated borane exposures on three occasions. The clinical symptoms including chest X-rays and the medical treatment were described in detail. The treatment of the acute exposures has been with oxygen by mask or with intermittent positive pressure breathing and the additional use of methocarbamol in many of the cases of pentaborane and decaborane intoxications. Severe neurologic impairment was managed by combined administration of meperidine hydrochloride (Demerol), promethazine (Phenergan), and chlorpromazine (Thorazine) intramuscularly. The chronic cases of diborane were treated with long-term bronchodilators, oxygen with intermittent positive pressure breathing at varying intervals, and expectorants.

Changes in bronchoalveolar lavage fluid (BALF) and blood were examined to assess the toxic effects of diborane on the lungs of rats that were exposed to diborane at 20 ppm (intended concentration) for 4 h (Phase I study) to evaluate time-course changes up to 14 days, and at 10 or 1 ppm to assess the dose-effect relationship after 3 days (Phase II study) [158]. BALF parameters were examined and biochemical and histopathological studies were also carried out. Alveolar capillary and alveolar cell damage were confirmed in rats exposed to 20, 10 or 1 ppm diborane for 4 h. A no-observed-effect level could not be established.

In order to clarify the acute and subacute toxicity of diborane at low concentrations, male ICR mice were exposed to diborane for 1, 2, 4, or 8 h at concentrations of 1 or 5 ppm (Phase I study), and for 6 h/day, 5 days/week, over 2 or 4 week at concentrations of 0.02 or 0.7 ppm (Phase II study) [159]. Hematological and biochemical tests, and histopathological examinations of the cornea, nasal mucosa, respiratory tract, and lung were carried out. All mice in both studies survived until they were sacrificed. In the Phase I study, lung weight increased significantly in mice exposed to 5 ppm of diborane for 8 h. In the Phase II study, slight infiltration of polymorphous neutrophil was observed mainly in the peribronchiolar region in mice exposed to 0.2 or 0.7 ppm of diborane for 2 or 4 weeks. In both studies, hematological and biochemical examinations failed to reveal any exposure-related changes. These results suggested that the no-observed-effect levels of diborane inhalation on the respiratory organs were 1 ppm in acute exposure, but 0.2 ppm of diborane inhalation for 2 or 4 weeks seems to be unsafe.

Diborane acute (15 ppm for 1, 2, 4, or 8 h) and subacute (5 ppm for 2 or 4 weeks) inhalation toxicity studies on mice resulted in a 50% kill after 4-h exposure to 31.5 ppm (interpolated) [160]. Body weight gain was suppressed and the lung weight was increased in diborane-exposed mice in both acute and subacute studies. In the acute study, diffuse bronchiolitis-like lesions developed in the lung in various degrees de-

pending on exposure time, which can be pathologically characterized as infiltration of inflammatory cells into the terminal bronchioles and surrounding alveoli, pulmonary congestion, and bleeding and/or edema. In the subacute study, lymphoid hyperplasia in the perivascular and peribronchial areas, and infiltration of macrophage and plasma cells into the alveoli was detected. In the mice exposed for 4 weeks, the lesions were more severe than in those exposed for 2 weeks, consisting of hyperplasia and desquamation of Clara cells. In the nasal cavity, mucous exudate and inflammatory cells suggested irritation caused by diborane. No significant changes were seen in hematological and serum biochemical examinations. In conclusion, the target organs of diborane inhalation poisoning are the respiratory organs, particularly the lung.

In order to investigate the sequential development of respiratory injuries following acute exposure to diborane, mice were exposed to 15 ppm diborane for 4 h and histopathological, hematological, and serum biochemical examinations were conducted immediately, 1 day, 3 days, and 2 weeks after exposure [161]. Changes progressed most severely on day 3, and lung weight significantly increased with the severity of the pulmonary lesions. At 2 weeks, few inflammatory cells in the bronchiolar lumen remained, and peribronchiolar thickening was disseminated at almost the same sites where inflammatory foci had been detected. The sequential changes in the histopathological observations from this study correlated very well with the clinical signs and symptoms of human acute diborane poisoning cases reported in the 1960s.

### 2.8.2 Olfactory Threshold of Boranes in Air

The median-detectable by odor concentration and the maximum allowable concentration for pentaborane, diborane, and decaborane are listed in Table 5. Diborane can be detected by odor at 2.8–3.6 ppm, but the recommended threshold limit value is 0.1 ppm [155].

**Table 5:** Olfactory threshold of boranes.

| Compound    | Median-detectable concentration |      | Maximum allowable concentration |
|-------------|---------------------------------|------|---------------------------------|
|             | mg/m <sup>3</sup>               | ppm  | ppm                             |
| Pentaborane | 2.5                             | 0.97 | 0.5                             |
| Diborane    | 3.7                             | 3.27 | 1.0                             |
| Decaborane  | 0.35                            | 0.07 | —                               |

Data source: [162]

### 2.8.3 Maximum Allowable Diborane Concentrations

The American Conference of Governmental and Industrial Hygienists revises and updates threshold limit values (TLVs) for hazardous chemicals every year. The 1993–1994 American Conference of Governmental Industrial Hygienists (ACGIH) TLV time-weighted average TWA, the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL), and the Occupational Safety and Health Administration (OSHA) permissible exposure limits (PEL) for diborane were all identical at 0.1 ppm (0.11 mg/m<sup>3</sup>). Such a low concentration is difficult to measure with the most common continuous analysis equipment. The olfactory threshold of diborane is around 3 ppm, and the human nose is thus not a reliable warning instrument. The NIOSH initially chosen immediately dangerous to life and health (IDLH) limit of 40 ppm was based on the statement by the ACGIH that Jacobson and Lawson (1962) [156] found the rat 4-h LC<sub>50</sub> to be 40 or 80 ppm, depending on the age or strain of rats used. The revised IDLH limit of 15 ppm was chosen on the basis of acute inhalation toxicity data in animals by Krackow (1953) [152]. Table 6 is a summary of diborane toxicity data used by NIOSH in their determination of the IDLH limit [163, 164].

**Table 6:** Lethal concentration (LC) data for diborane inhalation.

| Species | LC <sub>50</sub> (ppm) | LCLo (ppm) | Time   | Adjusted 0.5-h LC (CF) | Derived value | References |
|---------|------------------------|------------|--------|------------------------|---------------|------------|
| Rat     | 40                     | —          | 4 h    | 80 ppm (2.0)           | 8 ppm         | [6, 7]     |
| Mouse   | 29                     | —          | 4 h    | 58 ppm (2.0)           | 5.8 ppm       | [156]      |
| Rat     | 40–80                  | —          | 4 h    | 80–160 ppm (2.0)       | 8 ppm         | [156]      |
| Rat     | 159–181                | —          | 15 min | 126–143 ppm (0.79)     | 13–14 ppm     | [152]      |
| Dog     | —                      | 125        | 2 h    | 200 ppm (1.6)          | 20 ppm        | [165]      |
| Hamster | —                      | 50         | 8 h    | 125 ppm (2.5)          | 13 ppm        | [155]      |

Data source: [166]

### 2.8.4 Personnel Protective Equipment for Handling of Boranes

Candidate materials were screened as to their efficiency for removing boranes from contaminated air streams and to be used in gas masks and air filters [167]. The results of chemical tests and animal exposure studies showed that the following materials give temporary protection against: **(1)** diborane: chemical cartridge respirator charged with hopcalite; **(2)** pentaborane: chemical cartridge respirator charged with activated charcoal; **(3)** pentaborane and decaborane: a combination of silica gel and activated charcoal; and **(4)** diborane, pentaborane, and decaborane: a combination of silica gel, active hopcalite and activated charcoal.



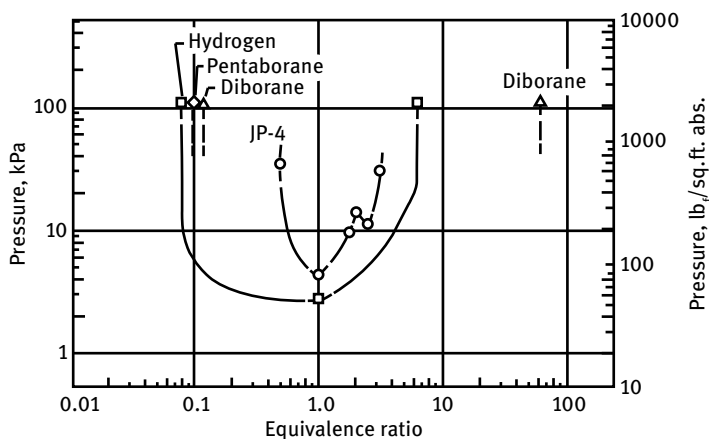
## 2.9 Fire Hazard of Diborane

### 2.9.1 Flammability Limits of Diborane

In general, mixtures of diborane in dry air do not ignite spontaneously at room temperatures, whereas pentaborane spontaneously ignites. No rich limit for pentaborane has ever been established because premature spontaneous ignition of the fuel-air mixture always occurred when attempting to obtain a rich mixture. The autoignition temperature and pressure of diborane in air is quite low, 408 K at 2.15 kPa (135 °C at 16.1 mm Hg) [168].

Because diborane in air may or may not autoignite over a wide range of compositions, it is difficult to determine the limits of flammability. Limits of flammability of diborane in air can be determined only with very lean and very rich mixtures.

Stoichiometric mixtures of diborane in air would contain 6.53 vol.-%  $B_2H_6$ . The lower limit of flammability in a tube measuring 5 cm in diameter at an initial pressure of 300 mm Hg is 0.8 vol.-% and the upper limit is 88 vol.-% [169]. The flammability limits of diborane and pentaborane as a function of fuel:air equivalence ratio and pressure are indicated in Figure 13 in comparison with hydrogen and JP-4 [170]. The rich limit for diborane occurred at an equivalence ratio of about 60, which is about eight times richer than the value for hydrogen, and about 15 times richer than for JP-4.

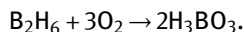


**Figure 13:** Flammable range of diborane and pentaborane in comparison with other fuels. (Reprinted and modified from [170], with permission from ©1958 Elsevier; permission conveyed through RightsLink.)

### 2.9.2 Explosive Limits in the Oxygen/Diborane System

Diborane gas does not always ignite spontaneously in dry air, but it has been reported that spilled liquid diborane ignited immediately in air. Because diborane and pure oxygen ignite spontaneously on contact, it is difficult to determine the limits of com-

bustibility at atmospheric pressure. Therefore, such measurements were conducted at very low partial pressures, but it is difficult to extrapolate the results to higher pressures such as those encountered in a rocket engine under sea-level starting conditions. It was found that oxygen/diborane gaseous mixtures ignite and explode only after the partial pressures of both reactants exceed a limited partial pressure [168, 171–173]. When diborane is ignited in air there is always a persistent odor characteristic of higher boron hydrides. Thus, it is very probable that in the heat of an explosion some of the diborane is converted to higher, more stable, hydrides and that the stoichiometry of the explosions does not correspond to the equation of complete combustion:



Explosions do occur within a range of composition and pressure, though only at temperatures at or above those corresponding to slow decomposition [168]. The latter strongly suggests sonic interaction with the decomposition process, but no mention is made of anything in the way of an induction period or of an oxygen-sensitized decomposition of diborane. Lower explosion limits were determined by slowly bleeding premixed gases into a clean reaction bulb until explosion occurred. Upper limits were observed by filling the cold reaction bulb to a higher pressure, bringing the thermostatted bath up around the bulb, and then slowly evacuating after a 1.5-min hold. Lower limits were found to be over a range from about 408 to 498 K (135 to 225 °C) for mixtures containing up to 33 vol-% diborane, but no limits could be found for 50% or richer mixtures. In another experiment, crossed streams of diborane and oxygen (presumably at 1 atm) were aimed into a mixing chamber, with gradually rising temperatures. Spontaneous ignition occurred only after the temperature was raised to 405 K (132 °C) or above.

## 2.10 Other Uses for Diborane

Diborane gas is used as a doping agent for the production of semiconductors. It is also an intermediate in the production of highly pure elemental boron for semiconductor production.

## 3 Pentaborane

There are two pentaboranes, pentaborane(9) and pentaborane(11). Pentaborane(9),  $\text{B}_5\text{H}_9$ , CAS RN [19624-22-7], is a volatile liquid that boils at 321 K (48 °C). In the pure state it is a water-clear colorless mobile liquid with a characteristic pungent and nauseating odor. Impurities, such as dissolved polymeric boron hydrides formed from decomposition of other lower boron hydrides present in commercial grade pentaborane, impart a slight yellow discoloration to the liquid if present in concentrations greater than 0.5 mass-%.

There are two known pentaboranes:  $B_5H_9$ , and  $B_5H_{11}$ . Both are colorless liquids. The name *pentaborane* alone is thus not specific as it could refer to either  $B_5H_9$  or  $B_5H_{11}$ . In most cases where no additional number designator is given, the data most often refer to pentaborane  $B_5H_9$ , also often called pentaborane-9 or pentaborane(9). Pentaborane(9) has an extremely disagreeable odor; it decomposes during storage over a long period of time to form hydrogen and a solid, colorless, non-volatile hydride. Pentaborane(11), dihydropentaborane,  $B_5H_{11}$  is less stable than  $B_5H_9$ . It dissociates at room temperature within 24 h to form hydrogen and polymeric solid deposits that stick to the container walls. When discussing properties of  $B_5H_{11}$ , one must always carry the full number designator with its name, pentaborane(11).

Pentaborane is insensitive to mechanical shock and is stable at room temperature under the blanket of an inert atmosphere. Pentaborane is an extremely hazardous rocket propellant owing to its high toxicity, high reactivity, and erratic pyrophoric or spontaneous ignition characteristics. When exposed to air, it may or may not ignite.

### 3.1 Production of Pentaborane

Pentaborane(9) is prepared by pyrolysis of diborane in the presence of excess hydrogen [32, 33, 103, 174]. A small amount of dihydropentaborane is formed along with the desired product, pentaborane(9) [175, 176].

It is difficult to control the diborane pyrolysis process so as to optimize the yields of pentaborane and decaborane and minimize the wasteful formation of unwanted, insoluble high-molecular mass boranes (“yellow solids”) [177].

The pyrolysis of diborane has been studied in single- and multi-pass flow systems to determine the optimal conditions for its conversion to pentaborane [178]. In a single-pass flow system the products consisted of tetraborane, dihydropentaborane ( $B_5H_{11}$ ), pentaborane ( $B_5H_9$ ), decaborane, and undesirable non-volatile solid hydrides. The most economical conversion of diborane to pentaborane was obtained under the following conditions: temperature  $523\text{ K} = 250^\circ\text{C}$ , flow rate  $400\text{ cm}^3/\text{min}$ . and ratio of diborane/hydrogen 1:5 when 15% of the diborane was converted into pentaborane, 4.4% to solid hydrides, and 80% recovered unreacted. In multi-stage reactors designed on the basis of single-pass experiments, the best yield of pentaborane was obtained in a 12-unit reactor operating at  $513\text{ K} = 240^\circ\text{C}$ , flow rate  $400\text{ cm}^3/\text{min}$ , and ratio diborane/hydrogen 1:5. Under these conditions, 57% of the diborane was converted into pentaborane, 14% to solid hydrides, and 29% was recovered unchanged.

Pentaborane(11) is an intermediate in the production of pentaborane(9). The production of pentaborane(11) was successfully scaled up to the point where about  $0.75\text{ cm}^3$  per min could be produced in runs lasting 10–20 min. by allowing diborane at 172 kPa (25 psig) to flow at 8 L/min. through a 16-L reactor maintained at  $393\text{ K}$  ( $120^\circ\text{C}$ ) [179].

## 3.2 Physical Properties of Pentaborane

### 3.2.1 Freezing Point, Boiling Point, and Critical Point of Pentaborane

The physical properties of pentaborane are summarized in Table 7.

**Table 7:** Physical properties of pentaborane(9).

| Property                       | SI units        | Other units | References |
|--------------------------------|-----------------|-------------|------------|
| Molecular mass                 | 63.126          |             | [53]       |
| Freezing point                 | 226.42 K        | −46.75 °C   | [60]       |
|                                | 226.41 ± 0.02 K | −46.74 °C   |            |
| Boiling point                  | 333.21 K        | 60.06 °C    | [180]      |
|                                | 331.5           | 58.4 °C     |            |
| Index of refraction $n_D^{24}$ | 1.4445          | —           | [60]       |
| Critical temperature           | 497 K           | 224 °C      | [1]        |
| Critical pressure              | 3.84 MPa        | 557 psia    | [1]        |

The melting point of pentaborane was found to be  $226.41 \pm 0.02$  K (−46.74 °C), and the purity as determined from fraction melted versus temperature curves was 99.9 mol-% [181].

### 3.2.2 Vapor Pressure of Pentaborane

The vapor pressure of pentaborane within the temperature range 226–298 K is given by the equation [181]:

$$\log p = 9.96491 - \frac{1951.14}{T} - 0.003688T,$$

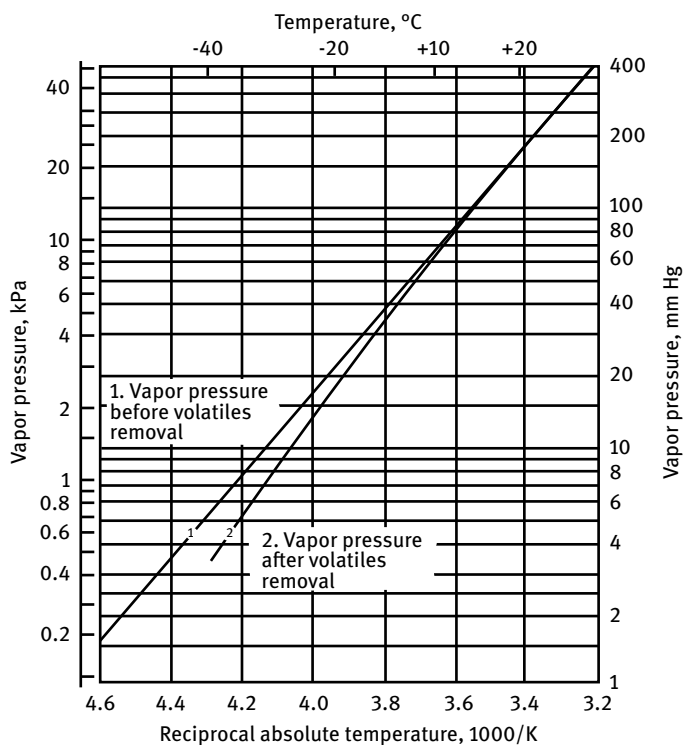
where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The vapor pressure between 298 and 348 K (25 and 75 °C) can be calculated from the following curve-fitted equation [182]:

$$\log p_D = 5.6352 - \frac{1384}{t + 250},$$

where  $p_D$  is the vapor pressure in psia and  $t$  is the temperature in °C. For higher temperatures from 348 to 398 K (75 to 125 °C), a slightly different equation was recommended:

$$\log p_D = 4.4803 - \frac{730}{t + 160},$$

where again  $p_D$  is the vapor pressure in psia and  $t$  is the temperature in °C. The vapor pressure of pentaborane as a function of temperature is illustrated in Figure 14. The vapor pressure changed a little after the volatiles were pumped off.



**Figure 14:** Vapor pressure of pentaborane as a function of temperature. (Reproduced and modified from [180].)

### 3.2.3 Density of Pentaborane

Density data for liquid pentaborane are listed in Table 8.

**Table 8:** Density of liquid pentaborane.

| Temperature |       | Density           |
|-------------|-------|-------------------|
| K           | °C    | g/cm <sup>3</sup> |
| 226.9       | -46.2 | 0.681             |
| 227         | -46.1 | 0.681             |
| 235.2       | -37.9 | 0.675             |
| 235.4       | -37.7 | 0.675             |
| 246.1       | -27   | 0.666             |
| 253         | -20.1 | 0.66              |
| 263.2       | -9.9  | 0.652             |
| 274.6       | 1.5   | 0.642             |
| 283.5       | 10.4  | 0.635             |
| 289.3       | 16.2  | 0.63              |

Data source: [52]

The data in Table 8 above can be described by the following equation:

$$\rho = 0.8674 - 0.00082T,$$

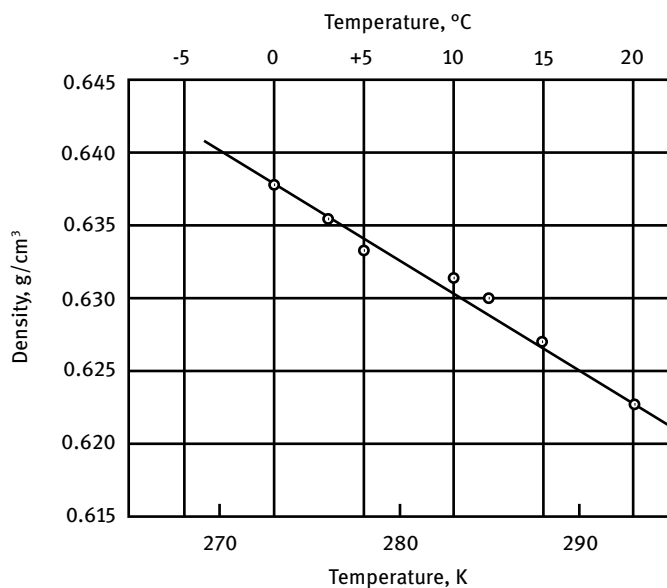
where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin. The density of liquid pentaborane from 288 to 388 K (15 to 115 °C) can also be described by the following equation:

$$\rho = 0.6404 - 0.000883t,$$

where  $\rho$  is density in  $\text{g}/\text{cm}^3$  and  $t$  is temperature in °C [183]. The density of liquid pentaborane between 265 and 298 K (−8 and +25 °C) was measured and curve-fitted by the equation:

$$\rho = 0.637 - 0.000733t,$$

where  $\rho$  is density in  $\text{g}/\text{cm}^3$  and  $t$  is temperature in °C [184]. The measured density at 273 K (0 °C) was  $0.637 \pm 0.002 \text{ g}/\text{cm}^3$ . The maximum deviation of any measured point from the curve-fitted curve was  $\pm 0.05\%$ . The raw density data points from which this curve-fitted equation was derived are shown in Figure 15.



**Figure 15:** Density of liquid pentaborane as a function of temperature. (Reproduced and modified from [180].)

Individual density data points reported by other sources are  $0.638 \text{ g}/\text{cm}^3$  at 273 K and  $0.623 \text{ g}/\text{cm}^3$  at 293 K [180].

3.2.4 Viscosity of Pentaborane

The viscosity of liquid pentaborane from 273 to 388 K (0 to 115 °C) can be described by the following equation:

$$\log \eta = \frac{344.75}{T} - 1.45851,$$

where  $\eta$  is the viscosity in centistokes, and  $T$  is temperature in K [183].

The viscosity of liquid pentaborane was measured over a range of temperatures from 245 to 313 K (–28 to 40 °C) (Table 9 and Figure 16). It was found necessary, however, to discard all values taken above 293 K (20 °C) as polymerization or some

Table 9: Viscosity of liquid pentaborane.

| Temperature |       | Density           | Viscosity  |
|-------------|-------|-------------------|------------|
| K           | °C    | g/cm <sup>3</sup> | millipoise |
| 232.2       | –40.9 | 0.6766            | 7.82       |
| 245.0       | –28.1 | 0.6662            | 5.29       |
| 246.5       | –26.6 | 0.6651            | 5.64       |
| 253.2       | –19.9 | 0.6598            | 5.14       |
| 258.4       | –14.7 | 0.6554            | 4.78       |
| 264.1       | –9.0  | 0.6509            | 4.45       |
| 269.0       | –4.1  | 0.6468            | 4.17       |
| 274.1       | 1.0   | 0.5426            | 3.94       |
| 279.6       | 6.5   | 0.6382            | 3.68       |
| 286.4       | 13.3  | 0.6326            | 3.42       |

Data source: [52]

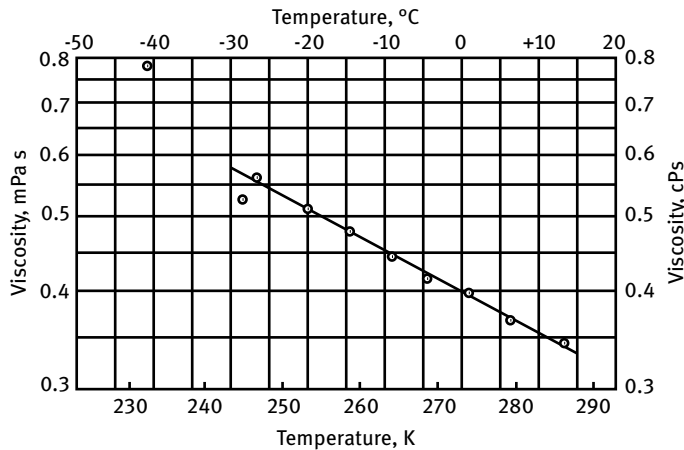


Figure 16: Viscosity of liquid pentaborane. (Reproduced and modified from [180].)

other phenomenon occurred above this temperature to increase the viscosity quite markedly.

The viscosity of liquid pentaborane, the same data as shown in Table 9 and Figure 4, as a function of temperature, can be expressed by the equation [52]:

$$\eta = 41.15 \times 10^{-5} \rho^{\frac{1}{3}} e^{\left(\frac{1024}{\rho T}\right)},$$

where  $\eta$  is the viscosity in Poise,  $\rho$  is the density in  $\text{g}/\text{cm}^3$ , and  $T$  is the temperature in kelvin. See also Wirth and Palmer for additional viscosity data [181].

### 3.2.5 Surface Tension of Pentaborane

The surface tension of pentaborane was measured within the range 234 to 303 K (−39 to +30 °C). An illustration of the surface tension data was already shown in Figure 6 (above in the diborane section). The numeric surface tension data are listed in Table 10.

The data in Table 10 can be fitted to a linear equation:

$$\sigma = (71.1 - 0.143T)\rho^{\frac{2}{3}},$$

where  $\sigma$  is the surface tension in  $\text{dyn}/\text{cm}$ ,  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin. Surface tension data from the same source are graphed in Figure 17.

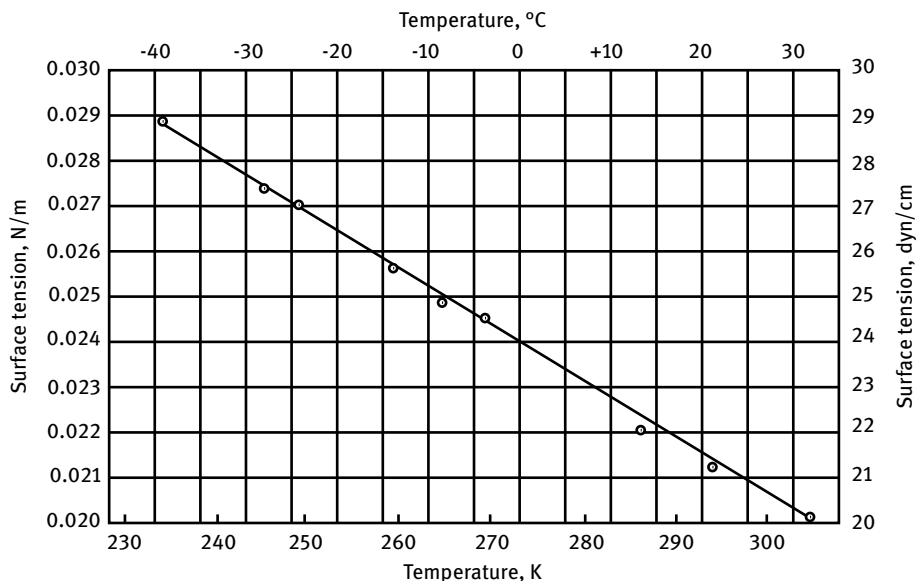
**Table 10:** Surface tension of pentaborane.

| Temperature |       | Surface tension |        |
|-------------|-------|-----------------|--------|
| K           | °C    | mN/m            | dyn/cm |
| 233.9       | −39.2 | 28.9            | 28.9   |
| 245.1       | −28   | 27.4            | 27.4   |
| 249.0       | −24.1 | 27.0            | 27.0   |
| 259.3       | −13.8 | 25.6            | 25.6   |
| 264.7       | −8.4  | 24.8            | 24.8   |
| 269.5       | −3.6  | 24.5            | 24.5   |
| 286.2       | +13.1 | 22.0            | 22.0   |
| 294.4       | +21.3 | 21.2            | 21.2   |
| 303.3       | +30.2 | 20.1            | 20.1   |

Data source: [52]

1 N =  $10^5$  dyn





**Figure 17:** Surface tension of pentaborane. (Reproduced and modified from [180], based on data from [181].)

### 3.2.6 Thermal Conductivity of Pentaborane

The thermal conductivity of liquid pentaborane from 294 to 314 K (70 to 105 °F) can be described by the following equation:

$$\kappa = 0.0874 - (0.0000684 \times t)$$

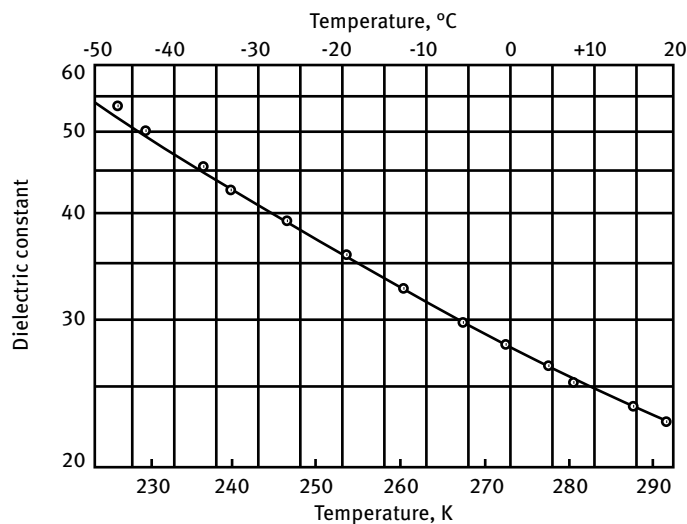
where  $\kappa$  is the thermal conductivity in  $\text{BTU h}^{-1} \text{ft}^{-2}$ , and  $t$  is the temperature in °F [182].

### 3.2.7 Heat Transfer to Liquid Pentaborane

Callery Chemical Co. conducted heat transfer experiments with liquid pentaborane at 1 to 3.4 MPa (145–495 psia), bulk temperatures 288 to 330 K (519–595°R), flow velocities of 6 to 19 m/s, and heat fluxes of up to  $326 \text{ W/cm}^2 = 78 \text{ cal cm}^{-2} \text{ s}^{-1}$  and discovered that pentaborane is not suitable as a coolant in regeneratively cooled rocket engines at high heat loads because the metal surface is quickly covered with solid deposits that reduce the heat transfer and in real life in a rocket engine would lead to burnout of the nozzle and chamber wall [185]. The wall temperature was limited to 394 K (710°R) [186].

### 3.2.8 Electric and Magnetic Properties of Pentaborane

In contrast to diborane, pentaborane is a highly polar substance, with an apparent dipole moment of the liquid varying between 3.37 Debye at room temperature to 4.54 Debye at the melting point. Within the temperature range 130–140 K there is a sluggish solid-solid phase transition that may be accompanied by the onset of free rotation in the solid [181]. The dielectric constant of pentaborane as a function of temperature is illustrated in Figure 18.



**Figure 18:** Dielectric constant of pentaborane as a function of temperature. (Reproduced and modified from [180].)

Nuclear (proton) magnetic resonance is the preferred way to identify the difference between hydrogen atoms in boron hydrides, depending on if they are part of a bridge structure or not. From nuclear magnetic resonance (NMR) data obtained for pentaborane, ethylpentaboranes, and  $^{13}\text{C}$ -enriched methylpentaboranes, estimates of differences in cage-boron charges and electronegativities can be made [187, 188]. The extra hydrogen that makes the difference between pentaborane(9) and pentaborane(11) is in a particularly labile (“anomalous”) position [189, 190].

### 3.2.9 Critical Point Parameters of Pentaborane

The critical temperature of pentaborane, calculated from theoretical calculations, is 500 K = 227 °C. In real life, pentaborane is unstable and would have decomposed a long time before reaching this temperature.

### 3.2.10 Solubility of Pressurant Gases

The solubilities of nitrogen, hydrogen, and helium in liquid pentaborane at 3.5, 7, and 10.5 MPa (500, 1000, and 1500 psig) from 303–423 K (30–150 °C) were reported [183].

### 3.2.11 Thermodynamic Properties of Pentaborane

The thermodynamic properties of pentaborane are listed in Table 11.

**Table 11:** Thermodynamic properties of pentaborane.

|                                 | SI units                                | Other units                                  | References |
|---------------------------------|-----------------------------------------|----------------------------------------------|------------|
| Molar heat capacity at 298 K    | 151 J mol <sup>-1</sup> K <sup>-1</sup> | 36.12 cal mol <sup>-1</sup> °C <sup>-1</sup> |            |
| Standard enthalpy of formation  | +42.8 ± 6.7 kJ/mol                      | +10.24 ± 1.6 kcal/mol                        |            |
| $\Delta H_f^{298}$ liquid       | +32.6 kJ/mol                            | +7.8 kcal/mol                                | [180]      |
|                                 | +32.38 ± 1.76 kJ/mol                    | +7.74 ± 0.42 kcal/mol                        | [191]      |
| Standard enthalpy of formation  | +73.2 ± 6.7 kJ/mol                      | +17.5 ± 1.6 kcal/mol                         |            |
| $\Delta H_f^{298}$ gaseous      | +62.8 kJ/mol                            | +15.0 kcal/mol                               | [180]      |
|                                 | +62.84 ± 1.67 kJ/mol                    | +15.02 ± 0.4 kcal/mol                        | [191]      |
| Heat of fusion at melting point | 6.14 kJ/mol                             | 1.468 kcal/mol                               |            |
| Heat of evaporation             | 30.5 kJ/mol                             | 7.28 kcal/mol                                |            |
| at 298 K = 25 °C                |                                         |                                              |            |
| Heat of evaporation             | 32.2 kJ/mol                             | 7.7 kcal/mol                                 | [180]      |
| at normal boiling point         |                                         |                                              |            |
| Enthalpy of phase change        | 1.8 kJ/mol                              | 0.430 kcal/mol                               |            |
| at 136.6 K = -136.5 °C          |                                         |                                              |            |
| Heat of combustion, liquid      | 4294 kJ/mol                             | 1026.4 kcal/mol                              | [180]      |

The heat of formation of pentaborane was determined by measurements of the heat of decomposition into amorphous boron and hydrogen in a calorimeter [90]. The heat of formation at 298 K (25 °C) from amorphous boron and hydrogen was +54.4 ± 1.6 kJ/mol (+12.99 ± 0.39 kcal/mol) for pentaborane (gas) and +23.8 ± 1.6 kJ/mol (+5.69 ± 0.40 kcal/mol) for liquid pentaborane.

The heat capacity of pentaborane vapor as a function of temperature can be calculated from the Shomate Equation:

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where  $C_p$  is the heat capacity in J mol<sup>-1</sup> K<sup>-1</sup>, A, B, C, D, and E are constants, and  $\tau$  is the absolute temperature in kelvin divided by 1000. The coefficients are listed in Table 12. The same coefficients (and others) are used for formulas expressing the standard enthalpy of formation of the vapor. These equations were curve-fitted from data covering ranges from 1500 to 6000 K. Of course at those temperatures pentaborane would long since have decomposed into the elements.

**Table 12:** Constants for vapor phase thermodynamic properties of pentaborane.

| Temperature range, K | 1500–6000 |
|----------------------|-----------|
| A                    | 302.0563  |
| B                    | 16.13748  |
| C                    | –3.133799 |
| D                    | 0.210327  |
| E                    | –64.33193 |
| F                    | –166.3023 |
| H                    | 73.22000  |

Data source: [53]

The vapor phase or liquid phase excess enthalpy above the standard enthalpy of formation  $\Delta H_f^{\circ 298}$  of pentaborane can be calculated from the Shomate Equation:

$$H^{\circ} - H_{298.15}^{\circ} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - H$$

where A, B, C, D, E, and F are constants, and  $\tau$  is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 12 (vapor phase) and Table 13 (liquid phase).

**Table 13:** Constants for thermodynamic properties of liquid pentaborane.

| Temperature range, K | 298–700   | 700–1500  |
|----------------------|-----------|-----------|
| A                    | 1777.865  | –50.81426 |
| B                    | –6068.264 | 647.6665  |
| C                    | 8247.877  | –432.3746 |
| D                    | –3628.812 | 101.0612  |
| E                    | –40.42346 | 9.259443  |
| F                    | –419.1448 | 55.06353  |
| H                    | 42.84416  | 42.84416  |

Data source: [53]

Additional physical properties of pentaborane are summarized in [180] and [192].

### 3.2.12 Optical, Electrical, and Magnetic Properties of Pentaborane

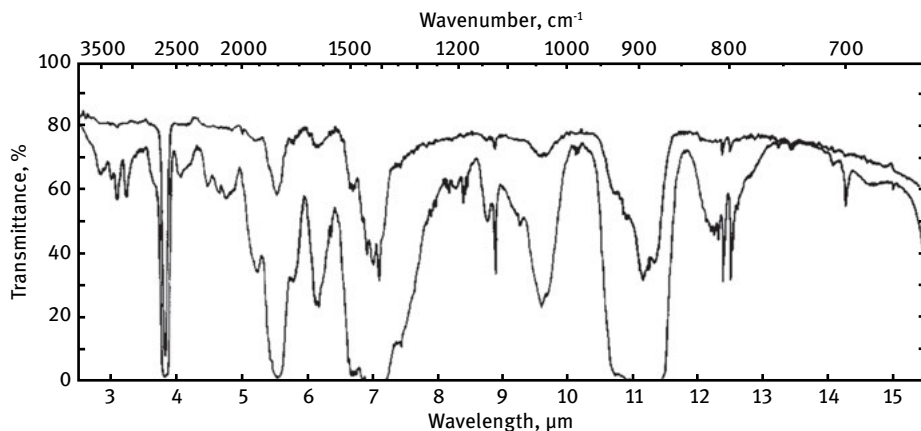
#### 3.2.12.1 Infrared Spectra of Pentaborane

The IR spectra of pentaborane are important for deriving thermodynamic properties and thermodynamic properties are important for calculating theoretical specific impulse of rocket engines with pentaborane. IR spectra of pentaborane are important for assuring the purity of the product and for identifying unwanted contaminants. Penta-

borane has been subjected to group theoretical reduction considerations to ascertain which overtone frequencies are IR active for this molecule. Ten bands were observed in the IR spectrum of liquid pentaborane. The pentaborane molecule is believed to belong to the  $C_{4v}$  symmetry group, as determined by electron and X-ray diffraction data. Assuming this symmetry point group and applying the usual group theoretical reduction methods, most bands could be assigned to fundamental vibrations [73]. On the basis of the data obtained, bond energies, bond distances, and force constants have been calculated for the B—H bonds in each of the three boranes.

Deuterated pentaborane can be prepared by catalytic exchange accelerated by a chromia-alumina catalyst between  $B_5H_9$  and excess deuterium at room temperature [193]. The vibrational modes of several fundamentals in the IR absorption spectra of gaseous  $B_5H_9$  and  $B_5D_9$  were identified by consideration of B isotopic band structure and the frequency shift on deuteration and assignment of the fundamental frequencies was possible.

The IR and the Raman spectra of liquid deuterated pentaborane, which was prepared by the catalytic exchange of normal pentaborane and deuterium, were measured and the polarization of the stronger Raman lines was determined [194] (Figure 19). Spectra of  $B_5H_9$  were recorded at two different pressures, 12 mm Hg (top trace) and 150 mm Hg (bottom trace). Based on these spectra, assignments of the vibrational frequencies of normal and deuterated pentaborane could be made, and the correlation of normal frequencies in deuterated and non-deuterated molecules was discussed. The thermodynamic functions of normal pentaborane vapor were calculated for the temperature range 296 to 2500 K from these assignments.



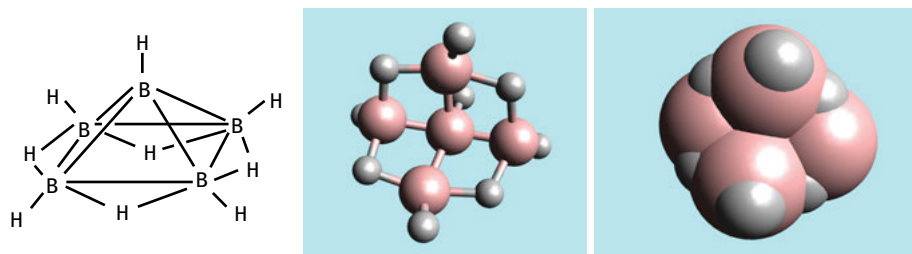
**Figure 19:** Infrared spectrum of pentaborane in the NaCl region. (Reproduced and modified from [194].)

### 3.2.12.2 Raman Spectra of Pentaborane

The Raman spectra of  $B_5H_9$  were recorded for the gas and liquid phases [195]. Moderately high resolution IR spectra of the gas phase were also recorded and then combined with the Raman data to assign natural isotopic data and verify previously proposed vibrational assignments [196].

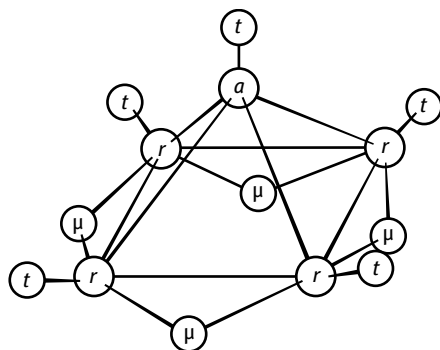
### 3.2.13 Molecular Structure of Pentaborane

Pentaborane is a symmetric top molecule with a large dipole moment of 2.13D in the direction of the symmetry axis. The pentaborane structure has five atoms of boron arranged in a square pyramid. Each boron has a terminal hydride ligand and four hydrides span the edges of the base of the pyramid (Figure 20). Note that each of the three images in Figure 20 shows the molecule from a different angle of view. The ball-and-stick diagram in the center shows the molecule “from below” with the apex pointing away.



**Figure 20:** Molecular structure of pentaborane(9).

Sometimes the position of the boron and hydrogen atoms are designated as **apical**, **ring**, **terminal**, or **bridge** by using the subscripts  $a$ ,  $r$ ,  $t$ , or  $\mu$ , respectively (Figure 21). The complete structure is determined by seven structural parameters.



**Figure 21:** Atom position designations in pentaborane(9).

The structure of pentaborane(9) has been investigated by XRD, electron diffraction and microwave absorption spectra. However, in all these studies the hydrogen positions were obtained only with large uncertainties. The investigation of the rotational spectra of the deuterated isotopes provided a more accurate method of determining the bridge hydrogen structure [197]. The microwave spectra of 15 isotopic species of  $B_5H_9$  were investigated. The complete molecular structure was determined from these data by assuming  $C_{4v}$  symmetry:  $B_r \cdots B_r = 1.803 \pm 0.002 \text{ \AA}$ ;  $B_r - B_a = 1.690 \pm 0.002 \text{ \AA}$ ;  $B_r - H_t = 1.186 \pm 0.002 \text{ \AA}$ ;  $B_a - H_a = 1.181 \pm 0.002 \text{ \AA}$ ;  $B_r \cdots H_\mu = 1.352 \pm 0.004 \text{ \AA}$ ;  $\angle B_a - B_r - H_t = 128.72 \pm 0.55^\circ$ ;  $\angle \phi = 193.10 \pm 2.9^\circ$ . Evidence is given of a large vibrational amplitude for the bridge hydrogens.

A study of free electron distributions in a hemispherical box and a hemispherical shell, and a study of simplified LCAO models for  $B_5H_9$  and  $B_5H_{11}$  indicated an uneven charge distribution in these unsymmetrical molecules [198].

The dipole moment of pentaborane(9) is  $2.13 \pm 0.04$  Debye [199]. The microwave spectra gave B—B distances of  $1.69 \pm 0.02 \text{ \AA}$  (ring-apex) and  $1.80 \pm 0.01 \text{ \AA}$  (ring-ring).

On cooling through the 136.7 K phase transition, the tetragonal unit cell of  $B_5H_9$  transforms to a tetragonal cell whose  $a$  and  $b$  axes correspond to the  $ab$  diagonals of the high temperature cell, and the  $c$ -axis is doubled [200]. The low temperature cell contains eight molecules,  $a = b = 10.201(5) \text{ \AA}$ ,  $c = 9.996(5) \text{ \AA}$ , space group  $P4_1$ .

### 3.3 Chemical Properties of Pentaborane

At a time when the US Government purchased pentaborane for high-energy fuels (mostly air breathing fuels) research and development, the procurement of pentaborane was covered by Military Specification MIL-P-27403(USAF) – Propellant, Pentaborane [201].

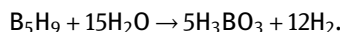
This specification required an assay of at least 99 mass-% (determined by a freezing point method), limited dissolved solids to a maximum of 1.1 mass-%, and specified a thermal stability of at most 1.5 mass-% decomposing in a vacuum evaporation apparatus. Some of the chemical properties of pentaborane are summarized in a very useful summary report [180].

#### 3.3.1 Reactions of Pentaborane

One would think that dinitrogen is an inert gas and it should be possible to use nitrogen as a pressurant gas for expulsion of pentaborane without any undue interaction. However, apparently at higher temperatures pentaborane will react even with dinitrogen, which until now was always considered an inert gas.

### 3.3.1.1 Hydrolysis of Pentaborane

Pentaborane does not hydrolyze as rapidly as diborane. Based on mass-spectrometric analysis of reaction products, the first step in the hydrolysis may be the removal of a borine  $\text{BH}_3$  from the cluster of  $\text{B}_5\text{H}_9$  [202]. Water and pentaborane are not miscible and the hydrolysis would take place only at the interphase of the two layers. If the two layers are dissolved in a mutually miscible solvent like dioxane, the hydrolysis reaction becomes very fast, near-catastrophically fast [203]:



The hydrolysis proceeds only at elevated temperatures (358 to 423 K = 85 to 150 °C) with measurable speed. Kinetic investigations have shown that in the presence of an excess of water, the reaction then proceeds as a first-order reaction with respect to pentaborane [204]. Pentaborane hydrolyzes with water to form hydrogen and boric acid [126, 205]. If an accidental spill of pentaborane ignites, the question is whether water is a suitable extinguishing agent or whether it will make matters worse by releasing hydrogen gas, which of course will burn too.

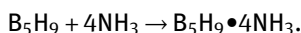
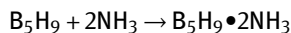
### 3.3.1.2 Reactions of Pentaborane with Lewis Bases

Reactions of pentaborane with amines lead to destruction of the pentaborane molecule and formation of fragments. At 195 K (−78 °C) pentaborane adds  $\text{Me}_3\text{N}$  to form  $\text{B}_5\text{H}_9 \bullet 2\text{Me}_3\text{N}$ , which on heating under vacuum will partially dissociate to the original components and partially decompose to  $\text{BH}_3\text{N}(\text{CH}_3)_3$  and  $(\text{BH})_x$  [206]. Bases strong enough for irreversible attachment to  $\text{BH}_3$  “steal”  $\text{BH}_3$  from  $\text{B}_5\text{H}_9$  [207].

Ammonia or methylamine, reacting with pentaborane(9) during sudden heating at 433–453 K (160–180 °C), can displace as much as 0.25 mol of  $\text{B}_2\text{H}_6$  per mole of  $\text{B}_5\text{H}_9$  consumed [208]. The reason for such anomalous behavior, whereby strong molecular bases displace a strong Lewis acid, is to be found in a series of reaction steps whereby the base first disrupts the  $\text{B}_5\text{H}_9$  to combine with the  $\text{B}_4\text{H}_6$  and  $\text{BH}_3$  fragments. Next, the  $\text{BH}_3$  complex makes borazane and hydrogen, then borazane accepts a second  $\text{BH}_3$  to make a  $\mu$ -aminodiborane, which finally dissociates into diborane and the borazane trimer, the latter at last going to the corresponding borazine.

These Lewis acid-Lewis base reactions are strongly exothermic and in the case of hydrazine can result in ignition and a new type of bipropellant rocket propellant combination that does not involve traditional oxidizers [209–211].

Pentaborane reacts with ammonia to form salt-like compounds, which are stable at room temperature [212]:





### 3.3.1.3 Reactions of Pentaborane with Strong Bases

Pentaborane is a weak acid and forms salts with potassium hydroxide, resulting in deprotonation [213, 214]. The potassium pentaborate salt is soluble in tetrahydrofuran.

### 3.3.1.4 Reactions of Pentaborane with Organic Compounds

Ethylene adds to pentaborane in an autoclave in the presence of aluminum chloride as a Friedel-Crafts catalyst, forming ethylpentaborane [215, 216]. Friedel-Crafts ethylation of pentaborane-9 with ethylene/aluminum chloride gave only monoethylpentaborane and there was no evidence of polysubstitution. Better yields of ethylpentaborane were obtained with lower ethylene pressures. The ethylpentaborane could be separated from unreacted pentaborane by fractionated distillation under a small positive pressure of nitrogen.

The Friedel-Crafts alkylation of pentaborane with ethylene/aluminum chloride in a heated Nimonic autoclave gave yields of 20 to 35% at 323 K (50 °C) with an ethylene pressure of 552 kPa (80 psi) [216–218].

The hydrogen atom at the apex of the pentaborane-9 molecule can be replaced by alkyl groups by reaction with alkenes or alkyl halides in the presence of Lewis acids such as  $\text{AlCl}_3$ ,  $\text{FeCl}_3$  or  $\text{SnCl}_4$  [219]. The mechanism appeared to be an electrophilic substitution. The following alkylpentaboranes have been prepared and characterized: 1-methylpentaborane, 1-ethylpentaborane, 1-isopropylpentaborane, and 1-*sec*-butylpentaborane.

The reaction of olefins with pentaborane-9 at 423 K (150 °C) gave the alkyl derivatives of pentaborane-9, with substitution at a base boron atom [220, 221]. *n*-Butyl-, *sec*-butyl-, isobutyl-, and ethylpentaborane could be prepared in this way. The direction of addition on the olefins, the position of substitutions on pentaborane-9, and the reactivity of the olefins were in accord with the expectations of a reaction involving a nucleophilic attack of olefins on pentaborane-9.

The reaction of pentaborane with acetylene leads to closo-carboranes [222]. See also [223].

### 3.3.1.5 Slow Oxidation of Pentaborane

Intermediates of the autoignition reaction can be trapped and identified if the reaction is slowed down by dilution with inert gases or carried out at lower temperatures and lower pressures. An intermediate compound of the slow oxidation of pentaborane had the composition  $\text{B}_2\text{H}_2\text{O}_3$  in which each H atom is attached directly to a B atom and in which the 2 B atoms exist in identical configurational environments [224].

The heat evolved during slow oxidation of pentaborane pyrolyzes unreacted pentaborane and forms a little diborane in a reversal of the traditional pentaborane synthesis. When dry air was admitted to a vessel containing pure pentaborane at 298 K and 6.7 kPa, partial oxidation took place and diborane, hydrogen and a white solid were formed [225]. The slow oxidation of pentaborane is accompanied by bluish light emission preceding a flame reaction [226].

A mass spectrometric technique was used to follow the stoichiometry of the slow oxidation of  $B_5H_9$  as oxygen was slowly added to a borane sample at pressure between (5 and 20 mm Hg) [227]. In the  $O_2/B_5H_9$  reaction boroxine ( $H_3B_3O_3$ ) was formed initially and further oxidation gave  $H_2B_2O_3$ . Results of isotope distribution experiments indicated that the precursor to  $H_3B_3O_3$  (and  $H_2B_2O_3$ ) in the  $O_2/B_5H_9$  reaction was probably HBO or  $H_2BOH$ . See also [228] and [229].

Rates of pyrolysis of pentaborane and ignition induction times of oxygen/pentaborane/argon mixtures were measured in a shock tube at 520 to 860 K [230]. The effects of pressure, mixture ratio, and a variety of additives on the flame speed of the pentaborane-air system were studied employing a low-pressure burner. Pyrolysis of pentaborane was shown to be the rate-controlling step in the ignition process, as induction times were independent of oxygen concentration. Butadiene, toluene, and benzene were most effective in reducing flame speed and in lengthening ignition induction times. The order of inhibitor effectiveness on the flame reaction bears a close resemblance to that of the air/hydrogen and air/diborane flame systems, indicating that flame propagation in the air/borane system may proceed by a mechanism resembling, to some extent, that of the oxygen/hydrogen where inhibitors function by removal of hydrogen atoms from the pre-flame zone.

### 3.3.2 Thermal Stability of Pentaborane

Pentaborane lacks thermal stability and at temperatures between 358 and 475 K (85 to 202 °C) decomposes in the course of a few days to hydrogen, a non-volatile solid boron hydride, and traces of decaborane [231, 232].

The thermal stability of  $B_5H_9$  was determined as the rate of pressure increase in 800-mL test cylinders filled to 7% ullage and was stored at different temperatures. In storage containers with insufficient ullage, for instance 7% ullage, the decomposition product pressure can increase to 8.27 MPa (80 atm = 1200 psig) within 3 h at 423 K (150 °C), 28 h at 398 K (125 °C) or 360 h at 373 K (100 °C), which may result in rupture of the vessel, depending on its pressure rating [233]. At 439 to 489 K (166 to 216 °C) the decomposition of pentaborane proceeded quite rapidly. At long hold times and high temperatures the predicted percentage decomposition was higher than the observed percentage decomposition. Investigations were made to determine the effects of added dihydrogen and  $B_{10}H_{14}$  on pentaborane thermal stability after 138 h, at a temperature of 383 K (110 °C) and an ullage of 52%. The addition of 26.8 mol-% dihydrogen (approximately 1175 psig) for one test and 9.2 mol-%  $B_{10}H_{14}$  for another test resulted in 6.5 and 8.1% decomposition respectively, whereas a blank  $B_5H_9$  control test resulted in 10.3% decomposition.

The formation of polymeric boron hydrides during storage of pentaborane must be kept at a minimum as precipitation of these solids tends to clog filters and valves during transfer or injector orifices in a rocket chamber. It was found that these non-volatile solids precipitate out at a concentration of 3 mass-% at 383 K (110 °C) and

1.3 mass-% at 80 °C. Dissolved solids in commercial grade pentaborane have been found as high as 1.3 mass-%. Approximately 25% of the precipitated solids may be decaborane.

The pyrolysis of pentaborane(9) was studied at 475, 486.6, and 501 K (202, 213.5, and 228 °C) at a pressure of about 5.33 kPa (40 mm Hg) and at 477 K (204 °C) at a pressure of about 10.7 kPa (80 mm Hg) [234]. The reaction was found to be first order and rate constants were  $1.68 \pm 0.03 \times 10^{-6}$ ,  $1.79 \pm 0.05 \times 10^{-6}$ ,  $2.62 \pm 0.2 \times 10^{-6}$ , and  $8.23 \pm 0.1 \times 10^{-6} \text{ s}^{-1}$  at 475, 477, 486.6, and 501 K (202, 204, 213.5, and 228 °C) respectively. The activation energy was  $130 \pm 6.3 \text{ kJ/mol}$  ( $31.1 \pm 1.5 \text{ kcal/mol}$ ). These results agreed relatively well with the values reported by Cheney et al. [235]. They obtained first-order rate constants of  $0.376 \times 10^{-2}$ ,  $1.73 \times 10^{-2}$ ,  $4.18 \times 10^{-2}$ , and  $11.6 \times 10^{-2} \text{ h}^{-1}$  at 467.6, 489.1, 501.6, and 516.1 K (194.5, 216, 228.5, and 243 °C) respectively, and an activation energy of  $142 \pm 4 \text{ kJ/mol}$  ( $33.9 \pm 1 \text{ kcal/mol}$ ). Converting the rate constants to common units gave rate constants of  $4.8 \times 10^{-6}$  and  $1.16 \times 10^{-5} \text{ s}^{-1}$  at 489.1 and 501.6 K (216 and 228.5 °C) respectively, which are approximately 20% larger than the rate constants reported by [234].

A mass spectrometer with an integral flow reactor was used to study the pyrolysis of  $\text{B}_5\text{H}_9$  and  $\text{B}_5\text{H}_{11}$  at very low pressures and to measure their molecular beam mass spectra [236]. The room-temperature molecular beam mass spectrum of  $\text{B}_5\text{H}_9$  agreed with the spectrum obtained with an instrument with a conventional ion source. The molecular beam mass spectrum of  $\text{B}_5\text{H}_{11}$  differed slightly from the conventional, but there were indications of contributions to the latter by pyrolysis products formed in the ion source. A study of the pyrolysis of  $\text{B}_5\text{H}_{11}$  has shown  $\text{B}_4\text{H}_8$  and  $\text{BH}_3$  to be decomposition products. No triborane species could be observed. Diborane and pentaborane(9) were seen, but no higher boranes could be detected under these experimental conditions.

The kinetics of homogeneous thermal decomposition of pentaborane(11) were investigated by a mass-spectrometric technique in the pressure range 1.75–10.5 mm Hg and temperature range 313–423 K (40–150 °C) and found to proceed by a first-order initial-rate gas-phase process. The main volatile products were dihydrogen, diborane, and a little pentaborane(9) [237]. In the thermolysis of  $\text{B}_5\text{H}_{11}$  there was a dramatic change in product distribution, but the order, activation energy, and initial rate of disappearance of  $\text{B}_5\text{H}_{11}$  were all unaffected by the presence of added dihydrogen [238].

The thermal stability of the various boranes has been ranked as follows:  $\text{B}_5\text{H}_9$  more stable than  $\text{B}_2\text{H}_6$  by a factor of 100;  $\text{B}_2\text{H}_6$  more stable than  $\text{B}_5\text{H}_{11}$  by a factor of 10,  $\text{B}_5\text{H}_{11}$  more stable than  $\text{B}_4\text{H}_{10}$  by a factor of 5.

### 3.3.3 Photolysis of Pentaborane

It was hoped that photolysis of pentaborane would lead to some other, more energetic or heretofore unknown boranes, but in reality the photolysis of pentaborane leads to a mix of several boranes that are difficult to separate. Pentaborane vapor at 20 mm Hg

was illuminated with the UV light from a hydrogen lamp. The rate of conversion was measured by IR absorption and an increase in total pressure owing to evolved hydrogen. The rate of conversion decreased with time as it approached a stationary equilibrium owing to reversible reactions. Added hydrogen would retard the reaction [239].

Illumination of  $B_5H_9$  in the gas phase by ArF laser radiation at 193 nm caused primary dissociation into  $BH_3$  and  $B_4H_6$  [240]. A reactive intermediate  $B_5H_7$ , upon addition to  $B_5H_9$ , forms  $B_{10}H_{14}$  and  $B_{10}H_{16}$ .  $B_6H_{10}$  formation as well as polymerization may proceed via the intermediate  $B_8H_{12}$ , which arises from the dimerization of  $B_4H_6$  fragments. See also [114] and [241].

### 3.3.4 Analysis of Pentaborane

#### 3.3.4.1 Physical Methods for Analysis of Pentaborane

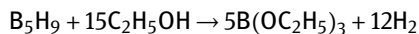
For quick-look data, the density, vapor pressure, and freezing point of pentaborane(9) may all be determined in a quality control laboratory with one basic transfer apparatus and test vessels of 1–5 mL in volume. These physical properties plus a determination of dissolved and total solids (hydrolysis products) are sufficient to certify that the pentaborane is suitable for use in a rocket engine but may not be sufficient if pentaborane is to be used for the synthesis of other fuels [180]. The freezing point depression in the presence of contaminants is an indication of the purity of a sample of pentaborane. The purity of  $B_5H_9$  could be determined within 10 mol-% on sample sizes of 2–10 mL. One of the possible contaminants is decaborane, which forms as a byproduct during the production of pentaborane from diborane.

#### 3.3.4.2 Methods for Analysis of Assay and Contaminants in Pentaborane

Gas chromatographic methods are quite suitable for the analysis of boron hydrides [129, 130].

Mixtures of pentaborane with other boron hydrides can be analyzed by IR-spectrometric methods, as the spectra of individual boranes are pretty well known. A method was developed for the determination of the four constituents, diborane, tetraborane, and dihydropentaborane in a relatively larger amount of pentaborane [73, 132]. The infrared spectrum of pentaborane was obtained from 2 to 15  $\mu\text{m}$  at 100 mm Hg pressure, and the concentrations of diborane, tetraborane, pentaborane, and dihydropentaborane were determined based on their absorption at specific wavelengths: 4.05, 4.65, 5.54, and 6.15  $\mu\text{m}$ . Base line points are chosen at 3.50 and 5.92  $\mu\text{m}$ . The spectrum must be obtained rapidly to prevent decomposition. The equations permit the direct calculation of the pressure in mm Hg for each boron hydride from measurement of the absorption at four wavelengths, 4.05, 4.65, 5.54, and 6.35  $\mu\text{m}$ . At a total pressure of 100 mm Hg, the minimum detectable amount of diborane was about 0.2 mol-%, for tetraborane it was 0.6 mol-% and for dihydropentaborane it was 0.7 mol-%.

For the determination of assay of pentaborane samples, pentaborane can be reacted with ethanol and the hydrogen gas evolved can be measured gas volumetrically [242]:



This reaction has also been proposed for the disposal of surplus pentaborane. See also [243].

### 3.3.4.3 Detection of Pentaborane in Workroom Air

Work room air must be monitored to ensure a safe working environment where pentaborane is used and stored. The instruments already described in the diborane section can also be used for monitoring work room air for traces of pentaborane [133, 135]. These instruments are more sensitive toward pentaborane than diborane.

Pentaborane and decaborane attack the central nervous system. A small hand-operated monitoring instrument sensitive to 0.4 ppm of pentaborane was developed, and was expected to be useful for detecting leaks or re-checking before re-entry after spillage and cleanup [244]. An electrical instrument that showed great promise was expected to detect concentrations below 0.1 ppm and possibly as low as 0.01 ppm.

One of the electrochemical pentaborane detection instruments was using a membrane electrode in a potentiometric circuitry. A feasibility study was made on the use of a membrane electrode for the detection and measurement of pentaborane in air [245, 246]. A number of plastic films were tested, but none was found to be sufficiently permeable to provide a sensitive and practical sensing device. Instead, a method was proposed to first convert pentaborane to hydrogen, which may then be sensed with the membrane electrode.

A direct reading, automatic and temperature-insensitive instrument for the detection and recording of pentaborane or any other borane in air was sensitive down to and below 0.1 ppm using the flame-emission principle [247]. A small hydrogen flame takes on a typical greenish cast in the presence of boranes, the radiation intensity being proportional to the borane concentration. A multiplier phototube with an appropriate interference filter would detect this colored light and the amplified current at the multiplier anode is sent to an amplifier.

Pentaborane reacts quite differently from diborane or decaborane when it has to be analyzed. It does not form a colored complex with quinoline as decaborane would. It does not hydrolyze as quickly as diborane. It does not react quickly with caustic solutions. Triphenyltetrazolium chloride gives colored products with pentaborane or decaborane. Instead of bubbling air that needs to be analyzed through impingers, pentaborane can be adsorbed on activated charcoal and then desorbed for analysis [248]. Several methods for the analysis of pentaborane vapors in workroom air were described in [180].

### 3.4 Materials of Construction for Pentaborane Equipment

Pentaborane installations can be made from anodized aluminum, brass, copper, lead, or stainless steel. The following non-metallic materials were listed as compatible: dry asbestos, polyethylene, Hycar, Garlock 230, Kel-F, and Teflon. Materials of construction that qualified as acceptable for contact with HEF fuels (alkylboranes) are also acceptable for contact with pentaborane. Very detailed summaries on the design of pentaborane installations are provided in the two reports by Rocketdyne [249, 250] and in some NASA reports [251].

### 3.5 Handling of Pentaborane

There are numerous publications, operating procedures and recommendations for the safe handling of pentaborane at rocket test sites and launch sites [252, 253]. A series of small-scale spill tests for the establishment of safe-distance values for the storage of the propellants was performed using propellant quantities not exceeding 2.5 kg (5 lb<sub>m</sub>) [254, 255]. Propellant quantities used on other large-scale tests conducted in the same test series ranged from 61 to 815 kg (135 to 1800 lb<sub>m</sub>) of total propellant. Similar spill tests were performed with N<sub>2</sub>H<sub>4</sub>, NTO, and ClF<sub>3</sub>. Although pentaborane itself is not shock sensitive, it has been shown that pentaborane can form shock-sensitive mixtures with many solvents commonly found in propellant test areas.

#### 3.5.1 Decontamination of Pentaborane

Pentaborane is soluble without reaction in inert hydrocarbon solvents such as toluene, kerosene, benzene, pentane, or hexane. Water-free kerosene is the standard solvent for washing systems that have been contaminated with pentaborane. Other solvents, especially those containing reactive carbonyl groups and highly halogenated or highly oxygenated solvents, must not be employed for use in pentaborane as they can form shock-sensitive solutions. Solvents of this type, which definitely must not be used, are acetone and other ketones, carbon tetrachloride, and aldehydes.

One method recommended for the decontamination of entire missile systems after use with pentaborane is to flush with a hydrocarbon solvent such as a kerosene to remove most of the material, followed by a flush with a mixture containing 80% methylene chloride and 20% ethyl alcohol and purge dry with gaseous nitrogen [180].

There are counterindications against the use of methylene chloride (dichloromethane) for this purpose: Not only is it quite toxic (causing symptoms similar to CO poisoning) but boranes can react vigorously with halocarbons, [252] specifically lists methylene chloride as a solvent that must be avoided. See also [256].

### 3.5.2 Fire Fighting of Pentaborane Fires

Pentaborane fires can be extinguished with chemical fire retardants [257]. Various phosphate, borate, silicate, and aluminate esters have been tested as extinguishants for pentaborane fires, acting mostly as diluents when mixed with the liquid in the burning puddle [258].

A study on fuels related to pentaborane (HEF compositions) indicated that complexing materials and foams made with inert gases were effective in fighting such fires [259]. This report also noted that hydrogen liberation on hydrolysis of boranes could lead to explosions and fires if oxygen were not excluded from the borane.

A wide range of flame suppressants, mostly halogenated compounds, were tested as inhibitors with an air/pentaborane diffusion flame burner [260]. Methyl iodide was the best material found, and was the only material that put out the flame at the higher pentaborane concentrations. A solution of iodine in carbon tetrachloride also showed some promise as a fire extinguishant. No nitrogen compounds, phosphorus compounds or aqueous solutions were found to be effective. Because pentaborane is not miscible with water and because it has a lower density than water, puddles of pentaborane may float on water and continue to burn.

### 3.5.3 Disposal of Pentaborane

After the termination of the borane-powered B-70 Valkyrie program in 1959, there were ample supplies of pentaborane and other alkylboranes stored and forgotten in some obscure munitions magazines and some cylinders were even buried in a landfill that later became the site for a residential development and then the cylinders needed to be unearthed for proper disposal. There have been two known incidents where people were injured or killed while handling pentaborane and attempting to destroy it [261, 262]. Two onsite treatment methods were identified for decontaminating the cylinders. They included pyrolytic incineration, if the cylinders contained pentaborane, and chemical treatment for decontaminating the empty cylinders. Upon excavating and inspecting the cylinders, all were found to contain only residual quantities of pentaborane, if any. The chemical treatment process was used to decontaminate the cylinders. After controlled venting of any hydrogen gas that may have accumulated in the cylinders, residual pentaborane was dissolved with dilute caustic solution. Methanol was used to rinse the cylinders and then they were flushed with large quantities of water.

Only decades later an enforcement of stricter environmental regulations led to a belated disposal effort for those chemicals inherited from the Cold War period. Some cylinders were disposed of by open pit burning in a remote test area. Various methods for controlled disposal of pentaborane by hydrolysis rather than open pit burning were tested [263, 264]. A pilot plant operation was planned that would use water-alcohol mixtures as the solvolysis reagent. The spontaneous self-ignition of

$B_5H_9$  was quenched by the addition of small concentrations of tetrahydrofuran or 1,2-dimethoxyethane. It was found that the addition of 10 vol.-% of ether provided efficient quenching. When these stabilized solutions were exposed to air, they decomposed and evaporated leaving a residue that was identified by NMR analysis as boric acid. The 90%  $B_5H_9$  + 10% THF solution was safer to handle and its solvolysis reactivity was virtually identical to that of 100%  $B_5H_9$ . Reaction rates were measured by collecting hydrogen evolved during the solvolysis reactions. The data indicated that 50/50 alcohol/water was the optimal solvolysis reagent. This reaction produced a mixture of boric acid and triethoxyborane,  $B(OC_2H_5)_3$ .

### 3.6 Safety Properties of Pentaborane

#### 3.6.1 Flammability Limits of Pentaborane

Stoichiometric mixtures of pentaborane in air would contain 3.37 vol.-%  $B_5H_9$ . The lower limit of flammability is 0.42 vol.-% but an upper limit for pentaborane has never been established because spontaneous ignition of the fuel-air mixture always occurred when attempting to obtain a rich mixture [265]. The flammability limits of pentaborane as a function of the air:fuel ratio and pressure were indicated in Figure 13 in comparison within limits of diborane, hydrogen, and JP-4.

#### 3.6.2 Autoignition of Pentaborane

Pentaborane is pyrophoric and autoignites in air as soon as its partial pressure exceeds 17.3 kPa = 130 mm Hg. Such high concentrations in air would usually be avoided for several reasons, flammability as well as toxicity hazard reasons.

Although this is a book on rocket propellants, information obtained during the examination of pentaborane as a fuel for airbreathing jet engines can be useful for the design of rockets with pentaborane as the fuel as well. The autoignition of pentaborane in a jet engine combustor would be a desirable feature to allow re-ignition after a flame-out or for cruising at high altitudes where the air is very thin [266].

The explosive oxidation and autoignition of pentaborane in air can be inhibited by iron pentacarbonyl vapors [267]. The addition of 1% iron pentacarbonyl suppressed autoxidation altogether. When 0.1% iron pentacarbonyl was added, upper and lower limits of flammability could be determined. This inhibitor raises the autoignition temperature and narrows the range of compositions that can autoignite in air (but it is very toxic and one would not want to prevent pentaborane fires by squirting iron pentacarbonyl all over the place).

At certain conditions of temperature and pressure, pentaborane-oxygen mixtures are spontaneously ignitable and explosive [173]. When oxygen was rapidly added to pentaborane, a first explosion limit region was found at low pressures at room tem-



perature, as well as a glow reaction at mixture pressures below the explosion limit pressures. Pentaborane sprays ignite spontaneously when injected into hot air [268, 269]. The spontaneous ignition limits of air/pentaborane mixtures were determined at 298 K (25 °C) and pressures ranging from 4 to 101 kPa [270]. A flash resulted when air was rapidly admitted to pentaborane vapor. The lean limit of spontaneous ignition in spherical bulbs measuring 6 cm in diameter was approximately 14 vol.-% at 101 kPa and about 55 vol.-% at 10 kPa. The rich limit was not determined, but mixtures containing 75% pentaborane ignited at 6.6 kPa. Stable mixtures of pentaborane and air could not be obtained by the addition of air to pentaborane vapor at 298 K (25 °C) except at pentaborane pressures less than 0.27 kPa. The ignition temperature of pentaborane droplets in air depends on the droplet size [271].

### 3.7 Toxicity of Pentaborane

As pentaborane reacts only slowly with water, it tends to concentrate in fatty tissues and lipids in the body. The primary damage caused by pentaborane poisoning is in the central nervous system.

The results of animal experimentation obtained from inhalation tests showed that pentaborane is more toxic than diborane or hydrogen cyanide. The Section 4 on decaborane contains a table comparing the hazard index of several boranes. Because of its low boiling point, pentaborane must be considered the most toxic of the several boranes.

The American Conference of Governmental and Industrial Hygienists revises and updates TLVs for hazardous chemicals every year. Most recently NIOSH REL has established a TWA for pentaborane of 0.005 ppm (0.01 mg/m<sup>3</sup>) (2005) and an ST of 0.015 ppm (0.03 mg/m<sup>3</sup>). Such a low concentration is difficult to measure with the most common continuous analysis equipment. The olfactory threshold of pentaborane is around 2.5 ppm, and the human nose is thus not a reliable warning instrument. It should be clearly understood that pentaborane concentrations that are detectable by odor are immediately dangerous to life. Additional information on the toxicity of pentaborane can be found in [147–149, 151, 272, 273].

#### 3.7.1 Acute Toxicity of Pentaborane

The LD<sub>50</sub> concentration, which is that concentration at which 50% of the test animals died for a 2-h exposure with pentaborane, was 14.1 ppm for male mice and 19.5 ppm for male rats. These same studies indicated that there may be an accumulative toxic effect build up in the rats with repeated subacute exposures to this compound. Detoxification owing to metabolism did not seem to occur within the animal body when exposed to low concentrations of pentaborane [274].

### 3.7.2 Chronic Toxicity of Pentaborane

In chronic inhalation exposure animal tests with lower subacute concentrations (about 3 ppm) and longer test durations, the effects of pentaborane were very similar to those of decaborane. The symptoms were primarily central nervous system damage and pathological changes in the blood counts [275, 276].

### 3.7.3 Symptoms of Pentaborane Poisoning

Typical symptoms of exposure to dangerous concentrations of pentaborane are nervousness, dizziness, lack of equilibrium, nausea, and frontal lobe headaches. Temporary impairment of higher mental functions, lack of coordination, and transient amnesia for recent events are common. Most frequently, intoxication cases occur from chronic exposure to low concentrations of pentaborane over long periods of time. The symptoms of such exposure are similar to those resulting from lack of sleep, alcoholic hangover, and general physical exhaustion.

Neurological symptoms are the most prominent manifestation of pentaborane poisoning, whereas decaborane produced only performance decrements of reinforced tasks in monkeys as test animals. In addition to CNS disturbance, the boron hydrides also cause cardiovascular effects and damage to both liver and kidney.

The first general symptoms shown are typical in many chemical exposure poisonings. These may include dizziness, blurred vision, nausea, fatigue, and nervousness. The more characteristic symptoms of severe pentaborane exposure are the abnormal muscular contractions or twitching of any part of the body followed by convulsions and then coma.

A lack of vitamin B may aggravate the toxic effects of boranes. Boron hydrides inhibit aspartate aminotransferase and lactic dehydrogenase in the liver, heart, brain, and kidneys of normal rats [277]. Decaborane does not cause a significant loss in activity in the tissues of pyridoxal-deficient rats.

### 3.7.4 Animal Toxicity Test Results with Pentaborane

The various government agencies considering the use of pentaborane and pentaborane derivatives as jet engine fuels and rocket propellants have carried out exhaustive series of animal exposure tests to obtain a better understanding of the toxicity hazard with pentaborane, to establish safe threshold levels for the work place, and to eventually develop better first aid post-accident treatment methods in the case of accidental poisonings in humans. They were also looking for preventive medications to be administered to personnel working in high-risk areas.

In animal tests with rats exposed 5 h/day to 3.3 ppm pentaborane the mortality was very high after only a few days of testing.

The acute LC<sub>50</sub> with rats exposed for 5 min was 66.6 ppm, after 15 min it was 31.2 ppm, after 30 min it was 15.2 ppm and after 1 h it was 10.4 ppm [278, 279]. The LC<sub>50</sub> concentrations for mice exposed for the same durations were 40.5, 18.6, 10.6, and

7.8 ppm respectively. Single exposures of dogs for 5-, 15-, and 60-min periods to 26, 12, and 3 ppm pentaborane vapor respectively produced borderline signs of toxicity [280]. Daily repeated exposures at approximately these levels caused convulsions, apprehensiveness, scleral injection, and miosis after the second exposure. Single exposures at 9.3, 5.0, and 1.4 ppm for 5-, 15-, and 60-min periods produced no detectable effects with the techniques employed. However, repeated daily exposure for 5 days to these levels caused irritability, miosis, and increased response time in a conditioned avoidance response test. Dogs exposed cutaneously for single 2-, 4-, and 6-h periods to 580, 550, and 710 ppm of  $B_5H_9$  respectively showed minimal or no signs of toxicity [281, 282].

In another test series the LC50 after 2 h of exposure was 14.1 ppm (0.037 mg/L) with male mice and 19.5 ppm (0.051 mg/L) with rats [283]. In similar tests where the animals were exposed for 4 h instead of 2 h, the LC50 was 10.9 ppm (0.028 mg/L) with male mice and 17.8 ppm (0.046 mg/L) with rats. The surviving animals recovered faster following a pentaborane poisoning episode than a decaborane poisoning episode.

In another test series with rats the LC50 after a 2-h exposure was reported to be 17 ppm [152]. The olfactory threshold in that source was listed as 2.5 ppm.

Median lethal doses of pentaborane-9 by intraperitoneal (*i.p.*) and inhalation administration to rats were determined to be 3.7 and 0.42 mg/kg respectively [284]. The intravenous (*i.v.*) median lethal dose to the rabbit was 0.52 mg/kg. The suggestion was made that pentaborane-9 might not oxidize appreciably prior to inhalation, and was almost quantitatively removed from respired air after passing through the lungs. Table 14 is a summary of acute toxicity data of pentaborane that were used by NIOSH to establish IDLH limits.

**Table 14:** Acute toxicity data summary for pentaborane.

| Species | LC50 (ppm) | Time   | Adjusted 0.5-h LC (CF) | Derived value | References |
|---------|------------|--------|------------------------|---------------|------------|
| Mouse   | 3          | 4 h    | 6 ppm (2.0)            | 0.6 ppm       | [285]      |
| Rat     | 6          | 4 h    | 12 ppm (2.0)           | 2 ppm         | [151]      |
| Mouse   | 3.4        | 4 h    | 6.8 ppm (2.0)          | 0.7 ppm       | [151]      |
| Dog     | 35         | 15 min | 28 ppm (0.79)          | 2.8 ppm       | [286]      |
| Monkey  | 244        | 2 min  | 100 ppm (0.41)         | 10 ppm        | [286]      |
| Rat     | 67         | 5 min  | 37 ppm (0.55)          | 3.7 ppm       | [280]      |
| Mouse   | 40         | 5 min  | 22 ppm (0.55)          | 2.2 ppm       | [280]      |
| Rat     | 31         | 15 min | 24 ppm (0.79)          | 2.4 ppm       | [280]      |
| Mouse   | 19         | 15 min | 15 ppm (0.79)          | 1.5 ppm       | [280]      |
| Rat     | 15         | 30 min | 15 ppm (10)            | 1.5 ppm       | [280]      |
| Mouse   | 11         | 30 min | 11 ppm (10)            | 1.1 ppm       | [280]      |
| Rat     | 10         | 1 h    | 13 ppm (1.25)          | 1.3 ppm       | [280]      |
| Mouse   | 6          | 1 h    | 7.5 ppm (125)          | 0.8 ppm       | [280]      |

Data source: [287]

### 3.7.5 Central Nervous System Effects of Pentaborane in Test Animals

Investigations of the influence of decaborane and pentaborane on biogenic amine metabolism were undertaken to assist in the elucidation of the toxic mechanisms and sites of action of boron hydrides in animals [288]. Brain and heart tissue serotonin and norepinephrine were found to be significantly depleted after treatment of test subjects with the boron hydrides. The testing of a number of potential antidotes for the treatment of the toxic symptoms and biogenic amine changes due to exposures to boron hydrides has resulted in the discovery of several new antidotal drugs for the toxic effects of decaborane. Some of the pentaborane effects were reversed following a norepinephrine infusion [289, 290].

Adverse cardiac and neurological symptoms were produced in animals following doses of decaborane(14) and pentaborane(9) [291]. Serotonin in adult rat brains was increased slightly at 4, 6, 8, and 12 h whereas norepinephrine was markedly lowered after 20 mg/kg IP of decaborane. A dose of 2.5 mg/kg IP of liquid pentaborane-9 lowered norepinephrine nearly 100% at 2 h, elevating serotonin 80%. Sedation and decreases in brain norepinephrine at 16 and 24 h after decaborane intoxication can be prevented by simultaneous or prior administration of 50 mg/kg IP of pargyline hydrochloride (*N*-methyl-*N*-benzyl-2-propynylamine hydrochloride). Similar treatments with 100 mg/kg IP of iproniazid phosphate did not block the fall in tissue norepinephrine due to decaborane.

### 3.7.6 Effects of Pentaborane on Metabolism of Test Animals

In a study of the fate of pentaborane-9, evenly labeled with tritium, in small animals, rats given B<sub>5</sub>H<sub>9</sub> by *i.p.* injection evolved 36–37% of the tritium label as molecular hydrogen over a 2- to 3-h period [292]. A non-volatile hydrolysis intermediate rapidly formed in the bloodstream concurrently as molecular hydrogen was evolved by treated animals. Tritium in the hydrolysis intermediate was found to be non-exchangeable into water. However, the hydrolysis intermediate slowly disappeared and approximately an equivalent amount of tritium could be detected in the body water of treated animals. A study of the effect of pentaborane-9 intoxication upon glucose catabolism by rats showed that total respiratory CO<sub>2</sub> production by intoxicated rats was slightly greater than that of normal rats. Catabolism of glucose via the glycolytic pathway appeared to be inhibited during the initial 4 h after B<sub>5</sub>H<sub>9</sub> administration by *i.p.* injection. Pentaborane-9 intoxication appeared to affect glucose catabolism for only a 6- to 8-h period.

### 3.7.7 Central Nervous System Damage in Persons Exposed to Pentaborane

Neuropsychological tests were administered to 14 workers and rescue squad personnel approximately 2 months following an accidental exposure to pentaborane [293]. Performance decrements were evident on 5 of 11 neuropsychological tests, including measures of sustained attention and recent memory. These results indicated mild residual brain dysfunction following pentaborane intoxication, including possible dysfunc-

tion in subcortical regions mediating memory processes and in cortical areas mediating visuo-spatial abilities.

Fourteen individuals briefly exposed accidentally to pentaborane by inhalation were evaluated for neuropsychiatric abnormalities 4–12 weeks after exposure [294]. Results of physical, neurological, and routine laboratory evaluations were normal. Initial and persistent psychiatric symptoms, neuropsychological deficits, electroencephalographic changes, elevated central nervous system neurotransmitter levels, and ventricular brain ratios (computed tomographic scan) provided evidence for central nervous system damage. Seven patients met the diagnostic criteria of the Diagnostic and Statistical Manual of Mental Disorders, Ed. 3, for post-traumatic stress disorder, and seven patients had neuropsychological test evidence for mild brain dysfunction. Patients suffered a combination of organic brain insult and psychological trauma. These results contradict previous literature that claimed that most symptoms resolved within the first week after exposure to pentaborane.

Pentaborane poisonings are unique with respect to the rapid and devastating neurologic consequences. Three cases of pentaborane poisoning resulting from accidental exposure were characterized by the rapid onset of seizures and spasms accompanied by severe metabolic acidosis without respiratory compensation [295]. Serum transaminase levels were elevated and liver damage was demonstrated histologically. One patient died and another sustained severe neurologic damage.

Fourteen individuals who had been briefly accidentally exposed to pentaborane were reevaluated for a period of 18 months following an initial neuropsychiatric study [296]. Psychiatric interviews utilizing standardized diagnostic criteria, neuropsychological and psychological assessment, and CT scan ventricular brain ratios were reevaluated and revealed worsening psychological factors. Post-traumatic stress disorder, major affective disorder, alcohol abuse and phobias were the most common diagnoses at follow-up.

### **3.7.8 Epidemiological Studies with Pentaborane Worker Cohorts**

During the period 1950–1962 a large quantity of pentaborane was produced by Callery Chemical Company without any serious poisoning accidents.

Psychodiagnostic testing was administered to personnel with a work history on a pentaborane project [297]. The tests consisted of questions referring to neuropsychiatric and psychosomatic symptoms, the results of which were related to job adjustment as measured by several criteria. Although the analysis of findings did not reveal statistically significant relationships, there was some evidence suggestive of the practical usefulness of such tests. Information obtained from these psychological measuring tools can serve a purpose as part of the personal medical history to assist physicians in diagnosing complaints of propellant intoxication, the symptomatology of which is often not clear.

During a thorough medical examination of 60 workers who were exposed to various subacute concentrations of pentaborane below the sensitivity threshold of moni-

toring equipment, 31 workers were found to have slight symptoms of pentaborane poisoning but without any pentaborane being detectable in their post-work shift blood samples. Even after one year of employment in the plant there were no pathological clinical changes in lung, liver, or kidney function [298]. A clinical evaluation of all of the exposed workers at the end of a year's production revealed no observable effects. The protective gear worn provided good, though not complete, protection. Further study of the hazards of the boranes will require a monitoring instrument of better sensitivity to evaluate the acute poisonings and the protective gear worn.

Extensive animal experiments, as well as limited observation upon humans, indicated that boron hydrides possess an unusual degree of toxicity. Intoxication may occur from inhalation, ingestion or skin absorption. Medical tests were performed on 154 technical personnel who had worked in a borane production plant for 3 years [299]. In order to maintain safe working conditions, the pentaborane concentration in the air should not exceed 5 parts per billion (by volume), but that is below the sensitivity of most analytical instruments.

It would have been very useful to have a clinical test to measure boron concentration in blood, skin wipes or urine of workers before and after each work shift, but instrumentation available at that time did not have the necessary sensitivity [300].

### 3.7.9 Maximum Allowable Pentaborane Concentrations

A very useful occupational health guideline for exposure of workers to pentaborane was published by CDC-NIOSH in 1978 [301]. As of May 1994, the NIOSH REL was 0.005 ppm (0.01 mg/m<sup>3</sup>) and the short-term exposure limit (STEL) was 0.015 ppm (0.03 mg/m<sup>3</sup>). The 1994 OSHA PEL was 0.005 ppm (0.01 mg/m<sup>3</sup>), unchanged from an earlier (1989) recommendation of 0.005 ppm (0.01 mg/m<sup>3</sup>) TWA, 0.015 ppm (0.03 mg/m<sup>3</sup>) STEL. The 1993–1994 ACGIH TLV recommendation was 0.005 ppm (0.013 mg/m<sup>3</sup>) TWA, and 0.015 ppm (0.039 mg/m<sup>3</sup>) STEL. The basis for the original (Standards Completion Program) IDLH of 3 ppm was the mouse 4-h LC50 of 3 ppm reported by Jacobson in 1958 [285] and cited by ACGIH in 1971. The IDLH was later revised to 1 ppm based on acute inhalation toxicity data in animals reported by Jacobson 1958 [285], Levinskis et al. 1958 [151], and Weir et al. 1964 [280].

The tentative emergency exposure limits for pentaborane vapor established in 1966 are listed in Table 15, but those limits are probably outdated and require re-examination in view of the extreme toxicity of this chemical:

**Table 15:** Emergency exposure limits for pentaborane vapor.

| Exposure duration, min | Emergency exposure limit, ppm |
|------------------------|-------------------------------|
| 5                      | 25                            |
| 15                     | 8                             |
| 30                     | 4                             |
| 60                     | 2                             |

Data source: [302].

## 4 Decaborane(14)

Decaborane(14),  $B_{10}H_{14}$ , CAS RN [17702-41-9], is a colorless, crystalline solid that melts at 372.8 K (99.7 °C) and sublimes readily. It dissolves in all organic solvents and in pentaborane.

### 4.1 Preparation of Decaborane

Decaborane(14) is formed along with other higher boron hydrides when diborane or pentaborane is heated to above 393 K (120 °C) [303]. The mixture of solid products formed by pyrolysis of diborane is usually extracted with saturated hydrocarbon solvents, which dissolve the decaborane, but not the higher boranes. The dissolved decaborane can be precipitated by reaction with a secondary alkyl amine [304]. It is difficult to control the diborane pyrolysis process so as to optimize the yields of pentaborane and decaborane and minimize the wasteful formation of insoluble high-molecular mass boranes [177]. A more selective laboratory procedure for the preparation of decaborane(14) consisted of three distinct steps [305, 306]:

- (1) Conversion of  $B_5H_9$  to  $[N(CH_3)_4]B_9H_{14}$  by reacting a 2:1 molar ratio of  $B_5H_9$  with NaH in THF in the presence of  $[N(CH_3)_4]Cl$  at room temperature.
- (2) Removal of THF and addition of  $BCl_3$  and reaction at 284 K (11 °C).
- (3) Sublimation of  $B_{10}H_{14}$  at 284 K (11 °C) from the solid reaction mixture.

A process for the preparation of decaborane that appears suitable for adoption by large-scale plant production involved the pyrolysis of diborane at constant temperature and pressure, using a closed recycle system with continuous diborane feed and decaborane withdrawal [303]. Optimal reaction occurred with a reactor residence time of 4 to 6 s, and temperatures of 453 to 458 K (180 to 185 °C), using diborane in concentrations of 30 to 40 mol-% at pressures of 170 to 180 kPa (10 to 11 psig). Diborane conversions of 80 to 90% and decaborane-corrected yields of 50 to 60% were attained, with a material accountability of 90%.

The synthesis of n-hexylcarborane, a burning rate modifier for improved solid propellants, depends on the availability of decaborane-14, a material that is not commercially available in large quantities. Laser-induced chemistry (LIC) can synthesize decaborane-14 from diborane in high yields and high purity using both  $CO_2$  and DF laser frequencies [307–309]. The products are decaborane-14 formed as white crystals and pentaborane-9 in the vapor state; the two are easy to separate. No polymer (which is an unwanted byproduct that is always present in thermal pyrolysis) was observed when the laser power was kept below a certain threshold (10 W/cm<sup>2</sup> for the  $CO_2$  laser). Also, the  $B_5H_{11}$  byproduct is always present in pyrolysis yet never observed in LIC synthesis.

## 4.2 Physical Properties of Decaborane

Some of the physical properties of decaborane are summarized in Table 16. Vapor pressure data are listed in Table 17.

**Table 16:** Physical properties of decaborane.

|                                    | SI units               | Other units     | References |
|------------------------------------|------------------------|-----------------|------------|
| Molecular mass                     | 122.221 g/mol          | 8.182 mol/kg    |            |
| Melting point                      | 372.8 K                | 99.7 °C         | [310]      |
| Triple point temperature           | 371.93 ± 0.02 K        | 98.78 ± 0.02 °C | [311]      |
| Boiling point (extrapolated)       | 486 K                  | 213.0 °C        |            |
| Density, solid at room temperature | 0.94 g/cm <sup>3</sup> | —               | [310]      |

**Table 17:** Vapor pressure of decaborane.

| Temperature |     | Vapor pressure |       |
|-------------|-----|----------------|-------|
| K           | °C  | kPa            | mm Hg |
| 328         | 55  | 0.04           | 0.3   |
| 338         | 65  | 0.186          | 1.4   |
| 366         | 93  | 1.70           | 12.7  |
| 373         | 100 | 2.53           | 19.0  |

Data source: [310]

The vapor pressure of decaborane between 315 and 395 K can be represented by the equation [311]:

$$\log_{10} p = -\frac{4225.345}{T} - 0.0107975T + 16.63911,$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.

### 4.2.1 Optical Properties of Decaborane

The IR spectrum of decaborane shows two bands, one at 5205 and the other at 7505 cm<sup>-1</sup>. These bands correspond to the two bands of pentaborane assigned to the first and second overtones of a B—H stretching frequency [73].



### 4.2.2 Thermodynamic Properties of Decaborane

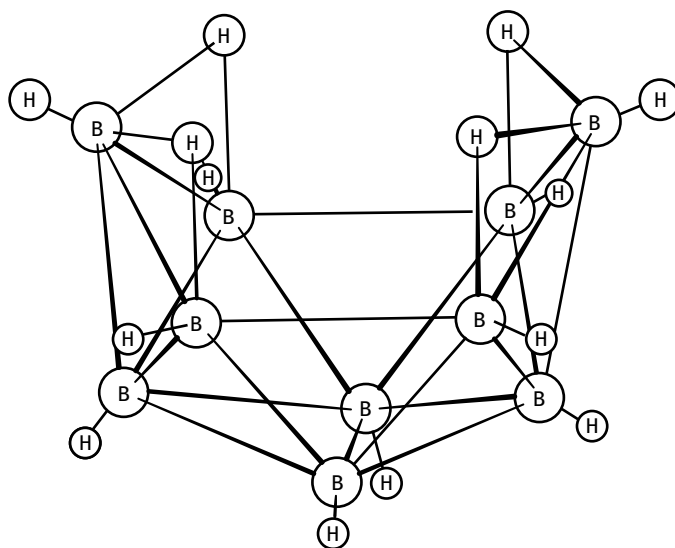
Thermodynamic properties of decaborane are summarized in Table 18

**Table 18:** Thermodynamic properties of decaborane.

|                                    | SI units                                   | Other units                                  | References |
|------------------------------------|--------------------------------------------|----------------------------------------------|------------|
| Enthalpy of formation, crystalline | -28.87 kJ/mol                              | -6.90 kcal/mol                               | [53]       |
| Enthalpy of formation, solid       | -28.294 · kJ/mol                           | -6.76 kcal/mol                               | [311]      |
|                                    | -66.11 kJ/mol                              | -15.8 kcal/mol                               | [191]      |
| Enthalpy of formation, liquid      | -7.13 kJ/mol                               | -1.70 kcal/mol                               | [53]       |
| Enthalpy of formation, vapor       | +47.28 kJ/mol                              | +11.30 kcal/mol                              | [53]       |
| Heat capacity at 298 K, solid      | 217.96 J K <sup>-1</sup> mol <sup>-1</sup> | 52.09 cal °C <sup>-1</sup> mol <sup>-1</sup> | [311]      |
| Heat of vaporization at 378 K      | 50.759 ± 0.1 kJ/mol                        | 12.13 ± 0.02 kcal/mol                        | [311]      |
| Heat of fusion                     | 21.965 ± 0.040 kJ/mol                      | 5.25 ± 0.01 kcal/mol                         | [311]      |

### 4.2.3 Molecular Structure of Decaborane

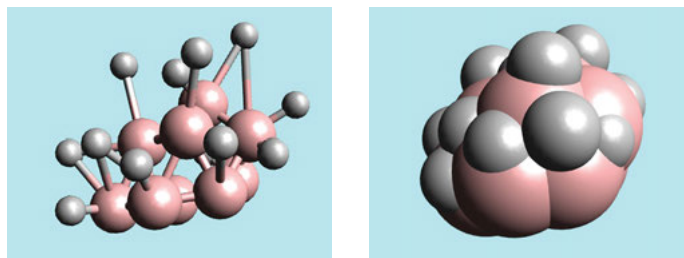
Decaborane(14) crystallizes in disordered orthorhombic crystals, space group *Pnnm*,  $a = 7.225 \text{ \AA}$ ,  $b = 10.44 \text{ \AA}$ ,  $c = 5.68 \text{ \AA}$  [312, 313]. The molecular structure of decaborane resembles that of a basket (Figure 22).



**Figure 22:** Molecular structure of decaborane(14).

When assembling a 3-D structure of decaborane with any of the chemical structure illustration programs, it is very difficult to get a clear view of the internal structure of decaborane. Regardless of how one rotates the molecule in any of the *x*-, *y*-, or *z*-axes to

obtain a different aspect, several atoms in the rear of the molecule are always occluded and out of view (Figure 23). It would be best to display this molecule as a .gif image and allow it to slowly rotate. The occlusion is even more hindering if the van der Waals radii of the atoms are displayed.



**Figure 23:** Molecular structure of decaborane(14).

### 4.3 Chemical Properties of Decaborane

A detailed review of the chemistry of decaborane [314] contains sections on the structure and reactivity of decaborane, pyrolysis, hydrolysis, alcoholysis, and thiolysis of decaborane, decaborane as an acid, nucleophilic substitution in decaborane, electrophilic substitutions, and the stable anion  $B_{10}H_{10}^{2-}$ . See also [315].

#### 4.3.1 Reactions of Decaborane

Decaborane is a strong acid in dimethylformamide as the solvent and forms salts with alkali metals, such as  $B_{10}H_{13}Na$  [316]. The  $B_{10}H_{10}^{2-}$  anion in  $B_{10}H_{10}[N(CH_3)_4]_2$  is quite stable [317].

The hydrolysis of decaborane takes place even more slowly than that of pentaborane. Likewise, the rate of autoxidation is much slower than that of pentaborane.

Decaborane forms adducts with Lewis bases, typical electron donors [318]. The best characterized adducts are those with aliphatic amines, but similar products are obtained with aromatic amines [319].

The adduct of decaborane with ammonia contains two moles of ammonia per mole of decaborane. The formation of the adduct is reversible [320]. Adducts of decaborane with one, two or three moles of diethylamine have been characterized by XRD [321]. These solid adducts release decaborane on treatment with acid. The reactions of decaborane with secondary or tertiary amines, forming Lewis adducts, can be used for the separation of decaborane from reaction mixtures during the production of decaborane [304].

Solutions of a hydrazinium decaboranate in hydrazine were patented as rocket fuels [322, 323]. This salt is soluble in hydrazine and can be prepared by a reaction

of diammonium decaboranate with hydrazine. Similar salts are formed by reaction of hydrazine or alkylhydrazines with undecaborane(14) [324].

Decaborane reacts with acetonitrile to form an adduct  $B_{10}H_{14} \bullet (H_3CCN)_2$ . Similar adducts are formed by reaction of alkyl decaboranes with dinitriles [325]. The reaction is believed to involve one mole of decaborane (alkyl decaborane) and two moles of the dinitrile, leading to a viscous, polymeric material with a putty-like consistency.

#### 4.3.2 Thermal Stability of Decaborane

Decaborane is quite stable and can be stored at room temperature indefinitely. The decomposition of decaborane starts only at temperatures above 473 K (200 °C) [326]. Differential thermal analysis curves of decaborane heated in air showed a slight exotherm up to 367 K (94 °C); then it began an endotherm due to melting at 373 K (100 °C). After melting, the curve returned to the base line and remained there from 378 to 398 K (105 to 125 °C). At 398 K (125 °C) it began to decompose and decomposition continued up to 433 K (160 °C). In helium only an endotherm due to melting was observed at 373 K (100 °C). No evidence of decomposition was to be seen up to 423 K (150 °C). On cooling, the freezing occurred at 361 K (88 °C), indicating supercooling. See also [327–330].

The thermal stability of decaborane was investigated at temperatures of 475 and 525 K (202 and 252 °C) [331]. The products of decomposition were hydrogen and a boron hydride, which is a solid or viscous liquid. The following equation was developed from which may be calculated the time required to decompose 20% of decaborane at any other temperature:

$$\log(t_{20\%} - 2) = 8.6 \times \frac{10^3}{T} - 16.0,$$

where  $T$  is temperature in kelvin and  $t$  is the time for decomposition of 20% of decaborane in minutes.

Rate constants for the homogeneous first-order disappearance of decaborane during vapor phase pyrolysis were measured over the range 443–511 K (170–238 °C), and an activation energy of 173 kJ/mol (41.4 kcal/mol) was calculated [332]. Inhibition by hydrogen, but not by other gases was demonstrated. Comparison of the rates for H-decaborane and deuterodecaborane indicated that the rupture of B–H or B–D bonds was rate determining. Decaborane disappeared by a rapid polymerization reaction without immediate loss of hydrogen to form an intermediate polymer consisting of decaborane-like units, followed by further loss of hydrogen and molecular weight increase with cross-linking to form non-volatile solid hydrides. No interim reactants more volatile than decaborane were observed. Hydrogen was found to split out preferentially at the external B–H bonds initially, rather than at the bridged hydrogen positions.

Premature decomposition of decaborane limits the yield during production of decaborane by pyrolysis of diborane. The kinetics of the pyrolysis of decaborane were

investigated in a static system within the temperature range 483–523 K (210–250 °C) and at decaborane pressures of 8–80 kPa (60–600 mm Hg) [333]. The decomposition led to non-volatile solid hydrides and hydrogen. Experiments were carried out in a sealed vessel for varying times at 483, 503, and 523 K (210, 230, and 250 °C) and initial decaborane pressures of 8, 16, 40, and 80 kPa (60, 120, 300, and 600 mm Hg). For experiments on retardation by hydrogen, a known pressure of hydrogen was admitted before sealing. The decomposition reaction was of first order with respect to decaborane, slightly retarded by hydrogen. The activation energy was  $174 \pm 2$  kJ/mol ( $41.6 \pm 0.5$  kcal/mol). Above 60% conversion, the reaction tended to be of greater than first order. Hydrogen was also formed by decomposition of the non-volatile solid hydrides, and its rate of formation in this way was strongly retarded by hydrogen. One of the objectives of the work was to see if the decomposition of decaborane was to blame for the formation of non-volatile (useless) solid hydrides during the pyrolysis of diborane at 513 K (240 °C). It was shown that at 513 K (240 °C), with 1:5 diborane:hydrogen ratio and a total flow rate of 0.4 l/min, only about 0.1% of decaborane was converted by thermal decomposition alone into non-volatile solid hydrides.

Even a long time after the excitement of boranes as jet engine and rocket fuels has subsided, pyrolysis of decaborane is still being used for boriding metal surfaces, deposition of boron thin films, doping semiconductors, and the production of nano-sized boron particles.

### 4.3.3 Analysis of Decaborane

The quantitative analysis of decaborane in solutions of inert solvents can be achieved by volumetric titration [326]. This method for the quantitative determination of decaborane performs an oxidation of the sample in glacial acetic acid with excess potassium iodate, reaction of excess iodate with potassium iodide, and titration of the liberated iodine with sodium thiosulfate.

Decaborane can be analyzed by reaction with potassium hexacyanoferrate(III) [334]. The reduction of hexacyanoferrate(III) by boranes forms hexacyanoferrate(II) and Prussian Blue, which can then be analyzed colorimetrically. Another method uses the reduction of phosphomolybdic acid to the blue dye. These reductions are not specific to decaborane or any borane.

An alkaline solution of triphenyl tetrazolium chloride can be reduced by boranes (pentaborane or decaborane) to form an insoluble red formazan, which can then be extracted with xylene and analyzed colorimetrically [335].

Nine methods for the determination of decaborane were evaluated by analyzing commercial samples ranging from 90 to 97% pure [336]. Gas chromatographic, IR, UV, and iodine redox volumetric procedures gave comparable results at the 95% confidence level. Decaborane was determined by five methods without significant interference by the impurities present. An alkaline titration method gave high results because of the acidic impurities. A 3-naphthoquinoline [benzo(f)quinoline] colorimetric method gave comparatively low results. Mole percent purity can be determined by

a freezing point depression method. The iodine titration method was recommended as a standard when high-purity decaborane is unavailable for calibration of other methods.

The  $\beta$ -naphthoquinone spectrophotometric method had a sensitivity of 0.1  $\mu\text{g}$  of decaborane/mL [337]. Another colorimetric reagent with even better sensitivity for the analysis of decaborane is 1,2-bis(4-dipyridyl)ethylene [338].

#### 4.4 Toxicity of Decaborane

Based on the quantity of borane absorbed into the body, decaborane is the most toxic of all boranes. The hazard in the handling of boranes, however, is determined not only by their toxicity as measured by LC50 or LD50, but also by their vapor pressure. Fortunately, the vapor pressure of decaborane at room temperature is very low, such that the quotient of vapor pressure divided by the LD50 or LC50 (also called the hazard index) is not the worst in the list examples shown in Table 19. The hazard index is a better measure for risk and hazards in handling than the LC50 or LD50.

**Table 19:** Hazard index of boranes and other chemicals.

| Compound           | Gross formula                  | Hazard index |
|--------------------|--------------------------------|--------------|
| Pentaborane        | $\text{B}_5\text{H}_9$         | 40300        |
| Diborane           | $\text{B}_2\text{H}_6$         | 25000        |
| Hydrazine          | $\text{N}_2\text{H}_4$         | 33           |
| Alkylborane        | $\text{B}_x\text{H}_y\text{R}$ | 11.5         |
| Benzene            | $\text{C}_6\text{H}_6$         | 7.8          |
| Tetrachloromethane | $\text{CCl}_4$                 | 6            |
| Decaborane         | $\text{B}_{10}\text{H}_{14}$   | 1.4          |

A review of literature data showed no cases of human accidental exposure to decaborane alone, but that was prior to the expansion of borane fuel production [147]. Most of the information that is available and discussed in the following paragraphs is based largely on animal experimentation. The mode of action of decaborane within the body is not quite understood. Available data indicated that it behaves somewhat like pentaborane, but to a lesser degree, in its toxicological effects. In general, toxicity studies show that recovery from pentaborane exposure is more rapid than from decaborane poisoning. Primary effects of decaborane exposure are disturbances of the central nervous system. Prolonged exposure may cause liver and kidney damage. Some animal exposure tests revealed corneal damage, hemorrhagic adrenal glands, and cardiovascular disturbances. A cumulative toxic effect may be exhibited by animals with repeated small exposures to decaborane. Detoxification of absorbed decaborane did not occur within the animal body. There is no quantitative information on

the cumulative or detoxifying action of decaborane in humans. Symptoms exhibited by animals exposed to decaborane may be compared with those exhibited by animals exposed to pentaborane (muscular incoordination, convulsions, and coma). Decaborane depleted the hepatic glycogen content in rats [339].

#### 4.4.1 Acute and Chronic Toxicity of Decaborane

In toxicity tests with intraperitoneal administration of decaborane the LD<sub>50</sub> was 33 mg/kg with mice and 23 to 28 mg/kg with rats [152]. When decaborane was administered to rats by way of stomach tube, the LD<sub>50</sub> was 64 mg/kg. Decaborane that was dissolved in oil and applied cutaneously to the skin of rabbits or rats resulted in an LD<sub>50</sub> of 113 mg/kg for rabbits and 640 mg/kg for rats, based on a 24-h exposure. The LC<sub>50</sub> for a 4-h exposure of mice to decaborane vapors was 26 ppm, based on a 48-h post-exposure observation period. The rate of survival of rats was higher than that of mice, but surviving animals exhibited greater irritability. The animals recovered more slowly after a decaborane poisoning than after a pentaborane poisoning.

In another test series, the acute toxicity LC<sub>50</sub> after a 4-h inhalation exposure period with mice was 36.5 ppm (0.182 mg/L) and 25.7 ppm (0.122 mg/L) after a 24- to 28-h inhalation period [283]. In a parallel test under identical conditions, all rats survived such that an LC<sub>50</sub> could not be determined. Exposure of test animals to subacute concentrations of 20 ppm caused rapid weight loss, disorders of the central nervous system, opacification of the cornea, nausea, and spasms with deadly consequences. The mammal metabolism does not appear to have a mechanism for the digestion of the poison, such that even small concentrations accumulated to toxic quantities over the course of time [275]. See also [244, 340–343]. The acute toxicity data in Table 20 were used by NIOSH in selecting a threshold for IDLH [344]. See also [345].

**Table 20:** Decaborane lethal concentration data.

| Species | LC <sub>50</sub>      | Time | Adjusted 0.5-h LC (CF)      | Derived value        | References |
|---------|-----------------------|------|-----------------------------|----------------------|------------|
| Rat     | 276 mg/m <sup>3</sup> | 4h   | 552 mg/m <sup>3</sup> (2.0) | 55 mg/m <sup>3</sup> | [244]      |
| Mouse   | 72 mg/m <sup>3</sup>  | 4 h  | 144 mg/m <sup>3</sup> (2.0) | 14 mg/m <sup>3</sup> | [244]      |
| Mouse   | 144 mg/m <sup>3</sup> | 4 h  | 288 mg/m <sup>3</sup> (2.0) | 29 mg/m <sup>3</sup> | [340, 341] |

Data source: [344]

#### 4.4.2 Central Nervous System Effects of Decaborane

Central nervous system damage due to inhalation or other absorption of decaborane is more pronounced and longer lasting for decaborane than for the other boranes [346, 347].

One single *i.p.* injection of 5 mg/kg decaborane in monkeys produced a marked behavioral depression, with only moderate electroencephalographic modifications, followed by death in 18 h [348]. Four daily doses of 3 mg/kg produced depression, som-

nolence, twitching in both arms, accompanied by bursts of high-voltage activity, localized in the internal capsule. Death occurred 3 days later. Daily doses of 1 mg/kg up to a total of 14 mg/kg produced depression, muscular twitching, anorexia, and a typical electroencephalographic pattern, but the animals recovered completely.

Ten adult monkeys were injected with either 1, 2 or 4 mg/kg of decaborane, and their performance on various operant tasks was compared with baseline performance [349, 350]. All animals exhibited a performance decrement on at least one task, with six of the subjects exhibiting a decrement on the remaining tasks. In over half the cases performance changes preceded clinical symptoms. There was no significant difference between the 2 and 4 mg/kg exposures. Subjects exposed to levels of decaborane such as those employed in this research may be expected to exhibit a performance decrement or clinical symptoms during the first 50 h. See also [351].

#### 4.4.3 Cardiovascular Effects of Decaborane

Decaborane (4–10 mg/kg, *i.v.*) produced bradycardia and an initial transient hypertensive effect in the anesthetized dog [352]. Decaborane caused an immediate decrease in cardiac output without affecting stroke volume, whereas right ventricular contractile force gradually decreased to below basal levels in approximately 60 min. The bradycardia produced by decaborane was partially antagonized in the initial stages by atropine and chlorisondamine. Subsequently, these agents had no effect on this response of decaborane. It was concluded that the initial hypertensive effect and increase in perfusion pressure were due to the acute release of norepinephrine from peripheral adrenergic neurons and the myocardial depression was induced by cholinergic stimulation as well as by a direct, non-specific depression of myocardial contraction induced by decaborane. See also [353].

#### 4.4.4 Enzyme Effects of Decaborane

Intermediates of decaborane hydrolysis inhibit glutamic-oxaloacetic transaminase (GOT) [354]. The inhibition of transaminase activity is kinetically irreversible when the ratio of apoenzyme to pyridoxal phosphate is kept constant, but is partially reversed when excess pyridoxal phosphate is added. The GOT-inhibitory activity disappeared when the intermediate was neutralized by pyridoxal phosphate. Prior loading of mice with pyridoxine raised the LD<sub>50</sub> of decaborane. It was postulated that toxicity of decaborane attendant upon inhibition of pyridoxal phosphate requiring enzymes is due not to decaborane per se, but to reduction of pyridoxal phosphate by a substance formed non-enzymically from decaborane in the presence of water.

Decaborane and carboranes inhibited hepatic microsomal enzymes isolated from adult male rats, ethylmorphine *N*-demethylase and aniline hydroxylase *in vitro* [355]. Pyridoxal phosphate, a coenzyme that alters the inhibitory actions of decaborane on certain enzyme systems, had no effect on the interaction of decaborane with these microsomal systems. Both decaborane and the carboranes are bound to cytochrome

P-450. The activity of some microsomal systems was unaltered after a single dose (12 mg/kg) of decaborane. During these studies morphologic changes of liver tissue occurred, confirming previous studies by other investigators that the liver is a site of pathology caused by decaborane.

#### 4.4.5 Accidental Exposures to Borane Fuels

A number of accidental exposures of personnel to borane fuels were described in Schoettlin et al. [149]. Here are some examples.

A rocket development company was conducting routine pentaborane firings. One research engineer working in the area wore no protective mask or equipment. At 3:30 PM he felt nervous. After this he had a lapse of memory. After arriving at work on the following morning, it was noted that he was sweating profusely and was very confused. He spoke slowly because of an inability to think, and was unable to describe what was wrong. He had a wide-awake stare and recent memory loss. Upon questioning, he complained of aching in all of his muscles. It was observed that when he was touched he developed muscle tremors. He complained of having not slept the previous night. He noted, on attempting to walk, that his "knees felt stiff, and back and hips felt as though they were slipping backwards." Oxygen therapy was started. At one time during observation he developed tetany and opisthotonos.

At another test site, a group of chemists were investigating the properties of high-energy fuels. Within 2 months of commencing this research, they admitted that minute amounts of the fuel had been spilled onto the chemist's hands and vapor had been inhaled. The chemists exposed to this developed frequent headaches in the frontal and occipital regions. These headaches persisted for 1 to 2 h.

A flight surgeon was conducting a series of electroencephalograms (EEG) on pilots to determine central nervous system damage from in-flight accidental inhalation of fuel fumes. Obvious abnormalities were observed on the EEG tracings made on the pilots.

A group of 119 rocket fuel handlers doing routine work and not involved in recent borane accidents and 22 controls were followed over time using serial electroencephalograms. Although observable, clinically important EEG changes were noted, the number of cases showing changes attributable to boranes was small. The pattern of central nervous system damage reconstructed from these few cases was as follows:

1. Known normals may convert to abnormal after exposure.
2. Not all normals may convert to abnormal after the initial exposure, but may do so after repeated exposure.
3. Post-exposure abnormalities tend to revert to normal about 1 year after exposure.

The EEG tracings showing post-exposure changes exhibited only slow activity in either or both the resting and hyperventilation records.



#### 4.4.6 Therapy of Decaborane Poisoning

Tests on therapy of decaborane poisonings in laboratory animals showed that the mortality can be substantially reduced by simultaneous administration of atrolactamide/sodium lactate 1:500 or methylene blue [356]. Themisone, also known as atrolactamide or M-144, was found in the 1950s to be a very potent anticonvulsant. Acute decaborane poisonings in animals have been treated with methocarbamol (Robaxin) or barbiturates. The survival rate of rabbits exposed to decaborane was improved by immediate administration of methylene blue [357, 358].

Rats were injected *i.p.* with decaborane and observed over a 7-day period to determine their toxic reactions, including death rate [359]. Pyridoxine, pyridoxal, and pargyline were tested in the decaborane-treated rats as antidotes for the observed manifestations of the boron hydride injection. In these studies pyridoxine (1 mmol/kg) given simultaneously with decaborane prevented the convulsions and hyperactivity usually seen in rats treated with decaborane alone (20 mg/kg) and caused a significant decrease in the number of deaths.

If decaborane comes into contact with skin, the contaminated areas should be washed first with a 1% solution of triethanolamine, followed by washing with soap and water.

#### 4.4.7 Maximum Allowable Concentrations of Decaborane in Workroom Air

The maximum allowable concentration of decaborane in workroom air established by the ACGIH in the 1993–1994 TLV is 0.25 mg/m<sup>3</sup> (0.05 ppm) TWA. Other recommended limits are NIOSH REL: 0.3 mg/m<sup>3</sup> (0.05 ppm) TWA, NIOSH STEL 0.9 mg/m<sup>3</sup> (0.15 ppm) [skin]; OSHA PEL: 0.3 mg/m<sup>3</sup> (0.05 ppm) TWA [skin]; 1989 OSHA PEL: 0.3 mg/m<sup>3</sup> (0.05 ppm) TWA, OSHA STEL 0.9 mg/m<sup>3</sup> (0.15 ppm) [skin]. The IDLH threshold was estimated at 100 mg/m<sup>3</sup>. The IDLH was based on the review by International Labour Office (1971) that the 4-h LC50 was 122 to 230 mg/m<sup>3</sup> for small animals [163, 164]. The olfactory threshold for decaborane is 0.3 mg/m<sup>3</sup> (for comparison: diborane 2 to 4 mg/m<sup>3</sup>; pentaborane 2.5 mg/m<sup>3</sup>).

#### 4.4.8 Protective Equipment

Gas masks containing a silica gel filter are effective in retaining decaborane vapors, but the filter capacity may be exhausted after only a few hours [360]. Activated charcoal filters are only half as effective as silica gel filters. Granulated soda lime or triethanolamine soaked into porous porcelain are usable only for short times. Gas mask filters containing combinations of these materials may be effective against decaborane and other boranes.

## 5 Complex Boron Hydrides

Complex boron hydrides can be formed with ionic or covalent bonds. Many complex boron hydrides have been evaluated as rocket propellants and gas generant constituents. Others were examined as potential hydrogen storage media [361].

### 5.1 Ionic Boron Hydrides

Salts containing the  $\text{BH}_4^-$  anion are called complex borohydrides, or, more specifically, tetrahydroborohydrides [362]. They are also called *boranates* or *tetrahydroborates*. Most of these ionic compounds are solids, but one of them, aluminum boranate,  $\text{Al}(\text{BH}_4)_3$ , with covalent and hydrogen bonds, is a liquid. Metal boranates can be used as rocket propellant fuels either in solution or dispersion in liquid fuels or as solids in solid or hybrid propellants.

Ionic boron hydrides would have the advantage over covalent boron hydrides that they have lower vapor pressure or no measurable vapor pressure at all, making them safer to handle, yet they still would be useful as rocket fuels.

The direct synthesis of metal borohydrides from the elements at substantially elevated pressures and temperatures was claimed for borohydrides of Li, Na, K, Mg, and Ba. In practice only indirect methods are used for the synthesis of metal borohydrides [363]. Four different methods can be used for the preparation of metal borohydrides: **(1)** addition of diborane to metal hydrides, **(2)** reaction of diborane with metal alkyls or metal alkoxides, **(3)** reaction of metal hydrides with boron compounds, and **(4)** exchange reactions between metal borohydrides and other metals salts, mostly halides. Complex borohydrides can be used in solid propellants, in hypergolic ignition formulations, or for the production of other borohydrides and boranes.

Ionic boron hydrides are widely used as reducing agents in organic chemistry [364]. Physical properties of complex borohydrides are summarized in Tables 21 and 22.

**Table 21:** Physical properties of complex borohydrides.

| Compound              | Gross formula   | Molecular mass | Melting point, °C | Density, g/cm <sup>3</sup> | Specific heat, cal g <sup>-1</sup> °C <sup>-1</sup> | Enthalpy of formation $\Delta H_f^{298}$ , kcal/mol |
|-----------------------|-----------------|----------------|-------------------|----------------------------|-----------------------------------------------------|-----------------------------------------------------|
| Lithium borohydride   | $\text{LiBH}_4$ | 21.79          | 284 (Dec.)        | 0.66                       | 0.84                                                | -44.1                                               |
| Sodium borohydride    | $\text{NaBH}_4$ | 37.86          | Dec. >400         | 1.074                      | 0.55                                                | -43.83                                              |
| Potassium borohydride | $\text{KBH}_4$  | 53.95          | Dec. >400         | 1.175                      | —                                                   | -57.7                                               |

Dec. = decomposition

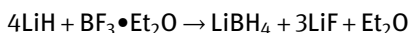
**Table 22:** Physical properties of complex borohydrides.

| Compound              | Gross formula                     | Molecular mass | Density           | Enthalpy of formation $\Delta H_f^{298}$ |          |           |
|-----------------------|-----------------------------------|----------------|-------------------|------------------------------------------|----------|-----------|
|                       |                                   | g/mol          | g/cm <sup>3</sup> | kJ/mol                                   | kcal/mol | kcal/100g |
| Lithium borohydride   | LiBH <sub>4</sub>                 | 21.792         | 0.681             | −194.3                                   | −46.44   | −213.11   |
| Sodium borohydride    | NaBH <sub>4</sub>                 | 37.86          | 1.08              | −191.0                                   | −45.65   | −120.63   |
| Beryllium borohydride | Be(BH <sub>4</sub> ) <sub>2</sub> | 38.717         | 0.604             | −107.9                                   | −25.8    | −66.6     |

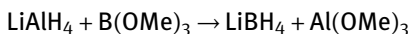
Data source: [365]

### 5.1.1 Lithium Borohydride

Lithium borohydride, lithium boranate, lithium tetrahydroborate, LiBH<sub>4</sub>, CAS RN [16949-15-8],  $M = 21.784$  g/mol, has a very high hydrogen content, 18.5 mass-% hydrogen. Lithium boranate is a white powder, which, in contradistinction to sodium boranate, reacts with water. At room temperature, diborane is readily absorbed into ethyllithium with the formation of various ethyldiboranes and a white solid, which is LiBH<sub>4</sub> [366]. LiBH<sub>4</sub> can be synthesized by several methods, for example, direct synthesis from elements. Other methods of preparing lithium borohydride are:



or



or



#### 5.1.1.1 Physical Properties of Lithium Borohydride

The crystal structure of LiBH<sub>4</sub> has been studied by synchrotron X-ray powder diffraction at room temperature and at 408 K [367]. At room temperature it has orthorhombic symmetry, space group *Pmna*, with unit cell parameters of  $a = 7.17858(4)$  Å,  $b = 4.43686(2)$  Å,  $c = 6.80321(4)$  Å. The tetrahedral (BH<sub>4</sub>)<sup>−</sup> anions (point symmetry *m*) are aligned along two orthogonal directions and are strongly distorted with respect to bond lengths [B—H = 1.04(2) to 1.28(1) Å] and bond angles [ $\angle$ H—B—H = 85.1(9)° and 120.1(9)°]. As the temperature is increased the structure undergoes a first-order transition and becomes hexagonal (space group *P6<sub>3</sub>mc*, with unit cell parameters of  $a = 4.27631(5)$  Å,  $c = 6.94844(8)$  Å at  $T = 408$  K). The (BH<sub>4</sub>)<sup>−</sup> tetrahedra align along *c*, become more symmetric [point symmetry *3m*, B—H = 1.27(2) and 1.29(2) Å,  $\angle$ H—B—H = 106.4(2)° and 112.4(9)°], and show displacement amplitudes that are consistent with dynamical disorder about their trigonal axis. Structurally, LiBH<sub>4</sub> has four different polymorph phases with the space groups *Pnma*, *P6<sub>3</sub>mc*, *Ama2*, and *Fm-3m*. Dynamically, the high temperature phase of LiBH<sub>4</sub> is a lithium fast-ion conductor.

The standard enthalpy of formation of lithium borohydride is −190.46 kJ/mol (−45.5 kcal/mol). Other sources gave an enthalpy of formation of −194 kJ/mol (−46.4 kcal/mol).

### 5.1.1.2 Chemical Properties of Lithium Borohydride

Lithium borohydride is hygroscopic and unstable in moist air. The reaction between lithium borohydride  $\text{LiBH}_4$  and atmospheric water vapor leads to premature material dehydrogenation and unwanted gas evolution in propellants. Lithium borohydride can be protected from the moisture by chemical vapor deposition metal coatings deposited from metal carbonyl decomposition [368].

Lithium borohydride can be dissolved in ammonia and this solution constitutes a hypergolic fuel [369, 370]. Lithium boranate forms adducts with ammonia in stoichiometric compositions, containing one or two ammonia molecules as solvates:  $\text{LiBH}_4 \cdot \text{NH}_3$  or  $\text{LiBH}_4 \cdot 2\text{NH}_3$ .

Lithium borohydride is considered as a hydrogen storage material owing to its high gravimetric hydrogen density (19.6%). Because of its hygroscopicity, lithium borohydride is a hazardous material that requires specific handling precautions. The reaction mechanism between  $\text{LiBH}_4$  and atmospheric water vapor, which leads to premature material dehydrogenation, was investigated using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, XRD, or thermogravimetric analysis (TGA)/differential thermal analysis (DTA), were investigated and led to the formation of lithium metaborate dihydrate  $\text{LiBO}_2 \cdot 2\text{H}_2\text{O}$  as hydrolysis product [371].

Lithium borohydride  $\text{LiBH}_4$  was introduced as an energetic component in solid propellants for its high hydrogen content, perfect burning performance and high reactivity. In order to reduce the hygroscopicity and to improve the stability in air,  $\text{LiBH}_4$  was coated with wax and polyester carbonate [372, 373]. The final product was characterized by scanning electron microscopy, electron spectroscopy for chemical analysis-XPS, and Raman spectroscopy, whereas the stability in air was investigated by monitoring weight changes. The results showed that a uniform coating layer was formed on the surface of  $\text{LiBH}_4$ , and the coverage was estimated from the boron content as approximately 82%. The activity of  $\text{LiBH}_4$  as an additive to promote the thermal decomposition of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and ammonium perchlorate was studied using differential scanning calorimetry (DSC), comparing the catalytic effects of pure and coated  $\text{LiBH}_4$ . This indicated that the coating did not decrease the reactivity of  $\text{LiBH}_4$ . It was suggested that surface coating with inert materials is a simple and effective method of improving the storage stability and performance of  $\text{LiBH}_4$ , while maintaining its reactivity.

### 5.1.1.3 Applications for Lithium Borohydride

Lithium borohydride would not only be a good fuel in rocket propellants, but it has also been considered as a hydrogen storage medium because it has high gravimetric hydrogen capacity [374]. In the hydrolysis of  $\text{LiBH}_4$  with the liberation of hydrogen gas, different byproducts form under different operating conditions. In the hydrogen desorption reaction of  $\text{LiBH}_4$ ,  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is a possible intermediate compound. Several methods have been proposed to improve the de-/rehydrogenation properties of  $\text{LiBH}_4$ . The first method is the “destabilization” of  $\text{LiBH}_4$ . The second method is the use of catalysts.

### 5.1.2 Sodium Borohydride

Sodium borohydride, sodium boranate, sodium tetrahydroborate,  $\text{NaBH}_4$ ,  $M = 37.833 \text{ g/mol}$ , CAS RN [16940-66-2], has a moderately high hydrogen content of 10.66 mass-% hydrogen. The hydrogen can be released by reaction with catalysts and water. Sodium borohydride is unusual because it is soluble in water without hydrolysis.

The standard enthalpy of formation of sodium borohydride is  $-191.84 \text{ kJ/mol}$  ( $-45.8 \text{ kcal/mol}$ ).

Sodium borohydride,  $\text{NaBH}_4$ , an air-stable white powder commonly referred to as sodium borohydride, is the most commercialized and readily available boron hydride material. Sodium borohydride or potassium borohydride do not react with water and are soluble in water. They are stable in aqueous solution as long as the pH does not drop into the acidic range and as long as contact with catalysts is avoided. Sodium borohydride is widely used as a reductant in organic chemistry, as a catalyst, and for bleaching high-brightness paper. Using sodium borohydride as a hydrogen storage medium for hydrogen-propelled automobiles is only economical if a simple method of converting the hydrolysis products back to sodium borohydride can be found.

Sodium borohydride can be prepared by electrolytic or hydrogen gas reduction of borax or other boron minerals. Reduction of sodium metaborate with magnesium produces sodium borohydride. Sodium borohydride, an important starting reactant in the preparation of boranes, can be prepared by the high-temperature reaction of sodium hydride with borate esters [375]. It is a very useful reducing agent for a wide range of industrial applications [376]. Various applications of sodium borohydride in the hypergolization of kerosene fuels will be discussed in a future volume on hypergolic propellants. See also [377, 378].

### 5.1.3 Magnesium Borohydride

Magnesium borohydride, magnesium bis(tetrahydroborate),  $\text{Mg}(\text{BH}_4)_2$ , is a potential rocket fuel, but very little is known about it. Metal tetrahydroborates, in general, form a large variety of structures ranging from simple ionic structures for  $\text{NaBH}_4$  to very complex structures for  $\text{Mg}(\text{BH}_4)_2$ . Despite the extensive discussion in the literature no clear explanation has been offered for this variety so far. A DFT computational analysis of the structural and electronic properties of a broad range of metal tetrahydroborates was done to study the factors that determine their structure: ionic bonding, the orientation of the  $\text{BH}_4$  groups, and the coordination number of the metal cation [379]. The charge transfer in the metal tetrahydroborates explains the structural diversity of these ionic compounds. By using the ionic radius for the  $\text{BH}_4$  group, structural predictions can be made for new and complex metal hydride compounds. The structure of magnesium borohydride is a transition between ionic and covalent borohydrides.

Magnesium borohydride has been evaluated as a hydrogen storage medium. Magnesium borohydride has the most complex crystal structures and the largest number

of phase polymorphs among other borohydrides. Some of these polymorphs possess a significant porosity, and on the other hand ultra-density with the second highest volumetric hydrogen content among all known hydrides. Additionally,  $\text{Mg}(\text{BH}_4)_2$  has the lowest theoretical stability, the lowest temperature of hydrogen release, and the mildest conditions for partial rehydrogenation among the alkali and alkaline-earth borohydrides [380].

#### 5.1.4 Other Ionic Boron Hydrides

Ionic boron hydrides would have the advantage over covalent boron hydrides that they have lower vapor pressure or no measurable vapor pressure at all, making them safer to handle and they still would be useful as rocket fuels.

In the thermolysis of tetraethylammonium tetraborohydride,  $\text{Et}_4\text{NBH}_4$ , the tetraethylammonium cation seems to survive, but the tetraborohydride anion changes to form di-tetraethylammonium decahydrodecaborate,  $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$  [381]. Thermolysis of  $\text{Et}_4\text{NBH}_4$  can be done using triethylamine borane ( $\text{Et}_3\text{NBH}_3$ ) as a boron-based solvent or using mineral oil as a non-boron-based solvent. See also [382, 383].

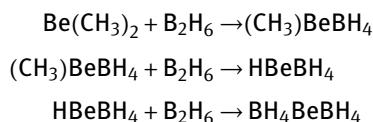
A series of hypergolic metal ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ) complexes with  $\text{B}_{12}\text{H}_{12}^{2-}$  were synthesized and fully characterized [384]. These complex metal hydrides possess good physicochemical properties (decomposition temperatures: 494.9–559.4 K (221.8–286.3 °C); densities: 1.215–1.264 g/cm<sup>3</sup>). Two of these six complexes exhibited ultrashort ignition delay times (approximately 1 ms), with white fuming nitric acid (WFNA) as the oxidizer, which makes them useful for bipropellant formulations.

## 5.2 Covalent Complex Boron Hydrides

### 5.2.1 Beryllium Borohydride

Beryllium borohydride, beryllium boranate; beryllium, bis[tetrahydroborato];  $\text{Be}(\text{BH}_4)_2$ ,  $M = 38.7$  g/mol, CAS RN [30374-53-9], is a solid that readily sublimates without decomposition.

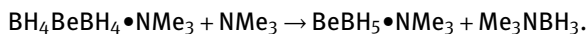
Beryllium borohydride,  $\text{Be}(\text{BH}_4)_2$ , can be prepared from dimethylberyllium and diborane [385]:



or, even better, from beryllium chloride and lithium borohydride or from beryllium chloride and sodium borohydride in a dry melt reaction at 323–423 K (50–150 °C) under nitrogen and at low pressure [386].

The vapors were collected in a cold trap, yielding 89% of theoretical of beryllium borohydride of high purity. Beryllium borohydride is a white solid that sublimates at room temperature, ignites instantly in air and reacts vigorously with water.

Beryllium borohydride forms 1:1 adducts with diethyl ether or trimethylamine. The ether adduct  $\text{Be}(\text{BH}_4)_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ , is a clear liquid that distills at 323 K at 0.13 Pa (50 °C at 0.001 mm Hg). The amine adduct,  $\text{Be}(\text{BH}_4)_2 \cdot \text{N}(\text{CH}_3)_3$ , is a low melting solid that melts at ~308 K (~35 °C). The amine adduct reacts further with additional  $\text{Me}_3\text{N}$ :



Under intense heat, the adducts decompose to hydrogen, diborane, and beryllium-bearing solids.

Studies of the  $\text{Be}(\text{BH}_4)_2/\text{AlR}_3$  reaction system led to the discovery of new forms of beryllium hydride, the borane-terminated beryllium hydrides,  $\text{H}_3\text{B}(\text{BeH}_2)_x\text{BH}_3$  [387]. These compounds have good physical and chemical stability and are essentially equivalent to pure  $\text{BeH}_2$  in theoretical propellant performance. They are, like  $\text{BeH}_2$ , amorphous and of low density, and studies aimed at inducing  $\text{H}_3\text{B}(\text{BeH}_2)_x\text{BH}_3$  crystallization met with very limited success.

### 5.2.1.1 Properties of Beryllium Borohydride

The vapor pressure of beryllium borohydride can be calculated from:

$$\log_{10} p = 11.772 - \frac{3240}{T}$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The normal sublimation temperature at sea level pressure is 364.4 K (91.3 °C) and the heat of vaporization is 62.0 kJ/mol (14.81 kcal/mol) [385]. The vapor pressure of the trimethylamine adduct with beryllium borohydride can be calculated from:

$$\log_{10} p = 8.353 - \frac{2909}{T}$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin and which gives an extrapolated b. p. of 533 K (260 °C).

The crystal structure of  $\text{Be}(\text{BH}_4)_2$  consists of a helical polymer of  $\text{BH}_4\text{Be}$  and  $\text{BH}_4$  units [388]. Within the  $\text{BH}_4\text{Be}$  unit the  $\text{Be} \cdots \text{B}$  distance is  $1.918 \pm 0.004 \text{ \AA}$ , whereas each Be is linked to two remaining  $\text{BH}_4$  units (and each  $\text{BH}_4$  to two Be) at a  $\text{Be} \cdots \text{B}$  distance of  $2.001 \pm 0.004 \text{ \AA}$ . Within the  $\text{BH}_4\text{Be}$  units there are two hydrogen bridges between B and Be, and in the helical polymer each  $\text{B} \cdots \text{Be}$  contact has two hydrogen bridges. The crystal structure is tetragonal, and the space group is  $I41cd$ , with  $a = 13.62 \pm 0.01 \text{ \AA}$  and  $b = 9.10 \pm 0.01 \text{ \AA}$ . Bonding from Be to  $\text{BH}_4$  occurs about equally directly from Be to B compared with bonding through bridge hydrogen atoms.

A first-principles study of the electronic structure and the energetics of beryllium boranate  $\text{Be}(\text{BH}_4)_2$  showed that (in contrast to the other boranates and alanates) hydrogen desorption directly to the elements is likely and is at least competitive with desorption to the elemental hydride ( $\text{BeH}_2$ ) [389]. The low formation enthalpy of  $\text{Be}(\text{BH}_4)_2$  indicated participation of all atoms in the covalent bonding, which is in contrast to the ionic bonding observed in other boranates.  $\text{Be}(\text{BH}_4)_2$  differs from other boranates and alanates in that its dehydrogenation to the elements is thermodynamically slightly more favorable than dehydrogenation via the simple hydride  $\text{BeH}_2$ . In alkali or alkaline earth boranates and alanates, dehydrogenations always occur via the alkali or alkaline earth simple hydride. Boranates are more stable than the corresponding alanates, lighter cations give compounds that are more unstable, and alkaline earth compounds are more unstable than alkali compounds.

### 5.2.1.2 Properties of Hybaline B3

Physical properties of the liquid adduct of methylamine and beryllium borohydride, which has been developed and tested under the code-name Hybaline B3, are summarized in Table 23.

**Table 23:** Physical properties of Hybaline B3.

| Property                 | SI units                                 | Other units                                 |
|--------------------------|------------------------------------------|---------------------------------------------|
| Freezing point           | 261.6 K                                  | −11.5 °C                                    |
| Density                  | 0.641 g/cm <sup>3</sup> at 293 K         | —                                           |
| Vapor pressure           | 0.2 kPa at 299 K                         | 1.5 mm Hg at 25.8 °C                        |
| Viscosity                | —                                        | 3.4 cPs at 20 °C                            |
| Surface tension          | 0.286 N/m at 293 K                       | 28.6 dyn/cm at 20 °C                        |
| Heat capacity            | 2.6133 J g <sup>−1</sup> K <sup>−1</sup> | 0.6246 cal g <sup>−1</sup> °C <sup>−1</sup> |
| Flash point              | 293 K                                    | 68 °F                                       |
| Autoignition temperature | 413 K                                    | 284 °F in air                               |

Data source: [390]

There is contradicting information about the pyrophoricity of Hybaline B3. Although one source states that it oxidizes slowly in dry air without ignition, other sources describe it as instantly pyrophoric in air.

The liquid adduct of methylamine and beryllium borohydride under the code-name Hybaline B3 has been the fuel for 87 test firings in a nominal 440-N (100 lb<sub>f</sub>) thrust uncooled rocket engine at a chamber pressure of 2.07 MPa (300 psia) [390, 391]. Thirty-seven tests were carried out with  $\text{N}_2\text{O}_4$ , 43 with 90%  $\text{H}_2\text{O}_2$ , and 7 with 98%  $\text{H}_2\text{O}_2$  as the oxidizer. An additional 25 tests were conducted with  $\text{N}_2\text{O}_4$  at a thrust level of 2.2 kN (500 lb<sub>f</sub>) and a chamber pressure of 6.89 MPa (1000 psia). Delivered performance with both oxidizers was low compared with theoretical impulse. Performance



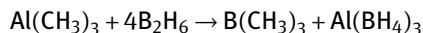
efficiencies significantly increased at weight oxidizer/fuel ratios where the combustion temperature was near or above the melting point of beryllium oxide. Hybaline B3 was compatible with standard materials of construction, and although it is pyrophoric, the fuel presented few handling problems other than toxicity.

### 5.2.2 Aluminum Borohydride

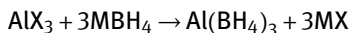
Aluminum borohydride, also known as aluminum boranate, aluminum tetrahydroborate, aluminum tris(tetrahydroborate),  $\text{Al}(\text{BH}_4)_3$ ,  $\text{AlB}_3\text{H}_{12}$ ,  $M = 71.510 \text{ g/mol}$ , CAS RN [16962-07-5], is a liquid instead of a solid and reacts vigorously with air, oxygen, or water. Aluminum borohydride can be used as an ignition fluid for large rocket engines with LOX as the oxidizer.

#### 5.2.2.1 Preparation of Aluminum Borohydride

Aluminum borohydride was first prepared from trimethylaluminum and excess diborane [392]:



Aluminum boranate and other borohydrides can be prepared by metathetical reactions from metal halogenides utilizing the alkali metal borohydrides [393, 394]:



where X is a halogen (Cl, Br) and M is an alkali metal (Li, Na, K). The THF adduct of aluminum boranate is not pyrophoric.

#### 5.2.2.2 Physical Properties of Aluminum Boranate

The molecular mass of aluminum boranate is  $71.510 \text{ g/mol} = 13.9841 \text{ mol/kg}$ .

#### Melting Point and Boiling Point of Aluminum Boranate

Aluminum boranate freezes at  $208.6 \text{ K} = -64.5^\circ\text{C}$  and boils at  $317.6 \text{ K} = 44.5^\circ\text{C}$ . The solid  $\text{Al}(\text{BH}_4)_3$  exists in two modifications with a phase transition temperature between 180 and 195 K ( $-93$  and  $-78^\circ\text{C}$ ). Weak interactions between aluminum borohydride molecules in the solid state explain the low melting point of the material.

#### Density of Aluminum Boranate

The density of aluminum boranate is less than that of water ( $\rho = 0.544 \text{ g/cm}^3$  at  $293 \text{ K} = 20^\circ\text{C}$ ). The density data for aluminum boranate are listed in Table 24.

**Table 24:** Density of aluminum boranate.

| Temperature |       | Density           |
|-------------|-------|-------------------|
| K           | °C    | g/cm <sup>3</sup> |
| 209.2       | −63.9 | 0.622             |
| 209.7       | −63.4 | 0.622             |
| 223.0       | −50.1 | 0.611             |
| 235.9       | −37.2 | 0.600             |
| 241.5       | −31.6 | 0.595             |
| 245.6       | −27.5 | 0.592             |
| 259.7       | −13.4 | 0.581             |
| 259.9       | −13.2 | 0.581             |
| 266.3       | −6.8  | 0.576             |
| 266.5       | −6.6  | 0.576             |
| 274.1       | +1.0  | 0.569             |
| 274.5       | +1.4  | 0.569             |

Data source: [52]

The data in Table 24 can be represented by the equation:

$$\rho = 0.7866 - 0.000793T$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $T$  is the temperature in kelvin.

### Vapor Pressure of Aluminum Boranate

Vapor pressure data for aluminum boranate are listed in Table 25.

**Table 25:** Vapor pressure of aluminum boranate.

| Temperature |       |       | Vapor pressure |       |       |
|-------------|-------|-------|----------------|-------|-------|
| K           | °C    | °F    | kPa            | mm Hg | psia  |
| 231.2       | −41.9 | −43.4 | 1.5            | 11.0  | 0.213 |
| 244.6       | −28.5 | −19.3 | 3.4            | 25.3  | 0.489 |
| 261.2       | −11.9 | 10.6  | 8.7            | 65.3  | 1.266 |
| 268.4       | −4.7  | 23.5  | 12.7           | 95.0  | 1.837 |
| 273.1       | 0     | 32    | 15.9           | 119.5 | 2.311 |
| 283         | 9.9   | 49.8  | 25.3           | 190.0 | 3.674 |
| 286.6       | 13.5  | 56.3  | 29.3           | 220.0 | 4.254 |
| 290         | 16.9  | 62.4  | 34.3           | 257.0 | 4.970 |

Data source: [310]

### Viscosity of Aluminum Boranate

The viscosity of aluminum borohydride was determined experimentally from 209.2 to 305.6 K (−63.9 to 32.5 °C) with an accuracy of  $\pm 2.5\%$ . The data are given in Table 26 and were plotted in Figure 4 (located above in the diborane section).

**Table 26:** Viscosity of liquid aluminum borohydride.

| Temperature |       | Density           | Viscosity  |
|-------------|-------|-------------------|------------|
| K           | °C    | g/cm <sup>3</sup> | millipoise |
| 209.3       | −63.8 | 0.620             | 9.28       |
| 217.3       | −55.8 | 0.614             | 7.58       |
| 228.9       | −44.2 | 0.605             | 5.91       |
| 239.6       | −33.5 | 0.597             | 4.69       |
| 250.3       | −22.8 | 0.588             | 3.93       |
| 261.7       | −11.4 | 0.581             | 3.39       |
| 265.0       | −8.1  | 0.577             | 3.12       |
| 280.5       | 7.4   | 0.564             | 2.58       |
| 287.4       | 14.3  | 0.559             | 2.34       |
| 305.6       | 32.5  | 0.545             | 1.93       |

Data source: [52]

The viscosity of liquid aluminum borohydride, the same data as shown in Table 26 and in Figure 4 (located in the diborane section), as a function of temperature can be expressed by the equation [52]:

$$\eta = 23 \times 10^{-5} \rho^{\frac{1}{3}} e^{\left(\frac{1291}{\rho T}\right)}$$

where  $\eta$  is the viscosity in Poise,  $\rho$  is the density in g/cm<sup>3</sup>, and  $T$  is the temperature in kelvin.

### Surface Tension of Aluminum Boranate

The surface tension of aluminum boranate was measured within the range 209 to 305 K (−63 to +32 °C). The surface tension data were already shown in Figure 6 (in the diborane section). The numeric surface tension data are listed in Table 27.

The data in Table 27 can be fitted to a linear equation:

$$\sigma = (61.0 - 0.130T)\rho^{\frac{2}{3}}$$

where  $\sigma$  is the surface tension in dyn/cm,  $\rho$  is the density in g/cm<sup>3</sup>, and  $T$  is the temperature in kelvin.

**Table 27:** Surface tension of aluminum boranate.

| Temperature |       | Surface tension     |
|-------------|-------|---------------------|
| K           | °C    | dyn/cm <sup>a</sup> |
| 209.6       | −63.5 | 24.6                |
| 216.2       | −56.9 | 23.8                |
| 227.4       | −45.7 | 22.6                |
| 238.3       | −34.8 | 21.3                |
| 248.9       | −24.2 | 20.0                |
| 258.7       | −14.4 | 19.0                |
| 260.3       | −12.8 | 18.8                |
| 263.7       | −9.4  | 18.6                |
| 286.8       | +13.7 | 16.0                |
| 305.1       | +32.0 | 14.3                |

Data source: [52]

<sup>a</sup> 1 N = 10<sup>5</sup> dyn

### IR Spectra of Aluminum Boranate

High-resolution ( $0.01\text{ cm}^{-1}$ ) Fourier transform infrared (FTIR) spectra of  $\text{Al}(\text{BH}_4)_3$  and  $\text{Al}(\text{BD}_4)_3$  recorded from low-pressure samples at room temperature showed only broad vibrational bands, with no trace of resolved rotational structure [395]. The BH bridge stretching and the  $\text{BH}_2$  deformation regions were examined at  $0.001\text{ cm}^{-1}$  resolution by tunable infrared diode laser spectroscopy for samples cooled to  $\sim 10\text{ K}$ . These too showed only near continua, with much more congestion than predicted by non-rigid rotor simulations based on boron isotopic shifts from *ab initio* calculations.

The normal mode frequencies and corresponding vibrational assignments of aluminum tetrahydroborate in  $D_3$  symmetry were examined theoretically [396]. All normal modes were successfully assigned to one of seven types of motion (B—H stretch, Al—B stretch, B—Al—B bend, H—B—H bend,  $\text{BH}_4$  wag,  $\text{BH}_4$  rock and  $\text{BH}_4$  twist) predicted by a group theoretical analysis. By comparing the vibrational frequencies with IR and Raman spectra available in the literature, a set of scaling factors was derived.

### Raman Spectra of Aluminum Boranate

Raman spectra of  $\text{Al}(\text{BH}_4)_3$  and  $^{11}\text{B}$  and  $^2\text{H}$  isotope-labeled isomers appeared to confirm a prismatic bridge structure  $D_{3h}$  [397]. There was no evidence for any significant structural change in the different phases when comparing IR spectra of gaseous, solid, and matrix-isolated IR spectra of  $\text{Al}(\text{BH}_4)_3$  and  $\text{Al}(\text{BD}_4)_3$  [398]. The data were consistent with a  $D_{3h}$  prismatic structure and all 23 of the optically allowed fundamental transitions were assigned for each molecular isotope. Some correlated NMR-Raman spectra were obtained over the temperature range 213 to 353 K ( $-60$  to  $+80\text{ }^\circ\text{C}$ ) and the results suggested that traces of decomposition products may act in a catalytic manner to profoundly change the NMR spectra of  $\text{Al}(\text{BH}_4)_3$ .

### Molecular Structure of Aluminum Boranate

The structures of several modifications of solid aluminum tetrahydroborates have been investigated, primarily by XRD of single crystals at low temperatures [399]. Solid aluminum tris(tetrahydroborate) exists in two phases with a transition temperature within the range 180–195 K. Each phase is made up of discrete  $\text{Al}(\text{BH}_4)_3$  units in which the angle between  $\text{AlB}_2$  and  $\text{Al}(\mu\text{-H})_2\text{B}$  planes is close to  $90^\circ$  and which conform within the limits of experimental error to  $D_{3h}$  symmetry; in the  $\alpha$  phase these molecular units are disposed around a  $2_1$  crystallographic screw axis.

### Thermodynamic Properties of Aluminum Boranate

The heat of formation of aluminum boranate was determined by calorimetry [400]. The enthalpy of formation of liquid aluminum boranate is  $-312.5 \text{ kJ/mol} = -74.7 \text{ kcal/mol}$  [52].

#### 5.2.2.3 Chemical Properties of Aluminum Boranate

##### Autoignition of Aluminum Boranate

There are numerous proposals for using aluminum boranate as the hypergolic ignition source for LOX-based rocket propellant applications and as a fuel in air-breathing hypersonic ramjets. The autoignition of aluminum boranate was therefore examined under a variety of conditions at different pressures and temperatures.

Additional experiments with aluminum boranate ignition and combustion will be described in a future volume on hypergolic bipropellant combinations. See also Fletcher et al. [401–404].

Here is one of the most unusual applications of a pyrophoric fluid: one can see why someone would want to select aluminum boranate for ignition of a rocket engine, but patenting aluminum boranate for use in a cigarette lighter appears to be extremely risky, a sure method of eradicating smokers by triggering accidental explosions of their lighters [405].

##### Reactions of Aluminum Boranate with Lewis Bases

Aluminum boranate forms adducts with amines and ethers. The adduct of aluminum boranate with dimethylamine is a liquid and has been tested as a rocket propellant under the code name Hybaline A4. Hybaline A4 is the reaction product of aluminum boranate and dimethylamine and was developed by Union Carbide [406]. The reaction was carried out in an inert solvent such as n-hexane or benzene. Hybaline A4 oxidizes slowly in dry air, but inflames in moist air or in contact with water. It has a very low vapor pressure, 267 Pa at 298 K = 2 mm Hg at  $25^\circ\text{C}$ , which makes it safer to handle than pentaborane. The boiling point was estimated at  $>493 \text{ K}$  ( $>220^\circ\text{C}$ ), but starts to decompose at that temperature. The freezing point is 265.6 K ( $-7.5^\circ\text{C}$ ) with supercooling. Once solidified, it melts at 277.6 K ( $+4.5^\circ\text{C}$ ). The density of Hybaline A4 is  $0.759 \text{ g/cm}^3$ . The viscosity of Hybaline A4 at 293 K is 9.2 cPs. The enthalpy of formation is  $-69 \text{ kJ/mol}$  ( $-16.5 \text{ kcal/mol}$ ).

A similar adduct can be formed between aluminum boranate and a 1:1 mol ratio mixture of dimethylamine and methylamine. This adduct has been evaluated as a rocket propellant under the code name Hybaline A5. Most of its properties are similar to those of Hybaline A4, but it has a lower freezing point than Hybaline A4. As a matter of fact, it has no sharp freezing point, but solidifies to a glassy sticky mess below 233 K ( $-40^{\circ}\text{C}$ ). The heat of formation of liquid Hybaline A4 was determined by oxygen bomb calorimetry [400].

Although this fuel has never found widespread application, substantial effort has been devoted to developing materials of construction that are compatible with Hybaline A. O-ring seals of selected elastomeric and compliant materials were evaluated for resistance to Hybaline A5 and pentaborane in a simulated end-use test at 296 K ( $73^{\circ}\text{F}$ ) [407]. The candidate elastomers were placed under compression in closed cells and exposed to the liquid and vapor of liquid rocket fuels and oxidizers for extended periods of time. Rate of fuel loss through the seal, and the change in physical properties of the seal materials were determined.

Compatibility and corrosion rates of 15 structural metals and three fluorinated plastics in Hybaline A5 liquid and vapor at 323 K ( $50^{\circ}\text{C}$ ) were investigated [408]. Corrosion rates of all metals were low ( $2.5\text{ }\mu\text{m}/\text{year} = 0.1\text{ mil}/\text{year}$  average). None of the metals actively catalyzed the decomposition of Hybaline A5. The plastics showed weight gains of 0.02 to 0.04% in 21-day exposures, and insignificant changes in appearance. No significant change in mechanical properties on 20-cm (8-in.) tensile specimens and no stress corrosion cracking on U-bend stressed specimens occurred.

Extensive materials compatibility testing was done on newly developed materials and other, well established materials that had already shown good compatibility with other rocket propellants. Several polymers were examined for resistance to Hybaline A5 and gelled aluminum/hydrazine [409, 410].

Hybaline  $\text{A}_{14}$  is similar to Hybaline A5 except that the amine ligand is different to assure better compatibility with RP-1. The amine ligand is 2-ethylhexylamine. It freezes below 195 K ( $-78^{\circ}\text{C}$ ) and has a density of  $0.78\text{ g}/\text{cm}^3$  at 293 K. It autoignites in air only above 373 K ( $100^{\circ}\text{C}$ ) and is best stored under nitrogen. Hybaline  $\text{A}_{14}$  is hypergolic with most oxidizers. It is more viscous than Hybaline A5 with a viscosity of 30 cPs at 293 K. Hybaline  $\text{A}_{14}$  has been tested as a combustion instability suppressant in a LOX/RP-1 rocket combustion chamber [411]. Hybaline A3 was a mixture of methylamine with aluminum boranate.

Propellant combinations of Hybaline A5 with six different oxidizers ( $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_4 + \text{NO}$ , inhibited red fuming nitric acid (IRFNA),  $\text{H}_2\text{O}_2$ ,  $\text{ClF}_5$ , and  $\text{F}_2$ ) were evaluated in terms of the effects of engine design parameters on their ignition characteristics at reduced ambient pressures. Additional applications of Hybalines as fuels in hypergolic rocket propellant combinations will be discussed in a future volume on hypergolic bipropellant combinations.

Aluminum borohydride forms adducts with 1–4 mol ethylenediamine that have been evaluated as hydrogen storage media [412].

### Reactions of Aluminum Boranate with Other Hydrides

Aluminum boranate reacts with a wide range of metal borohydrides, forming solid complex hydrides. The adduct of aluminum boranate with ammonia borane has been well characterized and evaluated as a hydrogen storage medium, but it decomposed to a viscous mass within 2 weeks of storage at room temperature. The advantage of this adduct as a hydrogen storage medium would be that it releases two moles of dihydrogen at moderate temperatures, although only stepwise, and its decomposition leading to release of dihydrogen is endothermic instead of exothermic, such as that of ammonia borane [413].

### Thermal Stability of Aluminum Boranate

In aluminum borohydride, the decomposition and the release of hydrogen start at around 313 K (40 °C). The material has not been investigated in detail for hydrogen storage by reversible reactions because of its extreme sensitivity to water and air.

The thermodynamical stability of  $\text{Al}(\text{BH}_4)_3$  has been investigated using first-principles calculations based on DFT and the heat of formation was predicted to be  $-132 \text{ kJ/mol}$  [414].

### Handling of Metal Borohydrides

When handling solid metal borohydrides (and other metal hydrides) in the laboratory, one should protect oneself from the dust by wearing dust masks and goggles because the finely ground dust particles are very fluffy and easily become airborne, irritating the mucous membranes.

In the case of metal borohydride fires, the fires may not be extinguished with water because hydrogen evolution would cause the situation to become even more dangerous. Even carbon dioxide fire extinguishers are useless against metal hydride or metal borohydride fires. To fight metal borohydride fires, it would be best to cover the burning material with sand, which would starve the burning material of oxygen.

### Toxicity of Aluminum Boranate

Aluminum boranate would inflame instantly in air or hydrolyze with moisture before it can be absorbed into living things. Aluminum boranate adducts with alkylamines, known under the code name Hybaline, are more stable and can potentially accidentally find their way into propellant handling personnel. Hybaline A, an adduct of aluminum boranate with alkylamines, has been administered to rats, rabbits, cats, and dogs via intragastric, *i.p.*, *i.v.*, cutaneous, subcutaneous, and inhalation routes [415]. All data indicated that effects of Hybaline A on mammals can be attributed to physiochemical changes caused by energy production during hydrolysis or thermal decomposition of Hybaline A. Those animals that survived the initial exposure showed no changes in any system that could be attributed to Hybaline A.

## 6 Borazines, Borazanes, and Boroxines

In addition to boron organic compounds containing only boron, carbon, and hydrogen, there are other compounds to be investigated as candidate rocket fuels that contain nitrogen as well.

### 6.1 Borazines (Borazoles)

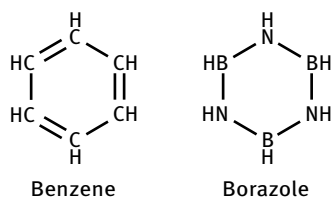
A ring structure formed of alternating boron and nitrogen atoms is isoelectronically similar to cyclohexane and benzene. These rings are called borazines, sometimes also called borazoles, although the name borazine is the more widely accepted nomenclature [416]. The name **borazole** hints at its structural similarity with benzene (*Benzol* in German).

Borazine is easier to handle than pentaborane, but its heat of combustion and performance as a rocket fuel is lower than that of pentaborane.

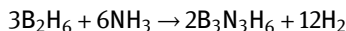
Borazine, also known as borazole,  $B_3N_3H_6$ , 1,3,5-triaza-2,4,6-triborinane, CAS RN [6569-51-3], with a molecular mass of 80.5 g/mol, contains 52.2 mass-% nitrogen and 40.2 mass-% boron. It freezes at 220 K ( $-58^\circ\text{C}$ ) and boils at 326 K ( $53^\circ\text{C}$ ). The density at 273 K ( $0^\circ\text{C}$ ) is  $0.824\text{ g/cm}^3$ . The vapor pressure of borazine in the range 223–325 K can be calculated from:

$$\log p_v = 6.5022 - \frac{960.099}{(T - 63.32)}$$

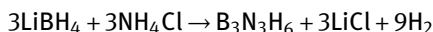
where  $p_v$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The six B–N bonds have lengths of  $1.436\text{ \AA}$ . For comparison, the carbon-carbon bonds in benzene are shorter at  $1.397\text{ \AA}$ .



Borazine was initially prepared by thermolysis of the DADB, which was obtained from diborane and ammonia [417]:



Borazine can be prepared by interaction of  $LiBH_4$  and  $NH_4Cl$  in the absence of solvents at moderately high temperatures [418].

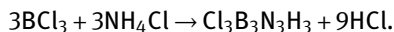




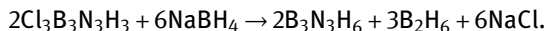
This method is preferred as it does not use high pressure. A similar method used the cheaper sodium borohydride and ammonium sulfate in diglyme as a solvent [419].

A four-step procedure involving the reaction of  $B_2H_6$  with liquid  $NH_3$  to give borazine is described in [420].

In a two-step process to borazine, boron trichloride is first converted to trichloroborazine [421]:



The B—Cl bonds are subsequently converted to B—H bonds:



The following density, viscosity, and surface tension data of borazine were taken from Eddy et al. [422]. The density of borazine as a function of temperature can be expressed by:

$$\rho = 1.1551 - 0.001074T$$

where  $\rho$  is the density in  $g/cm^3$  and  $T$  is the temperature in kelvin. Data for the viscosity of borazine were curve-fitted to the equation:

$$\eta = 47.3(10^{-5})\rho^{\frac{1}{3}}e^{665.5\frac{\rho}{T}}$$

where  $\eta$  is the viscosity in Poise,  $\rho$  is the density in  $g/cm^3$  and  $T$  is the temperature in kelvin. Just as check points for the equation above, here are three raw data points for three temperatures: 230 K: 6.39 mPs; 273 K: 3.65 mPs; and 300 K: 2.85 mPs. Data for the surface tension of borazine were curve-fitted to the equation:

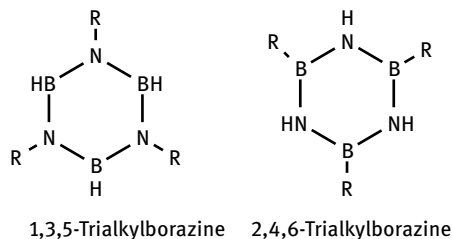
$$\sigma = (58.3 - 0.120T)\rho^{\frac{2}{3}}$$

where  $\sigma$  is the surface tension in dyn/cm,  $\rho$  is the density in  $g/cm^3$ , and  $T$  is the temperature in kelvin. The refractive index  $n_D^{20}$  of borazine is 1.3821. The freezing point of borazine is 216.9 K (with supercooling). Methods for the synthesis of borazine and its derivatives, synthetic methods based on reactions of functional derivatives of borazine, and properties of borazine and its derivatives are summarized in [423]. The heat of combustion of liquid borazine is  $2313.3 \pm 12.6$  kJ/mol ( $552.90 \pm 3.0$  kcal/mol), which translates into a heat of formation of  $-548.5 \pm 13.4$  kJ/mol ( $-131.1 \pm 3.2$  kcal/mol) [424].

Borazine does not react with diborane or lithium boranate, but ammonium chloride or hydrogen chloride will decompose it. Heating borazine at 343 K (70 °C) expels hydrogen with formation of a borazinyl polymer or polyborazylene, in which the monomer units are coupled in *para* position by new boron-nitrogen bonds. Boron nitride can be prepared by further heating of polyborazylene to 1273 K (1000 °C).

### 6.1.1 Substituted Borazines

In alkylborazines, the alkyl groups can be attached to either a boron atom or a nitrogen atom that is part of the ring structure:



Alkylborazines, for instance  $B,B',B''$ -triethylborazine, react hypergolically with fuming nitric acid [425]. In a ring of heterocyclic compounds, counting to indicate the location of substituents usually starts at the heteroatom. If the entire ring consists of heteroatoms, counting starts at the nitrogen (one of the nitrogen) atom(s).  $B,B',B''$ -triethylborazine could be called 2,4,6-triethylborazine.

The borazine ring undergoes some substitution reactions. However, unlike benzene, borazine and certain of its derivatives undergo addition reactions readily to give products such as  $B_3H_6N_3 \cdot 3HX$ , where  $X = Cl, Br, \text{ or } OH$  [426]. Borazine undergoes extensive decomposition in the liquid phase, even at room temperature.

$B,B',B''$ -triethylborazine decomposed below 373 K (100 °C), whereas  $B$ -trimethylborazine was reported to be stable at that temperature for extended periods.  $N$ -trimethylborazine (1,3,5-trimethylborazine) freezes at 265.6 K (−7.5 °C) and boils at 406 K (133 °C), whereas its  $B$ -substituted isomer ( $B$ -trimethylborazine, 2,4,6-trimethylborazine) melts at 304.9 K (31.8 °C) and sublimates at 393 K (120 °C). Hexamethylborazine was reported to survive treatment at 753 K (480 °C). Hexamethylborazine was more stable than phenyl or phenyl-methyl-borazoles [427]. Hexamethylborazine melts at 370 K (97 °C) and boils at 494 K (221 °C).

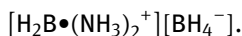
Attaching nitro groups to borazine would result in energetic explosives comparable with TNT [428, 429]. Similar energetic compounds are obtained by substituting three of the hydrogens in borazine with azido groups, such as in  $H_3B_3N_3(N_3)_3$  [430].

### 6.1.2 Borazanes

The nomenclature of adducts between boranes and amines is not always totally consistent. Some authors call them aminoborines in analogy to borine, others call them borazanes in analogy to alkanes.

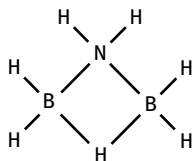
## 6.2 Diammonia Diborane

Reaction of diborane with ammonia at low temperatures forms a non-volatile compound, stable at 353 K (80 °C), which had the composition  $B_2H_6 \cdot 2NH_3$ , also called diborane diammine or diammonia diborane. It took a while until the structure could be identified as a tetrahydroborate (borohydride) anion and a diaminoboronium cation:



## 6.3 Aminodiborane

Aminodiborane is a byproduct in the preparation of borazole from diborane and ammonia. It can be made by passing a current of “diborane diammine” at 361 K (88 °C) and atmospheric pressure through a heated tube. It can be stored at room temperature for several days without appreciable decomposition. It melts at 206.6 K (−66.5 °C) and boils at 348.3 K (75.2 °C). The structure of aminodiborane has been established by electron diffraction and turned out to be similar to that of diborane, with one bridge hydrogen replaced by an amino group:

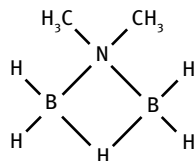


Cyclic aminodiborane,  $NH_2B_2H_5$ , ADB, can be made from ammonia borane ( $NH_3BH_3$ , AB) and THF  $\cdot BH_3$  [431]. Ammonia diborane ( $NH_3BH_2(\mu-H)BH_3$ ) and aminoborane ( $NH_2BH_2$ ) were identified as key intermediates in the formation of aminodiborane. Elimination of molecular hydrogen occurred from an ion pair,  $[H_2B(NH_3)(THF)]^+ [BH_4]^-$ . The structure of the aminodiborane  $\cdot$  THF complex was found from X-ray single crystal analysis to be a three-dimensional array of zigzag chains of aminodiborane and THF, maintained by hydrogen and dihydrogen bonding. The  $B \cdots H \cdots B$  bridge is opened when aminodiborane and NaH react to form sodium aminodiboronate,  $Na[NH_2(BH_3)_2]$ .

The DADB,  $[H_2B(NH_3)_2][BH_4]$ , is an ionic dimer of ammonia borane. It has received much less attention in the past few decades than ammonia borane, although it has the same high hydrogen content (19.6%) [432].

## 6.4 Alkylborazanes

*N*-alkylborazanes may be called dialkylamino-borines. Others just call them by the borane and the amine from which they were formed. In either case it is important to specify if the alkyl groups are attached to the boron atom or the nitrogen atom or both. The structure of *N*-dimethylaminodiborane has been established by electron diffraction and by nuclear magnetic resonance [433]. It is equivalent to diborane in which one bridge hydrogen has been replaced by a dimethylamino group



*N*-trialkylborazanes can be obtained by reaction of trialkylboron compounds in the presence of tertiary amines [45]. Borazanes such as  $\text{RBH}_2 \cdot \text{NR}_3$  that were formed from dialkyldiboranes and tertiary amines can be used as rocket fuels [434]. *N*-triethylborazane has been patented as a rocket fuel [435].

The ignition delay and the freezing point of *N*-triethylborazane can be lowered by the addition of 2 to 25% triethylborane, tetraethyldiborane, or triethylaluminum [436]. Triethylborazane has a density of  $0.791 \text{ g/cm}^3$ , a melting point of  $269 \text{ K}$  ( $-4^\circ\text{C}$ ), and a boiling point of  $373 \text{ K}$  at  $1.6 \text{ kPa}$  ( $100^\circ\text{C}$  at  $12 \text{ mm Hg}$ ). The heat of combustion is  $47642 \text{ kJ/kg}$  ( $20500 \text{ BTU/lb}$ ). The properties of numerous adducts between alkylboranes and alkyl amines are summarized in [98].

Boric acid triamides, tris(dialkylamino)boranes, of the  $\text{B}(\text{NR}_2)_3$  type where  $\text{R}=\text{C}_1-\text{C}_4$  alkyl or  $\text{C}_3-\text{C}_4$  cycloalkyl can ignite hypergolically with fuming nitric acid and have been patented as rocket propellants [437]. *N,N*-Dimethylaminodiborane  $[(\text{CH}_3)_2\text{N}]\text{HBH}_2\text{BH}_2$  is a potential liquid rocket or ramjet fuel. For this reason this compound has been investigated in more detail than some of the other borazanes.

*N,N*-Dimethylaminodiborane can be prepared by treatment of  $\text{K}(\text{H}_3\text{C})_2\text{NBH}_3$  in diglyme with a threefold excess of  $\text{NaBH}_4$  and one half mole of iodine, which produces a solution of  $\text{Na}(\text{H}_3\text{C})_2\text{N}(\text{BH}_3)_2$  that can later be converted to  $\mu\text{-(H}_3\text{C)}_2\text{NBH}_2\text{BH}_2$  by the addition of another half mole of iodine [438].

The maximum fundamental flame velocity in air for O: B = 0.8 at  $308 \text{ K} = 35^\circ\text{C}$  is  $115 \pm 5 \text{ cm/s}$ . Its lower heat of combustion of liquid fuel to gaseous nitrogen, carbon dioxide, steam, and solid boric oxide is  $44769 \text{ kJ/kg}$  ( $10700 \text{ kcal/kg} = 19.225 \pm 100 \text{ BTU/lb}$ ) [439]. It is a liquid and its spontaneous ignition temperature in air is  $383 \text{ K}$  ( $110^\circ\text{C} = 240^\circ\text{F}$ ).

The triple point temperature of *N,N*-dimethylaminodiborane is at  $218.4 \pm 0.2 \text{ K}$ , and the heat of fusion is  $1408 \pm 30 \text{ J/mol}$  [440]. The heat capacity of liquid

*N*-dimethylaminodiborane at 277.8 K is  $158.2 \text{ J mol}^{-1} \text{ K}^{-1}$ . The heat of vaporization of *N*-dimethylaminodiborane at 271.6 K (12.6 kPa = 94.3 mm Hg) is  $30119 \pm 30 \text{ J/mol}$ . The vapor pressure in the range from 220 to 290 K can be calculated from the equation:

$$\log p = 406.5734/T + 5.2095614 \times 10^{-2}T + 1.01048 \times 10^{-5}T^2 \\ - 1.390588 \times 10^{-7}T^3 - 11.63086$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. Based on the heat of reaction of its hydrolysis, the standard enthalpy of formation of *N*-dimethylaminodiborane is  $-151.5 \pm 3.1 \text{ kJ/mol}$  ( $-36.22 \pm 0.75 \text{ kcal/mol}$ ) [441].

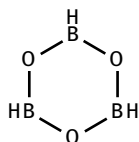
The far IR spectrum of *N,N*-dimethylaminodiborane showed a strong absorption band at  $420 \text{ cm}^{-1}$  and a weaker band at  $600 \text{ cm}^{-1}$  [442, 443]. A band at  $379 \text{ cm}^{-1}$  was assigned to the  $\mu\text{-H}_2$  bridge bending mode.

In trying to explain the molecular structure, a multiple origin method was used for the selection of atomic coordinates for the description of the normal vibrations of the *N*-dimethylaminodiborane molecule [444]. Symmetry considerations were used in order to obtain symmetry coordinates from these multiple origin method coordinates, and, under the assumption of a diagonal potential function, these coordinates were assigned to vibrational frequencies, which had been reported by Mann [442]. The valence force constants for the methyl-*N*-methyl framework vibrations were then calculated and the results compared with similar constants obtained from the dimethylamine molecule.

The molecular structure of *N,N*-dimethylaminodiborane has been determined from microwave spectra, including the boron-bonded hydrogen coordinates [445]. Structural parameters other than those of the hydrogens were in close agreement with earlier electron diffraction results. No internal rotation splittings were detected. The dipole moment was measured to be  $2.77 \pm 0.02 \text{ D}$ . The flame emission spectra of rocket engine plumes from engines operating on fluorine or oxygen as the oxidizer and dimethylaminodiborane as the fuel were measured in the visible and UV regions [446].

## 6.5 Boroxines

Boroxine ( $\text{B}_3\text{H}_3\text{O}_3$ ) CAS RN [289-56-5] is a six-membered, heterocyclic compound composed of alternating oxygen and boron atoms.



Boroxine derivatives (boronic anhydrides) such as trimethylboroxine make up a broader class of compounds called boroxines. These compounds are solids that are usually in equilibrium with their respective boronic acids at room temperature. Boroxine compounds are isoelectronic with benzene and, with the vacant *p*-orbital on the boron atoms, have partially aromatic character with a  $\pi$ -ring system. Boron single-bonds on boroxine compounds are mostly *s*-character. Ethyl-substituted boroxine has B—O bond lengths of 1.384 Å and B—C bond lengths of 1.565 Å. One of the most utilized boroxines is trimethylboroxine. It can be used for the synthesis of other alkylboron compounds, but has very little fuel value.

## 6.6 Ammonia Borane

Ammonia borane, borazane, also known as ammoniotrihydroborate, borane monoammoniate, ammonia borine, borine ammoniate,  $\text{H}_3\text{N}\cdot\text{BH}_3$ , CAS RN [13774-81-7], used to be a laboratory curiosity until its ability to reversibly store and release dihydrogen gas was discovered a few years ago and all of a sudden the number of publications dealing with this chemical has skyrocketed. The number of publications on ammonia borane, borohydrides, and similar boranes may soon exceed the number of publications on alkylboranes in the heyday of the Valkyrie ZIP HiCal fuels program. Dihydrogen as an energy carrier (it has been falsely called an energy source) has promises of a clean hydrogen energy economy without the worry about carbon dioxide pollution and global warming. The trouble with dihydrogen is that it is not easy to store and transport from the point of generation to the point of use. It takes the know-how of rocket engineers to store and transport liquid hydrogen. Compressed hydrogen gas is bulky and the cylinders are heavy. Other modes of hydrogen storage and transport suitable for the general population are needed and this is what motivated further research on ammonia borane.

Reversible hydrogen storage media have been sought for many decades. Much effort has been put into iron titanium hydride as a hydrogen storage medium, but the  $\text{LaNi}_5$  or Fe/Ti alloy is heavy and the tanks required for high-pressure storage are bulky, thick-walled, and heavy. The potential ability to store hydrogen in a lightweight fluid (instead of a solid) that is easy to regenerate has put the spotlight of energy research on ammonia borane and similar boron compounds. Ammonia borane has a hydrogen content of 19.6% by mass and most of that can be released when the chemical is decomposed [447, 448]. An entire chapter in a book on hydrogen storage is devoted to ammonia borane [449]. The fact that ammonia borane decomposes at moderate temperatures unfortunately eliminates it as a stable, storable rocket fuel, but opens new applications as a hydrogen storage medium. It must be emphasized that if any ammonia borane-type compound is to be used in rocket propellants or gas generators, it must be stable at room temperature and under tropical storage conditions. The current section only provides information on the preparation, properties, and safety

properties of ammonia borane and similar borazane compounds. These chemicals can be used in hydrogen gas generators (reversible or irreversible). The exothermic reaction leading to the release of dihydrogen can usually be initiated by means of an electrically heated nichrome wire. Once initiated, the reaction would propagate through the entire charge, it cannot be controlled, and it cannot deliver metered and varying amounts of hydrogen. It is with the application as a solid hydrogen gas generant in mind that the preparation and the properties of ammonia borane are discussed here in detail. The hydrogen may not only be used in combustion engines and fuel cells but may also be needed for chemical lasers (deuterium) or for inflation of weather or surveillance balloons at the battle front line.

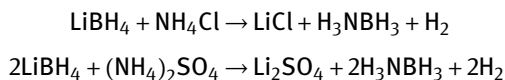
Ammonia borane has received a lot of attention not as a rocket propellant, but as a potential method for hydrogen storage. At one time, it was touted as a benefit to the general population as a derivative of military/space activity in borane fuels dating back to the 1950s, just as the Teflon-coated frying pans were advertised as a spinoff from the space program in the 1960s. However, the dehydrogenation of ammonia borane is stepwise, non-reversible, and results in the formation of undesirable byproducts. Volatile byproducts will be carried out with the evolved hydrogen and may contaminate the hydrogen-using equipment. In a critical review of the flurry of ammonia borane activity, one must conclude that its potential as a reversible storage medium for dihydrogen was highly overrated and that an economic method of regeneration (rehydrogenation) of its decomposition products was never demonstrated [450]. A short section below summarizes the efforts to regenerate spent ammonia diborane (Section 6.6.4.3). Although ammonia borane is a promising hydrogen storage medium, the world's limited supply of boron minerals would be insufficient to allow it to become a widespread storage medium for all automobiles and to compete with gasoline in the future. Ammonia borane is a solid and it would be awkward to load it into the apparatus that generates hydrogen. If a chemical with the same hydrogen storage capability was available that was a liquid instead of a solid, the chances for acceptance into the hydrogen economy would be much better. Future applications of solid ammonia borane would be in small portable devices (fuel cells) where energy density is at a premium.

In looking at the various hydrides tested as hydrogen storage candidates, some hydrides release hydrogen at too low a temperature and are unstable at room temperature, whereas others require very high temperature that would require parasitic energy and long warm-up periods.

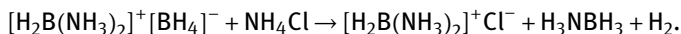
There are several reviews of the chemistry of ammonia borane and alkyl amine boranes that provide references for further study [449, 451–454]. Hydrazinoborane, which is discussed in one of the following sections, may offer similar hydrogen storage capability, similar to ammonia borane. It can also be used as a rocket propellant ingredient.

### 6.6.1 Preparation of Ammonia Borane

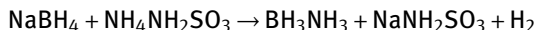
Ammonia borane can be prepared by reaction of lithium borohydride with ammonium salts in diethyl ether:



or by reaction of the DADB with ammonium chloride and a trace of excess ammonia [383, 455, 456]:



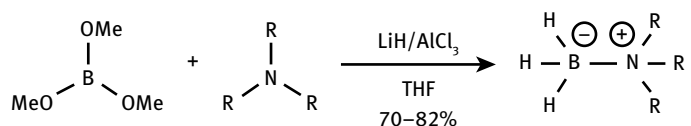
A more elegant method delivers the compound in a solution with diethyl ether [457]. In this synthesis,  $\text{NaBH}_4$  and ammonium sulfamate  $\text{NH}_4\text{NH}_2\text{SO}_3$ , under anhydrous conditions, are dissolved in liquid  $\text{NH}_3$  with vigorous stirring, diethyl ether is added, and the mixture is stirred continuously while it is allowed to warm. Near 273 K (0 °C) the reaction



begins to take place and continues for 3 to 4 h after the mixture reaches room temperature. The synthesis is completed by filtering the solution to remove the precipitate and distilling away the ether, leaving behind solid  $\text{BH}_3\text{NH}_3$ .

Another method used ammonium carbonate (carbamate) as the ammonium salt, giving a 80% yield of  $\text{BH}_3\text{NH}_3$  [458].

A one-pot synthesis of ammonia borane and trialkylamine-boranes starts with trimethyl borate, which is cheaper to obtain than sodium borohydride, yielding ammonia borane in 90% yield and >99% purity [459]. This method can also be applied to trialkylamine-boranes:

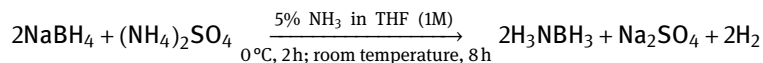


Ammonia promotes the synthesis of pure ammonia borane in excellent yields from sodium borohydride and ammonium sulfate in tetrahydrofuran under ambient conditions [460]. An examination of the influence of added ammonia revealed that it is incorporated into the product ammonia borane, contrary to its perceived function as a catalyst or a co-solvent.

In a simple, large-scale synthesis of ammonia borane from  $\text{NaBH}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  at temperatures between 0 °C and room temperature in THF containing 5%  $\text{NH}_3$ , the presence of ammonia is critical for the reaction to proceed and allows the reaction at



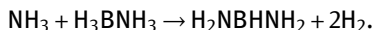
high concentrations and ambient temperature without the need for anhydrous solvent or an inert atmosphere [461, 462]. The yield can be up to 92%.



Usually when working with boron hydrides and metal hydrides one would want to work under anhydrous conditions. Thus, it is highly unusual to learn that a trace of water can enhance the synthesis of ammonia borane. Ammonia borane has been synthesized in very high purity (>99%) from sodium borohydride and ammonium sulfate under ambient conditions in tetrahydrofuran (THF) at 1 M concentration using water as the promoter [463].

Ammonia borane can be prepared by simple displacement reactions that may be more economical than the methods used in the past [464]. Simple displacement reactions have been thwarted by the formation of the DADB, an ionic byproduct. Preparation of pure ammonia borane by displacement reactions with either ammonia with dimethylsulfide borane or ammonia with dimethylaniline borane in toluene at room temperature may be a promising alternative.

A closely related compound is diaminoborane  $\text{H}_2\text{NBH}\text{NH}_2$ , which was prepared by passing a stream of ammonia gas through molten ammonia borane in a pressure vessel at 398 K (125 °C) [457, 465]:



The DADB, dihydridodiammineboron (III) borohydride,  $[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$ , was synthesized by a metathesis reaction between the diammoniate of monochloroborane and potassium borohydride in liquid ammonia [466].  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of the DADB helped to verify the structure of the molecule. The stability in THF was examined using variable-temperature  $^{11}\text{B}$  NMR spectroscopy.

### 6.6.2 Physical Properties of Ammonia Borane

Ammonia borane forms colorless crystals that have a density of  $0.78 \text{ g/cm}^3$  and melt at 377 K (104 °C) under decomposition. Other sources gave the density as  $0.73 \text{ g/cm}^3$ .

The heat of formation of solid ammonia borane is  $-174.2 \pm 5.8 \text{ kJ/mol}$  ( $-41.63 \pm 1.4 \text{ kcal/mol}$ ) and the heat of combustion is  $-1348.5 \pm 2.9 \text{ kJ/mol}$  ( $322.3 \pm 0.7 \text{ kcal/mol}$ ) [467].

The dipole moment of ammonia borane,  $\text{H}_3\text{NBH}_3$ , has been measured as 4.9 Debye units in dioxane solution [468] and 5.22 D in the dry state.

Ammonia borane is very soluble in liquid ammonia and this may be one of the methods by which ammonia borane will be transported and used as a hydrogen storage medium [469]. Ammonia borane can absorb ammonia to generate a series of liquid ammino complexes,  $\text{BH}_3\text{NH}_3 \cdot (\text{NH}_3)_n$ , after exposure to ammonia gas under the pressure range of 1 to 4 bar at 273 K (0 °C). Under an ammonia atmosphere, ammonia

borane reversibly absorbs up to at least six equivalents of  $\text{NH}_3$ . The strong classical hydrogen bond formed between the lone pair of  $\text{NH}_3$  and the  $-\text{NH}_3$  of ammonia borane is the driving force for the absorption of ammonia by ammonia borane. At 4 bar pressure, there were six moles of ammonia attached to each ammonia diborane molecule.

### 6.6.3 Molecular Structure of Ammonia Borane

The ammonia borane molecule structure is similar to that of ethane, with which it is isoelectronic. However, ammonia diborane is a solid and ethane is a gas at room temperature. The existence of the dihydrogen bonds largely explains the very different melting points of  $\text{BH}_3\text{NH}_3$  (383 K = 110 °C) and the isoelectronic compound ethane  $\text{CH}_3\text{CH}_3$  (92 K = -181 °C), as well as the higher volumetric hydrogen storage density of ammonia borane compared with ethane. Ammonia borane  $\text{H}_3\text{B}-\text{NH}_3$  is isoelectronic with ethane  $\text{H}_3\text{C}-\text{CH}_3$ , but it has very different properties owing to (1) the nitrogen and boron atoms (leading to a dipole moment), (2) the protic and hydridic hydrogens, and (3) the heteropolar dihydrogen bonding (rationalizing its solid state under ambient conditions). Ammonia diborane is expected to have a high dipole moment, as opposed to a dipole moment of zero for non-polar ethane.

The microwave spectra of nine isotopic species of ammonia borane with  $^{10}\text{B}$ ,  $^{11}\text{B}$ ,  $^1\text{H}$ ,  $^2\text{H}$  (= D),  $^{14}\text{N}$ , and  $^{15}\text{N}$  isotope substitution gave different sets of rotational constants, centrifugal distortion constants, dipole moments, torsional barriers, and molecular geometry [470]. The structural parameters of the ammonia borane molecule were:  $\text{B}-\text{N} = 1.6576(16) \text{ \AA}$ ,  $\text{B}-\text{H} = 1.2160(17) \text{ \AA}$ ,  $\text{N}-\text{H} = 1.0140(20) \text{ \AA}$ ,  $\angle\text{NBH} = 104.69(11)^\circ$ , and  $\angle\text{BNH} = 110.28(14)^\circ$ . The dipole moment was 5.216(17) Debye. The torsional barrier about the  $\text{B}-\text{N}$  bond was 2.047(9) kcal/mol for  $\text{H}_3^{11}\text{BND}_2\text{H}$  and 2.008(4) kcal/mol for  $\text{D}_2\text{H}^{11}\text{BNH}_3$ . It was not possible to determine, from the isotopic species studied, whether the staggered or eclipsed structure is the preferred geometry of the ground state.

The molecular structure of ammonia diborane at very high pressures under an atmosphere of hydrogen was investigated extensively because it was hoped that the low-pressure dehydrogenation of ammonia diborane would be reversible at high pressures, thus allowing a path to regenerate it as a hydrogen storage medium.

The effects of high pressures (up to 40 kbar) on dihydrogen-bonded  $\text{BH}_3\text{NH}_3$  molecular crystals were investigated using Raman spectroscopy in diamond and moissanite anvil cells [471]. The stretching mode frequencies of the  $\text{NH}_3$  proton donor groups exhibited moderate red shifts with increasing pressures, as found in many conventional hydrogen-bonded systems of weak to medium strength. The stretching modes corresponding to the  $\text{BH}_3$  proton acceptor group, on the other hand, showed large blue shifts with increasing pressure, which, however, were not related to the changes in the  $\text{N}-\text{H}\cdots\text{H}-\text{B}$  interactions. The  $\text{BH}_3\text{NH}_3$  crystals underwent a pressure-induced disorder-order phase transition around 8 kbar, which was facilitated by the presence of dihydrogen bonds.

The crystal structure of ammonia borane has been determined for the orthorhombic (at 90 K) and tetragonal (at 298 K) modifications using single-crystal XRD [472]. The orthorhombic structure (space group  $Pmn2_1$ ) agreed with a previously published neutron diffraction determination, whereas the tetragonal structure ( $I4mm$ ) exhibited halos of hydrogen atom occupancy around both the nitrogen and boron atoms. The bond angles to the regions of hydrogen occupancy were consistent with the expected tetrahedral geometry for  $\text{-BH}_3$  and  $\text{-NH}_3$  groups. A new model for bi-tetragonal  $\text{BH}_3\text{NH}_3$  was constructed, which accounted for the hydrogen disorder in the  $I4mm$  structure.

In ethane, the two halves of the molecule rotate freely around the C—C bond axis with only minor hindrances. In ammonia borane, the two halves do not rotate independently. The activation energies for rotations in low-temperature orthorhombic ammonia borane were analyzed and characterized in terms of electronic structure theory [473]. The barrier for independent  $\text{NH}_3$  rotation,  $E_a = 12.7$  kJ/mol, largely depends on the molecular conformational torsion in the solid-state geometry. The barrier for independent  $\text{BH}_3$  rotation,  $E_a = 38.3$  kJ/mol, results from the summation of the effect of molecular torsion and large repulsive intermolecular hydrogen-hydrogen interactions. However, a barrier of  $E_a = 31.1$  kJ/mol was calculated for internally correlated rotation with preserved molecular conformation. Analysis of the barrier heights and the corresponding rotational pathways showed that rotation of the  $\text{BH}_3$  group involves strongly correlated rotation of the  $\text{NH}_3$  end of the molecule.

Ammonia borane has three known structural phases in the temperature and pressure ranges 110–300 K and 0–1.5 GPa respectively. The boundaries between, and the ranges of stability of, these phases were located by *in situ* measurements of the thermal conductivity, whereas the actual structures in selected areas were identified using *in situ* Raman spectroscopy and XRD [474]. Below 0.6 GPa, reversible transitions involving only small hysteresis effects occurred between the room-temperature tetragonal plastic crystal  $I4mm$  phase and the low-temperature orthorhombic  $Pmn2_1$  phase. Transformations of the  $I4mm$  phase into the high-pressure orthorhombic  $Cmc2_1$  phase, occurring above 0.8 GPa, were associated with very large hysteresis effects, such that the reverse transition may occur at up to 0.5 GPa lower pressures. The thermal conductivity of the plastic crystal  $I4mm$  phase was about  $0.6 \text{ W m}^{-1} \text{ K}^{-1}$  and only weakly dependent on temperature, whereas the ordered orthorhombic phases had higher thermal conductivities limited by phonon-phonon scattering.

The effect of pressure on the low-temperature tetragonal ( $I4mm$ ) to orthorhombic ( $Pmn2_1$ ) phase transition of ammonia borane was investigated in a diamond anvil cell using Raman spectroscopy [475]. With applied pressure, the transition occurred at a higher temperature, which indicated that pressure enhances the ordering of the structure. Appearance of some of the characteristic Raman modes of the orthorhombic phase required undercooling of around  $\sim 15$  K below the transition, indicating the possible existence of an intermediate phase.

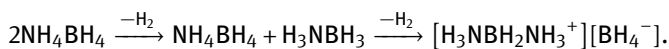
The phase transformation behavior of ammonia borane was examined at a low temperature (modified from room temperature down to 90 K) and high pressure (mod-

ified from ambient pressure to 9.5 GPa at room temperature and up to 15 GPa at 90 K) using a diamond anvil cell [476]. Ammonia borane showed four phase transitions in this pressure and temperature region. The phase transitions were indicated by the splitting of a peak and/or the appearance of a new peak in the Raman spectra as well as by the change of the pressure coefficient of the Raman modes. The phase boundaries between these phases were established during different cooling cycles. See also [477] and [478].

Raman spectroscopy studies indicated five transitions under compression up to 65 GPa at ambient temperature [479]. Diffraction experiments and theoretical studies demonstrated that three of these transitions were first-order phase transformations in the sequence of  $I4mm-Cmc2_1-P2_1$ -(different)  $P2_1$ , and two were iso-structural. A low-temperature phase ( $Pmn2_1$ ) and a high-temperature, high-pressure phase ( $Pmna$ ) were also recognized.

Under certain conditions at low temperatures, ammonia borane reverts to its ionic isomer, the DADB [480]. The structure of this compound was the object of debate for a significant period of time and was widely investigated in experiments using  $^{11}\text{B}$ -NMR and Raman studies. DADB is usually obtained as an X-ray amorphous white powder and appears in two modifications. DADB is stable up to 353 K (80 °C) and decomposes at 363 K (90 °C) with melting. It is soluble in liquid ammonia and is, in contrast to ammonia borane, not soluble in diethyl ether.

The diammoniate of diborane, dihydridodiammineboron (III) borohydride,  $[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$ , is formed from the room temperature decomposition of  $\text{NH}_4^+\text{BH}_4^-$ , via an  $\text{NH}_3\text{BH}_3$  intermediate [481]:



Its crystal structure has been determined and contains disordered  $\text{BH}_4^-$  ions in two distinct sites. Hydrogen release was similar to that from  $\text{NH}_3\text{BH}_3$  but with faster kinetics. Reaction of the DADB with ammonia in ether results in the formation of ammonia borane and hydrogen.

#### 6.6.4 Chemical Properties of Ammonia Borane

Ammonia borane is a white crystalline material that is relatively stable in air, although reports on its stability vary slightly. Unlike ionic hydrides, ammonia borane  $\text{H}_3\text{NBH}_3$  does not react violently with water. Aqueous solutions of ammonia borane decompose slowly at room temperature.

Ammonia borane is soluble in water and in many organic solvents. It is quite soluble (>5 mass-%) without reaction in EtOH, THF, diglyme, and triglyme; moderately (0.5–1 mass-%) soluble in  $\text{Et}_2\text{O}$  and dioxane; and poorly (<0.1 mass-%) soluble in toluene, benzene, or tetrachloromethane. Ammonia borane is soluble in water but slowly hydrolyzes at the rate of about 1%/day. The solubility of ammonia borane in water is high, 25 mass-% [482, 483]. Aqueous ammonia borane solutions are relatively

stable if kept under an inert gas atmosphere. In air the solution possesses much lower stability, which is believed to result from an increase in acidity in the solution due to the dissolution of  $\text{CO}_2$  [484]. Although the water solvent would need to be carried as unwanted ballast, ammonia borane solutions might be easier to accommodate in hydrogen-powered vehicles than solid ammonia borane. Hydrogen can be released by heating an aqueous ammonia borane solution to 353–408 K (80–135 °C) and 101–1379 kPa (14.7–200 psia) to release hydrogen by hydrothermolysis [485]. The hydrogen release temperature of ammonia borane solutions can be lowered by using transition metal catalysts [486].

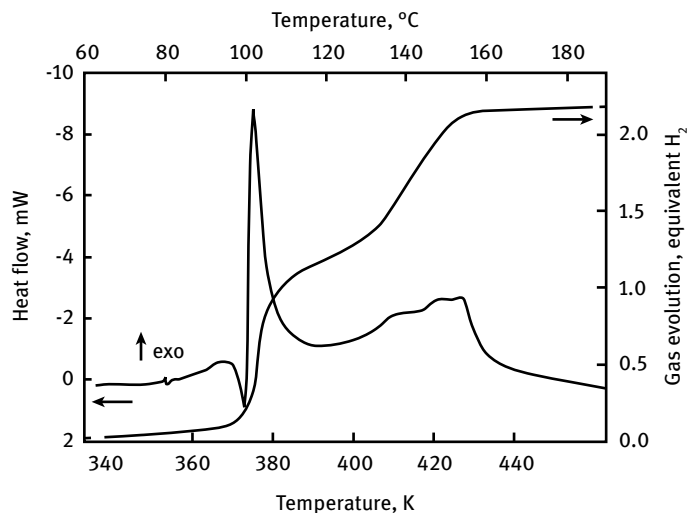
#### 6.6.4.1 Thermal Decomposition of Ammonia Borane

The controlled deliberate decomposition of ammonia borane as a source of dihydrogen gas has been extensively investigated, in the solid, molten, and dissolved states. There are hundreds of publications dealing with the decomposition of ammonia borane as a source of hydrogen, and only a few of those have been referenced here. The hydrogen release from ammonia borane is a multi-step process.

As the dehydrogenation reaction is exothermic, the applied temperature is only needed to initiate the desired dehydrogenation process. The exothermicity of ammonia borane is a positive feature if fast hydrogen release of the complete hydrogen content is desired in a one-shot device as for a chemical laser. With large storage containers where only a small portion of the hydrogen is supposed to be extracted, the exothermicity poses a control problem. If one does not want to run the risk of a thermal run-away from an unintentional emission of the complete hydrogen content in the case of a malfunction of the control mechanism, the storage of ammonia borane in small compartments is inevitable, as in an automobile that is started and stopped. A possible alternative to the pyrolytic decomposition of solid ammonia borane is the decomposition in solution. The decomposition of ammonia borane in solution has the advantage of separating the decomposition zone from the storage area because of the improved transport of the stored material in liquid form. Better ammonia borane transport properties in the form of liquid solutions also allow the application of heterogeneous catalysts for the controlled decomposition of ammonia borane, as the reactants and products can be easily moved to or away from the catalyst.

Differential scanning calorimetry, TGA, and volumetric measurements have shown that solid ammonia borane is thermally decomposed in two reaction steps, each releasing one molecule of hydrogen per formula unit at different temperature levels [487]. Both decomposition steps are exothermic (Figure 24).

The stepwise evolution of hydrogen is visible in Figure 24 above, but it becomes more clearly visible if the test is repeated as a lower heating rate of 0.1 K/min. If the temperature is increased at a comparably high heating rate of 10 K/min, the hydrogen release sets in shortly after the melting point at 385 K (112 °C) and reaches



**Figure 24:** Heat flow and  $\text{H}_2$  release during the thermal decomposition of ammonia borane, heating rate 1 K/min. (Republished and modified from [488], with permission of ©2010 John Wiley & Sons Books; permission conveyed through Copyright Clearance Center Inc.)

a maximum at 403 K (130 °C). The second step, releasing another equivalent of molecular hydrogen, occurs in the range 423–473 K (150–200 °C). Completion of the first dehydrogenation step below the melting temperature is possible, albeit only slowly, at isothermal conditions of approximately 343–363 K (70–90 °C). The hydrogen release rate is strongly temperature dependent, at 363 K (90 °C) the release is completed after 4 h, whereas at 343 K (70 °C) it takes 40 h to achieve completion. One problem is the contamination of the released hydrogen gas by volatile products. FTIR analysis of the evolved gases from the thermolysis of ammonia borane complex has shown that monomeric aminoborane ( $\text{BH}_2\text{NH}_2$ ), borazine, and diborane is also produced. Another problem is the slow, sluggish response after a demand of hydrogen is signaled to the gas generator and the heat is turned on. If the material is heated to 363 K (90 °C), almost no hydrogen release is initially observed. Subsequently, the release rate increases slowly and then reaches its maximum only after 40 min. The induction period can be shortened by additives [489].

The decomposition of ammonia borane has been studied at low [490] and at very high pressures. The thermal decomposition of ammonia borane at up to 450 K and 600 bar has been studied by DSC and volumetric analysis of the released volatile decomposition products [491]. Above 360 K ammonia borane underwent an exothermic decomposition, which proceeds in two steps with rising temperature. The heat evolution and hydrogen release terminates near 430 K. The final amount of released hydrogen is approximately equal to 2 mol  $\text{H}_2$ /mol ammonia borane.

Stored under vacuum at room temperature, no significant hydrogen loss was reported for a period of over 2 months and its solubility in organic solvents remained unchanged [492]. In contrast, other reports of its storage in air indicated a slow hydrogen loss, presumably induced by humidity. Ammonia borane melts with hydrogen release, leading to a strong volume expansion by foaming. After some time of continued heating, the product solidifies. Reports on the melting point vary strongly from 377 to 383–389 K (104 to 110–116 °C) and all the way up to 397 K (124 °C; under hydrogen pressure). Impurities have a strong effect on lowering the melting point and storage stability.

A study of the thermal decomposition of ammonia borane by TGA, DTA, and decomposition product measurements showed vigorous decomposition with hydrogen evolution that began near 393 K (120 °C) and proceeded in stages as the temperature was increased to 473 K (200 °C), leaving a white residue [493]. The composition of the residue was approximately  $\text{BNH}_{2.1}$  after heating to 443 K (170 °C) and  $\text{BNH}_{(0.8-1.2)}$  after heating to 473 K (200 °C). There was some evidence for further slow hydrogen loss above that temperature. The swelling and foaming of decomposing ammonia borane makes DTA and TGA analyses difficult [494].

The thermal dehydrogenation of solid ammonia borane preferentially leads to polymeric products whereas the non-hydrolytic decomposition in solution results primarily in cyclic liquid compounds such as borazine, the BN analog to benzene. Intermediates in this reaction include monomeric aminoborane  $\text{H}_2\text{NBH}_2$ , which has a tendency to polymerize [495].

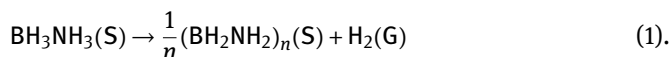
One equivalent of hydrogen gas was evolved from ammonia borane when it was heated above 343 K (70 °C). The initial stages of this process were examined using TGA/DSC, optical microscopy, and high temperature XRD [496]. Two exothermic events have been observed, the first of which took place without hydrogen evolution. During this stage, the sample lost its crystallinity and birefringence. The products were believed to be a more mobile form of  $\text{NH}_3\text{BH}_3$  and the diammoniate of diborane, dihydridodiammineboron (III) borohydride,  $[\text{NH}_3\text{BH}_2\text{NH}_3]^+[\text{BH}_4]^-$ . These products subsequently reacted in the second exothermic stage to generate hydrogen.

The ultimate product in the complete decomposition of ammonia borane is boron nitride [497]. Ammonia borane decomposition follows different reaction routes if the dehydrogenation occurs in a dissolved or solid state. A detailed study of ammonia borane dehydrogenation mechanism in diglyme and solid state showed that two main reaction pathways occur: one involves cyclization of monomers, which results in faster dehydrogenation at a lower temperature, whereas the other involves propagation to acyclic intermediates, which requires a higher temperature to carry out the cyclization step [498]. Ammonia borane dehydrogenation in the solid state was found to be initiated by B–N bond cleavage and not by direct dehydrogenation. It was found that diglyme plays a significant role in hindering B–N bond cleavage of ammonia borane, which facilitates the cyclization pathway.

Studies on ammonia borane decomposition have focused on relatively slow heating rates, showing that the mass lost because of decomposition increased with increasing heating rate. This trend has been confirmed, as mass loss continued to increase up to 50 K/min, the limit of most TGA/DSC instruments. Confined rapid thermolysis was used to examine the decomposition of ammonia borane under isothermal conditions [499–501]. FTIR spectroscopy and time-of-flight mass spectrometry were employed to identify the gaseous products, which included  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{NBH}_2$ , and cyclo- $\text{N}_3\text{B}_3\text{H}_6$ . The decomposition resulted in significant condensed-phase products as well, which were pressed into a KBr pellet and examined using FTIR spectroscopy. Condensable gas-phase products were collected from the stream of decomposition products, and FTIR spectroscopy showed that they have absorption bands similar to the polymeric species, indicating that the  $\text{H}_2\text{NBH}_2$  readily condenses out of the gas-phase products and polymerizes at low temperatures.

A Purdue University report is a mixture of reports on five different projects, but the section on pages 10 through 30 on confined rapid thermolysis of ammonia borane contains a thorough analysis of decomposition products of ammonia borane at different heating rates, supplemented by Molecular Dynamics Simulations calculations and many references to the relevant literature [502].

The decomposition of ammonia borane was studied using calorimetry, pressure measurements of evolved gases, and mass spectrometry methods [503]. It was shown that two competitive processes are taking place at 357 K, depending on the vapor pressure in the system. At atmospheric pressure, thermal decomposition with hydrogen evolution and polyamidoborane formation is the dominant process:



At low pressures (circa 4 mTorr) the major process is endothermic sublimation of ammonia borane:



At intermediate pressures both processes occur simultaneously. Enthalpies for the processes **(1)** and **(2)** have been determined by a drop-calorimetry method: for **(1)**  $\Delta H_{357} = -24.8 \pm 2.3 \text{ kJ/mol}$  and for **(2)**  $\Delta_{\text{sub}}H_{357} = 76.3 \pm 3.0 \text{ kJ/mol}$ . The activation energy for the process **(1)** within the range 327–351 K was  $94 \pm 11 \text{ kJ/mol}$  as determined by static pressure measurement. Based on the analysis of available thermodynamic characteristics, the standard enthalpy of formation  $\Delta H_f$  of solid ammonia borane was  $-133.4 \pm 5.2 \text{ kJ/mol}$  and for polyamidoborane a  $\Delta H_f$  of  $-156.7 \pm 5.8 \text{ kJ/mol}$  was recommended.



#### 6.6.4.2 Catalytic Decomposition of Ammonia Borane

The hydrogen release temperature of ammonia borane solutions can be lowered to more convenient temperatures by adding transition metal catalysts [486], dissolved Pt, Rh, and Pd salts injected into the ammonia borane solution [504], soluble rhodium, ruthenium, or platinum halogenide salts [505], salts of a weak base, and a strong acid such as  $\text{NH}_4\text{Cl}$  [506], or soluble rhodium or platinum halogenide salts [507].

#### 6.6.4.3 Regeneration of Ammonia Borane

The regeneration of exhausted ammonia borane residues may be mostly of interest for its use as a hydrogen storage medium and not so much for its use as a gas generant for lasers and balloon inflation. Nevertheless, this is part of ammonia borane chemistry and some of it is referenced here. The entire concept of hydrogen storage in ammonia borane hinges on an economic way to regenerate the spent residue. The ability to regenerate ammonia borane from its residues may affect its future availability from chemical suppliers as an ingredient in rocket propellants and gas generants.

To date, none of the proposed recycling schemes fulfills all of requirements for easy regeneration of the exhausted ammonia borane hydrogen storage medium. Ideally, the regeneration should proceed without additional energy requirements by pressurizing the exhausted medium with hydrogen gas at 10 MPa [508–510].

The spent fuel type derived from the release of more than two equivalents of  $\text{H}_2$  per molecule of ammonia borane (i.e., polyborazylene) can be converted back to ammonia borane nearly quantitatively by 24-h treatment with hydrazine in liquid ammonia at 313 K (40 °C) in a sealed pressure vessel [511, 512].

#### 6.6.5 Safety Properties of Ammonia Borane

An excellent survey of the methods of preparation, physical, chemical, and safety properties of ammonia borane and related alkylamine borane adducts is provided in [453]. This report, with 422 references, contains all the information one might need to safely handle ammonia borane, regardless if whether it is used as a rocket propellant or as a hydrogen storage medium.

#### 6.6.6 Applications of Ammonia Borane

Ammonia borane is a candidate medium for hydrogen storage and its properties and potential applications have been thoroughly investigated [488].

### 6.7 Ammonia Triborane

Another ammonia borane adduct that could be used as rocket propellant fuel or reversible hydrogen storage medium is ammonia triborane, also known as triborane(7), 3-amine-; triborane(7), ammoniate;  $\text{H}_3\text{NB}_3\text{H}_7$ , CAS RN [57808-44-3]. The melting point of ammonia triborane is 346 K (73 °C). Ammonia triborane is related

to the ammonium hydrotriborate salt  $[\text{NH}_4]^+[\text{B}_3\text{H}_8]^-$ , CAS RN [12447-26-6]. For its intended use as a hydrogen storage medium it turned out to be advantageous that it does not react with water in neutral or alkaline solutions and it is soluble in water. Ammonia triborane can be made from tetraborane by a series of reactions analogous to the preparation of ammonia borane from ammonia and diborane [513]. Ammonia triborane is a stable, white, crystalline solid when pure. Ammonia triborane is both soluble and stable in water, but upon the addition of acid or an appropriate transition metal catalyst it rapidly releases dihydrogen gas [514]. Ammonia triborane has a highly asymmetric structure in the solid state that results from intermolecular  $\text{N}-\text{H} + \cdots \text{H}-\text{B}$  dihydrogen bonding interactions [515, 516].

## 6.8 Hydrazine Borane

It is known that hydrazine reacts with pentaborane and other boranes in a highly exothermic, hypergolic reaction. So, in order to form adducts between hydrazine(s) and borane(s), one has to work in dilution with an inert solvent and provide cooling.

Hydrazine borane, also called hydrazine borane 1:1, borine hydrazine, hydrazine monoborane,  $\text{BH}_3 \cdot \text{N}_2\text{H}_4$ , CAS RN [14931-40-9], is a potential rocket propellant fuel and a source of dihydrogen for other energy conversion applications such as fuel cells. In parallel with the skyrocketing number of publications on ammonia borane as a hydrogen storage medium, the hydrazine boranes have also received recent attention, resulting in hundreds of publications. We are not interested in storage of hydrogen for non-rocket applications, which is the main topic of many publications on hydrazine borane and hydrazine bisborane. These publications are referenced here only because they provide information on the physical and chemical properties of these compounds. For their use as hydrogen storage media, the reversibility of the hydrogen release and hydrogen loading (regeneration) process has yet to be demonstrated. Once these compounds become available in larger quantities, they may even be used in rocket propellants or in hydrogen gas generators for chemical lasers. If ammonia borane, hydrazine borane, or hydrazine bisborane should evolve as a preferred hydrogen storage medium in the future, one can honestly claim that both building blocks of this hydrogen storage material have benefited substantially from a wealth of know-how that originated with their proposed or actual use as rocket propellants. Government-sponsored research into boranes and hydrazines in the 1950s, mostly aimed at propulsion for weapons, has now opened up an entire new field of chemistry for civilian uses.

### 6.8.1 Preparation of Hydrazine Borane

Hydrazine borane,  $\text{BH}_3 \cdot \text{N}_2\text{H}_4$ , can be made by reacting hydrazinium(2+) sulfate or hydrazinium(1+) chloride with sodium boranate  $\text{NaBH}_4$  [517–519].

Hydrazine borane,  $\text{N}_2\text{H}_4\text{BH}_3$ , stores 15.4 mass-% of hydrogen in hydridic and protic forms, and the challenge is to release  $\text{H}_2$  with maximum efficiency, if possible,

releasing all hydrogen stored in the material [520]. Hydrazine borane can be made by a two-step synthesis (salt metathesis and solvent extraction-drying) with a yield of about 80% and a purity of 99.6%.  $\text{N}_2\text{H}_4\text{BH}_3$  was characterized by NMR, IR, XRD, TGA, and DSC, its stability in dioxane and water was determined, and its thermolysis byproducts were characterized.

### 6.8.2 Physical Properties of Hydrazine Borane

Hydrazine borane has an enthalpy of formation of  $-975\text{ kJ/kg}$  ( $-233\text{ kcal/kg}$ ) and a density of  $0.95\text{ g/cm}^3$ . Hydrazine borane on heating decomposes partially to hydrazine bisborane, hydrazine diborane,  $\text{B}_2\text{H}_6\text{N}_2$ ,  $\text{H}_2\text{BNHNHBH}_2$ , CAS RN [13730-91-1], which exists mostly in a polymeric form and on further heating releases more dihydrogen gas (see Section 6.9 Hydrazine Bisborane).

Stable, solid adducts, which can be used in solid rocket propellants, are formed between hydrazine or alkylhydrazines and diborane, pentaborane, or decaborane [521]. The heat of combustion of  $\text{BH}_3\bullet\text{N}_2\text{H}_4$  is  $1644\text{ kJ/mol}$  ( $393\text{ kcal/mol}$ ).

Single-crystal XRD data showed that  $\text{BH}_3\bullet\text{N}_2\text{H}_4$ , m.p. =  $334\text{ K}$  ( $61^\circ\text{C}$ ), prepared in 70–75% yield from  $\text{NaBH}_4$  and  $(\text{N}_2\text{H}_5)_2\text{SO}_4$  in dioxane at  $303\text{--}343\text{ K}$  ( $30\text{--}70^\circ\text{C}$ ), is rhombic,  $a = 13.05\text{ \AA}$ ,  $b = 5.12\text{ \AA}$ ,  $c = 9.55\text{ \AA}$ ,  $Z = 8$ ,  $\rho_{25^\circ\text{C}} = 0.9475\text{ g/cm}^3$ , space group  $D102h\text{-Pccn}$  [522]. The observed frequencies in the IR spectra of  $\text{BH}_3\bullet\text{NH}_3$  and solid and liquid  $\text{BH}_3\bullet\text{N}_2\text{H}_4$  were assigned to molecular vibrations. The dipole moment of  $\text{BH}_3\bullet\text{N}_2\text{H}_4$ ,  $4.18\text{ D}$  was consistent with a largely *trans* form of the  $\text{N}_2\text{H}_4$  component. Data on dipole moment and molecular mass in dioxane showed that with increasing concentration,  $\text{BH}_3\bullet\text{N}_2\text{H}_4$  is increasingly associated.

An X-ray structural study has been made of crystals of borine hydrazine,  $\text{BH}_3\bullet\text{N}_2\text{H}_4$  [523]. Computation of the structure was carried out in parallel by two methods: a modified Monte Carlo method and Patterson function projections. The coordinates of the three atoms B, N1, and N2 were determined in both cases. The boron atoms and the nitrogen atoms closest to it have a tetrahedral valence configuration, the tetrahedra being arranged in *gauche* form. The length of the B–N bond was  $1.56 \pm 0.01\text{ \AA}$ . The crystal parameters were  $a = 9.53 \pm 0.07\text{ \AA}$ ;  $b = 5.12 \pm 0.06\text{ \AA}$ ;  $c = 13.01 \pm 0.08\text{ \AA}$ ; and  $\rho = 0.968\text{ g/cm}^3$ .

The electronic characteristics of the dative N–B bond in three Lewis acid-base adducts, hydrazine borane, hydrazine bisborane, and ammonia trifluoroborane, were analyzed using an approach combining experimental electron density determination with a broad variety of theoretical computations [524]. The main electronic effect of the formation of the Lewis acid-base adducts and of the crystallization is an increase in the charge separation within the ammonia/hydrazine fragments, which is supported by all investigated bond and atom properties. The nature of the dative N–B bond was found to be mainly electrostatic, but with a substantial contribution of covalency.

The structural behavior of hydrazine borane under mechanical stimulus was examined by synchrotron high-pressure XRD [525]. It was shown that hydrazine borane

undergoes a gradual pressure-induced decrease in its unit cell dimensions. The process is reversible when the applied pressure is released. The compressibility of this material was relatively low (high bulk modulus) and highly anisotropic. The mechanical behavior of hydrazine borane correlated with the pressure-induced changes of its crystal structure in terms of intra- and intermolecular bond lengths and angle parameters.

### 6.8.3 Chemical Properties of Hydrazine Borane

Unstable  $(\text{BH}_3 \bullet \text{N}_2\text{H}_5)_2\text{SO}_4$  and  $\text{BH}_3 \bullet \text{N}_2\text{H}_5\text{Cl}$  salts were obtained from solutions of hydrazine borane and the respective strong mineral acids in dioxane or THF [522]. Hydrazine borane forms salts with alkali metals, which release their hydrogen more readily than the parent compound [526, 527]. A clear correlation between sizes of metal cations in hydrazinoboranes and their corresponding melting and dehydrogenation temperatures was found, dependent on the melting temperature. Upon approaching the melting points, alkali metal hydrazinoboranes dehydrogenate rapidly in the first step, giving rise to the formation of intermediates that include  $\text{N}_2\text{BH}_2$ ,  $\text{N}_2\text{BH}$ , and  $\text{NBH}_3$  species.

Hydrazine borane ( $\text{N}_2\text{H}_4\text{BH}_3$ ) with a gravimetric hydrogen storage capacity of 15.4% can be used for the storage of hydrogen. Pyrolysis studies *in vacuo* over the temperature range 343–473 K (70–200 °C) showed that with release of some  $\text{N}_2\text{H}_4$  and, relatively rapidly, 1 mol of  $\text{H}_2$  per mol of hydrazine borane, a solid residue of variable composition resulted from which crystalline  $(\text{BH}_2\text{NH})_n$  was isolated [522].  $(\text{BH}_2\text{NH})_n$  resisted attack by  $\text{H}_2\text{O}$  or aqueous acids and probably has a polymeric structure composed of condensed six-membered rings; the N–N link is retained. At 473 K (200 °C),  $(\text{BH}_2\text{NH})_n$  slowly lost an additional  $\text{H}_2$  per mol of  $\text{BH}_3 \bullet \text{N}_2\text{H}_4$  to give an amorphous,  $\text{H}_2\text{O}$ -sensitive product of approximate composition  $(\text{HBN})_n$ . Loss of the second  $\text{H}_2$  from  $\text{BH}_3 \bullet \text{N}_2\text{H}_4$  occurred more rapidly if the initial decomposition products were not separated and led to unidentified, volatile, sometimes **explosive** products, which still had N–N bonds.

Metal-catalyzed hydrolysis of hydrazine borane at room temperature quickly released dihydrogen gas [528]. Among the catalyst systems tested, rhodium(III) chloride was found to provide the best catalytic activity. In the presence of dissolved rhodium(III) chloride, the aqueous solution of hydrazine borane underwent fast hydrolysis to release nearly 3.0 equivalents of  $\text{H}_2$  at room temperature. The reaction between hydrazine borane and water proceeded almost in stoichiometric proportion indicating that efficient hydrogen generation can be achieved even from highly concentrated solutions of hydrazine borane or in the solid state when water is added to the solid hydrazine borane.

Both hydrazine borane and ammonia borane have been evaluated as storage media for dihydrogen. The hydrogen release by hydrolysis of hydrazine borane can be catalyzed by rhodium nanoparticles supported on hydroxyapatite [529].

The hydrogen storage capabilities of hydrazine borane can be improved by adding an equimolar amount of lithium hydride [530]. The resulting mixture contains 14.8 mass-% hydrogen. The hydrogen release behavior of both the pure hydrazine borane and the LiH mixture showed hydrogen release rates at a reasonable operating temperature range of 373–523 K (100–150 °C). Similar improvements were observed with sodium hydride or potassium hydride instead of lithium hydride added to hydrazine borane [527]. Alkali metal hydrazidotrihydridoborates dehydrogenated rapidly in the first step with the formation of intermediates that contained  $\text{N}_2\text{BH}_2$ ,  $\text{N}_2\text{BH}$ , and  $\text{NBH}_3$  species. Further increasing temperature lead to the release of additional  $\text{H}_2$  and the formation of  $\text{N}_2\text{BH}$  species. Compared with bare  $\text{N}_2\text{H}_4\text{BH}_3$ , the alkali-metal-substituted hydrazidotrihydridoborates demonstrated significantly improved dehydrogenation behavior with no  $\text{N}_2\text{H}_4$  emission and greatly suppressed  $\text{NH}_3$  release. The hydrogen release temperatures of the potassium salt were then compared with the hydrogen release temperatures of the magnesium, calcium, and aluminum salts. Hydrazine borane  $\text{N}_2\text{H}_4\text{BH}_3$  can be destabilized by the addition of  $\text{MH}_x$  ( $x = 2, 3$ ;  $\text{M} = \text{Mg}, \text{Ca}, \text{Al}$ ), forming salts with better dehydrogenation properties [531]. In comparison with bare  $\text{N}_2\text{H}_4\text{BH}_3$ ,  $\text{MgH}_2$  had a catalytic effect;  $\text{CaH}_2$  strongly destabilized  $\text{N}_2\text{H}_4\text{BH}_3$ ; and unstable  $\text{AlH}_3$  can destabilize  $\text{N}_2\text{H}_4\text{BH}_3$  under heating. The most efficient salt was  $\text{CaH}_2 \cdot \text{N}_2\text{H}_4\text{BH}_3$ .

It was found that hydrazine borane and ammonia borane (mol ratio 1:1) destabilize each other [532]. The mixture can eventually be stabilized into a useful hydrogen storage material, which dehydrogenates in steps at temperatures up to 573 K (300 °C) to form boron nitride. Though stable at 293–298 K (20–25 °C), the mixture melted at ~303 K (~30 °C) and then underwent significant decomposition, with desorption of dihydrogen and hydrazine from 340 K (67 °C) on. Also, some dihydrogen was “explosively” liberated at around 363 K (90 °C). This was explained by the fact that the presence of hydrazine borane disrupts the  $\text{H}\delta + \cdots \text{H}\delta$  network of ammonia borane, and vice versa. The mixture is then much less stable than the borane adducts by themselves.

The presence of one mol of an alkaline borohydride ( $\text{LiBH}_4$  or  $\text{NaBH}_4$ ) per four mols of hydrazine borane  $\text{N}_2\text{H}_4 \cdot \text{BH}_3$  effectively destabilized  $\text{N}_2\text{H}_4 \cdot \text{BH}_3$ , which is then able to liberate dihydrogen as soon as it is heated to 323 K (50 °C) [533]. Upon heating up to 573 K (300 °C) at 5 °C/min, this mixture released 12.1 mol of dihydrogen (dehydrogenation extent of 76%) and 1.1 mol of  $\text{N}_2\text{H}_4$ . It may be possible to recycle and re-hydrate the solid residue of polyborazylene- and/or boron nitride-like materials.

The thermolytic dehydrogenation of hydrazine borane should be avoided because of the evolution of significant amounts of hydrazine and the formation of a shock-sensitive solid residue upon heating at >573 K (>300 °C) [534]. The alkali hydrazinidoboranes, obtained by reaction of hydrazine borane with alkali metal hydrides, would be more suitable to thermolytic dehydrogenation, with improved properties in comparison to the parent borane.

Hydrazinoboranes are of interest as sources of hydrogen for inflation of balloons and as rocket propellants. Their analysis is a difficult task, as simple iodometric titra-

tion would not only give the hydrazino group content, but to a varying extent some of the iodate would be consumed by the reducing properties of the borohydride. Simple gasometric analysis of the dinitrogen gas evolved by reaction of the BNH compound with iodate in aqueous solution does not work either, as the boron hydride develops some dihydrogen and would result in high nitrogen readings. A modified gasometric method for these BNH compounds reacts the sample with iodate solution and passes the  $N_2/H_2$  gas mixture over heated copper(II) oxide to remove dihydrogen [535]. A slow purge of carbon dioxide sweeps the gas into a gasometer (“nitrometer,” “azotometer”) filled with strong caustic where all the  $CO_2$  is absorbed.

## 6.9 Hydrazine Bisborane

### 6.9.1 Preparation of Hydrazine Bisborane

Hydrazine borane on heating decomposes partially to hydrazine bisborane,  $H_2BNHNHBH_2$ , CAS RN [13730-91-1], which exists mostly in a polymeric form and on further heating releases more dihydrogen gas [518, 536, 537].

### 6.9.2 Physical Properties of Hydrazine Bisborane

There is a discrepancy among the several values of the enthalpy of formation for hydrazine bisborane,  $B_2H_6 \bullet N_2H_4$ , with a molecular mass of 59.736 g/mol (16.7403 mol/kg). One source reported a heat of formation of  $-84.11 \text{ kJ/mol} = -1408 \text{ kJ/kg}$  ( $-20.10 \text{ kcal/mol} = -336.6 \text{ kcal/kg}$ ) and a density of  $0.94 \text{ g/cm}^3$ . Other sources gave a heat of formation of  $-125 \pm 21 \text{ kJ/mol} = -30 \pm 5 \text{ kcal/mol}$ .

The standard enthalpies of formation of hydrazine borane and hydrazine bisborane were obtained from a calorimetric study of the combustion of these compounds [538]. The  $\Delta H_f^\circ$  for solid  $N_2H_4BH_3$  and  $N_2H_4(BH_3)_2$  are  $-42.7 \pm 4.2 \text{ kJ/mol}$  ( $-10.2 \pm 1.0 \text{ kcal/mol}$ ) and  $-126.8 \pm 4.6 \text{ kJ/mol}$  ( $-30.3 \pm 1.1 \text{ kcal/mol}$ ) respectively.

The heat of combustion of crystalline  $(H_3B)_2N_2H_4$  was determined at 298 K (25 °C) and measured as  $2668 \pm 2.1 \text{ kJ/mol}$  ( $637.8 \pm 0.5 \text{ kcal/mol}$ ). Using this value and the  $\Delta H_f^\circ$ <sup>298.15</sup> of the combustion product, crystalline  $H_3BO_3$  ( $-261.71 \pm 0.31 \text{ kcal/mol}$ ), the standard heat formation of crystalline  $(H_3B)_2N_2H_4$  was calculated to be  $-22.2 \pm 0.8 \text{ kcal/mol}$  [539].

A lithium salt of hydrazine bisborane,  $LiNH(BH_3)NH_2BH_3$  can be synthesized via the reaction between hydrazine bisborane and BuLi in ether solution [540].  $^{11}\text{B}$  NMR and FTIR spectroscopy indicated a new structure, in which one of the N—H bonds is replaced by an N—Li bond. The XRD pattern of the product indicated the formation of a new crystal structure. This compound released  $H_2$  at 399 to 443 K (126 to 170 °C) with satisfactory purity and exhibited superior hydrogen storage properties compared with hydrazine bisborane. DSC measurements indicated that the dehydrogenation reaction of this compound was less exothermic than that of hydrazine bisborane.

### 6.9.3 Decomposition of Hydrazine Bisborane

Hydrazine bisborane is not stable in water, and is even less stable in alkaline aqueous solutions. Not only solid hydrazine bisborane [541] but also aqueous hydrazine bisborane solutions have been considered as a hydrogen storage medium [542]. The use of a metal-based catalyst accelerated the hydrolysis of the  $\text{BH}_3$  groups, but a bimetallic NiPt catalyst was more active, also being able to decompose the  $\text{N}_2\text{H}_4$  moiety. The best hydrogen evolution rate was at 343 K (70 °C) in alkaline solutions. However, the dehydrogenation was not complete, reaching a limit of only 80% of conversion.

Hydrazine bisborane contains two borine  $\text{BH}_3$  units per hydrazine molecule [543]. The hydrogen released by decomposition of hydrazine bisborane was shown to have a very high purity of >99%. The activation energy of the first-step dehydrogenation of hydrazine bisborane is 106.4 kJ/mol. Hydrazine bisborane also forms salts with lithium hydride that have a low hydrogen desorption temperature of 399 K (126 °C) [540].

Kinetics and mechanism of the thermal decomposition of hydrazine bisborane were determined by a manometric method using mass and IR spectrometry and thin-layer chromatography [544]. The decomposition proceeded according to a molecular mechanism and was first order, with a rate constant of  $k = 6.34 \times 10^7 \exp[-(24.1 \pm 0.5)/RT] \text{ s}^{-1}$ . Addition of  $\text{H}_3\text{B} \cdot \text{NH}_2\text{NH}_2$  accelerated the decomposition process.

Hydrazine bisborane has a relatively low dehydrogenation temperature (~100 °C), without generation of any unwanted gaseous products such as ammonia and diborane, and the released hydrogen had a very high purity of >99% [543]. The activation energy of the first-step dehydrogenation of hydrazine bisborane was calculated to be 106.4 kJ/mol using Kissinger's method. Based on  $^{11}\text{B}$  NMR and FTIR analysis of the products, the thermal decomposition of hydrazine bisborane produced  $[\text{HBN}_2\text{BH}]_2$  dimers.

The apparent activation energies of the first step for hydrazine bisborane and  $\text{NiCl}_2$ -doped hydrazine bisborane were 143.2 and 60.7 kJ/mol respectively [545]. DSC results showed that the addition of  $\text{NiCl}_2$  did not affect the enthalpy change of hydrazine bisborane dehydrogenation.

Experimental and computational methods were used to characterize hydrazine bisborane  $\text{N}_2\text{H}_4(\text{BH}_3)_2$  as a hydrogen storage medium, including XRD, NMR, FTIR, Raman, TGA, and DSC [546]. It was concluded that  $\text{N}_2\text{H}_4(\text{BH}_3)_2$  has the potential to be used as a hydrogen storage medium, assuming that both thermolytic and hydrolytic dehydrogenations were applied. In solid-state chemical hydrogen storage, it cannot be used because of the risk of explosions during dehydrogenation.

Borane compounds that are also being considered as reversible hydrogen storage media are hypergolic, with WFNA as the oxidizer [547]. When dissolved in ionic liquids, the borane solutions exhibited ignition delay times that were shorter than those of many known hypergolic ionic liquids.

## 7 Other Boron-Nitrogen Compounds

### 7.1 Alkylborane Alkylamine Adducts

Triethylborane is commercially available in the form of adducts with 1,3-diaminopropane or triethylenediamine.

### 7.2 Alkylborane Hydrazine Adducts

Trimethylborane forms Lewis adducts with hydrazine [548].

### 7.3 Aminoboranes

Aminoborane,  $\text{H}_2\text{NBH}_2$ , which has a tendency to polymerize, forms during the thermolysis of ammonia borane. The monomeric aminoborane is unstable at room temperature, oligomerizing to form a non-volatile white solid residue of poly(aminoboranes). Heating of poly(aminoboranes) releases dihydrogen and the ultimate product is boron nitride, which is difficult to convert back to ammonia borane if one wants to operate a hydrogen storage cycle [495]. There is a group of alkylaminoboranes where hydrogens on the nitrogen or the boron or both on nitrogen and boron are replaced by alkyl groups. These would be potential hypergolic fuels with a wide range of oxidizers. One example is dimethyl aminodimethylborane,  $(\text{H}_3\text{C})_2\text{N}-\text{B}(\text{CH}_3)_2$ , which is a liquid that freezes at 180.6 K ( $-92.5^\circ\text{C}$ ) and boils at 338 K ( $65^\circ\text{C}$ ).

### 7.4 Alkylamine-Borane Lewis Adducts

There are numerous adducts of the type  $\text{R}_{3-n}\text{H}_n\text{NBH}_3$  or  $\text{R}_{3-n}\text{H}_n\text{NBR}_3$  with  $n = 0, 1, 2$  that have acceptable properties as hypergolic fuels with WFNA or red fuming nitric acid (RFNA).

$\text{BH}_3$ -amine and  $\text{B}(\text{CH}_3)_3$ -amine adducts were investigated as potential additives for hypergolic rocket propellant combinations [549]. The investigation included the calculation of predicted properties for a variety of known and notional adducts. Property predictions were based on results from quantum chemistry methods. Predicted gas-phase properties included B–N bond dissociation energies and enthalpies of formation at 298 K [ $\Delta H_f^{298}(\text{G})$ ]. Predicted condensed-phase properties included enthalpies of sublimation, enthalpies of formation at 298 K [ $\Delta H_f^{298}(\text{S})$ ], and densities. The measured enthalpy of formation of trimethylamine borane in the gas phase was  $-85 \text{ kJ/mol}$  ( $-20.3 \text{ kcal/mol}$ ) and the predicted enthalpy of formation was  $-77 \text{ kJ/mol}$



(−18.4 kcal/mol). The measured enthalpy of formation of trimethylamine borane solid phase was −141 kJ/mol (−33.81 kcal/mol). The measured enthalpy of formation of trimethylamine trimethylborane in the gas phase was −220 kJ/mol (−52.6 kcal/mol) and the predicted calculated number was −212 kJ/mol (−50.6 kcal/mol). The measured enthalpy of formation of trimethylamine trimethylborane in the solid phase was −279 kJ/mol (−66.6 kcal/mol) and the predicted calculated number was −272 kJ/mol (−65.0 kcal/mol). The  $\Delta H_f^{298}(\text{S})$  estimates were then used as input for thermochemical code-based calculations of the specific impulse that adducts could potentially generate when combined with IRFNA. Several  $\text{BH}_3$ -amine adducts warrant further investigation as additives for liquid/gel hypergols or for solid fuels for hybrid concepts.

An alkylamine borane adduct of unusual inertness in air and thermal stability is bisborane-triethylenediamine, which was non-volatile and did not melt at temperatures up to 623 K (350 °C) [550]. Lewis adduct formation of amines with borane converts them to hypergols (if they were not hypergolic to start with) or decreases their ignition delays (if they already had some hypergolicity) multifold with WFNA or RFNA as the oxidizer. With consistently low ignition delays, amine boranes represent a class of compounds that can be promising alternatives to hydrazines as bipropellant fuels. A structure-hypergolicity relationship study revealed the necessary features for a low ignition delay [551].

Solid amine boranes, in particular, ethylenediamine bisborane, can be used as high-performance hypergolic hybrid rocket fuels and their combustion behavior in a hypergolic hybrid combustor has been investigated [552, 553]. The addition of a borane adduct to an amine fuel tends to reduce the ignition delay with WFNA by up to an order of magnitude.

The (mono-, di-, tri-)methylamine-borane adducts are solids like real salts and their crystalline structures are known [554]. The structures of methylamine borane,  $\text{MeH}_2\text{N}\cdot\text{BH}_3$  and dimethylamine borane,  $\text{Me}_2\text{HN}\cdot\text{BH}_3$ , have been investigated by gas-phase electron diffraction and quantum chemical calculations. The crystal structures have been determined for methylamine, dimethylamine, and trimethylamine borane,  $\text{Me}_n\text{H}_{3-n}\text{N}\cdot\text{BH}_3$  ( $n=1-3$ ), by XRD and revealed the intermolecular interactions and, particularly, the  $\text{N}-\text{H}\cdots\text{H}-\text{B}$  dihydrogen bonding in the cases where  $n=1$  or 2. The enthalpy of formation of solid trimethylamine borane is −146 kJ/mol (−34.8 kcal/mol). The ammonia-trimethylborane adduct melts at 347 K (74 °C), and its enthalpy of formation in the solid state is −286 kJ/mol (−68.3 kcal/mol). The methylamine-trimethylborane adduct melts at 300 K (27 °C) and boils at 420 K (147 °C) with dissociation. The trimethylamine-trimethylborane adduct melts at 401 K (128 °C) whereas the trimethylamine-triethylborane adduct is a liquid and freezes at 227 K (−46 °C).

The adduct of methylamine and diborane,  $\text{H}_3\text{CNH}_2\cdot\text{BH}_3$  is a solid and melts at 331 K (58 °C) [383]. It is soluble in diethyl ether or dioxane.

Instead of preparing the Lewis adducts directly from diborane and free amines, the adducts *N*-dimethylaminoborane, trimethylamine-borane, and *N*-tri-

methylborazole can be prepared more economically from lithium borohydride and the (bi, tri)methylammonium chloride [555].

It was hoped that forming addition compounds of diborane with alkylamines would reduce the vapor pressure and the toxicity of diborane. A comparison of the acute toxicity of dimethylamine-borane with the acute toxicity of pyridine-borane and trimethylamine-borane showed that, on a weight basis, the order of decreasing toxicity would be dimethylamine-borane > pyridine-borane > trimethylamine-borane [556]. However, when expressed in terms of mg B/kg, the LD50 values formed two distinct groups, still more toxic than hydrocarbon fuels such as RP-1.

Selected amine boranes (e.g., trimethylamine cyanoborane, *N*-methylmorpholine cyanoborane, and the base-boronated 2'-deoxynucleosides) are under evaluation as pharmaceutical drugs and have anti-inflammatory, analgesic, anti-arthritis, and anti-osteoporotic activities. Triethylamine borane has a short ignition delay with WFNA, but a high melting point. Methanol, triethylamine, and ammonium tetraphenylborate have been evaluated as freezing point depressants for triethylamine borane [557].

### 7.5 Ammonia-(Dinitramido)Boranes

Ammonia-(dinitramido)boranes,  $\text{H}_3\text{NH}_2\text{BN}(\text{NO}_2)_2$ , are members of a new class of chemicals that are potentially useful as rocket propellants. Two ammonia-(dinitramido)boranes were synthesized by the reaction of dinitroamine with ammonia borane [558]. Ammonia-mono(dinitramido)borane is a perfectly oxygen-balanced high-energy density material composed of an ammonia-BH<sub>2</sub> fuel group and a strongly oxidizing dinitramido ligand. Although it is thermally not stable enough for practical applications, its heat of explosion is 916 kJ/mol (219 kcal/mol) and its predicted specific impulse as a solid rocket propellant would be 333 s. Its predicted performance as an explosive matches that of pentaerythritol tetranitrate and significantly exceeds that of TNT. Its structure was established using XRD and vibrational and multi-nuclear NMR spectroscopy (Figure 25).

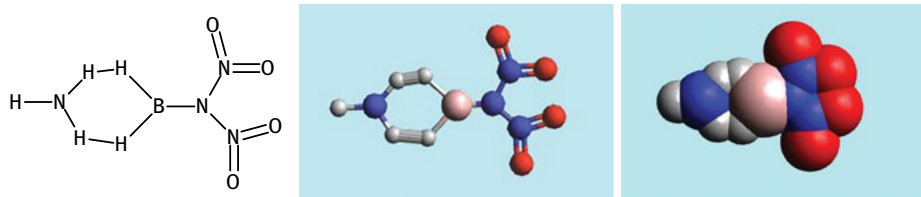


Figure 25: Molecular structure of ammonia-dinitramidoborane.

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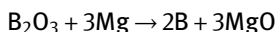


# Boron

Elemental boron has been tested as a fuel in solid propellants, ram-air rockets, gelled liquid fuel slurries, and hybrid fuel grains. Elemental boron is a solid, so it should not really be included in a volume entitled *Encyclopedia of Liquid Fuels*. However, we assume here that the boron is used as a finely divided powder suspended in a kerosene slurry, making it a liquid fuel. There is special interest in nanosize particles of boron that remain in suspension without the aid of a gelling agent. For general information on elemental boron, see [1] and [2].

## 1 Preparation of Elemental Boron

Amorphous boron solidifies from a melt in the shape of black, glass-like shards or is obtained in the form of a brown powder from thermite processes. Elemental boron can be made by a self-propagating high-temperature synthesis (SHS) thermite (*magnesiothermic*) process:



but the raw product is always contaminated with magnesium or carbon. Those contaminants do not interfere with the intended use of boron in rocket propellants or igniter pyrotechnic mixtures. Calculations showed that the adiabatic combustion temperature of the  $\text{B}_2\text{O}_3/\text{Mg}$  reaction system was 2604 K. This high thermite temperature causes unwanted coagulation of the boron particles that formed. Smaller particle sizes can be obtained if the reaction is conducted at lower temperatures in a diluent molten salt bath [3]. The diluent salt most often used is simple rock salt, NaCl. Nanosized amorphous boron powders were synthesized by an active dilution self-propagating high-temperature synthesis (SHS) method at moderate temperatures ranging from 973 to 1023 K (700–850 °C) in an SHS furnace using Mg,  $\text{B}_2\text{O}_3$ , and  $\text{KBH}_4$  as raw materials [4].

Amorphous boron nanoparticles can be synthesized by heating a  $\text{B}_2\text{O}_3 + 3\text{Mg} + n\text{NaCl}$  (where  $n$  is the number of moles of NaCl used as diluent) exothermic mixture in a laboratory oven at 1073 K (800 °C) under argon flow [5]. NaCl was used as an inert material to decrease the maximum combustion temperature of the reaction mixture when it was self-ignited after the melting of Mg at 923 K (650 °C). The sizes of the boron nanoparticles extracted from the final product by acid leaching ranged between 30 and 300 nm for  $n$  values ranging from 1 to 5.

Boron powders with sub-micron sizes can be prepared by salt-assisted combustion synthesis in an argon atmosphere using  $\text{B}_2\text{O}_3$  and Mg powders as starting materials and NaCl as diluent [6]. The average size of the boron particles decreased and



their dispersibility improved after starting to use diluent NaCl. The purity of samples prepared by adding 50% NaCl was the highest, 96% B, and the average particle size was within 0.4–0.8  $\mu\text{m}$ .

Pure boron can be obtained by reduction of boron trichloride with hydrogen or by thermal decomposition of diborane.

A review presented four main techniques for the preparation of elemental boron: molten salt electrolysis, metallic reduction, hydrogen reduction, and controlled decomposition of boron compounds [7]. Electrowinning of boron is conducted in molten salt systems. Four types of hydrogen reduction of boron compounds are in use. For chemical vapor deposition processes used in semiconductor and superconductor production, the purity, conversion rate, morphology, and deposition rate of the produced boron are major concerns. Like hydrogen reduction, decomposition of boron compounds can be used to produce high-purity and ultra-fine boron, but the high cost and severe reaction conditions will limit any applications of this process on a large scale. See also [8, 9].

Boron powders with high purity, a small particle size, and a narrow particle size distribution are preferred in high-tech industrial fields, but purity is not so critical if they are to be burned in a rocket propellant. Boron powder can be purified by leaching with acid [10].

In order to achieve complete combustion of boron or metal particles in an air-breathing or a rocket combustion chamber, the target during the past decades has been to produce boron (and aluminum) in smaller and smaller particle sizes. The production of nanoboron poses unique challenges, but both boron and aluminum in various nanoparticle sizes are now commercially available. Freshly ground boron powder should be exposed to air only slowly or it may autoignite.

### 1.1 Preparation of Nanoparticle-Size Elemental Boron

Nanoparticle and nanotube boron are more reactive forms of boron that potentially can result in higher burning rates of solid or slurry fuel propellants. Nanoboron particles may burn more completely than microboron particles, which sometimes become encrusted with  $\text{B}_2\text{O}_3$  slag before they burn to completion. Incomplete combustion results in performance losses. During the past two decades, a substantial amount of effort has been devoted to nanometal powders. There are now periodicals and conferences devoted exclusively to nanoparticles. Most of this effort was aimed at nanoaluminum as a means to increase performance and burning rates of solid rocket propellants. Similar efforts have been directed at nanoboron.

In order to increase the rate of energy release during the combustion of boron and make it a more attractive fuel for propellants and explosives, it is advantageous to prepare it in a nanoparticulate form. Boron nanoparticles have been obtained previ-

ously from diborane by thermolysis at temperatures between 1073 and 2523 K (700 and 2250 °C), although often the size distribution produced is broad or the particles are extensively aggregated [11]. Boron nanoparticles have also been obtained by reduction of boron trihalides with  $H_2$ . The difficulty with nanoboron is that it readily reacts with moisture or air, more readily so than aluminum. It loses some of its combustion value and becomes coated with an oxide layer as soon as it is exposed to air, which slows down the combustion kinetics. Some nanometals are pyrophoric and will autoignite in air, even at room temperature. Several methods are available for making nanoboron. One of the methods uses a thermal plasma system [12]. In another use of this method, a hydrogen thermal plasma jet was employed to prepare nanosized boron powder with hydrogen reduction of  $BCl_3$  vapor [13]. The maximum yield of nanosized boron powder from the hydrogen thermal plasma jet was about 50% with a  $H_2/BCl_3$  ratio of 4.5 : 1, a total feed of  $4.9\text{ m}^3/\text{h}$ , and a plasma power of 25 kW. The average diameter was about 50 nm, and the purity was 90.29%.

Nanoboron can be prepared by decomposition of diborane in a plasma discharge [14]. The reported diameters of boron nanoparticles synthesized in the gas phase and the liquid phase are in the ranges 10–150 and 1–45 nm, respectively.

Another method uses the dry-milling of reactive powders [15–17]. If a mixture of boron trioxide and magnesium is subjected to high-energy ball milling, the grinding forces will eventually trigger a mechanically induced self-sustaining reaction once the particle size is small enough, yielding nanosize boron powder.

Nanoboron can be obtained by ball-milling coarse boron powder in a ball mill with tungsten carbide rollers under either dry or wet conditions [18].

In order to obtain more reproducible results with different batches of nanoboron, the nanoparticles need to be better characterized. A variety of standard particle characterization techniques were applied to fifteen types of particles [19]. The parameters measured were average particle diameter, specific surface area, amount of active content, and oxide layer thickness. Trends in propulsion performance measured using a parameter of great interest to the hybrid rocket community (fuel mass burning rate) in general matched trends in particle characteristics (i.e., active content, surface area), but there were some noticeable exceptions. Other parameters that need to be examined include particle size distribution, degree of agglomeration, reactivity, and thermal effects.

Nanosized boron and  $MgB_2$  (a superconductor) can be prepared by boron oxide solubilization in hot water, cryogenic freezing of the liquid phase, a freezing–drying process, magnesiothermic reduction of boron oxide, and boron purification [20].

Boron combustion is inherently a heterogeneous process, which makes rapid and efficient combustion difficult. An obvious strategy is to increase the surface area/volume ratio by decreasing the particle size. This approach is limited by the fact that boron forms a ~0.5 nm thick native oxide layer that not only inhibits combustion but also consumes an increasing fraction of the particle mass as the size is decreased.

A simple, scalable, one-step process for generating air-stable boron nanoparticles that are unoxidized and soluble in hydrocarbons used ball milling to produce ~50 nm particles that were protected against room temperature oxidation by oleic acid functionalization and optionally coated with a combustion catalyst [21]. The high-energy milling method with subsequent sedimentation to separate aggregates produced gram quantities of nanoparticles in a narrow distribution of particle sizes centered around 50 nm [22].

Ball milling of boron in a hydrogen atmosphere was found to result in hydrogen uptake of up to 5% by mass (36 mol-%) [23]. The nature of the hydrogen binding to boron was probed by a combination of IR spectroscopy, TGA, and MS measurements of the gases evolved during sample heating. The dominant binding mode was found to be that of hydrogen atoms to boron atoms in the surface layer of the particles, and the high hydrogen loading resulted from the production of very high surface area, indicating that gaseous  $H_2$  is an effective agent for promoting size reduction in milling. Hydrogen incorporated into nanoboron was found to be stable for at least a month under ambient conditions. Hydrogen desorption began at ~333 K (~60 °C) and continued as the temperature was increased, with broad desorption features peaking at ~523 and ~723 K (~250 and ~450 °C) and ending at ~1073 K (~800 °C). Hydrogenated boron nanoparticles suspended in a fuel were found to promote more intense combustion upon contact with nitric acid.

Similar to carbon, boron atoms condensing from a hot plasma may also arrange themselves in the shape of nanotubes [24, 25].

### 1.1.1 Protective Coatings for Elemental Boron Particles

The exploitation of the high theoretical heat of combustion of boron has been limited by a few undesirable properties of boron powders. Among them, a resilient oxide layer on the particle surface affects the ignition and combustion of boron particles. Coating boron nanoparticles with a polymer to prevent autoxidation can provide a solution to the problem. The use of an energetic polymer can bring additional heat close to the surfaces of the nanoparticles and facilitate their ignition. Polymer-capped boron nanoparticles were produced by synthesis of surface-functionalized boron to obtain additional hydroxyl functional groups on the particles [26]. These hydroxyl sites were used to graft a diisocyanate and then produce an energetic polymer matrix based on polyurethane chemistry by addition of glycidyl azide polymer, resulting in boron nanoparticles coated with an energetic polymer. This led to improved boron particle combustion.

Energetic polymer coatings evaluated as protective coatings for boron particles include GAP [27, 28]. GAP-coated amorphous-boron-based fuel-rich propellants exhibited more vigorous combustion, higher burning rates, and less residue slag agglomeration than the uncoated baseline propellant. Two stages of combustion were observed

for a dust cloud of GAP-coated boron particles. The burning time was estimated to be approximately 37.5 ms [29].

A synthesis process has been evaluated for the preparation of boron fuel particles coated with titanium [30]. The titanium coating prevents oxide formation on exposure to air and aids in the combustion. Pure boron particles were produced by reaction of sodium vapor with boron trichloride vapor; the products were then expanded through a supersonic nozzle while titanium tetrachloride was added to produce titanium, coating the boron particles. Titanium-coated boron is resistant to oxidation and hydrolysis and has good burning characteristics [31].

Coating with magnesium is a good choice, since magnesium – with its low melting point and low boiling point – is easily vapor deposited on boron powder in a tumbler under vacuum, and some boron powders prepared by a thermite process already contain magnesium [32]. Magnesium-coated boron formulated into solid propellants has good burning characteristics [33, 34]. The same process can also be applied to make aluminum-coated boron.

Even a coating of ammonium perchlorate, a solid oxidizer, can protect the particles from air and moisture [35]. The method used involves dissolving ammonium perchlorate in liquid ammonia, adding a volatile non-solvent diluent and boron particles to the ammonia, and then vaporizing the ammonia and diluent to form a coated product.

Boron carbide is inert to moisture and makes a good coating on boron particles [36]. Boron particles that are coated with a ceramic layer of boron carbide in an atmosphere of decomposing lower hydrocarbons are resistant to oxidation and agglomeration. See also [37].

## 2 Physical Properties of Elemental Boron

Boron exists in the amorphous form and at least two crystalline allotropic forms. The main crystalline forms are  $\alpha$ -rhombohedral,  $\beta$ -rhombohedral, and  $\beta$ -tetragonal. Under special conditions, boron can also be synthesized as its  $\alpha$ -tetragonal and  $\gamma$ -orthorhombic allotropes. Amorphous boron powder and polycrystalline  $\beta$ -rhombohedral boron are the most common forms [38].

One highly unusual allotropic form of boron is borospherene,  $B_{40}$ , which is a cluster molecule containing 40 boron atoms. It is similar to buckminsterfullerene ( $C_{60}$ ), the “spherical” carbon structure, but with a different symmetry. The physical properties of elemental boron are summarized in Table 1.

**Table 1:** Physical properties of elemental boron.

| Property                              | SI units                 | Other units              |
|---------------------------------------|--------------------------|--------------------------|
| Atomic mass                           | 10.811 g/g-atom          | 92.498 g-atom/kg         |
| Density, $\alpha$ -rhombohedral phase | 2.46 g/cm <sup>3</sup>   | —                        |
| Density, $\beta$ -rhombohedral phase  | 2.35 g/cm <sup>3</sup>   | —                        |
| Melting point                         | 2450 K                   | 2177 °C                  |
| Boiling point                         | 3931 K                   | 3658 °C                  |
| Heat of fusion                        | 50.2 $\pm$ 1.7 kJ/g-atom | 12 $\pm$ 0.4 kcal/g-atom |

## 2.1 Thermodynamic Properties of Elemental Boron

The solid- and liquid-phase heat capacities of boron can be calculated with the following equation:

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where  $C_p^\circ$  is the heat capacity in J mol<sup>-1</sup> K<sup>-1</sup>,  $\tau$  is the absolute temperature in kelvin divided by 1000, and A, B, C, D, and E are constants listed in Table 2.

**Table 2:** Coefficients for thermodynamic properties of solid and liquid boron.

| Temperature range (K) | Solid boron |           | Liquid boron               |
|-----------------------|-------------|-----------|----------------------------|
|                       | 298–1800    | 1800–2350 | 2350–4138                  |
| A                     | 10.18574    | 25.12664  | 31.75003                   |
| B                     | 29.24415    | 1.975493  | 2.556177 $\times 10^{-7}$  |
| C                     | -18.02137   | 0.338395  | -6.456792 $\times 10^{-8}$ |
| D                     | 4.212326    | -0.040032 | 5.616644 $\times 10^{-9}$  |
| E                     | -0.550999   | -2.635578 | 2.705970 $\times 10^{-7}$  |
| F                     | -6.036299   | -14.43597 | 27.94205                   |
| H                     | 0.000000    | 0.000000  | 48.92686                   |

Comment: Values for solid boron are for the  $\beta$ -rhombohedral phase  
Data source: [39]

By definition, the enthalpy of formation of solid boron at 298 K is zero. The solid-phase differential heat of formation of boron as a function of temperature can be calculated with the following equation:

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - H$$

where  $H^\circ - H^\circ_{298,15}$  is the differential heat of formation in kJ/g-atom,  $\tau$  is the absolute temperature in kelvin divided by 1000, and A, B, C, D, E, F, and H are constants listed in Table 2. The heat of formation of amorphous boron is a little higher than the heat of formation of crystalline boron, which, by definition, would be zero. The heat of formation of amorphous boron is +0.9 kcal/g-atom. The heat of fusion at the melting point is  $50.2 \pm 1.7$  kJ/g-atom ( $12 \pm 0.4$  kcal/g-atom) and the heat of evaporation at the boiling point is 479.56 kJ/g-atom (114.6 kcal/g-atom).

## 3 Chemical Properties of Elemental Boron

### 3.1 Reactions of Elemental Boron

#### 3.1.1 Autoxidation Reactions of Elemental Boron

Amorphous boron will absorb moisture and react with moisture in the atmosphere if it is not stored under dry conditions. The rate of water absorption of amorphous boron is dependent on the particle size and the relative humidity of the atmosphere where boron is stored. Samples that had been stored at various controlled humidities in humidity test chambers showed increased water-soluble boron content. Oxidation of boron to boric acid is accompanied by water absorption; at lower humidities, only about 25% of the sample weight gain was due to oxidation, while oxidation accounted for over half the weight gain above 50% relative humidity (Table 3). Less than 0.03% of the boron stored in dry air in the absence of moisture at 298 K for 13 d was oxidized.

**Table 3:** Cumulative % increase in weight of amorphous boron at various relative humidities.

| Day | Relative humidity, % |      |      |      |      |      |
|-----|----------------------|------|------|------|------|------|
|     | 20                   | 35   | 45   | 66   | 81   | 90   |
| 1   | 0.65                 | 0.83 | 1.02 | 1.30 | 1.76 | 2.1  |
| 10  | 1.05                 | 1.37 | 1.70 | 2.10 | 2.66 | 3.80 |
| 25  | 1.38                 | 2.05 | 2.58 | 3.10 | 3.85 | 5.77 |

Data source: [40]

The reaction between boron and water has been considered as a source of hydrogen gas for fuel cells and automobile propulsion, although at the current cost of boron powder this approach may not be economical [41]. The boron–water reaction can produce 277 g H<sub>2</sub> per kg B. Room-temperature boron hydrolysis is of interest from both scientific and practical perspectives. It was demonstrated that high-purity amorphous boron nanoparticles can be oxidized by water to produce H<sub>2</sub> at room temperature.

### 3.1.1.1 Autoignition Reactions of Elemental Boron

Boron is used as the fuel in many igniter compositions. Therefore, it is important to know the ignition behavior of boron powder in air in the absence and in the presence of solid oxidizers. The autoignition temperature in air is dependent on particle size. Boron is less susceptible to autoignition than aluminum. Replacing aluminum powder in pyrotechnic flash formulations with boron powder raised the autoignition temperature in air per ASTM standard E1492-06 from 623 to 773 K (350 to 500 °C).

## 3.2 Analysis and Specifications of Elemental Boron

Boron purity for pyrotechnic applications is controlled by MIL-SPEC MIL-B51092 [42].

## 3.3 Combustion of Elemental Boron

The use of boron is very attractive for rocket and ramjet applications due to its high heat of combustion on both a gravimetric (58 kJ/g) and a volumetric (136 kJ/cm<sup>3</sup>) basis. The heat of combustion of elemental boron is 58448 kJ/kg = 25150 BTU/lb. Boron slurries in gelled hydrocarbons can be used as fuels in ramjets.

## 4 Applications of Elemental Boron

The main non-pyrotechnic, non-propulsion use of boron, also in the form of boron carbide, is as a neutron absorber in nuclear reactors. Elemental boron is used in many solid igniter formulations such as KNO<sub>3</sub>/B or KClO<sub>4</sub>/B.

### 4.1 Slurries of Boron in Inert Fuels

The best way to protect boron powder particles from air oxidation and moisture hydrolysis is to suspend them in an inert fluid that serves both as a continuous phase suspension and as a fuel. In order to prevent particles from settling, the fluid is usually gelled, similar to metallized gelled fuels with other metal particles. Most of the work has been done with (micron-size or nanosize) boron particles suspended in kerosene. Other inert fuels suitable for boron suspensions are ethanol [43] and ionic liquids. Suspending boron nanoparticles by milling in the presence of a hypergolic energetic ionic liquid (EIL) retains hypergolicity, leading to the ignition of the boron with WFNA [44, 45]. It was found that the ionic liquids 1-methyl-4-amino-1,2,4-triazolium dicyanamide and 1-butyl-3-methylimidazolium dicyanamide bind to boron well enough to resist removal by ultrasonic washing and to protect the boron surface from oxidation during

air exposure of the washed powder. The data suggest that both the cation and the anion of each ionic liquid interact with the boron surface [46]. The interaction of B-H-functionalized boron nanoparticles with alkenes was investigated by a combination of XPS, FTIR, TGA, and helium ion microscopy. Surface B—H bonds were shown to react with terminal alkenes to produce alkyl-functionalized boron particles [47].

## 4.2 Slurries of Boron in Monopropellants

Although most organic nitropropellants such as nitroalkanes or alkyl nitrates are underoxidized, and addition of another fuel such as boron shifts the oxygen balance toward an even more fuel-rich stoichiometry, addition of nanoboron powder to organic monopropellants has been shown to improve performance and combustion rates [48]. The reaction of boron with hydrazine is highly exothermic and forms the basis for a good monopropellant.

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# Cyano Compounds and Nitriles

## Cyano Compounds and Nitriles

This chapter contains information on inorganic and organic cyanides. Cyano compounds carry triple bonds. Triple bonds, regardless of whether they are between two carbon atoms or a carbon atom and a nitrogen atom, carry extra energy that make these compounds useful as rocket propellant ingredients. In addition, many of these compounds contain a large amount of nitrogen, which makes them valuable as ingredients in nitrogen gas generators, such as in airbag inflators.

### 1 Inorganic Cyanogen Derivatives

Cyanogen compounds contain a nitrile bond, a carbon–nitrogen triple bond  $C\equiv N$ , which is chemically quite stable. Examples of inorganic cyanogen compounds include hydrogen cyanide  $HC\equiv N$ , cyanogen (dicyanogen)  $N\equiv C-C\equiv N$ , and cyanogen azide  $N\equiv C-N=N\equiv N$ . These compounds have been investigated as high-energy fuels because, when burned with the right oxidizer, they achieve extremely high flame temperatures. Of course, every rocket propulsion student knows that a high flame temperature alone does not imply a good rocket propellant; in addition to a high temperature, one also needs low-molecular-weight combustion products. In this case, the average molecular weight of cyanogen combustion products is relatively high because they contain mostly carbon monoxide and/or carbon dioxide and no or very little hydrogen or water. The products from the combustion of cyanogen with oxygen consist mostly of carbon monoxide and nitrogen, with an average molecular weight of 28 g/mol.

A high flame temperature may be good for a welding torch but it is not easy to tame in a rocket engine. It makes the cooling of rocket engines extremely difficult. Therefore, instead of using cyanogen compounds by themselves, it may be possible to use them as energetic additives to other fuels that contain at least some hydrogen [1].

While the high heats of combustion of cyanogen compounds may not necessarily make them suitable as rocket propellants, they would make good fuels for air-breathing turbojet and ramjet or ram-rocket engines, which have already been demonstrated using methylacetylene as the fuel [2].

All cyanogen compounds are very toxic and would have to be handled with special safety precautions if one ever wanted to use them as rocket propellants. The only cyanogen compound that has ever been used as a rocket propellant is acetonitrile,  $H_3C-C\equiv N$  (see Section 2.1).

## 1.1 Hydrogen Cyanide

Hydrogen cyanide, also known as hydrocyanic acid, prussic acid, formonitrile, HCN, CAS RN [74-90-8],  $M = 27.03 \text{ g/mol}$ , is a colorless, highly toxic liquid with the characteristic odor of bitter almonds. Hydrogen cyanide in aqueous solution was first prepared by Scheele in 1782. The acid occurs naturally among the hydrolysis products of amygdalin and has been the cause of numerous poisoning accidents. Pure hydrogen cyanide is not stable in the liquid state but tends to polymerize to a brown residue. Hydrogen cyanide would not be a good rocket propellant and is discussed here only because it is the parent compound for many other more useful propellant ingredients. Hydrogen cyanide has been detected in the spectra of comet plumes, and there is speculation that it may be a precursor to amino acids in interstellar chemistry. Hydrogen cyanide forms as an unwanted combustion product during fuel-rich combustion of amines and alkylhydrazines in rocket engines. In vacuum rocket engine test facilities where the vacuum is created by steam ejectors, hydrogen cyanide will dissolve in the condensate water. If the condensate water is reused and recycled for the steam generator in a closed loop, hydrogen cyanide may accumulate in the condensate. This has been the case in one of the vacuum test facilities for the third stage of ELDO in Germany in 1965.

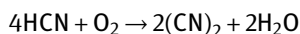
Because hydrogen cyanide is very toxic, it is important to detect it quickly in the air in workplaces and take corrective action (i.e., stop the combustion process that emits HCN and increase ventilation). Hydrogen cyanide in air can be detected easily with a reagent-impregnated test paper [3] or with Draeger tubes. Additional information on inorganic cyano compounds is provided in [4].

## 1.2 Cyanogen

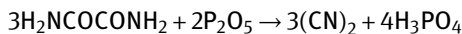
Cyanogen, also known as dicyanogen, oxalic acid dinitrile, oxalonitrile, carbon nitride, ethanedinitrile,  $(\text{CN})_2$ , CAS RN [460-19-5], is the simplest representative of the family of cyanogen compounds. It can be used for high-temperature flame studies and as an intermediate in the synthesis of heterocyclic compounds [5]. The hydrolysis of cyanogen leads to oxamide. Cyanogen has been detected in interstellar gas and in the spectra of comet plumes.

### 1.2.1 Preparation of Cyanogen

Cyanogen can be produced in industrial quantities by oxidation of hydrogen cyanide with air in the presence of copper salts as catalysts [6]:



In smaller quantities in the laboratory, cyanogen can be prepared by dehydration of ammonium oxalate or oxamide with phosphorus pentoxide:



by treatment of sodium cyanide or potassium cyanide with copper(II) sulfate, by reacting hydrogen cyanide with chlorine gas, by electrolysis of cyanide solutions or molten cyanides, by heating mercuric cyanide, silver cyanide, or auric cyanide, by pyrolysis of triazine compounds, and by dehydration of glyoxime with acetic anhydride. Cyanogen can be prepared by pyrolysis of diacetylglyoxime, which can be easily prepared from glyoxime [7]. Cyanogen can be prepared from the elements by a consumable carbon electrode in a nitrogen/argon electric arc [8] or by reduction of cyanogen chloride with hydrogen in a quartz tube at 1123 K (850 °C) [9].

### 1.2.2 Physical Properties of Cyanogen

Cyanogen is a colorless, very poisonous gas that can be condensed to a liquid at 252 K = −21.15 °C. Once ignited, the gas will burn in air with a pink-shrouded, very hot flame. Properties of cyanogen are summarized in Table 1.

**Table 1:** Physical properties of cyanogen.

| Property                                               | SI units                      | Other units                     | References |
|--------------------------------------------------------|-------------------------------|---------------------------------|------------|
| Molecular mass                                         | 52.0348 g/mol                 | 19.217 mol/kg                   | [10]       |
| Freezing point                                         | 245.31 K                      | −27.84 °C                       | [11]       |
|                                                        | 245.27 K                      | −27.88 °C                       | [12]       |
| Boiling point                                          | 252 K                         | −21.15 °C                       | [10]       |
| Triple point                                           | 245.32 K                      | −27.83 °C                       | [12]       |
| Density, liquid, at 256 K = −17 °C                     | 0.866 Mg/m <sup>3</sup>       | 0.866 g/cm <sup>3</sup>         | [11]       |
| Density, liquid, at 252 K = −21 °C                     | —                             | 0.9537 g/cm <sup>3</sup>        | [13]       |
| Critical temperature                                   | 401 K                         | 128.3 °C                        |            |
| Critical pressure                                      | 5.978 MPa                     | 59.3 atm                        |            |
| Surface tension, liquid at normal boiling point        | 2.198 × 10 <sup>−4</sup> N/cm | 21.98 dyn/cm                    |            |
| Standard enthalpy of formation, gas $\Delta H_f^{298}$ | +307.9 kJ/mol                 | +73.6 kcal/mol                  | [11]       |
|                                                        | +309.07 kJ/mol                | +73.87 kcal/mol                 | [10]       |
|                                                        | +308.94 ± 1.8 kJ/mol          | +73.84 ± 0.43 kcal/mol          | [14]       |
| Heat of fusion at 245 K = −27 °C                       | 8.109 kJ/mol                  | 1.938 kcal/mol = 37 cal/g       | [12]       |
| Heat of vaporization at 252 K = −21 °C                 | 23.33 kJ/mol                  | 5.58 kcal/mol = 107 cal/g       |            |
| Heat of sublimation in the range 202–245 K             | 34.4 kJ/mol                   | 8.22 kcal/mol                   |            |
| Dipole moment                                          | —                             | 0.38 × 10 <sup>−18</sup> e.s.u. | [11]       |

### 1.2.2.1 Vapor Pressure of Cyanogen

Cyanogen has a very narrow liquid range, only 6° wide. The vapor pressure of liquid cyanogen in the range 252–391.3 K can be calculated from the Antoine equation:

$$\log_{10}P = A - (B/(T + C))$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. The parameters  $A$  through  $C$  are listed in Table 2.

**Table 2:** Parameters of the Antoine vapor pressure equation for cyanogen.

| Temperature range, K | A       | B        | C       |
|----------------------|---------|----------|---------|
| 252–391.3            | 4.51661 | 1041.518 | –21.288 |

Data source: [10]

The vapor pressure of solid cyanogen in the range 202–245 K (–69 to –28 °C) can be calculated from the equation

$$\log_{10}P = -1795.9/T - 0.001464T + 9.42442$$

where  $P$  is the pressure in cm Hg and  $T$  is the temperature in kelvin [12]. The vapor pressure of liquid cyanogen in the range 245–253 K (–28 to –20 °C) can be calculated from the equation

$$\log_{10}P = -1525.7/T - 0.0040842T + 8.96542$$

where  $P$  is the pressure in cm Hg and  $T$  is the temperature in kelvin. See also [15].

### 1.2.2.2 Heat Capacity of Cyanogen

The heat capacity of gaseous cyanogen can be calculated from the Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where  $C_p$  is the heat capacity in J mol<sup>–1</sup> K<sup>–1</sup>,  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$  are constants, and  $\tau$  is the absolute temperature in kelvin divided by 1000. The coefficients are listed in Table 3. The same coefficients (and others) are used for formulas expressing the standard enthalpy of formation and the standard entropy of the vapor (see Section 1.2.2.3). These equations were obtained by curve fitting data covering the ranges 298–1300 and 1300–6000 K. The heat capacity of liquid cyanogen at 255 K ( $C_p$ ) is 105.73 J mol<sup>–1</sup> K<sup>–1</sup> [12]. See also [16].

**Table 3:** Constants for vapor-phase thermodynamic properties of cyanogen.

| Temperature range, K | 298–1300  | 1300–6000 |
|----------------------|-----------|-----------|
| A                    | 51.69290  | 83.01014  |
| B                    | 36.79351  | 2.209166  |
| C                    | -12.46154 | -0.419735 |
| D                    | 0.701803  | 0.027676  |
| E                    | -0.428743 | -9.308648 |
| F                    | 290.6951  | 264.0342  |
| H                    | 309.0725  | 309.0725  |

Data source: [10]

**1.2.2.3 Heat of Formation and Heat of Combustion of Cyanogen**

The vapor-phase excess enthalpy above the standard enthalpy of formation  $\Delta H^\circ_{f,298}$  of cyanogen can be calculated from the Shomate equation:

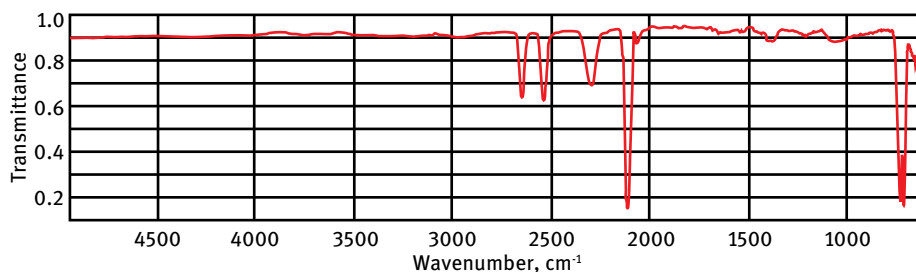
$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - \Delta H^\circ_{f,298}$$

where A, B, C, D, E, and F are constants and  $\tau$  is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 3. The same coefficients (and others) were used for a formula expressing the heat capacity of the vapor. These equations were obtained by curve fitting data covering the range from 298 to 6000 K.

The heat of combustion of cyanogen gas at 298 K is  $1096.0 \pm 1.8$  kJ/mol ( $261.94 \pm 0.43$  kcal/mol) [14].

**1.2.2.4 Infrared Spectrum of Cyanogen**

The IR spectrum of cyanogen is shown in Figure 1.

**Figure 1:** IR spectrum of cyanogen. Reproduced and modified with permission from [17]



The vibrational Raman spectrum of cyanogen has been obtained in the gas, liquid, and solid states [18]. The three Raman-active fundamentals,  $\nu_1$ ,  $\nu_2$ , and  $\nu_4$ , have been identified in all three phases. Whereas the spectra for the gaseous and liquid phases were consistent with  $D_{\infty h}$  molecular symmetry, the solid-state spectrum clearly showed the presence of the infrared-active and Raman-forbidden  $\nu_3$  mode. This is in contradiction to the XRD results. See also [19].

#### 1.2.2.5 Molecular Structure of Cyanogen

The carbon and nitrogen atoms in cyanogen are in a linear configuration, and the  $\angle \text{C}-\text{C}-\text{N}$  bond angle is  $180^\circ$ . The C—C distance is 1.37 Å and the C—N distance is 1.16 Å.

#### 1.2.3 Chemical Properties of Cyanogen

Cyanogen can serve as an intermediate in syntheses of numerous organic compounds, mostly heterocyclic compounds. A survey of the chemistry of cyanogen lists many reactions involving cyanogen [13].

Although cyanogen has an energy content similar to that of acetylene, cyanogen does not explode in either the solid, liquid, or gaseous state. Under the influence of catalysts, cyanogen can polymerize to a brown solid, such as hydrogen cyanide polymerization products.

A comprehensive study of the stability of pure cyanogen to heat, pressure, chemical additives, and severe mechanical shock found that pure cyanogen was unchanged after 18–23 d at 338 K ( $65^\circ\text{C}$ ), and that it contained only small quantities of solid polymerization products after storage for 100 d under similar conditions [20]. The presence of acids, bases, and salts as contaminants caused an acceleration of the decomposition and polymerization reactions. It was concluded that pure cyanogen did not decompose or polymerize rapidly at moderate temperatures and could be stored safely in Monel or stainless-steel cylinders, even in the absence of a stabilizer. The shock tests of liquid and solid cyanogen indicated that the material is insensitive to mechanical shocks greater than those expected in shipment and laboratory handling.

Cyanogen (dicyanogen) dissociates into cyanogen (CN) free radicals, which can be detected in interstellar space [21, 22].

Paracyanogen, the solid polymeric form of cyanogen, is often a troublesome by-product that forms during reactions of cyanogen, particularly at elevated temperatures. The structure of paracyanogen has not been elucidated but, owing to the chemical inertness and insolubility of paracyanogen, it is presumed to be either a three-dimensional network system or a fused ring system. Paracyanogen is formed when cyanogen is heated to 573–673 K ( $300\text{--}400^\circ\text{C}$ ) at atmospheric pressure. When heated in the presence of an inert carrier purge gas, such as carbon dioxide or nitrogen, paracyanogen depolymerizes to monomeric cyanogen.

### 1.2.4 Safety Properties of Cyanogen

#### 1.2.4.1 Flammable Range of Cyanogen

The flammable range of cyanogen vapor in air is LFL = 6.6 vol.-% to UFL = 32 vol.-%.

### 1.2.5 Toxicity of Cyanogen

Cyanogen (ethanedinitrile) has found a new application as a soil fumigant in agriculture, where it replaces methyl bromide. The use of methylbromide should be discontinued because it is an ozone-depleting chemical with global warming potential. Cyanogen (ethanedinitrile) can be used, often in combination with carbon dioxide, to sterilize soil and control insects, diseases, nematodes, weeds, and other parasites before planting fruit and vegetables, leaving little residue. Unlike most fumigants,  $C_2N_2$  is readily soluble in water, with one volume of water dissolving four volumes of  $C_2N_2$ . In aqueous solutions,  $C_2N_2$  is slowly hydrolyzed to form oxalic acid and ammonia, forming ammonium oxalate. Ammonia adds fertilizer nitrogen to the soil. At low pH,  $C_2N_2$  reacts to form derivatives of formic acid and hydrogen cyanide. The threshold limit value (TLV) for  $C_2N_2$  workplace exposure is 10 ppm.

## 2 Organic Nitriles

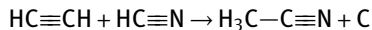
Because of their high enthalpies of formation, many cyano compounds have been considered as propellant ingredients [23, 24] and as binders for solid propellants [25].

### 2.1 Acetonitrile

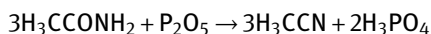
Acetonitrile, also known as methyl cyanide, cyanomethane,  $CH_3C\equiv N$ ,  $C_2H_3N_1$ , CAS RN [75-05-8], was used as an additive to increase the heat of combustion of the HYDYNE fuel mixture, which was used to power the JUPITER-C rocket that launched the first US artificial satellite in 1958. Acetonitrile is often used as a non-aqueous, polar solvent. Acetonitrile,  $H_3CC\equiv N$ , has a structural isomer, methyl isocyanide,  $H_3C-NC$ .

#### 2.1.1 Preparation of Acetonitrile

Acetonitrile can be prepared by addition of hydrogen cyanide to acetylene:



or by dehydration of acetamide:



In industry, most of the acetonitrile is obtained as a by-product of ammoxidation of higher ( $C_{n\geq 2}$ ) hydrocarbons.

### 2.1.2 Physical Properties of Acetonitrile

Physical properties of acetonitrile are listed in Table 4.

The vapor pressure of acetonitrile can be calculated from an Antoine equation,

$$\log_{10}P = A - [B/(T + C)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. Two different sets of constants are offered for this property for two different temperature ranges. The coefficients are listed in Table 5.

**Table 4:** Physical properties of acetonitrile.

| Property                                | SI units                                  | Other units                                  | References |
|-----------------------------------------|-------------------------------------------|----------------------------------------------|------------|
| Molecular mass                          | 41.0519 g/mol                             | 24.359 mol/kg                                | [10]       |
| Freezing point                          | $228 \pm 1$ K                             | $-45 \pm 1$ °C                               |            |
| Boiling point                           | $354.8 \pm 0.4$ K                         | $+81.7 \pm 0.4$ °C                           |            |
| Triple point                            | $229.315 \pm 0.02$ K                      | $-43.84 \pm 0.02$ °C                         | [26]       |
| Critical temperature                    | 548 K                                     | —                                            | [27]       |
| Critical pressure                       | —                                         | 47.7 atm                                     | [27]       |
| Density, at 293 K                       | —                                         | 0.7828 g/cm <sup>3</sup>                     |            |
| Vapor pressure, at 298 K                | 11.7 kPa                                  | 87.9 mm Hg                                   |            |
| Viscosity, at 298 K                     | $3.5 \times 10^{-4}$ Pa s                 | 0.35 cPs                                     | [28]       |
| Index of refraction ( $n_D^{16.5}$ )    | 1.3496                                    | —                                            | [29]       |
| Enthalpy of formation, liquid, at 298 K | $+40.56 \pm 0.40$ kJ/mol                  | $+9.69 \pm 0.1$ kcal/mol                     | [30]       |
| Enthalpy of formation, vapor, at 298 K  | $+74.04 \pm 0.37$ kJ/mol                  | $+17.70 \pm 0.1$ kcal/mol                    |            |
| Heat of combustion, liquid              | 1256.33<br>$\pm 0.30$ kJ/mol              | $300.3 \pm 0.1$ kcal/mol                     |            |
| Heat of vaporization, at 298 K          | 33.225 kJ/mol                             | 7.94 kcal/mol                                | [26]       |
| Heat of fusion, at 229.3 K              | 8.17 kJ/mol                               | 1.95 kcal/mol                                |            |
| Heat capacity, liquid, at 298 K         | $91.46 \text{ J mol}^{-1} \text{ K}^{-1}$ | $21.86 \text{ cal mol}^{-1} \text{ °C}^{-1}$ |            |
| Critical temperature                    | $545 \pm 2$ K                             | $272 \pm 2$ °C                               | [10]       |
| Critical pressure                       | $48.7 \pm 0.9$ bar                        | 706 psia                                     |            |
| Flash point, Cleveland open cup         | 285.9 K                                   | 12.78 °C                                     | [29]       |

**Table 5:** Coefficients for the Antoine vapor pressure equation of acetonitrile.

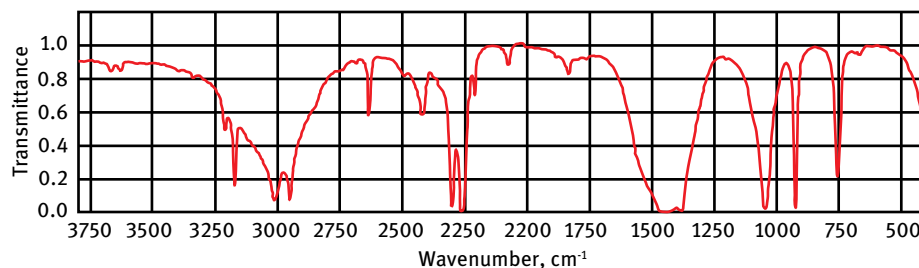
| Temperature range, K | A       | B        | C       | References |
|----------------------|---------|----------|---------|------------|
| 288.3–362.3          | 4.27873 | 1355.374 | –37.853 | [31]       |
| 280.41–300.53        | 5.93296 | 2345.829 | 43.815  | [26]       |

Coefficients were calculated by NIST from the author's data.

The heat capacity of liquid acetonitrile in the range 253–353 K can be calculated from

$$C_p = 1.2838 + 0.0004369T + 5.3125 \times 10^{-6}T^2$$

where  $C_p$  is the heat capacity in  $\text{J g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. The IR spectrum of liquid acetonitrile is shown in Figure 2.



**Figure 2:** IR spectrum of liquid acetonitrile liquid. Reproduced and modified with permission from [32].

### 2.1.3 Chemical Properties of Acetonitrile

All cyanides are poisonous. Thus, the OSHA PEL TWA of methyl cyanide is 40 ppm and the IDLH is 500 ppm. The LC50 in rabbits is 2828 ppm.

Using standard textbook methods for synthesizing more energetic materials, attempts were made to synthesize the energetic acetonitrile derivatives nitroacetonitrile  $\text{O}_2\text{N}-\text{CH}_2-\text{CN}$  (mononitroacetonitrile, nitrocyanomethane) and azidoacetonitrile  $\text{N}_3-\text{CH}_2-\text{CN}$ , but both compounds are detonable and quite sensitive to shock. Nitroacetonitrile and dinitroacetonitrile form salts with alkali metal hydroxides and ammonium hydroxide.

### 2.1.4 Rocket Fuel Blends Containing Acetonitrile

Acetonitrile mixed with UDMH was an essential fuel component in the REDSTONE rocket that launched the first US satellite. One fuel mixture used at that time consisted of 50% UDMH, 39% diethylene triamine, and 10% acetonitrile. A mixed amine fuel, MAF-1, was composed of 50.5% UDMH, 40.5% diethylene triamine (DETA), and 9.0% acetonitrile. MAF-5 consisted of 29.5% UDMH, 50.5% diethylene triamine (DETA), and 20.0% acetonitrile.

When an equimolar quantity of acetonitrile was mixed with anhydrous hydrazine, a drop in temperature of about  $10^\circ\text{C}$  occurred, indicating endothermic mixing [33]. However, this solution showed liquid phase separation at  $266.6 \text{ K}$  ( $-6.5^\circ\text{C}$ ). Methyl alcohol was added to increase the mutual miscibility of the two liquids. An equimolar mixture of the three components froze at  $214.6 \text{ K}$  ( $-58.5^\circ\text{C}$ ).

## 2.2 Propionitrile

Propionitrile, also known as ethyl cyanide, cyanoethane, propanenitrile,  $\text{C}_2\text{H}_5\text{CN}$ , CAS RN [107-12-0], has physical properties similar to acetonitrile and could be used for the same purposes. Properties of propionitrile are summarized in Table 6.

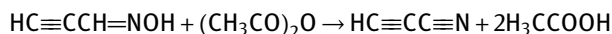
**Table 6:** Physical properties of propionitrile

| Property                                | SI units                                  | Other units                                       | References |
|-----------------------------------------|-------------------------------------------|---------------------------------------------------|------------|
| Molecular mass                          | 55.0785 g/mol                             | 18.156 mol/kg                                     | [10]       |
| Freezing point                          | $180 \pm 7 \text{ K}$                     | $-93 \pm 7 ^\circ\text{C}$                        |            |
| Boiling point                           | 370 K                                     | $97 ^\circ\text{C}$                               |            |
| Triple point                            | 180.37 K                                  | $-92.78 ^\circ\text{C}$                           |            |
| Critical temperature                    | 561.3 K                                   | $288.2 ^\circ\text{C}$                            |            |
| Critical pressure                       | 42.60 bar                                 | 42.04 atm                                         |            |
| Density, at 293 K                       | —                                         | $0.772 \text{ g/cm}^3$                            | [27]       |
| Vapor pressure, at 295 K                | 5.33 kPa                                  | 40 mm Hg                                          |            |
| Index of refraction ( $n_D^{20}$ )      | 1.3655                                    | —                                                 | [27]       |
| Enthalpy of formation, liquid, at 298 K | +15.5 kJ/mol                              | +3.70 kcal/mol                                    | [10]       |
| Enthalpy of formation, vapor, at 298 K  | +51.46 kJ/mol                             | +12.3 kcal/mol                                    |            |
| Heat of vaporization at 298 K           | 36.116 kJ/mol                             | 8.63 kcal/mol                                     | [10]       |
| Heat of fusion at 180.4 K               | 5.03 kJ/mol                               | 1.20 kcal/mol                                     |            |
| Heat of combustion, liquid              | $1948.3 \pm 0.54 \text{ kJ/mol}$          | 465.6 kcal/mol                                    |            |
| Heat capacity, liquid, at 298 K         | $105.3 \text{ J mol}^{-1} \text{ K}^{-1}$ | $25.17 \text{ kcal mol}^{-1} ^\circ\text{C}^{-1}$ | [27]       |

## 2.3 Cyanoacetylene

Cyanoacetylene, also known as ethynylcyanide,  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ ,  $\text{C}_3\text{H}_1\text{N}_1$ , CAS RN [68010-34-4],  $M = 51.0467 \text{ g/mol}$ , is a very energetic compound that burns in air or oxygen with a very hot flame. Cyanoacetylene has been detected in interstellar gas. It may even be present in the hydrocarbon-rich atmosphere of Titan.

Cyanoacetylene boils at 314–316 K (41–43 °C) and can be made by dehydration of propargyl aldehyde oxime with acetic anhydride [34–36]:



After examining the IR and Raman spectra of cyanoacetylene, band assignments were made for eight of the nine fundamental frequencies that explained the observed combination tones very satisfactorily [37]. All features of the spectra are compatible with  $D_{\infty h}$  symmetry, in particular the IR band contours, the lack of coincidences between IR and Raman frequencies, and the operation of selection rules for the combination tones.

The IR spectra of gaseous, liquid, and solid cyanoacetylene have been observed [38] in the region from 450 to 3400  $\text{cm}^{-1}$ . Five of the seven fundamental vibrational frequencies expected for cyanoacetylene based on a linear structure have been assigned, and the remaining frequency has been estimated from the observed combination bands. Based on these data, a force constant calculation was carried out using a simple valence potential function.

IR band assignments for a total of 28 frequencies – the complete set – were made with improved confidence by comparing the spectrum of the normal hydrogen-containing cyanoacetylene with that of its deuterated isotopomer [39].

Crystalline cyanoacetylene is monoclinic, with unit cell parameters of  $a = 6.96 \text{ \AA}$ ,  $b = 6.90 \text{ \AA}$ ,  $c = 3.84 \text{ \AA}$ ,  $\beta = 110.5^\circ$  [40]. The probable space group is  $P2_1/m$ , with two molecules per unit cell. Cyanoacetylene molecules are joined together by  $\text{CH}\cdots\text{N}$  hydrogen bonds into parallel, approximately linear, infinite chains that are nearly close packed. The bond lengths are:  $\text{C}\equiv\text{N}$  1.14  $\text{\AA}$ ,  $\text{C}-\text{C}$  1.38  $\text{\AA}$ ,  $\text{C}\equiv\text{C}$  1.18  $\text{\AA}$ , and  $\text{C}-\text{H}$  0.9  $\text{\AA}$ . The molecules are linear within experimental error. The enthalpy of formation of cyanoacetylene is +529 kJ/mol (+126.5 kcal/mol) [41]. For comparison, the enthalpy of formation of dicyanodiacetylene is +751 kJ/mol (+179.4 kcal/mol) (estimated).

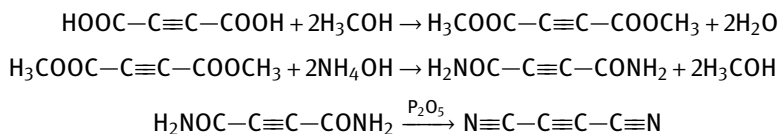
## 2.4 Dicyanoacetylene

Cyanogen compounds with more than two  $\text{C}\equiv\text{N}$  or  $\text{C}\equiv\text{C}$  triple bonds have even higher energy contents than cyanogen  $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$  itself. Higher energy is achieved by inserting one or two acetylene  $\text{C}\equiv\text{C}$  linkages between the terminal  $-\text{C}\equiv\text{N}$  groups. The first compound of this kind to be synthesized was dicyanoacetylene, also known as acetylene dicarbonic acid dinitrile, 2-butyne dinitrile, 1,2-dicyanoacetylene, dicyanoethyne, carbon subnitride,  $\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ , CAS RN [1071-98-3],  $M = 76.0562 \text{ g/mol}$ . This compound is a solid at cool room temperature but melts at 293.5–294 K (20.5–21  $^\circ\text{C}$ ) to give a clear, colorless liquid and boils at 349 K at 100.4 kPa (76  $^\circ\text{C}$  at 753 mmHg) [42]. It readily sublimates at room temperature but gradually decomposes and turns brown during storage at room temperature. The molten compound has a density of 0.9703  $\text{g/cm}^3$  at 298 K (25  $^\circ\text{C}$ ). The heat of combustion is 2160 kJ/mol = 516 kcal/mol = 6790 cal/g. Early data for this compound included a standard enthalpy of formation  $\Delta H_f^{298}$  of the liquid of +493.7 kJ/mol = +118.0 kcal/mol [27] and an enthalpy of formation  $\Delta H_f^{298}$  of the vapor of +627 kJ/mol (149.81 kcal/mol). NIST-Chase [43] gives an enthalpy of formation of the vapor of +533.46 kJ/mol (+127.5 kcal/mol), and NIST-Armstrong [44] gives the enthalpy of formation of the liquid as +500.4 kJ/mol (+119.6 kcal/mol). This compound can instantly explode, forming just carbon soot and nitrogen. During its combustion with oxygen in a calorimeter bomb, some of it decomposed instead of burned, and the heat of combustion had to be corrected for the amount of unburnt carbon found. The corrected heat of combustion of the liquid is 2074 kJ/mol (495.7 kcal/mol), and the

heat of formation derived from this number is +495.5 kcal/mol (+118.4 kcal/mol) [44, 45]. See also [46–48].

It is interesting to note that methyl cyanide  $\text{H}_3\text{CCN}$ , cyanoacetylene  $\text{HC}_3\text{N}$ , dicyanoacetylene  $\text{C}_4\text{N}_2$ , cyanodiacetylene  $\text{HC}_5\text{N}$ , cyanotriacetylene  $\text{HC}_7\text{N}$ , and cyanotetraacetylene  $\text{HC}_9\text{N}$  have been detected in interstellar space by radioastronomy [49]. They may be precursors to amino acids and constituents of tholins.

Dicyanoacetylene can be prepared by the pyrolysis of 1,2-dichloro-1,2-dicyanoethylene [50]. One synthetic method for dicyanoacetylene starts with acetylene and proceeds via propiolic acid, propiolic acid amide, and dehydration [51]. Forming the amide in liquid ammonia at low temperature and suspending  $\text{P}_2\text{O}_5$  powder in xylene for dehydration improves the overall yield.



The infrared and Raman spectra of dicyanoacetylene were analyzed [52]. Assignments were given for eight of the nine fundamental frequencies that explained the observed combination tones very satisfactorily. All features of the spectra were compatible with  $D_{\infty h}$  symmetry, in particular the IR band contours, the lack of coincidences between IR and Raman frequencies, and the operation of selection rules for the combination tones.

In a continuation of that work, the IR spectrum of dicyanoacetylene was extended down to  $320\text{ cm}^{-1}$  and one more combination tone was located [53]. When a larger sample and a better instrument was used, 15 Raman lines were detected instead of the four reported earlier, allowing the vibrational assignments to be revised and extended. All but one of the fundamentals have been observed directly, and the one exception ( $107\text{ cm}^{-1}$ ) is well established from combination tones. The totally symmetric fundamentals have been reassigned to 2290, 2119, and  $692\text{ cm}^{-1}$ .

Near to 278 K ( $5^\circ\text{C}$ ), dicyanoacetylene forms monoclinic crystals belonging to the space group  $C_{2h}-P2_1a$  [54]. The unit cell dimensions are  $a = 8.93\text{ \AA}$ ,  $b = 6.04\text{ \AA}$ ,  $c = 3.86\text{ \AA}$ ,  $\beta = 99^\circ 20'$ . The two molecules per unit cell are linear and have a center of symmetry. Bond lengths within the molecule are:  $\text{C}\equiv\text{N}1.14\text{ \AA}$ ,  $\text{C}-\text{C}1.37\text{ \AA}$ , and  $\text{C}\equiv\text{C}1.19\text{ \AA}$ .

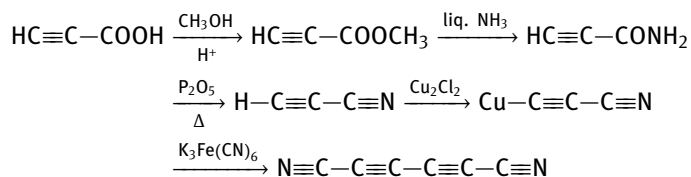
## 2.5 Dicyanodiacetylene

An even more energetic compound is obtained by inserting not just one, but two acetylene groups between the terminal cyanogen groups:  $\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$ . The compound thus obtained is called dicyanodiacetylene, butadiyne dicarbonic acid dinitrile, hexadiynedinitrile, hexacarbon dinitride, CAS RN [16419-78-6],  $M = 100.0776\text{ g/mol}$ .

Dicyanodiacetylene was first synthesized by the action of aqueous potassium ferricyanide on the cuprous derivative of propiolonitrile (cyanoacetylene). With newer methods, yields as high as 36% have been obtained [55]. The product was characterized as dicyanodiacetylene ( $C_6N_2$ ) by elementary analysis and molecular weight determinations and by conversion on hydrogenation to hexamethylenediamine. Dicyanodiacetylene is an unstable, volatile, white solid with a marked irritating odor. It can be obtained by sublimation in a stream of carbon dioxide gas as fine, elongated crystals that melt at 337.6–338.6 K (64.5–65.5 °C). Dicyanodiacetylene gradually turns brown at room temperature but may be stored at 273 K (0 °C) without decomposition. This discoloration is more rapid in the presence of water.

This compound has a very high heat of combustion and gives very high flame temperatures when burned in oxygen or in air [46, 56]. At 335 K = 62 °C it has a vapor pressure of 10.66 kPa = 80 mm Hg. The extrapolated boiling point would be 427 K = 154 °C, but it is unstable at that temperature and needs to be sublimed under vacuum for purification. The heat of vaporization is 30.25 kJ/mol = 7.23 kcal/mol. The heat of sublimation is 35.9 kJ/mol at 295–335 K.

Dicyanodiacetylene,  $N\equiv C-C\equiv C-C\equiv C-C\equiv N$ , was prepared by the sequence of reactions



and the IR spectrum of dicyanodiacetylene was measured from 35 to 4000  $cm^{-1}$  in the vapor and solution phases [57]. Raman spectra with polarizations were obtained for solutions.  $D_{\infty h}$  symmetry is fully satisfactory for assigning IR absorption and Raman fluorescence lines, and most fundamentals have been assigned. All other candidate symmetries present serious problems. The three polarized Raman lines at 2235, 2183, and 1287.5  $cm^{-1}$  are surely  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ , respectively, but there was no polarized line for  $\nu_4$ . The experimental evidence clearly supported the expected linear symmetrical structure. As of 1967, dicyanodiacetylene was believed to be the longest confirmed linear molecule known.

## 2.6 Malonic Acid Dinitrile

Malonic acid dinitrile, also known as dicyanomethane, methylene cyanide, malononitrile,  $H_2C(CN)_2$ ,  $C_3H_2N_2$ , CAS RN [109-77-3],  $M = 66.0614$  g/mol, is a useful intermediate in the synthesis of other energetic chemicals. It is not anticipated that it would be used as a rocket fuel as such.



Malonic acid dinitrile can be prepared by reacting acetonitrile and cyanogen chloride in the gaseous phase at temperatures between 1053 and 1473 K (780–1200 °C) [58]. Yields exceeding 80% can be obtained when the reactants flow through the reactor in a condition exceeding laminar flow and extending into turbulent flow, with molar ratios of acetonitrile to cyanogen chloride of 4:1 and with residence times at reaction temperatures of less than 5 s. Preheating the acetonitrile to 873–923 K (600–650 °C) considerably increased the space–time yield (capacity) of the reactor, and use of an excess of acetonitrile aided in the removal of HCl [59].

Malonic acid dinitrile melts at 305 K (32 °C) and boils at 493 K (220 °C) at atmospheric pressure or at 382 K at a reduced pressure of 0.027 bar.

The heat of formation of malonic acid dinitrile vapor is +265.7 kJ/mol (+63.5 kcal/mol) [60]. Other sources give the heat of formation of solid malonic acid dinitrile as  $+187.9 \pm 0.2$  kJ/mol. Dicyanomethane,  $\text{CH}_2(\text{CN})_2$ , has an active proton that acts as an acid ( $\text{p}K_{\text{a}} = 11.2$ ) and can form salts with strong bases. Dicyanomethanide salts of heterocyclic amines such as triazole or tetrazole are high-nitrogen compounds that are useful as additives for gas generants. Some have enthalpies of formation as high as 1579 kJ/mol [61].

Dicyanomethanide salts of heterocyclic amines such as imidazole have very low melting points and qualify as ionic liquids. These ionic liquids are particularly useful as hypergolic ionic liquids with very low vapor pressures, potential replacements for MMH (see the chapter “Ionic Liquids” in *Encyclopedia of Liquid Fuels*). Nitrodicyanomethanide and dinitrocyanomethanide anions can be used in similar applications.

## 2.7 Other Nitrile Compounds

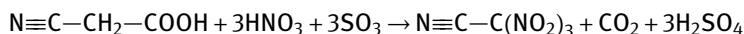
### 2.7.1 Dinitroacetonitrile

Dinitroacetonitrile,  $(\text{O}_2\text{N})_2\text{CHC}\equiv\text{N}$ ,  $\text{C}_2\text{H}_1\text{N}_3\text{O}_4$ , can be prepared by hydrolysis of dinitrocyanoacetic acid esters or by reduction of trinitroacetonitrile with hydrogen sulfide or bromide ion. The hydrogen atom is acidic, and it forms salts with a variety of bases. The product is most stable if crystallized with four molecules of water as a hydrate that melts at 311–313 K (38–40 °C). Dinitroacetonitrile has never been isolated in a pure, anhydrous state. Instead of isolating the pure compound, it is best isolated in the form of its salts with alkali metals or organic amines [62, 63]. The potassium salt of dinitroacetonitrile is sparingly soluble in most solvents and best suited for isolation, and most other salts can be prepared from the sodium salt. Dinitroacetonitrile can be used for the synthesis of dinitrocyanoethanol by reaction with formaldehyde [64], dinitroacetamide [65], and esters of dinitrocyanoacetic acid [66].

### 2.7.2 Trinitroacetoneitrile

Trinitroacetoneitrile, also known as trinitrocyanomethane, cyanotrinitromethane,  $(\text{O}_2\text{N})_3\text{CC}\equiv\text{N}$ ,  $\text{C}_2\text{N}_4\text{O}_6$ ,  $M = 176.0446 \text{ g/mol}$ , CAS RN [630-72-8], forms yellow volatile crystals with a pungent odor that melt at 314.6 K (41.5 °C) and explode on rapid heating to 493 K (220 °C). It is a very hazardous substance and its synthesis would be avoided if alternatives were available. It is soluble in ether but reacts with water or alcohols. In the Trauzl test, the lead block expansion is 182% of that of picric acid. The drop weight sensitivity is 15 cm or less with a 2 kg weight.

Trinitroacetoneitrile can be made by complete nitration of cyanoacetic acid in carbon tetrachloride as the solvent:



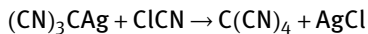
When the molar ratio of nitric acid to cyanoacetic acid was reduced to 2:1 or 1:1, and with less sulfuric acid, 3,4-dicyanofuroxan was obtained as the major by-product.

The heat of combustion of trinitroacetoneitrile is  $961 \pm 1 \text{ kJ/mol}$ , and its enthalpy of formation  $\Delta H_f^\circ \text{ solid} = +174 \pm 1 \text{ kJ/mol}$  [67].

### 2.7.3 Tetracyanomethane

Tetracyanomethane, also known as methanetetracarbonitrile,  $\text{C}(\text{C}\equiv\text{N})_4$ ,  $\text{C}_5\text{N}_4$ , CAS RN [24331-09-7],  $M = 116.0803 \text{ g/mol}$ , is a pernitride containing only carbon and nitrogen [48, 68].

The silver salt of tricyanomethane (*cyanofom*) reacts with cyanogen chloride to form tetracyanomethane and AgCl [69].



Tetracyanomethane is crystalline, sublimes at 333 K (60 °C) under vacuum, begins to decompose at 433 K (160 °C), and is soluble in polar solvents. Tetracyanomethane is stable as long as moisture is excluded. If a solution is allowed to sit in moist air, it discolors to yellow and forms an insoluble orange residue (a polymer).

There is a contradiction in the literature about the crystal structure of tetracyanomethane. One source described the crystals as trigonal, space group  $R3c$ . Tetracyanomethane,  $\text{C}(\text{CN})_4$ , is monoclinic and crystallizes in space group  $Cc$  or  $C2/c$  with  $a = 9.361 \text{ \AA}$ ,  $b = 8.881 \text{ \AA}$ ,  $c = 6.241 \text{ \AA}$ ,  $\beta = 91.30^\circ$ , and with four molecules per unit cell [70]. No crystallographic phase transitions were observed at standard pressure between 123 K (−150 °C) and the decomposition temperature of 433 K (+160 °C). An analysis of the data available for several methylcyanomethane compounds indicated that dipole–dipole interactions are more important in these compounds than hydrogen-bond formation.

Other publications described the crystal structure of tetracyanomethane as trigonal with hexagonal axes  $a = 9.062(2) \text{ \AA}$  and  $c = 11.625(3) \text{ \AA}$ ,  $Z = 6$ , space group  $R3c$  [71]. The molecule has full tetrahedral symmetry within experimental error, and its aver-

age bond lengths are: C—C 1.481, corrected to 1.488 Å; C≡N 1.147, corrected to 1.168 Å. The structure is a trigonal distortion of the cubic SiF<sub>4</sub> structure. One nitrogen atom points directly at the central carbon atom of an adjacent molecule, with a N...C (in CN) distance of 3.03 Å. The remaining three (equivalent) nitrogen atoms point approximately at the central carbon atoms of three adjacent molecules, with N...C (in CN) distances of 3.00, 3.10, and 3.19 Å. These short distances are regarded as evidence of donor–receptor interactions. The Britton [71] and Rubin [70] papers contradict each other. This needs clarification.

Tetracyanomethane was burned in a rotating-bomb combustion calorimeter in order to determine its thermodynamic properties. The standard enthalpy of combustion  $\Delta H_c(c)$  was  $2579 \pm 1.7 \text{ kJ/mol} = 616.43 \pm 0.4 \text{ kcal}_{th}/\text{mol}$ , which yields a standard enthalpy of formation  $\Delta H_f^\circ(c)$  of  $+611.6 \pm 1.8 \text{ kJ/mol} = +146.18 \pm 0.43 \text{ kcal/mol}$  [72]. The enthalpy of formation of tetracyanomethane vapor is  $672.8 \pm 9.2 \text{ kJ/mol}$ . The mean bond dissociation energy is  $\langle D \rangle(\text{C}—\text{CN}) = 469 \text{ kJ/mol} = 112 \text{ kcal/mol}$ .

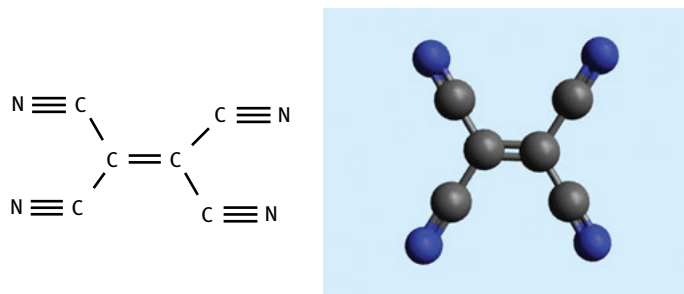
The IR spectrum of tetracyanomethane dissolved in acetonitrile solution was recorded and a full set of fundamental frequencies were assigned to vibrations and oscillations in the molecule [73]. A normal coordinate analysis was then carried out and the values of the calculated force constants were compared with those of related molecules. Some thermodynamic functions were computed from the spectroscopic data.

#### 2.7.4 Tetracyanoethylene

Tetracyanoethylene, also known as tetracyanoethene, ethenetetracarbonitrile,  $(\text{CN})_2\text{C}=\text{C}(\text{CN})_2$ , C<sub>6</sub>N<sub>4</sub>, CAS RN [670-54-2],  $M = 128.0910 \text{ g/mol}$ , is a dienophile and forms  $\pi$  complexes and charge-transfer complexes with many aromatic compounds. It is the strongest  $\pi$  acid in the inventory. Heats of reaction for the formation of complexes between tetracyanoethylene and methylbenzenes were found to range from  $-9.6 \text{ kJ/mol}$  ( $-2.3 \text{ kcal/mol}$ ) for benzene to  $-29.3 \text{ kJ/mol}$  ( $-7.0 \text{ kcal/mol}$ ) for pentamethylbenzene. Tetracyanoethylene is not likely to be used as a rocket propellant, but it has been tested for some pyrotechnic formulations (IR decoy flares).

Tetracyanoethylene has been synthesized from malononitrile by four different methods: by reaction with sulfur monochloride, by chlorination/dehydrochlorination of malononitrile in the vapor phase, by condensation with malononitrile followed by pyrolysis of the product, and by debromination of dibromomalononitrile with copper powder in boiling benzene.

Tetracyanoethylene is a colorless, crystalline solid that sublimes readily at temperatures above 393 K (120 °C) at atmospheric pressure and melts at 471–473 K (198–200 °C) in a sealed capillary. The IR spectrum of tetracyanoethylene has a divided band in the nitrile region that is characteristic of conjugated, unsaturated nitriles. The heats of combustion and sublimation of tetracyanoethylene are 3021 and 78 kJ/mol (722 and 18.65 kcal/mol), respectively. The enthalpy of formation of solid tetracyanoethylene is  $+633 \pm 2 \text{ kJ/mol}$ . Given this high enthalpy of formation, it should make



**Figure 3:** Molecular structure of tetracyanoethylene.

a good rocket propellant ingredient, but it lacks the hydrogen. The molecular structure of tetracyanoethylene is illustrated in Figure 3.

Additions to the double bond of tetracyanoethylene occur rapidly, even at room temperature, with several types of reagents, including dienes, aromatics, ketones, and hydrogen. Tetracyanoethylene is an unusually active dienophile; its reaction with butadiene and other 1,3-dienes gives tetracyanocyclohexenes [74].

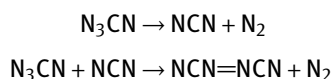
The heats of combustion of several cyanocarbons were measured, as well as their heats of vaporization (from vapor pressures), and heats of solution were determined in order to calculate the heats of formation [75]. The cyano-olefins tricyanoethylene and tetracyanoethylene have negative stabilization energies, indicating that electrostatic repulsion between the highly polar cyano groups predominates over electronic delocalization stabilization ( $-62.8$  and  $-113$  kJ/mol =  $-15$  and  $-27$  kcal/mol, respectively).

### 2.7.5 Hexacyanoethane

Hexacyanoethane is a colorless solid that decomposes in a sealed tube above 403 K (130 °C). Its most striking property is its instability, decomposing spontaneously at room temperature to tetracyanoethylene and polymeric materials. It can be sublimed at 348 K and 0.67 kPa (75 °C at 2 mm Hg), but some decomposition to tetracyanoethylene and, presumably, cyanogen occurs during sublimation. It has been stored at 195 K ( $-78$  °C) for long periods without change.

### 2.7.6 Azodicarbonitrile

Azodicarbonitrile,  $\text{N}\equiv\text{C}-\text{N}=\text{N}-\text{C}\equiv\text{N}$ ,  $\text{C}_2\text{N}_4$ , has been synthesized in good yield by the pyrolysis of cyanogen azide at 473 K (200 °C) [76, 77]. The reaction in the vapor phase is believed to involve cyanonitrile ( $[\text{N}=\text{C}=\text{N}]$ ) as an intermediate:



Azodicarbonitrile is a crystalline, orange-red, volatile solid with a melting point of 308.6–310.1 K (35.5–37 °C). Vapor pressure measurements and gas liquid chromatography indicated that both *cis* and *trans* isomers are present; however, these have not been separated [78]. The *trans* isomer is energetically favored by 83 kJ/mol (20 kcal/mol). Vapor phase decomposition of azodicarbonitrile at 373 K (100 °C) is slow. However, crystalline azodicarbonitrile detonates when mechanically shocked or heated in a closed vessel. Because of the hazardous nature of pure cyanogen azide, azodicarbonitrile has been synthesized only on a limited scale. Azodicarbonitrile is soluble without reaction in benzene, acetonitrile, ethyl acetate, 1,1,2-trichloro-1,2,2-trifluoroethane, or nitromethane. It is decomposed by methanol, water, or ether. The reaction of azodicarbonitrile with 1,3-dienes causes the red color to disappear, and can be used as an analytical reagent for conjugated double bonds.

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# Cycloaliphatic Hydrocarbons

## Introduction

*Encyclopedia of Liquid Fuels* contains eight chapters dealing with hydrocarbon fuels. The topic of hydrocarbon fuels had to be subdivided into several smaller chapters, which were easier to arrange in alphabetical order into five sub-volumes of equal size. The titles of the eight hydrocarbon chapters are “Alkanes,” “Alkenes and Alkynes,” “Aromatic Hydrocarbons,” “Cycloaliphatic Hydrocarbons,” “Hydrocarbons,” “Jet Fuels,” “Kerosenes,” and “Ramjet Fuels.”

## 1 Cycloaliphatic Hydrocarbons

Cycloaliphatic (“hydroaromatic,” “alicyclic”) hydrocarbons may have certain advantages over open-chain hydrocarbons. Alicyclic compounds are both aliphatic and cyclic. They contain one or more all-carbon rings that may be either saturated or unsaturated, but they do not have aromatic character and do not contain a heteroatom. Alicyclic compounds may have one or more aliphatic side chains attached. Cycloalkanes are named by adding the prefix “cyclo” to their normal alkane counterparts of the same carbon count: cyclopropane, cyclobutane, cyclopentane, cyclohexane, etc. The larger cycloalkanes, with more than 20 carbon atoms, are also called cycloparaffins. The simplest alicyclic compounds are the monocyclic cycloalkanes: cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, and cyclooctane. Cycloalkanes are also called naphthenes but should not be confused with naphthalene, which is an aromatic hydrocarbon.

Cycloaliphatic hydrocarbons occur naturally as constituents of petroleum and crude oil and in plant oils (terpenes). The percentage of cycloaliphatic hydrocarbons in these fossil fuels varies significantly from source to source. Oil pumped in the Caucasus region was one of the first petroleums to be identified as having a high content of cycloaliphatic hydrocarbons compared to oil pumped in other regions of the world. The most common cycloaliphatic hydrocarbon is cyclohexane, which is easily dehydrogenated to benzene or, in a reversal of this reaction, easily made from benzene by hydrogenation. Six-ringed cycloaliphatic hydrocarbons are thermally more stable than rings containing fewer or more than six carbon atoms in the ring. Other cycloaliphatic hydrocarbons are contained in turpentine distilled from the resins of certain coniferous trees, giving the name “terpenes” to this group of hydrocarbons.

In addition to occurring naturally, certain cycloaliphatic compounds with increased internal energy due to strained ring (three-ring and four-ring) structures are synthesized in the laboratory, and some are produced industrially, but they do not occur in nature in the unsubstituted hydrocarbon form. Many of these hydrocarbons

combine more than one ring in the molecule, and many of these are used as fuels in air-breathing cruise missiles.

The potential of increasing the rocket performance of hydrocarbon fuels by using three- and four-ringed compounds was recognized relatively early in the sequence of historical events leading to today's state of rocket technology [1].

If one or more of the carbon atoms in an alicyclic compound is replaced by B, N, O, S, Si, or another heteroatom, we arrive at the vastly complex group of heterocyclic compounds. Some of these are used as rocket fuels, and others are or have been used as monopropellants, e.g., ethylene oxide. These fuels are discussed in the chapters "Ethers" and "Heterocyclic Amines" of this volume.

There are numerous literature summaries on the chemistry and applications of cycloaliphatic hydrocarbons [2–6]. In a review of fuels for air-breathing supersonic propulsion, cycloaliphatic hydrocarbons were identified to offer the best compromise for future supersonic propulsion [7]. Multi-cyclic, strained, and caged fuels have higher density and higher energy content than open-chain hydrocarbons and must be synthesized from other precursors [8].

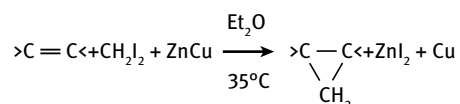
## 2 Cyclopropane

Cyclopropane, trimethylene,  $C_3H_6$ , CAS RN [75-19-4], is a strained ring molecule, the lowest member of the cycloaliphatic hydrocarbon family of compounds. It has a high heat of combustion but is difficult to synthesize in quantity and therefore not used as a rocket propellant. However, hydrocarbons containing cyclopropyl rings as attachments have been used as rocket propellants (Syntin, see Section 2.3). This is why we include cyclopropane in this chapter. See also [9, 10].

### 2.1 Preparation of Cyclopropane

Cyclopropane was first prepared by dehalogenating 1,3-dibromopropane with sodium metal. Later the sodium metal was replaced by zinc metal in moist ethanol. The reaction also works with 1-bromo-3-chloropropane or 1,3-dichloropropane.

The conversion of ethene with methylene iodide and a brass alloy in ether gave a yield of 29% cyclopropane [11–14]:



The reaction of olefins with dialkyl zinc and methylene iodide gives cyclopropane derivatives [15]. Another source of methylene carbenes is the photolysis of dia-

zomethane. The light-induced reaction of diazomethane with olefins gives a mixture of cyclopropane derivatives.

## 2.2 Physical Properties of Cyclopropane

The physical properties of cyclopropane are summarized in Table 1.

**Table 1:** Physical properties of cyclopropane.

| Property                            | SI units                                  | Other units                                  | References |
|-------------------------------------|-------------------------------------------|----------------------------------------------|------------|
| Molecular mass                      | 42.0797 g/mol                             | 23.764 mol/kg                                |            |
| Freezing point                      | 145.54 K                                  | −127.61 °C                                   | [16]       |
| Boiling point                       | 240.3 K                                   | −32.85 °C                                    |            |
| Density at normal boiling point     | 0.68 g/cm <sup>3</sup>                    | 0.68 g/cm <sup>3</sup>                       |            |
| Standard enthalpy of formation, gas | +53.3 kJ/mol                              | +12.74 kcal/mol                              | [17, 18]   |
| Heat capacity, liquid at 150 K      | 75.81 J mol <sup>−1</sup> K <sup>−1</sup> | 18.12 cal mol <sup>−1</sup> °C <sup>−1</sup> | [16]       |
| Heat capacity, liquid at 240 K      | 81.34 J mol <sup>−1</sup> K <sup>−1</sup> | 19.44 cal mol <sup>−1</sup> °C <sup>−1</sup> |            |
| Enthalpy of fusion                  | 5443 J/mol                                | 1301 cal/mol                                 |            |
| Enthalpy of vaporization at 240 K   | 20.054 kJ/mol                             | 4.793 ± 3 kcal/mol                           |            |
| Entropy, gas, at 298 K              | 237.8 J mol <sup>−1</sup> K <sup>−1</sup> | 56.84 cal mol <sup>−1</sup> °C <sup>−1</sup> |            |
| Critical temperature                | 398.0 ± 0.3 K                             | 124.9 ± 0.3 °C                               | [17]       |
| Critical pressure                   | 55.4 ± 0.5 bar                            | 54.7 atm                                     |            |
| Critical specific volume            | 0.162 L/mol                               | —                                            |            |
| Critical density                    | 6.15 ± 0.05 mol/L                         | —                                            |            |

The vapor pressure of cyclopropane in the range between 183 and 241 K can be calculated from

$$\log P = 9.03877 - 1348.2/T - 0.00823 T + 7.45 \times 10^{-6} T^2$$

where  $P$  is the vapor pressure in cmHg and  $T$  is the temperature in kelvin [16]. The same data in the form of an Antoine equation is

$$\log P = 4.05015 - [870.393/(T - 25.063)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. The Wagner equation for the vapor pressure of cyclopropane is

$$\ln\left(\frac{P}{P_c}\right) = (A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6) / \left(\frac{T}{T_c}\right)$$

where  $T$  is temperature in K,  $\tau = 1 - (T/T_c)$  with the following constants  $A = -6.60088$ ,  $B = 1.27594$ ,  $C = -1.78063$ , and  $D = -2.07475$  [19]. From the same source, the density

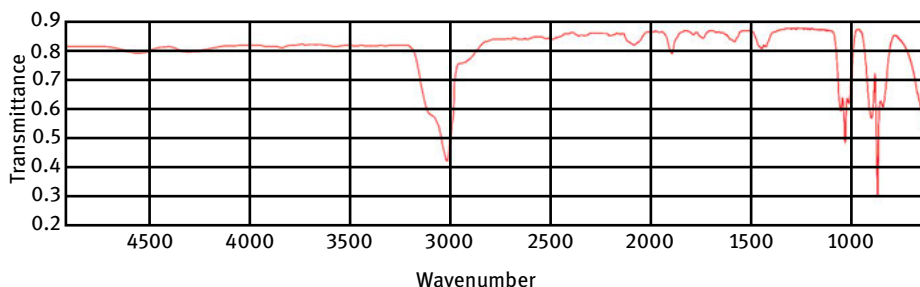
of cyclopropane for  $T/T_c = 0.38$  to 1.0 can be expressed by the following generalized Rackett equation

$$\ln(\rho') = A + B\left(\frac{1-T}{C}\right)^D$$

where  $\rho'$  is the density in mol/L,  $T$  is the temperature in kelvin, and the constants are as follows:  $A = 1.42272$ ,  $B = -1.63206$ ,  $C = 399.266$ , and  $D = 0.187411$ .

### 2.2.1 Optical Properties of Cyclopropane

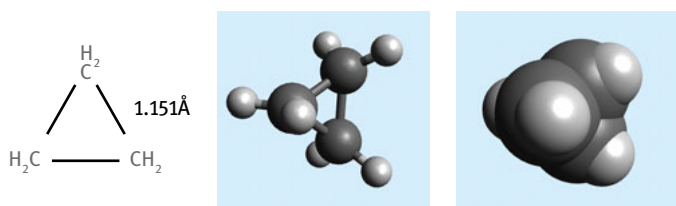
The infrared (IR) spectrum of cyclopropane has absorption bands at 3125, 3030, 1031 to 1020  $\text{cm}^{-1}$ , and between 909 and 833  $\text{cm}^{-1}$  (3.2, 3.3, 9.7 to 9.8  $\mu\text{m}$ , and between 11 and 12  $\mu\text{m}$ ) (Figure 1).



**Figure 1:** Infrared spectrum of cyclopropane. (Reproduced and modified with permission from [20])

### 2.2.2 Molecular Structure of Cyclopropane

The tetrahedron bond angle of the stress-free carbon atom, as in methane ( $109.4^\circ$ ), has been forced into a strained ring with a C—C—C bond angle of  $104^\circ$ , and the bonds (electron clouds) are not straight as shown in Figure 2 but rather are banana-shaped. The distance of the carbon atoms is 1.151 Å. The  $\angle\text{H—C—H}$  angle formed by the hydrogen atoms surrounding the carbon atoms is  $115.1^\circ$ . The length of the C—C bonds is shorter than in cyclohexane but still weaker than in cyclohexane.



**Figure 2:** Molecular structure of cyclopropane.

### 2.2.3 Thermodynamic Properties of Cyclopropane

Thermodynamic properties of cyclopropane are listed in Table 2.

**Table 2:** Thermodynamic properties of cyclopropane.

| Property                            | SI units                                  | Other units                                  | References |
|-------------------------------------|-------------------------------------------|----------------------------------------------|------------|
| Standard enthalpy of formation, gas | +53.3 kJ/mol                              | +12.74 kcal/mol                              | [17, 18]   |
| Heat capacity, liquid at 150 K      | 75.81 J mol <sup>-1</sup> K <sup>-1</sup> | 18.12 cal mol <sup>-1</sup> °C <sup>-1</sup> | [16]       |
| Heat capacity, liquid at 240 K      | 81.34 J mol <sup>-1</sup> K <sup>-1</sup> | 19.44 cal mol <sup>-1</sup> °C <sup>-1</sup> |            |
| Enthalpy of fusion                  | 5443 J/mol                                | 1301 cal/mol                                 |            |
| Enthalpy of vaporization at 240 K   | 20.054 kJ/mol                             | 4.793 ± 3 kcal/mol                           |            |
| Entropy, gas, at 298 K              | 237.8 J mol <sup>-1</sup> K <sup>-1</sup> | 56.84 cal mol <sup>-1</sup> °C <sup>-1</sup> |            |

Note: Molecular mass 42.0797 g/mol = 23.764 mol/kg

The enthalpy and entropy of cyclopropane were calculated from experimental pressure-volume-residual temperature data [21]. The heat capacity of the ideal gas cyclopropane in the range 291–458 K (525–825 °R) can be expressed by the following equation

$$c_p = 2.520225 + 9.055728 \times 10^{-3} T + 2.968219 \times 10^{-5} T^2 - 1.650501 \times 10^{-8} T^3$$

where  $c_p$  is the heat capacity in BTU lb<sup>-1</sup> °F<sup>-1</sup> and  $T$  is the temperature in °R.

## 2.3 Chemical Properties of Cyclopropane

The chemical properties of cyclopropane are quite different from those of the other cycloalkanes. Cyclopropane is thermally less stable and more reactive, very often resulting in ring opening.

### 2.4 Toxicity of Cyclopropane

Cyclopropane (in mixture with 15–30 vol.-% oxygen) had been used for anesthesia, but this application was quickly abandoned because of the explosivity of the mixture.

### 2.5 Flammability of Cyclopropane

The flammable range of cyclopropane in air with upward propagation is from 2.4 vol.-% to 10.4 vol.-% C<sub>3</sub>H<sub>6</sub>. The autoignition temperature in air is 768 K (495 °C).

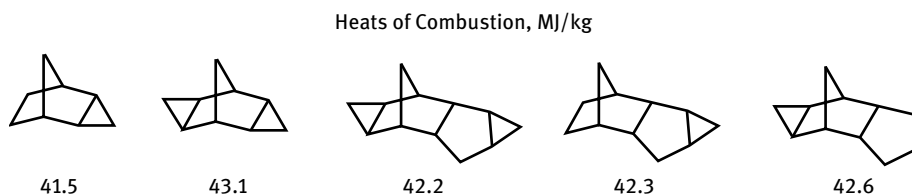
### 3 Cyclopropane Derivatives – Polycyclic Isocyclic Hydrocarbons

The chemistry of cyclopropane and compounds containing cyclopropyl groups is of particular interest to all rocket propellant chemists [22].

In a study to prepare and purify 19 hydrocarbon derivatives of cyclopropane and evaluate them as rocket or air-breathing engine fuels, 13 of these hydrocarbons were synthesized for the first time [23]. In addition to the hydrocarbons, six cyclopropylcarbinols, five alkyl cyclopropyl ketones, three cyclopropyl chlorides, and one cyclopropanedicarboxylate were prepared as intermediates for subsequent syntheses. The melting points, boiling points, refractive indices, densities, and, in some instances, heats of combustion of both the hydrocarbon and non-hydrocarbon derivatives of cyclopropane were determined, including the very sharp IR spectra of each of the 34 cyclopropane compounds. The IR absorption bands characteristic of the cyclopropyl ring were identified. Many of the cyclopropane derivatives have bands at  $3.23 \pm 0.02 \mu\text{m}$  and at  $3.33 \pm 0.02 \mu\text{m}$ . Nearly all the cyclopropane derivatives showed strong absorption between  $9.7$  and  $9.8 \mu\text{m}$  and between  $11$  and  $12 \mu\text{m}$ . Some observations were made on the contribution of the cyclopropyl ring to the molecular refractions of cyclopropane compounds. A total of 12 cyclopropylalkenes and five cyclopropylalkanes were prepared from methyl cyclopropyl ketone. Vinylcyclopropane had a melting point of  $164 \text{ K}$  ( $-109^\circ\text{C}$ ), a boiling point of  $313 \text{ K}$  ( $40^\circ\text{C}$ ), a density of  $0.72105 \text{ g/cm}^3$ , and a refractive index of  $n_D^{20} = 1.4138$ .

Cyclopropyl derivatives carrying an energetic substituent such as a nitrile group or a vinyl group, have been evaluated as fuels for air-breathing engines [24].

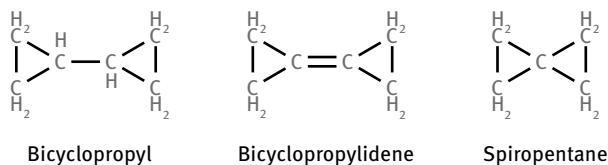
Cyclopropyl compounds synthesized by cyclopropanation have high density and high energy caused by internal ring tension, which gives the molecule a high enthalpy of formation. Three different methods for cyclopropanation, i.e., conversion of a ring-contained  $\text{C}=\text{C}$  double bond to an external cyclopropane ring, were used for adding one or two cyclopropane rings to norbornene, norbornadiene, or dicyclopentadiene [25]. The volumetric heat of combustion of several of these compounds was higher than that of RJ-4 or JP-10 (Figure 3). For comparison, the heat of combustion of JP-10 is  $42.1 \text{ MJ/kg}$ .



**Figure 3:** Heat of combustion of cyclopropane derivatives. (Based on data from [25].)

### 3.1 Bicyclopropyl and Spiropentane

Other energetic fuels of interest are cyclopropyl cyclopropane (“bicyclopropane,” “bicyclopropyl”) and di(cyclopropyl)methane. Strained ring hydrocarbons with two cyclopropane rings in the molecule can be formed by either connecting two cyclopropanes through an external C—C bond or by sharing a carbon atom.



Bicyclopropyl,  $C_6H_{10}$ , CAS RN [5685-46-1], has a molecular mass of 82.1436 g/mol, a melting point of 191 K ( $-82^\circ\text{C}$ ), a boiling point at 760 mm Hg of 349 K ( $76^\circ\text{C}$ ), a refractive index  $n_D^{20}$  of 1.4239, a density of  $0.7898\text{ g/cm}^3$ , an enthalpy of formation (liquid) of  $96.0 \pm 3.8\text{ kJ/mol}$ , and a net heat of combustion of  $3703\text{ kJ/mol}$  ( $885\text{ kcal/mol}$ ). Solid bicyclopropyl has a density of  $1.035\text{ g/cm}^3$  at 173 K [26]. The central C—C bond in bicyclopropyl is shorter than a typical aliphatic C—C bond, more like a single bond in a conjugated system.

Spiropentane,  $C_5H_8$ , CAS RN [157-40-4], has a freezing point of 168 K ( $-105^\circ\text{C}$ ), a boiling point at 760 mm Hg of 311.9 K ( $38.8^\circ\text{C}$ ), a density of  $0.7551\text{ g/cm}^3$ , a heat of fusion of  $6.43\text{ kJ/mol}$ , a heat of vaporization of  $27.7\text{ kJ/mol}$ , and a refractive index of  $n_D^{20} = 1.4122$  [27].

Bicyclopropylidene, made up from two cyclopropane rings linked by a C=C double bond, is a particularly strained derivative of cyclopropane. It undergoes a thermal rearrangement and dimerization [28, 29]. Bicyclopropylidene was tested in a 220-N (50-lb<sub>f</sub>) rocket engine with LOX as the oxidizer in a side-by-side test in comparison to RP-1 [30]. The density is 1.5% greater than that of RP-1, and the  $I_{sp}$  is approximately 2 to 4% better than that of RP-1. However, the volume benefit is negative. The boiling point of bicyclopropylidene is 374 K ( $101^\circ\text{C}$ ) at 101 kPa. The freezing point is 261 K ( $-12^\circ\text{C}$ ). The density is  $0.8454\text{ g/cm}^3$  at 293 K. The vapor pressure is 11.4 kPa at 298 K ( $85.9\text{ mm Hg}$  at  $25^\circ\text{C}$ ). The kinetic viscosity is  $0.808\text{ cSt}$  at 313 K ( $40^\circ\text{C}$ ). The flash point is  $266.7\text{ K}$  ( $-6.4^\circ\text{C}$ ). The standard enthalpy of formation is  $+264\text{ kJ/mol}$  ( $+63.1\text{ kcal/mol}$ ). The heat of combustion is  $44.4\text{ MJ/kg}$  ( $19113\text{ BTU/lb}$ ).

A laboratory-scale flow reactor was developed to subject small amounts (approximately 1 mL) of deoxygenated fuels to controlled conditions of temperature and residence-time-at-temperature at constant pressure (34 atm) in the liquid or supercritical phase [31]. The thermal stability of the parent material and the thermal fragmentation products of each fuel were measured. Some of the candidate materials tested (quadricyclane and bicyclopropylidene) showed only marginal thermal stability, with major decomposition already occurring before 673 K ( $400^\circ\text{C}$ ) ( $\sim 3\text{ s}$

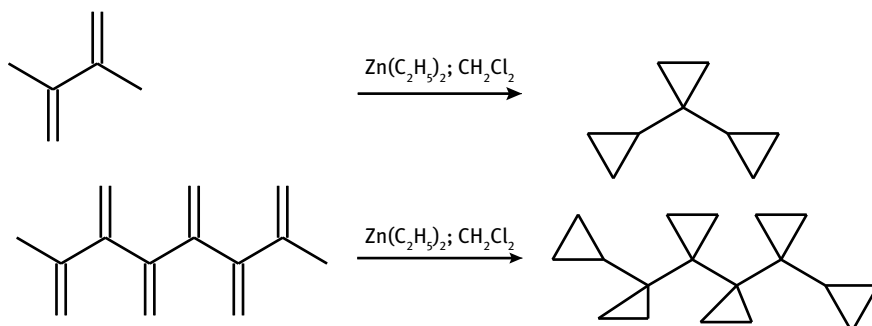


residence time). Other fuels (JP-10, RP-1, RG-1, RJ-6, and RJ-7) showed excellent thermal stability with little decomposition even at 873 K (600 °C). Results showed the pyrolytic stability of candidate materials relative to each other and provided insights into the mechanisms of thermal decomposition for specific fuel candidates.

### 3.2 Ivyanes and Triangulanes

Hydrocarbons with cyclopropane rings in the molecules, called ivyanes, with several cyclopropane rings attached to each other, were proposed as fuels for hybrid rockets [32, 33].

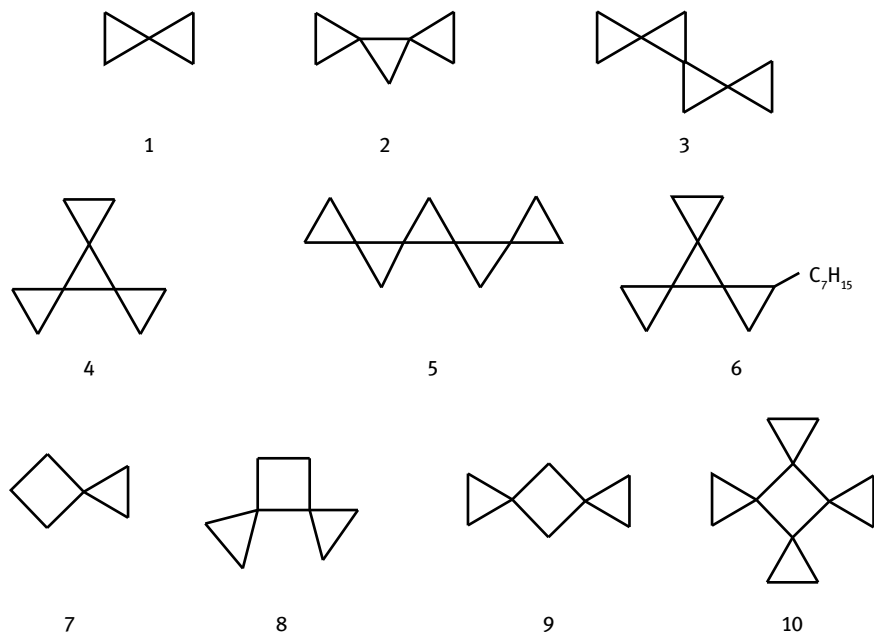
Practical synthesis of the first six members of the ivyane (1,1-oligocyclopropane) family of energetic hydrocarbons was achieved from the cross-conjugated polyenes known as dendralenes. Dendralenes are unsaturated hydrocarbons with multiple *exo*-ene double bonds in their side chains. The C=C double bonds can be converted to connected cyclopropane rings with three to eight cyclopropane rings in the molecule [34].



These molecules may have helical conformations in both the solid state and in solution. Ivyanes have the highest experimental heats of combustion recorded for any hydrocarbon. Ring-opening reactions of ivyanes are common. [3]- to [6]-ivyanes are oils at ambient temperature, but [7]- and [8]-ivyanes are solids. The ivyanes are kinetically stable up to moderate temperatures. [8]-ivyane, for example, melts at 368 K (95 °C) in air without significant decomposition, and [6]-ivyane is kinetically stable to about 473 K (200 °C). The heat of combustion of [6]-ivyane was found to be  $50.8 \pm 2.5 \text{ MJ/kg} = 12.3 \pm 0.6 \text{ MJ/mol}$ , which is one of the highest reported for any hydrocarbon and is significantly higher than that of cubane. The molar heat of combustion of [6]-ivyane is roughly six times that of cyclopropane (2.1 MJ/mol).

Highly strained oligospirocyclopropane systems would make good fuels, but they are difficult to obtain [35, 36]. Ivyanes can form not only linear chains but also ring structures. There are numerous exotic two-dimensional (2D) and three-dimensional

(3D) molecule structures that can incorporate three-ring and four-ring elements [37]. These include [1.1.1]propellane, prismane, cubane, bicyclopropylidene, triangulanes, and tetrahedrane, but some of these have not yet been isolated [38]. The molecules described in the following are exotic examples of unique molecular structures; some look like atomic artwork.

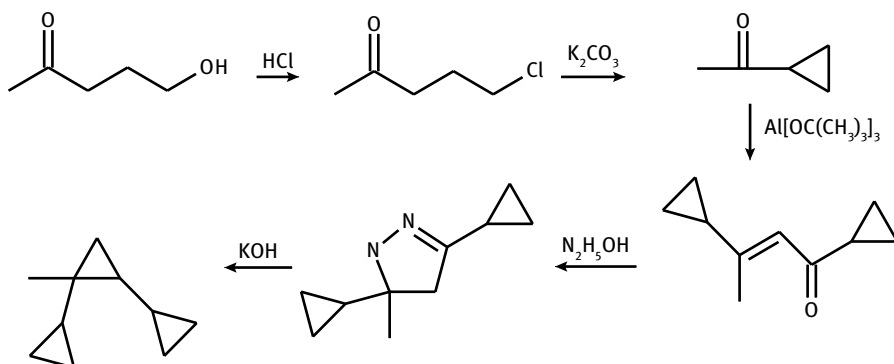


These compounds have been obtained only in milligram quantities, so they will never be used as rocket propellants. The enthalpies of formation of trispiro[2.0.0.2.1.1]-nonane (3), [3]rotane (4), *n*-heptyl[3]rotane (6), spiro-[2.3]hexane, and isomeric dispiro[2.0.2.2]octane (8) and dispiro[2.1.2.1]octane (9), as well as [4]rotane (10), were determined by measuring their heats of combustion in a microcalorimeter [39]. The enthalpy of formation values and the strain energies derived from them were compared with values from quantum mechanical calculations. The results confirmed previously reported theoretical and experimental values for spiropentane and established an additivity scheme for strain energies in different types of [*n*]triangulanes, with an excessive strain energy increment of 36 kJ/mol (8.6 kcal/mol) per spiro carbon atom. A simple additivity of strain energies without an excess increment can be employed for spirocyclopropanated cyclobutanes as well as for larger rings including [*n*]rotanes ( $n > 4$ ).

There are many spirocyclic compounds that have high heats of combustion and are candidates for high-energy fuels. These can either be synthesized in the lab or their performance can be predicted by computational methods [40].

### 3.3 Syntin (1-Methyl-1,2-dicyclopropylcyclopropane)

Syntin,  $C_{10}H_{16}$ , 1-methyl-1,2-dicyclopropylcyclopropane, 1'-methyl-1,1':2',1''-tercyclopropane, synthin, tsycklin, cyclane, CAS RN [93223-46-2], is a synthetic hydrocarbon and was used as a rocket fuel in the former Soviet Union. Syntin is a mixture of four possible *cis* and *trans* isomers. It has a density of  $0.851\text{ g/cm}^3$  and a boiling point of  $431\text{ K}$  ( $158^\circ\text{C}$ ). Because of the presence of three strained cyclopropane rings in the molecule, the compound has a very high positive enthalpy of formation:  $\Delta H_f^\circ(\text{L}) = +133\text{ kJ/mol}$  ( $+980\text{ kJ/kg} = +234\text{ cal/g}$ ), the average value for the isomeric mixture, bringing additional energy during the combustion process. Thus, it has advantages over the traditional hydrocarbon fuels, such as RP-1, because of higher density, lower viscosity, and higher heat of combustion. Syntin was used in the Soviet Union, and later Russia, in the 1980s and 1990s as fuel for the Soyuz-U2 rocket. It was first synthesized in the USSR in the 1960s and was brought to mass production in the 1970s. It was prepared in a multi-step synthetic process from common hydrocarbon sources [41, 42].



The production of this fuel is very expensive, and eventually it was halted.

Syntin was originally used on the Buran reaction control system (RCS)/orbital maneuvering system (OMS), which evolved to be used on the 11D58S (also known as RD-58S) engine on the Proton DM upper stage and in the second-stage engine of the Soyuz-U2 rocket [43]. It is reportedly denser than standard RG-1 (or RP-1) and provides a performance boost of approximately 8–10 s of vacuum-specific impulse. In 1996, the Russians discontinued production of Syntin, citing its high production cost and stating that they had sufficient stockpiles to meet their commercial launch needs until the DM stage was replaced by the  $LO_2/LH_2$  KM stage (powered by the RD-56M) and the  $N_2O_4/UDMH$  Briz (Breeze) upper stage (powered by the S5.98M engine). The termination of syntin production also forced the abandonment of the Soyuz 11A511U2 “Rus” booster, an updated version of the standard Soyuz 11A511U booster, which used syntin instead of standard kerosene in the first stage for launch of premium reconnaissance satellites and manned payloads that required extra payload performance.

Syntin can be analyzed by chromatography in combination with mass spectrometry (MS) [44]. As an example of gas chromatography (GC)–MS analysis capabilities, the total ion current chromatogram of a syntin propellant sample containing other hydrocarbon impurities was shown in [44].

### 3.4 Alkylcyclopropanes

Alkylcyclopropanes combine the energetic ring structure of cyclopropane with the favorable hydrogen content of alkanes in one molecule. Table 3 lists physical properties of alkylcycloalkanes [45].

**Table 3:** Physical properties of alkylcyclopropanes.

| Compound                               | Density at 298 K  | Heat capacity at 298 K            |                                      | Boiling point |       |
|----------------------------------------|-------------------|-----------------------------------|--------------------------------------|---------------|-------|
|                                        | g/cm <sup>3</sup> | J g <sup>-1</sup> K <sup>-1</sup> | cal g <sup>-1</sup> °C <sup>-1</sup> | K             | °C    |
| Methylcyclopropane                     | 0.634             | 2.30                              | 0.55                                 | —             | —     |
| Ethylcyclopropane                      | 0.679             | 2.26                              | 0.54                                 | 309.08        | 35.93 |
| <i>cis</i> -1,2-Dimethylcyclopropane   | 0.6889            | 2.26                              | 0.54                                 | 310.18        | 37.03 |
| <i>trans</i> -1,2-Dimethylcyclopropane | 0.6648            | 2.26                              | 0.54                                 | 301.36        | 28.21 |
| 1,1,2-Trimethylcyclopropane            | 0.6897            | 2.22                              | 0.53                                 | 325.6         | 52.44 |
| 1,1,2,2-Tetramethylcyclopropane        | 0.702             | 2.18                              | 0.52                                 | 344           | 71    |

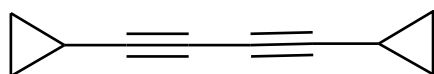
Data source: [45]

The enthalpies of combustion of six alkylcyclopropanes were measured by oxygen-bomb combustion calorimetry, and values of the enthalpies of formation of the liquids were derived therefrom. Table 4 lists the constant volume energy of combustion, the constant pressure enthalpy of combustion, and the standard enthalpy of formation of liquid alkylcyclopropanes.

1,3,3-trimethylcyclopropene is very sensitive to oxygen in air, causing formation of a thick polymeric gum [46]. This energetic fuel can be dissolved in RP-1.

### 3.5 Alkenyl- and Alkynyl-cyclopropanes

Another cyclopropane derivative considered as rocket propellant is ECP dimer, ethynyl cyclopropyl dimer, 1,4-dicyclopropyl-1,3-butadiyne. It has been considered as a bipropellant fuel with HTP or PERSOL-2 as the oxidizer [47].



**Table 4:** Thermodynamic properties of liquid alkylcyclopropanes at 298.15 K.

| Compound                                    | $\Delta E_c^{298}$  |                       | $\Delta H_c^{298}$  |                       | $\Delta H_f^{298}$  |                      |
|---------------------------------------------|---------------------|-----------------------|---------------------|-----------------------|---------------------|----------------------|
|                                             | kJ/mol              | kcal/mol              | kJ/mol              | kcal/mol              | kJ/mol              | kcal/mol             |
| Methylcyclopropane                          | 2714.1<br>$\pm 0.6$ | 648.69<br>$\pm 0.14$  | 2719.1<br>$\pm 0.6$ | 649.87<br>$\pm 0.14$  | $1.7 \pm 0.7$       | 0.41<br>$\pm 0.16$   |
| Ethylcyclopropane                           | 3365.7<br>$\pm 0.8$ | 804.43<br>$\pm 0.18$  | 3371.9<br>$\pm 0.8$ | 805.91<br>$\pm 0.18$  | -24.8<br>$\pm 0.8$  | -5.92<br>$\pm 0.19$  |
| <i>cis</i> -1,2-Dimethyl-<br>cyclopropane   | 3364.2<br>$\pm 0.6$ | 804.06<br>$\pm 0.14$  | 3370.4<br>$\pm 0.6$ | 805.55<br>$\pm 0.14$  | -26.3<br>$\pm 0.7$  | -6.29<br>$\pm 0.16$  |
| <i>trans</i> -1,2-Dimethyl-<br>cyclopropane | 3359.8<br>$\pm 0.8$ | 803.01<br>$\pm 0.18$  | 3366.0<br>$\pm 0.8$ | 804.494<br>$\pm 0.18$ | -30.7<br>$\pm 0.8$  | -7.34<br>$\pm 0.19$  |
| 1,1,2-Trimethyl-<br>cyclopropane            | 3972.4<br>$\pm 0.8$ | 949.43<br>$\pm 0.18$  | 3979.9<br>$\pm 0.8$ | 951.21<br>$\pm 0.18$  | -96.2<br>$\pm 0.8$  | -22.99<br>$\pm 0.20$ |
| 1,1,2,2-Tetramethyl-<br>cyclopropane        | 4626.9<br>$\pm 0.8$ | 1105.86<br>$\pm 0.20$ | 4635.6<br>$\pm 0.8$ | 1107.94<br>$\pm 0.20$ | -119.8<br>$\pm 0.9$ | -28.63<br>$\pm 0.22$ |

Data source: [45]

Ethynylcyclopropane, cyclopropylacetylene,  $C_5H_6$ , CAS RN [6746-94-7], has been considered as a high-energy bipropellant fuel [48]. Ethynylcyclopropane can be prepared from (1,1-dimethoxyethyl)cyclopropane by a two-stage elimination of methanol [49]. The freezing point of ethynylcyclopropane is less than 248 K (less than  $-25^\circ\text{C}$ ). The boiling point of ethynylcyclopropane is 325–338 K ( $52$ – $65^\circ\text{C}$ ). The density is  $0.7801\text{ g/cm}^3$ . The vapor pressure is 34.1 kPa. The enthalpy of formation of cyclopropyl methyl acetylene is  $+218\text{ kJ/mol}$  ( $+52.0\text{ kcal/mol}$ ). Ethenylcyclopropane (vinylcyclopropane, cyclopropylethylene) and cyclopropylcyanide have been considered as energetic fuels [24].

## 4 Cyclobutane and Cyclobutane Derivatives

Cyclobutane, also known as cyclotetramethylene,  $C_4H_8$ , CAS RN [287-23-0] is a cycloaliphatic hydrocarbon and part of the skeleton of many naturally occurring chemicals. This is surprising because the four-membered ring is still strained and not easy to form. There are no known applications of cyclobutane or cyclobutane derivatives as rocket propellants. Many polycyclic hydrocarbons contain a four-membered ring, but that does not make them cyclobutane derivatives.

## 4.1 Preparation of Cyclobutane

Cyclobutane can be prepared by dehalogenation of 1,4-dihalobutanes with zinc or magnesium [50]. Ethylene may dimerize under the influence of ultraviolet (UV) light.

## 4.2 Physical Properties of Cyclobutane

Physical properties of cyclobutane are summarized in Table 5.

**Table 5:** Physical properties of cyclobutane.

| Property                                                         | SI units                | Other units          | References |
|------------------------------------------------------------------|-------------------------|----------------------|------------|
| Molecular mass                                                   | 56.1063 g/mol           | 17.8233 mol/kg       | [17]       |
| Freezing point                                                   | 183 K                   | −90 °C               |            |
| Boiling point                                                    | 284 ± 5 K               | 11 ± 5 °C            |            |
| Density at 293 K under pressure                                  | 0.720 g/cm <sup>3</sup> | —                    |            |
| Vapor pressure at 273 K                                          | 0.62 bar                | 466.74 mm Hg         | [17]       |
| Standard enthalpy of formation, gas, $\Delta H_f^{29}$           | +28.4 kJ/mol            | +6.79 kcal/mol       | [18]       |
| Heat of combustion, liquid                                       | 2720.4 ± 0.5 kJ/mol     | 650.2 ± 0.1 kcal/mol | [17]       |
| Enthalpy of formation, liquid under pressure, $\Delta H_f^{298}$ | +3.0 kJ/mol             | +0.72 kcal/mol       |            |
| Enthalpy of vaporization at normal boiling point                 | 23.92 kJ/mol            | 5.72 kcal/mol        | [51]       |

The vapor pressure of cyclobutane in the range 213–285 K can be calculated from an Antoine equation with the coefficients

$$\log P = 4.07143 - [1038.009 / (T - 30.334)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. See also [50].

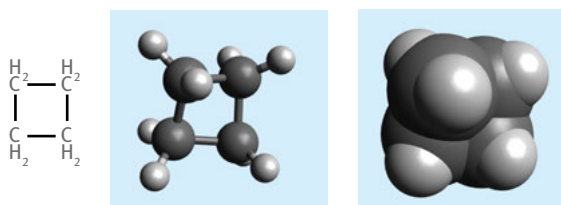
The unusually high enthalpy of formation of cyclobutane and many of its derivatives can be explained by strain energy [52]. The term strain energy is usually considered relative to a theoretical unstrained state of the molecule. The strain energy can be calculated from the difference between the experimentally determined enthalpy of formation and the enthalpy of formation predicted from additive behavior of unstrained bonds:

$$\text{Strain energy} = \Delta H_{f,\text{exp.}} - \Delta H_{f,\text{calc.}}$$

The standard enthalpy of formation of cyclobutylacetylene is +236 kJ/mol (+56.3 kcal/mol).

### 4.3 Molecular Structure of Cyclobutane

The molecular structure of cyclobutane is that of a four-membered ring, but the ring is not flat (Figure 4). The cyclobutane ring is strained, and the C—C—C bond angle is different from the unstrained tetrahedral angle of  $109.45^\circ$ . The bond angles are not  $90^\circ$  as in a perfect flat square because the bonds are banana-shaped and the four-membered ring is not flat. One of the carbon atoms sticks out and makes a  $25^\circ$  angle with the plane formed by the other three carbons. Cyclobutane is a molecule that undergoes inversion, which may split some absorption bands. IR, Raman, and electron diffraction spectra suggest that the equilibrium configuration of cyclobutane is  $D_{2d}$  symmetry and that the barrier hindering inversion is sufficiently low so that even at room temperature, an appreciable number of molecules obey  $D_{4h}$  selection rules [53].



**Figure 4:** Molecular structure of cyclobutane.

Another strained multi-ring compound would be [1.1.0]-bicyclobutane, a cyclobutane in which opposite corners are connected by an internal C—C bond [54–56]. This molecule could also be described as the combination of two cyclopropane rings that share a base of the triangles.

An even more strained ring molecule is [1.1.1]propellane, in which not just two but three cyclopropyl rings share a common side of three triangles.

## 5 Cyclopentane and Cyclopentane Derivatives

Cyclopentane,  $C_5H_{10}$ , CAS RN [287-92-3], in small quantities may be found in cracked petroleum products along with cyclopentadiene. It is not used as a rocket propellant in the pure state.

## 5.1 Physical Properties of Cyclopentane

Physical properties of cyclopentane are summarized in Table 6.

**Table 6:** Physical properties of cyclopentane.

| Property                                                         | SI units                                       | Other units                                         | References |
|------------------------------------------------------------------|------------------------------------------------|-----------------------------------------------------|------------|
| Molecular mass                                                   | 70.1329 g/mol                                  | 14.2586 mol/kg                                      | [17]       |
| Freezing point                                                   | 179.2 ± 0.8 K                                  | −93.9 °C                                            |            |
| Boiling point                                                    | 322.4 ± 0.3 K                                  | 49.3 °C                                             |            |
| Density at 293 K                                                 | 0.7457 g/cm <sup>3</sup>                       | —                                                   | [57]       |
| Vapor pressure at 293 K                                          | 0.344 bar                                      | 258 mm Hg                                           | [17]       |
| Viscosity at 286.6 K                                             | 493 μPa s                                      | 0.493 cPs                                           | [57]       |
| Heat capacity, gas, at 298 K                                     | 82.8 ± 2.0 J mol <sup>−1</sup> K <sup>−1</sup> | 19.79 ± 0.48 cal mol <sup>−1</sup> °C <sup>−1</sup> | [17]       |
| Heat capacity, liquid, at 298 K                                  | 126.74 J mol <sup>−1</sup> K <sup>−1</sup>     | 30.29 cal mol <sup>−1</sup> °C <sup>−1</sup>        |            |
| Standard enthalpy of formation, gas, $\Delta H_f^{298}$          | −78.4 kJ/mol                                   | −18.74 kcal/mol                                     | [18]       |
|                                                                  | −76.40 ± 0.79 kJ/mol                           | −18.26 kcal/mol                                     | [17]       |
| Heat of combustion, liquid                                       | 3291.4 ± 0.6 kJ/mol                            | 786.7 kcal/mol                                      | [17]       |
| Enthalpy of formation, liquid under pressure, $\Delta H_f^{298}$ | −105.6 ± 1.8 kJ/mol                            | −25.24 ± 0.43 kcal/mol                              |            |
| Enthalpy of vaporization at 322.4 K                              | 27.3 kJ/mol                                    | 6.52 kcal/mol                                       | [51]       |
| Enthalpy of fusion at 179.7 K                                    | 0.6 kJ/mol                                     | 0.143 kcal/mol                                      | [17]       |
| Critical temperature                                             | 511.7 ± 0.2 K                                  | 238.6 °C                                            |            |
| Critical pressure                                                | 45.1 ± 0.4 bar                                 | 654 psia                                            |            |
| Critical volume                                                  | 3.85 ± 0.04 mol/L                              | —                                                   |            |

The vapor pressure of cyclopentane in the range 288.86–323.18 K can be calculated from the Antoine equation

$$\log P = A - [B/(T + C)] = 4.00288 - [1119.208/(T - 42.412)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

## 5.2 Physical Properties of Cyclopentadiene

Cyclopentadiene, C<sub>5</sub>H<sub>6</sub>, CAS RN [542-92-7], is an important raw material in the synthesis of dicyclopentadiene and the intermediates for the synthesis of JP-10. Cyclopentadiene is a byproduct of petroleum refining [58, 59]. Cyclopentadiene and dicyclopentadiene



tadiene (DCPD) occur as by-products in the steam-cracking process in ethylene plants and are the major ingredients in the production of hydrocarbon resins, unsaturated polyester resins, elastomers, pesticides, flame retardants, and many specialty chemicals. Cyclopentadiene dimerizes readily, via the Diels-Alder mechanism, to DCPD at ambient conditions. The dimerization is highly exothermic. Because of its reactivity, cyclopentadiene is normally available only in the stable dimer form. Pure cyclopentadiene can be produced by the thermal cracking of DCPD at a temperature near the normal boiling point of DCPD. Cyclopentadiene traces may be present as incomplete conversion or depolymerization products of JP-10. Physical properties of cyclopentadiene are summarized in Table 7.

**Table 7:** Physical properties of cyclopentadiene.

| Property                                                         | SI units                                         | Other units                                                       | References |
|------------------------------------------------------------------|--------------------------------------------------|-------------------------------------------------------------------|------------|
| Molecular mass                                                   | 66.1011 g/mol                                    | 15.1283 mol/kg                                                    | [17]       |
| Freezing point                                                   | 183 K                                            | -90 °C                                                            |            |
| Boiling point                                                    | 314 K                                            | +41 °C                                                            |            |
| Density at 293 K                                                 | 0.8021 g/cm <sup>3</sup>                         | —                                                                 |            |
| Vapor pressure at 293 K                                          | 48 kPa                                           | 363 mm Hg                                                         | [17]       |
| Heat capacity, $C_p$ , vapor, at 298 K                           | $75.4 \pm 2.0 \text{ J mol}^{-1} \text{ K}^{-1}$ | $18.02 \pm 0.48 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$ |            |
| Heat capacity, $C_p$ , liquid, at 298 K                          | $115.3 \text{ J mol}^{-1} \text{ K}^{-1}$        | $27.56 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$          |            |
| Standard enthalpy of formation, vapor, $\Delta H_f^{298}$        | +130.8 kJ/mol                                    | +31.26 kcal/mol                                                   | [18]       |
|                                                                  | +139 kJ/mol                                      | +33.22 kcal/mol                                                   | [17]       |
| Heat of combustion, vapor                                        | $2960 \pm 30 \text{ kJ/mol}$                     | $707 \pm 7 \text{ kcal/mol}$                                      |            |
| Enthalpy of formation, liquid under pressure, $\Delta H_f^{298}$ | +110 kJ/mol                                      | 26.29 kcal/mol                                                    |            |
| Enthalpy of vaporization at NBP                                  | 29 kJ/mol                                        | 6.93 kcal/mol                                                     |            |

## 6 Cyclohexane

Cyclohexane,  $\text{C}_6\text{H}_{12}$ , CAS RN [110-82-7], also known as hexahydrobenzene, hexamethylene, is the main representative of the family of cycloalkyl hydrocarbons and the most readily available chemical in this group [60]. The cyclohexyl ring can be found in many natural and synthetic fuel products. There are numerous derivatives of cyclohexane in use in various functions in rocket propellants, and cyclohexane is a constituent of many fuel mixtures derived from petroleum refining. The only other six-ring compound of more importance is benzene, which can be obtained by dehydrogenation of cyclohexane.

## 6.1 Production of Cyclohexane

Cyclohexane is produced by reduction of benzene.

## 6.2 Physical Properties of Cyclohexane

### 6.2.1 Mechanical and Thermal Properties of Cyclohexane

Physical properties of cyclohexane are listed in Table 8.

**Table 8:** Physical properties of cyclohexane.

| Property                                                  | SI units                                            | Other units                                             | References |
|-----------------------------------------------------------|-----------------------------------------------------|---------------------------------------------------------|------------|
| Molecular mass                                            | 84.1595                                             | 11.8822 mol/kg                                          |            |
| Freezing point                                            | $279.6 \pm 0.3$ K                                   | $6.5$ °C                                                | [17]       |
| Boiling point                                             | $353.9 \pm 0.2$ K                                   | $80.8$ °C                                               |            |
| Density at 298 K                                          | $0.77379$ g/cm <sup>3</sup>                         | —                                                       | [61]       |
| Vapor pressure at 293 K                                   | $10.3$ kPa                                          | $77.1$ mm Hg                                            |            |
| Surface tension at 298 K                                  | $24.57$ mN/m                                        | —                                                       | [61]       |
| Heat capacity, $C_p$ , vapor at 298 K                     | $105.3 \pm 2.0$ J mol <sup>-1</sup> K <sup>-1</sup> | $25.17 \pm 0.48$ cal mol <sup>-1</sup> °C <sup>-1</sup> | [17]       |
| Heat capacity, $C_p$ , liquid at 298 K                    | $156.00$ J mol <sup>-1</sup> K <sup>-1</sup>        | $37.38$ cal mol <sup>-1</sup> °C <sup>-1</sup>          |            |
| Standard enthalpy of formation, vapor, $\Delta H_f^{298}$ | $-123.3$ kJ/mol                                     | $-29.47$ kcal/mol                                       | [18]       |
| Heat of combustion, liquid                                | $3930 \pm 20$ kJ/mol                                | $930 \pm 4.8$ kcal/mol                                  | [17]       |
| Enthalpy of formation, liquid, $\Delta H_f^{298}$         | $-157.7 \pm 1.8$ kJ/mol                             | $-37.69 \pm 0.43$ kcal/mol                              |            |
| Enthalpy of vaporization at NBP                           | $29.97$ kJ/mol                                      | $7.16$ kcal/mol                                         | [51]       |
| Index of refraction, $n_D^{20}$                           | $1.42618$                                           | —                                                       | [62]       |
| Critical temperature                                      | $554 \pm 1$ K                                       | $281 \pm 1$ °C                                          | [17]       |
| Critical pressure                                         | $40.7 \pm 0.5$ bar                                  | $40.2$ atm                                              |            |
| Critical density                                          | $3.24 \pm 0.03$ mol/L                               | $0.273$ g/cm <sup>3</sup>                               |            |

The vapor pressure of cyclohexane can be calculated from the Antoine equation

$$\log P = A - B/(T + C) = 5.9655598 - [1200.428/(T - 50.6773)]$$

where  $P$  is the vapor pressure in kPa and  $T$  is the temperature in kelvin [62]. The data in Table 9 were calculated with this equation.

**Table 9:** Vapor pressure of cyclohexane.

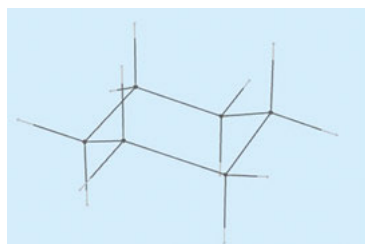
| Temperature<br>K | Vapor pressure |       |
|------------------|----------------|-------|
|                  | kPa            | mm Hg |
| 273              | 3.7            | 27.6  |
| 280              | 5.4            | 40.4  |
| 290              | 8.9            | 66.8  |
| 293              | 10.3           | 77.1  |
| 298              | 12.9           | 97.1  |
| 300              | 14.2           | 106   |
| 310              | 21.7           | 163   |
| 320              | 32.2           | 242   |
| 330              | 46.6           | 349   |
| 340              | 65.5           | 492   |
| 350              | 90.2           | 676   |
| 353.9            | 101.5          | 762   |

A wide range of reference equations for the thermal conductivity of cyclohexane as a function of temperature and density was based in part on a body of experimental literature data that had been critically assessed for internal consistency and for agreement with theory whenever possible [63]. Uncertainties in the critical region were significant, since the thermal conductivity approaches infinity at the critical point and is very sensitive to small changes in density.

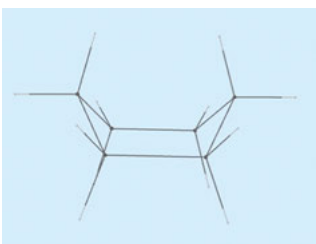
### 6.2.2 Molecular Structure of Cyclohexane

The symmetrical six-membered ring structure of cyclohexane is the ideal precursor for stable aromatic six-membered rings, and many pyrolytic and dehydrogenating conversions of cyclohexane and cyclohexane derivatives end up with aromatic structures that are favored from a standpoint of energy.

Electron diffraction studies, dynamic nuclear magnetic resonance (NMR) spectroscopy, analysis of vibrational spectra, and theoretical calculations indicate that the chair conformation ( $D_{3d}$  symmetry) is the most stable form of cyclohexane. The strain-energy calculations showed that there are also two other conformations, twist-boat ( $D_2$  symmetry) and boat ( $C_2$  symmetry), with an energy of about 20–25 kJ/mol above that of the chair form. The twist-boat and boat forms can interconvert by pseudo-rotation. Calculations have suggested that the twist-boat forms are at the minima of the pseudo-rotation path and that the boats are transition states about 4 kJ/mol above the twist boats.



Chair Conformation



Boat Conformation

### 6.3 Chemical Properties of Cyclohexane

There are numerous publications about the dehydrogenation of cyclohexane (not included here for lack of space), and many of those relate to the dehydrogenation of methylcyclohexane, using the same catalysts and the same methods of investigation. The dehydrogenation of methylcyclohexane has more practical importance as a step for endothermic fuels than the dehydrogenation of cyclohexane.

The reaction mechanisms for thermal decomposition of cyclohexane in the gas phase have been investigated using quantum chemical calculations and transition-state theory [64]. The predicted rate constants and kinetic parameters in the modified Arrhenius equation form were in good agreement with data available from the literature.

## 7 Methylcyclohexane

Methylcyclohexane,  $C_7H_{14}$ , CAS RN [108-87-2], is rarely used as such in the pure state, but it is a constituent of JP-9. Methylcyclohexane (MCH) has been selected as the constituent of some surrogate fuel mixtures. It has disadvantages in some high-speed air-breathing vehicle applications because of its relatively high vapor pressure, low density, and comparatively low volumetric heat of combustion.

### 7.1 Production of Methylcyclohexane

Methylcyclohexane can be prepared by reduction of toluene. MCH and decahydronaphthalene (decalin) are potential fuels that could provide the heat sink that is required for high-Mach air-breathing vehicles. At the beginning of these programs, domestic suppliers of methylcyclohexane and decalin were identified, and production rates were determined. Two producers of MCH and one producer of decalin were identified, but production capacity of these materials was limited at that time, and the

materials were sold only as specialty chemicals with an associated high cost. Technologies were sought to allow expansion of production facilities and to reduce the cost of MCH.

## 7.2 Physical Properties of Methylcyclohexane

Physical properties of methylcyclohexane are listed in Table 10.

**Table 10:** Physical properties of methylcyclohexane.

| Property                                                  | SI units                                                                             | Other units                                                               | References |
|-----------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------|------------|
| Molecular mass                                            | 98.1861                                                                              | 10.1847 mol/kg                                                            |            |
| Freezing point                                            | $146.6 \pm 0.4$ K                                                                    | $-126.5 \pm 0.4$ °C                                                       | [17]       |
| Boiling point                                             | $374.0 \pm 0.8$ K                                                                    | $101 \pm 0.8$ °C                                                          |            |
| Density at 298 K                                          | 0.77 g/cm <sup>3</sup>                                                               | —                                                                         |            |
| Density at 293 K                                          | 0.7694 g/cm <sup>3</sup>                                                             | —                                                                         | [65]       |
| Vapor pressure at 293 K                                   | 4.8 kPa                                                                              | 36 mm Hg                                                                  |            |
| Viscosity, liquid                                         | 0.731 mPa s at 293 K                                                                 | 0.731 cPs at 20 °C                                                        | [66, 67]   |
| Viscosity, liquid                                         | 0.679 mPa s at 298 K                                                                 | 0.679 cPs at 25 °C                                                        | [65]       |
| Surface tension                                           | 0.0237 N/m at 298 K                                                                  | —                                                                         | [68]       |
|                                                           | 23.42 mN/m at 298 K                                                                  | —                                                                         | [61]       |
| Thermal conductivity, liquid, at 300 K                    | 0.106 W m <sup>-1</sup> K <sup>-1</sup><br>for a density of<br>763 kg/m <sup>3</sup> | 0.06128 BTU h <sup>-1</sup> ft <sup>-1</sup> °F <sup>-1</sup><br>at 80 °F | [69]       |
| Heat capacity, $C_p$ , vapor, at 298 K                    | 135.8 J mol <sup>-1</sup> K <sup>-1</sup>                                            | 32.46 cal mol <sup>-1</sup> °C <sup>-1</sup>                              | [17]       |
| Heat capacity, $C_p$ , liquid, at 298 K                   | 184.38 J mol <sup>-1</sup> K <sup>-1</sup>                                           | 44.07 cal mol <sup>-1</sup> °C <sup>-1</sup>                              |            |
| Standard enthalpy of formation, vapor, $\Delta H_f^{298}$ | $-154.8 \pm 1.0$ kJ/mol                                                              | $-36.99 \pm 0.25$ kcal/mol                                                | [70]       |
| Heat of combustion, liquid                                | $4565.3 \pm 1.0$ kJ/mol                                                              | $1091.13 \pm 0.23$ kcal/mol                                               |            |
| Enthalpy of formation, liquid, $\Delta H_f^{298}$         | $-190.2 \pm 1.0$ kJ/mol                                                              | $-45.45 \pm 0.25$ kcal/mol                                                |            |
| Enthalpy of vaporization at NBP                           | 31.27 kJ/mol                                                                         | 7.47 kcal/mol                                                             | [51]       |
| Refractive index, $n_D^{20}$                              | 1.42308                                                                              | —                                                                         | [62]       |
| Critical temperature                                      | $573 \pm 2$ K                                                                        | $300 \pm 2$ °C                                                            | [17]       |
| Critical pressure                                         | $34.8 \pm 0.2$ bar                                                                   | 34.3 atm                                                                  |            |
| Critical density                                          | $2.71 \pm 0.02$ mol/L                                                                |                                                                           |            |
| Critical temperature                                      | 572.2 K                                                                              | 299.1 °C                                                                  | [69]       |
| Critical pressure                                         | 3.47 MPa                                                                             | 503 psia                                                                  |            |
| Critical density                                          | 267.07 kg/m <sup>3</sup>                                                             | —                                                                         |            |

Physical and thermochemical properties of pure MCH were measured so that it could be used as a constituent of surrogate fuel mixtures. This was done as part of an effort to develop surrogate fuels to represent the thermophysical properties of aviation kerosenes described under the umbrella names of Jet-A and JP-8 [71].

### 7.2.1 Density of Methylcyclohexane

The density, velocity of sound, and adiabatic compressibility of MCH and propylcyclohexane were measured over the temperature range 278–343 K. The data are listed in Table 11.

**Table 11:** Density, velocity of sound, and adiabatic compressibility of methylcyclohexane and propylcyclohexane.

| Temperature<br>K | Methylcyclohexane             |                                           |                                                   | Propylcyclohexane             |                                           |                                                   |
|------------------|-------------------------------|-------------------------------------------|---------------------------------------------------|-------------------------------|-------------------------------------------|---------------------------------------------------|
|                  | Density<br>$\text{kg m}^{-3}$ | Velocity of<br>sound<br>$\text{m s}^{-1}$ | Adiabatic<br>compressibility<br>$\text{TPa}^{-1}$ | Density<br>$\text{kg m}^{-3}$ | Velocity of<br>sound<br>$\text{m s}^{-1}$ | Adiabatic<br>compressibility<br>$\text{TPa}^{-1}$ |
| 278.15           | 782.3                         | 1304.7                                    | 750.94                                            | 805.4                         | 1371.3                                    | 660.26                                            |
| 283.15           | 778.0                         | 1281.9                                    | 782.27                                            | 801.5                         | 1349.6                                    | 685.01                                            |
| 293.15           | 769.3                         | 1236.9                                    | 849.67                                            | 793.7                         | 1307.1                                    | 737.38                                            |
| 303.15           | 760.7                         | 1192.9                                    | 923.93                                            | 785.9                         | 1265.5                                    | 794.47                                            |
| 313.15           | 751.9                         | 1149.7                                    | 1006.1                                            | 778.1                         | 1224.7                                    | 856.81                                            |
| 323.15           | 743.1                         | 1107.4                                    | 1097.4                                            | 770.2                         | 1184.7                                    | 925.02                                            |
| 333.15           | 734.3                         | 1065.6                                    | 1199.3                                            | 762.3                         | 1145.4                                    | 999.94                                            |
| 343.15           | 725.3                         | 1024.5                                    | 1313.6                                            | 754.4                         | 1106.9                                    | 1081.9                                            |

Data source: [71]

The density of methylcyclohexane can be calculated from the equation

$$\rho = 0.80217 - 0.0004830t$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $t$  is the temperature in  $^{\circ}\text{F}$  [72].

### 7.2.2 Vapor Pressure of Methylcyclohexane

The vapor pressure of MCH can be calculated from the Antoine equation

$$\log P = A - B/(T + C) = 5.9140199 - [1250.905/(T - 54.0054)]$$

where  $P$  is the vapor pressure in kPa and  $T$  is the temperature in kelvin [62]. The data in Table 12 were calculated with this equation.

The density and velocity of sound of liquid MCH and propylcyclohexane from 270 to 470 K with pressures to 40 MPa were measured with two vibrating-tube densime-

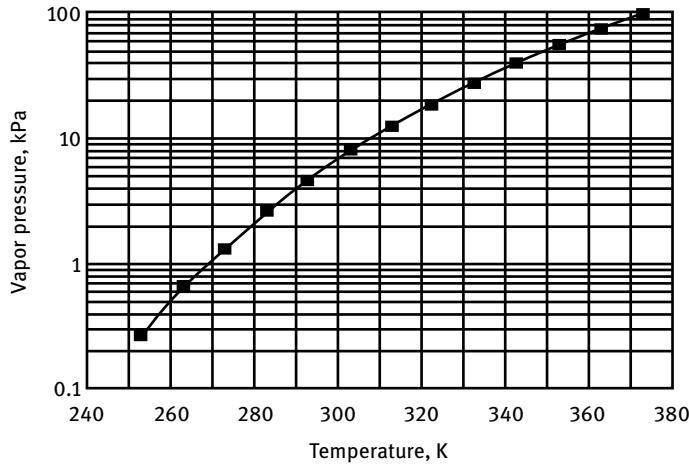
**Table 12:** Vapor pressure of methylcyclohexane.

| Temperature<br>K | Vapor pressure |       |
|------------------|----------------|-------|
|                  | kPa            | mm Hg |
| 273              | 1.6            | 12    |
| 280              | 2.4            | 18    |
| 290              | 4.1            | 31    |
| 298              | 6.1            | 46    |
| 300              | 6.7            | 51    |
| 310              | 10.7           | 80    |
| 320              | 16.3           | 122   |
| 330              | 24.1           | 181   |
| 340              | 34.7           | 260   |
| 350              | 48.7           | 366   |
| 360              | 67.0           | 503   |
| 370              | 90.2           | 677   |
| 374              | 101.1          | 759   |

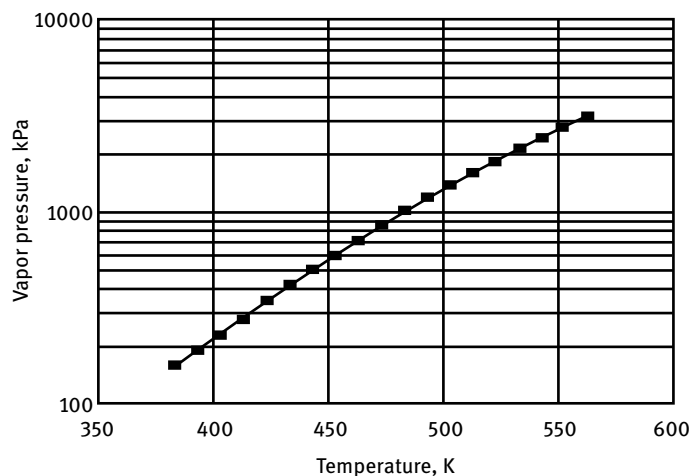
Data source: [62]

ters and a time-of-flight method, respectively [73]. Comparisons with literature data showed good agreement in overlapping ranges. See also [74].

The graphs in Figures 5 and 6 are based on numerical data first published in [68] and then graphed by other users. Vapor pressures of methylcyclohexane over two different temperature ranges are illustrated in Figures 5 and 6.



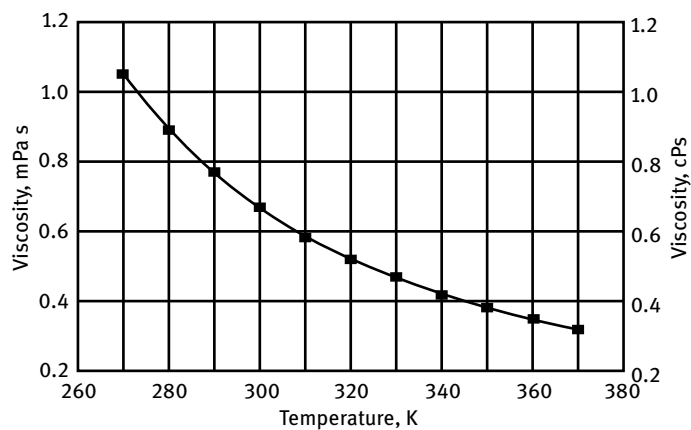
**Figure 5:** Vapor pressure of methylcyclohexane (low temperature range). (Chart created by Schmidt 2020 based on data from [68].)



**Figure 6:** Vapor pressure of methylcyclohexane (high temperature range). (Chart created by Schmidt 2020 based on data from [68].)

### 7.2.3 Viscosity of Methylcyclohexane

The dynamic viscosity of liquid MCH based on data from [75] is illustrated in Figure 7.



**Figure 7:** Dynamic viscosity of liquid methylcyclohexane. (Chart created by Schmidt 2020 based on data from [75].)

The viscosities of MCH and propylcyclohexane were measured between 300 and 360 K [71]. The results are listed in Table 13. The kinematic viscosity and density of MCH were measured in the temperature range of 219 to 341 K (−65 to +155 °F), as listed in Table 14.



**Table 13:** Viscosities of methylcyclohexane and propylcyclohexane.

| Methylcyclohexane |                                                    | Propylcyclohexane |                                                    |
|-------------------|----------------------------------------------------|-------------------|----------------------------------------------------|
| Temperature<br>K  | Kinematic viscosity<br>$\text{mm}^2 \text{s}^{-1}$ | Temperature<br>K  | Kinematic viscosity<br>$\text{mm}^2 \text{s}^{-1}$ |
| 293.23            | 0.9480                                             | 293.15            | 1.2770                                             |
| 303.21            | 0.8387                                             | 303.15            | 1.1120                                             |
| 313.15            | 0.7488                                             | 313.15            | 0.9830                                             |
| 323.15            | 0.6736                                             | 323.15            | 0.8759                                             |
| 333.15            | 0.6107                                             | 333.15            | 0.7877                                             |
| 343.15            | 0.5568                                             | 343.15            | 0.7140                                             |
| 353.16            | 0.5113                                             | 353.15            | 0.6499                                             |
| 363.15            | 0.4707                                             | 363.15            | 0.5966                                             |
|                   |                                                    | 373.15            | 0.5500                                             |

Data source: [71]

**Table 14:** Kinematic viscosity and density of methylcyclohexane.

| Temperature                |        |        |        |        |
|----------------------------|--------|--------|--------|--------|
| -65                        | -30    | 32     | 77     | 155 °F |
| -54                        | -34    | 0      | 25     | 68 °C  |
| 219                        | 239    | 273    | 298    | 341 K  |
| Viscosity, cSt             |        |        |        |        |
| 3.796                      | 2.358  | 1.235  | 0.881  | 0.562  |
| Density, g/cm <sup>3</sup> |        |        |        |        |
| 0.8335                     | 0.8167 | 0.7867 | 0.7650 | 0.7273 |

Data source: [72]

#### 7.2.4 Thermal Conductivity of Methylcyclohexane

The thermal conductivities of MCH and propylcyclohexane liquid and vapor were measured covering a temperature range of 300 to 600 K and a pressure range of 0.1 to 60 MPa and were used to develop correlations for the thermal conductivity [69]. The data included a contribution due to thermal radiation that increased in proportion to temperature cubed up to an estimated value from 2 to 3% near 600 K. Two graphs in this publication show the thermal conductivities of the alkylcyclohexanes as a function of density rather than as a function of temperature. That format of data representation may be of scientific interest, but the more practical graphs with properties shown as a function of temperature or pressure are missing. The thermal conductivity of liquid MCH at 300 K is  $0.106 \text{ W m}^{-1} \text{ K}^{-1}$  at a density of  $763 \text{ kg/m}^3$ . The thermal conductivity of liquid MCH at 450 K under 50 MPa pressure is  $0.099 \text{ W m}^{-1} \text{ K}^{-1}$  at a density of  $702 \text{ kg/m}^3$ .

The thermal conductivity of MCH and propylcyclohexane at temperatures from 300 to 595 K and pressures up to 60 MPa was again measured and resulted in a second set of data, but the results were displayed only as a function of density instead of as a function of temperature [71].

### 7.2.5 Surface Tension of Methylcyclohexane

The surface tension of MCH at 298 K is 23.42 mN/m [61]. The density of the same sample was 0.76499 g/cm<sup>3</sup>. The surface tension of MCH is 32.843, 30.806, 24.465, and 19.519 dyn/cm at 219, 239, 295, and 343 K (−65, −30, +72, and +158 °F), respectively [72].

### 7.2.6 Thermodynamic Properties of Methylcyclohexane

The isobaric heat capacity data of MCH in the temperature range of 298.1 to 775.4 K and the pressure range of 3.5 to 5 MPa was measured by a mixing technique [76]. In the low-temperature region, the isobaric heat capacity of MCH increased gently with increasing temperature. At the pseudo-critical region, the isobaric heat capacity increased sharply to a peak value and then decreased dramatically in a nearly symmetrical way.

The heat capacity of MCH at 233, 293, and 339 K (−40, +20, and +66 °C) is, respectively, 1.653, 1.929, and 2.171 J g<sup>−1</sup> K<sup>−1</sup> (0.395, 0.461, and 0.519 cal g<sup>−1</sup> °C<sup>−1</sup>) (average of five consecutive tests) [72].

Thermodynamic properties of MCH and several other alkylcycloalkanes are summarized in Table 15. The gross heat of combustion of MCH is 19989 BTU/lb = 11105 cal/g, and the net heat of combustion is 18700 BTU/lb = 10389 cal/g (average of two repeated tests) [72]. See also [77].

The enthalpy of vaporization of MCH as a function of temperature in the range 298–374 K can be calculated from the equation

$$\Delta H_v = A \exp(-\beta T_r)(1 - T_r)^\beta$$

where  $T_r$  is the reduced temperature  $T_r = T/T_c$  with  $T_c = 572.1$  K,  $\Delta H_v$  is the enthalpy of vaporization at saturation pressure in kJ/mol, and  $T$  is the temperature in kelvin.  $A$  and  $\beta$  are constants, with  $A = 49.56$  and  $\beta = 0.2685$ .

### 7.2.7 Electrical Properties of Methylcyclohexane

The dielectric constant of methylcyclohexane is 2.129, 2.055, 2.024, and 1.960 at 219, 273, 295, and 342 K (−65, 32, 72.5, and 156 °F), respectively [72].

**Table 15:** Thermodynamic properties of alkylcycloalkanes.

| Compound                     | Heat of combustion at 298 K (25 °C) |                   |                 |                   | Enthalpy of formation at 298 K (25 °C) |                  |                 |                  |
|------------------------------|-------------------------------------|-------------------|-----------------|-------------------|----------------------------------------|------------------|-----------------|------------------|
|                              | Liquid                              |                   | Vapor           |                   | Liquid                                 |                  | Vapor           |                  |
|                              | kJ/mol                              | kcal/mol          | kJ/mol          | kcal/mol          | kJ/mol                                 | kcal/mol         | kJ/mol          | kcal/mol         |
| Cyclopentane                 | 3290.9<br>± 0.7                     | 786.54<br>± 0.17  | 3319.5<br>± 0.7 | 793.39<br>± 0.17  | -105.9<br>± 0.8                        | -25.31<br>± 0.18 | -77.2<br>± 0.8  | -18.46<br>± 0.18 |
| Methylcyclopentane           | 3937.7<br>± 0.8                     | 941.14<br>± 0.18  | 3969.4<br>± 0.8 | 948.72<br>± 0.18  | -138.4<br>± 0.8                        | -33.08<br>± 0.20 | -106.7<br>± 0.8 | -25.5<br>± 0.20  |
| Ethylcyclopentane            | 4591.9<br>± 0.9                     | 1097.5<br>± 0.22  | 4628.4<br>± 1.0 | 1106.21<br>± 0.23 | -163.5<br>± 1.0                        | -39.08<br>± 0.24 | -127.1<br>± 1.0 | -30.37<br>± 0.25 |
| <i>n</i> -propylcyclopentane | 5245.6<br>± 1.2                     | 1253.74<br>± 0.28 | 5286.7<br>± 1.2 | 1263.56<br>± 0.28 | -189.2<br>± 1.3                        | -45.21<br>± 0.30 | -148.1<br>± 1.3 | -35.39<br>± 0.30 |
| Cyclohexane                  | 3919.9<br>± 0.7                     | 936.88<br>± 0.17  | 3953.0<br>± 0.7 | 944.79<br>± 0.17  | -156.2<br>± 0.8                        | -37.34<br>± 0.19 | -123.1<br>± 0.4 | -29.43<br>± 0.10 |
| Methylcyclohexane            | 4565.3<br>± 1.0                     | 1091.13<br>± 0.23 | 4600.7<br>± 1.0 | 1099.59<br>± 0.23 | -190.2<br>± 1.0                        | -45.45<br>± 0.25 | -154.8<br>± 1.0 | -36.99<br>± 0.25 |
| Ethylcyclohexane             | 5222.6<br>± 1.5                     | 1248.23<br>± 0.35 | 5263.1<br>± 1.5 | 1257.9<br>± 0.35  | -212.2<br>± 1.5                        | -50.72<br>± 0.37 | -171.8<br>± 1.5 | -41.05<br>± 0.37 |
| <i>n</i> -Propylcyclohexane  | 5875.8<br>± 1.1                     | 1404.34<br>± 0.27 | 5920.9<br>± 1.1 | 1415.12<br>± 0.27 | -238.4<br>± 1.3                        | -56.98<br>± 0.30 | -193.3<br>± 1.3 | -46.2<br>± 0.30  |

Data source: [70]

### 7.3 Chemical Properties of Methylcyclohexane

For its application as a fuel in air-breathing engines, the most important chemical property of MCH is the endothermicity of its thermal decomposition, making it a good coolant for hot parts of the engine or leading edges of hypersonic aircraft. The evaluation of MCH as an endothermic fuel in comparison to decalin or bicyclohexyl is discussed in Section 2.2.1.3 on endothermic fuels in chapter “Hydrocarbons.”

The maximum-cruise Mach capability of most endothermic fuels was found to be Mach 6. Significant increases in fuel heat capacity would be necessary to increase the maximum-cruise Mach number. At Mach 7, the propulsive energy in methylcyclohexane was not sufficient to complete the mission range using turboramjets.

The addition of methyl groups to the cycloalkane ring may decrease the stability of the catalyst system used to effect dehydrogenation. The addition of methyl groups may improve equilibrium conversion at lower temperatures.

### 7.3.1 Thermal Decomposition of Methylcyclohexane

The vapor-phase thermal decomposition of four jet fuel candidates (MCH, toluene, *trans*-decalin, and naphthalene) has been measured under precisely controlled conditions of reaction atmosphere, exposure temperature, and residence time at atmospheric pressure and temperatures from 300 to 1050 K [78]. Differences in fuel thermal decomposition were analyzed with respect to molecular structure and thermochemical bond energy analysis. The thermal decomposition data for these compounds were used to evaluate their potential heat-sink capacities. In a separate but related study, the gas-phase thermal degradation behavior of MCH was examined for a broad range of reaction conditions. The results indicated that removal of oxygen from the fuel-handling system and a reduction in high-temperature exposure time will greatly enhance the fuel's gas-phase stability.

The kinetics of thermal unimolecular decomposition of MCH were studied at temperatures in the range 861–1218 K using the technique of very-low-pressure pyrolysis (VLPP) [79]. Multiple reaction pathways and secondary decomposition of primary products resulted in a complex array of reaction products. VLPP rate data (fall-off regime) were obtained for the overall decompositions and interpreted via the application of Rice-Ramsperger-Kassel-Marcus (RRKM) theory. The data for methylcyclopentane and methylcyclohexane were interpreted in terms of ring-opening bond fission pathways and bond fission to methyl and cycloalkyl radicals. By selecting Arrhenius parameters consistent with the analogous pathways in open-chain alkanes, a good fit to the overall decomposition was obtained. The VLPP data were consistent with the following high-pressure rate expression (at  $T = 1100$  K) for the dominant primary reaction channel of ring opening adjacent to the substituent group:

$$\log k = (16.4 \pm 0.3) - (341 \pm 10)/\theta$$

where  $k$  is the rate constant in  $\text{s}^{-1}$  and  $\theta = 2.303RT \text{ kJ/mol}$ .

Methylcyclohexane was an essential part of the U.S. Air Force endothermic fuel program. Besides methylcyclohexane, multi-ringed hydrocarbons such as methyldecalin were evaluated as endothermic fuels.

In flight vehicles, the cross-section and aerodynamic drag can be reduced if the fuel has a high density. The search was on for high-density endothermic fuel systems. Additives and impurities have a pronounced effect on the rate of methylcyclohexane pyrolytic dehydrogenation. Cycloalkanes are the preferred endothermic fuels. See also [80].

High-temperature (1050–1200 K) pyrolysis studies of pure methylcyclohexane and oxidation studies of pure methylcyclohexane and methylcyclohexane/toluene blends were performed in a turbulent flow reactor [81]. Decomposition rates were reported at four temperatures between 1058 and 1192 K and at 1 atm, while fuel and ethene time histories were reported only at 1155 K. Ethene, 1,3-butadiene, methane, and propene were found to be the major intermediates produced by

methylcyclohexane pyrolysis. Oxidation of methylcyclohexane also produced the same intermediates. As expected, the observed oxidation reaction rates were faster than the pyrolysis reaction rates.

Pyrolysis of MCH has been investigated in a tubular reactor at atmospheric pressure in the temperature range 953–1073 K [82]. Using non-linear regression, the overall decomposition was found to be approximately first order, with a pre-exponential factor and activation energy of  $A = 1.71 \times 10^{11} \text{ s}^{-1}$  and  $E_{\text{act}} = 209.0 \text{ kJ/mol}$ . The experimental product yields and rates of conversion could be satisfactorily simulated using a molecular model consisting of an overall primary reaction and 24 secondary reactions.

Methylcyclohexane decomposition studies and analysis of the resulting products were carried out in non-pre-mixed air/methane flames at atmospheric pressure. The height above the burner was set such that the temperatures studied were near 1400 K [83]. The observed hydrocarbon products indicated that the specific dissociation pathways for the cycloalkanes were ring-opening isomerization to alkenes. All of the cycloalkanes produced similar distributions of aromatic hydrocarbons, which showed that they formed aromatics by addition reactions between their aliphatic decomposition products, not by direct dehydrogenation of their alkyl rings. Dimethylcyclohexanes produced more benzene than MCH did. The benzene production from MCH was comparable to that from the most-branched heptane isomer (2,3,3-trimethylbutane), which indicated that the cycloalkane portion of practical fuels will have a proportionately greater effect on soot production than the non-cyclic alkane portion.

A detailed kinetic investigation of the dehydrogenation of MCH over a wide range of operating conditions was conducted as part of an evaluation of MCH as a reversible hydrogen storage medium for on-board use of hydrogen in earthbound vehicles where the dehydrogenated product (mostly toluene) would be recycled to a hydrogenation station [65, 84]. The reaction kinetics were incorporated into a 2D pseudo-homogeneous model to predict observed longitudinal temperature profiles in reactors. Kinetic experiments were performed in a laboratory fixed-bed tubular reactor with a 1.0 mass-% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The dehydrogenation of MCH is very selective toward toluene. As well as the main product toluene, a number of condensable by-products were also identified. Benzene, cyclohexane, and ring-closed products (ethylcyclopentane and dimethylcyclopentanes) were the major by-products [85]. See also [86].

Coke deposition during thermal decomposition of MCH may foul catalysts, clog orifices, and impede heat transfer through reactor walls [87]. An abundance of alkyl-substituted C<sub>5</sub> ring hydrocarbons caused the formation of polycyclic aromatic hydrocarbons, which were precursors for coke under supercritical conditions.

Monoalkylcyclohexanes are some of the typical constituents in certain jet fuels. As the first step to study the combustion chemistry of monoalkylcyclohexanes, the unimolecular reactions of MCH were investigated by both theoretical calculations and

experimental measurements for MCH pyrolysis and flames [88]. The temperature- and pressure-dependent kinetics of unimolecular reactions of MCH, including its dissociation and isomerization channels, were computed by high-level quantum chemical calculations, which also revealed the competitive relationship between the two reaction channels. The theoretical predictions were compared to the experimental observations, including species identification, measured by photoionization efficiency spectra. The unimolecular reaction mechanism and corresponding temperature- and pressure-dependent rate constants provided a useful reference for exploring the combustion chemistry of cyclohexanes by kinetic modeling.

A kinetic model consisting of 1216 free-radical and 87 molecular reactions and implying 239 species was developed to describe the thermal decomposition of MCH [89]. The model was tested against experimental published data over a wide range of temperatures (723–1192 K) and conversion (up to more than 90%), at near atmospheric pressure. The model appeared robust enough to be simulated over a wider range of temperatures (523–1273 K) in order to identify the main consumption and production pathways, in particular the aromatization pathways vs. temperature. Under these conditions, the aromatic compounds are mainly formed by dehydrogenation and dealkylation reactions of cyclohexene and alkylcyclohexenes, whatever the temperature. One key point is the formation of cyclohexene and alkylcyclohexenes. It was shown that, at high temperature, they are exclusively formed by free-radical reactions with decompositions by  $\beta$ -scission of C—C and C—H bonds. At low temperature, molecular Diels-Alder reactions become the main pathway.

The thermal decomposition of MCH follows a radical chain mechanism, which mainly includes the C—C bond scission, H-atom abstraction, secondary reactions, and biradical reactions [90]. Thermodynamic data for selected species involved in this study were computed, and the rate constants for all elementary reactions were evaluated with conventional transition state theory in the temperature range of 298–2000 K, where the Eckart method was adopted to correct the quantum mechanical tunneling effect. The rate constants were in reasonable agreement with experimental measurements and previous theoretical reports. The final products of MCH thermal decomposition are methane, ethene, propene, 1,3-butadiene, isoprene, and 1,3-pentadiene.

Synchrotron vacuum UV photoionization mass spectrometry (PIMS) combined with molecular-beam sampling was used to investigate the species formed during the pyrolysis of methylcyclohexane and in pre-mixed flames of methylcyclohexane [91]. A number of pyrolysis and flame intermediates were identified and quantified, especially including radicals (e.g.,  $\text{CH}_3$ ,  $\text{C}_3\text{H}_3$ ,  $\text{C}_3\text{H}_5$ , and  $\text{C}_5\text{H}_5$ ) and cyclic  $\text{C}_6$ - and  $\text{C}_7$ -intermediates (benzene, 1,3-cyclohexadiene, cyclohexene, toluene,  $\text{C}_7\text{H}_{10}$ , and  $\text{C}_7\text{H}_{12}$ ). The observation of cyclic  $\text{C}_6$ - and  $\text{C}_7$ -intermediates provided important experimental evidence to clarify the special formation channels of toluene and benzene that were observed with high concentrations in both pyrolysis and flame of methylcyclohexane. A kinetic model of methylcyclohexane combustion with 249 species and 1570 reactions was developed including a new sub-mechanism of MCH decomposition.

A combined experimental and chemical kinetic modeling study of the high-temperature ignition and pyrolysis of 1,3-dimethylcyclohexane measured ignition-delay times behind reflected shock waves over a temperature range of 1049–1544 K and pressures of 3.0–12 atm [92]. Pyrolysis was investigated at average pressures of 4 atm at temperatures of 1238, 1302, and 1406 K. By means of mid-infrared direct laser absorption at 3.39  $\mu\text{m}$ , fuel concentration time histories were measured under ignition and pyrolysis conditions. Ignition measurements showed that the ignition-delay times of 1,3-dimethylcyclohexane were longer than those of its isomer, ethylcyclohexane.

The thermal decomposition of MCH was investigated using reactive molecular dynamics and density functional theory calculations in order to better understand the initiation and intermediate reaction mechanisms associated with the high-temperature pyrolysis of methylcyclohexane [93]. It was shown that the pyrolysis of MCH is initiated by four types of reaction channels. The initiation of the decomposition is mainly through the C–C bond homolysis of the six-membered ring, leading to ring opening and the formation of  $\text{C}_7\text{H}_{14}$  diradicals. Subsequently, the biradicals undergo successive decomposition by the  $\beta$ -scission of the C–C bonds to form ethene. The apparent activation energy extracted from the simulations was 263 kJ/mol at temperatures from 2300 to 3100 K, which was reasonably consistent with experimental results.

### 7.3.2 Catalytic Decomposition (Dehydrogenation) of Methylcyclohexane

There are numerous publications about the dehydrogenation of cyclohexane (not included here), and many of those relate to the dehydrogenation of MCH. The rapid dehydrogenation of MCH as an endothermic fuel and as a hydrogen storage medium depends on the availability of active catalysts [94–105], some of which are based on zeolites [106]. Similar catalysts and reactors are applicable to the dehydrogenation of decalin. Catalyst development work for this dehydrogenation reaction may initially have been motivated by the petroleum refining industry in trying to improve the octane rating of gasoline, but most of the recent work was in support of the use of MCH as a reversible hydrogen storage medium. Its use in endothermic fuels for cooling of hypersonic flight vehicles would benefit from all of these previous uses. The effect of propane on the catalytic dehydrogenation of MCH was investigated [97].

Rhodium catalysts supported on  $\text{SiO}_2\text{--Al}_2\text{O}_3$  oxides with varying  $\text{SiO}_2$  content were evaluated in the cracking reaction of methylcyclohexane at 873–1023 K (600–750  $^\circ\text{C}$ ) and 4 MPa [107]. It was found that  $\text{Rh/SiO}_2/\text{Al}_2\text{O}_3$  catalysts exhibited better cracking activity than thermal cracking tested in parallel tests under identical operating conditions. The catalytic activity of these Rh-supported catalysts depended greatly on the  $\text{SiO}_2$  content. The activity initially increased with the content of  $\text{SiO}_2$ , until about 60 mass-%, and then it declined when  $\text{SiO}_2$  constituted a majority (85 and 100 mass-%) in the catalyst carrier. Particularly, catalysts with 60 mass-%  $\text{SiO}_2$  achieved the best catalytic performance with regard to the gas yield, methylcyclohex-

ane conversion, and heat sink capability, which were increased by 56.1%, 16.0%, and 0.28 MJ/kg, respectively, in comparison to thermal cracking at 948 K (675 °C).

Three types of  $\text{ZrO}_2/\text{TiO}_2/\text{Al}_2\text{O}_3$  catalysts with and without platinum active metal were prepared to investigate the coke deposition during pyrolysis of supercritical MCH at 923 K (650 °C) and 4 MPa [108]. Based on GC/MS analysis results, it was observed that the alkene content in liquid products over platinum-loaded catalysts was higher than that in products obtained on bare supports. But for the aromatics, e.g., benzene and toluene, the yields over platinum-loaded samples were obviously less than those on bare supports. It was found that the deposition of platinum on the metal oxide catalyst supports prevented the formation of aromatics. The coke formed over pure supports was more crystalline ordered, with a higher dehydrogenation extent than those produced on the platinum-loaded samples. Platinum-loaded catalysts restrained the generation and polymerization of coke intermediates.

Cracking of MCH in a micro-channel reactor was investigated under supercritical conditions with a series of transition metal M (M = Fe, Co, Ni)-loaded  $\text{SiO}_2$  catalysts coated on the inner wall of stainless-steel tubes in micro-channel reactors [109]. The results showed that the cracking activity and endothermic capacity of MCH increased in the following order:  $\text{Fe}/\text{SiO}_2 < \text{Co}/\text{SiO}_2 < \text{Ni}/\text{SiO}_2$ . The gas yield, conversion, and heat sink capability at 1023 K (750 °C) over  $\text{Ni}/\text{SiO}_2$  increased by 15.4%, 21.3%, and 0.32 MJ/kg, respectively, compared with non-catalyzed thermal cracking.

Monolithic catalysts made from a skeleton of high-thermal-conductivity open-celled metal foam coated with a catalytic coating of zeolites were characterized by Fourier-transform infrared spectroscopy (FTIR) analysis and  $\text{NH}_3$ -temperature programmed desorption analysis [110]. In initial experiments of H-ZSM-5 catalyst pellets, the conversion of MCH was only about 82%. In the case of the H-ZSM-5 catalyst supported on metal foam, the conversion of MCH was about 93%, and the conversion was 11% higher than that of the pelletized zeolite catalyst itself.

### 7.3.3 Oxidation of Methylcyclohexane

Oxidation of MCH leading to ignition and combustion will be discussed in more detail in Volume 5 together with non-hypergolic bipropellant combinations. Here are a few publications that deal both with decomposition and oxidation, and they may be referenced in both places. In many instances, decomposition precedes ignition and combustion.

Although the combustion chemistry of aliphatic hydrocarbons has been extensively documented, the oxidation of cyclic hydrocarbons has been studied to a much lesser extent. To provide a better understanding of the combustion chemistry of cycloaliphatics, the oxidation of MCH was studied in a series of high-temperature shock tube experiments [111]. Ignition-delay times for a series of mixtures of varying MCH/oxygen equivalence ratios ( $\varphi = 0.5, 1.0, 2.0$ ) were measured over reflected shock



temperatures of 1200–2100 K and reflected shock pressures of 1.0, 2.0, and 4.0 atm. A detailed chemical kinetic mechanism was assembled to simulate the shock tube results and flow reactor experiments, with good agreement observed.

#### 7.4 Safety Properties of Methylcyclohexane

Based on information in material safety data sheets (MSDSs), the flammability range of methylcyclohexane in air is 1.2 to 6.7 vol.-%. The closed-cup flash point is 269 K ( $-3.9^{\circ}\text{C} = 25^{\circ}\text{F}$ ). The autoignition temperature of methylcyclohexane in air is 538 K ( $265^{\circ}\text{C} = 509^{\circ}\text{F}$ ).

#### 7.5 Toxicity of Methylcyclohexane

Four animal species were exposed for 1 year to selected vapor concentrations of MCH to determine its long-term toxic effects [112, 113]. Year-long exposures of animals were conducted to MCH at 0, 400, and 2000 parts per million (ppm). Rats, mice, and hamsters were held for 1 year post exposure, while dogs were held for 5 years post exposure. Mean body weight depression was observed in the MCH-exposed hamsters and male rats. The only significant lesion noted in any of the animals was progressive renal nephropathy, which was seen in virtually all of the male rats. The acute toxicity of MCH is as follows: oral mouse LD<sub>50</sub>, 2250 mg/kg; inhalation mouse LC<sub>50</sub>, 41500 mg/m<sup>3</sup> for two hours.

The American Conference of Governmental Industrial Hygienists (ACGIH) recommended threshold limit value (TLV) for methylcyclohexane is 400 ppm (time-weighted average [TWA]). The U.S. Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) TWA is 500 ppm (2000 mg/m<sup>3</sup>), and the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) TWA is 400 ppm (1600 mg/m<sup>3</sup>). The NIOSH Immediately Dangerous to Life and Health (IDLH) limit is 1200 ppm, which is also the lower limit of flammability in air [114, 115].

#### 7.6 Applications of Methylcyclohexane

Methylcyclohexane is used as a fuel constituent in JP-9. The air-launched cruise missile uses PF-1 priming fluid (MIL-P-87173) to aid in engine ignition. PF-1 is approximately 90% JP-10 and 10% MCH. Physical properties have been estimated for binary mixtures of MCH and low molecular weight hydrocarbons for mixtures containing ethane, propane, and *n*-butane [97].

## 8 Ethylcyclohexane and Diethylcyclohexane

Rocketdyne conducted extensive experimentation with diethylcyclohexane (DECH) in 1959 and proposed it as an alternative to RP-1 because of its reduced coking, lower sulfur content, higher heat transfer coefficient, and lower freezing point. Of the relatively few candidate chemicals that had sufficiently wide commercial availability and physical properties similar to RP-1 to enable direct substitution, DECH and *p*-menthane were selected for detailed experimental evaluation [116]. DECH is a highly reproducible mixture of isomers readily available from the polymer industry. Even though the experiments succeeded in showing DECH as being appreciably superior to RP-1, it was too late for a changeover. The development of the Atlas and Titan-I intercontinental ballistic missile (ICBM) systems had proceeded too far to justify changing from RP-1 fuel to DECH, and RP-1's incumbency as the standard U.S. hydrocarbon rocket fuel has continued from then to the present day [117] (or until it was replaced by RP-2). It now appears that current batches of RP-1 and its more advanced versions do contain large quantities of the branched cyclohexanes, but at a cost of only 20% of that of the projected cost of DECH.

The pyrolysis of ethylcyclohexane (ECH) was studied in a flow reactor at atmospheric pressure [118]. The pyrolysis products were analyzed by synchrotron vacuum UV PIMS and gas chromatography. Dozens of species were identified and quantified, including many isomers, in order to investigate the primary decomposition of ECH, including its initial decomposition, isomerization, and further reactions of the cyclic  $C_8H_{15}$  radicals formed from the H-abstraction of ECH. The observation of  $C_8H_{16}$  alkene indicated the existence of ring-opening isomerization reaction of ECH. The ring-opening isomerization reaction of cyclic  $C_8H_{15}$  radicals produces alkenyl radicals, whose further decomposition constitutes the various chain and branched intermediates in ECH pyrolysis. The formation of isoprene and vinylcyclopentane is due to isomerization reactions of radical addition on the double bond of alkenyl radicals.

Ethylcyclohexane is a model compound for cycloalkanes with long alkyl side chains [119]. The flow reactor pyrolysis of ECH at various pressures (30, 150, and 760 mm Hg) was studied using synchrotron vacuum UV PIMS and gas chromatography. The mole-fraction profiles of numerous major and minor species were evaluated, and good agreement was observed between the PIMS and GC data sets. A detailed kinetic model for ECH high-temperature pyrolysis and oxidation was developed and validated against the pyrolysis and flame data. Further validation of the kinetic model was presented by comparison with literature data, including species concentrations in jet-stirred reactor oxidation, ignition-delay times in a shock tube, and laminar flame speeds at various pressures and equivalence ratios. The model predicted the rate of consumption of ECH, the growth of aromatics, and the global combustion properties. Reaction flux and sensitivity analysis were used to explain chemical kinetic features of ECH combustion under various reaction conditions.

The standard enthalpy of formation of a similar homologue molecule, dimethylcyclohexane vapor, is  $-181 \text{ kJ/mol}$  ( $-43.26 \text{ kcal/mol}$ ) [120].

## 9 Propylcyclohexane

Propylcyclohexane,  $\text{C}_9\text{H}_{18}$ , CAS RN [1678-92-8], has not been used as a rocket fuel as such, but the physical and thermochemical properties of pure propylcyclohexane were measured so that it could be used as a constituent of surrogate fuel mixtures. This was done as part of an effort to develop surrogate fuels to represent the thermophysical properties of aviation kerosenes with the more general description of Jet-A and JP-8 [71]. It was not always clear whether the compounds tested were *n*-propylcyclohexane or isopropylcyclohexane. One must assume that the properties of these two structural isomers differ slightly.

### 9.1 Physical Properties of Propylcyclohexane

Data for density, velocity of sound, and adiabatic compressibility of propylcyclohexane are listed in Table 11 in the section on methylcyclohexane. The thermal conductivity of propylcyclohexane liquid and vapor was measured in comparison to that of methylcyclohexane, covering a temperature range of 300 to 600 K and a pressure range of 0.1 to 60 MPa and was used to develop a correlation for the thermal conductivity [69]. The thermal conductivity of liquid propylcyclohexane at 300 K is  $0.111 \text{ W m}^{-1} \text{ K}^{-1}$  at a density of  $788 \text{ kg/m}^3$ . The thermal conductivity of liquid propylcyclohexane at 450 K under 50 MPa pressure is  $0.105 \text{ W m}^{-1} \text{ K}^{-1}$  at a density of  $729 \text{ kg/m}^3$ .

### 9.2 Chemical Properties of Propylcyclohexane

Aliquots of propylcyclohexane were thermally stressed in sealed stainless-steel ampule reactors with an initial pressure of 34.5 MPa (5000 psi) and temperatures of 648, 673, 698, and 723 K (375, 400, 425, and 450 °C) [121]. These conditions represented the high-pressure conditions that existed during some of physical property measurements. This temperature range was chosen because it allowed for reaction times of a convenient length. At 648 K (375 °C), the reaction was relatively slow, so reaction times ranged from 16 to 32 h. At 723 K (450 °C), the reaction was much faster, so reaction times ranged from 10 to 40 min. At each temperature, the extent of decomposition was determined as a function of time by gas chromatography. These data were used to derive first-order rate constants for the decomposition of propylcyclohexane. Decomposition rate constants ranged from  $3.66 \times 10^{-7} \text{ s}^{-1}$  at 648 K (375 °C) to  $8.63 \times 10^{-5} \text{ s}^{-1}$  at

723 K (450 °C). The kinetic data were used to determine Arrhenius parameters of  $A = 2.56 \times 10^{16} \text{ s}^{-1}$  and  $E_{\text{act}} = 283 \text{ kJ/mol}$ .

In a similar test, the thermal decomposition kinetics of 1,3,5-triisopropylcyclohexane were studied between 623 and 698 K (350 and 425 °C) in stainless-steel ampule reactors [122]. At each temperature, the extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase by gas chromatography. These data were used to derive pseudo-first-order rate constants that ranged from  $2.38 \times 10^{-7} \text{ s}^{-1}$  at 623 K (350 °C) to  $7.28 \times 10^{-5} \text{ s}^{-1}$  at 698 K (425 °C). The Arrhenius parameters of the thermal decomposition of 1,3,5-triisopropylcyclohexane were  $A = 5.67 \times 10^{16} \text{ s}^{-1}$  and  $E_{\text{act}} = 279 \text{ kJ/mol}$ . The kinetics of *n*-alkylcyclohexane pyrolysis depend on the chain length of the attached alkyl group [123].

### 9.3 Fused-Ring Cycloaliphatic Compounds

Attaching one or several cycloaliphatic rings to each other or making bridging bonds across the inside of a ring from two opposite carbon atoms opens up a new field of high-energy fuels that are used mostly for air-breathing engines but may have potential use as high-density rocket fuels. Illustrating the chemical structures of many of these molecules requires 3D drawings, which are hard to reproduce here in 2 dimensions on flat paper. It would be desirable to display these 3D molecular structures in this book as GIF images that would rotate in front of the viewer and allow observation of the molecules from all angles of view. Some websites already have that capability.

## 10 Tetralin

Tetralin, also known as 1,2,3,4-tetrahydronaphthalene, tetrahydronaphthalene,  $\text{C}_{10}\text{H}_{12}$ , CAS RN [119-64-2], is an aromatic hydrocarbon and should be discussed in the chapter “Aromatic Hydrocarbons.” Because it is so closely related to decalin, it is discussed here next to decalin, the result of complete hydrogenation of naphthalene.

### 10.1 Physical Properties of Tetralin

Tetralin freezes at 237.3 K (−35.8 °C) and boils at 481 K (207.6 °C). The density of tetralin at 293 K is  $0.9702 \text{ g/cm}^3$  [124]. The vapor pressure of liquid tetralin in the temperature range 370–446 K can be calculated from the equation

$$\log P = (-2797.9/T) + 11.954 - 1.187 \log T$$

where  $P$  is the vapor pressure in mmHg and  $T$  is the temperature in kelvin [2]. The enthalpy of formation of tetralin vapor is  $+22.1 \pm 3.4$  kJ/mol ( $+5.29 \pm 0.81$  kcal/mol). The enthalpy of formation of liquid tetralin is  $-33.1 \pm 2.1$  kJ/mol ( $-7.91 \pm 0.51$  kcal/mol). The heat of combustion of liquid tetralin is  $5617 \pm 2$  kJ/mol ( $1342.6 \pm 0.51$  kcal/mol). The heat of evaporation of liquid tetralin is  $55.2 \pm 1.2$  kJ/mol ( $13.20 \pm 0.3$  kcal/mol) at 298 K and  $49.9 \pm 0.8$  kJ/mol ( $11.92 \pm 0.2$  kcal/mol) at 380 K. The refractive index  $n_D^{20}$  of tetralin is 1.5413.

The results of heat capacity measurements of subcritical tetralin at saturation pressure between 300 and 720 K were given only in table format [125]. It would have been more practical to give the parameters for a curve-fitted polynomial equation.

## 10.2 Safety Properties of Tetralin

### 10.2.1 Flammability of Tetralin

The autoignition temperature of tetralin in air is 696 K ( $423^\circ\text{C} = 794^\circ\text{F}$ ), which is much higher than that of decalin.

### 10.3 Toxicity of Tetralin

The LD50 (rats, oral) of tetralin is 2.68 g/kg. Tetralin induces methemoglobinemia.

## 11 Decalin

Decalin, also known as decahydronaphthalene, bicyclo[4.4.0]decane,  $\text{C}_{10}\text{H}_{18}$ , *cis*-decalin [CAS RN 493-01-6], *trans*-decalin [CAS RN 493-02-7], also CAS RN [91-17-8], has been used as an endothermic fuel and as a fuel additive. Decalin is thermally stable and readily available and has advantages in high-speed vehicle applications because of its relatively low vapor pressure, high density, and good volumetric heat of combustion.

### 11.1 Preparation of Decalin

Decalin is prepared by hydrogenation of naphthalene in the presence of a catalyst. A commercial mixture of *trans/cis*-decahydronaphthalene produced by DuPont may be sold as a brand-marked chemical and is spelled with a capital first letter: Decalin.

Decahydronaphthalene (decalin) is a potential fuel that could provide the heat sink required for high-Mach air-breathing vehicles. At the beginning of these programs, domestic suppliers of decalin were identified, and production rates were deter-

mined. Only one producer of decalin was identified, but production capacity of these cycloalkane materials was limited at that time, and the materials were sold only as specialty chemicals with an associated high cost.

## 11.2 Physical Properties of Decalin

Physical properties of decalin are listed in Table 16. A separate table, Table 19, gives the thermodynamic properties of decalin.

**Table 16:** Physical properties of decalin.

| Property                                                      | SI units                                               | Other units                                              | References |
|---------------------------------------------------------------|--------------------------------------------------------|----------------------------------------------------------|------------|
| Molecular mass                                                | 138.2499 g/mol                                         | 7.2333 mol/kg                                            |            |
| Freezing point, <i>cis</i>                                    | 230.3 K                                                | −42.9 °C = −45.2 °F                                      | [17]       |
| Freezing point, <i>trans</i>                                  | 242.7 K                                                | −30.4 °C = −22.7 °F                                      |            |
| Boiling point, <i>cis</i>                                     | 469 K                                                  | 196 °C = 384 °F                                          |            |
| Boiling point, <i>trans</i>                                   | 460 K                                                  | 187 °C = 369 °F                                          |            |
| Density at 293 K                                              | 0.8837 g/cm <sup>3</sup><br>0.896 g/cm <sup>3</sup>    | 7.375 lb <sub>m</sub> /gal<br>7.477 lb <sub>m</sub> /gal | [126]      |
| Vapor pressure at 293 K                                       | 0.353 kPa                                              | 2.6 mm Hg                                                | [126]      |
| Viscosity                                                     | 2.702 × 10 <sup>−3</sup> Ns/m <sup>2</sup><br>at 293 K | 2.702 cPs at 20 °C                                       | [126]      |
| Viscosity, <i>cis</i> -decalin, at 303 K                      | 2.723 mPa s                                            | 2.723 cPs                                                | [127]      |
| Viscosity, <i>trans</i> -decalin, at 303 K                    | 1.774 mPa s                                            | 1.774 cPs                                                |            |
| Surface tension, <i>cis</i> -decalin                          | 32.18 mN/m                                             | 32.18 dyn/cm                                             | [128]      |
| Surface tension, <i>trans</i> -decalin                        | 29.89 mN/m                                             | 29.89 dyn/cm                                             |            |
| Thermal conductivity, <i>cis</i> -decalin,<br>at 302 to 391 K | 1.365 to<br>1.183 mW cm <sup>−1</sup> K <sup>−1</sup>  | —                                                        | [129]      |
| Thermal conductivity, <i>trans</i> -decalin,<br>at 302–391 K  | 1.381 to<br>1.223 mW cm <sup>−1</sup> K <sup>−1</sup>  | —                                                        |            |
| Refractive index, <i>n</i> <sub>D</sub> <sup>20</sup>         | 1.481                                                  | —                                                        |            |
| Critical temperature, <i>cis</i> -decalin                     | 704 ± 3 K                                              | 431 ± 3 °C                                               | [17]       |
| Critical temperature, <i>trans</i> -decalin                   | 687 ± 3 K                                              | 414 ± 3 °C                                               |            |
| Critical pressure, <i>cis</i> -decalin                        | 32 ± 2 bar                                             | 31.6 ± 2 atm                                             |            |

### 11.2.1 Freezing Point of Decalin

The freezing points of the two conformers of decalin are quite different: *trans*-decalin melts at 242.7 K (−30.4 °C = −22.7 °F) and *cis*-decalin melts at 230.3 K (−42.9 °C = −45.2 °F). The fusion temperature listed in NIST Chemistry WebBook (149 K) is in error.

### 11.2.2 Boiling Point of Decalin

The boiling points of the two conformers of decalin are quite different: *trans*-decalin boils at 460 K (187 °C = 369 °F), and *cis*-decalin boils at 469 K (196 °C = 384 °F).

### 11.2.3 Vapor Pressure of Decalin

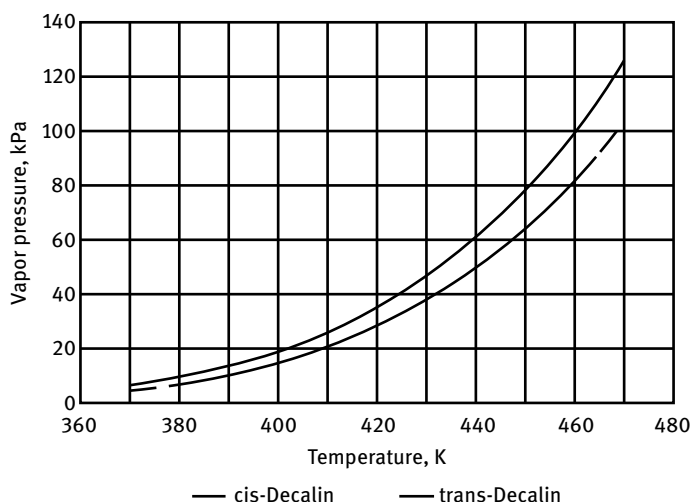
The NIST Chemistry WebBook website gives Antoine equations for decalin for the range 373–469 K, both for *cis*- and *trans*-decalin. The first equation is for *cis*-decalin:

$$\log P = A - [B/(T + C)] = 4.00047 - [1594.687/(T - 69.731)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. And the same type of equation for the vapor pressure of *trans*-decalin is

$$\log P = A - [B/(T + C)] = 3.99304 - [1572.899/(T - 65.947)]$$

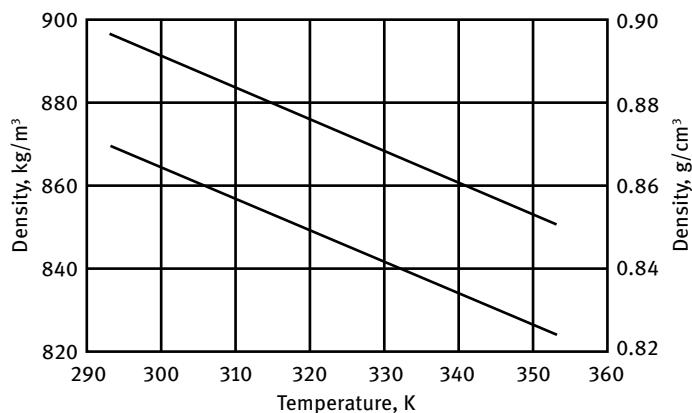
Vapor-pressure data derived from these equations are shown in Figure 8 to illustrate the difference between the two conformers.



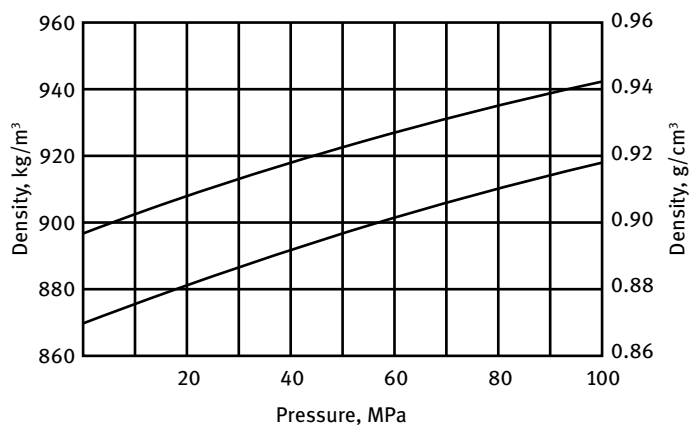
**Figure 8:** Vapor pressures of *cis*- and *trans*-decalin. (Image created by Schmidt 2020 based on data from [17].)

### 11.2.4 Density of Decalin

A study of the stereoisomeric influence and effect on the density of decalin was performed by carrying out experimental measurements up to 100 MPa in the temperature range 293–353 K in increments of 10 K [130]. The density of *cis*- and *trans*-decalin as a function of temperature is shown in Figure 9. The density of *cis*-decalin is substantially higher than that of *trans*-decalin. Similar data were reported 60 years earlier [128]. A similar relationship was observed for viscosity.



**Figure 9:** Density of *cis*- (—) and *trans*- (---) decalin as a function of temperature. (Image created by Schmidt 2020 based on data from [130].)



**Figure 10:** Density of *cis*- (—) and *trans*- (---) decalin as a function of pressure. (Image created by Schmidt 2020 based on data from [130].)

The density of *cis*- and *trans*-decalin at 293 K as a function of pressure is shown in Figure 10. Data for density and dynamic viscosity of a decalin isomer mixture (41.06% *cis* and 58.69% *trans*), a commercial grade of decalin, are listed in Table 17. That reference also contains data on mixtures of decalin with cyclohexane or toluene. Single-point measurements for densities of *cis*- and *trans*-decalin gave *cis*-decalin  $\rho = 0.89685 \text{ g/cm}^3$  and *trans*-decalin  $\rho = 0.86978 \text{ g/cm}^3$  [131].



**Table 17:** Density and dynamic viscosity of a decalin isomer mixture (41.06% *cis* and 58.69% *trans*).

| Temperature<br><i>T</i> | Density<br>kg/m <sup>3</sup> | Viscosity<br>mPa s |
|-------------------------|------------------------------|--------------------|
| 283                     | 0.88780                      | 3.09742            |
| 293                     | 0.88025                      | 2.50378            |
| 303                     | 0.87270                      | 2.06586            |
| 313                     | 0.86515                      | 1.73385            |
| 323                     | 0.85765                      | 1.47722            |

Data source: [132]

### 11.2.5 Viscosity of Decalin

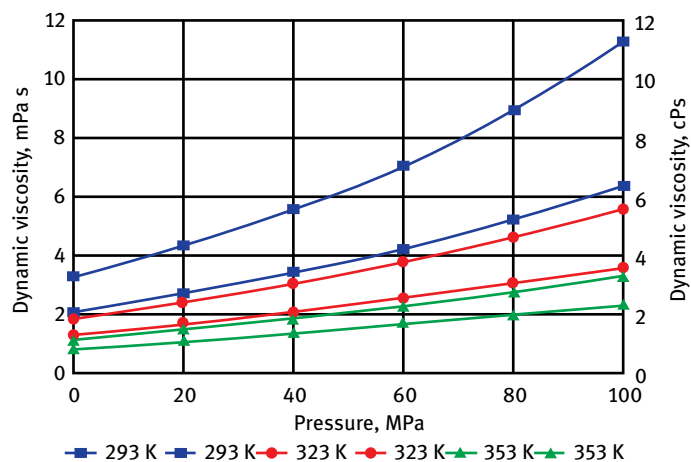
The viscosity of the *cis* and *trans* isomers of decalin has been measured in the range 243 to 453 K (−30 to +180 °C) [127]. The viscosity of the *trans* isomer was always less than that of the *cis* isomer. Viscosity measurements have been made on nine pure hydrocarbon liquids, including *cis*- and *trans*-decalin, at six temperatures ranging from 288 to 408 K (15 to 135 °C) and at pressures as high as 4000 bars [133].

A study of the stereoisomeric influence and effect on the dynamic viscosity was performed by carrying out experimental measurements up to 100 MPa in the temperature range 293 to 353 K in increments of 10 K [130]. Decahydronaphthalene (decalin) exists in two stereoisomeric molecular configurations, a *cis* and a *trans* configuration. The *cis* and *trans* isomers have different physical properties. In a study of the stereoisomeric effect on the dynamic viscosity (and density) versus pressure and temperature at up to 100 MPa in the temperature range 293 to 353 K, it was found that the viscosity of *cis*-decalin is higher than that of *trans*-decalin in the considered temperature and pressure ranges due to the twisted structure of *cis*-decalin compared to the relatively more symmetrical and rigid structure of *trans*-decalin (Figures 11 and 12). The density of *cis*-decalin is around 3% higher than for *trans*-decalin.

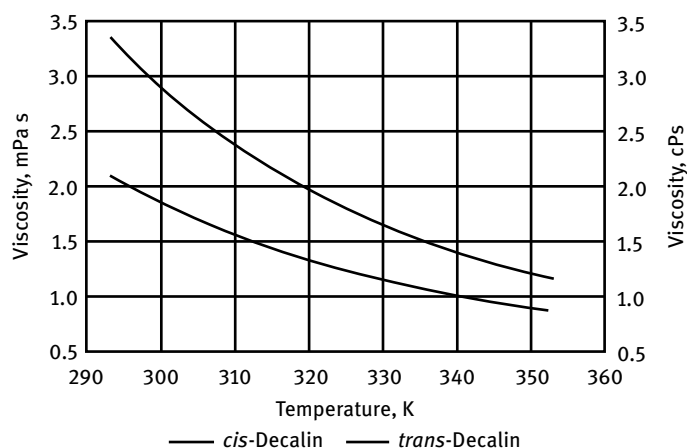
The dynamic viscosity of decalin at atmospheric pressure as a function of temperature is illustrated in Figure 12. The viscosity of liquid *cis*-decalin is higher than that of *trans*-decalin. The higher viscosity of liquid *cis*-decalin is due to its more twisted and less symmetrical molecular structure compared to the relatively more symmetrical and rigid molecule of *trans*-decalin.

Data for dynamic viscosity of a decalin isomer mixture (41.06% *cis* and 58.69% *trans*) are included in Table 17 (in the density section) [132]. That reference also includes viscosity data for mixtures of decalin with cyclohexane or toluene.

Viscosity and density measurements for binary mixtures composed of methylcyclohexane and *cis*-decalin in the temperature range 293 to 353 K and at pressures up to 100 MPa were carried out with a falling-body viscometer, except at atmospheric pressure, where an Ubbelohde viscometer was used [134]. The density was measured up to 60 MPa and was extrapolated by a Tait-type relationship to 100 MPa.

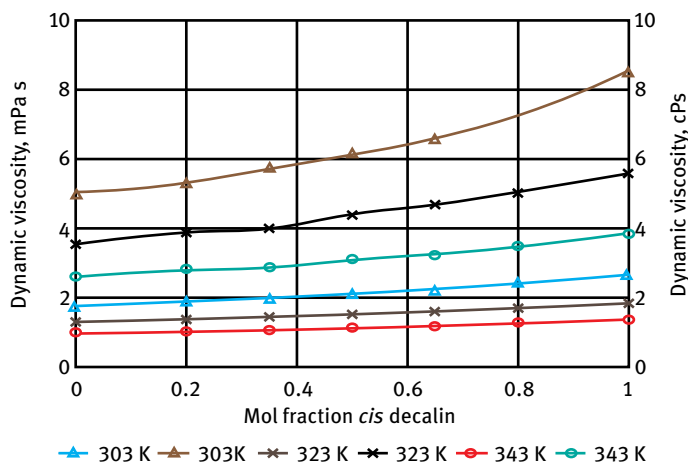


**Figure 11:** Viscosity as a function of pressure for *cis*-decalin (—) and *trans*-decalin (---). (Image created by Schmidt 2020 based on data from [130].)



**Figure 12:** Dynamic viscosity as a function of temperature for *cis*-decalin and *trans*-decalin. (Image created by Schmidt 2020 based on data from [130].)

The dynamic viscosities of controlled mixtures of *cis*- and *trans*-decalin were measured as a function of the *cis* : *trans* ratio for five different mixtures at three temperatures K and six isobars up to 100 MPa, as shown in Figure 13 [135, 136]. The variations of dynamic viscosity versus composition were discussed with respect to their behavior due to stereoisomerism. Four different models with a physical and theoretical background were studied in order to investigate how they take the stereoisomeric effect into account through their required model parameters. All the models were able to distinguish between the two stereoisomeric decalin compounds.



**Figure 13:** Dynamic viscosity versus mol fraction  $x$  for *cis*-decalin. (Image created by Schmidt 2020 based on data from [135].)

Legend: At 20 MPa (bottom three lines, thin lines —) and 100 MPa (top three lines, heavy lines —) for various isotherms (open triangle = 303 K,  $\times$  = 323 K, and open circles = 343 K).

The viscosities, flash points, and refractive indices of mixtures of decalin with  $C_9$  to  $C_{11}$  *n*-alkanes were measured at pressure  $p = 0.1$  MPa and different temperatures ranging from 293 to 323 K [131]. In addition to data for hydrocarbon mixtures, that study included viscosity data for the pure compounds, with the results shown in Table 18.

The transport properties of mixtures of decalin with propane were modeled. Propane was added to decalin as a supercritical fluid solvent that was supposed to help transfer heat from the wall to the suspended decalin molecules for dehydrogenation and release of dihydrogen. The density and viscosity of propane mixed with 66/34 *trans/cis*-decahydronaphthalene were measured over a wide range of

**Table 18:** Dynamic viscosity of *cis*- and *trans*-decalin

| Temperature, K | Dynamic viscosity, mPa s |                       |
|----------------|--------------------------|-----------------------|
|                | <i>cis</i> -decalin      | <i>trans</i> -decalin |
| 293.15         | 3.355                    | 2.112                 |
| 298.15         | 3.011                    | 1.925                 |
| 303.15         | 2.718                    | 1.769                 |
| 308.15         | 2.470                    | 1.628                 |
| 313.15         | 2.252                    | 1.505                 |
| 318.15         | 2.079                    | 1.394                 |
| 323.15         | 1.912                    | 1.295                 |

Data source: [131]

temperatures (323–423 K), pressures (2.5–208 bar), and compositions (0–65 mol-% propane) [137].

### 11.2.6 Surface Tension of Decalin

The surface tension of *cis*- and *trans*-decalin was measured over the temperature range 253 to 453 K (–30 to +180 °C) along with the density of the same samples [128]. The surface tensions of *cis*- and *trans*-decalin at 293 K (20 °C) were 32.18 and 29.89 mN/m (32.18 and 29.89 dyn/cm) for samples with densities of 0.8967 and 0.8700 g/cm<sup>3</sup>, respectively.

### 11.2.7 Thermal Conductivity of Decalin

The thermal conductivity  $\lambda$  was measured in the temperature range 302–392 K for the *cis* and *trans* isomers of decahydronaphthalene and their commercially available mixture (32.15 mass-% *trans*) [129]. See also [138].

### 11.2.8 Thermodynamic Properties of Decalin

Thermodynamic properties of decalin are summarized in Table 19.

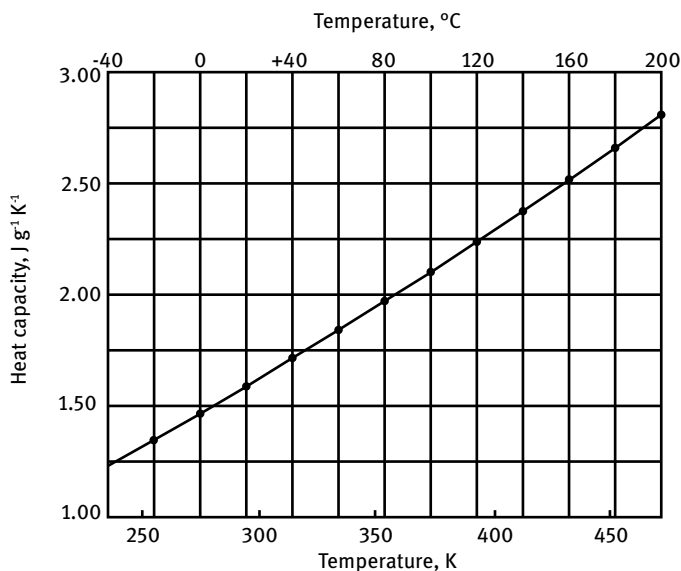
**Table 19:** Thermodynamic properties of decalin.

| Property                                                                          | SI units                                          | Other units                                              |
|-----------------------------------------------------------------------------------|---------------------------------------------------|----------------------------------------------------------|
| Molecular mass                                                                    | 138.2499 g/mol                                    | 7.2333 mol/kg                                            |
| Heat capacity, $C_p$ , vapor, at 298 K, <i>cis</i> -decalin                       | $168.1 \pm 1.0 \text{ J mol}^{-1} \text{ K}^{-1}$ | $40.18 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| Heat capacity, $C_p$ , vapor, at 298 K, <i>trans</i> -decalin                     | $168.6 \pm 1.0 \text{ J mol}^{-1} \text{ K}^{-1}$ | $40.30 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| Heat capacity, $C_p$ , liquid, at 298 K                                           | $232.08 \text{ J mol}^{-1} \text{ K}^{-1}$        | $55.46 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| Heat capacity, $C_p$ , liquid, at 298 K, <i>trans</i> -decalin                    | $229.17 \text{ J mol}^{-1} \text{ K}^{-1}$        | $54.77 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| Standard enthalpy of formation, vapor, $\Delta H_f^{298}$ , <i>cis</i> -decalin   | $-169.2 \pm 2.3 \text{ kJ/mol}$                   | $-40.44 \pm 0.55 \text{ kcal/mol}$                       |
| Standard enthalpy of formation, vapor, $\Delta H_f^{298}$ , <i>trans</i> -decalin | $-182.2 \pm 2.3 \text{ kJ/mol}$                   | $-43.55 \pm 0.55 \text{ kcal/mol}$                       |
| Heat of combustion, liquid, <i>cis</i> -decalin                                   | $6288.22 \pm 0.92 \text{ kJ/mol}$                 | $1502.8 \pm 0.22 \text{ kcal/mol}$                       |
| Heat of combustion, liquid, <i>trans</i> -decalin                                 | $6276.96 \pm 0.92 \text{ kJ/mol}$                 | $1500.2 \pm 0.22 \text{ kcal/mol}$                       |
| Enthalpy of formation, liquid, $\Delta H_f^{298}$ , <i>cis</i> -decalin           | $-281.05 \text{ kJ/mol}$                          | $-67.17 \text{ kcal/mol}$                                |
| Enthalpy of formation, liquid, $\Delta H_f^{298}$ , <i>trans</i> -decalin         | $-230.7 \pm 0.92 \text{ kJ/mol}$                  | $-55.14 \pm 0.22 \text{ kcal/mol}$                       |
| Enthalpy of vaporization at NBP, <i>cis</i> -decalin                              | $50.2 \pm 2.1 \text{ kJ/mol}$                     | $12.00 \pm 0.50 \text{ kcal/mol}$                        |
| Enthalpy of vaporization at NBP, <i>trans</i> -decalin                            | $48.5 \pm 2.1 \text{ kJ/mol}$                     | $11.59 \pm 0.50 \text{ kcal/mol}$                        |

NBP = normal boiling point; Data source: [17]

### 11.2.8.1 Heat Capacity of Decalin

The heat capacity of a commercial mixture of decalin stereoisomers as a function of temperature is illustrated in Figure 14.



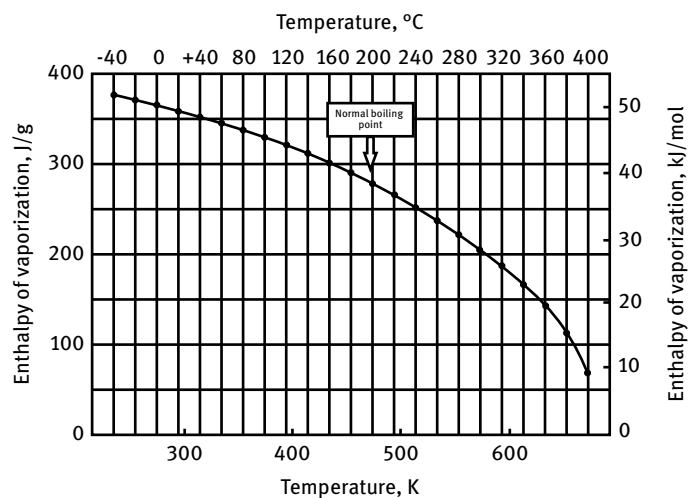
**Figure 14:** Heat capacity of a commercial mixture of liquid decalin stereoisomers as a function of temperature. (Reproduced and modified from [126].)

### 11.2.8.2 Enthalpy of Formation of Decalin

The stereoisomers of decalin have slightly different enthalpies of formation:  $\Delta H_f^{298}$ , *cis*-decalin =  $-281.05 \text{ kJ/mol} = -67.17 \text{ kcal/mol}$  and  $\Delta H_f^{298}$  and *trans*-decalin =  $-230.7 \pm 0.92 \text{ kJ/mol} = -55.14 \pm 0.22 \text{ kcal/mol}$ .

### 11.2.8.3 Enthalpy of Vaporization and Enthalpy of Sublimation of Decalin

The heat of sublimation of *cis*-decahydronaphthalene is  $64.8 \text{ kJ/mol}$  at  $230 \text{ K}$  and  $62.5 \text{ kJ/mol}$  at  $298 \text{ K}$ . The heat of sublimation of *trans*-decahydronaphthalene is  $66.2 \text{ kJ/mol}$  at  $241 \text{ K}$  and  $64.3 \text{ kJ/mol}$  at  $298 \text{ K}$  [139]. The enthalpy of vaporization of a stereoisomer mixture of decalins as a function of temperature at the saturation point is illustrated in Figure 15.

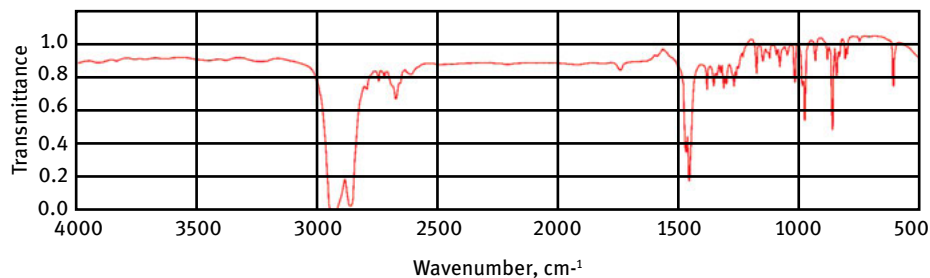


**Figure 15:** Enthalpy of vaporization of a stereoisomer mixture of decalins as a function of temperature at the saturation point. (Reproduced and modified from [126].)

## 11.2.9 Optical Properties of Decalin

### 11.2.9.1 Infrared Spectrum of Decalin

The IR spectrum of *cis*-decalin is shown in Figure 16.



**Figure 16:** Infrared spectrum of *cis*-decahydronaphthalene. (Reproduced and modified with permission from [140].)

### 11.2.9.2 Refractive Index of Decalin

Extended measurements of refractive indices of both stereoisomers of decalin over a range of temperatures from 298 to 318 K gave the data listed in Table 20. These data are useful for checking the purity of decalin.

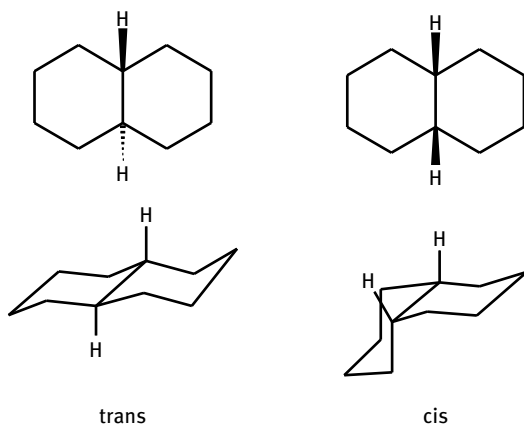
**Table 20:** Refractive indices of *cis*- and *trans*-decalin.

| Temperature, K | Refractive indices, $n_D$ |                       |
|----------------|---------------------------|-----------------------|
|                | <i>cis</i> -decalin       | <i>trans</i> -decalin |
| 293            | 1.4806                    | 1.4691                |
| 298.15         | 1.4776                    | 1.4662                |
| 308.15         | 1.4736                    | 1.4618                |
| 318.15         | 1.4696                    | 1.4581                |

Data source: [131]

### 11.2.10 Molecular Structure of Decalin

Decalin occurs in *cis* and *trans* forms. The *trans* form is energetically more stable because of fewer steric interactions. *Cis*-decalin is a chiral molecule without a chiral center; it has a two-fold rotational symmetry axis but no reflective symmetry. However, the chirality is canceled through a chair-flipping isomerization process that turns the molecule into its mirror image. *Trans*-decalin is relatively symmetrical and rigid compared to *cis*-decalin, which is a twisted and less symmetrical molecule but more flexible, as it can flip from one configuration to another. Although *cis* and *trans* molecules have the same molecular constitution, they have different physical properties because of their different molecular configurations.



### 11.3 Chemical Properties of Decalin

Technical-grade decalin may contain several percent of tetralin as contaminant, a result of incomplete hydrogenation when decalin is made by reducing naphthalene.

#### 11.3.1 Thermal Decomposition of Decalin

The vapor-phase thermal decomposition of *trans*-decalin and naphthalene has been measured under precisely controlled conditions of reaction atmosphere, exposure temperature, and residence time at atmospheric pressure and at temperatures from 300 to 1050 K [78]. Differences in fuel thermal decomposition were analyzed with respect to molecular structure and thermochemical bond energy analysis. The thermal decomposition data for these compounds were used to evaluate their potential heat-sink capacities. In a separate but related study, the gas-phase thermal degradation behavior of decalin was examined for a broad range of reaction conditions. The results indicated that removal of oxygen from the fuel-handling system and a reduction in high-temperature exposure time will greatly enhance the fuel's gas-phase stability. Under pyrolytic reaction conditions, the nature of *trans*-decalin reaction products was consistent with an initial degradation pathway involving bond homolysis followed by H-atom abstraction reactions.

Studies on the effect of low oxygen concentrations on the thermal stability of decalin indicated that stringent control of the oxygen content of fuels in the sub-parts-per-million region markedly improved thermal stability, and hence decreased heat exchanger fouling. A test program was conducted to determine the thermal stability and thermal cracking properties of decalin. Compared to JP-7, decalin was more stable to thermal decomposition.

The pyrolysis of decalin as an endothermic fuel was measured in a flow reactor using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) at 4, 20, and 101 kPa and 920–1500 K [141]. Dozens of pyrolysis species, particularly several free radicals and aromatic species, were identified, and their mole fraction profiles were measured as a function of temperature. A detailed kinetic model consisting of 484 species and 1774 reactions was developed and used to simulate the experimental data. A rate of production analysis and sensitivity analysis was performed in order to provide insight into the pyrolysis kinetics of decalin. The decomposition of decalin is initiated by C—C bond dissociation reactions of both decalin and its C<sub>10</sub>H<sub>18</sub> isomers, while the H-atom abstraction reactions consume most of decalin. Monocyclic aromatic hydrocarbons (MAHs) are mainly produced in the fuel decomposition process instead of the mass growth process from small molecules, indicating that the two fused six-membered ring structure offers a solid infrastructure to form MAHs. Polycyclic aromatic hydrocarbons (PAHs) are mainly produced in the mass growth pro-



cess from PAH precursors such as benzyl radical ( $\phi\text{CH}_2^\bullet$ ), phenyl radical ( $\phi^\bullet$ ), and 1,3-cyclopentadienyl radical. The high degree of saturation of decalin facilitates ring-opening pathways in its decomposition. This enhances the formation of MAHs but limits the formation of PAHs, leading to the lower sooting tendency of decalin compared with tetralin.

### 11.3.2 Catalytic Decomposition of Decalin

The catalyzed decomposition of decalin as an endothermic fuel has been thoroughly investigated [97, 98]. Several publications on this topic have are discussed in the section on endothermic fuels; see chapter “Kerosenes.”

Laboratory studies of the dehydrogenation of decalin to naphthalene over a  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst have indicated that the reaction proceeds in two stages (with tetralin as the intermediate). Hyperbranched polymer-encapsulated metal nanoparticles (HEMNs) with  $(\text{Pd}, \text{Pt}, \text{Au})@\text{CPAMAM}$  were tested as integrated catalysts for the supercritical cracking of decalin [142]. The metal precursor was extracted into the organic phase using a hydrocarbon-soluble hyperbranched poly(amidoamine) (CPAMAM) and then reduced *in situ* by  $\text{NaBH}_4$  to produce HEMNs with virtually a single-size distribution. The new encapsulation method allowed metal nanoparticles to have a smaller particle size beneficial to their overall specific surface area and a higher proportion of active surface atoms for better catalytic activity. The three HEMNs were highly dispersed in decalin and exhibited good stability under storage tests for up to 12 months and high-temperature stability tests at 453 K (180 °C). During the supercritical cracking of decalin,  $\text{Pd}@\text{CPAMAM}$  had much better catalytic performance than  $\text{Pd}@18\text{N}$  and plain CPAMAM. To obtain the same heat-sink capability of 3.02 MJ/kg, the temperature could be lowered from 998 K (725 °C) (thermal cracking) to 974, 966, and 972 K (701, 693, and 699 °C) for palladium, platinum, and gold HEMNs, respectively. Platinum HEMN turned out to be the best catalyst because of its excellent catalytic dehydrogenation/cracking performance, with the conversion of decalin increasing from 22.3 to 50.7% and the heat-sink capability rising from 2.18 to 2.62 MJ/kg with the addition of only 50 ppm  $\text{Pt}@\text{CPAMAM}$  to decalin, operating at 923 K (675 °C).

### 11.4 Safety Properties of Decalin

Decalin forms explosive organic peroxides upon extended storage in the presence of air. Therefore, it should be stored under nitrogen.

The flammable range of decalin vapors in air is from 0.7 vol.-% to 4.9 vol.-%. The autoignition temperature of decalin in air is 545 K (272 °C = 521 °F), which is much lower

than that of tetralin. Other sources (MSDSs) gave an autoignition temperature of 523 K ( $250^{\circ}\text{C} = 482^{\circ}\text{F}$ ). The autoignition temperature of undecomposed endothermic fuels is an important safety criterion. The flash point of commercial decalin is at 330 K ( $57^{\circ}\text{C} = 135^{\circ}\text{F}$ ). The flash point of *cis*-decalin is 332.6 K, and the flash point of *trans*-decalin is 326.8 K [131].

### 11.5 Toxicity of Decalin

The toxicity of decalin is as follows: oral rat LD<sub>50</sub>, 4170 mg/kg; skin rabbit LD<sub>50</sub>, 5900 mg/kg; inhalation rat LC<sub>50</sub>, 710 ppm/4 h. Decalin has been investigated as a tumorigen.

## 12 Alkyldecalins

Isomerized mixed methyl decalin (MMD-I) is an attractive fuel for ramjets and turbojets. *Exo*-tetrahydrodicyclopentadiene (*exo*-THDC) and isomerized RJ-4 (RJ-4-I) would be excellent fuels for ramjets and liquid propellant guns, but along the same line, MMD-I would also be an attractive fuel for ramjets and turbojets, and *exo*-THDC/60 mass-% RJ-5 and *exo*-THDC/60 mass-% *exo*-tetrahydrotricyclopentadiene mixtures could be used for ramjets.

Branched alkyldecalins are promising jet fuel components with high density, high thermal stability, and low freezing point, but availability is limited by fossil resources. A catalytic one-pot synthesis process using cyclic alcohols (cyclohexanol, cyclopentanol) and branched cycloalkanes (methylcyclohexane, methylcyclopentane) that can be derived from lignocellulose and/or refineries as feedstock is based on consecutive dehydration, alkylation, rearrangement, and hydrogen transfer to produce branched decalins [143]. The dehydration/oligomerization of alcohols also produces branched cycloalkanes, but the carbon yield and selectivity are very low, and the presence of branched cycloalkanes significantly improves the reaction. The reaction goes smoothly at room temperature, and continuous feeding of alcohols can further increase the yield. Under optimized reaction conditions, the carbon yield and branched decalins selectivity vary in the range of 61–87%, depending on the reactants used. The branched decalins have good fuel properties, such as density as high as 0.88 g/mL and freezing point as low as 163 K ( $-110^{\circ}\text{C}$ ), and they can be produced on a large scale.

### 13 Other Fused-Ring Alicyclic Hydrocarbon Fuels

Methylstyrene can be dimerized to 1,1,3-trimethyl-3-phenylindane and can then be hydrogenated to 1,1,3-trimethyl-3-cyclohexyl-hydrindane, which has been patented as a rocket fuel [144].

### 14 Bridged-Ring Alicyclic Polycyclic Hydrocarbons

Bridges connecting opposite atoms in a ring can contain one, two, or several carbon atoms. The bridges are then called methylene, ethylene, or *n*-alkene bridges. Methylene bridges are the ones that will generally increase strain in the molecules and increase their energy content, more so than bridges with two or more carbon-atom members. Bridge formation usually adds to the energy of the molecule and favorably influences physical properties such as low freezing points and low viscosity.

Hydrocarbon fuels with strained molecular conformations or more densely packed molecular structures have high energy content but often exhibit low reactivity, and their ability to improve the performance of practical combustion systems relies strongly on their interaction with the dynamics of the surrounding fluid flow [145]. The intensity of the combustion processes of these materials is dictated, in general, by evaporation, pyrolysis, mixing, and exothermic reactions processes. Unlike other conventional hydrocarbon fuels, the time scales of all these processes are often comparable with each other. It is difficult to devise simpler theoretical models to predict combustion characteristics.

Some fuels that are composed of compact hydrocarbon molecules have energy contents or heating values significantly greater than that of currently used standard missile fuel JP-10 (up to 160000 BTU/gal [44.7 GJ/m<sup>3</sup>] vs. 141700 BTU/gal [39.6 GJ/m<sup>3</sup>] for JP-10) [146].

High-density hydrocarbon fuels consist of naphthenic hydrocarbons, caged hydrocarbons, and fuels with nanoparticles [147]. Through a combination of polymerization, hydrogenation, and isomerization, high-energy fuels with high density, high combustion value, and good quality can be synthesized to satisfy the requirements of hypersonic aircraft and missiles. The high-strain caged hydrocarbons and high-density fuels with nanoparticle additives are promising candidate fuels because of their higher density (usually over 1 g/cm<sup>3</sup>) and combustion value.

Polycyclic and caged hydrocarbons with small rings are promising propellants, and their heats of combustion can be predicted by quantum-chemical calculations [148]. Molecular design, shape-selective syntheses, and blending technology are key paths for successful development of better fuels. The synthesis of high-density liquid hydrocarbon fuels and their applications has made substantial progress over the past two decades [149]. This includes a description of feedstock, synthesis routes, properties, and cost of fuels already in use or under development.

Three high-density hydrocarbons with the gross chemical formulas of  $C_{10}H_{16}$  (C10),  $C_{15}H_{22}$  (C15), and  $C_{20}H_{28}$  (C20) were synthesized using dicyclopentadiene as feedstock [150]. The density of the fuels increased in the order of increasing number of carbon atoms C10, C15, and C20, whereas the low-temperature properties showed the inverse tendency. To obtain higher density and acceptable low-temperature property, binary and ternary mixtures of these fuels were prepared. The dependence of density and viscosity on the composition of blends was analyzed, and an equation was derived to predict the density of mixtures. C10 can improve the low-temperature properties of mixtures, whereas C20 can enhance the density. According to the density-viscosity-composition ternary diagrams, an optimized blending composition of  $C15 \geq 75 \text{ mass-}\%$ ,  $C20 \leq 20 \text{ mass-}\%$ , and  $C20 \leq 5 \text{ mass-}\%$  was selected. The resulting fuel had a density above  $1.0 \text{ g/cm}^3$  at  $288 \text{ K} = 15^\circ\text{C}$ , volumetric heat of combustion higher than  $42 \text{ MJ/L}$ , viscosity less than  $500 \text{ mm}^2 \text{ s}^{-1}$  (at  $233 \text{ K} = -40^\circ\text{C}$ ), and pour point less than  $203 \text{ K} = -70^\circ\text{C}$ , which is very promising for future propulsion applications.

Two polycyclic alkane-based, high-density, thermally stable hydrocarbon fuels for liquid fuel ramjet applications, designated DPCR-2 and DPCR-3, were prepared from processed special petroleum fraction DPCR-1 by addition of decalin and JP-10 or RJ-4 [151]. These fuels were subjected to detailed physicochemical characterization and were found to have improved density ( $0.844$  to  $0.846 \text{ g/cm}^3$  at  $293 \text{ K} = 20^\circ\text{C}$ ), low aromatic content ( $<5\%$ ), low sulfur content, and high flash point ( $>335 \text{ K} = >62^\circ\text{C}$ ). These fuels exhibited better engine performance properties than aviation turbine fuel (ATF/Jet A-1). The theoretical as well as experimental ramjet performance factors such as characteristic velocity and chamber pressure for both the fuels were higher than ordinary Jet-A1 and comparable with similar high-density T-6 fuel.

## 15 Terpenes

Terpenes are a large and diverse class of naturally occurring hydrocarbons, produced by a variety of plants, particularly conifers, and by some insects [152, 153]. The name turpentine indicates a plant-derived oil, often extracted by steam distillation. Steroids, for example, are derivatives of the triterpene squalene, including sex hormones, cholesterol, and vitamin  $D_3$ . Terpenes and terpenoids are the primary constituents of the essential oils extracted from many types of plants. There are hundreds of other uses for essential oils, and one would not want to use them as fuels in rockets or other combustion engines unless there is an objective to use replenishable, renewable, nature-derived fuels (biofuels) as opposed to fossil fuels that spew out more carbon dioxide into Earth's atmosphere [154, 155]. High-density terpene dimer fuels can be mixed with JP-8, JP-10 [156], or hydrogenated pinene.

## 15.1 Pinene

Pinene,  $C_{10}H_{16}$ , CAS RN [80-56-8], is a bicyclic monoterpene natural hydrocarbon. There are two structural isomers of pinene found in nature:  $\alpha$ -pinene and  $\beta$ -pinene. The two isomers of pinene are the major constituents of turpentine. The use of pinene as a biofuel in spark ignition engines and as a rocket fuel has been explored.

### 15.1.1 Physical Properties of Pinene

$\alpha$ -pinene has a density of  $0.86 \text{ g/cm}^3$  at 288 K (15°C) and  $0.8539 \text{ g/cm}^3$  at 298 K, a melting point of 211–218 K (−62 to −55°C = −80 to −67°F), and a boiling point of 428–429 K (155–156°C = 311–313°F).  $\alpha$ -pinene has a refractive index of  $n_D^{25} = 1.4631$ .  $\beta$ -pinene has a density of  $0.8667 \text{ g/cm}^3$  at 298 K with a refractive index of  $n_D^{25} = 1.4768$ .  $\alpha$ -pinene boils at 429 K (155.9°C), and  $\beta$ -pinene boils at 439 K (166°C) [157]. The enthalpy of vaporization of  $\alpha$ -pinene is 45.4 kJ/mol at 298 K and 43.4 kJ/mol at 308 K [158].

### 15.1.2 Chemical Properties of Pinene

Because of ring strain, pinenes have a higher heating value than linear molecules of similar molecular weights, and dimerization can effectively increase their fuel density considerably. Catalytic  $\beta$ -pinene dimerization fuels can be used as high-energy-density fuels.  $\beta$ -pinene condensation was performed to obtain dimers, which are candidates for use in renewable jet fuels [159]. To suppress the production of oligomers composed of more than two pinene units, which are undesirable in liquid fuels because of their high boiling temperatures and viscosities, the pore width of the silica-alumina aerogel catalysts was modified, and their surfaces were treated chemically. The chemical treatment of the catalyst surface improved the selectivity of fuel-grade dimer production and suppressed oligomer formation. Pinene trimers are not appropriate for use in liquid fuels because of their high viscosity and high boiling temperatures.  $\alpha$ -pinene,  $\beta$ -pinene, and crude turpentine give similar product distribution in isomerization/dimerization [160].

In the presence of Al-MCM-41 mesoporous catalyst, both  $\alpha$ - and  $\beta$ -pinenes are quickly transformed into isomerized products, which then couple to form homodimers and heterodimers [161]. Lewis acid sites are active in triggering both the isomerization and dimerization reactions, but weak Brønsted acid sites seem inactive for the dimerization. Al-MCM-41 has greater activity than many other microporous and layered materials and can be easily regenerated.

## 15.2 Other Terpenes

The heat of combustion of several terpenes was determined in a bomb calorimeter [162]. The heats of combustion were as follows:  $\alpha$ -pinene, 6205 kJ/mol (1483 kcal/mol);  $\beta$ -pinene, 6213 kJ/mol (1485 kcal/mol); and d-limonene, 6167 kJ/mol (1474 kcal/mol).

3-cyclopropylnorcarane is a high-energy fuel that can be prepared by reaction of 4-vinylcyclohexene with a carbene generator [163]. It has a three-membered ring fused to a cyclohexyl ring and a loose cyclohexyl group attached by a conventional C—C bond. It has a density of 0.89967 g/cm<sup>3</sup> and a net heat of combustion of 43.03 MJ/kg (18514 BTU/lb).

## 15.3 Hydrocarbon Fuels Derived from Naturally Occurring Plant Materials

A liquid fuel blend consisting of natural oil products carene (a distillation fraction of turpentine) and cardanol (a distillation product of cashew nutshell liquid [CNSL]) in a 70 : 30 mixture ratio (mass ratio) has been evaluated as a replacement for the aromatic amine/aliphatic amine fuel mixture G-Fuel that was used in the Prithvi missile in India. It is hypergolic with red fuming nitric acid (RFNA) and dinitrogen tetroxide (NTO). This fuel was supposed to have lower freezing point, higher boiling point, higher density, and higher density impulse compared with other storable fuels. The addition of norbornadiene would increase the performance further. A fuel blend consisting of 40 carene/40 norbornadiene/20 cardanol has been tested as a replacement for RFNA/G-Fuel [164–169]. 3-carene has better storage stability than  $\alpha$ - and  $\beta$ -pinenes. It has less of a tendency to form resins during storage but can also be polymerized on command to form a resin.

The low-temperature properties of high-density terpene dimer fuels and fuel mixtures with hydrogenated pinene, JP-8 and JP-10, have been studied using shear viscometry and thermomechanical analysis [170]. Neat terpene dimers have a viscosity of  $3.94 \times 10^3$  mPa s at 263 K (−10 °C), while 50 : 50 mixtures with JP-10, RJ-4, pinane, and JP-8 have viscosities two to three orders of magnitude lower, at 23.9, 53.0, 24.9, and 3.7 mPa s, respectively. Blending conventional fuels with terpene dimers is an effective strategy for mitigating the high viscosity of the C<sub>20</sub> molecules. In addition, blending these renewable fuels with conventional jet fuel (JP-8) imparts both a higher density and an improved volumetric net heat of combustion while maintaining an acceptable low-temperature viscosity compared to JP-8 alone.

## 16 Quadricyclane

Quadricyclane, also known as quadracyclane, QC,  $C_7H_8$ , quadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]-heptane, tetracyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane, CAS RN [278-06-8], is a seven-membered bridged-ring structure containing two cyclopropyl, one cyclobutyl, and one cyclopentyl ring. It is a liquid that is stable at room temperature with a low vapor pressure and boils at 381 K (108 °C) at 740 mm Hg. Isomerization of quadricyclane proceeds slowly at low temperatures without the use of a catalyst. The unusual reactivity of QC is due to ring strain, and one of the first steps of conversion is cleavage of the C2-C6 cyclopropyl bond. It easily undergoes photochemical, electrochemical, or thermal conversion to its lower-energy-level valence isomer, 2,5-norbornadiene.

When converting back to norbornadiene via irradiation, quadricyclane's ring strain energy is liberated in the form of heat ( $\Delta H = -89$  kJ/mol). This reaction has been proposed to store solar energy. However, the absorption edge of light does not extend past 300 nm, whereas most solar radiation has wavelengths longer than 400 nm. Quadricyclane undergoes thermal decomposition at relatively low temperatures (<673 K = 400 °C). This property limits its applications because propulsion systems may operate at temperatures exceeding 773 K = 500 °C.

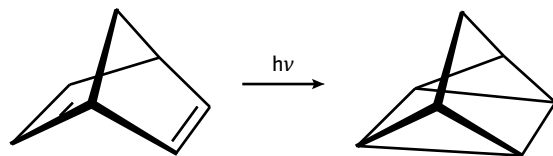
Quadricyclane has been identified as a possible replacement for, or additive to, kerosene-based rocket propellant RP-1 or RP-2. Density, viscosity, thermal conductivity, heat capacity, flash point, purity, 90-day aging, high temperature decomposition, impact sensitivity, friction sensitivity, and detonation sensitivity (card gap) have been measured [171, 172]. Thermal decomposition and rapid compression sensitivity test results indicated that quadricyclane can be easily handled as a liquid propellant fuel and should have performance advantages over RP-1. However, since the performance and physical properties of quadricyclane differ from those of RP-1, implementation of QC would require some modification of current rocket engine hardware.

The performance of quadricyclane as a rocket fuel was tested in a 220-N (50-lbf) rocket engine with LOX as the oxidizer in a side-by-side test in comparison to RP-1 [30]. Other fuels tested in that series were bicyclopropylidene, 2-azidoethyldimethylamine, and 1,7-octadiyne. The density of quadricyclane is 17% higher than that of RP-1, and the specific impulse is better. This yields a 17% fuel tank volume and an approximate 10% propellant volume benefit to a launch vehicle. The results of this fuel test warrant scaling to higher thrust levels and additional tests.

### 16.1 Preparation of Quadricyclane

In the presence of a catalyst, norbornadiene is converted into quadricyclane via ~300 nm UV radiation. Quadricyclane can be synthesized with high yield and selectivity, close to the theoretical value, by irradiation of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) in a photochemical reactor with a high-pressure mercury

vapor lamp and in the presence of a small amount of Michler's ketone (bis-4,4'-dimethylaminobenzophenone) or ethyl Michler's ketone [173].



Synthesis of quadricyclane from norbornadiene

Other sensitizers, such as acetone, benzophenone, acetophenone, etc., may be used but with a lesser yield [174].

The reversible photoisomerization of norbornadiene/quadricyclane has been proposed to store solar energy in power plants. A large number of catalysts have been identified to accelerate this reaction or drive it in the desired direction. When converting back to norbornadiene via irradiation, quadricyclane's ring strain energy is liberated in the form of heat ( $\Delta H = -89 \text{ kJ/mol}$ ) [175, 176].

The quadricyclane yield is higher for freshly distilled norbornadiene, but commercial reagents will suffice [177]. A sensitizer, such as a substituted diaminobenzophenone having a solubility in norbornadiene greater than that of Michler's ketone, may be added to the norbornadiene to form a solution [178].

The photoisomerization of norbornadiene to quadricyclane was studied with petroleum ether and acetone as mixed solvents, including the influences of initial concentration, amount and type of photosensitizer, and reaction time [179]. The optimum reaction conditions were obtained as follows: room temperature, initial reaction concentration 1.0 mol/L, 6% benzophenone, UV radiation 15 h, resulting in norbornadiene conversion up to 93% and selectivity of 100%. After vacuum distillation, high-purity quadricyclane fuel (95% purity) was obtained with 73% isolated yield.

The synthesis of quadricyclane on a kilogram scale was studied without the use of any solvents [180]. After 16 h of photoisomerization reaction and further purification, the purity and yield of quadricyclane product can reach 99.5 and 96.2%, respectively. Quadricyclane is a hypergolic fuel and ignites spontaneously with either  $\text{N}_2\text{O}_4$  or white fuming nitric acid (WFNA) [181].

### 16.1.1 Catalysts for Quadricyclane Synthesis and Photoisomerization

A large number of catalysts have been identified to accelerate the photoisomerization equilibrium of norbornadiene and quadricyclane or drive it in the desired direction.

Heterogeneous titanium-containing MCM-41 materials were prepared for the photocatalytic isomerization of norbornadiene to quadricyclane with the aim of replacing homogeneous sensitizers [182]. Chemical grafting produced quantum-size  $\text{TiO}_2$  crystallites highly dispersed in the pore of MCM-41. Isomorphous substitution gener-



ated titanium species in the framework of MCM-41, but some non-framework species were formed with increasing titanium content. It was found that titanium-containing MCM-41 materials showed significantly higher photocatalytic activity than bulk  $\text{TiO}_2$ , and the framework titanium species were more active than the surface-dispersed species.

Zinc-doped and lanthanum/zinc co-doped  $\text{TiO}_2$  nanoparticles were prepared by a sol-gel method and used as the photocatalysts for the isomerization of norbornadiene to quadricyclane and has significant potential for solar energy storage and high-energy fuel synthesis [183]. The isomerization reaction over semiconductors was proposed to proceed through an exciplex (charge-transfer) intermediate.

### 16.1.2 Quadricyclane Synthesis by Photoisomerization

Quadricyclane can be made by photoisomerization of norbornadiene using transition metal-doped  $\text{TiO}_2$  [184]. The photoreactivity is correlated with the surface lattice oxygen, and a mechanism was proposed to explain the photoisomerization and role of iron dopant. Under UV irradiation, the transition metal ions can improve the photoisomerization activity in order of decreasing activity  $\text{V} > \text{Fe} > \text{Cr}$  [185, 186].

## 16.2 Physical Properties of Quadricyclane

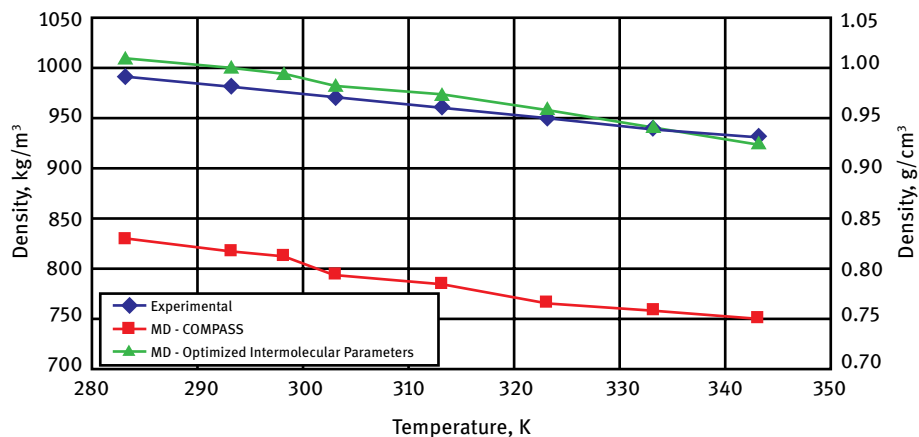
The physical properties of quadricyclane are listed in Table 21.

**Table 21:** Physical properties of quadricyclane.

| Property                                         | SI units                               | Other units                                                                                | References     |
|--------------------------------------------------|----------------------------------------|--------------------------------------------------------------------------------------------|----------------|
| Molecular mass                                   | 92.1384 g/mol                          | 10.8532 mol/kg                                                                             |                |
| Freezing point                                   | 229 K<br>233 K                         | $-44^\circ\text{C} = -47^\circ\text{F}$<br>$-40^\circ\text{C}$                             | [187]          |
| Boiling point                                    | 381 K at 0.0987 MPa<br>343 K at 27 kPa | $108^\circ\text{C} = 226^\circ\text{F}$ at<br>740 mm Hg<br>$70^\circ\text{C}$ at 200 mm Hg | [174]<br>[177] |
| Vapor pressure                                   | 3.1 kPa                                | 23 mm Hg at room temp.                                                                     |                |
| Density                                          | $0.982\text{ g/cm}^3$ at 293 K         | 8.195 lb/gal                                                                               | [187]          |
| Enthalpy of formation, liquid $\Delta H_f^{298}$ | $+253.3 \pm 1.1\text{ kJ/mol}$         | $60.54 \pm 0.26\text{ kcal/mol}$                                                           | [188]          |
| Enthalpy of formation, vapor $\Delta H_f^{298}$  | $+339.1 \pm 2.3\text{ kJ/mol}$         | $+81.05 \pm 0.55\text{ kcal/mol}$                                                          | [17, 189]      |
| Enthalpy of formation, liquid $\Delta H_f^{298}$ | $+302.1 \pm 2.2\text{ kJ/mol}$         | $+72.20 \pm 0.53\text{ kcal/mol}$                                                          |                |
| Enthalpy of vaporization at NBP                  | $37.3 \pm 0.8\text{ kJ/mol}$           | $8.91 \pm 0.19\text{ kcal/mol}$                                                            |                |
| Enthalpy of fusion                               | 1.09 kJ/mol at 228 K                   | 0.26 kcal/mol at $-45^\circ\text{C}$                                                       |                |
| Heat of combustion, liquid                       | $4200.0 \pm 2.2\text{ kJ/mol}$         | $1003.8 \pm 0.53\text{ kcal/mol}$                                                          | [17, 189]      |
| Index of refraction                              | $n_D^{26} 1.4830$                      | —                                                                                          | [174]          |

### 16.2.1 Density of Quadricyclane

The density of quadricyclane as a function of temperature is illustrated in Figure 17. This figure compares density predictions from two different molecular orbital mechanics calculations with measured data. The measured density of three different samples of quadricyclane from three different suppliers is listed in Table 22. The data from Table 22 are illustrated in Figure 18.

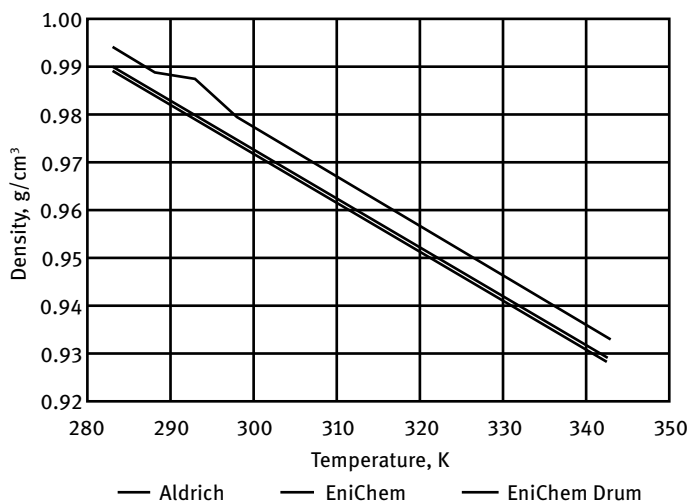


**Figure 17:** Predicted and measured density of quadricyclane. (Reproduced and modified from [190] with permission of Dr. Tim Kokan 3 July 2020.)

**Table 22:** Density of three different samples of quadricyclane.

| Temperature |    | Aldrich           | EniChem (small can) | EniChem (45 kg drum) |
|-------------|----|-------------------|---------------------|----------------------|
| K           | °C | g/cm <sup>3</sup> |                     |                      |
| 283         | 10 | 0.9944            | 0.9897              | 0.9894               |
| 288         | 15 | 0.9894            | 0.9848              | 0.9844               |
| 293         | 20 | 0.9875            |                     | 0.9787               |
| 298         | 25 | 0.9796            | 0.975               | 0.9746               |
| 303         | 30 | 0.9743            | 0.9698              | 0.9693               |
| 308         | 35 | 0.9692            | 0.9647              | 0.9642               |
| 313         | 40 | 0.9642            | 0.9597              | 0.9592               |
| 323         | 50 | 0.9537            | 0.9493              | 0.9487               |
| 333         | 60 | 0.9435            | 0.939               | 0.9384               |
| 343         | 70 | 0.9332            | 0.9288              | 0.9281               |

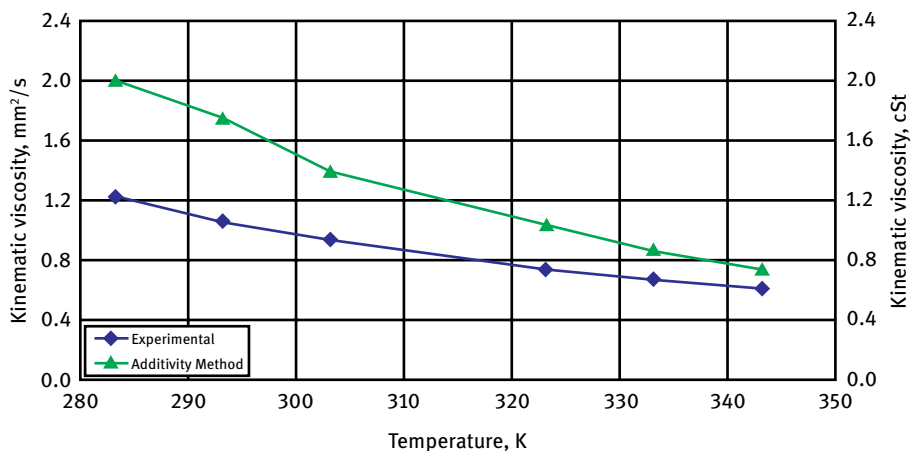
Data source: [172]



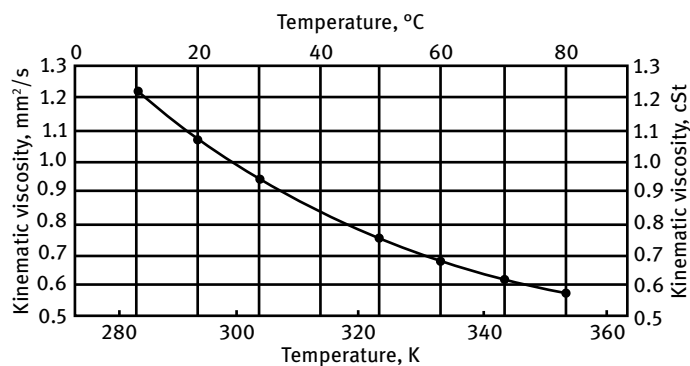
**Figure 18:** Density of three different samples of quadricyclane. (Image created by Schmidt 2020 based on data from [172].)

### 16.2.2 Viscosity of Quadricyclane

The kinematic viscosity of quadricyclane as a function of temperature is illustrated in Figure 19. This figure compares viscosity predictions from molecular orbital mechanics calculations with measured data. Experimental data for the kinematic viscosity of quadricyclane as a function of temperature are illustrated in Figure 20.



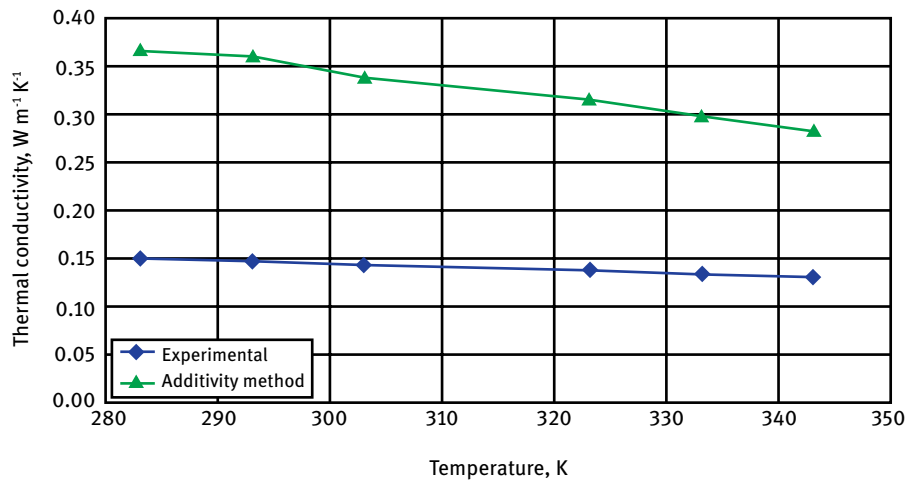
**Figure 19:** Predicted and measured kinematic viscosity of quadricyclane. (Reproduced and modified from [190] with permission of Dr. Tim Kokan, 3 July 2020.)



**Figure 20:** Kinematic viscosity of quadricyclane as a function of temperature. (Reproduced and modified from [172].)

### 16.2.3 Thermal Conductivity of Quadricyclane

The thermal conductivity of quadricyclane as a function of temperature is illustrated in Figure 21. This figure compares thermal conductivity predictions from molecular orbital mechanics calculations with measured data. Table 23 lists thermal conductivity of quadricyclane in comparison to that of RP-1.



**Figure 21:** Predicted and measured thermal conductivity of quadricyclane. (Reproduced and modified from [190] with permission of Dr. Tim Kokan, 3 July 2020.)

**Table 23:** Thermal conductivity of quadricyclane in comparison to that of RP-1.

|             |     | Quadricyclane (EniChem)           |                                                       | RP-1                              |                                                       |
|-------------|-----|-----------------------------------|-------------------------------------------------------|-----------------------------------|-------------------------------------------------------|
| Temperature |     | Thermal conductivity              |                                                       |                                   |                                                       |
| K           | °C  | W m <sup>-1</sup> K <sup>-1</sup> | cal cm <sup>-1</sup> s <sup>-1</sup> °C <sup>-1</sup> | W m <sup>-1</sup> K <sup>-1</sup> | cal cm <sup>-1</sup> s <sup>-1</sup> °C <sup>-1</sup> |
| 233         | -40 | 0.166                             | 0.000397                                              | 0.142                             | 0.000339                                              |
| 263         | -10 | 0.159                             | 0.000379                                              | 0.138                             | 0.000331                                              |
| 293         | 20  | 0.147                             | 0.000352                                              | 0.137                             | 0.000327                                              |
| 323         | 50  | 0.136                             | 0.000325                                              | 0.135                             | 0.000323                                              |
| 353         | 80  | 0.131                             | 0.000312                                              | 0.133                             | 0.000318                                              |
| 373         | 100 | 0.119                             | 0.000284                                              | 0.130                             | 0.000310                                              |

Data source: [172]

### 16.2.4 Thermodynamic Properties of Quadricyclane

The enthalpy of vaporization of quadricyclane is  $36.99 \pm 0.02$  kJ/mol ( $8.84 \pm 0.004$  kcal/mol). The heat of combustion of quadricyclane is  $348.7 \pm 1.1$  kJ/mol ( $83.34 \pm 0.26$  kcal/mol). The enthalpy of formation of liquid quadricyclane is  $+216.3 \pm 1.1$  kJ/mol ( $+51.70 \pm 0.26$  kcal/mol) [189]. This enthalpy of formation for quadricyclane differs from a value reported earlier,  $\Delta H_f = +302.1$  kJ/mol =  $+72.2$  kcal/mol [191].

A technique for determining thermophysical properties of rocket engine propellants used a combination of three different computational methods to predict these properties [190, 192–194]. Quantum mechanics and molecular dynamics methods were used to model new propellants at a molecular level in order to calculate density, enthalpy, and entropy. Additivity methods were used to calculate the kinematic viscosity and thermal conductivity of new propellants. This technique was validated by comparing results for two propellants: quadricyclane and 2-azido-*N,N*-dimethylethanamine (DMAZ). In each case, the new technique was better than the best current computational methods at accurately matching the experimental data of the two propellants. Table 24 gives a comparison of the enthalpies and entropies of formation of quadricyclane and DMAZ, two candidate hypergolic fuels. See also [189].

**Table 24:** Thermodynamic properties of liquid DMAZ and liquid quadricyclane

| Compound      | Enthalpy of formation $\Delta H_f$ |          | $\Delta S_f$ at 101 kPa             | $\Delta S_f$ at 1 atm                  |
|---------------|------------------------------------|----------|-------------------------------------|----------------------------------------|
|               | kJ/mol                             | kcal/mol | J mol <sup>-1</sup> K <sup>-1</sup> | cal mol <sup>-1</sup> °C <sup>-1</sup> |
| Quadricyclane | +302                               | +72.2    | 167                                 | 39.9                                   |
| DMAZ          | +280                               | +66.9    | 154                                 | 36.8                                   |

Data source: [190]

### 16.2.5 Molecular Structure of Quadricyclane

Quadricyclane has a very high strain energy, 393 kJ/mol (94 kcal/mol), because of the degree of stressing of carbon-carbon bonds away from tetrahedral bonds inside its molecule. The molecular structure of quadricyclane is illustrated in Figure 22.

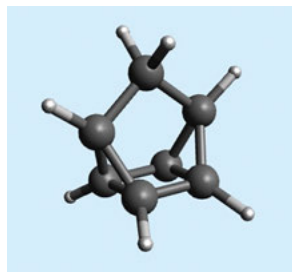


Figure 22: Molecular structure of quadricyclane.

## 16.3 Chemical Properties of Quadricyclane

### 16.3.1 Isomerization of Quadricyclane

The energy-releasing isomerization of quadricyclane back to norbornadiene was thoroughly investigated as part of a photochemical energy-storage scheme. While the thermal barrier for reversion of quadricyclane back to norbornadiene is relatively high, the energy-releasing conversion of quadricyclane to norbornadiene can be achieved readily via a free-radical-cation chain reaction initiated by one-electron oxidations [195]. The difference in enthalpy of formation of the two hydrocarbons is 96 kJ/mol (23 kcal/mol).

Quantum mechanical *ab initio* calculations were performed to explain the thermal isomerization of quadricyclane to norbornadiene, which occurs via a forbidden pathway [196]. The predicted activation barrier was 142 kJ/mol (34 kcal/mol), consistent with the 138 kJ/mol (33 kcal/mol) measured by earlier investigators. The transition state has a biradical character. The reaction is highly asynchronous, with one bond cleaving entirely before the transition state and the second bond cleaving afterward on the intrinsic reaction coordinate.

### 16.3.2 Reactions (Other than Isomerization) of Quadricyclane

Quadricyclane can undergo cycloaddition reactions with olefins, acetylenes, carbonyl, nitrogen, sulfur-containing compounds, carbenes, and silenes, along with cycloaddition reactions involving transition metals, photochemical transformations, ionic reactions (electrophilic and nucleophilic), oxidation, and reduction [197].

### 16.3.3 Thermal Decomposition of Quadricyclane

The pyrolysis/combustion mechanisms of quadricyclane were studied in an apparatus consisting of a resistively heated reactor (1000 °C) for flow and static pyrolysis studies, a pulsed IR laser pyrolysis source, and a gas chromatographic analyzer with flame ionization, thermal conductivity, and mass spectrometric detectors [198]. The flow reactor and the gas chromatographic analysis system were validated at 978 and 1033 K (705 and 760 °C) with the well-established pyrolysis of propane in helium. Gas-phase thermal decomposition studies of quadricyclane and its decomposition products were conducted in the presence and in the absence of oxygen at atmospheric pressure in helium.

Pyrolysis and isomerization of the  $C_7H_8$  isomers quadricyclane, norbornadiene, cycloheptatriene, and toluene have been studied in a micro-flow tube reactor with detection/isomer identification by guided ion beam tandem mass spectrometry [199]. This methodology permits pyrolysis studies with product isomer identification with samples of only a few milligrams. The samples were pre-mixed with buffer gas and then passed through a temperature-controlled flow tube reactor with millisecond residence time. The sample/pyrolysis products exiting the flow tube were ionized by methane chemical ionization, and both mass spectra and low-energy collision-induced dissociation were used to determine the composition. Quadricyclane began to decompose at ~500 K, and the dominant decomposition processes were the acetylene elimination and isomerization to toluene, with a small amount of norbornadiene production.

A laboratory-scale flow reactor was developed to subject small amounts (approximately 1 mL) of deoxygenated fuels to controlled conditions of temperature and residence-time-at-temperature at constant pressure (34 atm) in the liquid or supercritical phase [31]. The reactor was made from 316 stainless-steel high-performance liquid chromatography (HPLC) tubing. Using an inline analytical system, as well as offline chromatographic analysis of products, the thermal stability of the parent material and the thermal fragmentation products of each fuel were measured. Quadricyclane and bicyclopentylidene showed only marginal thermal stability, with major decomposition occurring before 400 °C (~3 s residence time). Other fuels (JP-10, RP-1, RG-1, RJ-6, and RJ-7) showed excellent thermal stability with little decomposition even at 873 K (600 °C). Results showed the pyrolytic stability of candidate materials relative to each other and provided insights into the mechanisms of thermal decomposition for specific fuel candidates.

Pyrolysis experiments of quadricyclane at 473–1073 K and 1.0–2.0 MPa were conducted in a micro-reactor equipped with online GC-MS/flame ionization detection to investigate the dependence of pyrolysis mechanism on pressure [200]. It was found that quadricyclane first isomerizes into 2,5-norbornadiene (NBD) below 598 K under 1.0 MPa with an activation energy of  $68.50 \pm 5.95$  kJ/mol, and then NBD decomposes through three major pathways: the retro-Diels-Alder reaction to acetylene plus cyclopentadiene, the isomerization into 1,3,5-cycloheptatriene, and the isomerization

into toluene. The high pressure inhibits the isomerization of quadricyclane into NBD and the retro-Diels-Alder reaction of NBD, but it promotes the isomerization reactions of NBD into 1,3,5-cycloheptatriene and into toluene. The further reactions of cyclopentadiene and toluene produce small molecules and aromatic products, mainly from the combination of cyclopentadiene and cyclopentadienyl. Based on the detailed analysis of the decomposition products and kinetics, a possible kinetic mechanism of quadricyclane pyrolysis was then proposed.

#### 16.4 Other Quadricyclane Derivatives

Attempts have been made to synthesize more energetic fuels by attaching explosophoric groups, such as azido groups, to quadricyclane [201, 202].

#### 16.5 Safety Properties of Quadricyclane

The flash point of quadricyclane is at 275 K (+2°C) [187].

#### 16.6 Toxicity of Quadricyclane

Quadricyclane caused 100% mortality in male Fischer 344 rats within 24 h following gavage at 3.5 g/kg [203, 204]. The LC<sub>50</sub> is somewhere between 1.2 and 3.5 g/kg. Gavage treatment with a quadricyclane/kerosene mixture (70% quadricyclane, 30% kerosene), similar to the proposed rocket fuel mixture, produced toxic effects at a dose level below the U.S. Environmental Protection Agency (EPA) limit test. No treatment-related deaths occurred in rabbits following a 24-h dermal exposure to the EPA limit dose of 2 g test material/kg body weight.

Measurements of the inhalation toxicity of quadricyclane in acute 4-h exposures of male Sprague-Dawley rats to QC vapor resulted in an LC<sub>50</sub> value of 0.78 mg/L [205]. Subchronic (2-week) inhalation exposure of groups of male and female Sprague-Dawley rats at 0.0, 0.025, 0.075, and 0.25 mg/L quadricyclane resulted in no mortality. Body weights of exposed rats were significantly less than those of the controls after 10 exposures. No exposure-related gross lesions were noted at necropsy. A 90-d general toxicity/reproductive screen using concentrations of 0.0, 0.01, 0.025, and 0.10 mg/L quadricyclane produced no significant exposure-related differences in the reproductive or litter parameters measured. The only lesion noted at necropsy was minimal pulmonary inflammation in the lungs of the mid-concentration and high-concentration male rats. Significant treatment-related increases in brain dopamine and 5-hydroxytryptamine levels were detected in all quadricyclane-exposed rats.



The low-concentration level of 0.01 mg/L quadricyclane represents a no observable adverse effect level (NOAEL).

The biodegradation and hydrolysis of quadricyclane in water yielded two hydroxy-substituted compounds, tricyclic or bicyclic alcohols [206]. Both quadricyclane and its hydroxy-substituted compounds were toxic to bacterial cultures. LC50 concentrations were 0.88 and 0.82 mM for *Pseudomonas aeruginosa* and *Pseudomonas putida*, respectively.

## 16.7 Applications of Quadricyclane

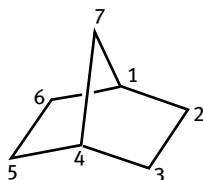
The use of quadricyclane as a high-energy fuel, a potential replacement for RP-1 or RP-2, has been investigated, but due to a limited supply, QC has never found a practical application. Quadricyclane as a rocket fuel can be mixed with RP-1 or *n*-hexane [207].

Quadricyclane is hypergolic with NTO, in particular if it is used as a suspension of sub-micron-sized boron particles in quadricyclane [180, 181]. The ignition-delay time of NTO/quadricyclane was 29 ms, which decreased to 18 ms by addition of boron nanoparticles to the fuel. Quadricyclane is hypergolic with WFNA, NTO, and high-test peroxide (HTP) [208].

The heat of combustion of quadricyclane can be increased by dissolving acetylene in the fuel. The solubility of acetylene in quadricyclane can be enhanced by adding triethylamine [209]. The solubility of acetylene in quadricyclane at 298 K and pressures up to 200 kPa was studied. The solubility of acetylene in the presence of triethylamine showed that such additives could significantly increase the solubility of acetylene in the fuel.

## 17 Norbornane

Norbornane, also known as C<sub>7</sub>H<sub>12</sub>, bicyclo[2.2.1]heptane, CAS RN [279-23-2], is an organic compound and a saturated hydrocarbon. It is a crystalline, readily subliming compound with a melting point of 358 to 361 K (85 to 88 °C). The carbon skeleton is derived from a cyclohexane ring with a methylene bridge in the 1,4-position, and thus it is a bridged bicyclic compound (Figure 23). This compound is a prototype of the class of strained bicyclic hydrocarbons. Norbornane is prepared by reduction of norbornene.



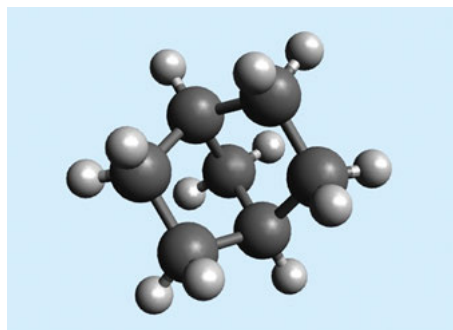


Figure 23: Molecular structure of norbornane.

### 17.1 Physical Properties of Norbornane

Norbornane melts at 358 to 361 K (85 to 88 °C) and sublimes readily. The vapor pressure of crystalline norbornane in the temperature range 284–327 K can be calculated from the equation

$$\log P = (-2097.5/T) + 8.479$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin [2].

The enthalpy of formation of solid norbornane is  $-92.1 \pm 2.2$  kJ/mol ( $-22.01 \pm 0.52$  kcal/mol). The enthalpy of formation of norbornane vapor is  $-51.96 \pm 2.9$  kJ/mol ( $-12.42 \pm 0.70$  kcal/mol). The enthalpy of vaporization of norbornane is 40.12 kJ/mol (9.59 kcal/mol) [188].

The thermal decomposition of norbornane (dissolved in benzene) has been studied in a jet-stirred reactor at temperatures between 873 and 973 K, at residence times ranging from 1 to 4 s, and at atmospheric pressure, leading to conversions from 0.04 to 22.6% [210]. A total of 25 reaction products were identified and quantified by gas chromatography, among which the main ones were hydrogen, ethene, and 1,3-cyclopentadiene. Reactions involved in a proposed mechanism include unimolecular initiations by C–C bond scission of norbornane, generation of diradicals, the reactions of transfer and propagation of norbornyl radicals, the reactions of benzene, and cross-coupling reactions.

### 17.2 Other Norbornane Derivatives

Spiro[cyclopentane-1,2'-norbornane],  $C_{11}H_{18}$ , has been synthesized by a one-pot Mannich-Diels-Alder reaction from cyclopentanone, formaldehyde, and cyclopentadiene [211]. It has a density of 0.952 g/cm<sup>3</sup> at 293 K (20 °C), a freezing point of 220 K (–53 °C), and a net heat of combustion of 42.21 MJ/kg.

## 18 Norbornene

Norbornene,  $C_7H_{10}$ , bicyclo[2.2.1]hept-2-ene, CAS RN [498-66-8], is a bridged cyclic hydrocarbon. It is a white readily subliming solid with an unpleasant odor. The molecule consists of a cyclohexene ring with a methylene bridge between carbons 1 and 4. The molecule carries a double bond that induces significant ring strain and significant reactivity. Norbornene can be prepared by a Diels-Alder reaction of cyclopentadiene and ethene.



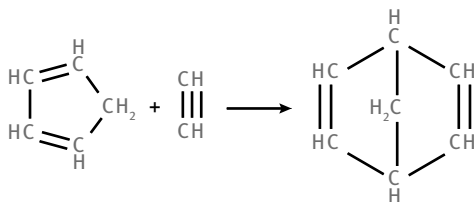
It has a melting point of 315 to 319 K (42 to 46 °C = 108 to 115 °F) and a boiling point of 369 K (96 °C = 205 °F). The heat of combustion of norbornene is  $4213 \pm 1.7$  kJ/mol ( $1007.04 \pm 0.40$  kcal/mol). The enthalpy of formation of liquid norbornene is  $+29.7 \pm 1.7$  kJ/mol ( $+7.09 \pm 0.40$  kcal/mol). The enthalpy of vaporization of norbornene is  $33.6$  kJ/mol ( $8.03$  kcal/mol) [188]. Photochemical dimerization of norbornene catalyzed by copper(I) chloride leads to a dimer with a cyclobutane ring, which can be used as a rocket fuel [212].

## 19 Norbornadiene

Norbornadiene,  $C_7H_8$ , 2,5-norbornadiene, bicyclo[2.2.1]hepta-2,5-diene, CAS RN [121-46-0], is a homocyclic hydrocarbon that achieved most interest because of its ability to isomerize to quadricyclane (see Section 15.1).

### 19.1 Preparation of Norbornadiene

Norbornadiene can be prepared by a Diels-Alder reaction between cyclopentadiene and acetylene:



The dimers and trimers of norbornadiene have a unique polycyclic strained structure and are useful as high-density fuels. A systematic study of the synthesis of norbornadiene from dicyclopentadiene and acetylene under pressure investigated the effects of various operating parameters on product distribution [213]. The optimum conditions for the synthesis were as follows: temperature, 563 K = 290 °C; residence period, 16 min; mol ratio of  $C_2H_2:N_2$ : dicyclopentadiene, 1:1:0.4; and initial pressure at ambient temperature, 0.8 MPa. Under these conditions the conversion of norbornadiene was 41% on the basis of dicyclopentadiene consumed. The loss of dicyclopentadiene due to polymerization was estimated from the material balance.

## 19.2 Physical Properties of Norbornadiene

### 19.2.1 Freezing Point of Norbornadiene

Norbornadiene freezes at 254 K ( $-19\text{ °C} = -2\text{ °F}$ ).

### 19.2.2 Boiling Point of Norbornadiene

Norbornadiene boils at 362 K ( $89\text{ °C} = 192\text{ °F}$ ).

### 19.2.3 Density of Norbornadiene

Norbornadiene has a density of  $0.906\text{ g/cm}^3$  at 293 K.

### 19.2.4 Thermodynamic Properties of Norbornadiene

The heat of combustion of norbornadiene is  $311.1 \pm 1.0\text{ kJ/mol}$  ( $74.35 \pm 0.24\text{ kcal/mol}$ ). The enthalpy of formation of liquid norbornadiene is  $+178.7 \pm 1.00\text{ kJ/mol}$  ( $+42.72 \pm 0.24\text{ kcal/mol}$ ). The enthalpy of vaporization of norbornadiene is  $32.93 \pm 0.08\text{ kJ/mol}$  ( $7.87 \pm 0.02\text{ kcal/mol}$ ) [188].

### 19.2.5 Molecular Structure of Norbornadiene

The molecular structure of norbornadiene is illustrated in Figure 24.

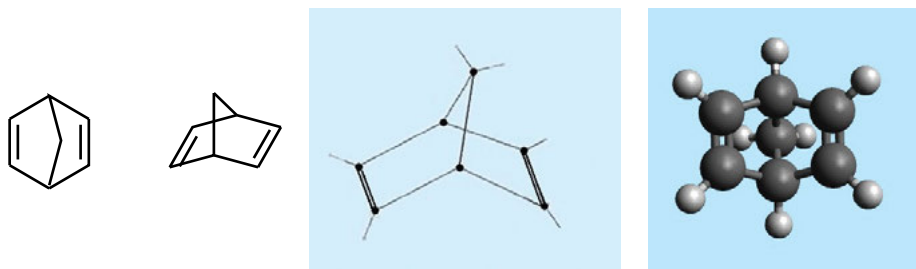


Figure 24: Molecular structure of norbornadiene.

### 19.3 Chemical Properties of Norbornadiene

#### 19.3.1 Thermal Stability of Norbornadiene

##### 19.3.1.1 Isomerization of Norbornadiene

In the past, the isomerization of norbornadiene to quadricyclane was investigated mostly as an energy-storage reversible reaction and not so much as a method for producing a rocket propellant. The valence photoisomerization of norbornadiene to quadricyclane or quadricyclane can be catalyzed by copper(I) salts [214, 215], copper complexes [216], orthometalated transition-metal complexes [217], rhodium(III) salts [218], or zeolites [219].

Pyrolysis and isomerization of the  $C_7H_8$  isomers norbornadiene, quadricyclane, cycloheptatriene, and toluene have been studied in a micro-flow tube reactor with detection/isomer identification by guided ion beam tandem mass spectrometry [199]. This methodology permits pyrolysis studies with product isomer identification with samples of only a few milligrams. The samples were premixed with buffer gas and then passed through a temperature-controlled flow tube reactor with millisecond residence time. The sample/pyrolysis products exiting the flow tube were ionized by methane chemical ionization, and both mass spectra and low-energy collision-induced dissociation were used to determine the composition. For the experimental residence time, decomposition of norbornadiene sets in at  $\sim 600$  K. The dominant decomposition processes are acetylene elimination via a retro-Diels-Alder reaction and isomerization to toluene. See also [220].

##### 19.3.1.2 Oligomerization of Norbornadiene

Under the influence of zeolites, the dimerization of norbornadiene can go beyond the linking of two norbornadiene molecules, resulting in higher oligomers that can also be used as high-density fuels [221].

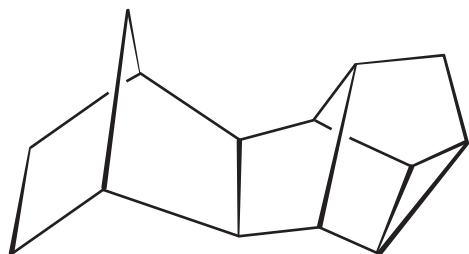
## 20 Dinorbornadiene

Norbornadiene readily dimerizes to form dinorbornadiene. Dinorbornadiene was an intermediate product in the synthesis of Shellldyne-H, the main ingredient of RJ-5. The storage stability of this bridged cycloparaffin was improved by hydrogenating all unsaturated C=C bonds, resulting in perhydrodinorbornadiene, the main ingredient of Shellldyne-H and RJ-5.

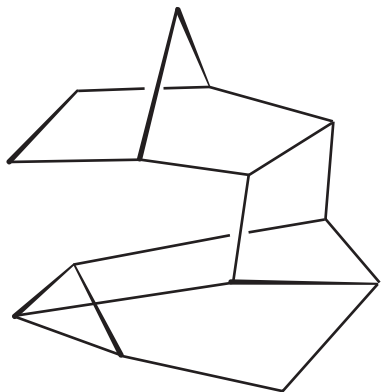
## 21 Perhydrodinorbornadiene

Perhydrodinorbornadiene, also known as dihydrodinorbornadiene, hexacyclic dihydrodinorbornadiene,  $C_{14}H_{18}$ , is formed by hydrogenation of dinorbornadiene. A mixture of structural isomers of perhydrodinorbornadiene is the main ingredient of Shellldyne-H and RJ-5. The properties of RJ-5 are discussed in the chapter “Ramjet Fuels.” The molecular structures of two valence isomers are shown in the following images (Figure 25). These are the most complex structures shown in this entire book.

There are eight structural isomers of perhydrodinorbornadiene, so only two typical ones are shown here.



Hexacyclic *exo,exo*-dihydrodinorbornadiene



Hexacyclic *endo,endo*-dihydrodinorbornadiene

**Figure 25:** Molecular structures of HXX (top) and HNN (bottom) perhydrodinorbornadiene (DHDNBD).

## 21.1 Preparation of Perhydrodinorbornadiene

Perhydrodinorbornadiene can be prepared by reduction of dinorbornadiene with hydrogen over a 10% palladium/carbon catalyst in methylcyclohexane at 373 K and 68 atm [222].

## 21.2 Physical Properties of Perhydrodinorbornadiene

### 21.2.1 Melting Point of Perhydrodinorbornadiene

One of the most remarkable findings of a study on polycyclic hydrocarbons was the observation of two distinct melting points for the HNN and HXX isomers of perhydrodinorbornadiene (PHDNBD) [223]. This was first detected in measuring the melting point of pure HNN, where it was found that about half of the time the sample would melt at 273.65 K (0.5 °C), and the other half of the time it would melt at 280.65 K (7.5 °C). With the HXX isomer, if the melting point was measured immediately after crystallization, it was found to be 284.4 K (11.3 °C), whereas if the crystallized sample was held for 1 to 2 h near dry-ice temperature, it was found to be 290.1 K (17.0 °C). The explanation for this phenomenon is that there are two crystalline forms or polymorphs of the HNN and of the HXX isomers, which were designated as “low melting point” and “high melting point,” respectively. It can be shown from thermodynamics that in the vicinity of the lower melting point, the low-melting-point form is metastable with respect to the high-melting-point form. Seeding with high-melting-point HNN crystals causes crystallization of only high-melting-point HNN, which melts at 253.6 K (−19.5 °C).

### 21.2.2 Density of Perhydrodinorbornadiene

For single data points, the density of HNN isomer at 298 K is 1.085 g/cm<sup>3</sup>, compared to a density of 1.073 g/cm<sup>3</sup> for the HXX isomer [224]. Densities of the purified liquid PHDNBD isomers and their mixtures with *exo*-tetrahydrodicyclopentadiene (THDCPD) are linear functions of temperature. Table 25 gives the parameters obtained from least squares fits to the equation

$$\rho = \rho_0 - Bt$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $t$  is the temperature in °C. The parameters for density equations for HNN, HXX, isomer I, and *exo*-THDCPD are given in Table 25.

**Table 25:** Parameters for density equations for HNN, HXX, isomer I, and *exo*-THDCPD.

| Compound                  | Temperature range |            | $\rho_0$ | $B \times 10^4$ | Standard deviation |
|---------------------------|-------------------|------------|----------|-----------------|--------------------|
|                           | K                 | °C         |          |                 |                    |
| HNN                       | 223–323           | –50 to +50 | 1.105    | 7.49            | 0.0004             |
| HXX                       | 259–323           | –14 to +50 | 1.098    | 7.50            | 0.0004             |
| Isomer I                  | 263–323           | –10 to +50 | 1.097    | 7.81            | 0.0002             |
| <i>exo</i> -THDCPD run I  | 219–323           | –54 to +50 | 0.951    | 7.60            | 0.0003             |
| <i>exo</i> -THDCPD run II | 218–323           | –55 to +50 | 0.951    | 7.60            | 0.0004             |

Data source: [223]

### 21.2.3 Vapor Pressure of Perhydrodinorbornadiene

The vapor pressure of perhydrodinorbornadiene is similar to that of RJ-5, which was calculated to be 0.96 kPa (0.00952 atm = 7.2 mm Hg) at 366.7 K (200 °F).

### 21.2.4 Viscosity of Perhydrodinorbornadiene

Shear viscosities of four isomeric hydrogenated norbornadiene dimers and their mixtures were measured over the viscosity range 0.04–200 Ps [225]. On a logarithmic viscosity scale, all of the liquids exhibited identical temperature dependences. The combined effects of composition and temperature on the viscosity could be described accurately by a modified free-volume equation. It was found that the viscosity differences among the different isomers were due to differences in their molecular dimensions along the direction of the long axis.

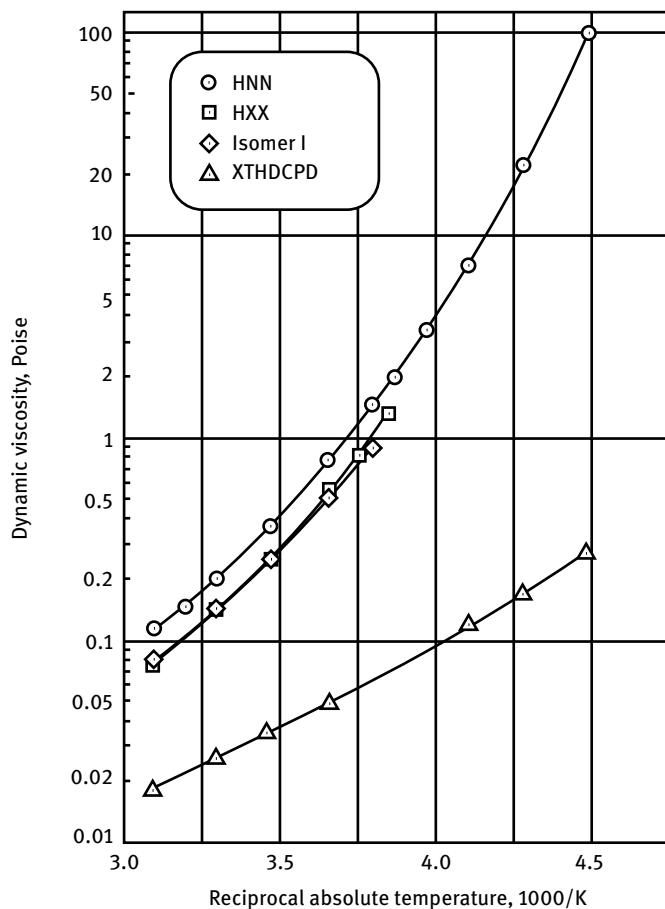
Shear viscosity results are listed in Table IV from [226]. The data for HNN, HXX, isomorph I, and *exo*-THDCPD are shown in Figure 26 in the form of Arrhenius plots of  $\log \eta$  vs.  $1/T$ . These plots are typical of those observed for nearly all liquids, i.e., they are not linear, but curved.

Viscosity as a function of temperature can be expressed by the equation

$$\ln \eta = A + B/(T - T_0)$$

where  $\eta$  is the viscosity in Poise and  $T$  is the temperature in kelvin.  $A$ ,  $B$ , and  $T_0$  are constants listed in Table 26. Additional density and viscosity data are available in [226] for mixtures of the PHDNBD isomers with *exo*-THDCPD.





**Figure 26:** Viscosity of HNN, HXX, isomorph I, and *exo*-THDCPD. (Reproduced and modified from [226].)

**Table 26:** Coefficients for viscosity equations for perhydrodinorbornadiene isomers and *exo*-tetrahydrodicyclopentadiene.

| Compound                  | Temperature range |            | A      | B      | $T_0$ | Standard deviation |
|---------------------------|-------------------|------------|--------|--------|-------|--------------------|
|                           | K                 | °C         |        |        |       |                    |
| HNN                       | 223–323           | –50 to +50 | –7.168 | 850.75 | 150   | 0.0043             |
| HXX                       | 259–323           | –14 to +50 | –6.765 | 656.87 | 166   | 0.0006             |
| Isomer I                  | 263–323           | –10 to +50 | –7.041 | 768.95 | 152   | 0.0325             |
| <i>exo</i> -THDCPD run I  | 219–323           | –54 to +50 | –7.752 | 881.78 | 86    | 0.0060             |
| <i>exo</i> -THDCPD run II | 218–323           | –55 to +50 | –7.653 | 847.96 | 89    | 0.0016             |

Data source: [226]

### 21.2.5 Thermodynamic Properties of Perhydrodinorbornadiene

Enthalpies of fusion and heat capacities of crystals below the melting point and liquid above the melting point were measured with a Perkin-Elmer model DSC-2 differential scanning calorimeter (DSC) [223, 226, 227]. Table 27 lists the molar heats of fusion,  $\Delta H_f$ , of pure low-melting-point and high-melting-point HNN and HXX, along with the melting points  $T_{\text{melt}}$  determined by the American Society for Testing and Materials (ASTM) method. The  $\Delta H_f$  values are averages of between two and 13 DSC measurements carried out at a heating rate of 0.625 K/min on each crystal. Two heat capacity data are also in that table.

**Table 27:** Enthalpy of fusion and heat capacity of perhydrodinorbornadiene isomers.

| Compound       | Melting point, K | $\Delta H_f$ , cal/mol | $C_p$ , cal mol <sup>-1</sup> K <sup>-1</sup> |
|----------------|------------------|------------------------|-----------------------------------------------|
| HNN, high m.p. | 280.7 ± 0.3      | 3720 ± 50              | 11.6 ± 1.7                                    |
| HNN, low m.p.  | 273.7 ± 0.3      | 2000 ± 70              | —                                             |
| HXX, high m.p. | 290.2 ± 0.3      | 2850 ± 40              | 7.3 ± 0.7                                     |
| HXX, low m.p.  | 284.5 ± 0.3      | 3150 ± 70              | —                                             |

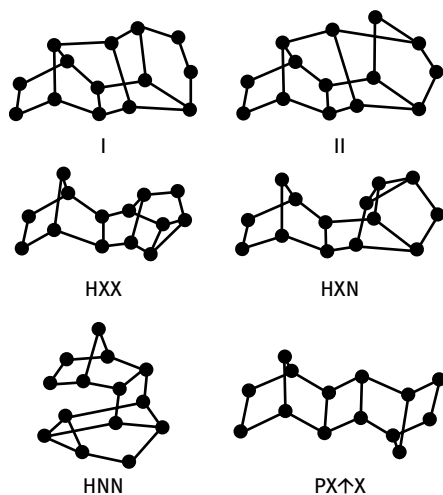
m.p. = melting point

Enthalpy of fusion and heat capacity results were reported previously for impure samples of HNN (96.8% by GC) and HXX (98.6% by GC). The heat of combustion of HNN is 8150 ± 1.5 kJ/mol (1948.11 ± 0.36 kcal/mol), and the heat of combustion of HXX is 8121 ± 1.9 kJ/mol (1940.88 ± 0.46 kcal/mol) [224]. The standard enthalpy of formation of liquid HNN is  $\Delta H_f^{298} = +65.1 \pm 1.7$  kJ/mol (+15.56 ± 0.40 kcal/mol), and the standard enthalpy of formation of liquid HXX is  $\Delta H_f^{298} = +39.1 \pm 1.7$  kJ/mol (+9.34 ± 0.40 kcal/mol) [224]. The standard enthalpies of formation for the same compounds in the vapor state are +134.6 ± 1.7 kJ/mol (+32.18 ± 0.41 kcal/mol) for HNN and +104.5 ± 2.1 kJ/mol (+24.97 ± 0.50 kcal/mol) for the HXX isomer. The difference between these numbers should be the enthalpy of vaporization, which we calculated as 69.5 kJ/mol for the HNN and 65.4 kJ/mol for the HXX isomer.

Isomers of the major JP-9 constituent, hydrogenated norbornadiene (RJ-5), were separated by preparative gas chromatography, and enthalpies of fusion for each were measured using a DSC [72].

### 21.2.6 Molecular Structure of Perhydrodinorbornadiene Isomers

The molecular structures of perhydrodinorbornadiene isomers are drawn in Figure 27.



**Figure 27:** Molecular structures of perhydrodinorbornadiene RJ-5 isomers. (From [226].)

### 21.3 Chemical Properties of Perhydrodinorbornadiene

Chemical synthesis of RJ-5 (perhydrodinorbornadiene) gives a mixture of many isomers. Depending on synthesis conditions, one of these isomers will be the predominant form. Three different types of “as synthesized” perhydrodinorbornadiene in which the main isomeric constituents were respectively HNN (93%), HXX (75%), and isomer I (57%) were used for a characterization of physical properties [223, 226, 227]. The main isomeric constituent of each fuel was isolated by recrystallizing it from acetone at dry-ice temperature. HNN and HXX could be purified to 99.9% (as determined by GC) in three recrystallizations, but 13 recrystallizations of isomer I gave a purity of only 97%.

### 21.4 Perhydrodinorbornadiene Mixtures

Tetrahydrodicyclopentadiene (JP-10) is used as a viscosity and melting point lowering diluent for RJ-5. An RJ-5/JP-10 mixture with 36–42 mass-% JP-10 is referred to as RJ-6 (see chapter “Ramjet Fuels”). All of the liquids studied here showed a strong tendency to supercool. Often there was considerable difficulty in inducing them to crystallize prior to measuring the melting point, particularly with those liquids blended from “as synthesized” RJ-5.

## 22 Dicyclopentadiene

Dicyclopentadiene is a precursor for the synthesis of tetrahydrodicyclopentadiene, commonly known as JP-10. Dicyclopentadiene, *exo*-tetrahydrodicyclopentadiene,  $C_{10}H_{12}$ , tricyclo[5.2.1.0<sup>2,6</sup>]deca-3,8-diene, 1,3-dicyclopentadiene, DCPD, CAS RN [77-73-6] is a white crystalline solid with a camphor-like odor with a density of  $0.98\text{ g/cm}^3$ , melting point of 305.6 K (32.5 °C), and boiling point of 443 K (170 °C).

### 22.1 Production of Dicyclopentadiene

Dicyclopentadiene is co-produced in large quantities as a side product in the steam cracking of naphtha and gas oils to ethene. The major use is in resins, particularly unsaturated polyester resins. Polymers based on polymerization of dicyclopentadiene were tested for compatibility with HTP [228]. There is an ample supply of dicyclopentadiene as a raw product for the production of JP-10 and other high-density hydrocarbons.

Dicyclopentadiene (tricyclo(5.2.1.0)deca-3,8-diene) is synthesized by a Diels-Alder reaction of cyclopentadiene. The heat of reaction of this dimerization is  $-75.4\text{ kJ/mol}$  and yields two stereo-isomer forms (*endo* and *exo*). If the exothermic reaction occurs unexpectedly during storage of cyclopentadiene, this can lead to accidents. For this reason, cyclopentadiene is traded as its dimer and de-dimerized at the point of use. But even the *endo*-dimer can cause problems. There have been several thermal runaway accidents related to uncontrolled *endo*-to-*exo* conversions [229]. The energy difference of enthalpy of formation between the two isomers was estimated as  $2.9 \pm 0.4\text{ kJ/mol}$  ( $0.7 \pm 0.1\text{ kcal/mol}$ ) based on various computational methods.

The spontaneous dimerization of cyclopentadiene at room temperature to form dicyclopentadiene proceeds to around 50% conversion in the course of 24 h and yields the *endo* isomer in a better than 95:5 *endo*:*exo* ratio as the kinetically favored product. Prolonged heating results in more complete isomerization to the *exo* isomer.

Dimerization of cycloolefins may be achieved catalytically using commercially available Fe(III) salts, and the reaction is applicable to a range of ring sizes (C5–C8) and limited ring-substitution patterns [230].

## 22.2 Physical Properties of Dicyclopentadiene

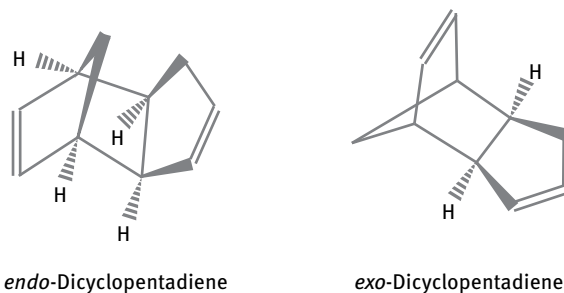
Dicyclopentadiene has a density of  $0.98 \text{ g/cm}^3$ , melting point of  $305.6 \text{ K}$  ( $32.5^\circ\text{C}$ ), and boiling point of  $443 \text{ K}$  ( $170^\circ\text{C}$ ). The vapor pressure at  $293 \text{ K}$  ( $20^\circ\text{C}$ ) is  $180 \text{ Pa}$ . The *endo* isomer is more viscous and has a higher freezing point than the *exo* isomer, and the ratio of the two isomers is not reproducible from batch to batch, which results in undesirable variations of the properties of RJ-4. For this reason, the *endo* isomers are converted to the *exo* isomer by isomerization over  $\text{AlCl}_3$  catalysts, and the isomerized fuel has the designation RJ-4I. This isomerization improves the low-temperature viscosity. The viscosity at  $233 \text{ K}$  ( $-40^\circ\text{C}$ ) is reduced from  $60 \text{ cSt}$  to  $28 \text{ cSt}$ . However, this isomerization causes a slight drop in the heating value, from  $39.0$  to  $38.5 \text{ MJ/L}$ .

## 22.3 Thermodynamic Properties of Dicyclopentadiene

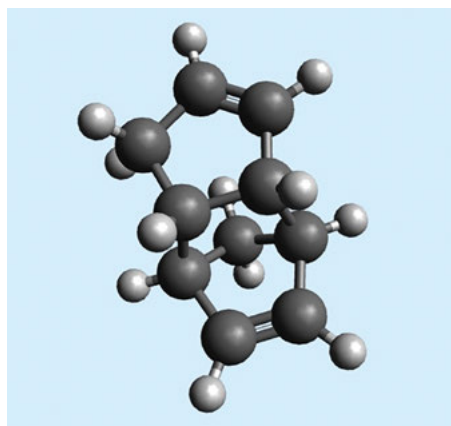
Dicyclopentadiene exists in the form of two structural isomers, the *exo* and *endo* isomers. There have been several thermal runaway accidents related to this hazardous compound. It is well known that enthalpy of formation is one of the most important parameters for investigating thermal runaway reactions. The enthalpy of formation for the *endo* isomer has been characterized via computational and experimental studies; however, there was no thorough computational or experimental study on the enthalpy of formation for the *exo* isomer. Computational chemistry methods with homodesmotic reaction schemes were used to predict the enthalpy of formation for the *exo* isomer [229]. First, the computational methodology was validated by comparing predicted results of the *endo* isomer with its existing experimental value ( $+176 \pm 2 \text{ kJ/mol} = +42.2 \pm 0.6 \text{ kcal/mol}$ ). The results from high-level *ab initio*, density functional theory, and composite methods were shown to be in good agreement with the experimental value. The same methodology was then applied to predict the enthalpy of formation for the *exo* isomer. The energy difference of enthalpy of formation between two isomers was estimated at  $2.9 \pm 0.4 \text{ kJ/mol} = 0.7 \pm 0.1 \text{ kcal/mol}$  based on various computational methods. Therefore, combining the experimental and computational data, the predicted enthalpy of formation for the *exo* isomer is  $+174 \pm 2.5 \text{ kJ/mol} = +41.5 \pm 0.6 \text{ kcal/mol}$ . Thermodynamically, the *exo* isomer is about  $2.9 \text{ kJ/mol}$  ( $0.7 \text{ kcal/mol}$ ) more stable than the *endo* isomer.

## 22.4 Molecular Structure of Dicyclopentadiene

Dicyclopentadiene exists in two stereoisomers, *endo*- and *exo*-dicyclopentadiene (Figures 28 and 29).



**Figure 28:** Molecular structure of *endo*- and *exo*-dicyclopentadiene.



**Figure 29:** Molecular structure of *endo*-dicyclopentadiene.

## 22.5 Chemical Properties of Dicyclopentadiene

### 22.5.1 Reactions of Dicyclopentadiene

Above 423 K (150 °C), dicyclopentadiene undergoes a retro-Diels-Alder reaction at an appreciable rate to yield cyclopentadiene. The reaction is reversible, and at room temperature cyclopentadiene dimerizes again over the course of several hours to re-form dicyclopentadiene [231].

### 22.5.2 Hydrogenation of Dicyclopentadiene

Hydrogenation of dicyclopentadiene gives *endo*-tetrahydrodicyclopentadiene (TH-dimer), the main ingredient in JP-10 (see chapter “Jet Fuels”). It is thus a reaction that is conducted on an industrial scale.

Continued hydrogenation of dicyclopentadiene gives the saturated derivative cycloaliphatic compound  $C_{10}H_{16}$ , which can undergo acid-catalyzed rearrangement to adamantane. The Diels-Alder synthesis from cyclopentene and cyclopentadiene leads

to mixtures of both isomers of dihydrodicyclopentadiene as well as dicyclopentadiene [232].

The kinetics of dicyclopentadiene hydrogenation were investigated in a laboratory stirred autoclave using a powdered palladium catalyst [233]. The time function of reaction mixture composition for different hydrogen partial pressures, temperatures, catalyst weights, and initial concentrations of dicyclopentadiene in a cyclohexane solution was measured, and kinetic data were described using Langmuir-Hinshelwood kinetics. The kinetic rate constant of the first reaction step was 5.5 times higher with respect to the second one. Adsorption constants of unsaturated hydrocarbons are often proportional to the number of double bonds in their molecule. The values of activation energy of both consecutive reactions (25 and 18 kJ/mol) correspond to the interval typical for liquid-phase hydrogenation of unsaturated hydrocarbons.

The intrinsic kinetics of dicyclopentadiene (DCPD) hydrogenation into *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts was investigated using stirred semi-batch reactors in the absence of transport limitations over ranges of temperature (358–438 K) and hydrogen pressure (0.5–3 MPa) [234]. A Langmuir-Hinshelwood-type model was proposed to fit the experimental data. The kinetic parameters were regressed by numerically integrating the differential mass balance equations for the stirred semi-batch reactors. The activation energy for the first- and second-step reactions was 7.8945 and 12.2068 kJ/mol, respectively.

Hydrogenation of DCPD into *endo*-THDCPD in the presence of a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was experimentally and theoretically studied in a quasi-adiabatic trickle-bed reactor with a diameter of 24 mm and a length of 850 mm [235]. Effects of several operating parameters, including the liquid hourly space velocity (LHSV) (6–14 h<sup>-1</sup>), hydrogen pressure (1–2 MPa), inlet liquid concentration (0.5–1.3 mol/L), and inlet temperature (319–379 K) on the trickle-bed reactor performance were investigated systematically in terms of DCPD conversions, THDCPD yields, global hydrogenation rates, and axial temperature profiles. A plug-flow model for the trickle-bed reactor incorporating partial wetting, mass and enthalpy balance, and phase equilibria behavior was developed to simulate the experimental results, based on a phenomenological pellet-scale model. A comparison of experimental and simulated results indicated that the developed model reliably predicted the performance and axial temperature profiles.

The unsteady-state operation of a trickle-bed reactor was investigated using a multi-step exothermic reaction, the hydrogenation of dicyclopentadiene in the presence of a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst [236]. The influence of five operation strategies on the reactor performance was studied and compared with the steady-state operation, including ON-OFF and PEAK-BASE modulations of the liquid flow rate or concentrations, and a simultaneous modulation of both liquid flow rate and concentration. Attempts were also made to develop an unsteady-state operated trickle-bed reactor model based on a plug-flow model incorporating fluid flowing behavior, three-zone partial wetting catalyst, vapor-liquid phase equilibrium, and

enthalpy balance to predict the overall performance under unsteady-state operating conditions. Compared with the experimental observations, the model was generally reliable to predict performance enhancement for different modulation strategies.

GC/MS analysis of reactants and products during the hydrogenation of DCPD to THDCPD over nickel alloy catalyst SRNA-4 showed that the reaction is a consecutive process with two hydrogenated intermediates [237]. Density functional theory simulation confirmed that the double bond in the norbornene ring is easier to saturate than that in the cyclopentene ring, so the major intermediate is 8,9-dihydrodicyclopentadiene (8,9-DHDCPD). In comparison with Raney nickel, SRNA-4 had a significantly higher activity and allowed the reaction to proceed at lower temperature. The reaction conditions, including temperature and hydrogen pressure, were optimized. The optimal hydrogen pressure was 1.5 MPa. To avoid the decomposition of DCPD, a two-stage operation was designed: 373 K for 1 h and then 403 K for another 4 h. Under these conditions, the yield of THDCPD reached 98.5%. The apparent kinetics was calculated using the concentration-time data obtained during the experiments. The activation energy for DCPD to 8,9-DHDCPD and 8,9-DHDCPD to THDCPD reaction was 22.8 and 40.9 kJ/mol, respectively.

The kinetics of dicyclopentadiene hydrogenation were measured at different temperatures (323–353 K) under varying hydrogen pressure (0.5–1.5 MPa) with a range of Pd/C catalyst loading (0.25–1.00 mass-%) using ethanol as a solvent in a batch reactor [238]. The time-dependent concentration variations for each component were traced under the conditions of removing both the internal and external diffusion effects. A Langmuir-Hinshelwood mechanism was proposed with consideration of the non-competitive adsorption between the organic species with hydrogen, and the surface reaction was assumed to be the rate-determining step. The kinetic equations for the sequential reaction were derived on the basis of the analysis of mechanisms, and the model parameters were determined by fitting the experimental data in differential temperature using the method of Runge-Kutta. The reaction activation energies for the first and second steps were 3.19 and 31.69 kJ/mol, respectively, and the reliability of the model was verified by these experimental results in response to changed hydrogen pressure, reactant concentration, and catalyst loading.

A one-step, continuous-flow, catalytic hydrogenation-isomerization of DCPD directly to *exo*-THDCPD has been performed in a fixed-bed reactor [239]. This method is an environmentally friendly and more cost-effective single-step route than the use of  $\text{AlCl}_3$  and noble metals (palladium, platinum, and gold) and instead employs a combination of  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$  catalyst for hydrogenation and  $\text{Ni}/\text{H}\beta$  catalyst for isomerization. The bifunctional catalysts provided 100% DCPD conversion and 70% selectivity for *exo*-THDCPD and displayed a high stability without obvious deactivation during 200 h of testing. The influence of the operating conditions, including temperature, pressure, reaction time, reduction time, liquid hourly space velocity, nickel loading, catalyst weight ratio, calcination temperature of the catalysts, and type of solvent, was studied in detail.



A skeletal nickel catalyst supported on  $\text{Al}_2\text{O}_3$  achieved high dicyclopentadiene conversion (95%) and appropriate THDCPD selectivity (50%) during a 1000-h evaluation for dicyclopentadiene hydrogenation [240]. The optimum operating conditions were  $T = 393\text{K} = 120^\circ\text{C}$ ,  $P = 2.0\text{MPa}$ ,  $\text{LSHV} = 2.0\text{h}^{-1}$ , and hydrogen:oil ratio = 300:1.

The kinetic parameters that characterize the effect of the solvent nature, catalyst concentration, and temperature on the rate of hydrogen uptake in the hydrogenation process during the conversion of dicyclopentadiene (tricyclo[5.2.1.0<sup>2,6</sup>]decadiene-3,8) to dicyclopentene (tricyclo[5.2.1.0<sup>2,6</sup>]decene-3) in the liquid phase under mild conditions at atmospheric pressure over a finely divided 1% Pd/C catalyst have been measured [241]. To substantiate the theory of a stepwise sequence of saturation of the dicyclopentadiene double bonds in terms of the mechanism of heterogeneous catalysis, their reactivity was compared. It was shown that in the presence of a number of functionalized aromatic compounds as stabilizing additives, the yield of desired dicyclopentene increased to 98.5–99 mol-% with complete conversion of all dicyclopentadiene.

### 22.5.3 Oligomerization of Dicyclopentadiene

Cyclopentadiene dimer can be converted to higher-density oligomers by treatment with zeolites [242]. Oligomerization of dicyclopentadiene may be desirable for the synthesis of tricyclopentadiene or polymers, but it would result only in high-molecular-weight, viscous chemicals not suitable as liquid propellants. The synthesis of dicyclopentadiene is discussed in Section 24.1.

The processes of homo-oligomerization and co-oligomerization of dicyclopentadiene were investigated on the laboratory and pilot-plant scale under controlled isothermal or boiling conditions [243]. Reaction conditions and their effect on the quality of products were optimized. The oligomerization of dicyclopentadiene can proceed by two different mechanisms: **(1)** the Diels-Alder polyaddition at temperatures below 473 K (200 °C) and **(2)** thermal oligomerization at temperatures close to 533 K (260 °C). Products obtained by these two mechanisms differed significantly in their physical properties.

An investigation of the oligomerization of cyclopentadiene and its dimer, dicyclopentadiene, to tricyclopentadiene through Diels-Alder reaction at temperatures between 393 and 423 K (120 and 150 °C) showed that reaction temperature, pressure, and solvent influence the product yield [244]. At 423 K (150 °C), a yield of tricyclopentadiene up to 50% was obtained in the absence of solvents. The ratios of isomers in the product can be adjusted by using different solvents. The kinetics indicated that the rate was more sensitive to the concentration of cyclopentadiene than to that of dicyclopentadiene.

The oligomerization of *endo*-dicyclopentadiene in a continuous-flow reactor at elevated pressure was studied to produce tricyclopentadiene that was the precursor for the synthesis of high-energy-density fuels [245]. The composition of the products and

possible reaction pathways were analyzed, and the effects of reaction conditions were evaluated. Compared with the batchwise reaction at atmospheric pressure, the continuous-flow process could significantly enhance the reaction, increase the *exo/endo* ratio of tricyclopentadiene, and produce a new product *exo*-dicyclopentadiene. The *exo/endo* ratio was linearly dependent on the selectivity of *exo*-dicyclopentadiene. A high pressure above 1.2 MPa was necessary to facilitate the reaction. The conversion of *endo*-dicyclopentadiene increased with an increase of temperature, while the yield of tricyclopentadiene reached the highest value at 433 K (160 °C). However, the *exo/endo* ratio decreased with an increase of temperature. Increasing the pressure can improve the conversion, but the *exo/endo* ratio of tricyclopentadiene is unchanged. The conversion of dicyclopentadiene and the yield of tricyclopentadiene increased when the residence time was increased, but the reaction rate decreased. A short residence time was favorable because it led to a high *exo/endo* ratio for tricyclopentadiene. Under the optimal operating conditions, the conversion of *endo*-dicyclopentadiene was 82%, and the yield of tricyclopentadiene was 41%.

The effect of aluminum incorporation over KIT-6 on the catalytic performance in dicyclopentadiene oligomerization reaction has been investigated [246]. Al-KIT-6 was prepared by inserting alumina into KIT-6. The Al-KIT-6 prepared through aluminum grafting over KIT-6 was shown to have a well-arranged mesoporous structure, a large surface area, and a large pore size. Grafting of aluminum on KIT-6 generated Lewis acid sites with weak acid strength. The tricyclopentadiene yield over the Al-KIT-6 catalysts was higher than that over KIT-6 during dicyclopentadiene oligomerization and tricyclopentadiene isomerization. It might be attributed to the higher number of acid sites in the Al-KIT-6 catalyst. Higher *endo*-dicyclopentadiene conversion and higher tricyclopentadiene isomerization selectivity can be achieved by using Al-KIT-6 as compared with Al-MCM-41, likely due to the 3D mesopores and larger pore diameters of the KIT-6 aluminosilicates.

#### 22.5.4 Isomerization of Dicyclopentadiene

Isomerization of dicyclopentadiene is an important step in the production of JP-10. Accordingly, this reaction has been thoroughly investigated. *Endo*-dicyclopentadiene can be isomerized to the *exo*-isomer by thermal treatment at elevated temperature and pressure. The reaction temperature and pressure are key factors for this isomerization [247, 248].

The *endo*- to *exo*-isomerization of dicyclopentadiene can be performed in the liquid phase using acidic zeolites [249]. Among the several zeolites tested, the activity decreased in the sequence  $H\beta > HY > HUSY > HZSM-5 \approx H\text{-mordenite}$ . Beta and Y-type zeolites exhibited higher activity because of their large 3D channels. Surface passivation of  $H\beta$  confirmed that the reaction proceeds in the inner channels. Thermogravimetric measurements verified that HY is deactivated very quickly because the strong acidity induces serious coke formation, but this phenomenon was much less serious over

beta zeolites. Evaluation on H $\beta$  with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios indicated that both the weak Lewis acid concentration and isomerization activity of zeolites monotonically decrease with the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. Thus, a weak acid, especially a weak Lewis acid, of H $\beta$  favors the isomerization reaction. Calcination at 773 K (500 °C) provided the highest activity due to complete removal of template residues, generation of large amounts of weak Lewis acid, and good crystal structure. Zeolites deactivated due to coke deposition could be regenerated by calcination in air flow at 773 K (500 °C), and there was no obvious activity loss after they had been regenerated four times.

The isomerization of *endo*-dicyclopentadiene using aluminum-grafted MCM-41 zeolite was studied as an industrial practical synthesis route for *exo*-dicyclopentadiene [250]. The catalyst showed higher activity than microporous zeolites because its mesoporous structure gives free diffusion and excellent coke formation avoidance. A good correlation between the conversion of *endo*-dicyclopentadiene and the amount of Lewis acid was observed. Specifically, the weak Lewis acid sites catalyzed the *endo*-to-*exo*-isomerization. The moderate acidity sites accounted for the [2 + 2] cycloaddition of two dicyclopentadiene molecules. A catalyst with a Si/Al ratio of 8 was most active due to its highest concentration of weak Lewis acid sites. The addition of inert solvent, relatively low reaction temperature, and high catalyst dosage can improve the isomerization. The deactivated catalyst can be easily regenerated by calcination.

Mesoporous materials synthesized from commercial zeolite beta were applied to dicyclopentadiene oligomerization/dicyclopentadiene oligomer isomerization reactions [251]. A highly ordered mesoporous aluminosilicate, MMZ-H $\beta$ , was synthesized using commercially available zeolite beta as its framework. The MMZ-H $\beta$  catalyst showed high reaction activity and selectivity in dicyclopentadiene oligomerization/dicyclopentadiene oligomer isomerization reactions.

Isomerizing *endo*-dicyclopentadiene into the *exo*-isomer and some *exo*-tricyclopentadiene has great potential in synthesizing high-density fuels, but microporous acidic zeolites showed low activity due to the mass transfer limitation and shape selectivity. A modified HZSM-5 zeolite showed a higher *exo*-dicyclopentadiene yield than those of microporous H $\beta$  and mesoporous Al-MCM-41 [252]. In the oligomerization reaction, hierarchical HZSM-5 showed a higher tricyclopentadiene yield than that of H $\beta$ , and the yield was comparable to that obtained with Al-MCM-41.

MIL-100 (Fe, Cr) and MIL-101 (Fe, Cr) metal-organic frameworks have been used for the solvent-free isomerization of dicyclopentadiene from the *endo* to the *exo* form [253]. In the isomerization reaction, the conversion of *endo*-dicyclopentadiene and selectivity for the *exo*-dimer strongly depended on the nature of the active metal center. The MIL-100 (Fe) catalyst possessing more acid sites showed the highest catalytic activity among the metal-organic frameworks.

### 22.5.5 Thermal Decomposition of Dicyclopentadiene

When heated above 423 K (150 °C), dicyclopentadiene de-dimerizes in a reverse Diels-Alder reaction to yield cyclopentadiene. The reaction is reversible, and at room temperature cyclopentadiene slowly dimerizes to re-form dicyclopentadiene.

### 22.5.6 Hypergolic Ignition Reactions of Dicyclopentadiene

Dicyclopentadiene is produced as a by-product during the high-temperature steam cracking of petroleum gas oil. Dicyclopentadiene, methyldicyclopentadiene, and mixtures containing these fuels will ignite hypergolically with WFNA or RFNA [254, 255].

Solid dicyclopentadiene below its melting point has been evaluated as a binder in hybrid rocket fuel grains. The performance and the regression rate of this fuel can be increased by adding up to 25% sodium borohydride [256]. Similar improvements might be possible by suspending sodium borohydride in gelled liquid fuels containing dicyclopentadiene.

### 22.5.7 Fuel Mixtures with Dicyclopentadiene

*Endo*-dicyclopentadiene is a solid at room temperature, so it would have to be dissolved in a suitable solvent to make a liquid propellant fuel. Isobaric densities and viscosities of five binary liquid mixtures of *endo*-dicyclopentadiene with 2,2-dimethylbutane, 3-methylpentane, *n*-hexane, *n*-heptane, and 2,2,4-trimethylpentane were measured between 288 and 318 K at 5-K intervals [257]. Excess molar volume,  $V_{E_m}$ , viscosity deviation,  $\Delta\eta$ , and excess Gibbs energy of activation of viscous flow,  $G_E$ , have been calculated from these data.

## 23 *exo*-Tetrahydrodicyclopentadiene (JP-10)

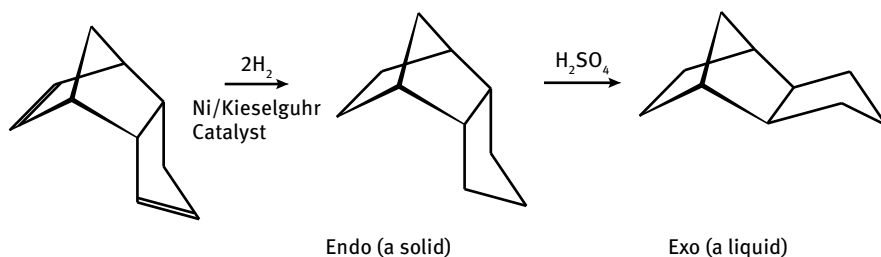
*Exo*-tetrahydrodicyclopentadiene, also known as  $C_{10}H_{16}$ , tricyclo[5.2.1.0<sup>2,6</sup>]-decane, JP-10, CAS RN [2825-82-3], is a liquid with a favorable density (0.94 g/cm<sup>3</sup>) and a low freezing point of 194 K = -79 °C for a mixture of the three stereoisomers. *Exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD) is the main ingredient of JP-10. The difference between pure *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD) and JP-10 is that the formulation meeting the military specification for JP-10 may contain additives to prevent corrosion and autoxidation.

*Exo*-tetrahydrodicyclopentadiene may also be known under one of the following names: tricyclo[5.2.1.0<sup>2,6</sup>]decane; 4,7-methano-1*H*-indene, octahydro-, (3 $\alpha$ ,4 $\beta$ ,7 $\beta$ ,7 $\alpha$ )-; 4,7-methanoindan, hexahydro-, *exo*-; *exo*-hexahydro-4,7-methanoindan; JP-10; *exo*-tetrahydrobicyclopentadiene; *exo*-tetrahydrodi(cyclopentadiene); *exo*-tricyclo(5.2.1.0<sup>2,6</sup>)decane; *exo*-trimethylenenorbornane; *exo*-5,6-trimethylenenorbornane; *exo*-octahydro-4,7-methano-1*H*-indene; *exo*-3,4,8,9-tetrahydrodicyclopent-

tadiene; endo-octahydro-4,7-methano-1*H*-indene; (3 $\alpha$ ,4 $\beta$ ,7 $\beta$ ,7 $\alpha$ )-octahydro-4,7-methano-1*H*-indene. The CAS RN for the endo stereoisomer is [2825-83-4].

### 23.1 Production of *exo*-Tetrahydrodicyclopentadiene

*Exo*-tetrahydrodicyclopentadiene is produced by hydrogenation of dicyclopentadiene, followed by isomerization. *Endo*-tetrahydrodicyclopentadiene is a solid at room temperature and has to be converted to its *exo*-tetrahydrodicyclopentadiene isomer to obtain a liquid fuel.



Several synthetic methods for making *exo*-tetrahydrodicyclopentadiene, including hydrogenation of dicyclopentadiene and isomerization from *endo*-tetrahydrodicyclopentadiene to *exo* form, have been summarized [258, 259]. Different hydrogenation catalysts and process were described, and several hydrogenation catalysts were compared. *Exo*-tetrahydrodicyclopentadiene can be made by continuous or intermittent batch processes, all of which involve isomerization catalysts. The mechanism of isomerization with Lewis acid catalysts has been explained. Additional work was aimed at improved hydrogenation catalysts and isomerization catalysts [149, 150, 259, 260].

An enantiomeric mixture of tricyclodecane can be obtained by hydrogenating dicyclopentadiene in an autoclave over a nickel/MgO/kieselguhr catalyst [261].

Hydrogenation of DCPD into *endo*-THDCPD in the presence of a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was experimentally and theoretically studied in a quasi-adiabatic trickle-bed reactor with a diameter of 24 mm and a length of 850 mm [235]. Effects of several operating parameters, including the liquid hourly space velocity (6–14 h<sup>-1</sup>), hydrogen pressure (1–2 MPa), inlet liquid concentration (0.5–1.3 mol/L), and inlet temperature (319–379 K) on the trickle-bed reactor performance were investigated systematically in terms of DCPD conversions, THDCPD yields, global hydrogenation rates, and axial temperature profiles. A plug-flow model for the trickle-bed reactor incorporating partial wetting, mass and enthalpy balance, and phase equilibria behavior was developed to simulate the experimental results, based on a phenomenological pellet-scale

model. A comparison of experimental and simulated results indicated that the developed model reliably predicted the performance and axial temperature profiles.

Hydrocarbon-soaked  $\text{AlCl}_3$  is a waste product that must be disposed of at the end of *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD) synthesis. H-type zeolites have been evaluated as a replacement for  $\text{AlCl}_3$  in *exo*-THDCPD production [262]. H-type Y zeolites with large pore size (0.74 nm) had sufficient activities for isomerization of *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) to form *exo*-THDCPD. As for acidity strength, the moderate strength of zeolite acidity was favorable. The incorporation of fluorine generated more moderate acids, which improved the catalytic performance of zeolites to *endo*-to-*exo* yield of 92% and *exo* selectivity of 96% and suppressed the adamantane byproduct yield to 2.3%. When  $\text{NH}_4\text{F}/\text{SSY} = 6.57\%$ , calcined at 773 K (500 °C), was used, this showed a performance equivalent to  $\text{AlCl}_3$ .

Tetracyclo[74.0.0<sup>2,7</sup>.1<sup>3,6</sup>]tetradecane was synthesized from dicyclopentadiene and indene by a Diels-Alder reaction and hydrogenation [263]. Under the optimal conditions, the yield of tetracyclo[74.0.0<sup>2,7</sup>.1<sup>3,6</sup>]tetradecane was 68%. Properties of tetracyclo[74.0.0<sup>2,7</sup>.1<sup>3,6</sup>]tetradecane were measured. Density was 0.986 g/cm<sup>3</sup>, volumetric heat of combustion heat was 43.7 MJ/L, viscosity at 255 K (−18 °C) was 97.44 mm<sup>2</sup>s<sup>−1</sup>, flash point was 323 K (50 °C), and freezing point was 228 K (−45 °C). The thermal decomposition of tetracyclo[74.0.0<sup>2,7</sup>.1<sup>3,6</sup>]tetradecane was analyzed by a DSC. Results showed that tetracyclo[74.0.0<sup>2,7</sup>.1<sup>3,6</sup>]tetradecane has high thermal stability.

In a new process for continuous preparation of *exo*-THDCPD using a cascade of two reactors (a continuous-flow bubbling hydrogenation reactor and a continuous-flow isomerization tank reactor), DCPD was hydrogenated to *endo*-THDCPD over a Pd/C catalyst, and the *endo*-THDCPD was isomerized to *exo*-THDCPD over an  $\text{AlCl}_3$  catalyst [264]. Results showed that the optimum liquid-phase continuous-flow process conditions of preparing *exo*-THDCPD were mass hourly space velocity of 2.4 h<sup>−1</sup>, hydrogenation pressure of 0.1 MPa,  $\text{H}_2$  gas flow rate of 80 mL/min, DCPD concentration of 0.76 mol/L, hydrogenation reaction temperature of 303 K (30 °C), and isomerization reaction temperature of 343 K (70 °C), with an *exo*-THDCPD yield of 92.5%.

It is very difficult to separate *endo*- and *exo*-tetrahydrodicyclopentadiene by distillation because the vapor pressures are so similar. The minimum reflux ratio and minimum number of stages were calculated to obtain products having at least a quality of 99.0 mass-% of each component [265]. Separation by distillation would require a tall, fractionated distillation column with 60 theoretical plates operating at a high reflux ratio. The theoretical number of stages was estimated from the correlation of number of stages and reflux ratio.

### 23.1.1 Catalysts for Preparation of *exo*-Tetrahydrodicyclopentadiene by Hydrogenation

THDCPD can be produced through fixed-bed catalytic hydrogenation of DCPD [266]. The effects of catalyst composition and surface pretreatment methods of  $\gamma$ - $\text{Al}_2\text{O}_3$  support on reaction activity were investigated. An impregnated single-ingredient nickel catalyst suitable for this catalytic hydrogenation system with an active metal load of 15% Ni and a support that was physically and chemically pretreated  $\gamma$ - $\text{Al}_2\text{O}_3$  was tested. The activation conditions and the optimum activation process were determined, which were as follows: 423–433 K (150–160 °C),  $P_{\text{H}_2}$ : 1 MPa, space velocity 20–30  $\text{h}^{-1}$ ,  $\text{H}_2/\text{DCPD}$  (mole ratio) 3:1. Under these conditions, the conversion of DCPD was better than 98%, and the yield of THDCPD was close to 95%.

The synthesis of THDCPD from DCPD by catalytic hydrogenation has been studied using a Ziegler-Natta homogeneous catalyst [267]. The results showed that the catalyst had good activity and selectivity; the amount of nickel in the homogeneous catalyst was only 1% that of the heterogeneous catalyst.

Liquid-phase hydrogenation of DCPD to form *endo*-THDCPD was investigated by using SRNA-4 amorphous catalyst under different reaction conditions, including agitation speed, reaction temperature, pressure, and the amount of catalyst used [268]. It was found that the hydrogenation of the DCPD intermediate is a consecutive reaction, during which 9,10-dihydrodicyclopentadiene (9,10-DHDCPD) is a main intermediate and 1,2-dihydrodicyclopentadiene (1,2-DHDCPD) is a minor one. The hydrogenation of DCPD to form 9,10-DHDCPD could be conducted under a mild condition, but more severe conditions are needed for hydrogenating 9,10-DHDCPD to form *endo*-THDCPD. The hydrogenation of DCPD to form *endo*-THDCPD should be carried out in two steps. A temperature of 383 K (110 °C) is used for the first step, and 403 K (130 °C) is used for the second step. A pressure of 1.5 MPa and catalyst amount of 1.18 mass-% were used for both steps. The SRNA-4 amorphous catalyst exhibited hydrogenation activity superior to that of Raney nickel catalyst. When the SRNA-4 amorphous catalyst was used, the intermediate 1,2-DHDCPD could be produced during hydrogenation of DCPD, the reaction temperature and pressure could be lower, the catalyst amount used and reaction time could be less, and the number of by-products could also be fewer than when a Raney nickel catalyst is used.

Hydroconversion of DCPD into tetrahydrodicyclopentadiene has been carried out with a single-step route over a supported gold catalyst [269]. The physicochemical properties of the catalysts were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM),  $\text{N}_2$ -adsorption, and  $\text{NH}_3$ -temperature-programmed desorption (TPD). The influence of reaction conditions such as temperature, pressure, and reaction duration were studied in detail. The studies revealed that pressure and temperature play crucial roles in the reaction. Moderate acid sites in the catalysts are chiefly involved in isomerization, and gold catalyzes hydrogenation of the intermediates. Analysis of the product stream at different intervals

indicated a dissociation-recombination mechanism for the reaction. Reusability of the catalyst was demonstrated by conducting five runs with the same catalyst. Even after the fifth run, the catalyst retained relatively high conversion and selectivity to *exo*-THDCPD.

A one-step, continuous flow phase, catalytic combined hydrogenation-isomerization of DCPD directly into *exo*-THDCPD was carried out in a fixed-bed reactor [239]. This method is an environmentally friendly and more cost-effective single-step route than the use of  $\text{AlCl}_3$  or noble metals (palladium, platinum, and gold) and instead employs a combination of  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$  for hydrogenation and  $\text{Ni}/\text{H}\beta\text{-zeolite}$  for isomerization. The bifunctional catalysts provided 100% DCPD conversion and 70% selectivity for *exo*-THDCPD and displayed a high stability without obvious deactivation over 200 h of testing. The synergistic effect of nickel hydrogenation activity and the isomerization activity of the supports is a key factor for the catalytic combined hydrogenation-isomerization of DCPD. The reaction operating conditions, including temperature, pressure, reaction time, reduction time, liquid hourly space velocity, nickel loading, catalyst weight ratio, calcination temperature of the catalysts, and type of solvents, were optimized.

There are several chemical methods for the synthesis of *exo*-THDCPD. However, it is still a challenge to synthesize *exo*-THDCPD economically. *Exo*-THDCPD has successfully synthesized from DCPD through a simple and environmentally compatible single-step hydroconversion reaction over a mesoporous supported nickel nanocatalyst ( $\text{Ni}/\text{MCM-41}$ ) [270]. The reaction was carried out in an autoclave under a hydrogen pressure ranging from 2.07 to 2.76 MPa (300–400 psia) and temperature ranging from 403 to 423 K (130–150 °C). Progress was monitored by gas chromatography, which revealed that the reaction mechanism goes through dissociation-recombination of DCPD. The major reaction parameters such as temperature, pressure, and nanocatalyst have been experimentally examined for the best yield (85%) of the product. A structural analysis of freshly produced *exo*-THDCPD was carried out using  $^1\text{H}$  NMR and FTIR, and the physicochemical properties were evaluated and confirmed. Good-quality nanocatalyst  $\text{Ni}/\text{MCM-41}$  has been synthesized by the impregnation incipient wetness method and characterized using XRD, energy-dispersive X-ray analysis (EDAX), TEM, and Brunauer-Emmett-Teller (BET) techniques. The nanocatalyst is highly reactive due to its mesoporous structure having appropriate size and shape, which gives free diffusion of the molecules. Repeatability of the nanocatalyst showed good reactivity up to four consecutive runs.

### 23.1.2 Isomerization of Tetrahydrodicyclopentadiene

The isomerization of freshly hydrogenated dicyclopentadiene is part of the production process, and there is some overlap between the following and the previous sections when it comes to the selection of catalysts for hydrogenation and isomerization.



### 23.1.2.1 Aluminum Chloride Catalysts for Isomerization of Tetrahydrodicyclopentadiene

For a very long time, aluminum chloride,  $\text{AlCl}_3$ , was the preferred catalyst for isomerization of *endo*-tetrahydrodicyclopentadiene (*endo*-THDCPD) [271, 272], along with an aluminum halide hydrate as a cocatalyst [273]. The resulting product has a density of  $0.936 \text{ g/cm}^3$  and a heat of combustion of  $39.4 \text{ MJ/L}$  ( $149 \text{ MJ/gal} = 141720 \text{ BTU/gal}$ ).

For the isomerization of *endo*-THDCPD, anhydrous  $\text{AlCl}_3$  was used as catalyst [274]. The effects of catalyst amount, reaction temperature on reaction rate, conversion, yield, selectivity, and by-product formation were investigated. Optimal reaction conditions were catalyst 3%, temperature  $353 \text{ K}$  ( $80^\circ\text{C}$ ), and reaction time 100 min, with conversion of 94.67%, yield 92.26%, and selectivity 97.36%.

Aluminum chloride was again used as a catalyst, but with different solvents for the isomerization of *endo*-THDCPD to *exo*-THDCPD [275]. The effect of the solvents on reaction rate, conversion, yield, selectivity, and by-products was investigated. The results showed that different solvents have different effects on the isomerization. Reaction conversion and yield decreased greatly with toluene as the only solvent. Compared with the isomerization without solvent, using 1,2-dichloroethane as solvent had the best effect on the isomerization under the optimal reaction conditions of a temperature of  $333 \text{ K}$  ( $60^\circ\text{C}$ ) and 3 mass-% catalyst. Less adamantane and no tar were found in the product. The reaction results were conversion 97%, yield 97%, and selectivity 99.9%. A kinetic equation for *endo*-THDCPD isomerization was derived from the measured conversion rates.

Modified clays were pretreated with a pyridine hydrochloride/ $\text{AlCl}_3$  mixture and used for supporting a chloroaluminate ionic liquid catalyst for the isomerization of *endo*-tetrahydrodicyclopentadiene into the corresponding *exo*-isomer [276]. Nearly quantitative conversion to the desired product and nearly quantitative selectivity were achieved by isomerization of *endo*-tetrahydrodicyclopentadiene into the corresponding *exo*-isomer using clay-supported ionic liquid catalysts.

The effects of solvents, catalyst loadings, solvent amount, and reaction time during the preparation of *exo*-tetrahydrodicyclopentadiene by isomerization of *endo*-tetrahydrodicyclopentadiene over  $\text{AlCl}_3$  catalyst were investigated [277]. The optimum operating conditions were obtained as follows:  $(\text{CH}_2\text{Cl}_2):(\text{endo-tetrahydrodicyclopentadiene})$  ratio = 0.8, catalyst loading = 20%, and reaction time = 3 h. Conversion of 97% and selectivity of 99% were attained under these optimum conditions.

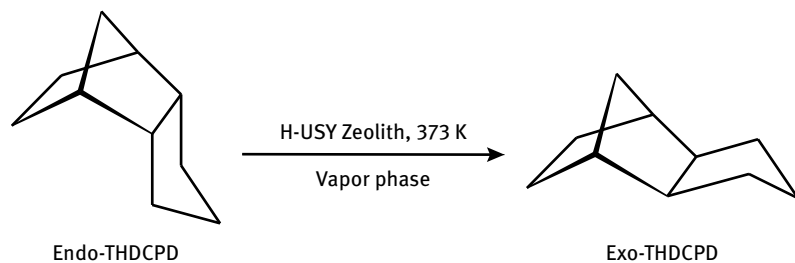
### 23.1.2.2 Zeolite Catalysts for Isomerization of Tetrahydrodicyclopentadiene

The *endo*- to *exo*-isomerization of tetrahydrodicyclopentadiene can be catalyzed by commercially available zeolites [278]. Several zeolites were tested, and the influences of calcination temperatures, Si/Al ratio, and cations of the zeolites on the reaction were investigated. The results showed that, because of their large pore size and relative strong acidity, HY zeolites were more active than other zeolites and Y zeolites

with other cations. In all HY zeolites with different Si/Al ratios, H-USY was the best choice. On one hand, H-USY has more moderate acid sites than others. On the other hand, the high thermal stability of H-USY makes it a suitable choice for recycling catalysts. In all the zeolites tested, H-USY calcined at 723 K (450 °C) was the most favorable catalyst. Regeneration of H-USY showed no decrease of *exo*-yield, while it had better *exo*-selectivity.

Aluminum chloride, which is generally used as catalyst for the isomerization of *endo*-THDCPD, is considered environmentally unsafe to dispose of in landfills. Instead, zeolites were used as catalysts to develop an environmentally more friendly process for the production of *exo*-THDCPD [279]. Among the several zeolites tested, Y type zeolites with larger pores were the most active. HUSY zeolite was more efficient than HSSY due to the abundance of weak acidic sites. Loading of fluorine could suppress the medium acid and increase the weak acid, promoting the selectivity to *exo*-THDCPD. The optimal reaction conditions were as follows: 6.6% F/HSSY as catalyst, temperature 468 K (195 °C), and catalyst percentage 20%. In this case, the conversion of *endo*-THDCPD was 94%, and the selectivity to *exo*-THDCPD was 98.4%. The deactivated catalyst could be effectively regenerated by calcination at 823 K (550 °C).

Vapor-phase isomerization of *endo*-THDCPD to *exo*-THDCPD over zeolite catalysts (HY, H-USY, H $\beta$ , HZSM-5, and HMOR) was studied as an environmentally more friendly synthesis route for *exo*-THDCPD [280]. The HY and H-USY catalysts showed catalytic activity, whereas the H $\beta$ , HZSM-5, and HMOR catalysts did not. Higher yield of *exo*-THDCPD was obtained over the H-USY catalyst than over the HY catalyst, which was attributed to the presence of strong acid sites and mesopores in the H-USY catalyst. The yield of *exo*-THDCPD obtained via vapor-phase isomerization was better than that reported via liquid-phase isomerization. Under the optimized conditions, high-purity (98 mass-%) *exo*-THDCPD was directly obtained without any separation processes. Although some deactivation of the catalyst with time on-stream was observed, the activity could be recovered easily via regeneration in air.



The synthesis of *exo*-THDCPD through the isomerization of *endo*-THDCPD was investigated over HY zeolite catalysts [281]. Conversion of *endo*-THDCPD increased with an increase of the Si/Al<sub>2</sub> ratio of HY zeolite catalysts, which was attributed to an increase of acid strength with increasing Si/Al<sub>2</sub> ratio. The yield of *exo*-THDCPD, however, was

highest over an HY catalyst with an Si/Al<sub>2</sub> ratio of 30 because the production of cyclopentadiene and oligomers was minimized. The optimal reaction temperature was 453 K (180 °C) because the higher reaction temperature increased the production of unwanted by-products. The yield of *exo*-THDCPD also increased with the amount of catalyst in the feed. In the isomerization reaction of *endo*-THDCPD using the HY zeolite catalysts, it was confirmed that the internal diffusion resistance in the pore of catalysts would have more significant effects on the reaction activity than that of the external diffusion resistance of catalysts.

### 23.1.2.3 Other Catalysts for Isomerization of Tetrahydrodicyclopentadiene

The isomerization of *endo*-THDCPD to *exo*-THDCPD (JP-10) and adamantane was investigated using ionic liquids as acid catalysts to explore a less contaminating alternative to the widely used AlCl<sub>3</sub> [282]. Ionic liquids composed of various 1-alkyl-3-methylimidazolium chlorides ([Rmim]Cl) and metal chlorides were tested, and [Bmim]Cl/AlCl<sub>3</sub> was the best candidate. The effects of acidity and dosage of ionic liquids, reaction temperature, and time were studied for *endo*- to *exo*-isomerization of THDCPD. The reaction occurred quickly under mild conditions, with both conversion and selectivity beyond 98%. Purifying the reactant could suppress deactivation of ionic liquids, and the used ionic liquids could be recycled four times by heating under vacuum after each run. By adjusting the reaction conditions to more severe conditions, i.e., higher ionic liquid dosage, higher temperature, and longer time, *exo*-THDCPD was further isomerized to adamantane. The highest yield of adamantane was only 50.9% [283].

*Endo*-THDCPD can be isomerized to its *exo*-isomer (JP-10) by using chloroaluminate ionic liquids as catalysts [284]. The catalyst activity and selectivity could be optimized by varying the mole fraction of AlCl<sub>3</sub> in the ionic liquid. The formation of undesirable by-products derived from side reactions such as skeletal rearrangement, alkylation, cracking, and dimerization could be minimized by appropriate catalyst design and adjustment of the reaction conditions. The catalyst system was further optimized by selecting 1-butyl-3-methylimidazolium chloride as the basic ionic liquid and adding 0.60–0.65 mole fraction of AlCl<sub>3</sub> as the promoter. Using the optimized catalyst system, the isomerization of *endo*-THDCPD to *exo*-THDCPD proceeded at a fast rate at 323 K (50 °C), with 98.9% conversion and 100% selectivity. The catalyst longevity was demonstrated by recycling the ionic liquid several times without a noticeable reduction in catalytic activity.

A palladium or nickel compound, PdCl<sub>2</sub>, Pd(acac)<sub>2</sub>, or Ni(acac)<sub>2</sub>, can be used as a catalyst for the catalytic isomerization of *endo*-tetrahydrodicyclopentadiene to *exo*-tetrahydrodicyclopentadiene [285].

A series of heterogeneous catalysts for the isomerization of *endo*-THDCPD to its *exo*-isomer (*exo*-THDCPD) based on different metal chlorides (AlCl<sub>3</sub>, NbCl<sub>5</sub>, ZnCl<sub>2</sub>) immobilized on silica gel were investigated [286]. The physicochemical properties of the catalysts were studied using SEM, low-temperature nitrogen adsorption, and NH<sub>3</sub>-

TPD. Supported  $\text{AlCl}_3$  exhibited the best catalyst activity and a high selectivity without side reactions such as skeletal rearrangement or alkylation, whereas  $\text{NbCl}_5$  and  $\text{ZnCl}_2$  immobilized on  $\text{SiO}_2$  showed much less catalytic activity.

## 23.2 Physical Properties of *exo*-Tetrahydrodicyclopentadiene

This section overlaps with a similar section, Section 7.2 of chapter “Jet Fuels” in *Encyclopedia of Liquid Fuels*, on the physical properties of JP-10. The main ingredient of JP-10 is *exo*-tetrahydrodicyclopentadiene, and thus the physical properties of JP-10 and the pure *exo*-tetrahydrodicyclopentadiene compound are very similar. The difference between the two is that JP-10 may contain some additives, which would change the physical properties of pure *exo*-tetrahydrodicyclopentadiene. If no better data are available, they could be substituted for each other. If a reader is looking for *exo*-tetrahydrodicyclopentadiene physical property data in this section and does not find them, it would be advisable to go back to the JP-10 section and start looking there.

Physical properties of tetrahydrodicyclopentadiene are summarized in Table 28 and discussed in more detail in individual sections following the table. A separate table, Table 31, summarizes the thermodynamic properties of tetrahydrodicyclopentadiene. A summary of physical properties of *exo*-tetrahydrodicyclopentadiene is available online at [287].

**Table 28:** Physical properties of tetrahydrodicyclopentadiene.

| Property                                 | SI units                              | Other units   | References |
|------------------------------------------|---------------------------------------|---------------|------------|
| Molecular mass                           | 136.2340 g/mol                        | 7.3403 mol/kg |            |
| Freezing point, <i>endo</i>              |                                       |               | [17]       |
| Freezing point, <i>exo</i>               | 183.2 K                               | −89.9 °C      |            |
| Boiling point, <i>endo</i>               | 463.60 K                              | 190.5 °C      | [265]      |
| Boiling point, <i>exo</i>                | 459.38 K                              | 186.23 °C     |            |
| Density at 293 K, mixed                  | 0.9358 g/cm <sup>3</sup>              | 7.810 lb/gal  | [223]      |
| Density at 298 K, <i>exo</i>             | 0.93179 g/cm <sup>3</sup>             | 7.776 lb/gal  | [288]      |
| Density at 293 K, <i>exo</i>             | 0.9563 g/cm <sup>3</sup>              | 7.981 lb/gal  | [265]      |
| Density at 293 K, <i>endo</i>            | 0.9360 g/cm <sup>3</sup>              | 7.811 lb/gal  |            |
| Vapor pressure at 298 K, <i>exo</i>      | 0.34 kPa                              | 2.5 mm Hg     | [288]      |
| Vapor pressure at 298 K, <i>endo</i>     | 0.20 kPa                              | 1.5 mm Hg     |            |
| Kinematic viscosity at 298 K, <i>exo</i> | 2.653 mm <sup>2</sup> s <sup>−1</sup> | 2.653 cSt     | [288]      |
| Critical temperature, <i>exo</i>         | 633.90 K                              | 360.8 °C      | [265]      |
| Critical temperature, <i>endo</i>        | 639.90 K                              | 366.8 °C      |            |

### 23.2.1 Freezing Point of *exo*-Tetrahydrodicyclopentadiene

The freezing point of *exo*-tetrahydrodicyclopentadiene is 183.2 K (−89.9 °C). Other sources list a freezing point of 182.4 K (−90.7 °C) [223].

### 23.2.2 Boiling Point of *exo*-Tetrahydrodicyclopentadiene

In an effort to separate *endo*- and *exo*-tetrahydrodicyclopentadiene by distillation, the boiling points of the two stereoisomers were determined [265]: 459.38 K for *exo*-tetrahydrodicyclopentadiene and 463.60 K for *endo*-tetrahydrodicyclopentadiene.

### 23.2.3 Density of *exo*-Tetrahydrodicyclopentadiene

The density of JP-10 per MIL-DTL-87107E is 0.934–0.943 g/cm<sup>3</sup> at 288 K (15 °C). The density of *exo*-tetrahydrodicyclopentadiene (JP-10) in the temperature range 219–323 K (−54 to +50 °C) can be expressed by a linear equation [222]

$$\rho = \rho_0 - Bt$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $t$  is the temperature in °C. The constants  $\rho_0$  and  $B$  are listed in Table 25 (in the section on perhydrodininorbornadiene). A similar equation for the range 203 to 348 K (−70 to +75 °C) was given in an earlier report [227]:

$$\rho = \rho_0 - bt = 0.950 - 7.7 \times 10^{-4}t$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $t$  is the temperature in °C. A similar equation uses a Fahrenheit temperature scale

$$\rho = 0.96407 - 0.0004391t$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $t$  is the temperature in °F [72].

The density and velocity of sound measurements with JP-10 are summarized in *Encyclopedia of Liquid Fuels* in the chapter “Jet Fuels,” Sections 7.2.2 and 7.2.4 [289].

### 23.2.4 Vapor Pressure of *exo*-Tetrahydrodicyclopentadiene

The vapor pressure of liquid *exo*-tetrahydrodicyclopentadiene (tricyclo[5.2.1.0<sup>2,6</sup>]-decane) in the temperature range 358–417 K can be calculated from the equation

$$\log P = (-2273.7/T) + 7.782$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin [2]. The enthalpy of formation is  $-60.17 \pm 3.8$  kJ/mol ( $-14.38 \pm 0.90$  kcal/mol).

The vapor pressures of *endo*- and *exo*-tetrahydrodicyclopentadiene were measured over the range 335 to 460 K and can be expressed by the Antoine equation [288]

$$\ln P = A - [B/(T + C)]$$

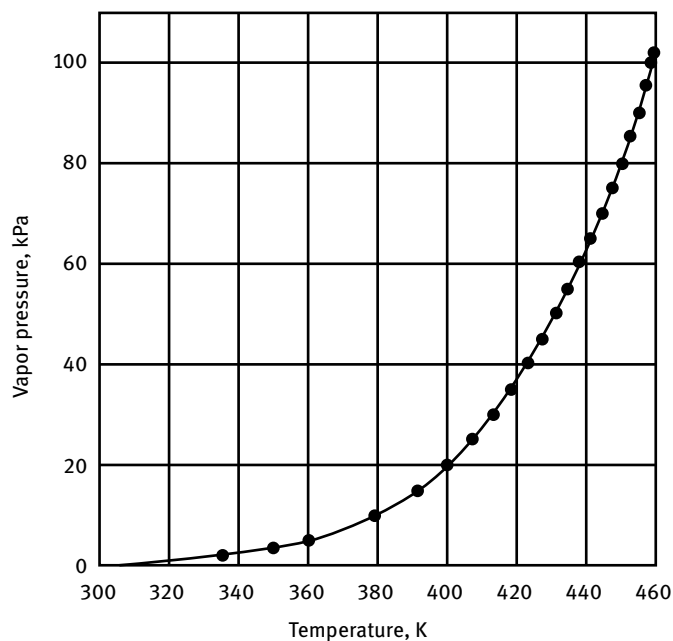
where  $P$  is the vapor pressure in kPa and  $T$  is the temperature in kelvin. The constants A, B, and C are listed in Table 29.

**Table 29:** Antoine constants and standard deviations for the fitted vapor pressures of *exo*-THDCPD and *endo*-THDCPD.

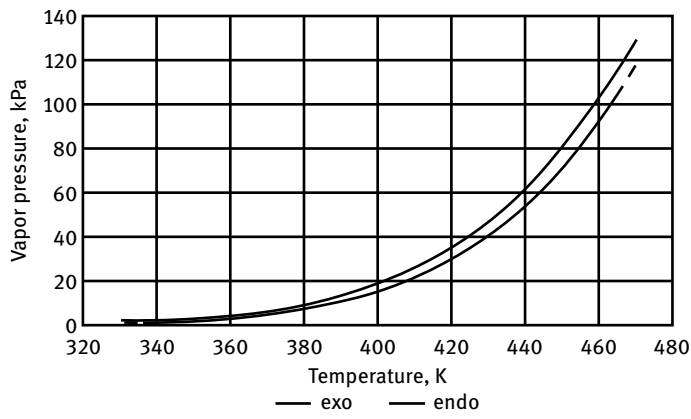
| Component           | A        | B        | C      | Standard deviations |
|---------------------|----------|----------|--------|---------------------|
| <i>Exo</i> -THDCPD  | 17.01851 | 6339.506 | 52.047 | 0.00081             |
| <i>Endo</i> -THDCPD | 16.84102 | 5992.073 | 26.870 | 0.00075             |

Data source: [288]

The vapor pressure of *exo*-tetrahydrodicyclopentadiene is shown in Figure 30, where the solid circles are measured data points and the solid line is the result of the Antoine equation. A similar chart is available for *endo*-tetrahydrodicyclopentadiene. As can be seen from Figure 31, the vapor pressure of *exo*-tetrahydrodicyclopentadiene is slightly higher than that of the *endo*-conformer.



**Figure 30:** Vapor pressure of *exo*-tetrahydrodicyclopentadiene. (Reprinted and modified from [288], with permission from ©2006 Elsevier; permission conveyed through RightsLink.)



**Figure 31:** Comparison of vapor pressures of *exo*- and *endo*-tetrahydrodicyclopentadiene. (Image created by Schmidt 2020 based on data from [288].)

**23.2.5 Viscosity of *exo*-Tetrahydrodicyclopentadiene**

The kinematic viscosity of JP-10 is 40 mm<sup>2</sup>/s = 40 cSt at 219 K (−54 °C) and 10 mm<sup>2</sup>/s = 10 cSt at 255 K (−18 °C). The viscosity of *exo*-tetrahydrodicyclopentadiene (JP-10) in the temperature range 219–323 K (−54 to +50 °C) can be expressed by the following equation [223]:

$$\ln \eta = A + B/(T - T_0)$$

where  $\eta$  is the viscosity in Poise and  $T$  is the temperature in kelvin.  $A$ ,  $B$ , and  $T_0$  are constants listed in Table 26 (in the section on perhydrodinorbornadiene). Additional density and viscosity data are available in [223] for mixtures of *exo*-THDCPD with the isomers of PHDNBD.

The viscosity of *exo*-tetrahydrodicyclopentadiene at 233 K (−40 °C) is 17 cPs [290]. The density of this sample was 0.9369 g/cm<sup>3</sup> at 293 K. The viscosity and density of *exo*-THDCPD was measured between 239 and 341 K (−30 and +155 °F) as listed in Table 30.

**Table 30:** Kinematic viscosity and density of *exo*-tetrahydrodicyclopentadiene.

| Temperature                |        |        |        |
|----------------------------|--------|--------|--------|
| −30                        | 32     | 77     | 155 °F |
| −34                        | 0      | 25     | 68 °C  |
| 239                        | 273    | 298    | 341 K  |
| Viscosity, cSt             |        |        |        |
| 14.55                      | 5.001  | 2.957  | 1.492  |
| Density, g/cm <sup>3</sup> |        |        |        |
| 0.9772                     | 0.9500 | 0.9303 | 0.8960 |

Data source: [72]

### 23.2.6 Surface Tension of *exo*-Tetrahydrodicyclopentadiene

The surface tension of *exo*-tetrahydrodicyclopentadiene is 37.850, 35.928, 32.926, 30.534, and 26.097 dyn/cm at 219, 239, 273, 295, and 343 K (−65, −30, +32, +72, and +158 °F), respectively [72].

### 23.2.7 Thermodynamic Properties of *exo*-Tetrahydrodicyclopentadiene

Thermodynamic properties of *exo*-tetrahydrodicyclopentadiene are listed in Table 31. For some of the literature sources, it was not clear whether the experiments had been done with the *exo* or *endo* conformer or a mixture of the two. Most likely the data reported for the solid state were for the *endo* conformer.

**Table 31:** Thermodynamic properties of *exo*-tetrahydrodicyclopentadiene.

| Property                                                                | SI units                                   | Other units                                  | References |
|-------------------------------------------------------------------------|--------------------------------------------|----------------------------------------------|------------|
| Molecular mass                                                          | 136.2340 g/mol                             | 7.3403 mol/kg                                | [17]       |
| Heat capacity, $C_p$ , vapor, at 293 K, <i>exo</i>                      | 1.573 J g <sup>−1</sup> K <sup>−1</sup>    | 0.376 cal g <sup>−1</sup> °C <sup>−1</sup>   | [72]       |
| Heat capacity, $C_p$ , liquid, at 298 K, <i>exo</i>                     | 213.87 J mol <sup>−1</sup> K <sup>−1</sup> | 51.12 cal mol <sup>−1</sup> °C <sup>−1</sup> | [224]      |
| Standard enthalpy of formation, liquid, $\Delta H_f^{298}$ , <i>exo</i> | −122.8 ± 1.5 kJ/mol                        | −29.35 ± 0.35 kcal/mol                       | [291]      |
| Heat of combustion, liquid, <i>exo</i>                                  | 6099 ± 1 kJ/mol                            | 1457.74 ± 0.26 kcal/mol                      | [77]       |
| Enthalpy of formation, vapor, $\Delta H_f^{298}$                        | −60.17 ± 3.8 kJ/mol                        | −14.38 ± 0.90 kcal/mol                       | [2]        |
| Enthalpy of fusion                                                      | 1.2 kJ/mol at 183.2 K                      | 0.287 kcal/mol at −89.9 °C                   | [292]      |
|                                                                         | 1.1 kJ/mol at 182.4 K                      | 0.263 kcal/mol at −90.7 °C                   | [227]      |
|                                                                         | 2.95 kJ/mol                                | 0.705 kcal/mol                               | [2]        |
| Enthalpy of vaporization at 409 K                                       | 46.0 kJ/mol                                | 11 kcal/mol                                  | [17]       |
| Enthalpy of vaporization at 359–443 K                                   | 43.5 ± 0.8 kJ/mol                          | 10.40 ± 0.2 kcal/mol                         | [2]        |

#### 23.2.7.1 Heat Capacity of *exo*-Tetrahydrodicyclopentadiene

The heat capacity of liquid *exo*-THDCPD in the range 210 to 340 K can be calculated from

$$c_p = 0.254 + 0.00088 (T - 182.4)$$

where  $c_p$  is the heat capacity in cal g<sup>−1</sup> °C<sup>−1</sup> and  $T$  is the temperature in kelvin [227]. The heat capacity of JP-10 in the range 260 to 465 K can be calculated from the equation

$$c_p = 0.10423 + 0.76872 \times 10^{-3} T + 0.46992 \times 10^{-6} T^2$$



where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin [224]. This equation gives a heat capacity of  $213.87 \text{ J mol}^{-1} \text{ K}^{-1}$  at 298 K. Other sources gave heat capacities of  $236.6 \text{ J mol}^{-1} \text{ K}^{-1}$  at 298.15 K ( $0.415 \text{ cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$  at  $25 \text{ } ^\circ\text{C}$ ) [77].

Another equation for the heat capacity of JP-10 in the range 275 to 365 K was listed as

$$c_p = 0.046061 + 0.0012371 T$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin [293, 294]. This equation gives a heat capacity of  $236.5 \text{ J mol}^{-1} \text{ K}^{-1}$  at 298 K.

The heat capacity of *exo*-THDCPD at 233, 293, and 339 K ( $-40$ ,  $+20$ , and  $+66 \text{ } ^\circ\text{C}$ ) is 1.335, 1.573, and  $1.791 \text{ J g}^{-1} \text{ K}^{-1}$  ( $0.319 \text{ cal}$ ,  $0.376$ , and  $0.428 \text{ cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$ ), respectively (average of two consecutive tests [72]).

The isobaric molar heat capacity of *exo*-THDCPD was measured at temperatures from 323 to 523 K with an interval of 10 or 20 K and at pressures from 0.1 to 6.0 MPa with an interval of about 1 MPa by using a flow calorimeter [295]. The results showed that the isobaric heat capacities of *exo*-THDCPD increased gradually with increasing temperature at fixed pressure and decreased with increasing pressure at fixed temperature. A polynomial equation was derived that expresses the heat capacity as a function of both temperature and pressure:

$$C_p = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 + a_6 \ln p + a_7 \ln p^2$$

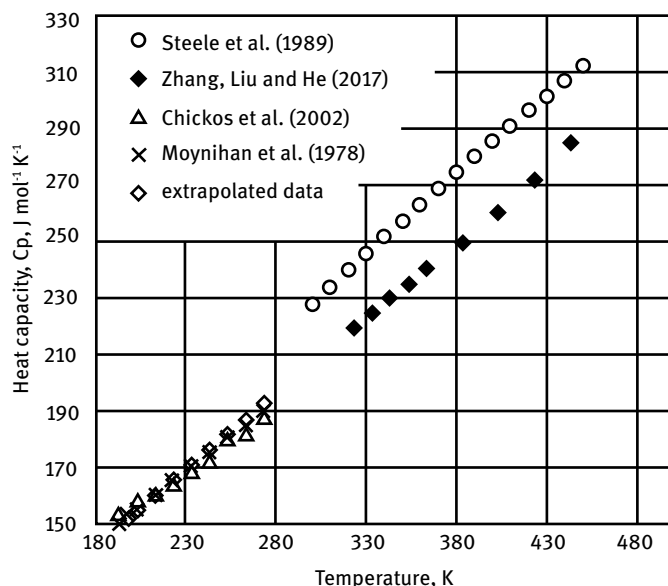
where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{ K}^{-1}$ ,  $T$  is the temperature in kelvin, and  $p$  is the pressure in MPa;  $a_1$  through  $a_7$  are the constants listed in Table 32.

**Table 32:** Parameters of the correlation equation for the heat capacity of *exo*-THDCPD at pressures from 0.1 to 6 MPa and at temperatures from 323 to 523 K.

| Parameter | Value                       | Units                                               |
|-----------|-----------------------------|-----------------------------------------------------|
| $a_1$     | -4112.1053                  | $\text{J K}^{-1} \text{ mol}^{-1}$                  |
| $a_2$     | 41.466491                   | $\text{J K}^{-2} \text{ mol}^{-1}$                  |
| $a_3$     | -0.14878625                 | $\text{J K}^{-3} \text{ mol}^{-1}$                  |
| $a_4$     | $2.3636990 \times 10^{-4}$  | $\text{J K}^{-4} \text{ mol}^{-1}$                  |
| $a_5$     | $-1.3821147 \times 10^{-7}$ | $\text{J K}^{-5} \text{ mol}^{-1}$                  |
| $a_6$     | -1.1282113                  | $\text{J K}^{-1} \text{ mol}^{-1} \text{ MPa}^{-1}$ |
| $a_7$     | -0.58042910                 | $\text{J K}^{-1} \text{ mol}^{-1} \text{ MPa}^{-2}$ |

Data source: [295]

Figure 32 shows a comparison of measured and extrapolated isobaric heat capacity data in the Zhang, Liu, and He 2017 [295] work and reported data in literature. The extrapolated data agreed well with the earlier data reported by Chickos et al. 2002 [292] and Monihan et al. 1978 [226], but the measured data were about 18% below the data reported by Steele et al. 1989 [125].



**Figure 32:** Measured, extrapolated, and reported heat capacity data of *exo*-THDCPD at 0.1 MPa. (Reprinted and modified from [295], with permission from ©2017 Elsevier; permission conveyed through RightsLink.)

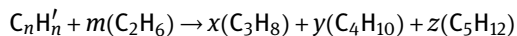
### 23.2.7.2 Enthalpy of Formation of *exo*-Tetrahydrodicyclopentadiene

The enthalpy of formation of *exo*-tetrahydrodicyclopentadiene vapor is  $-60.17 \pm 3.8$  kJ/mol ( $-14.38 \pm 0.90$  kcal/mol) [2]. The heat of combustion of crystalline *exo*-(*endo*-?) tetrahydrodicyclopentadiene is  $6109 \pm 3$  kJ/mol ( $1460.04 \pm 0.60$  kcal/mol). This source does not provide a number for this fuel in the liquid state.

Thermodynamic parameters for the parent *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane molecule and of all the tricyclodecyl radicals corresponding to the loss of hydrogen atoms from different carbon sites were determined using several density functional theory (DFT) and composite computational chemistry methods [296]. Five isodesmic reactions, three involving bridged hydrocarbon reference molecules with similar ring strains, were employed to produce a cancelation of systematic calculation errors in evaluation of standard, gas-phase formation enthalpies at 298 K. The enthalpy of formation  $\Delta H_f^{o298}$  for *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane was predicted to be  $-81.6 \pm 5.4$  kJ/mol ( $-19.5 \pm 1.3$  kcal/mol), which is several kcal/mol lower than the commonly used values. Results from the use of five different DFT methods were in very good agreement with composite level values for all reactions used for the radicals. The *exo* and *endo* isomers of *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane were both determined to have chair and boat conformers.

Combining calculated values for the gas-phase heat of formation with recent measurements of the heat of vaporization yielded recommended values for  $\Delta H_f^\circ(298)_{\text{liq}}$  of  $-126.4$  and  $-114.7$  kJ/mol for the *exo* and *endo* isomers, respectively [297].

The efficiency of DFT was investigated for estimating the gas-phase and condensed-phase heats of formation of 27 polycyclic saturated hydrocarbons  $C_nH_n$  ( $5 \leq n \leq 12$ ) [298]. The homodesmotic reactions



were used where the experimental reference data are available in the literature. The reliability of predicted results through these density functionals was also compared with the corresponding values calculated by other computational approaches. All three methods showed excellent linear relationships with the experimental data.

Based on the reported heat of combustion of liquid XTHDCPD of  $10682.01 \pm 0.90$  cal/g =  $1457.68 \pm 0.33$  kcal/mol, the enthalpy of formation was assumed to be  $-122.8 \pm 1.5$  kJ/mol ( $-29.35 \pm 0.35$  kcal/mol) [291].

### 23.2.7.3 Enthalpy of Fusion of *exo*-Tetrahydrodicyclopentadiene

The molar heat of fusion of *exo*-tetrahydrodicyclopentadiene (XTHDCPD,  $C_{10}H_{16}$ ,  $M = 136.2$  g/mol) at 182.4 K is 1.1 kJ/mol [227]. Later measurements gave similar data: 1.2 kJ/mol at 183.2 K [292]. Low-temperature DSC studies of both isomers revealed solid-to-solid phase transitions. The *endo* isomer, which is a plastic at room temperature, exhibited a solid-to-solid phase transition at  $T = 214$  K with  $\Delta H = 10.7 \pm 0.13$  kJ/mol and a melting temperature of 356.8 K with some evidence of polymorphism. The *exo* isomer exhibited a solid-phase transition at  $T = 162.1$  K with  $\Delta H = 3.18 \pm 0.11$  kJ/mol and a melting temperature of 183.2 K. The more recent data do not quite match older heat of fusion data measured at 352 K with  $2.95 \pm 0.04$  kJ/mol ( $0.705 \pm 0.01$  kcal/mol) [2].

### 23.2.7.4 Enthalpy of Vaporization and Sublimation of *exo*-Tetrahydrodicyclopentadiene

The vaporization enthalpies ( $\Delta H_m$  (298.15 K) of *endo*- and *exo*- tetrahydrodicyclopentadiene THDCPD) have been measured by correlation gas chromatography [292]. Values of  $\Delta H = (50.2 \pm 2.3)$  kJ/mol and  $\Delta H = (49.1 \pm 2.3)$  kJ/mol were obtained for the *endo*- and *exo*-configurations, respectively. The sublimation enthalpy of the *endo* isomer is  $\Delta H = 51.2 \pm 2.4$  kJ/mol and was obtained by combining fusion and vaporization enthalpies adjusted as necessary to  $T = 298.15$  K. Enthalpies of vaporization and sublimation were combined with the respective enthalpies of formation previously reported to yield gas-phase values for *endo*-THDCPD and *exo*-THDCPD of  $\Delta H = -61.9 \pm 3.2$  kJ/mol and  $\Delta H = -73.7 \pm 2.7$  kJ/mol, respectively. Based on vapor-pressure measurements in the range 359 to 443 K, the heat of sublimation at 298 K was calculated to be  $52.96 \pm 1.3$  kJ/mol at 298 K [139].

Older sources reported an enthalpy of vaporization of the liquid of  $53.4 \pm 0.8$  kJ/mol ( $10.40 \pm 0.2$  kcal/mol), calculated from vapor pressure measurements in the range 359 to 443 K [2].

### 23.2.7.5 Heat of Combustion of *exo*-Tetrahydrodicyclopentadiene

It is inconvenient that the heat of combustion and the enthalpy of formation of *exo*-tetrahydrodicyclopentadiene reported in [2] contain data only for the solid and vapor states but not for the liquid state at 298 K. Heat of combustion of JP-10, which would not be very different from that of pure tetrahydrodicyclopentadiene, is reported in this volume in chapter “Jet Fuels.”

The net (lower) heat of combustion of JP-10 per ASTM D240 or D4809 is 42.1 MJ/kg. The heat of combustion of *exo*-tetrahydrodicyclopentadiene is  $6099 \pm 1$  kJ/mol ( $1457.74 \pm 0.26$  kcal/mol) [77]. An earlier report gave the heat of combustion of *exo*-THCPD as  $10682.01 \pm 0.90$  cal/g =  $1457.68 \pm 0.33$  kcal/mol [291]. The gross heat of combustion of *exo*-THCPD is 19156 BTU/lb = 10642 cal/g, and the net heat of combustion is 18083 BTU/lb = 10046 cal/g [72].

### 23.2.7.6 Computational Chemistry of Thermodynamic Properties of *exo*-Tetrahydrodicyclopentadiene

Computational methods to estimate some physical and chemical properties, such as melting point, normal boiling point, standard enthalpy of vaporization at 298 K, standard enthalpy of formation at 298 K, standard enthalpy of combustion at 298 K, density, and flash point of polycyclic alkanes, were validated, despite the scarcity of experimental data, with several tens of polycyclic alkanes [299]. The methods were used to estimate properties of some polycyclic alkanes that are currently in use as missile fuels, such as JP-10, RJ-4, and RJ-5. Estimates and experimental data were found to be in good agreement for these fuels. This methodology was then used to evaluate new missile fuel candidates to be used in the pure state or as additives to JP-10 or to blends such as RJ-6.

The process of screening promising hydrocarbon propellants and eliminating less promising ones can be based on calculating the specific impulse of a rocket engine from the results of quantum-chemical calculation of their heats of combustion [148]. This approach ensures high accuracy irrespective of the composition and structure of the compounds under consideration. Polycyclic and framework hydrocarbons with small rings have been suggested as promising propellants.

Thermodynamic parameters for the parent *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane molecule and of all the tricyclodecyl radicals corresponding to the loss of hydrogen atoms from different carbon sites were determined using several DFT and composite computational chemistry methods [296]. The enthalpy of formation  $\Delta H_f^{o298}$  for *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane was predicted to be  $-81.6 \pm 5.4$  kJ/mol ( $-19.5 \pm 1.3$  kcal/mol), which is several kcal/mol lower than the commonly used values. Results from the use of five

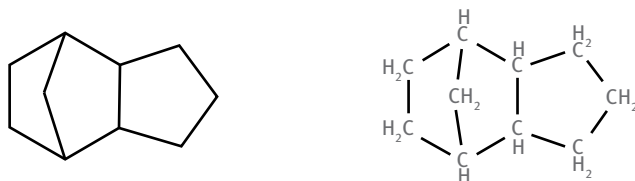
different DFT methods were in very good agreement with composite level values for all reactions used for the radicals.

High-level *ab initio* calculations have been performed on the *exo* and *endo* isomers of gas-phase tetrahydrodicyclopentadiene (THDCPD), a principal component of JP-10, using Gaussian composite methods, as well as the CBS-QB3 method, and have been done using a variety of isodesmic and homodesmotic reaction schemes [297]. The impetus for this work was to resolve large discrepancies between literature data reported for the enthalpy of formation  $\Delta H_f^\circ(298)$  for *exo*-THDCPD. Isodesmic bond separation calculations for the *endo* isomer gave a heat of formation in excellent agreement with the experimental measurements. Combining calculated values for the gas-phase heat of formation with recent measurements of the heat of vaporization yields recommended values for  $\Delta H_f^\circ(298)_{\text{liq}}$  of  $-126.4$  and  $-114.7$  kJ/mol for the *exo* and *endo* isomers, respectively.

DFT calculations were performed to explore the molecular structure, electronic structure, C—H bond dissociation enthalpy, and reaction enthalpies for five isodesmic reactions of tetrahydrodicyclopentadiene [300]. On the basis of the calculations, it was found that the carbonium ion C-6 isomer formed from the catalytic cracking at the C6 site of tetrahydrodicyclopentadiene has the lowest energy, and the R-5 radical generated from the thermal cracking at the C5 site of tetrahydrodicyclopentadiene is the most stable isomer. A series of hypothetical and isodesmic work reactions containing similar bond environments was used to calculate the reaction enthalpies for target compounds. For the same isodesmic reaction, the reaction enthalpy of each carbon site radical was calculated. This method provided some valuable insights into the component design and energy utilization of advanced endothermic fuels.

### 23.2.8 Molecular Structure of *exo*-Tetrahydrodicyclopentadiene

The molecular structure of tetrahydrodicyclopentadiene is illustrated in Figure 33.

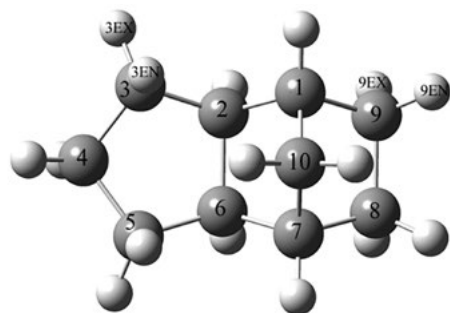


**Figure 33:** Simple plan view of tetrahydrodicyclopentadiene molecule

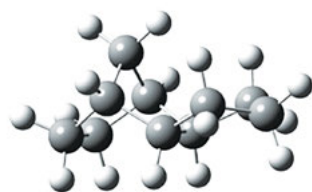
Alternate names for *exo*-tetrahydrodicyclopentadiene are tricyclo[5.2.1.0<sup>2,6</sup>]decane, *exo*-trimethylenenorbornane, *exo* isomer of 4,7-methano-1*H*-indene, octahydro 12a  $\alpha$ , 4 $\alpha$ , 7 $\alpha$ , 7a  $\alpha$ , CAS RN [2825-83-4] and [2825-82-3].

Tetrahydrodicyclopentadiene (THDCP, TCD) exists in either *exo* or *endo* form depending on the respective hydrogen atom/cyclopentane ring positions relative to the single CH<sub>2</sub> bridge carbon of the cyclohexane moiety in the molecule. In addition, there are chair and boat conformations for each of these two isomers. This results from the CH<sub>2</sub> group at C(4) position flop in this non-bridged cyclopentane ring; see Figure 34 for the position numbering scheme [296].

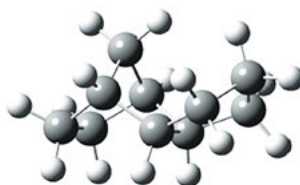
Figures 35 and 36 illustrate the *exo*- and *endo*-isomers along with their respective chair/boat conformations.



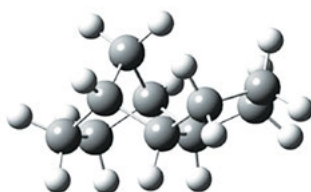
**Figure 34:** Numbering scheme for carbon and hydrogen atoms in tetrahydrodicyclopentadiene. (Reprinted from [296], with permission from ©2010 American Chemical Society; permission conveyed through RightsLink.)



exo-TCD Chair

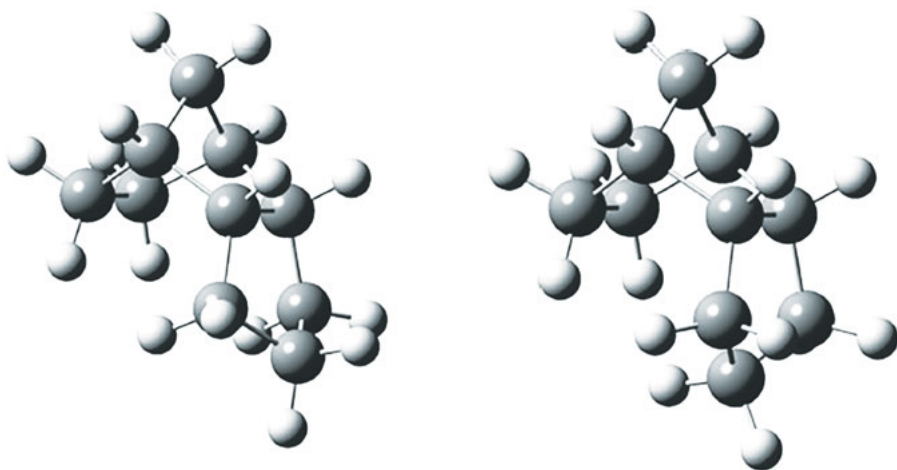


exo-TCD Boat



exo-TCD TS

**Figure 35:** Tetrahydrodicyclopentadiene *exo* isomers along with their respective chair/boat conformations. (Reprinted from [296], with permission from ©2010 American Chemical Society; permission conveyed through RightsLink.)



**Figure 36:** Tetrahydrodicyclopentadiene endo isomers along with their respective chair/boat conformations. (Reprinted from [296], with permission from ©2010 American Chemical Society; permission conveyed through RightsLink.)

The molecular surface properties, including the molecular surface area and the positive, negative, and total average potentials, variances, average deviation, and electrostatic balance parameter on the molecular surface, were used for calculating the heats of vaporization and sublimation of 45 polycyclic saturated hydrocarbons with the general formula  $C_nH_n'$  ( $5 \leq n \leq 16$ ) in order to test 14 well-known isomers of tetrahydrodicyclopentadiene with molecular formulas of  $C_{10}H_{16}$  [301]. These properties were calculated using quantum chemical computational methods. For several compounds where experimental data were available, the agreement between predicted and published results was rather good. For polycyclic isomers of tetrahydrodicyclopentadiene, the highest values of heats of vaporization and sublimation were related to dispiro[2.2.2.2]decane and 1,7,7-trimethyltricyclo[2.2.1.0<sup>2,6</sup>]heptane, respectively. This method provided a suitable pathway to study phase transformations and molecular surface properties of polycyclic saturated hydrocarbon isomers.

DFT calculations were performed to explore the molecular structure, electronic structure, C—H bond dissociation enthalpy, and reaction enthalpies for five isodesmic reactions of *exo*-tetrahydrodicyclopentadiene [300].

### 23.2.9 Electrical Properties of *exo*-tetrahydrodicyclopentadiene

The dielectric constant of *exo*-tetrahydrodicyclopentadiene is 2.554, 2.489, 2.463, and 2.407 at 219, 273, 295, and 342 K (−65, 32, 72.5, and 156 °F) [72].

### 23.3 Fuel Mixtures with *exo*-Tetrahydrodicyclopentadiene

There are numerous fuel mixtures with tetrahydrodicyclopentadiene, the most prominent being RJ-6. RJ-6 is a blend of RJ-5 and JP-10 in the weight-percent ranges shown below. The nominal composition range was 58–64 mass-% perhydrodinorbornadiene (RJ-5) and 36–42 mass-% *exo*-tetrahydrodicyclopentadiene (JP-10).

Another fuel mixture consisted of 50 mass-% tetrahydromethylcyclopentadiene dimer (TH-dimer) with about 50 mass-% *exo*-tetrahydrodicyclopentadiene (*exo*-THDC, JP-10) [290]. The mixture exceeds U.S. Navy flash point requirements of 60 °C while yielding a lower viscosity than TH-dimer alone. Volumetric heating properties of the mixture make it an excellent ramjet fuel.

Other fuel mixtures described in the literature are tetrahydrodicyclopentadiene with *n*-undecane or *n*-tetradecane [302], *n*-nonane, *n*-dodecane or *n*-tridecane [303], cyclohexane, methylcyclohexane, ethylcyclohexane, butylcyclohexane or 1,2,4-trimethylcyclohexane [304], or isopropyl ether [305].

### 23.4 Chemical Properties of *exo*-Tetrahydrodicyclopentadiene

The chemical gross formula for *exo*-tetrahydrodicyclopentadiene (THDCPD) is C<sub>10</sub>H<sub>16</sub> with 11.84 mass-% hydrogen and a molecular mass of 136.24 g/mol. *Exo*-tetrahydrodicyclopentadiene is an isomer of adamantane, limonene, pinene, and camphene.

#### 23.4.1 Thermal Decomposition of *exo*-Tetrahydrodicyclopentadiene

This section overlaps significantly with Section 7.4.3 in the chapter “Jet Fuels” of *Encyclopedia of Liquid Fuels*, concerning the thermal decomposition of JP-10. Most investigators made no distinction between JP-10 and *exo*-tetrahydrodicyclopentadiene (THDCPD), but JP-10 may actually contain additives that influence its thermal decomposition and autoxidation behavior.

There are numerous publications about the thermal decomposition of THDCPD, and just as we have done in a preceding chapter on the thermal decomposition of JP-10, the literature references are given here in chronological order by the date of publication. The decomposition of JP-10 (tricyclo[5.2.1.0<sup>2,6</sup>]decane) was studied in a micro-flow-tube reactor in the temperature range 298 to 1300 K and on a millisecond time scale [306]. Decomposition was found to start at 840 K and was complete by the time the sample reached 1000 K. Thermal decomposition was compared to electron impact dissociation and chemical ionization of JP-10.

During an investigation of the thermal stability of *exo*-tetrahydrodicyclopentadiene (THDCPD), methylcyclohexane (MCH), and aviation kerosene RP-3, it was found that there was a maximum in the rate of thermal oxidation deposit formation at 473, 513, and 493 K (200, 240, and 220 °C) for RP-3, MCH, and THDCPD, respectively [307].



Pyrolytic deposits of three fuels increased dramatically and approximately followed an exponential function with the reaction temperature. The thermal stability of RP-3 was worst among the three fuels, while that of THDCPD was close to that of MCH, and THDCPD displayed even better thermal stability than that of MCH at high temperatures. Under SEM, the oxidation deposits and pyrolytic deposits of the three fuels showed different structure. Filamentous carbon, which contained metal particles that had been removed from the heat transfer surface, was found in the pyrolytic deposits of three fuels. This phenomenon was most obvious in the pyrolytic deposit of MCH.

The thermal decomposition of tricyclodecane was studied in a jet-stirred reactor at temperatures from 848 to 933 K for residence times between 0.5 and 6 s and at atmospheric pressure, corresponding to a conversion between 0.01 and 25% [308]. The main products of the reaction were hydrogen, methane, ethene, ethane, propene, 1,3-cyclopentadiene, cyclopentene, benzene, 1,5-hexadiene, toluene, and 3-cyclopentylcyclopentene. A primary mechanism containing all the possible initiation steps, including those involving diradicals as well as propagation reactions, has been developed and allows experimental results to be satisfactorily modeled. The main reaction pathways of consumption of tricyclodecane and of formation of the main products have been derived from flow rate and sensitivity analyses.

The effects of temperature and contact with metals on the thermal stability of *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane (tricyclodecane, *exo*-THDCP) contained in a temperature-controlled batch reactor were investigated using GC/MS [309]. The surfaces of metals in contact with tricyclodecane were analyzed using SEM-EDAX. In the fuel temperature variation test, thermal decomposition of *exo*-THDCP took place at 623 K (350 °C). In the case of fuel in contact with metals, titanium was less catalytic to decomposition of *exo*-THDCP than stainless-steel CRES-304 or -316.

Thermal stability and the primary initiation mechanism of *exo*-tetrahydrodicyclopentadiene (*exo*-THDCP, C<sub>10</sub>H<sub>16</sub>) decomposition were investigated in a batch-type reactor [310]. The catalytic role of the stainless steel inside the reactor was eliminated by inserting a quartz flask. *Exo*-THDCP decomposed at temperatures over 623 K, and 1-cyclopentylcyclopentene (1-CPCP, C<sub>10</sub>H<sub>16</sub>) and 4-methyl-2,3,4,5,6,7-hexahydro-1*H*-indene (4-MHI, C<sub>10</sub>H<sub>16</sub>) were the primary decomposition products of *exo*-THDCP. C<sub>10</sub> hydrocarbons were determined to be the major products. The amounts of C<sub>5</sub>–C<sub>7</sub> hydrocarbons such as cyclopentene, benzene, and toluene were relatively small. A computer-based molecular modeling on some of the compounds, including 1-CPCP and 4-MHI produced from *exo*-THDCP, was done to evaluate the activation energy and molecular structure of the intermediates. The experimental and molecular modeling results showed that 1-CPCP and 4-MHI were independently formed from *exo*-THDCP. The experimental results closely corresponded with the molecular modeling result. The products that were only produced in small quantities after the reaction had qualitatively higher activation energies than the other products.

The thermal stability of *exo*-THDCP was investigated in the absence and presence of 1,2,3,4-tetrahydroquinoline (THQ), which acts as a hydrogen donor [311]. It

was found that conversion of *exo*-THDCP was faster at the higher temperature, which was to be expected. The increase in the rate of  $C_{<10}$  product formation with increasing temperature was higher than that of  $C_{\geq 10}$  product formation. Conversion of *exo*-THDCP was found to be slowed in the presence of THQ. The THQ-induced decrease in the conversion of *exo*-THDCP was smaller at the higher temperature. In addition, the THQ-induced decrease in the rate of  $C_{<10}$  product formation was smaller than that of  $C_{\geq 10}$ . A mechanism for the thermal decomposition of *exo*-THDCP was proposed, which explained the THQ-induced thermal stability improvement of *exo*-THDCP and suggested a mechanistic basis for developing effective additives capable of lowering decomposition product formation at high temperatures.

The thermal stability of *exo*-THDCP was investigated in the absence and presence of three additives, 3,4-dihydro-2*H*-1,4-benzoxazine (Benzox), THQ, and 1,2,3,4-tetrahydroquinoxaline (THQox), which act as hydrogen donors [312]. Conversion of *exo*-THDCP was slowed in the presence of hydrogen donors. The order of increasing H-donor effects on the decrease in the conversion of *exo*-THDCP was Benzox  $\ll$  THQ  $<$  THQox. The H-donor-induced decrease in the conversion of *exo*-THDCP was less pronounced at higher temperatures. In addition, the H-donor-induced decrease in the rate of  $C_{<10}$  product formation was smaller than that of  $C_{\geq 10}$ . A mechanism was proposed for the thermal decomposition of *exo*-THDCP in the presence of the H donor. The proposed mechanism explains the unusual thermal decomposition kinetics of *exo*-THDCP and H donors in the following way: **(1)** *exo*-THDCP does not follow first-order kinetics, and **(2)** THQ and THQox show the S-shaped concentration-time curves. A proposed mechanism for H donations by Benzox, THQ, and THQox elucidates that THQox performs faster H donation than THQ and has higher thermal stability than Benzox, which accounts for the more effective thermal stability improvement of *exo*-THDCP by THQox compared to THQ and Benzox.

During a further investigation of the decomposition of *exo*-tetrahydrodicyclopentadiene (*exo*-THDCP,  $C_{10}H_{16}$ ) in the absence and presence of  $O_2$  at various temperatures, it was found that the conversion of *exo*-THDCP was faster in the presence of  $O_2$  than in its absence [313]. The  $O_2$ -induced increase in the conversion of *exo*-THDCP was hardly affected by variations in temperature. In addition, the  $O_2$ -induced increase in the rate of  $C_{10}$  product formation was higher than those of  $C_{<10}$  and  $C_{>10}$  product formation. A mechanism was proposed for the oxidative decomposition of *exo*-THDCP, which occurs independently of its thermal decomposition and induces distinct product formation near and below its thermal decomposition starting temperature.

The thermal decomposition properties of *endo*-tetrahydrodicyclopentadiene, *exo*-tetrahydrodicyclopentadiene, tetrahydrotricyclopentadiene, and pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane were studied using DSC and thermogravimetric analysis (TGA)/differential thermogravimetry (DTG) [314]. The thermal decomposition products of pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane were identified by thermogravimetry-DSC-MS. The results showed that the decomposition of high-density hydrocarbon fuels is an endothermic process, and the endothermic heat

of decomposition increases with the pressure. The pyrolysis products are  $C_1$ – $C_5$  of alkanes, alkenes, and alkynes, etc., small molecular compounds. High-density hydrocarbons can be used as the components of endothermic hydrocarbon fuels.

The initial pathways of *exo*-tetrahydrodicyclopentadiene decomposition are expected to have a significant effect on combustion and pyrolysis behavior of the fuel, affecting, for example, product distribution and ignition delay [315]. Modeling of JP-10 decomposition should capture these initial decomposition processes as accurately as possible. Two classes of computational approaches have been applied to study intramolecular disproportionation, an important class of reactions in the initial stages of JP-10 decomposition: **(1)** the second-order, multi-configurational, quasi-degenerate perturbation theory employing the complete active space self-consistent field (CASSCF), and **(2)** the size-extensive, left-eigenstate, completely renormalized coupled-cluster method with singles, doubles, and non-iterative triples, termed CR-CC(2,3), capable of describing reaction pathways involving biradicals. With application of higher levels of theory to points along the CASSCF reaction paths, the barriers to intramolecular disproportionation are much smaller, and some barriers appear to vanish. The conventional ring-opening and disproportionation pathway was compared with an alternative concerted reaction pathway.

The pyrolysis of *exo*-TCD (*exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane) (3 vol.-% *exo*-TCD in argon) was performed in a flow-tube reactor at a temperature range of 900 to 1600 K under low pressure (667 Pa) [316]. The identification of products or intermediates and the distinction of stereoisomers were accomplished by synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). Approximately 28 species were identified and quantified by near-threshold measurements of photoionization mass spectra and photoionization efficiency spectra. The initial unimolecular decomposition rate of *exo*-TCD was estimated using transition states theory and Rice-Ramsperger-Kassel-Marcus (RRKM) theory. A detailed kinetic model of *exo*-TCD pyrolysis was developed including 316 species and 807 reactions. The simulation results generally agreed well with the experimental data. Rate of production and sensitivity analysis indicated that under lower pressure, the initial decomposition of *exo*-TCD proceeds dominantly by a diradical channel rather than the unimolecular decomposition or H-abstraction channels, and that the methyl-cyclic  $C_5$  and methylene-cyclic  $C_5$  species may be one of the principal precursors for the formation of aromatics (benzene, toluene).

*Exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane (TCD) or *exo*-tetrahydrodicyclopentadiene is an interesting strained-ring compound and is the main constituent or single-component of the high-energy density hydrocarbon fuel known as JP-10. Important initial reactions of TCD at high temperatures could cleave a strained carbon–carbon (C–C) bond in the ring system, thereby creating diradicals also constrained by the remaining ring system. The thermochemical properties of these diradicals (TCD-H 2mJ-nJ where m and n correspond to the cleaved carbons sites) including the carbon–carbon bond dissociation energy (C–C BDE) corresponding to the cleaved TCD site, were inves-

tigated [317]. Thermochemical properties, including enthalpies ( $\Delta H_f^{298}$ ), entropies, heat capacities, and C—H and C—C BDEs for the parent (TCD-H2 m-n), radical (TCD-H2 mJ-n and m-nJ), diradical (TCD-H 2mJ-nJ), and carbene (TCD-H 2mJJ-n and m-nJJ) species, were determined by computation. Structures, vibrational frequencies, moments of inertia, and internal rotor potentials were calculated. Standard enthalpies of formation in the gas phase for the TCD-H 2m-n parent and radical species were predicted using DFT and the higher-level composite methods. The bond energies calculated with these methods were shown to be comparable to those obtained by other calculation methods. C—C bond dissociation energies ranged from 324 to 354 kJ/mol (77.4 to 84.6 kcal/mol) for TCD diradical singlet species. C—H BDEs for the parent TCD-H 2m-n carbon sites ranged from 389 to 423 kJ/mol (93–101 kcal/mol), with a similar range seen for loss of the second hydrogen to generate the diradical singlet species.

Two sets of experiments were performed to study the high-temperature pyrolysis of tricyclo[5.2.1.0<sup>2,6</sup>]decane (JP-10) using high-temperature reactors over temperature ranges of 1100 to 1600 K and 927 to 1083 K, with residence times of a few tens of microseconds to, typically, 144 ms [318].

### 23.4.2 Catalyzed Decomposition of *exo*-Tetrahydrodicyclopentadiene

The catalytic cracking of tricyclo [5.2.1.02.6] decane (JP-10) over HZSM-5 molecular sieves with different Si/Al mole ratios was investigated over a temperature range from 773 to 873 K [319]. This reaction of an endothermic fuel is of interest for the cooling of hypersonic flight vehicles. Compared with the thermal cracking and the catalytic cracking over ZSM-5, conversions of JP-10 from the catalytic cracking over HZSM-5 molecular sieves at the same temperature were more rapid. The predominant hydrocarbon products from the catalytic cracking, analyzed at room temperature and atmospheric pressure, were methane, ethane, ethene, propane, and propylene in the gaseous phase and benzene, indene, naphthalene, and their homologues in the liquid phase. The contents of ethane, propane, and propene decreased with increasing Si/Al mole ratio of a catalyst, while those of methane and ethene increased simultaneously with the increase of Si/Al mole ratio of HZSM-5. The contents of the main components in the liquid products produced on the catalyst surface at a given temperature also decreased with the increase of Si/Al mole ratio. A HZSM-5 catalyst with a high Si/Al mole ratio could be chosen to obtain high yields of alkenes.

The thermal decomposition of *exo*-tetrahydrodicyclopentadiene (*exo*-THDCP, C<sub>10</sub>H<sub>16</sub>) was investigated in the absence and presence of various metals, Ti, SS316, SS304, Fe, Ni, and Cu [320]. It was found that conversion of *exo*-THDCP was faster in the presence of metals compared to tests conducted in the absence of metals. The increasing order of the metal catalytic effects on the increase in the conversion of *exo*-THDCP was Ti < SS316 < SS304 < Fe < Ni < Cu. The metal-induced increase in the conversion of *exo*-THDCP was more pronounced at the higher temperature. In addition, the metal-induced increases in the rates of C<sub>5–9</sub>, C<sub>15–</sub>, and C<sub>sd</sub> product for-

mations were higher than those of  $C_{\leq 4}$  and  $C_{10-14}$ . The composition and crystallinity of metal surfaces were found to be associated with the distinct metal effects on the thermal decomposition of *exo*-THDCP.

Catalytic endothermic reactions of *exo*-tetrahydrodicyclopentadiene (*exo*-THDCP) with different zeolites were investigated in a batch reactor to increase the rates and change the product distribution of endothermic reactions [321]. The heat of reaction with each zeolite was calculated by the NIST SUPERTRAPP program. The conversion and product distribution were investigated because they affected the heat of reaction. The heat of reaction of HZSM-5 was greater than those of other zeolites due to its total acid density and pore structures. It showed the highest conversion and highest composition percentage of low molecular weight products. Because dehydrogenation can increase endothermic heat, Pt/HZSM-5 (1 mass-% Pt loaded) was used in the endothermic reaction. The metal sites led to the dehydrogenation of saturated hydrocarbons and an increase in olefins. High conversion and high yields of low molecular weight hydrocarbons and olefins were necessary to increase the overall heat of reaction.

### 23.4.3 Computational Modeling of *exo*-Tetrahydrodicyclopentadiene Decomposition

The initial pathways of *exo*-tetrahydrodicyclopentadiene decomposition are expected to have a significant effect on the combustion and pyrolysis behavior of the fuel, affecting, for example, product distribution and ignition delay [315]. Modeling of *exo*-tetrahydrodicyclopentadiene decomposition should capture these initial decomposition processes as accurately as possible. Two classes of computational approaches have been applied to study intramolecular disproportionation, an important class of reactions in the initial stages of *exo*-tetrahydrodicyclopentadiene decomposition: **(1)** the second-order, multi-configurational, quasi-degenerate perturbation theory employing the complete active space self-consistent field (CASSCF) reference, and **(2)** the size-extensive, left-eigenstate, completely renormalized, coupled-cluster method with singles, doubles, and non-iterative triples, termed CR-CC(2,3), capable of describing reaction pathways involving biradicals. With the application of higher levels of theory to points along the CASSCF reaction paths, the barriers to intramolecular disproportionation were much smaller, and some barriers appeared to vanish. The conventional ring-opening and disproportionation pathway was compared with an alternative concerted reaction pathway.

The  $C < 5$  products predicted by molecular dynamics simulations were consistent with those detected using experimental techniques [322]. Particularly, the product evolution tendency of methane, ethane, ethylene, propylene, acetylene, allene, 1-butene, propyne, 1,3-butadiene, and cyclopentadiene with temperature was in good agreement with the results of single-pulse shock tube experiments. The simulation results indicated that JP-10 pyrolysis reactions proceed in three stages: the initial ring-opening through C—C bond homolysis in stage I, the initiation and growth of

chain radicals through  $\beta$ -scission reactions as well as chain propagation via C—H bond scission in stage II, and the chain propagation through further C—H bond cleavage and the chain termination reactions in stage III.

#### 23.4.4 Oxidation of *exo*-Tetrahydrodicyclopentadiene

Traces of oxygen have been identified as having a pronounced effect on the onset of thermal decomposition of many hydrocarbons.

The exothermicity of oxidation of *exo*-tetrahydrodicyclopentadiene ultimately leads to ignition of the fuel if sufficient air or oxygen is present. The kinetics of oxidation of *exo*-tetrahydrodicyclopentadiene is discussed here, while actual combustion properties (ignition energy, flame speed, detonation speed) will be discussed in a future *Encyclopedia of Nonhypergolic Bipropellant Combinations*.

The ignition of JP-10 was examined from computational and theoretical viewpoints [323]. A detailed chemical mechanism consisting of 174 elementary steps among 36 chemical species was obtained by adding 27 steps, including JP-10, cyclopentene, and 1,3-butadiene, to an earlier scheme. See also [324]. The ignition of *exo*-tetrahydrodicyclopentadiene droplets in air is different if the fuel is doped with aluminum nanoparticles to enhance its fuel value [325].

#### 23.4.5 Analysis of *exo*-Tetrahydrodicyclopentadiene

The constituents of four types of JP-10 were analyzed using GC/MS [326]. The purity of JP-10 fuels was measured with an external standard method. Results showed that JP-10 contained not only the main component *exo*-tetrahydrodicyclopentadiene but also decahydronaphthalene, *endo*-tetrahydrodicyclopentadiene, adamantane, and their methylated derivatives. The suitable concentration range for external standard method to measure the purity of JP-10 is 0.5–20 mg/mL.

### 23.5 Safety Properties of *exo*-Tetrahydrodicyclopentadiene

The flash point of JP-10 is 327.5 K (54.4 °C), and it is assumed that the flash point of *exo*-tetrahydrodicyclopentadiene would be the same. One sample of *exo*-tetrahydrodicyclopentadiene had a flash point of 329 K (56 °C) [290].

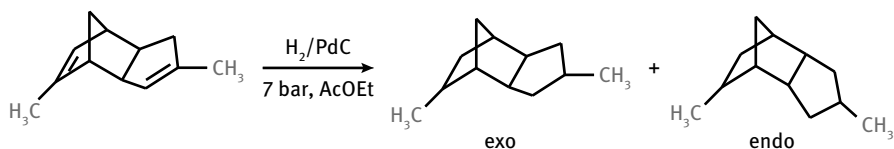
## 24 Tetrahydrodimethyldicyclopentadiene

Tetrahydrodimethyldicyclopentadiene, C<sub>12</sub>H<sub>20</sub>, CAS RN [26472-00-4], is the main ingredient of RJ-4. The properties of RJ-4 are described in the chapter “Ramjet Fuels” of *Encyclopedia of Liquid Fuels*.

In the following section are listed the properties of the pure compound tetrahydromethylcyclopentadiene, not those of the RJ-4 mixture.

### 24.1 Production of Tetrahydromethylcyclopentadiene

Tetrahydromethylcyclopentadiene can be prepared by hydrogenation of dimethylcyclopentadiene, followed by isomerization.



The precursor, dimethylcyclopentadiene, can be prepared by dimerization of methylcyclopentadiene. Both the hydrogenation and the isomerization steps use a nickel on silica-alumina catalyst [327]. The temperature of the hydrogenation should be in the range of about 343–533 K (70–260 °C) and the temperature of the isomerization in the range of about 473–553 K (200–280 °C) [328]. The pressure range for hydrogenation is about 1.38–20.7 MPa (200–3000 psig) and for isomerization is between 0.07 and 10.3 MPa (10–1500 psig). Hydrogen is present during the isomerization.

*Endo*-tetrahydromethylcyclopentadiene isomers within the raw fuel stock can be isomerized to *exo*-isomers by treatment of the fuel stock with catalysts such as aluminum chloride, nickel, or pulverized, acid-treated firebrick, resulting in a fuel with a lower viscosity than the original raw fuel stock [329].

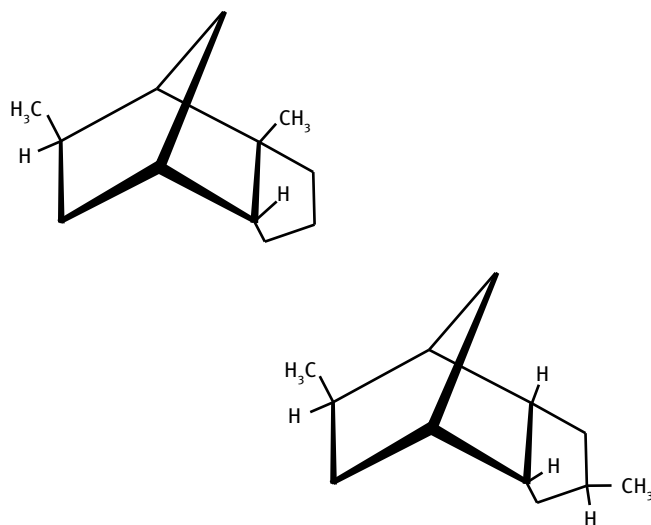
Tetrahydromethylcyclopentadiene can be catalytically isomerized to a liquid isomeric mixture having a suitable low temperature viscosity, making it suitable as a missile fuel. One catalyst proposed for the isomerization was an acidic alumina. Hydrogen was also kept present and in an amount sufficient to maintain the isomerization activity of the alumina. Moderately elevated temperature is sufficient to cause isomerization. The temperature of the isomerization is in the range of about 473–553 K (200–280 °C) [328].

The kinetics of hydrogenation of methylcyclopentadiene dimer (MCPD) to *endo*-tetrahydromethylcyclopentadiene over Pd/C catalysts were investigated, and the reactivity of the C=C bond in the MCPD molecule was analyzed using DFT calculations [330]. A kinetic model was developed based on the Langmuir-Hinshelwood mechanism with the consideration of the non-competitive adsorption between the organic species and atomic hydrogen. The model parameters were obtained by fitting experimental data at differential temperatures using the non-linear least squares and Runge-Kutta methods. The reaction activation energies for the two steps of hydrogenation

were 22.86 and 41.21 kJ/mol. The good correlation between the kinetic model and the experimental data contributed to a better understanding of the consecutive hydrogenation mechanism of high-density polycyclic hydrocarbon fuels.

## 24.2 Physical Properties of Tetrahydrodimethyldicyclopentadiene

The physical properties of tetrahydrodimethyldicyclopentadiene depend on the proportions of stereoisomers, in particular the ratio of *endo*- to *exo*-isomers. The *endo* isomers have higher melting points and may solidify at room temperature. There are only a few exact physical property data for the isolated isomers with a clean structure. Pure compounds are not required for the RJ-4 application. The two structural isomers shown in Figure 37 are liquids at room temperature, while other, undesirable isomers are solids and not suitable as liquid fuels.



**Figure 37:** Molecular structure of tetrahydrodimethyldicyclopentadiene isomers

## 24.3 Chemical Properties of Tetrahydrodimethyldicyclopentadiene

The empirical, gross chemical formula of tetrahydrodimethyldicyclopentadiene is  $C_{12}H_{20}$ , with a hydrogen content of 12.27 mass-% and a molecular mass of 164.29 g/mol.



## 25 Tricyclopentadiene

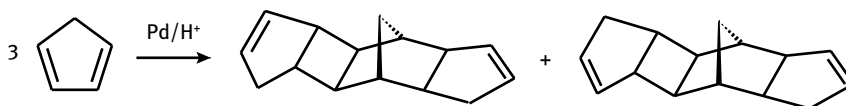
Tricyclopentadiene, also known as  $C_{15}H_{18}$ , cyclopentadiene trimer, TCPD; 4,9:5,8-dimethano-1*H*-benz[*f*]indene, 3a,4,4a,5,8,8a,9,9a-octahydro-; CAS RN [7158-25-0], is a by-product of the synthesis of dicyclopentadiene.

### 25.1 Production of Tricyclopentadiene

Tricyclopentadiene, a product of dicyclopentadiene/cyclopentadiene cycloaddition, is a precursor for synthesis of a high-energy-density fuel, tetrahydrotricyclopentadiene. Tricyclopentadiene can be prepared by heating feed streams containing dicyclopentadiene or cyclopentadiene or mixtures of the two [331]. The yield of tricyclopentadiene is better if the feed stream is mostly dicyclopentadiene, for instance 50% dicyclopentadiene in benzene as the process solvent. The reactor temperature should be between 533 and 583 K (260 and 310 °C) because no trimerization occurs below 533 K (260 °C), and temperatures above 583 K (310 °C) lead to undesirable tetramers and higher oligomers. The residence time in the reactor zone should be 10–20 min.

Mixtures of cyclopentadiene and methylcyclopentadiene dimers can be co-reacted at 483 K (210 °C) for 1 h to generate a mixture of trimers that can subsequently be hydrogenated to give a high-density fuel, tetrahydrotricyclopentadiene, with a density of 1.018 g/cm<sup>3</sup> and a freezing point below 219 K (–65 °F) [332].

Nearly total suppression of the unwanted dimerization and selective trimerization of cyclopentadiene can be achieved by a mixed catalyst formed from a palladium complex, a phosphane, and a carboxylic acid [333]. The cyclopentene ring attached to the norbornane system of the trimers 1a, 1b is in the endo conformation and differs only in the location of the double bonds.



The processes of homo-oligomerization and co-oligomerization of dicyclopentadiene were investigated on the laboratory and pilot-plant scale under controlled isothermal or boiling conditions [243]. Reaction conditions and their effect on the quality of products were optimized. The oligomerization of dicyclopentadiene can proceed by two different mechanisms: **(1)** the Diels-Alder polyaddition at temperatures below 473 K (200 °C) and **(2)** thermal oligomerization at temperatures close to 533 K (260 °C). Products obtained by these two mechanisms differed significantly in their physical properties. Realistic models of Diels-Alder and thermal oligomerization processes considering reversible reaction kinetics and vapor-liquid-phase equilibrium were developed.

Pressure and the presence of high-boiling process solvents had an effect on the Diels-Alder oligomerization process and product properties.

Oligomerization reactions of cyclopentadiene and dicyclopentadiene are discussed in Section 22.5.3. Tricyclopentadiene can be made by oligomerization of *endo*-dicyclopentadiene at elevated pressure [244, 245, 334].

Thermal  $[4 + 2]$  cycloaddition of dicyclopentadiene/cyclopentadiene was simulated using a computer program to predict the product distribution [335]. There are four concerted but slightly asynchronous pathways leading to four adducts for *endo*-dicyclopentadiene/cyclopentadiene and *exo*-dicyclopentadiene/cyclopentadiene additions, respectively. The pathways connecting *endo*-adduct are kinetically preferred compared with those connecting *exo*-adduct. Norbornadiene-adducts showed higher stability than corresponding cyclopentadiene adducts. *Exo*-isomers are more stable for cyclopentadiene adducts, but the tendency is inverse for norbornadiene adducts.

Tricyclopentadiene was synthesized by oligomerization of dicyclopentadiene and cyclopentadiene, with a yield up to 83.2% [336]. A study of the effects of catalyst amount, temperature, and type of solvent on the reaction showed that the optimum conditions were a molar ratio of  $[\text{Ni}(\text{PPh}_3)_2]\text{Cl}_2:\text{Zn}:\text{cyclopentadiene} = 0.05:0.6:1$ , reaction temperature 333 K (60 °C), and reaction duration 8 h. Compared to the Diels-Alder method, the oligomerization method proceeds at a lower reaction temperature and pressure (0.1 MPa) and gives a higher yield.

Cyclopentadiene trimer (tricyclopentadiene) is an important raw material for the synthesis of high-energy-density fuels. Tricyclopentadiene can be synthesized through a  $[4 + 2]$  cycloaddition between *endo*-dicyclopentadiene and cyclopentadiene over microporous zeolites (ZSM-5, HY) and mesoporous Al-MCM-41 catalysts [337]. The catalytic activity was strongly influenced by the average pore size and the Brønsted acidity of the catalyst. Of the several catalysts tested, an  $\text{NH}_4\text{F}$ -treated Al-MCM-41 catalyst, which had meso-sized pores (3.4 nm in average) and enhanced Brønsted acidity, exhibited the best dicyclopentadiene conversion, tricyclopentadiene selectivity, and yield. The average pore size of the catalyst influenced the isomer distribution of the tricyclopentadiene products. The mesoporous catalysts produced mixtures of *exo*- and *endo*-tricyclopentadiene, which favored the *exo*-fraction (approximately 40 mol-%) compared to the microporous catalysts (approximately 20 mol-%).

Homogeneous palladium catalysts enable the  $[2 + 2]$  isomer synthesis of tricyclopentadiene in good yield (up to 98% from cyclopentadiene and up to 78% from dicyclopentadiene) with high selectivity. The effects of a variety of palladium precursors, phosphorus ligands, and acids were investigated to improve the productivity and selectivity of the tricyclopentadiene synthesis [338]. The reaction conditions were optimized, and their effects on the product distribution were evaluated.

Tricyclopentadiene is one of the precursors for making tetrahydrotricyclopentadiene, a fuel with high energy density. Tricyclopentadiene was obtained by polymerization reaction of DCPD using ionic liquid-supported mesoporous silica catalysts [339].

Ionic liquid-supported mesoporous silicas showed better catalytic performance with regard to tricyclopentadiene yield and dicyclopentadiene conversion than those not using ionic liquids. Among four kinds of ionic liquid-supported mesoporous silica catalysts, the CuCl-based ionic liquid-supported MCM-41 system showed the highest tricyclopentadiene yield.

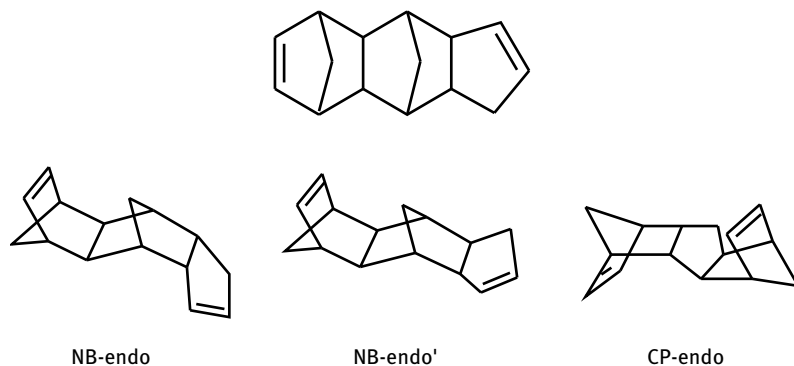
The catalytic potential of metal oxide/MCM-41 catalysts, including molybdenum oxide, tungsten oxide, and titanium oxide on MCM-41, for the dicyclopentadiene oligomerization and dicyclopentadiene oligomer isomerization was evaluated [340]. The number of acid sites with weak strength were increased through metal oxide deposition. The oligomer yield in dicyclopentadiene oligomerization and dicyclopentadiene oligomer isomerization did not change with an increasing number of acid sites. The highest tricyclopentadiene isomer selectivity over the MoO<sub>3</sub>/MCM-41 catalyst could be attributed to having the highest overall number of acid sites among the several catalysts tested.

A catalyst composed of microporous and mesoporous material prepared from ferrierite was evaluated as a catalyst for oligomerization of *endo*-dicyclopentadiene (DCPD) [341]. Physical and chemical characteristics of the catalysts were analyzed using NH<sub>3</sub>-TPD, N<sub>2</sub> adsorption, XRD, and IR spectroscopy of adsorbed pyridine. The catalyst showed a weak acid site composed of Brønsted acid site, Lewis acid sites, and H acid sites, whereas strong acid sites were not observed. In the case of the dicyclopentadiene oligomerization that utilized this catalyst, the yield of tricyclopentadiene and tetracyclopentadiene reached 30.4 and 19.9%, respectively, which were higher than those obtained with other catalysts. This is a good catalyst for the isomerization selectivity to *exo*-tricyclopentadiene. Weak acid sites on this catalyst play a role as active sites for *endo*-dicyclopentadiene oligomerization. The higher activity in dicyclopentadiene oligomerization is probably due to the large pore size of this catalyst.

The oligomerization of *endo*-dicyclopentadiene (*endo*-DCPD) over a mesoporous catalyst in a continuous-flow reactor at elevated pressure was studied to produce tricyclopentadiene (TCPD) and tetracyclopentadiene (TeCPD) [342]. A mesoporous material prepared from a zeolite was used as a catalyst. TCPD and TeCPD were continuously produced through DCPD oligomerization over the zeolite catalyst in a fixed-bed reactor. At early time-on-stream, the conversion of *endo*-DCPD, the yield of TCPD and TeCPD, and the isomerization selectivity of TCPD in the fixed-bed reactor were comparable to those in a batch-type reactor. The yield of oligomer containing TCPD and TeCPD decreased drastically from 28.5% at 3 h time-on-stream to 21.5% at 12 h time-on-stream, indicating that the catalyst was being deactivated, but *in situ* calcination in air flow at 773 K (500 °C) was found to be effective for the regeneration of the used catalyst.

## 25.2 Physical Properties of Tricyclopentadiene

There are no summaries of physical properties of tricyclopentadiene in the literature. It is difficult to obtain samples with pure isomers for physical property determination. The molecular structures of three possible isomers of tricyclopentadiene are shown in Figure 38.



**Figure 38:** Three possible isomers of tricyclopentadiene

## 25.3 Chemical Properties of Tricyclopentadiene

The hydrogenation of tricyclopentadiene results in the formation of tetrahydrotricyclopentadiene. Therefore, the publications dealing with this reaction will be discussed in the following section.

## 26 Tetrahydrotricyclopentadiene

Tetrahydrotricyclopentadiene, *exo*-THTC, THTCPD,  $C_{15}H_{22}$ , CAS RN [56086-31-8], exists in several stereoisomers, of which the *exo*-conformer is the one with importance as a candidate high-density fuel, a possible successor to and future replacement of JP-10 with even better properties. Other names for this compound are 4,9:5,8-dimethano-1*H*-benz[*f*]indene, dodecahydro-; 4,9,5,8-dimethano-1- $\beta$ -naphthindene, dodecahydro- (3CI); and dodecahydro-4,9:5,8-dimethano-1*H*-benz[*f*]indene.

## 26.1 Preparation of Tetrahydrotricyclopentadiene

As the first step in this synthesis, dicyclopentadiene is heated in a closed system to 443 K (170 °C), forming tricyclopentadiene, tetracyclopentadiene, and pentacyclopentadiene as products. The reaction mixture is distilled, and the 438–448 K (165–175 °C) fraction is then hydrogenated in the presence of a Ni/kieselguhr catalyst, giving a mixture of stereoisomers [343]. Isomerizing the *endo*-tetrahydrotricyclopentadiene by treatment with aluminum chloride at a temperature from 273 to 293 K (0 to 20 °C) in a methylene chloride solvent forms the desired *exo*-tetrahydrotricyclopentadiene, a low-freezing, high-density liquid fuel.

Pd – B/γ-Al<sub>2</sub>O<sub>3</sub> amorphous catalysts were prepared through impregnation and KBH<sub>4</sub> reduction and then used for the hydrogenation of tricyclopentadiene [344]. The kinetics of tricyclopentadiene hydrogenation to tetrahydrotricyclopentadiene over Pd – B/γ-Al<sub>2</sub>O<sub>3</sub> amorphous catalyst was studied in a stirred semi-batch reactor over a range of temperatures (353–413 K), hydrogen pressures (1.0–3.5 MPa), initial feed concentrations (0.2–0.4 mol/L), and catalyst concentrations (0.60–5.33 g/L) [345]. The reaction was found to be a consecutive reaction, with 14,15-dihydrotricyclopentadiene as the intermediate product. Analysis verified that the kinetic experiments were conducted in the absence of mass transfer resistance. A kinetic model was formulated with the assumptions that single-site adsorbed organic species are saturated by hydrogen dissolved in the liquid phase and that the surface reaction is rate-determining. This model was able to accurately fit the experimental data in the ranges studied and correctly explained the observed tendencies. The activation energies for the first-step and second-step reactions were 11.11 and 34.71 kJ/mol, respectively.

Crystallized Pd – B/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were obtained by thermal treatment of the prepared amorphous catalyst at elevated temperatures. For comparison, a conventional H<sub>2</sub>-reduced Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was also prepared. The catalysts were characterized by inductively coupled plasma, XRD, SEM, TEM, DSC, and TPD, and were used for the hydrogenation of tricyclopentadiene [346]. All the catalysts demonstrated similar activities for partial hydrogenation of tricyclopentadiene to dihydrotricyclopentadiene. However, the amorphous alloy catalyst showed significantly higher activity for the further hydrogenation of dihydrotricyclopentadiene to the final product tetrahydrotricyclopentadiene.

Tetrahydrotricyclopentadiene has been prepared by the reaction of dicyclopentadiene with cyclopentadiene by first reacting dicyclopentadiene with cyclopentadiene to produce tricyclopentadiene, which was then converted into the final product in the presence of H and Raney nickel [347]. A study of the effects of temperature, pressure, and reaction time as well as the solvent amount on conversion and yield showed that the optimal conditions were a temperature of 493 K (220 °C), a pressure of 0.5 MPa, a solvent concentration of 50 mass-%, and a reaction duration of 4 h. Under these conditions, the conversion of dicyclopentadiene was 85.4%, and the yield of tetrahydrotri-

cyclopentadiene was able to reach 76.5%. The last step of the process, the reaction of tricyclopentadiene with hydrogen, promoted by Raney nickel, achieved a high yield of tetrahydrotricyclopentadiene of 99.6%.

The reaction intermediate and final products of the hydrogenation of tricyclopentadiene (TCPD) were characterized using GC-MS, IR,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR [348]. The double bond in the norbornene ring (NB bond) of TCPD was easily saturated at a low temperature, and an intermediate 12,13-dihydrotricyclopentadiene (12,13-DHTCPD) was formed. Higher temperature and hydrogen pressure were required for the saturation of the remaining double bond in the cyclopentene ring (CP bond) to generate a completely hydrogenated compound tetrahydrotricyclopentadiene (THTCPD). A DFT calculation was conducted by using Gaussian 03 series programs to clarify the reactivity of double bonds in TCPD molecules. The bond parameters confirmed that the NB double bond was more reactive than the CP bond. Total energy calculation also showed that 12,13-DHTCPD was thermodynamically preferred, compared with the other possible intermediate 5,6-DHTCPD. The computational result was in good agreement with the experiments.

THTCPD was synthesized from dicyclopentadiene and indene by a Diels-Alder reaction and hydrogenation [349]. The density of THTCPD thereby obtained was  $1.082\text{ g/cm}^3$ . The volumetric heat of combustion was  $47.5\text{ MJ/L}$ . The flash point was  $393\text{ K}$  ( $120^\circ\text{C}$ ), and the melting point was  $321\text{--}322\text{ K}$  ( $48\text{--}49^\circ\text{C}$ ). Thermal decomposition of THTCPD was studied in a decomposition reactor at atmospheric pressure in the temperature range of  $973$  to  $1153\text{ K}$ . Decomposition products detected by GC/MS were methane, ethene, propylene, cyclopentene, cyclopentadiene, benzene, and toluene. The conversion of THTCPD at different temperatures was investigated. A primary mechanism including nine pathways was proposed according to the main products of the reaction and a monoradical mechanism. DFT calculations of the potential energy surface were performed to investigate the mechanisms of THTCPD breakdown, and relative energy and ratio of reaction routes were computed. The kinetic equation of thermal decomposition was obtained by relation of the conversion and temperature. The pre-exponential factor and activation energy overall reaction order for thermal cracking of THTCPD were determined by linear regression analysis to be  $133.75$  and  $6.67 \times 10^4\text{ kJ/mol}$ , respectively.

*Exo*-tetrahydrotricyclopentadiene (*exo*-THTCPD) has a high volumetric energy content ( $43.2\text{ MJ/L}$ ), high density ( $1.04\text{ g/mL}$ ), and low freezing point ( $233\text{ K} = -40^\circ\text{C}$ ). A one-pot catalytic synthesis of *exo*-THTCPD directly from dicyclopentadiene (DCPD) was performed in one-pot in three steps [350]. First, tricyclopentadiene (TCPD) was prepared directly from the dissociation-recombination of DCPD at  $473\text{ K}$  ( $200^\circ\text{C}$ ). Then the reaction mixture (the majority being TCPD, mixed with small amounts of DCPD and tetracyclopentadiene) was hydrogenated using supported noble metal catalysts at  $423\text{ K}$  ( $150^\circ\text{C}$ ) under  $4.0\text{ MPa}$  hydrogen. Finally, the hydrogenated mixture was treated by  $\text{AlCl}_3$ -catalytic isomerization at  $288\text{ K}$  ( $15^\circ\text{C}$ ). Fractionated distillation was needed to obtain the final product of *exo*-THTCPD. See also [351].

THTCPD can be produced by the hydrogenation of TCPD using ruthenium/nanoporous silica catalysts for TCPD hydrogenation [352]. Ru/KIT-6 and Ru/SBA-15 catalysts showed significantly higher activity compared to Ru/kieselguhr catalyst during TCPD hydrogenation. The nanoporous structures of Ru/KIT-6 and Ru/SBA-15 help overcome the diffusion limitations of reactants and products during the TCPD hydrogenation process. In addition to the diffusion factors, the distribution of ruthenium crystallites on the support plays an important role in the TCPD hydrogenation activity.

## 26.2 Isomerization of Tetrahydrotricyclopentadiene

Mixed *endo*- and *exo*-tetrahydropolycyclopentadienes can be isomerized in the presence of anhydrous aluminum trichloride,  $\text{AlCl}_3$ , to produce a high-energy missile fuel [353]. The amount of aluminum trichloride present is such that its weight ratio to tetrahydropolydiene is in the range of about 0.005 to about 0.75. The isomerization is carried out in an inert solvent in the presence of anhydrous hydrogen chloride and at a temperature between 253 and 298 K (−20 and +25 °C).

Aluminum trichloride was used as a catalyst to transform a THTCPD mixture into a high-energy-density liquid fuel [354]. The reactant contained three inseparable isomers (I, II, and III) to start with. Quantum computations showed the possibility of *endo* fragments of THTCPD turning into *exo* counterparts. However, experiments indicated that the isomerization only happens on norbornyl fragments, and cyclopropyl fragments remain unchanged. Reactants I and II containing both norbornyl and cyclopropyl fragments were only slowly isomerized, and the reactions are reversible, whereas component III without a cyclopropyl fragment was converted quickly. A 5% concentration of  $\text{AlCl}_3$  showed enough catalytic activity. A temperature higher than 288 K (15 °C) is not preferred because it lowers the equilibrium conversion. A halohydrocarbon solvent such as 1,2-dichloroethane is necessary. Pseudo-first-order reversible kinetics was established for the isomerization of I and II. The heat of reaction was 22.94 and 17.69 kJ/mol, respectively. The resulting mixture showed good potential as a fuel for advanced propulsion due to its high energy content and low freezing point.

Instead of using aluminum chloride for the catalytic isomerization of THTCPD, the use of chloroaluminate ionic liquid catalysts gave a totally different product distribution [355]. The *endo*-cyclopropyl fragments of THTCPD that cannot be isomerized by  $\text{AlCl}_3$  catalysis were easily transferred to the desirable *exo* conformation. The hydrocarbons were transferred to diamondoids as by-products, including methyl-1,2-tetramethyleneadamantane, methyl-diethyl-adamantane, and methyl-diamantane via skeletal rearrangement, with the first diamondoid as the primary and dominant product (selectivity 80%). The ionic liquid showed much higher activity than superacid  $\text{CF}_3\text{SO}_3\text{H}$ . Increasing the temperature, ionic liquid dosage, and

addition of  $\text{AlCl}_3$  can promote the rearrangement rate with a slight decrease in the selectivity of methyl-1,2-tetramethylenadamantane. The diamondoid-based product had a low freezing point and high hydrogen content and thus would be superior as a high-energy-density fuel.

The ionic liquid-catalyzed isomerization of tetrahydrotricyclopentadiene can also be achieved using various chloroaluminate complexes [356], Y zeolites [281], copper(I) chloride or iron(III) chloride in ionic liquids [357] or chloroaluminate ionic liquid catalysts [358].

The isomerization of *endo*- to *exo*-tetrahydrotricyclopentadiene over alumino-silicate catalysts (ZSM-5, MOR, HY, Cu-HY, Al-MCM-41) was evaluated using a batch reactor, and the catalytic performances were significantly affected by the microchannel or pore size, acid strength, and acid type of each catalyst [359].  $\text{N}_2$  adsorption-desorption,  $\text{NH}_3$ -temperature-programmed desorption, and pyridine FTIR analyses indicated that the pore size of the catalyst and the acid strength on the catalyst surface affected the conversion rate of *endo*-THTCPD, and the type of acid on the catalyst surface affected the *exo*-THTCPD selectivity. The HY catalyst showed the highest yield and productivity among all of the catalysts evaluated.

The reaction conditions for a facile route to synthesize alkyl-diamondoids via solvent-free rearrangement of tetrahydrotricyclopentadiene catalyzed by acid were optimized, varying catalysts, temperature, catalyst dosage, and process solvent [360]. Notably, under the optimal conditions (10.7 mass-% catalyst, 453 K = 180 °C, 20 h), an extremely high content of alkyl-diamondoids (85.6%) was found in liquid phase, and a high carbon yield of alkyl-diamondoids (60.0%) was obtained. The reaction kinetics of rearrangement were investigated, and the reaction rate constants and apparent activation energies were calculated based on the experimental kinetic data. The resultant diamondoid-based product showed excellent low-temperature performance and a higher energy content than reported for diamondoids and widely used JP-10 fuel, and thus would be superior as a high-energy-density fuel.

The oligomerization of cyclopentadiene and dicyclopentadiene to tricyclopentadiene through the Diels-Alder reaction at temperatures between 393 and 423 K (120 and 150 °C) depends on the type of solvent used in the process [361]. A study showed that the reaction temperature has the most pronounced effect on the reaction, and at a lower reaction temperature near 403 K (130 °C), pressure has a considerable effect on the oligomerization. The use of different solvents had a totally different effect on the reaction in that it changed the reaction rate of conversion, yield, and product composition. Without higher oligomers, the oligomerization showed high selectivity at any given reaction temperature. These findings are similar to the solvent effects observed during the isomerization of *endo*-THDCPD to *exo*-THDCPD [275].

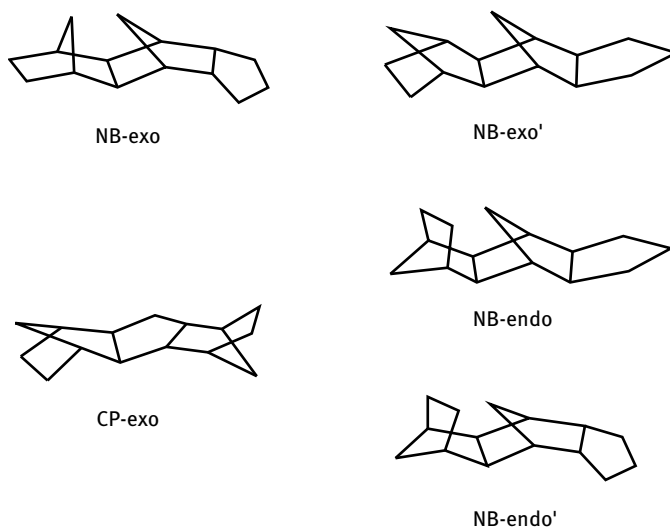
A homologue of tetrahydrotricyclopentadiene, tricycloundecane, has similar isomerization behavior [362]. Tricycloundecane is an intermediate in the formation of adamantane.



## 26.3 Physical Properties of Tetrahydrotricyclopentadiene

*Exo*-tetrahydrotricyclopentadiene (*exo*-THTC) has a freezing point less than 233 K (less than  $-40^{\circ}\text{C}$ ), a density of  $1.0376\text{ g/cm}^3$ , a flash point of 424 K ( $151^{\circ}\text{C}$ ), and viscosity of 37 cPs at 293 K ( $20^{\circ}\text{C}$ ), 97 cPs at 273 K ( $0^{\circ}\text{C}$ ), and 510 cPs at 253 K ( $-20^{\circ}\text{C}$ ). The net heat of combustion is  $\Delta H_{\text{comb}} = 42095\text{ kJ/kg}$  ( $18110\text{ BTU/lb}$ ) [343].

There are about 14 structural and stereo isomers for tetrahydrotricyclopentadiene [363]. Five examples of possible molecular structures of tetrahydrotricyclopentadiene are shown in Figure 39.



**Figure 39:** Molecular structures of tetrahydrotricyclopentadiene.

## 26.4 Chemical Properties of Tetrahydrotricyclopentadiene

### 26.4.1 Isomerization of Tetrahydrotricyclopentadiene

Isomerization of tetrahydrotricyclopentadiene, usually from the *endo*- to the *exo*-conformer, is part of the manufacturing process; therefore, it is discussed in a subsection of Section 25.1.

### 26.4.2 Thermal Decomposition of Tetrahydrotricyclopentadiene

The thermal decomposition properties of tetrahydrotricyclopentadiene were studied using DSC and TGA/DTG [314]. The pyrolysis products were C1–C5 alkynes, alkenes, and alkanes.

In a study of the thermal decomposition of tetrahydrotricyclopentadiene in a batch reactor at 658–698 K (385–425 °C), the reaction activation energy and pre-exponential coefficient were established as 248.5 kJ/mol and  $1.5 \times 10^{15} \text{ s}^{-1}$ , respectively [364]. A detailed analysis of the decomposition products indicated that THTCPD was first cracked into ethene,  $\text{C}_5$  (1,3-cyclopentadiene, cyclopentene, and cyclopentane), benzene, and  $\text{C}_{10}$  (JP-10 and its isomers), which then formed secondary products. The possible primary mechanism was the cleavage of the C–C bond of THTCPD, which produced diradicals that were further converted into monoradicals through intermolecular hydrogen abstraction. The monoradicals then generated primary products through  $\beta$ -scission, isomerization, and intermolecular hydrogen abstraction reactions. Possible secondary decomposition of primary products ( $\text{C}_{10}$  and  $\text{C}_5$  species) may form small molecules ( $\text{C}_1$ – $\text{C}_4$  species, methyl- and ethyl-cyclopentane, etc.), while some bimolecular reactions of  $\text{C}_5$  species may form naphthalene and 2,3-dihydro-4-methyl-1*H*-indene.

The high-pressure thermal decomposition of tetrahydrotricyclopentadiene (THTCPD) and binary high-density hydrocarbon fuels containing JP-10/THTCPD were investigated at 773–933 K (500–660 °C) and 4.0 MPa in an electrically heated tubular reactor [365]. The decomposition of THTCPD under high temperature, high pressure, and short residence time was conducted to analyze the effects of these variable on the product composition. The experimental results of JP-10/THTCPD pyrolysis showed that the THTCPD pyrolysis is easier than the thermal cracking of JP-10, and the addition of JP-10 can significantly promote the THTCPD pyrolysis, which was evidenced by the fact that THTCPD conversion increased up to 80% at 933 K (660 °C) when blended with 50% JP-10. The free radicals generated by the decomposition of THTCPD may help promote the decomposition of JP-10 via H-abstraction reactions.

## 27 Bicyclo[2.2.2]octane

Bicyclo[2.2.2]octane,  $\text{C}_8\text{H}_{14}$ , CAS RN [280-33-1], is a bridged cyclic hydrocarbon, but it has not found any applications as a fuel. It occurs as a contaminant in other polycyclic cycloaliphatic hydrocarbons. Other names for bicyclo[2.2.2]octane are 1,4-endoethylenecyclohexane and “cyclohexane, 1,4-*endo*-(1,2-ethanediyl)-.”

### 27.1 Physical Properties of Bicyclo[2.2.2]octane

Bicyclo[2.2.2]octane melts at 442–443 K (169–170 °C) and sublimes readily at room temperature. The vapor pressure of crystalline bicyclo[2.2.2]octane in the temperature range 323–363 K can be calculated from the equation

$$\log P = (2416.4/T) + 8.628$$

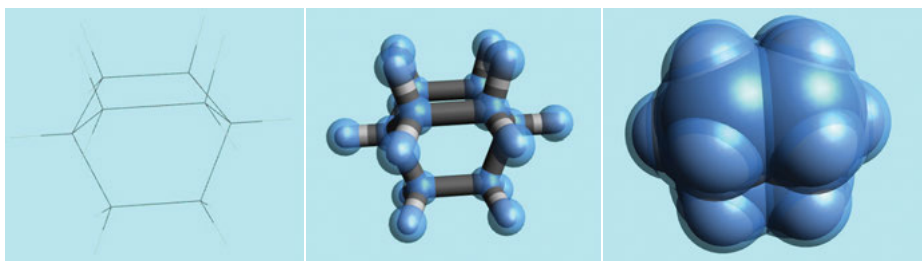
where  $P$  is the vapor pressure in mmHg and  $T$  is the temperature in kelvin [2]. The enthalpy of formation of bicyclo[2.2.2]octane vapor is  $-99.37 \pm 1.3$  kJ/mol ( $-23.75 \pm 0.30$  kcal/mol). The enthalpy of formation of solid bicyclo[2.2.2]octane is  $-147.1 \pm 0.4$  kJ/mol ( $-35.15 \pm 0.10$  kcal/mol). The heat of combustion of solid bicyclo[2.2.2]octane is  $5002 \pm 0.4$  kJ/mol ( $1195.49 \pm 0.10$  kcal/mol).

The enthalpy of sublimation in the range 323–363 K is  $46.36 \pm 0.8$  kJ/mol [139]. The enthalpy of sublimation at 298 K is  $47.76 \pm 0.8$  kJ/mol.

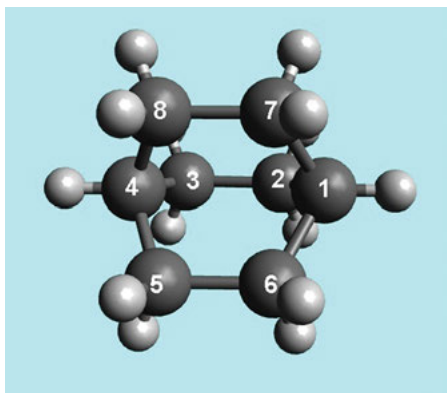
## 27.2 Molecular Structure of Bicyclo[2.2.2]octane

Bicyclo[2.2.2]octane is a homologue of bicyclo[2.2.1]heptane, norbornane. Bicyclo[2.2.2]octane is a cyclohexane with a  $-\text{CH}_2-\text{CH}_2-$  bridge from the 1 to the 4 position (Figures 40 and 41).

There are some heterocyclic amines with similar structures, with nitrogen atoms in the 1 position or both the 1 and 4 positions (triethylenediamine, DABCO). A bicyclo[3.3.0]octane also exists, which essentially consists of two cyclopentane rings sharing one side of the pentagons.



**Figure 40:** Molecular structure of bicyclo[2.2.2]octane.



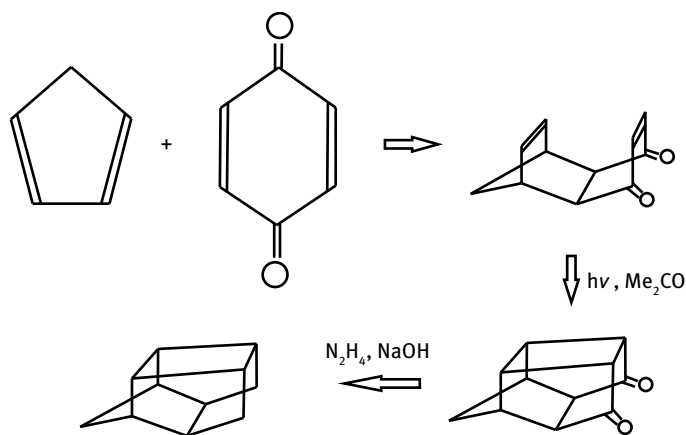
**Figure 41:** Atom position numbering in molecular structure of bicyclo[2.2.2]octane.

## 28 Pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane

Pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane is one of the most unusual caged molecule structures, jokingly called a “bird cage.” It consists of three co-joined pentagons and one square. It is available only in small quantities and will not be used as a rocket propellant or jet fuel. It is shown here only to indicate that there are few limits to the complexity of these molecules, and initially nobody would have predicted that a complex molecule like *exo*-tetrahydrodicyclopentadiene would ever gain importance as the main ingredient of JP-10. So we continue to look at other complex molecules in the hope that there might be some more energetic ones and others that are easier to synthesize.

### 28.1 Synthesis of Pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane

Various laboratory methods have been developed for the synthesis of these unusual molecules [366, 367]. One of the synthesis methods starts with readily available ingredients, cyclopentadiene and *p*-quinone [368, 369].



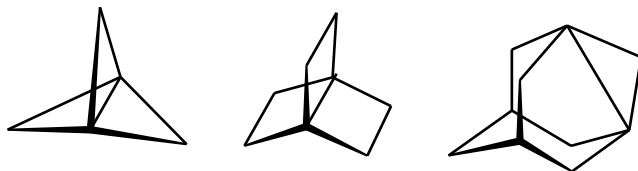
The melting point of pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane (PCU) is 475.8 K, and the molar enthalpy of fusion is  $\Delta H_{\text{fus}}^\circ = 6.38 \pm 0.12 \text{ kJ/mol}$  [370]. The enthalpy of sublimation at 336.86 K was measured with a heat-conduction differential microcalorimeter as  $\Delta H_{\text{subl}}^\circ = 54.71 \pm 0.94 \text{ kJ/mol}$ . The weight-averaged value of the molar sublimation enthalpy at 298.15 K was  $\Delta H_{\text{subl}}^\circ = 55.85 \pm 1.00 \text{ kJ/mol}$ , based on  $\Delta C_p = 49 \text{ J K}^{-1} \text{ mol}^{-1}$ . The energy of combustion in oxygen was  $43332 \pm 31 \text{ J/g}$ , and the molar enthalpy of combustion was  $6345.2 \pm 4.8 \text{ kJ/mol}$ . The standard molar enthalpy of formation in the crystalline state was  $\Delta H_f^\circ(\text{cr}, 298.15 \text{ K}) = 15.8 \pm 4.9 \text{ kJ/mol}$ .

## 28.2 Molecular Structure of Pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecane

The molecular structure and energy content of PCU has been studied using DFT [371]. Based on the optimized geometrical parameters, the strain energy of the PCU molecule was calculated. The density of PCU was predicted using a Monte Carlo method based on the optimized results. The predicted IR frequencies and the NMR chemical shifts were calculated and were in good agreement with experimental results, and the calculated results were used to interpret the experimental spectra and to help determine the structure of PCU. The standard thermodynamic properties of PCU have been calculated by a statistical thermodynamic method.

## 29 Propellanes

Propellanes are polycyclic hydrocarbons with three rings that share a side of a three-, four-, five-, or six-membered ring. This symmetrical shape gives them the appearance of an airplane propeller, and that is where their name is derived from. The name *propellane* was proposed for compounds having three non-zero bridges and one zero bridge between a pair of bridgehead carbons. Although these strained-ring polycyclic hydrocarbons are predicted to be energetic molecules suitable as fuels in rockets or air-breathing engines, they are very difficult to synthesize, and they will most likely never find applications as rocket fuels. At this point, these compounds are mostly of theoretical interest. The shapes of some of these molecules have artistic appeal (“the synthetic chemist as artist”).

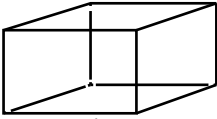
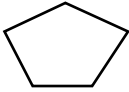
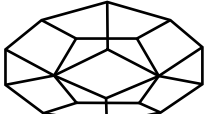
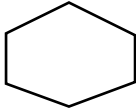
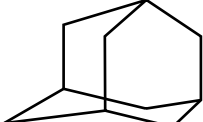


Some propellanes are shown above. From left to right are [1.1.1]propellane, [2.2.2]propellane, and 1,3-dehydroadamantane (a methylene-bridged derivative of [1.3.3]propellane).

The following sources in the literature offer additional information on propellanes, but for now this book cannot provide any more detail on the methods of preparation and physical properties of propellanes [372–379].

### 30 Caged Cycloaliphatic Hydrocarbons

Caged cycloaliphatic hydrocarbons are attractive rocket fuels because they have high densities, which is apparent when comparing 3D cages with flat building blocks that make up their flat sides (Figure 42).

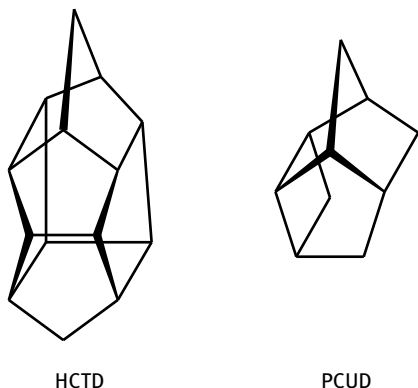
| MONOCYCLE                                                                         | DENSITY, g/cm <sup>3</sup> | CAGED                                                                             | DENSITY, g/cm <sup>3</sup> |
|-----------------------------------------------------------------------------------|----------------------------|-----------------------------------------------------------------------------------|----------------------------|
|  | 0.70                       |  | 1.28                       |
|  | 0.74                       |  | 1.45                       |
|  | 0.78                       |  | 1.07                       |

**Figure 42:** Caged hydrocarbons with high densities.

Bicyclic and cage compounds have high heats of combustion and can be used as fuels. A literature survey of the field of bicyclic and cage compounds was conducted with the objective of identifying those types of compounds with unusual physical and chemical stability [380]. There are many caged alicyclic and heterocyclic compounds that are potentially useful as rocket propellants [381, 382].

Calculations of thermodynamic properties (heat capacities, standard entropies, and enthalpies of formation) of some caged hydrocarbons of the general formula  $C_nH_n$  in the ideal-gas state were performed for tetrahedrane  $C_4H_4$ , triprismane  $C_6H_6$ , cubane  $C_8H_8$ , pentaprismane  $C_{10}H_{10}$ , hexaprismane  $C_{12}H_{12}$ , truncated tetrahedrane  $C_{12}H_{12}$ , heptaprismane  $C_{14}H_{14}$ , octaprismane  $C_{16}H_{16}$ , dodecahedrane  $C_{20}H_{20}$ , truncated octahedrane  $C_{24}H_{24}$ , and truncated cubane  $C_{24}H_{24}$  [383].

The synthetic routes to the synthesis of prismanes are summarized in [384]. Some of the more exotic caged hydrocarbons, promising fuel candidates heptacyclo-[6.6.0.0<sup>2,5</sup>.0<sup>3,13</sup>.0<sup>4,11</sup>.0<sup>5,9</sup>.0<sup>10,14</sup>]tetradecane (HCTD) and pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]-undecane (PCUD), were synthesized and evaluated as ramjet fuels [385]. The density of HCTD is 1.26 g/cm<sup>3</sup>, and the density of PCUD is 1.23 g/cm<sup>3</sup>. Some of these caged and bridged structures are related to homocubanes [386].



Reductive dimerization of methylated pentacycloundecan-8-ones gave mixtures of methylated pentacycloundecane (PCU) alkene dimers [387].

Thermal properties of four high-energy-density PCU-derived hydrocarbons were investigated [388]. All of these fuels were stable and non-volatile at room temperature and pressure. Two fuels were solid, and the third was a viscous liquid. The PCU alkene dimer,  $C_{22}H_{24}$ , was a mixture of isomers with a high enthalpy of formation (+408 kJ/mol), high density (1.2–1.3 g/cm<sup>3</sup>) and a melting point of 451–452 K (178–179 °C). The calculated heat of combustion was 11900 kJ/mol. The methylated PCU alkene dimer,  $C_{22}H_{28}$ , was a mixture of up to 64 isomers. The methylated fuel was a wax-like material with a melting point of 328 K (55 °C). In contrast to the base PCU alkene dimer, the methylated PCU alkene dimer was soluble in kerosene. The spirocyclic alkene dimer,  $C_{22}H_{26}$ , was a mixture of two isomers in the form of a powder with a melting point of 432 K (159 °C). Methylenecyclopropane,  $C_{18}H_{22}$ , a mixture of two isomers, was semi-solid at room temperature and formed a viscous oil.

### 31 Cubane

Cubane, pentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane, C<sub>8</sub>H<sub>8</sub>, CAS RN [277-10-1], is a highly energetic hydrocarbon and the parent compound of a group of high-energy materials including tetranitrocubane and octanitrocubane. It was believed for a long time that a molecule like cubane would not be stable and might be impossible to synthesize, but cubane has a surprising stability. Cubane is now the parent molecule of a large number of energetic compounds that are of interest as rocket propellants and explosives [389].

### 31.1 Preparation of Cubane

The first synthesis of cubane in a nine-step reaction was reported in 1964 [390, 391]. Similar methods are available for the synthesis of methylcubane [392]. Methylcubane melts at 307 K (34 °C) and sublimates at 310 K (37 °C). There are now several methods for cubane synthesis [393, 394]. One new method allows the synthesis of cubane in a four-step reaction [395].

Cubane and methylcubane are of interest as high-density fuels and as parent molecules for energetic compounds. The most readily accessible starting material for the synthesis of energetic cubanes is cubane-1,4-dicarboxylic acid, which can be prepared in a seven-step process [396]. Functional group transformations of this diacid have yielded energetic derivatives such as 1,4-dinitrocubane, 1,4-di(hydrazomethyl)-cubane, and 1,4-di(*N*-nitroamino)cubane. The diacid has been converted to both 1,2,4,7- and 1,3,5,7-cubane-tetracarboxylic acids, from which the energetic molecules 1,2,4,7-cubane-tetraammonium tetraperchlorate and 1,3,5,7-tetranitrocubane have been synthesized.

### 31.2 Physical Properties of Cubane

Cubane is a solid at room temperature and has a molecular mass of 104.15 g/mol and a density of 1.29 g/cm<sup>3</sup> (remarkable for a hydrocarbon). It melts at 406.6 K (133.5 °C = 272.3 °F) and boils at 434.8 K (161.6 °C = 322.9 °F).

Cubane crystallizes as small rhombs (*O<sub>h</sub>* point group) and is one of the densest hydrocarbons known. The measured enthalpy of formation of solid cubane is +620 kJ/mol (+148 kcal/mol). This is a notably high value and quite unlike that of common hydrocarbons. Most of these saturated hydrocarbons have negative heats of formation.

#### 31.2.1 Lattice Dynamics of Cubane Crystals

Solid cubane, which is composed of weakly interacting cubic molecules, exhibits many unusual and interesting properties, such as a very large coefficient of thermal expansion and a first-order phase transition at 394 K from an orientationally ordered phase of *R*3 symmetry to a non-cubic disordered phase of the same symmetry with a volume expansion of 5.4%, among the largest ever observed [397]. A study of the lattice dynamics of solid cubane within the quasi-harmonic and rigid-molecule approximation tried to explain some of these unusual dynamical properties. The experimental melting temperature of cubane is 405 K, indicating a strong crystal lattice.



### 31.2.2 Thermodynamic Properties of Cubane

The measured enthalpy of formation of solid cubane is  $+620 \text{ kJ/mol}$  ( $+148 \text{ kcal/mol}$ ). This is a notably high value and is quite unlike that of common hydrocarbons. Most of these more common saturated hydrocarbons have negative heats of formation.

The sublimation enthalpy of cubane was measured by combining the vaporization enthalpy at  $298.15 \text{ K}$  with the sum of the fusion enthalpy measured at  $405 \text{ K}$  and a solid-solid phase transition that occurs at  $394 \text{ K}$  [398]. The fusion and solid-solid phase transitions were measured previously. A sublimation enthalpy value of  $55.2 \pm 2.0 \text{ kJ/mol}$  at  $298.15 \text{ K}$  was obtained. This value compared quite favorably with the value obtained by comparing the sublimation enthalpy of similar substances as a function of their molar masses, but it is different from earlier measurements. The heat of combustion for cubane is  $46.5 \text{ MJ/kg}$ , which corresponds to an enthalpy of formation of  $+602 \text{ kJ/mol} = +144 \text{ kcal/mol}$  [399, 400].

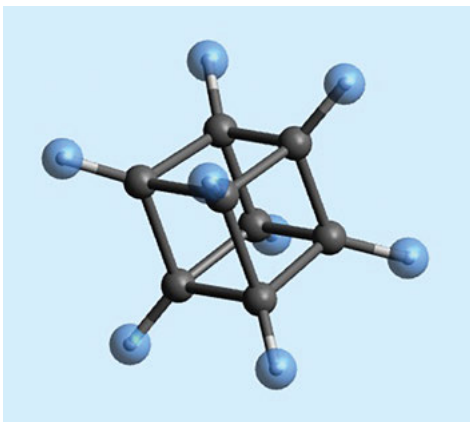
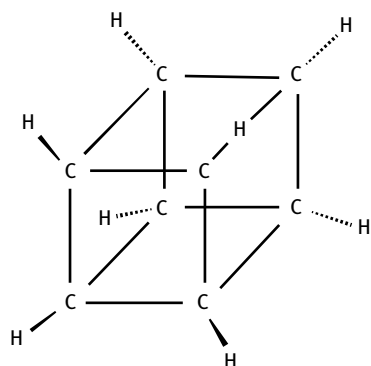
Three commonly used density functional methods for computing heats of formation for cubane vapor were compared [401]. Heats of formation were computed from the total energies of this strained hydrocarbon and building elements (carbon and hydrogen molecule), with the experimental carbon enthalpy of formation given ( $+710.9 \text{ kJ/mol} = +169.9 \text{ kcal/mol}$ ). It was demonstrated that the complete basis-set *ab initio* method computes heats of formation that are very close to the experimental, as well as G2, values. Hybrid DFT computes almost identical values and was recommended as the method of choice for computing heats of formation, while local spin density approximation generates energies that are a few hundred  $\text{kcal/mol}$  different from the experimental value and should be avoided for these calculations. For cubane vapor, there is an experimental enthalpy of formation of  $+622.2 \pm 4.2 \text{ kJ/mol} = +148.7 \pm 1 \text{ kcal/mol}$  at  $298 \text{ K}$ . Again, the estimated energy agreed well with this value. In fact, it differed by only  $3.3 \text{ kJ/mol} = 0.8 \text{ kcal/mol}$ . The computed cubane enthalpy of formation deviated slightly more from this value. Similarly, as it was in the case of tetrahydronaphthalene, the enthalpy of formation for cubane was substantially different (for more than  $1255 \text{ kJ/mol} = 300 \text{ kcal/mol}$ ) than estimated from the experimental data.

The heat of combustion of solid cubane is  $4837 \text{ kJ/mol}$  ( $1156 \text{ kcal/mol}$ ), which translates into an enthalpy of formation of  $+541.8 \pm 3.3 \text{ kJ/mol}$  ( $+129.5 \pm 0.8 \text{ kcal/mol}$ ) for the solid and  $+622.2 \pm 4.1 \text{ kJ/mol}$  ( $+148.7 \pm 1.0 \text{ kcal/mol}$ ) for the vapor [402]. The strain energy of  $157 \text{ kcal/mol}$  distributed over the six faces of the cube gives  $26.2 \text{ kcal/mol}$  per cube face, which is very similar to that of cyclobutane at  $26 \text{ kcal/mol}$ . The unusually high enthalpy of formation of cubane and many of its derivatives can be explained by strain energy [52]. The term strain energy should be considered relative to a theoretical unstrained state of the molecule. The strain energy can be calculated from the difference between the experimentally determined enthalpy of formation and the enthalpy of formation predicted from additive behavior of unstrained bonds:

$$\text{Strain energy} = \Delta H_{\text{f,exp.}} - \Delta H_{\text{f,calc.}}$$

### 31.2.3 Molecular Structure of Cubane

The molecular structure of cubane shows that the molecule is highly stressed, because on eight carbon atoms the bonds are bent away from the stress-free tetrahedron bond angle of  $109.45^\circ$  to those of the corners of a cube with  $90^\circ$  angles (Figure 43).



**Figure 43:** Molecular structure of cubane.

Cubane is named appropriately because its skeleton is in the shape of a cube. At each corner of this cube is a carbon atom (carrying a hydrogen) bound to three identical neighboring carbons. The internuclear  $\angle CCC$  angles are  $90^\circ$ , bent far off from the standard  $109.5^\circ$  typical of tetravalent,  $sp^3$ -hybridized carbons like those in methane. This departure from normal bond orientation is energetically expensive. Cubane is strained by about  $695 \text{ kJ/mol}$ , corresponding to a substantial weakening of its bonds. The large bond angle deformations in cubane make it a treasure of stored energy. Each strained bond is like the spring in a set mousetrap. It was once thought that cubane would be impossible to synthesize or stabilize. Neither concern proved to be the case. The cubane system and cubane itself were first synthesized in 1964 at the University of Chicago.

Bicubyl consists of two cubes connected by a single C—C bond. Bicubyl has a density of  $1.336 \text{ g/cm}^3$ , significantly higher than cubane ( $1.29 \text{ g/cm}^3$ ). Other polycubyls are known and together make an interesting set of stable rigid chains to which each cubyl link adds  $0.42 \text{ nm}$  to the length of the chain. Nitro derivatives of these polycubyls are not yet known. Even if they were, they would be prohibitively expensive.

### 31.2.3.1 Computational Chemistry for Polycyclic Strained-Ring Caged Energetic Materials

Compounds containing carbon-based (no hetero atoms) cage structures have highly strained molecular structures and have become the subject of practical interest in recent decades because they possess high enthalpy of formation. *Ab initio* molecular modeling calculations have been performed for 28 carbon-cage structures with the aim of identifying the best candidates for future synthesis work in order to improve propellant compositions [403]. DFT was employed for the geometric optimization of the proposed molecules. Calculated heats of formation and densities of the compounds have been used from the optimized structures to compute their specific impulses and density-specific impulses in various configurations (solid and liquid rocket propellants). Detonation properties of air/fuel mixtures of these compounds have been predicted.

### 31.2.3.2 Computational Chemistry for Tetrahedrane

Three commonly used density functional methods for computing heats of formation for tetrahedrane were compared [401]. Enthalpies of formation were computed from the total energies of tetrahedrane. The enthalpy of formation of tetrahedrane vapor was estimated, through homodesmotic reactions, to be  $+535 \pm 4$  kJ/mol ( $+127.9 \pm 1.0$  kcal/mol) at 298 K. The same approach was used for the DFT evaluation of the tetrahedrane enthalpy of formation. The values computed with three different basis sets were +600, +523, and +610 kJ/mol (+143.4, +125.1, and +145.7 kcal/mol), respectively.

Tight-binding molecular dynamics simulations were carried out to analyze the thermal stability of the  $C_4H_4$  tetrahedrane molecule over a wide temperature range from 400 to 1000 K [404]. The temperature dependence of the  $C_4H_4$  lifetime  $\tau$  was related to the Arrhenius law. The height of the minimum energy barrier preventing the tetrahedrane decomposition was found to be 0.46 eV. Possible channels and final products of the tetrahedrane decay were identified.

### 31.2.3.3 Computational Chemistry for Prismanes

The group of prismanes includes the polyhedral hydrocarbons tetrahedrane, cubane (tetraprismane), and dodecahedrane. An *ab initio* computational study was performed to obtain the bond energies and geometries of the lower prismanes [405]. See also [406].

### 31.2.3.4 Computational Chemistry of Cubane Structures

The enthalpy of formation of cubane,  $C_8H_8$ , pentacyclo[4.2.0.0<sup>2,5</sup>.0<sup>3,8</sup>.0<sup>4,7</sup>]octane, CAS RN [277-10-1], can be derived from the properties of its fragments. A composite molecular orbital method was used to calculate standard enthalpies of formation and hydrogenation ( $\Delta H_f^{298}{}_0$ ,  $\Delta H_{hyd}^{298}{}_0$ ) of a series of compounds obtained from cubane by successively breaking one C—C single bond at a time [407]. The enthalpy of

isomerization of each cubane derivative was compared to the corresponding isomer in the sequence obtained by stepwise hydrogenation of cycloocta-1,3,5,7-tetraene to cyclooctane [401].

The gas-phase enthalpy of formation of cubane ( $603.4 \pm 4$  kJ/mol) was calculated using an explicitly correlated composite method [408]. The results obtained for cubane, together with the experimental value for the enthalpy of sublimation,  $54.8 \pm 2.0$  kJ/mol, led to a value of  $+548.6 \pm 4.5$  kJ/mol for the solid-phase enthalpy of formation of cubane. This value was only 6.8 kJ/mol higher than the 50-year-old original calorimetric result. The carbon-hydrogen bond dissociation enthalpy of cubane is  $438.4 \pm 4$  kJ/mol. The strain energy of cubane (667.2 kJ/mol) and cubyl radical (689.4 kJ/mol) were independently estimated via quasi-homodesmotic reactions.

### 31.3 Other Information on Cubanes

Cubanes with methylene bridges across the sides are called homocubanes, with *bis* and *tris* indicating the number of methylene bridges. It is hard enough to synthesize cubane and cubane derivatives and test them as energetic materials, but making homocubanes is even more difficult, and it is very unlikely that they could ever be used as rocket propellants. These molecules are mostly of theoretical interest [386]. An alternative name for homocubane is pentacyclo[4.3.0.0<sup>2,5</sup>.0<sup>2,8</sup>.0<sup>4,7</sup>]nonane [409].

Homocubane is a potential support backbone for a family of high-energy-density materials [410]. Six polynitro and polyazido diesters of homocubane-2,4-dicarboxylic acid were synthesized as possible energetic plasticizers. 2,4-dicyano and dinitro homocubanes were synthesized as models for more highly substituted homocubanes. Dinitrate and diperchlorate salts of 2,4-diaminohomocubane were prepared via proper ion exchange resins. The energy content of bishomocubane molecules can be increased by attaching tetrazole rings [411]. A variety of cubane derivatives was synthesized in a search for more energetic fuels, including 1,4-diazidomethylcubane and 1,4-dihydroxymethylcubane [202].

### 31.4 Chemical Properties of Cubane

Interest in cubane chemistry was triggered by potential applications of the molecule and its derivatives to the production of high-energy fuels and propellants [389]. Once initial substitution of hydrogen in cubane by amino groups or iodine is achieved, this will open new paths for the synthesis of polysubstituted energetic cubane derivatives [412, 413]. New cubane derivatives have been prepared by developing new methodology for direct substitution on the cubane nucleus [414].

### 31.5 Thermal Decomposition of Cubane

The decomposition chemistry of cubane and other high-energy-density fuels was investigated by flow tube mass spectrometry [415]. Pyrolysis reactions of cubane and methylcubane were studied in a micro-flow tube reactor from room temperature to 1000 K [416]. The composition of the flow tube eluent was analyzed by chemical ionization in a tandem guided beam mass spectrometer. It was found that cubane and methylcubane have nearly identical breakdown temperature dependence, suggesting that methyl functionalization has minimal effect on the stability of cubane cage bonds. There is, however, a substantial effect of the methyl group on product branching, resulting in more stable isomers at intermediate temperatures and a propensity to eliminate fragments containing the methyl group at high temperatures.

The reasons for the anomalously high thermal stability of cubane  $C_8H_8$  and the mechanisms of its decomposition were studied by numerically simulating the dynamics of this metastable cluster at  $T = 1050 - 2000$  K using a tight-binding potential method [417]. The decomposition activation energy was found from the temperature dependence of the cubane lifetime obtained from the numerical experiment. The activation energy is fairly high,  $E_a = 1.9 \pm 0.1$  eV. The decomposition products are either  $C_6H_6$  and  $C_2H_2$  molecules or the isomer  $C_8H_8$  with a lower energy. The thermodynamic instability of cubane, due to having a positive enthalpy of formation, is not accompanied by kinetic instability. Cubane and most of its derivatives are amazingly stable. The energy of activation for thermal decomposition of cubane in the gas phase is very large, about 180 kJ/mol at 503–533 K (230–260 °C), so the molecule decomposes only slowly at such temperatures. The reason for this is that there are no kinetically viable paths along which cubane can rearrange thermally.

A detailed chemical kinetics mechanism was developed for the decomposition of cubane [418]. Quantum mechanics-based *ab initio* calculations have been carried out to elucidate the various chemical pathways that lead to the formation of previously known product species from cubane. Optimized structures of ground states and transition states appearing in the chemical reaction scheme were obtained by using various levels of theory. Minimum energy paths were traced for each elementary reaction. The mechanism thus obtained, along with the computed rate parameters and thermodynamic data, was used in a flow reactor model to simulate a flow reactor experiment that was carried out previously by others. Comparison of the simulation and experimental results validated the formulated reaction mechanism and provided valuable insights into the chemical decomposition behavior of cubane.

## 32 Adamantane

Adamantane, also known as  $C_{10}H_{16}$ , tricyclo[3.3.1.1<sup>2,6</sup>]decane, CAS RN [281-23-2], contains 12.27 mass-% hydrogen and has a molecular mass of 164.29 g/mol.

Adamantane is a colorless, crystalline chemical compound with a camphor-like odor. It is a cycloalkane and the simplest diamondoid and is related to many compounds that are of interest as air-breathing engine fuels or rocket propellants [419]. Attaching explosophoric groups leads to nitroadamantane or difluoroaminoadamantane, potential high-energy-density materials. Adamantane and a variety of alkyl-substituted adamantanes (“diamondoid hydrocarbons”) occur naturally in some deep petroleum reservoirs. Because of their ease of sublimation, they are carried to the surface with natural gas from those underground formations.

### 32.1 Preparation of Adamantane

A simple two-step reaction allows the synthesis of adamantane from the readily available dicyclopentadiene by first reducing it to tetrahydrodicyclopentadiene and then refluxing the tetrahydrodicyclopentadiene for 10 h over an  $AlCl_3$  catalyst [420]. Strong sulfuric acid catalyzes isomerization of trimethylenenorbornane = tetrahydrodicyclopentadiene to adamantane [421].

As part of a study of the synthesis of adamantane on zeolite catalysts and the reaction conditions, it was found that Ni(3–5% Ni)/USY catalyst exhibited a higher activity and good selectivity for adamantane preparation [422]. The best reaction conditions were temperature 523–553 K (250–280 °C), catalyst content 25–28%, and hydrogen pressure 10–15 MPa. It was found that the presence of a little dry HCl increased the yield of adamantane.

Adamantane can be synthesized in a batch reactor system under hydrogen using *endo*-tetrahydrodicyclopentadiene (*endo*-TCD) as feedstock and solid super-acid  $ZrO_2-SO_4$  (SZ)-loaded REY, USY, or Si-MCM-41 molecular sieves as isomerizing catalysts [423]. Loading  $ZrO_2-SO_4$  on the surface of a molecular sieve increased the yield of adamantane. The effects of reaction temperature, hydrogen pressure, content of the surface-loaded  $ZrO_2$ , and types of molecular sieves on synthesis of adamantane were investigated. The results showed that higher temperature 540 K (270 °C) will increase the yield of hydrocracking (by-products), which led to a decrease in adamantane yield. The highest yield of adamantane (22.77%) was obtained by using (SZ(20%))/REY as isomerizing catalyst under the following conditions: catalyst/reactant mass ratio 0.625, reaction temperature 523 K (250 °C), hydrogen pressure 1.5 MPa, and reaction time 3 h. The total selectivity of adamantane conversion was 95%.

The catalytic activity of 12-tungstophosphoric acid-supported PW/C catalysts in the isomerization of *endo*-tetrahydrodicyclopentadiene (*endo*-TCD) to adamantane was investigated in a batch reactor [424]. Under optimum conditions, the PW loading was 30% by weight, the reaction temperature was 413 K (240 °C), the reaction time was 3 h, the mass ratio of catalyst and material was 0.6:1.0, the initial pressure was 1.1 MPa, and the molar ratio of cyclohexane solvent and *endo*-TCD was 5:1. The maximum yield of adamantane was up to 21.6%.

Adamantane can be made by isomerization of *exo*-tetrahydrodicyclopentadiene to adamantane using an acidity-adjustable chloroaluminate ionic liquid [283]. The zeolite catalytic method is considered to be the most typical and the more active method for the synthesis of adamantane and is likely to become the preferred replacement for the conventional  $\text{AlCl}_3$  method on an industrial scale [425]. Some adamantane is obtained as an unwanted by-product during the production of *exo*-tetrahydrodicyclopentadiene, the main ingredient of JP-10.

## 32.2 Physical Properties of Adamantane

### 32.2.1 Melting Point of Adamantane

The melting point of adamantane is 542.7–543.9 K (269.6–270.8 °C) in a sealed vial. At 540 K (270 °C), the melting point of adamantane is much higher than that of other hydrocarbons with the same molecular weight, such as camphene (318 K = 45 °C) or limonene (199 K = –74 °C). Other sources reported the melting point of adamantane as 552 K.

### 32.2.2 Vapor Pressure of Adamantane

Adamantane sublimates readily. The vapor pressure of crystalline adamantane in the temperature range 366–443 K can be calculated from the equation

$$\log P = (-2746.8/T) + 8.617$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin [2]. A similar equation applies to a wider temperature range from 313 to 443 K:

$$\log P = (-4054.4/T) + 29.220 - 6.666 \log T$$

The enthalpy of formation of solid adamantane is  $-128.2 \pm 4.1$  kJ/mol ( $-30.65 \pm 0.98$  kcal/mol) [2]. The heat of combustion of adamantane is  $6033 \pm 3$  kJ/mol ( $1441.95 \pm 0.68$  kcal/mol).

Other sources [158] gave the following equations for the vapor pressure of adamantane, the first for the solid in the temperature range 483–543 K and the second

one for the liquid at temperatures above 543 K

$$\ln p = A - \frac{B}{T} = 18.18 - \frac{6570}{T} \quad 483 < T < 543 \text{ K}$$

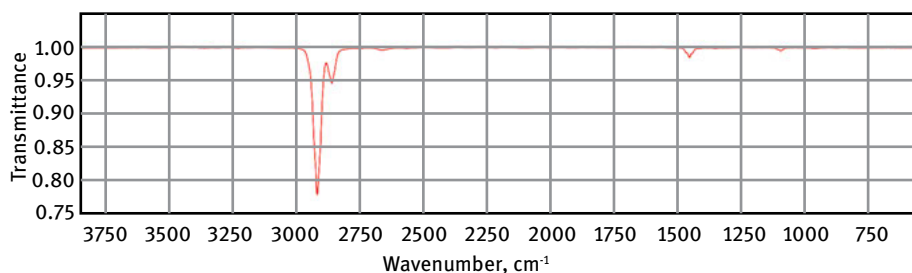
$$\ln p = A - \frac{B}{T} = 14.75 - \frac{4670}{T} \quad T > 543 \text{ K}$$

where  $p$  is the pressure in kPa and  $T$  is the temperature in kelvin.

### 32.2.3 Optical Properties of Adamantane

#### 32.2.3.1 Infrared Spectrum of Adamantane

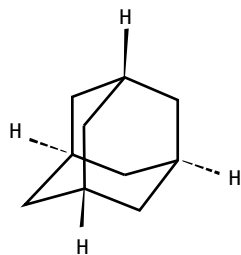
The IR spectrum of adamantane is shown in Figure 44. Due to the high symmetry of the molecule, the number of absorption bands is very small.



**Figure 44:** Infrared spectrum of adamantane. (Reprinted and modified with permission from [426].)

#### 32.2.4 Molecular Structure of Adamantane

Adamantane molecules consist of four connected cyclohexane rings arranged in the “chair” configuration. Adamantane is unique in that it is both rigid and virtually stress free and is highly symmetrical. A boat-shaped configuration can also exist. Adamantane is the most stable among all the isomers with the empirical formula  $C_{10}H_{16}$ , which include the somewhat similar twistane. The spatial arrangement of carbon atoms in adamantane molecule is the same as in the diamond crystal, which is where the name adamantane is derived from. The molecular structure of adamantane is illustrated in Figure 45.



**Figure 45:** Molecular structure of adamantane.



The molecular and crystal structure of adamantane was examined using XRD, FTIR, MS, NMR, enhanced MS, differential ion mobility spectrometry, Raman, and DSC, revealing phase transitions of adamantane at different temperature or pressure conditions [427]. The molecular parameters were deduced by electron diffraction and X-ray crystallography. The carbon-carbon bond length is 1.54 Å and is almost identical to that of diamond, and the carbon-hydrogen distance is 1.112 Å. Adamantane crystallizes in a face-centered cubic structure (space group  $Fm\bar{3}m$ ,  $a = 9.426 \pm 0.008$  Å,  $Z = 4$ ) containing orientationally disordered adamantane molecules. This structure transforms into an ordered body-centered tetragonal phase ( $a = 6.641$  Å,  $c = 8.875$  Å) with  $Z = 2$  either upon cooling to 208 K or pressurizing to above 0.5 GPa.

### 32.2.5 Thermodynamic Properties of Adamantane

#### 32.2.5.1 Heat Capacity of Adamantane

The constant-pressure heat capacity of crystalline adamantane at 298 K is  $189.74 \text{ J mol}^{-1} \text{ K}^{-1}$  ( $45.3 \text{ cal mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ). The heat capacity of adamantane vapor at 298 K is  $148.91 \text{ J mol}^{-1} \text{ K}^{-1}$  ( $35.6 \text{ cal mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ).

#### 32.2.5.2 Enthalpy of Formation of Adamantane

Based on a measured heat of combustion of solid adamantane of  $6033 \pm 3 \text{ kJ/mol}$  ( $1441.95 \pm 0.68 \text{ kcal/mol}$ ), an enthalpy of formation for solid adamantane was calculated as  $-188.7 \pm 2.8 \text{ kJ/mol}$  ( $-45.10 \pm 0.68 \text{ kcal/mol}$ ) [2]. The enthalpy of formation of adamantane vapor is  $-132.9 \pm 1.3 \text{ kJ/mol}$  ( $-31.76 \pm 0.32 \text{ kcal/mol}$ ). The enthalpy of formation of crystalline adamantane is  $-192.5 \pm 0.4 \text{ kJ/mol}$  ( $-46.02 \pm 0.09 \text{ kcal/mol}$ ) [428].

The standard enthalpy of combustion of adamantane is  $\Delta H_c = 6033 \pm 3 \text{ kJ/mol}$  ( $1442.01 \pm 0.78 \text{ kcal/mol}$ ), which yields a standard enthalpy of formation of  $\Delta H_f^{298} = -188.4 \pm 3.3 \text{ kJ/mol}$  ( $-45.02 \pm 0.79 \text{ kcal/mol}$ ) [429].

#### 32.2.5.3 Enthalpy of Fusion of Adamantane

The enthalpy of fusion of adamantane is  $13.8 \text{ kJ/mol}$  ( $3.3 \text{ kcal/mol}$ ) [430].

#### 32.2.5.4 Enthalpy of Sublimation of Adamantane

The heat of sublimation of adamantane is  $59.7 \text{ kJ/mol}$  ( $14.26 \text{ kcal/mol}$ ). Other sources reported the enthalpy of sublimation of adamantane at 308 K as  $58.3 \text{ kJ/mol}$  ( $13.93 \text{ kcal/mol}$ ) [430].

The enthalpy of sublimation of adamantane is  $59.1 \text{ kJ/mol}$  at 298 K and  $58.3 \text{ kJ/mol}$  at 308 K [139]. Other sources gave an enthalpy of vaporization of  $52.6 \text{ kJ/mol}$  or  $48.5 \pm 3.8 \text{ kJ/mol}$  at 298 K [158].

#### 32.2.5.5 Heat of Combustion of Adamantane

The heat of combustion of adamantane is  $6029 \pm 4 \text{ kJ/mol}$  ( $1441 \pm 1 \text{ kcal/mol}$ ) [428].

### 32.3 Alkyladamantanes

Alkyladamantanes have the advantage over adamantane in that they are liquids at room temperature and thus are easier to use as rocket fuels.

The most thoroughly investigated alkyladamantane is 1,3-dimethyladamantane, 1,3-DMA, CAS RN [702-79-4]. The boiling point of 1,3-dimethyladamantane is 476.4 K. The enthalpy of vaporization of 1,3-dimethyladamantane was reported as  $49.37 \pm 0.33$  kJ/mol [431] or  $51.2 \pm 0.5$  kJ/mol [158].

The thermal stability of 1,3-dimethyladamantane was investigated under different conditions because it is a candidate for high-energy-density hydrocarbon fuels [432]. The thermal decomposition kinetics in a batch reactor between 693 and 743 K proceeded with rate constants ranging from  $4 \times 10^{-7} \text{ s}^{-1}$  at 693 K to  $35 \times 10^{-7} \text{ s}^{-1}$  at 743 K, along with the Arrhenius parameters of  $A = 2.39 \times 10^7 \text{ s}^{-1}$  and activation energy  $E_a = 183$  kJ/mol. The rate constants for the thermal decomposition of 1,3-DMA were smaller than those of some typical model fuels such as decalin, propylcyclohexane, butylcyclohexane, and *n*-dodecane, demonstrating that the thermal stability of 1,3-DMA is satisfactory. On the basis of component analysis, a hypothetical mechanism of thermal decomposition of 1,3-DMA was proposed to explain the product distribution. It was shown that the different products are mainly obtained through a combination of isomerization, hydrogen transfer,  $\beta$ -scission, and dehydrogenation.

The heat capacities of the crystalline and liquid phases of 1,3-dimethyladamantane and 1-ethyladamantane have been measured over the temperature range 8 to 373 K [433]. 1,3-dimethyladamantane was found to exist in two crystalline phases; 1-ethyladamantane exists in only one crystalline phase.

### 32.4 Natural Occurrence of Adamantane Derivatives (Diamondoids)

Naturally occurring diamondoids are the most stable remnants of petroleum degradation over geologic time. These compounds have survived the severe geologic time/temperature/pressure conditions at great depths where most other hydrocarbons, except methane, are destroyed by either thermal cracking and/or thermochemical reduction. Some geochemists have tried to explain their presence as the result of acid-catalyzed rearrangements of alicyclic hydrocarbons in petroleum. Diamondoids are known to occur as trace components in some crude oils, but they are also found subliming in natural gas. There have been only two reported occurrences of diamondoids in natural gas reservoirs worldwide. Diamondoids are predominantly adamantane, diamantane, triamantane, and their methyl- and ethyl-substituted counterparts. For the most part, alkyl side chains longer than propyl have been cracked off in thermal reactions over the past millions of years. Analysis of these natural gas condensates has revealed several dozen diamondoids with structures similar to that of adamantane [146]. Mixtures of diamondoids have been proposed as high-density fuels under the

name Mobildym Fuels RF. The energy released per unit volume of the RF-1, RF-2, and RF-3 fuels in a ramjet combustor was found to be significantly greater than that of JP-10 over a wide range of air/fuel equivalence ratios. Efforts have started for synthesizing fuels with properties similar to those of diamondoid fuels but beginning with readily available feedstocks instead – the same as those used for the production of JP-10, except continuing the dimerization reaction by building multi-ringed caged molecules by oligomerization of DCPD to C15+ molecules.

### 33 Dodecahedrane

Dodecahedrane, also known as pentagonal dodecahedrane, undecacyclo [9.9.0.0<sup>2,9</sup>.0<sup>3,7</sup>.0<sup>4,20</sup>.0<sup>5,18</sup>.0<sup>6,16</sup>.0<sup>8,15</sup>.0<sup>10,14</sup>.0<sup>12,19</sup>.0<sup>13,17</sup>]dodecane, C<sub>20</sub>H<sub>20</sub>, CAS RN [4493-23-6], is a platonic hydrocarbon that has been the subject of many experimental and theoretical studies. It consists of 12 pentagons linked in a spherical structure. A platonic hydrocarbon is a hydrocarbon (molecule) whose structure matches one of the five platonic solids, with carbon atoms replacing its vertices, carbon–carbon bonds replacing its edges, and hydrogen atoms as needed on the apex points. The synthesis of dodecahedrane, a 20-step reaction, makes this compound very difficult to obtain, and it will never be used as a rocket propellant. It would be interesting to see how many nitro groups or amino groups can be attached to the carbon skeleton to make a new oxidizer or fuel.

#### 33.1 Physical Properties of Dodecahedrane

The physical properties of dodecahedrane are listed in Table 33.

**Table 33:** Physical properties of dodecahedrane.

| Property                                                                 | SI units                | Other units        | References |
|--------------------------------------------------------------------------|-------------------------|--------------------|------------|
| Molecular mass                                                           | 260.3728 g/mol          | 3.8406 mol/kg      |            |
| Melting point                                                            | 703 ± 10 K              | 430 ± 10 °C        |            |
| Density                                                                  | 1.448 g/cm <sup>3</sup> | —                  |            |
| Enthalpy of formation (estimated)                                        | +79.1 kJ/mol            | +18.9 kcal/mol     | [434]      |
| Enthalpy of formation, vapor, computed                                   | +76.1 kJ/mol            | +18.2 kcal/mol     | [120]      |
| Enthalpy of formation, vapor (from heat of combustion of dimethyl ester) | +93.7 kJ/mol            | +22.4 ± 1 kcal/mol | [39]       |

### 33.1.1 Molecular Structure of Dodecahedrane

The molecular structure of dodecahedrane is illustrated in Figure 46. Each apex carries one hydrogen atom.

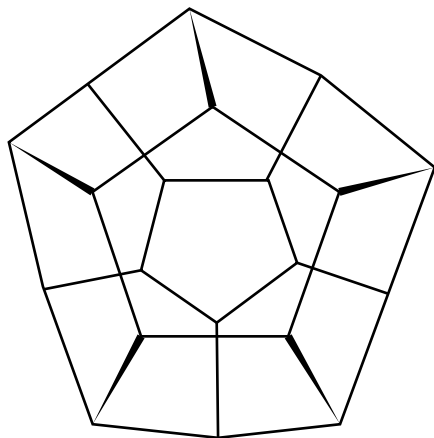


Figure 46: Molecular structure of dodecahedrane.

### 33.1.2 Thermodynamic Properties of Dodecahedrane

*Ab initio* molecular orbital calculations to predict accurate geometries and enthalpies of formation have been applied to cyclohexane, cubane, adamantane, and dodecahedrane [435]. Good agreement with experimental data was obtained for geometries in all cases. In the 6-31G basis set, enthalpies of formation of cyclohexane, adamantane, and cubane were in error by 0.5, 2.1, and 9.9 kcal/mol, respectively. For dodecahedrane, the enthalpy of formation was predicted to be  $-20.9$  kJ/mol ( $-5.0$  kcal/mol). This number had to be revised later when a different computational method was used. The enthalpy of formation of dodecahedrane was estimated from the difference of *ab initio* energies of dodecahedrane and pagodane, as well as from two homodesmotic reactions [434]. The results,  $+79.1$ ,  $+73.2$ , and  $+69.9$  kJ/mol ( $+18.9$ ,  $+17.5$ , and  $+16.7$  kcal/mol), depending on the method of calculation, were in modest agreement with a value estimated by others,  $+93.7 \pm 4.1$  kJ/mol ( $+22.4 \pm 1$  kcal/mol).

## 33.2 Chemical Properties of Dodecahedrane

It would be of interest to attach explosophoric groups to the dodecahedrane sphere, similar to what has been done with cubane, where substitution of eight hydrogens by nitro groups resulted in the formation of octanitrocubane. The other possibility with dodecahedrane is to insert small molecules into the cavity formed by the sphere.

## 34 Buckminsterfullerene C<sub>60</sub>

Fullerene also known as C<sub>60</sub>, (C<sub>60</sub>-Ih)[5,6]fullerene, Buckminsterfullerene, Buckyball, [60]fullerene, CAS RN [99685-96-8], has unique properties that would make it and its derivatives useful as propellant ingredients. Of course, these compounds are solids and not liquids, so their use would be restricted to solid propellants [436].

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# Dimethylhydrazines

## Dimethylhydrazines

*Encyclopedia of Liquid Fuels* contains six chapters that discuss hydronitrogen compounds and four chapters that discuss hydrazines. The chapter on hydrazine deals with the parent compound, which is an inorganic compound. The chapter regarding alkylhydrazines discusses alkylhydrazines compounds but not methylhydrazine or dimethylhydrazines. This is followed by a chapter focused on methylhydrazine, and finally, a chapter regarding dimethylhydrazines, which is the chapter at hand.

There are two dimethylhydrazines, which will be the focus of this chapter. They differ in location regarding where the two methyl groups are attached to the two nitrogen atoms. The unsymmetrical dimethylhydrazine (UDMH), where both methyl groups are attached to the same nitrogen atom, is of more importance than symmetrical dimethylhydrazine, where two methyl groups are attached to different nitrogen atoms. UDMH is widely used as rocket fuel. In contrast, symmetrical dimethylhydrazine (SDMH) with the two methyl groups attached to different, adjacent nitrogen atoms, is not used as a rocket propellant and is only an unwanted contaminant and decomposition product that must be dealt with carefully due to its toxicity. The following sections discuss dimethylhydrazines in the order of importance, UDMH first and SDMH last.

## 1 Unsymmetrical Dimethylhydrazine

Unsymmetrical dimethylhydrazine and asymmetrical dimethylhydrazine, 1,1-dimethylhydrazine, *N,N*-dimethylhydrazine, 2-methyl-2,3-diazapropane, UDMH, also referred to as “Dimazine,”  $(\text{CH}_3)_2\text{NNH}_2$ ,  $\text{C}_2\text{H}_8\text{N}_2$ , CAS RN [57-14-7], also [88733-28-2], is the most commonly produced hypergolic fuel (see [1, 2]).

### 1.1 Production of Unsymmetrical Dimethylhydrazine

Unsymmetrical dimethylhydrazine did not have any industrial applications before it was identified and developed as a rocket propellant. UDMH is a textbook example of how the use of a chemical expanded from a rarely used chemical (used only in test tube quantities) to a major industrial product. It would be interesting to trace back the history of UDMH from when it was first made to the point of large-scale production when it became an important ingredient [3]. The history of all hydrazines deserves to be explored in a book similar to the very entertaining, anecdotal book on the history of boranes written in 1991.

Next to hydrazine (and hydrazine hydrate), 1,1-dimethylhydrazine is probably the hydrazine derivative with the largest cumulative production quantity on record. This is due to its use as a bipropellant fuel in liquid-fueled rockets in many countries around the world. To satisfy the temporarily high demand for this chemical, several alternate production methods have been developed as an intermediate solution [4], including industrial-scale production methods and one involving *N*-nitrosodimethylamine,  $(\text{H}_3\text{C})_2\text{NNO}$ , NDMA, which is a proven animal carcinogen. However, concern about the toxicity of nitrosamine intermediates has caused a major shift in the industrial practice of UDMH production over the past 50 years. At one point, it even led to aerospace managers initiating an intensive search during the 1970s to look for alternate methods that avoid the use of carcinogenic intermediates [5].

A temporary UDMH shortage in the United States (US) in 1973 prompted the formation of a Joint UDMH Task Group which studied a variety of alternative processes that do not require the use of NDMA. This included chloramination [6], hydrazine methylation, urea processes, nitramine processes [7, 8], and others [9]. A cost comparison of different processes to produce monomethylhydrazine (MMH) and UDMH was conducted in 1978. This concluded that (based on a 6.5-year amortization schedule) the estimated product cost for UDMH using the chloramine-Sisler process would have been \$4.53/lb. MMH was estimated to cost \$6.12/lb rather than \$6.73/lb as reported from the Raschig process used in 1978 (1978 US dollars) [10]. A preferred process would have been one that can produce both UDMH and MMH using the same equipment. Methylation of hydrazine might have resulted in a price of \$8/lb for UDMH and \$12/lb for MMH (1978 US dollars). The nitramine process was expected to be even more expensive, namely, \$15/lb UDMH. As the search for alternate UDMH production methods continued, the US supply of Aerozine-50 dropped to 380000 lb at one point, which was equivalent to only six Titan-II launches [11].

### 1.1.1 Preparation of UDMH Using a Modified Raschig Process

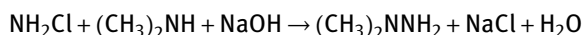
A variation of the Raschig process involves a chloramine solution (which is prepared using the same method as when hydrazine itself is the desired product) that is reacted with dimethylamine (DMA) instead of ammonia. In one example [12, 13], a 17-kg/h stream of 10%  $\text{NH}_3$  solution with 0.06% glue was reacted at 273 K (0 °C) with 25 kg/h of NaOCl solution containing 115 g of active chlorine per liter. DMA was added to the primary reactor effluent at a rate of 10 kg/h. The temperature was then raised to ambient to allow the reaction to go to completion. The UDMH can be extracted from the reaction mixture with an inert solvent that does not mix with water. Solvents proposed for this purpose are aniline, *o*-toluidine, *m*-toluidine, *N,N*-dimethylaniline, and xyli-dine.

When producing UDMH, MMH, or hydrazine, it is important during all modifications of the Raschig process that an efficient way of making chloramine without losing too much active chlorine is employed. The chloramine yield depends on the pH of

the ammonia or ammonium chloride solution reacting with sodium hypochlorite and needs to be optimized [14].

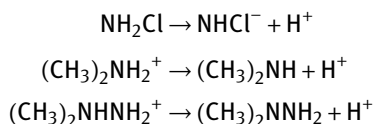
The production of UDMH using the modified Raschig process may form small amounts of hydrazine as a by-product. While the presence of a little hydrazine does not interfere when UDMH is used as a rocket fuel, it may lead to undesirable side reactions when UDMH is intended to be used for the synthesis of pharmaceutical or agrochemical products. Traces of hydrazine can be selectively removed from UDMH solutions by heating it in contact with catalysts that do not destroy any alkylhydrazines, for instance nickel supported on silica/alumina, nickel-nickel oxide mixture supported on silica/alumina, or rhodium supported by carbon at a temperature of between 333 and 393 K (60 and 120 °C) [15].

The kinetics of the reaction



were studied at different reactant ratios, pH (between 12 and 6 mol/L of alkali hydroxide), and temperature (298–333 K = 25–60 °C) [16]. The reaction is first order in both reactants, and the reaction is independent of the concentration of alkali hydroxide up to about pH = 12.5. At higher alkalinities, catalysis by hydroxide ions was observed and the rate constant was a linear function of hydroxide ions activity. The yield of the reaction increased from pH = 12 to 13.5 on account of the decrease of the rate of dimethylhydrazine oxidation by monochloramine, and the reaction went beyond 14 on account of the diminution of monochloramine decomposition.

Another kinetic model of UDMH formation using the Raschig process covered an application range from pH 8 to 14.64 (4 mol/L NaOH) [17]. It assumed that the synthesis is controlled by the acid-base dissociation equilibria:



and by the following concurrent elementary reactions: **(1)** dimethylhydrazine formation molecular ( $\text{NH}_2\text{Cl}/(\text{CH}_3)_2\text{NH}$ ) and ionic ( $\text{NHCl}^-/(\text{CH}_3)_2\text{NH}$ ) processes; **(2)** dimethylchloramine formation from  $\text{NH}_2\text{Cl}$  and  $(\text{CH}_3)_2\text{NH}_2^+$ ; **(3)** UDMH catalytic oxidation by  $\text{NH}_2\text{Cl}$  and dimethyldiazene  $(\text{CH}_3)_2\text{N}^+=\text{N}^-$  intermediate formation; **(4)** diazene decomposition to yield formaldehyde dimethylhydrazone (FDMH); **(5)** degradation of  $(\text{CH}_3)_2\text{N}^+=\text{N}^-$  by  $\text{NH}_2\text{Cl}$ ; **(6)** alkaline hydrolysis of chloramine. The synthesis can be expressed by a differential system of which the integration allows the prediction of the evolution of mixtures in terms of concentration, pH, and temperature. It also allows a numeric evaluation of FDMH, which is a troublesome by-product of the UDMH manufacture. Significant examples were selected in different pH ranges and concentrations to test the agreement between experimental and

calculated curves. It was found that the reaction is first order in each of the first two reactants and is independent of alkali concentration in the range of pH 12.5. Beyond this point, a catalytic action of alkali was observed and the rate became dependent on pH. The UDMH yield went through a maximum at pH = 14. One of the yield-limiting reactions is a reaction of UDMH with chloramine that leads to tetramethyltetrazene and ammonium chloride.

In a laboratory study, a 0.9-kg/h (2-lb/h) bench-scale reactor for chloramine production was operated to determine optimum operating conditions [10]. An empirical equation was derived that calculates the chloramine yield (as a fractional decimal) as a function of reactant ratios and temperatures:

$$\text{Yield} = A(1 - e^{-B\lambda})$$

$$A = a + bt + ct^2$$

$$B = d + f \frac{[\text{N}_2]}{[\text{Cl}_2]}$$

$$\lambda = \frac{[\text{NH}_3]}{[\text{Cl}_2]}$$

with  $a = -2.447695$ ,  $b = 0.013631$ ,  $c = -8.331248$ ,  $d = 0.146832$ ,  $e = 2.7182818$ ,  $f = 0.023463$ , and  $t = \text{temperature, } ^\circ\text{F}$ . Other topics investigated were the analysis of  $\text{ClNH}_2$  in effluent from the first-stage reactor, kinetics of  $\text{ClNH}_2$  reaction with amines (MMH or UDMH), the efficiency of the reactor stirrer, phase diagrams of  $\text{CH}_3\text{NH}_2$ - $\text{NaOH-H}_2\text{O}$  and  $(\text{CH}_3)_2\text{NH-NaOH-H}_2\text{O}$ , product purification by extraction, and by-product analysis. Recommended molar ratios of  $\text{NH}_3:\text{Cl}_2$  for first-stage reaction were 10:1. In the contactor second-stage reactor, the preferred amine: $\text{NaOH}:\text{ClNH}_2$  ratios were 4.5:1.6:1.4 for UDMH and 9.0:1.2:1.0 for MMH. Based on data obtained with the 0.9-kg/h reactor, scale-up to an 18-kg/h pilot plant and 182-kg/h production plant was considered feasible as the next step.

Synthesizing different hydrazines by an indirect Raschig process by introducing a substituted chloramine ( $\text{R}_1\text{R}_2\text{NCl}$ ) into liquid ammonia under pressure to obtain the corresponding hydrazine ( $\text{R}_1\text{R}_2\text{NNH}_2$ ) led chemists to propose a new mechanism involving a chlorine transfer reaction. This was in disagreement with mechanisms reported in the literature [18]. Thus, the reaction of chloramine and the amine ( $\text{R}_1\text{R}_2\text{NH}$ ) occurs first. Chloramine reacts immediately with the substituted amine, in agreement with the direct Raschig process, to produce the hydrazine. Under these conditions, the nature of the hydrazine is kinetically controlled by the excess amine. As such, it becomes possible to synthesize different hydrazines from the same substituted chloramine. This mechanism was validated by synthesizing UDMH, *N*-aminopiperidine, and *N*-amino-3-azabicyclo[3.3.0]octane.

After an exhaustive study of the system ammonia/dimethylchloramine in liquid ammonia, it was interesting to compare the reactivity of this system in liquid ammo-

nia with the same system in an aqueous medium [19]. Dimethylchloramine prepared in a pure state underwent dehydrohalogenation in an alkaline medium. The principal products formed were *N*-methylmethanimine, 1,3,5-trimethylhexahydrotriazine, formaldehyde, and methylamine. The kinetics of this reaction was studied using ultraviolet (UV), gas chromatography (GC), and high-performance liquid chromatography (HPLC) as a function of temperature, initial concentrations of sodium hydroxide, and chlorinated derivative. The reaction was of the second-order and obeyed an E2 mechanism

$$k_1 = 4.2 \times 10^{-5} \text{ mol}^{-1} \text{ s}^{-1}, \quad \Delta H = 82 \frac{\text{kJ}}{\text{mol}}, \quad \Delta S = -59 \text{ J mol}^{-1} \text{ K}^{-1}.$$

The oxidation of unsymmetrical dimethylhydrazine by dimethylchloramine involves two consecutive processes. The first step follows the first-order law for haloamine and hydrazine, leading to the formation of an aminonitrene intermediate

$$k_2 = 150 \times 10^{-5} \text{ mol}^{-1} \text{ s}^{-1}.$$

The second step corresponds to the conversion of aminonitrene into FDMH at pH 13. This reaction followed the first-order law

$$k_3 = 23.5 \times 10^{-5} \text{ s}^{-1}.$$

The dimethylchloramine-ammonia interaction corresponds to an SN2 bimolecular mechanism

$$k_4 = 0.9 \times 10^{-5} \text{ mol}^{-1} \text{ s}^{-1}, \quad \text{pH} = 13, \quad \text{and} \quad T = 298 \text{ K} = 25^\circ \text{C}.$$

The kinetic model formulated based on the above reactions showed that the formation of UDMH in an aqueous medium is limited by strong competition from the dehydrohalogenation of dimethylchloramine and the oxidation of UDMH formed by the original chlorinated derivative.

The formation of FDMH by oxidation of UDMH by chloramine during the UDMH synthesis is a very undesirable side reaction. Therefore, conditions favoring this reaction must be avoided. The kinetics of UDMH oxidation by chloramine have been investigated in an aqueous solution in terms of concentration, pH (8–13.5), and temperature (288–308 K = 15–35 °C) [20]. The overall reaction, first-order in both reactants, is the result of two competitive steps. Catalysis by hydrogen ions was observed and the apparent rate constant involved two terms, one being pH-independent the other one varying linearly with the acidity function. The entropy and enthalpy of activation of the molecular process have been established at 298 K (25 °C). In alkaline media (pH ≥ 13), the major product of the reaction identified by mass spectrometry (MS) was FDMH (CH<sub>3</sub>)<sub>2</sub>NN=CH<sub>2</sub>. In neutral or weakly basic solution (pH ≤ 8), the only organic product formed was tetramethyl-2-tetrazene (CH<sub>3</sub>)<sub>2</sub>NN=NN(CH<sub>3</sub>)<sub>2</sub>. A mixture of these two compounds was obtained for intermediate pH values.

The effect of acidification on the chloramine-dimethylamine reactivity was further investigated as a function of pH (13–8) and temperature (292–305 K = 19–32 °C) [21]. Kinetics results showed the existence of two competitive reactions involving chloramine with neutral and ionic forms of the amine. According to a second-order process, they lead to the formation of dimethylhydrazine ( $k_1 = 68 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ ;  $T = 298 \text{ K}$ ) and dimethylchloramine ( $k_2 = 210 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ ;  $T = 298 \text{ K} = 25^\circ \text{C}$ ). The rate bimolecular constant calculated from the total concentration of reactants may be expressed by an equation of the form

$$k_{\text{obs}} = k_1 \alpha_A + k_2 \beta_A$$

where  $\alpha_A$  and  $\beta_A$  are coefficients that depend on pH and the protonation constants of dimethylamine. The enthalpy and entropy of activation for the ionic process have been determined at 298 K (25 °C). Another potential mechanism involving  $\text{NH}_3\text{Cl}^+$  and  $(\text{CH}_3)_2\text{NH}$  have been examined and a correlation between the two models was established.

While modeling the kinetics of the preparation of UDMH under industrial conditions, an analysis of the kinetic data enabled the operators to define the optimal range for synthesis (pH = 13–14.64) [22, 23]. For this interval, a theoretical model was established and physical correlations between the initial and final states were developed. This model was based on the following reactions: **(1)** dimethylhydrazine formation via molecular and ionic processes; **(2)** UDMH oxidation by  $\text{NH}_2\text{Cl}$  and FDMH formation; **(3)** alkaline hydrolysis of chloramine. The influence of the absolute concentration of starting materials showed that the yields  $p_1 = [\text{UDMH}]_\infty / [\text{NH}_2\text{Cl}]_0$  and  $P_2 = [\text{UDMH}]_\infty / [(\text{CH}_3)_2\text{NH}]_0 - [(\text{CH}_3)_2\text{NH}]_\infty$ , approach the limiting values  $p_1$  and  $p_2$ , which depend solely upon the initial molar ratio  $p = [(\text{CH}_3)_2\text{NH}]_0 / [\text{NH}_2\text{Cl}]_0$ , the pH, and the temperature. The concentrations of the by-product FDMH as a function of the degree of conversion of the reactants have been calculated and operating conditions for the synthesis that avoids the troublesome FDMH formation have been proposed.

Conditions leading to the formation of FDMH by UDMH oxidation by chloramine must be avoided [24]. The kinetics of UDMH oxidation by chloramine has been investigated in aqueous solutions as a function of concentration, pH (8–13.5), and temperature (288–308 K = 15–35 °C). The overall reaction, first-order in both reagents, is the result of two competitive steps. Catalysis by hydrogen ions was observed and the apparent rate constant involved two terms, one being pH-independent the other one varying linearly with acidity function  $h_0$ . The entropy and enthalpy of activation of the molecular process have been established at 298 K (25 °C). In alkaline media (pH  $\geq$  13), the major product of the reaction identified using MS was the FDMH  $(\text{CH}_3)_2\text{NN}=\text{CH}_2$ . In neutral or weakly basic solution (pH  $\leq$  8), the only organic product formed is tetramethyl-2 tetrazene  $(\text{CH}_3)_2\text{NN}=\text{NN}(\text{CH}_3)_2$ . A mixture of these two compounds was obtained for intermediate pH values.

### 1.1.2 Methods of UDMH Product Separation

Because the UDMH content in Raschig primary product effluents is only 3% or less, a multi-step distillation in a very efficient distillation column is required to separate unreacted reactants, products, and by-products. The distillation is facilitated by adding 1–30% NaOH [25, 26]. For instance, 100 parts of synthesis liquor containing 3% UDMH, 8% H<sub>2</sub>O, and 10% NaCl (balance amine and ammonia) were mixed with 12.8 parts of solid NaOH. The distillation in a column with 11 theoretical trays, operating at a 75:1 reflux ratio, resulted in a 90% recovery of 95% UDMH. A typical reaction raw product prior to distillation was described as consisting of 1.27 mol/kg ammonia, 4.38 mol/kg dimethylamine, 0.026 mol/kg FDMH, 0.56 mol/kg UDMH, 33.0 mol/kg water, 2 mol/kg NaCl, and 0.45 mol/kg NaOH [27]. It was separated in a distillation apparatus consisting of two columns, one with two plates to remove volatiles and small amounts of water and a second with seven plates to separate water and UDMH from the other volatiles. This method is said to avoid the precipitation of salts that may clog the pipes.

There have been attempts to extract UDMH from the reaction mixture by crystallization or by distillation from a concentrated solution. To do that, the solid-liquid and liquid-liquid equilibria in the ternary-systems (*N,N*-dimethylhydrazine sodium-hydroxide water and *N,N*-dimethylhydrazine sodium-chloride water) had to be measured [28]. In another example, the UDMH was recovered by adding 50% NaOH, filtering off the NaCl, and extracting with aniline [12]. The extract, which contained 3.5% UDMH, was dried over solid NaOH and separated via distillation. At 298 K, a single solid phase (NaCl) was observed in the UDMH-NaCl-H<sub>2</sub>O system. In the ternary system UDMH-NaOH-H<sub>2</sub>O, a very wide miscibility gap was observed. The invariant point compositions were (in percent by weight) 94.5% UDMH + 5.5% H<sub>2</sub>O (no NaOH) and 48.1% NaOH + 1.4% UDMH + 51.5% H<sub>2</sub>O [29–31].

### 1.1.3 Single-Step SNPE Process

A particularly elegant route to UDMH is the continuous SNPE process developed in France that starts with aqua ammonia, dimethylamine, and sodium hypochlorite [32]. The undesirable formation of the *N,N*-dimethylhydrazone of formaldehyde (CH<sub>3</sub>)<sub>2</sub>N=N=CH<sub>2</sub> (also called methylene dimethyl hydrazine) as a by-product can be suppressed by adding 0.5–2 vol.-% hydrazine in the form of hydrazine hydrate to the reaction mix [33]. The use of hydrazine reduces the by-product concentration from 6.4 to 2.4% in the raw product. A raw product containing 16% UDMH, 8% NH<sub>3</sub>, 8% (CH<sub>3</sub>)<sub>2</sub>NH, 2.3% H<sub>2</sub>C=N–N(CH<sub>3</sub>)<sub>2</sub>, and 71% H<sub>2</sub>O can be separated by distillation using 2-propanol as an auxiliary fluid [34]. The hydrazone goes over with the 2-propanol and can then be hydrolyzed to obtain more UDMH. Under slightly different conditions, but still using 2-propanol, UDMH can be obtained directly from raw reaction products after adding sufficient sodium hydroxide to form two separate layers (32% NaOH) and distilling on a column at 361–363 K (190–195 °F) [35]. In a batch process, the end of



distillation of pure UDMH was indicated when the pot temperature rapidly increased to 372 K (210 °F).

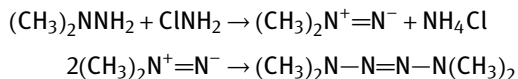
#### 1.1.4 Preparation of UDMH Using the Sisler Process

Using the Sisler process, UDMH can be prepared either from chloramine and DMA [36–38] or from chlorodimethylamine and ammonia [39]. Both can be prepared in either the gas phase or in a non-aqueous solvent system. Improved yields can be obtained by operating in a two-phase system [40]. *N*-Chlorodialkylamines are not sufficiently reactive with ammonia at ambient temperature to give good dialkyl-hydrazine yields. Thus it takes alkali or temperatures above the normal boiling point of ammonia or both to achieve acceptable conversion. Reacting dimethylchloramine with ammonia in a pressure bomb at 0.9 MPa and 293 K for 45 minutes in the presence of solid KOH produced only a modest UDMH yield of 26% of the theory [39].

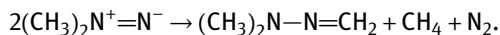
To find a suitable replacement for the nitrosamine process, the Sisler process was one of several investigated at the Martin Marietta Corp. as an alternative approach [7, 8].

The chloramination of DMA in a solution of KOH in 1-butanol was carried out in the presence of NH<sub>3</sub> at room temperature [41]. The major products were 1,1-dimethylhydrazine, the dimethylhydrazone of formaldehyde, and 1,1,4,4-tetramethyl-2-tetrazene. Subsequently, 1,1-dimethylhydrazine was reacted with ammonia-free chloramine in ether solution. The products included CH<sub>4</sub>, N<sub>2</sub>, the dimethylhydrazone of formaldehyde, and 1,1,4,4-tetramethyl-2-tetrazene. This is a UDMH yield-limiting reaction that must be suppressed. The reactions of 1,1-dimethylhydrazine with HgO and with Ag<sub>2</sub>O also resulted in 1,1,4,4-tetramethyl-2-tetrazene.

Attempts to manufacture UDMH by the anhydrous Sisler process from DMA and chloramine were not always very successful [42]. Although yields as high as 71% UDMH were achieved in pure DMA at low chloramine concentrations, there was a marked decrease in product yield when higher ClNH<sub>2</sub> concentrations were employed [43]. The problem is caused by undesirable side reactions, leading to tetramethyltetrazene



or FDMH



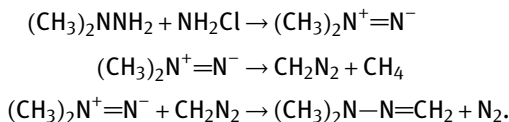
Hydrazone is a particularly troublesome by-product because it cannot be removed by conventional distillation procedures. While tetramethyltetrazene may accumulate in UDMH distillation columns and cause explosions. As such, tetramethyltetrazene accumulations must be avoided by periodically purging the column.

A process for the preparation of UDMH in an anhydrous reaction medium was developed on a laboratory scale [6]. The method consisted of generating chloramine in the gas phase by reacting an excess of ammonia with chlorine diluted with nitrogen. After removal of the ammonium chloride by-product, the gaseous reaction product was absorbed in a suitable hydrocarbon solvent such as xylene. The yield of chloramine (based on chlorine input) was 90%. The chloramine solution was then reacted with excess liquid DMA or a solution of DMA in xylene at temperatures of 273 to 278 K (0 to 5 °C) with efficient stirring. The yields of UDMH obtained were 50 to 60%. Isolation of UDMH was achieved by distillation. It was found that MMH can be prepared using this method as well. UDMH can also be prepared by a variation of the above process in which the chloramine from the gas-phase generator is introduced directly into a liquid two-phase system consisting of aqueous sodium hydroxide and dimethylamine. UDMH was produced in high yields (80%) in relatively high concentrations. The activation energy of UDMH formation was found to be 41 kJ/mol (9.8 kcal/mol), in agreement with that reported by other authors (40.2 kJ/mol = 9.6 kcal/mol) [7]. The activation energy of the troublesome side reaction leading to FDMH was 14.5 kcal/mol. Therefore, the undesired side reaction becomes more important at higher temperatures. The rate of this side reaction is 600 times faster than the one leading to the product UDMH (in anhydrous organic solvents at 273 K) [43]. It is obvious that under these conditions, one is fighting an uphill battle. The UDMH concentration achieves only a low stationary concentration early in the reaction, and any further additions of  $\text{ClNH}_2$  do not improve the UDMH yield. The relative ratios of formation of FDMH to UDMH are more favorable to UDMH production in water or ammonia as a process solvent than in anhydrous organic solvents. The extraction of the product hydrazines from the slush reaction mix of the Sisler-Kelmers process is facilitated by the addition of 2–5 parts of hydrocarbon, such as *n*-heptane, filtering the undissolved hydrochlorides, and distilling the filtrate [44, 45].

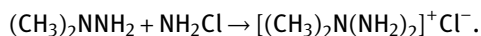
A stopped-flow technique was used to study the kinetics of the  $\text{ClNH}_2 + (\text{CH}_3)_2\text{NH}$  reaction in chloroform, dioxane, and diethyl ether [43].

A report by the University of Florida included six appendices that examined the chloramination of dimethylamine, synthesis of MMH in non-aqueous solvents, and also the oxidation of UDMH and MMH by oxygen, which are unwanted side reactions. The chloramination of DMA in a solution of KOH in *n*-butanol in the presence of  $\text{NH}_3$  at room temperature produced UDMH but also formed large amounts of by-products in the form of tetramethyltetrazene (TMTZ) and the dimethylhydrazone of formaldehyde [46]. The UDMH yield was only 30% of the theoretical yield based on the amount of chloramine consumed. To study the yield-limiting follow-on reactions, UDMH was reacted with chloramine in ether at 293 K (20 °C). Reaction products included methane, nitrogen,  $(\text{CH}_3)_2\text{NN}=\text{CH}_2$ ,  $(\text{CH}_3)_2\text{N}-\text{N}=\text{N}-\text{N}(\text{CH}_3)_2$ , and some unreacted UDMH. Relatively pure tetramethyltetrazene could be obtained by oxidizing UDMH with mercuric oxide in ether solution. The TMTZ yield was 97% after 1 h. However, with continued stirring, the TMTZ decomposed to FDMH (also called methylene

dimethyl hydrazine) within 23 h. In earlier reports [47], the formation of TMTZ during the reaction of UDMH with chloramine was postulated to occur by way of the dimethyldiazene radical  $(\text{CH}_3)_2\text{N}^+=\text{N}^-$ , the dimerization of which would lead to TMTZ. The exact mechanism is still uncertain. A similar mechanism involving dimethyldiazene and diazomethane had been proposed [48]:



The dimethyldiazene could also be prepared by oxidation of UDMH with silver oxide. By reacting the dimethyldiazene thus formed with diazomethane derivatives, it could be shown that this mechanism is not the one that leads to FDMH. Another undesirable follow-on product during the reaction of UDMH with chloramine is 2,2-dimethyltriazanium chloride [48]:



If samples of this salt are needed for comparison purposes, it can be prepared in good yield by reaction of UDMH with chloramine in ethereal solution. It is stable at room temperature and reacts with neither ammonia nor UDMH. It can be recrystallized from UDMH in which it is moderately soluble.

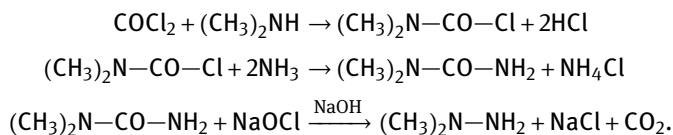
Theoretically, UDMH can be made from dimethylchloramine and ammonia. However, the reaction of the excess dimethylchloramine with the UDMH thus formed leads to unwanted by-products that limit the UDMH yield [49]. Quite often in various UDMH production processes, FDMH is obtained as an undesirable by-product. Controlled hydrolysis of these unwanted hydrazones can yield some additional UDMH.

### 1.1.5 Preparation of UDMH from Urea

A temporary UDMH shortage in the US in 1973 prompted a variety of studies on alternative processes for the production of UDMH, which included chloramination [6], hydrazine direct methylation, urea processes [50], and nitramine processes [7]. These studies were sponsored by the Space and Missile Systems Organization (SAMSO), the Air Force Logistics Center (AFLC) in San Antonio, and the Air Force Rocket Propulsion Laboratory (AFRPL), based in Edwards AFB, CA [9]. After completion of the urea process study [50], SAMSO awarded a contract to the Illinois Institute of Technology Research Institute (IITRI) to investigate product purification and waste product disposal of the crude amine mixtures resulting from the chloramine process. In evaluating the chloramine versus the urea process, it was concluded that both are feasible, however, the capital costs for the urea process were considerably greater [10]. A cost comparison of different processes to produce MMH and UDMH was conducted in 1978. This was based on a six-and-a-half-year amortization schedule. The exercise concluded

that the estimated product cost using the chloramine-Sisler process would be \$4.53/lb for UDMH and \$6.12/lb for MMH compared to \$6.73/lb MMH using the Raschig process used in 1978 (1978 US dollars). Another process, the methylation of hydrazine, was said to result in \$8/lb for UDMH and \$12/lb for MMH. The nitramine process was expected to be even more expensive, namely, \$15/lb UDMH. Of course, these cost comparisons mean nothing in view of the process equipment improvements that may have been made in the interim.

To avoid the use of carcinogenic NDMA as an intermediate in the production of UDMH, numerous other synthesis routes have been evaluated. One such route was the modification of the urea process for hydrazine, starting with *N,N*-dimethylurea instead of urea [51, 52]. Another possibility to produce UDMH is by the urea process based on phosgene [53]:



Initially, they attempted to run the process without removing the  $\text{NH}_4\text{Cl}$  from the dimethylurea. Removal of  $\text{NH}_4\text{Cl}$  by reaction with 50% aqueous NaOH was possible in laboratory tests but less effective in a production plant. Optimization of process conditions and the identification of reaction intermediates during the reaction of dimethylurea with hypochlorite were hampered by a lack of analytical methods. *N,N'*-Dimethyl-*N*-chlorourea and *N,N*-dimethylamino isocyanate are likely intermediates in the reaction leading to UDMH. Hypochlorite not only initiated the desired Hoffmann rearrangement of the amide but also reacted with the methyl groups, which was very undesirable. Dichloro- and trichloromethane were found in the by-products.

UDMH can be made by base-assisted chlorination of urea by dimethylchloramine [54]. Dimethylchloramine prefers to abstract the H-atom from urea. However, the chlorination of urea occurs, and tetramethylhydrazine forms as a result of the coupling of the dimethylamino radicals. Fairly good yields of UDMH are obtainable in methanol.

### 1.1.6 Preparation of UDMH by Direct and Indirect Methylation of Hydrazine

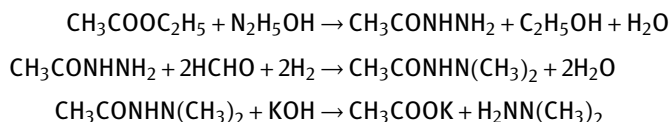
Direct methylation of hydrazine or hydrazine hydrate with dimethyl sulfate in an ice bath with vigorous agitation resulted in a mixture of 32% MMH and 67.6% UDMH with a trace (0.3%) of trimethylhydrazine [55]. Whereas this mixture may be undesirable for a purely organic chemist, the mix is perfectly suitable as a rocket fuel without further separation. A laboratory method was developed for the preparation of MMH and UDMH in good yields by the direct methylation of hydrazine with dimethyl sulfate [56]. The relative quantities of MMH and UDMH obtained can be varied by altering the mol ratios of dimethyl sulfate to hydrazine (hydrate). Small amounts of symmetrical

dimethylhydrazine and trimethylhydrazine can also be formed as by-products in this reaction. The methylation procedure was employed to manufacture several hundred pounds of MMH and UDMH for distribution to various agencies for their test programs in the 1950s.

Methylation of hydrazine hydrate results in an azeotrope of UDMH and methanol that is difficult to separate. If dimethyl sulfate is added to UDMH, the reaction product consists of 1,2-dimethylhydrazine (SDMH) and trimethylhydrazine.

### 1.1.7 Reductive Methylation of Acethydrazide

Reductive methylation of acethydrazide (acetyl hydrazine, prepared by condensing hydrazine with ethyl acetate) forms an alkylated product that can be hydrolyzed to yield 84% UDMH [57–59].



Reductive alkylation of acetyl hydrazine, which is then hydrolyzed and converted to UDMH, is an attractive process for getting high yields of UDMH in a safe production process. The effects of pressure, temperature, and the amount of Pd/C catalyst on the yield of the reductive alkylation of acetyl hydrazine were studied to optimize the yield of this process [60]. The reductive methylation with formaldehyde and hydrogen is achieved via Pd-C catalysts. Catalyst poisoning due to unreacted hydrazine is avoided by bubbling carbon dioxide through the mixture. This process was temporarily used by Uniroyal Inc. to produce UDMH after other UDMH producers had withdrawn from the market. Uniroyal later discontinued this operation and returned to purchasing UDMH from other sources.

### 1.1.8 Isotope-Labeled UDMH

Isotope-labeled UDMH is needed for toxicokinetic studies of UDMH metabolism in animals, for spectroscopic studies of the molecular structure by identifying molecular vibrations, and for kinetic studies in the formation and decomposition of UDMH. Substitution of hydrogen on nitrogen by deuterium is relatively easy and the rate of substitution can be measured by proton exchange rate measurements.

*N,N*-[Methyl-<sup>14</sup>C]-Dimethylhydrazine hydrochloride was synthesized in two steps: dimethylation of acetophenone hydrazone with <sup>14</sup>C-methyl iodide in the presence of potassium in liquid ammonia, followed by acid-catalyzed hydrolysis of the hydrazone. This afforded this chemical a yield of 60% (>97% radiochemical purity) [61].

### 1.1.9 Preparation of UDMH via NDMA

Several of the processes for the production of UDMH described on the following pages are dependent on NDMA as an intermediate. Because NDMA and other nitrosamines are human carcinogens, these processes must be used with extreme precaution to avoid worker exposure and environmental pollution. One UDMH-production plant operated by FMC in Baltimore, MD, had to be shut down in 1975 because NDMA in levels of 0.3 to 12 ppb was found in the air surrounding the plant.

Methods for NDMA production have become very unpopular due to occupational hygiene and environmental pollution concerns. Nonetheless, the methods are listed here for reference purposes. If nothing else, this is the type of reaction one should avoid. An NDMA 98.8% yield can be obtained by a continuous process by reacting DMA with a mixture of nitric oxide (NO) and air, maintaining an excess of NO, and maintaining acidic conditions with the addition of hydrochloric acid [62, 63]. In another process, NDMA was obtained in 94% yield by reacting a mixture of dimethylammonium sulfate and sodium nitrite (initial pH 9.5) slowly with sulfuric acid [64]. After the pH had dropped to four and the reaction had ceased, a slight excess of sodium nitrite was added as a 40% solution before distillation. This procedure has been used for large-scale NDMA production at the rate of 450 kg/h.

NDMA can be separated from the reaction mix by distillation and phase separation with caustic [65]. One-pot synthesis of UDMH avoids the isolation of NDMA. This is prepared using DMA and dinitrogen tetroxide with potassium carbonate. A palladium catalyst is added, which reduces the raw product with high-pressure hydrogen immediately after the nitrosation is complete [66].

The more detailed chapter on reduction methods for NDMA that was published in an earlier book [67] has been abbreviated and is not repeated here. Reduction methods include the reduction of NDMA with metals in acidic or alkaline solution, electrolytic reduction, catalytic reduction with hydrogen gas, and NDMA reduction with metal hydrides or sodium dissolved in liquid ammonia.

### 1.1.10 UDMH Preparation from Sodium Amide and Dimethylchloramine

Admittedly it is more expensive to react chloramines with alkaline metal amides instead of free ammonia. However, the yields can be better because the alkaline metal chloride precipitates in the presence of tertiary amine solvents. The only advantage of this method is that it avoids the use of water and it results directly in anhydrous hydrazines. Thus, UDMH is obtained in 60% yield by reacting *N*-chlorodimethylamine in tripropylamine with sodium amide in liquid ammonia at 238 K [68–72].

### 1.1.11 Separation of Water and UDMH

As explained earlier, mixtures of UDMH and water are not easy to separate by simple distillation because UDMH forms an azeotrope with water. The problem with separating the desired alkylhydrazine from the reaction mixture is similar to the problem encountered earlier with MMH and water. Usually, the azeotrope is broken by adding sodium hydroxide to the mixture, following which the pure MMH or UDMH can be distilled off [25]. Monoethanolamine can be used as an auxiliary fluid to separate UDMH and water by distillation [73].

The methods used for separating UDMH and water depend on the amount of water in the UDMH or the amount of UDMH in the water [74]. Process liquors from the Raschig process usually contain only 3% UDMH.

#### 1.1.11.1 Concentrating Dilute Solutions of UDMH in Water

Pervaporation of process liquid containing only less than five percent of UDMH in water is a more economical process than distillation. In pervaporation, the feed mixture is contacted with a non-porous perm-selective membrane. Separation is, in general, explained by the steps of sorption into, diffusion through, and desorption from the membrane. The latter is usually considered to be fast and expected to take place at equilibrium, while diffusion is kinetically controlled and the slowest step of the process. Permeation is dependent on sorption and diffusion steps. The driving force for the separation is created by maintaining a pressure lower than the saturation pressure on the permeate side of the membrane. The mechanism of separation is usually explained in terms of sorption-diffusion processes.

Dehydration of hydrazine or MMH using ethyl cellulose membranes has been demonstrated and similar techniques can be used for UDMH, except that ethyl cellulose is not compatible with UDMH [75, 76]. However, ethyl cellulose membranes cannot be used to dehydrate UDMH because ethyl cellulose is degraded rapidly in UDMH.

Chitosan, a derivative of the naturally abundant biopolymer chitin, is fully stable in anhydrous UDMH and hence can be selected for its dehydration ability, keeping in mind its highly hydrophilic nature and good mechanical strength. The promising potential of chitosan as a pervaporation membrane has already been exploited for the dehydration of alcohols such as ethanol and isopropanol [77].

Cross-linked chitosan membranes synthesized using glutaraldehyde and characterized by IR and XRD spectroscopic methods were applied to the pervaporation-based dehydration of UDMH [78]. The characterization techniques were an efficient tool in identifying polymer-liquid interaction sites and the separation mechanisms involved. The cross-linked polymer was found to have good potential for the separation of the aqueous azeotrope (20 mass-% UDMH) and its enrichment to >90% purity. An equilibrium sorption study examined the preferential affinity of the membrane toward the two penetrating liquids. The pervaporation performance of the membrane was eval-

uated by varying the experimental parameters of feed composition, membrane thickness, and permeate pressure. Similar membranes can be used for the pervaporation of MMH from aqueous solutions.

NaA zeolite membranes have been formed on porous mullite tubes and tested for the pervaporation of dilute UDMH solutions in water [79]. The seeded supports were prepared by dipping the mullite supports in an 8% NaA zeolite suspension in a single step. After dipping, the supports were dried at 373 K (100 °C) for 3 h. Other tubes received five coatings. Most initial tests were conducted with ethanol/water mixtures as a surrogate liquid and only a few tests were conducted with 2% UDMH solutions at a temperature of 303 K (30 °C) and a pressure of 1.5 mbar at the permeate side, with test durations of 30–60 minutes. For low concentrations of UDMH, the zeolite NaA membrane was better than the zeolite hydroxy sodalite membrane. However, for high concentrations of UDMH, a zeolite hydroxy sodalite membrane was recommended.

Hydroxysodalite zeolite was coated on an external surface of porous mullite supports using hydrothermal synthesis and water/UDMH mixtures were separated at ambient temperature and atmospheric pressure by pervaporation using the hydroxysodalite zeolite membranes [80–83]. The membranes demonstrated very high selectivity of water for all water/UDMH mixtures. A separation factor as high as 52000 was obtained for a UDMH feed concentration of 5%. Total mass flux was up to  $3.95 \text{ kg m}^{-2} \text{ h}^{-1}$ . The results confirmed the good performance of hydroxysodalite zeolite membranes for the dehydration of water/UDMH mixtures.

Mordenite is another zeolite mineral that was evaluated in pervaporation experiments. Mordenite membranes were prepared on the outer surface of mullite ceramic tubes via hydrothermal synthesis and evaluated for dehydration pervaporation of water/UDMH mixtures [84]. Highly water-selective mordenite membranes were prepared and the optimum reaction condition was found to be 24 h crystallization time and 443 K (170 °C) crystallization temperature. The effect of gel composition on the separation factor and water flux of the water-UDMH mixtures was investigated. XRD patterns showed that mordenite was the only zeolite material that was present in the membrane. The morphology of the supports subjected to crystallization was characterized by scanning electron microscope (SEM). In pervaporation of the water or in UDMH mixtures with higher UDMH contents, the membrane exhibited a hydrophilic behavior. The best membranes had a water flux of  $2.67 \text{ kg m}^{-2} \text{ h}^{-1}$  at 303 K (30 °C). The best pervaporation selectivity was 264 ([85, 86]).

#### 1.1.11.2 Removal of Trace Water from UDMH

Traces of water can be removed from UDMH by passing the mixture through a column packed with molecular sieves. The adsorption isotherms of trace water in UDMH on 3A, 4A, and 5A molecular sieves were determined and curve-fitted by using the Langmuir equation and Freundlich equation [87]. The adsorption isotherms on 3A and 4A



molecular sieves were most consistent with results curve-fitted by the Langmuir equation. The adsorption isotherm on the 5A molecular sieve was more suitable to that curve-fitted by the Freundlich equation. The adsorption process had no influence on other contaminants, including FDMH or dimethylamine.

The isothermal adsorption data of small amounts of water in UDMH on 4A molecular sieves were measured and curve-fitted well according to the models by Langmuir and Freundlich [88]. The activation energy of water adsorption on 4A molecular sieves was  $E_a = 28.22 \text{ kJ/mol}$ . The dynamic breakthrough curves in fixed-bed columns were measured for a residence time of 60 minutes. These results can be used as the basis for the design of a full-scale adsorption process. Out-of-spec UDMH with excessive water content can be regenerated by fractionated distillation [89].

#### 1.1.11.3 Purification of UDMH

Even with the best care devoted to the manufacturing of UDMH, the carryover of some contaminants from the reaction mixture is inevitable. Other contaminants form during storage if air is not carefully excluded from the storage containers.

Charcoal that was activated by treatment with strong ammonia water, 1 mol/L  $\text{NH}_4\text{Cl}$ , and 0.5 mol/L NaOH solution or by microwave treatment could remove yellow discoloration from aged UDMH [90, 91]. The adsorption isotherm showed that the adsorption process of a yellow substance in UDMH on the activated carbon is endothermic.

### 1.2 Physical Properties of Unsymmetrical Dimethylhydrazine

The physical properties of UDMH are summarized in Table 1. There used to be several widely distributed manufacturer's marketing brochures regarding the physical properties and safe handling of UDMH [92, 93]. These are no longer available because UDMH ceased to be produced in the US. Other bibliographies and handbooks on the properties of UDMH were compiled by UDMH users or produced under US Government contracts [94–98].

#### 1.2.1 Density of UDMH

The measurements of the density of UDMH performed by various authors and organizations agreed quite well when it came to the temperature range of between 210 to 330 K. The composite smoothed data from several sources [95, 99, 100] can be expressed by the equation

$$\rho = 1.06041 - 7.7507 \times 10^{-4} T - 4.8648 \times 10^{-7} T^2$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. This is the equation used to construct the density curve in Figure 1.

**Table 1:** Physical properties of UDMH.

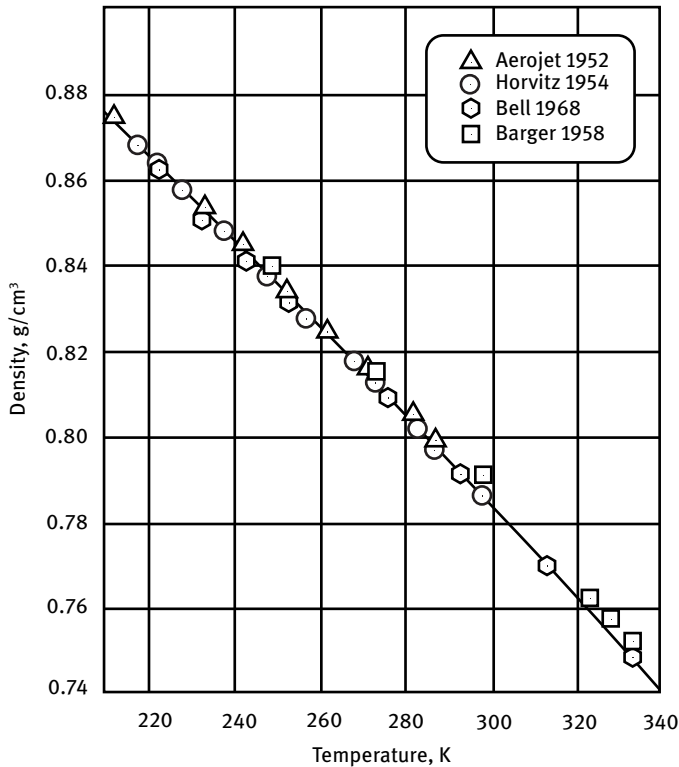
| Property                           | Unit                                                 | UDMH                    |
|------------------------------------|------------------------------------------------------|-------------------------|
| Molecular mass (weight)            |                                                      | 60.0986                 |
| Melting point                      | K                                                    | 215.94                  |
|                                    | °C                                                   | −57.21                  |
|                                    | °F                                                   | −70.97                  |
| Boiling point                      | K                                                    | 335.47                  |
|                                    | °C                                                   | 62.32                   |
|                                    | °F                                                   | 144.18                  |
| Vapor pressure                     | kPa                                                  | 22.3                    |
|                                    | mm Hg                                                | 167.1                   |
|                                    | psia                                                 | 3.23                    |
| Density, liquid                    | g/cm <sup>3</sup> (lb/ft <sup>3</sup> )              | 0.7861 (49.073)         |
| Viscosity, liquid                  | cPs                                                  | 0.492                   |
| Surface tension                    | mN/cm = dyn/cm × 10 <sup>2</sup>                     | 0.2409                  |
| Thermal conductivity, liquid       | cal cm <sup>−1</sup> K <sup>−1</sup> s <sup>−1</sup> | 3.76 × 10 <sup>−4</sup> |
| Heat capacity, liquid              | J g <sup>−1</sup> K <sup>−1</sup>                    | 2.945                   |
|                                    | cal g <sup>−1</sup> °C <sup>−1</sup>                 | 0.704                   |
| Enthalpy of formation, liquid      | kJ/mol                                               | +51.626                 |
|                                    | kcal/mol                                             | +12.339                 |
| Heat of fusion, solid              | kJ/mol                                               | 10.073                  |
|                                    | kcal/mol                                             | 2.4074                  |
| Heat of vaporization, at normal bp | kJ/mol                                               | 32.623                  |
|                                    | kcal/mol                                             | 7.797                   |
| Standard entropy, liquid           | J mol <sup>−1</sup> K <sup>−1</sup>                  | 200.24                  |
|                                    | cal mol <sup>−1</sup> °C <sup>−1</sup>               | 47.86                   |
| Standard entropy, vapor            | J mol <sup>−1</sup> K <sup>−1</sup>                  | 304.72                  |
|                                    | cal mol <sup>−1</sup> °C <sup>−1</sup>               | 72.83                   |
| Dipole moment, liquid, Debye units | 1.72                                                 | —                       |
| Index of refraction $n_D$          | 1.4053                                               | —                       |

A simpler linear equation,

$$\rho = 1.09450 - 1.0343 \times 10^{-3}T,$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $T$  is the temperature in kelvin, may be used with almost equal accuracy. Other authors obtained the following relationship for pure UDMH, reporting slightly higher densities [101]:

$$\rho = 0.4478 + 4.2160 \times 10^{-3}T - 1.028 \times 10^{-5}T^2$$



**Figure 1:** Density of liquid UDMH. (Reproduced and modified from [95].)

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. At elevated temperatures, the liquid and vapor densities converge at the critical density and critical temperature, as shown in Figure 2. Only saturated liquid and saturated vapor densities are included in this chart.

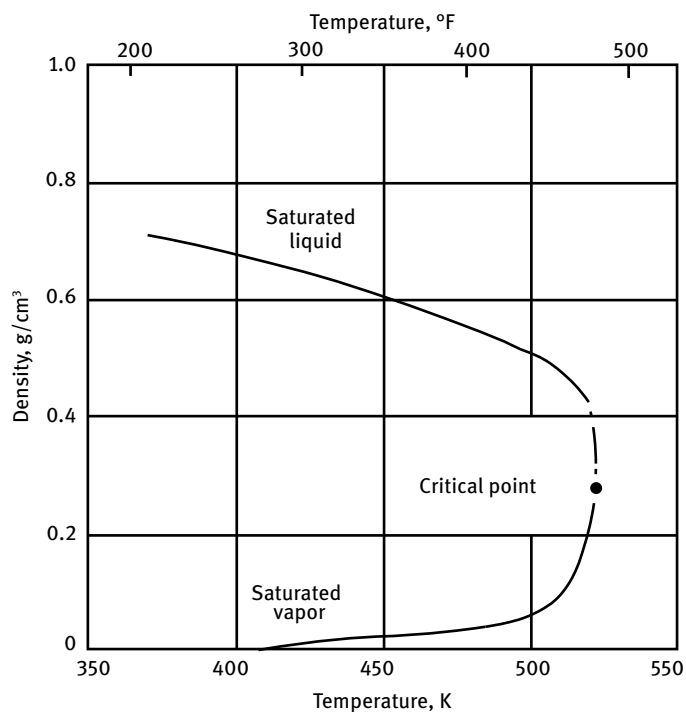
### 1.2.2 Compressibility and Sonic Velocity of UDMH

Data are available for both the isothermal and adiabatic compressibility of UDMH. Data for the isothermal compressibility are summarized in Table 2.

The adiabatic compressibility of UDMH was derived from measured sonic velocity data. The temperature dependence of the adiabatic compressibility can be expressed by the following equation:

$$\beta_a = 3.9348 \times 10^{-4} - 2.8074 \times 10^{-6} T + 5.9151 \times 10^{-9} T^2$$

where  $\beta_a$  is the adiabatic compressibility in  $\text{atm}^{-1}$  and  $T$  is the temperature in kelvin. The curve in Figure 3 was derived from this equation.



**Figure 2:** Density of UDMH saturated liquid and vapor as a function of temperature. (Reproduced and modified from [95] and [102].)

**Table 2:** Isothermal compressibility of UDMH.

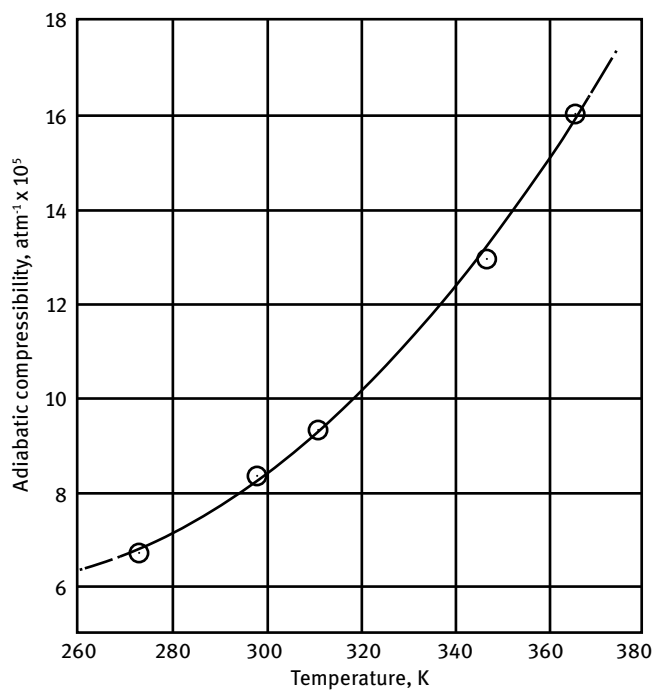
| Temperature, K                        | 373                        | 403   | 433   | 463   |
|---------------------------------------|----------------------------|-------|-------|-------|
| Units                                 | Isothermal compressibility |       |       |       |
| $\text{cm}^2/\text{kg}_f \times 10^4$ | 2.049                      | 2.776 | 3.874 | 6.447 |
| $\text{m}^2/\text{N} \times 10^9$     | 2.089                      | 2.830 | 3.949 | 6.572 |

Data source: [102].

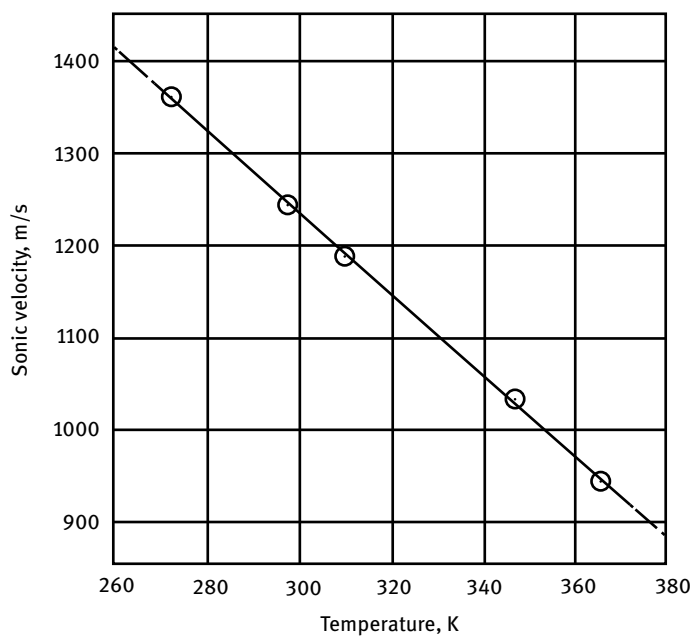
The temperature dependence of the sonic velocity of compression waves in UDMH can be expressed using the following equation:

$$c = 2582.1 - 4.4781 T$$

where  $c$  is the sonic velocity in m/s and  $T$  is the temperature in kelvin. The sonic velocity curve in Figure 4 was drawn based on this equation.



**Figure 3:** Adiabatic compressibility of liquid UDMH. (Reproduced and modified from [95].)



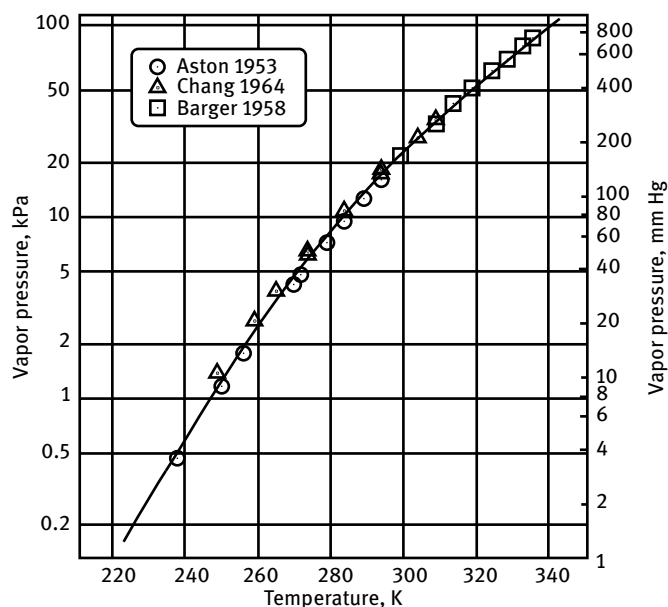
**Figure 4:** Sonic velocity of liquid UDMH. (Reproduced and modified from [95].)

### 1.2.3 Vapor Pressure of UDMH

The composite vapor pressure equation for UDMH, as constructed from combined data obtained by Aston [103], Barger [102], and Chang [104], is

$$\log p = 6.73578 - \frac{875.89}{T} - \frac{140001.0}{T^2}$$

where  $p$  is in mm Hg and  $T$  is in K. It represents the combined data from the three different authors with only small deviations and indicates a normal boiling point of 335.5 K (144.2°F). The curve in Figure 5 for the vapor pressure below the normal point was derived from this equation.



**Figure 5:** Vapor pressure of UDMH below the normal boiling point. (Reproduced and modified from [95].)

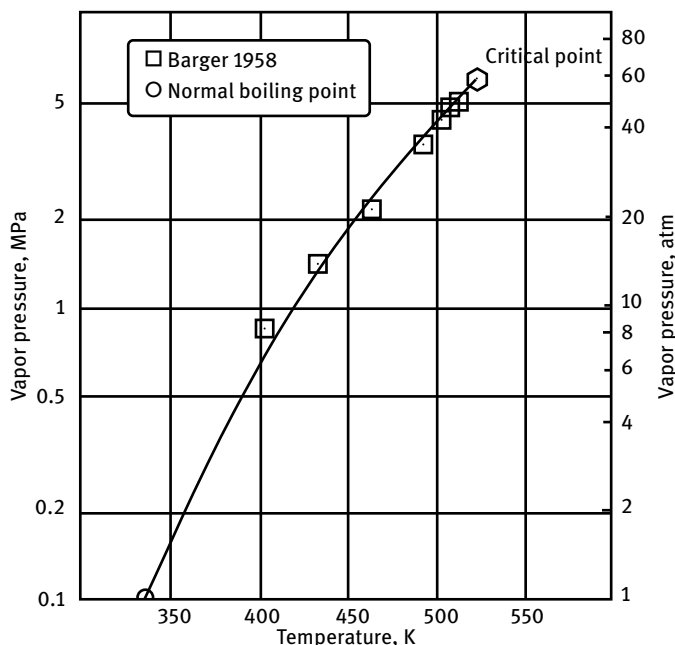
A more recent source [105, 106] determined the vapor pressure of UDMH as

$$\ln p = 22.394289 - \frac{6551.0134}{T} + \frac{424700.9}{T^2}$$

where  $p$  is in mm Hg and  $T$  is in K. The vapor pressure between the boiling point and the critical point can be described using

$$\log p = 4.9439 - \frac{1659.84}{T}$$

where  $p$  is in atm and  $T$  is in K [102]. This is the data illustrated in Figure 6.



**Figure 6:** Vapor pressure of UDMH above normal boiling point. (Reproduced and modified from [95].)

In general, the vapor pressure data in the range of 248 to 308 K (–25 to +35 °C) reported by Chang and Gokcen [104] are higher than those reported by Aston [103] and those for low temperatures reported by Pannetier and Mignotte [107]. At temperatures above 308 K, the data from Chang and Gokcen [104] are lower than those reported by previous authors. Vapor pressures reported by Lawrence [94] in the range of 298 K (25 °C) up to the critical point (523 K = 250 °C, 53.5 atm) for vapor pressures above one atmosphere and at the higher temperatures are suspect since these measurements were made in an apparatus that used mercury (a material which reacts with UDMH) as a confining fluid [94].

Table 3 provides a comparison of UDMH vapor pressure data from various literature sources. There is quite a bit of scatter among these data, especially at higher temperatures.

### 1.2.3.1 Vapor-Phase Composition of UDMH Mixtures

The vapor-phase compositions of UDMH/H<sub>2</sub>O mixtures are discussed in Section 2.1.2. The vapor-phase compositions of UDMH/N<sub>2</sub>H<sub>4</sub> mixtures are discussed later in this chapter (see [109]). A model was deduced from the study of the water-alkylhydrazines vapor-liquid equilibria. It represents strong interactions between molecules as chemical associations and allows one to correctly reproduce all the liquidus curves. This modeling was based on the evolution of the Raman spectra of the liquid phase. The model can also be used to reproduce the system of UDMH/water (see [110]).

**Table 3:** Comparison of UDMH vapor pressure data.

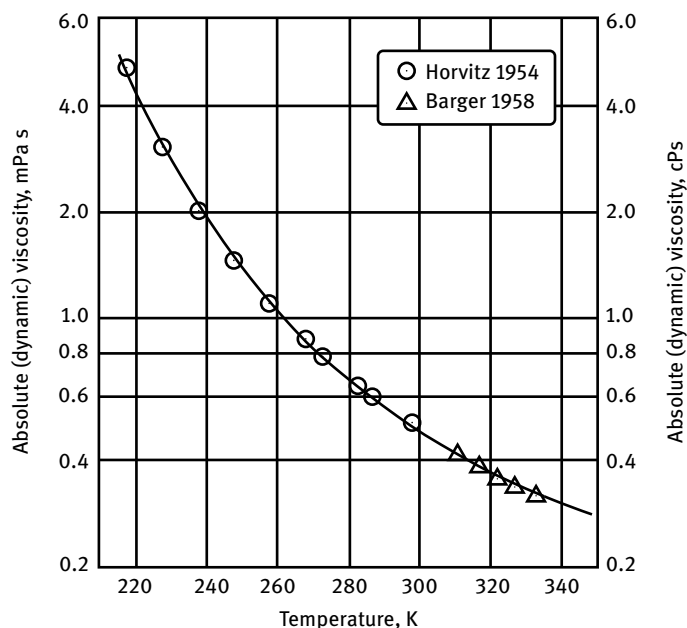
|             |     | Reference                        |                                    |                       |                              |                 |
|-------------|-----|----------------------------------|------------------------------------|-----------------------|------------------------------|-----------------|
| Temperature |     | Copeland and<br>Simmons<br>[108] | Pannetier and<br>Mignotte<br>[107] | Aston et al.<br>[103] | Chang and<br>Gokcen<br>[104] | Barger<br>[102] |
| K           | °C  | Vapor pressure, mm Hg            |                                    |                       |                              |                 |
| 273         | 0   | 44.1                             | 44.7                               | 41.1                  | 48.0                         | 45.2            |
| 323         | 50  | 465.9                            | 460.2                              | 515.0                 | 496.3                        | 483.5           |
| 373         | 100 | 2616                             | 2535                               | 3278                  | 2746                         | 2739            |
| 423         | 150 | 9768                             | 9331                               | 13480                 | 10040                        | 19300           |

### 1.2.4 Viscosity of UDMH

Viscosity data for UDMH from Horvitz and Osborg [100] and Barger [102] have been combined in the following equation:

$$\log \mu = 0.25411 - \frac{623.532}{T} + \frac{1.811518 \times 10^5}{T^2}$$

where  $\mu$  is the viscosity in cPs and  $T$  is the temperature in kelvin. A curve calculated from this formula is illustrated in Figure 7.

**Figure 7:** Absolute (dynamic) viscosity of liquid UDMH. (Reproduced and modified from [95].)



### 1.2.5 Surface Tension of UDMH

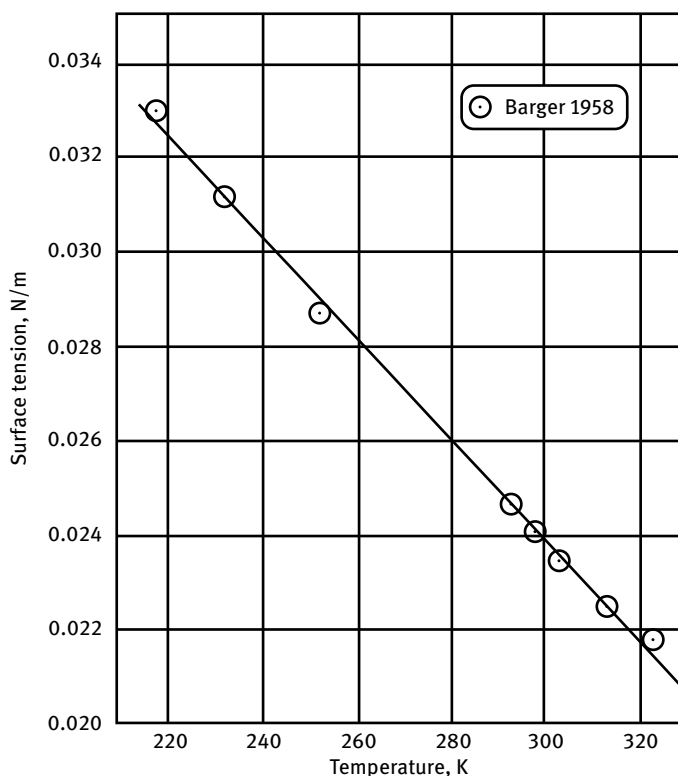
Knowledge of the surface tension of methylhydrazines is of both theoretical and practical interest for two reasons; **(1)** the surface tension can be used to derive parachor data and gain information on the molecular structure of these compounds and, secondly, **(2)** the design of fuel tanks for retaining fluids by capillary forces in the weightlessness of outer space requires the knowledge of the surface tension and wetting angles.

The surface tension of UDMH as a function of temperature can be expressed by the following equations [95, 111]:

$$\sigma_{\text{UDMH}} \left( \frac{\text{dyn}}{\text{cm}} \right) = 56.705 - 0.1094T$$

$$\sigma_{\text{UDMH}} \left( \frac{\text{N}}{\text{m}} \right) = 0.056705 - 1.094 \times 10^{-4} T$$

where  $T$  is the temperature in kelvin. The surface tension curve in Figure 8 was derived from this equation.



**Figure 8:** Surface tension of UDMH. (Reproduced and modified from [95].)

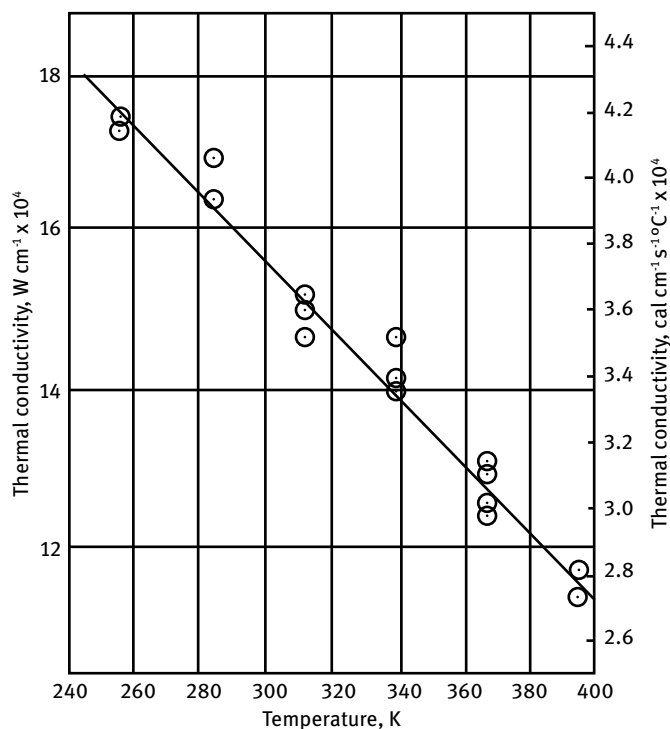
### 1.2.6 Thermal Conductivity of UDMH

The following linear relationship, which is more simple than the one for MMH, has been obtained for the thermal conductivity of 99.8% liquid UDMH [112]:

$$\lambda(\text{cal cm}^{-1} \text{K}^{-1} \text{s}^{-1}) = 6.7975 \times 10^{-4} - 1.0187 \times 10^{-6} T$$

$$\lambda(\text{W K}^{-1} \text{m}^{-1}) = 2.8441 \times 10^{-1} - 4.2622 \times 10^{-4} T.$$

where  $T$  is the temperature in kelvin. The thermal conductivity curve in Figure 9 was derived from this equation. At 298 K, a single data point for the thermal conductivity of liquid UDMH was reported as  $4.8 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ K}^{-1} = 2.0 \times 10^{-1} \text{ W m}^{-1} \text{ K}^{-1}$  [93]. The thermal conductivity of UDMH vapor at 0.17 atm was determined as being between 278.9 and 306.2 K using a hot-wire method [113]. Thermal conductivity was  $272, 274, 293, \text{ and } 301 \times 10^{-7} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  at 278.9, 282.3, 302.6, and 306.2 K, respectively. A linear relationship between temperature and thermal conductivity was assumed for extrapolation purposes. This inferred  $266 \times 10^{-7} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  and  $316 \times 10^{-7} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  at 273 and 323 K, respectively. To convert units from  $\text{cal cm}^{-1} \text{ K}^{-1} \text{ s}^{-1}$  to  $\text{W K}^{-1} \text{ m}^{-1}$ , it should be multiplied by 418.4.



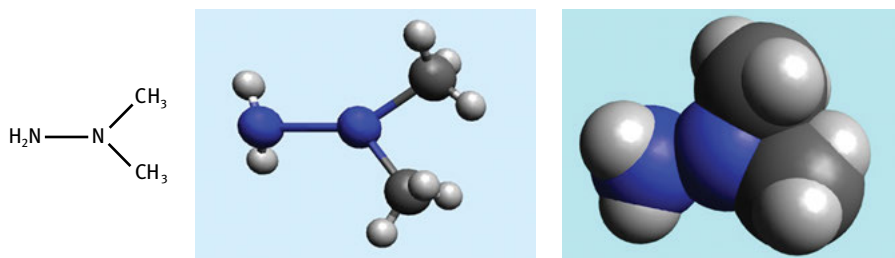
**Figure 9:** Thermal conductivity of liquid UDMH. (Reproduced and modified from [95].)

### 1.2.7 Heat-Transfer Properties of UDMH

As opposed to anhydrous hydrazine, which is likely to explode during soakback and cooldown of an engine at the end of a run, UDMH can be safely used as fuel in regeneratively fuel-cooled engines [114, 115]. An excellent summary of heat flux limits of storable rocket propellants, including hydrazine, MMH, UDMH, and their mixtures, are provided in [116].

### 1.2.8 Molecular Structure of UDMH

The molecular structure of UDMH is illustrated in Figure 10.

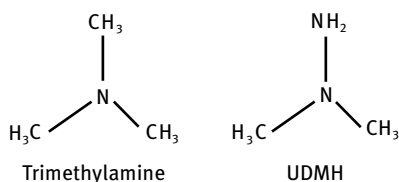


**Figure 10:** Molecular structure of UDMH.

The following atom distances and angles of UDMH were determined from electron diffraction studies [117]:

|       |                                             |
|-------|---------------------------------------------|
| C—N   | $(7 \pm 0.03) \times 10^{-10} \text{ m}$    |
| C—N   | $\sim 1.09 \times 10^{-10} \text{ m}$       |
| N—N   | $(1.45 \pm 0.03) \times 10^{-10} \text{ m}$ |
| N—H   | $\sim 1.04 \times 10^{-10} \text{ m}$       |
| C—N—C | $110 \pm 4^\circ$                           |
| C—N—H | $110 \pm 4^\circ$                           |

In general, the more symmetrical a molecule is, the more stable it is (consider adamantane). Because the atomic weight of an  $\text{—NH}_2$  group is very similar to that of a  $\text{—CH}_3$  group, UDMH can be written as an ammonia molecule with all three hydrogens substituted by groups of similar atomic weight.



It was pointed out that this arrangement favors the possibility of resonance structures. Notably, the shorter the N—N distance ( $1.45 \times 10^{-10}$  vs.  $1.5 \times 10^{-10}$  m for  $\text{N}_2\text{H}_4$ ) the higher the N—N bond energy ( $301 \text{ kJ/mol} = 72 \text{ kcal/mol}$  instead of  $251 \text{ kJ/mol} = 60 \text{ kcal/mol}$ ), which seems to confirm this theory [118]. The N—N bond energy in UDMH has been measured and compared to that in MMH or hydrazine [119].

Bond energies are identical with dissociation energies required to break a particular bond (but there may be contributions by energy stored in other degrees of freedom of the molecule). Table 4 is a summary of bond dissociation energy (BDE) data in UDMH in comparison to other methylhydrazines. The bond lengths and angles in the molecular structure of UDMH based on Raman spectra [103] agreed with those obtained by electron diffraction [117].

**Table 4:** BDEs in UDMH in comparison to other methylhydrazines.

| Bond                                                   | Dissociation energy |            |
|--------------------------------------------------------|---------------------|------------|
|                                                        | kJ/mol              | kcal/mol   |
| <i>1,1-Dimethylhydrazine</i>                           |                     |            |
| $(\text{CH}_3)_2\text{NNH—H}$                          | 368                 | 88         |
| $(\text{CH}_3)_2\text{NNH—H}$                          | $356 \pm 21$        | $85 \pm 5$ |
| $\text{H}_2\text{NN}(\text{CH}_3)\text{—CH}_3$         | 377                 | 90         |
| $\text{H}_2\text{N—N}(\text{CH}_3)_2$                  | $156 \pm 21$        | $38 \pm 5$ |
| $\text{H}_2\text{NN}(\text{CH}_3)\text{CH}_2\text{—H}$ | 410                 | 98         |
| For comparison:                                        |                     |            |
| <i>Methylhydrazine</i>                                 |                     |            |
| $\text{CH}_3\text{NHNH—H}$                             | 368                 | 88         |
| $\text{CH}_3\text{NHNH—H}$                             | $276 \pm 21$        | $66 \pm 5$ |
| $\text{HNN}(\text{CH}_3)\text{—H}$                     | $222 \pm 25$        | $53 \pm 6$ |
| $\text{H}_2\text{NNH—CH}_3$                            | 347                 | 83         |
| $\text{H}_2\text{N—NHCH}_3$                            | 280                 | 67         |
| $\text{H}_2\text{NNHCH}_2\text{—H}$                    | 410                 | 98         |
| <i>Tetramethylhydrazine</i>                            |                     |            |
| $(\text{CH}_3)_2\text{N—N}(\text{CH}_3)_2$             | $209 \pm 21$        | $50 \pm 5$ |

Data sources: [118, 120, 121].

Entropies calculated and compared to those expected from Raman data indicated that a *trans* configuration is very unlikely for UDMH. Other electron-diffraction measurements for UDMH vapor reported an N—N distance of  $1.437 \times 10^{-10}$  m, an N—C distance of  $1.469 \times 10^{-10}$  m, a  $\angle\text{CNC}$  angle of  $111.2 \pm 0.5^\circ$ , and an  $\angle\text{NNC}$  angle of  $108.2 \pm 0.4^\circ$  [122]. The rotation around the N—N bond was studied using MNDO/2 and *ab initio* methods. The skew shape of UDMH was supported by the photoelectron spectra of UDMH vapor [123, 124]. An electron diffraction spectroscopy study of the molecular structure of SDMH and UDMH provided exact atomic distances and bond angles [117].

The molecular structures of UDMH and other hydrazines have been modeled in an effort to predict the enthalpies of formation of the molecules in the vapor state and to identify the weak links in the molecule (those that break first when the molecule is heated).

Based on quantum mechanical and molecular mechanics (MM3) studies of hydrazines, the N—N bond lengths are much longer in the *syn* and *anti* conformations of UDMH than in the *gauche* conformation [125].

Calculations in a combined density functional theory (DFT, B3LYP) and G2MP2 theoretical study resulted in enthalpies of formation ( $H^\circ_f$ ) and bond dissociation enthalpies (BDE) for UDMH of  $80 \pm 4$  kJ/mol and  $259 \pm 12$  kJ/mol, respectively [126].

Improved molecular models for hydrazine, methylhydrazine, and 1,1-dimethylhydrazine were developed to study the fluid-phase behavior of these compounds [127, 128]. A parameterization of classical molecular interaction models was carried out by using quantum chemical calculations and subsequent fitting to experimental vapor pressure and saturated liquid density data. To validate the molecular models, vapor-liquid equilibria for the pure hydrazines and binary hydrazines mixtures with water or ammonia were calculated and compared with available experimental data. In addition, the Henry's-law constant for the physical solubility of argon, nitrogen, and carbon monoxide in liquid UDMH was computed. In general, the simulation results were in good agreement with the experimental data. The computed results for saturated densities, vapor pressure, and heat of vaporization were compared to the available experimental data and the simulation results published by Gutowski et al. [129]. The saturated liquid density based on the model by Gutowski et al. [129] followed an opposite trend relative to hydrazine and methylhydrazine, i.e., the density from the simulation was larger than that reported in the experiment. Over the temperature range of 273 to 339 K, the values by Gutowski were in excellent agreement with the experiment, being only slightly higher (0.5 to 1.7%). Notably, at higher temperatures, the density deviations increased. The Elts et al. [127] model reported average deviations from the experimental saturated liquid density of about 1.3% over the whole temperature range. For the vapor pressure, the data derived from the Elts et al. model deviated from the experiment only by about 3.7%, while the values reported by Gutowski et al. [129] underestimated the experimental vapor pressure by more than 80% above 340 K. The enthalpy of vaporization predicted by Gutowski et al. [129] at 298 and 339 K were higher than the experimental values by around 8 kJ/mol, which is 24% in relative terms. For the Elts et al. [127] model, these deviations were minor, yielding a mean unsigned error of about 1.0%.

Composite *ab initio* methods and DFT methods were used to calculate accurate BDEs of UDMH [130]. It was found that the results calculated by composite *ab initio* methods were in good agreement with literature values for all other types of bonds of the molecule except the N—C bond. Of the results calculated using DFT methods, the Boese–Martin for Kinetics (BMK) method produced results very similar to composite *ab initio* methods. For the N—H and C—H bonds, the B3P86 method performed slightly

better than the BMK method, while the B3LYP data set generally underestimated the BDE of UDMH. Results from restricted open-shell-method calculations were superior to an unrestricted method due to spin contamination.

Full geometrical optimizations of the 1,1-dimethylhydrazine molecular structure have been carried out by quantum-mechanical methods Restricted Hartree-Fock (RHF), Becke, 3-parameter, Lee–Yang–Parr (B3LYP) (B3LYP), and Møller-Plesset perturbation theory (MP2), respectively, and the optimal geometric structure parameters have been obtained [131]. The predicted structure parameters were compared to experimental results. Except for two predicted parameters ( $\angle\text{C–N–N–H}$  dihedral angle and C–H bond length, which showed smaller values), all others agreed well with the experimental results. All these calculations indicated a *gauche* conformation. The predicted N–N bond length was about 0.143 nm and the C–N bond length was about 0.147 nm. The bond angles of  $\angle\text{N–N–C}$  and C–N–C were about 112 and 113.8°, respectively. The  $\angle\text{C–N–N–H}$  dihedral angle was about 86°.

Dimethyldiazene is an important intermediate product in the reaction of UDMH and  $\cdot\text{OH}$ . A DFT calculation was performed to study the reaction mechanism of dimethyldiazene formation [132]. All transition states were characterized by one imaginary frequency on the potential energy surface. The energy curve of the reaction was obtained using vibrational energy calculations.

Full geometrical optimizations of UDMH structures have been carried out to study the nucleophilicity difference between  $-\text{NH}_2$  and  $-\text{N}(\text{CH}_3)_2$  of the two halves of the molecule [133]. The calculated results of nucleophilicity by molecular orbital theory agreed with the experimental results, showing that the nucleophilicity of  $-\text{N}(\text{CH}_3)_2$  is stronger than that of  $-\text{NH}_2$ .

### 1.2.9 Optical Properties of UDMH

The optical properties of UDMH and other methylhydrazines are important for analytical applications, verifying the purity of propellant before it is being loaded into spacecraft or missiles, and detecting the presence of leaked UDMH vapors in areas where it does not belong and constitutes a hazard to both equipment and personnel. Spectra of UDMH enabled us to better understand the structure of this molecule and derive thermochemical properties that are important for its use as a rocket propellant.

#### 1.2.9.1 UV Absorption Spectra of UDMH

Vacuum UV (VUV) absorption coefficients for hydrazine, MMH, and UDMH were measured from 115 to 185 nm to determine the interference of leaked propellants with UV sensors in space applications [134]. VUV absorption coefficients for  $\text{N}_2\text{H}_4$ ,  $\text{CH}_3\text{HNNH}_2$ , and  $(\text{CH}_3)_2\text{NNH}_2$  were measured for wavelengths between 115 and 185 nm with an estimated experimental error of  $\pm 15\%$ . The measurements were made in a hydrazine-compatible flow-cell apparatus at room temperature.

For the UV absorption of UDMH at 213.9 nm, a UV absorption cross-sections of  $\sigma = 399.9 \times 10^{-20} \text{ cm}^2/\text{molecule}$  was assumed for UDMH photolysis and autoxidation studies in the atmosphere [135, 136].

### 1.2.9.2 Infrared Spectra of UDMH

The IR and Raman spectra of liquid and gaseous UDMH between 700 and 1600  $\text{cm}^{-1}$  for the gas phase and between 700 and 3500  $\text{cm}^{-1}$  for the liquid phase and of trimethylhydrazine have been measured [137, 138]. The wavenumbers and intensity of IR and Raman lines are listed in Table 5.

**Table 5:** Infrared and Raman band wavenumbers for UDMH spectra.

| Infrared                            |                |           |                                     |           |           | Raman                          |                    |              |                   |
|-------------------------------------|----------------|-----------|-------------------------------------|-----------|-----------|--------------------------------|--------------------|--------------|-------------------|
| Vapor                               |                |           | Liquid                              |           |           | Liquid                         |                    |              |                   |
| Wavenumber $\nu$ , $\text{cm}^{-1}$ | Intensity      | Structure | Wavenumber $\nu$ , $\text{cm}^{-1}$ | Intensity | Structure | $\Delta\nu$ , $\text{cm}^{-1}$ | Intensity          | Polarization | Breadth           |
|                                     |                |           |                                     |           |           | 282                            | w                  | p            | Diffuse and broad |
|                                     |                |           |                                     |           |           | 418                            | m                  | p            | Narrow            |
|                                     |                |           |                                     |           |           | 445                            | m                  | p            | Narrow            |
| 803                                 | vs             | PQR       | 793                                 | s         | Broad     | 809                            | vs                 | p            | Narrow            |
| 904                                 | s              | PQR       | 848                                 |           |           |                                |                    |              |                   |
| 961                                 | m              | Q         | 944                                 | s         | Broad     | 957                            | w                  | pp           | Diffuse           |
| 1016                                | vw             |           | 1009                                | s         | Broad     | 1027                           | m                  | p            | Narrow            |
| 1046                                | vs             | PQR       |                                     |           |           |                                |                    |              |                   |
| 1090                                | m              | Q         | 1069                                | s         | Broad     | 1061                           | w                  | pp           | Diffuse           |
| 1139                                | s              | Q?        | 1140                                | s         | ?         | 1150                           | s                  | p            | Narrow            |
| 1153                                | Branch on 1139 |           |                                     |           |           |                                |                    |              |                   |
| 1214                                | m              | PQR       | 1201                                | s         | ?         | 1212                           | m                  | dp?          | Narrow            |
|                                     |                |           | 1243                                | m         | ?         | 1248                           | m                  | pp           | Diffuse           |
| 1301                                | m              | PQR       | 1321                                | s         | ?         | 1325                           | vw                 | dp?          | Diffuse           |
|                                     |                |           |                                     |           |           | 1405                           | m                  | dp           | Narrow            |
| 1457                                | m              | PQR       | Too strong to measure               |           |           | 1423                           | s                  | dp           | Broad             |
| 1593                                | m              | ?         | —                                   |           |           | 1599                           | w                  | pp           | Diffuse           |
|                                     |                |           | 2764                                | m         |           | 2774                           | Covered by Hg line |              |                   |
|                                     |                |           | 2811                                | m         |           | 2817                           | ?                  | p?           | Narrow            |
|                                     |                |           | 2844                                |           |           | 2849                           | m-s                | p            | Narrow            |
|                                     |                |           |                                     |           |           | 2881                           | w                  | p            | Narrow            |
|                                     |                |           | 2944                                | m         |           | 2950                           | s                  | p            | Narrow            |
|                                     |                |           | 2975                                | w         |           | 2988                           | m                  | dp           | Diffuse           |
|                                     |                |           | 3126                                | vw        |           | 3141                           | m                  | p            | Narrow            |
|                                     |                |           | 3298                                | w         |           | 3330                           | vw                 | dp?          | Diffuse           |

Data source: [138].

**Table 6:** Fundamental vibration band assignments for UDMH IR and Raman spectra.

| Assignment            | Wavenumber, $\text{cm}^{-1}$ |
|-----------------------|------------------------------|
| Skeletal bend         | 418                          |
| Skeletal bend         | 445                          |
| Skeletal stretch      | 803                          |
| Skeletal stretch      | 904                          |
| Skeletal stretch      | 961                          |
| Rocking               | 961                          |
| Rocking               | 1046                         |
| Rocking               | 1090                         |
| Rocking               | 1139                         |
| $\text{CH}_3$ bend    | 1301                         |
| $\text{CH}_3$ bend    | 1405                         |
| $\text{CH}_3$ bend    | 1457                         |
| $\text{NH}_2$ bend    | 1593                         |
| $\text{CH}_3$ stretch | 2950                         |
| $\text{CH}_3$ stretch | 2988                         |
| $\text{NH}_2$ stretch | 3741                         |
| $\text{NH}_2$ stretch | 3330                         |

Data source: [138].

The infrared and Raman fundamental vibration band assignments for UDMH are listed in Table 6. Some unassigned frequencies were later identified as combinations of assigned frequencies (wavenumbers). The line at  $282\text{cm}^{-1}$  in the Raman spectrum of UDMH is probably due to internal rotation. Similar assignments were made for a spectrum of trimethylhydrazine.

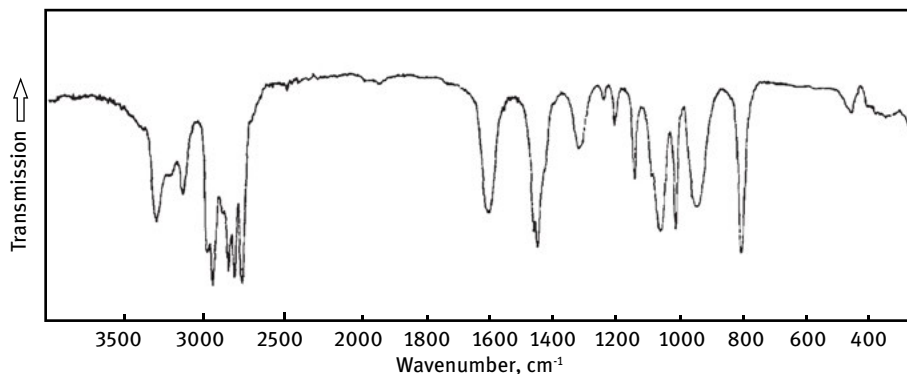
The IR spectra of MMH, UDMH, SDMH, formaldehyde-*N,N*-dimethylhydrazone,  $\text{H}_2\text{C}=\text{N}-\text{N}(\text{CH}_3)_2$ , trimethylhydrazine, and tetramethylhydrazine are contained in a catalog of IR spectra for qualitative analysis of gases [139]. This useful summary also includes the IR spectra of 30 other compounds found in propellant mixtures.

The preliminary band assignments by Shull et al. [139] were superseded by more accurate measurements by Durig and Harris [140] reported 14 years later. The IR spectra of UDMH and  $\text{D}_2\text{NN}(\text{CH}_3)_2$  have been recorded in both liquid and vapor states from  $33$  to  $4000\text{cm}^{-1}$  [140], as demonstrated in Figures 11 and 12.

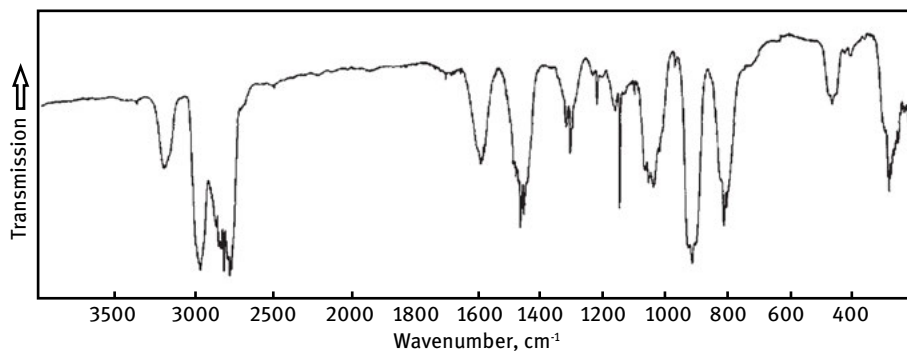
In addition, the spectra of deuterated UDMH and IR spectra of solid UDMH were recorded as being between  $33$  to  $4000\text{cm}^{-1}$ . Raman spectra of liquid UDMH between  $200$  to  $4000\text{cm}^{-1}$  could be correlated with the IR spectra recorded. The spectra were interpreted based on  $C_1$  symmetry. All 30 vibrations were assigned based on intensity, position, and isotope shift. The band assignments in Table 7 supersede the older assignments listed in Table 6.

The methyl torsional fundamentals were identified and found to correspond to a barrier hindering the free rotation of the methyl group that was equivalent to  $19.6\text{kJ/mol}$  ( $4.69\text{kcal/mol}$ ). The amino group free rotation is restrained by





**Figure 11:** Infrared spectrum of liquid UDMH. (Reprinted and modified from [140], with the permission of ©1969 AIP Publishing.)



**Figure 12:** Infrared spectrum of UDMH vapor. (Reprinted and modified from [140], with the permission of ©1969 AIP Publishing.)

a barrier of 13.4 kJ/mol (3.2 kcal/mol). Individual vibration assignments in UDMH were considerably more complex than the MMH spectrum analyzed before it. Based on the spectroscopic measurements of vibrations and inertia, thermodynamic functions of the *gauche* conformation were calculated from 200 to 3000 K. At 298.16 K,  $S^0$  was 296.3 J mol<sup>-1</sup> K<sup>-1</sup> (70.82 cal mol<sup>-1</sup> K<sup>-1</sup>),  $-(F^0 - E_0^0)/T$  was 239.8 J mol<sup>-1</sup> K<sup>-1</sup> (57.31 cal mol<sup>-1</sup> K<sup>-1</sup>),  $(H^0 - E_0^0)/T$  was 56.5 J mol<sup>-1</sup> K<sup>-1</sup> (13.51 cal mol<sup>-1</sup> K<sup>-1</sup>), and  $C_p$  was calculated to be 90.33 J mol<sup>-1</sup> K<sup>-1</sup> (21.59 cal mol<sup>-1</sup> K<sup>-1</sup>).

Several of the 30 fundamental vibrations ascribed to the UDMH molecule by Shull et al. [138] had to be reassigned because of the more recent data supplied by Durig and Harris [140]. These data, in turn, have been superseded. Further to this, some of the contradictions may have been eliminated by later examinations by Anthoni, Larsen, and Nielsen [141]. They were able to assign most of the 30 possible funda-

**Table 7:** Fundamental vibration band assignments for UDMH spectra.

| Number     | Approximate description of vibration       | Wavenumber, cm <sup>-1</sup> |
|------------|--------------------------------------------|------------------------------|
| $\nu_1$    | NH <sub>2</sub> anti-symmetric stretching  | 3338                         |
| $\nu_2$    | NH <sub>2</sub> symmetric stretching       | 3315                         |
| $\nu_3$    | CH <sub>3</sub> anti-symmetric stretching  | 2980                         |
| $\nu_4$    | CH <sub>3</sub> anti-symmetric stretching  | 2980                         |
| $\nu_5$    | CH <sub>3</sub> anti-symmetric stretching  | 2961                         |
| $\nu_6$    | CH <sub>3</sub> anti-symmetric stretching  | 2961                         |
| $\nu_7$    | CH <sub>3</sub> symmetric stretching       | 2816                         |
| $\nu_8$    | CH <sub>3</sub> symmetric stretching       | 2777                         |
| $\nu_9$    | NH <sub>2</sub> deformation                | 1587                         |
| $\nu_{10}$ | CH <sub>3</sub> anti-symmetric deformation | 1464                         |
| $\nu_{11}$ | CH <sub>3</sub> anti-symmetric deformation | 1464                         |
| $\nu_{12}$ | CH <sub>3</sub> anti-symmetric deformation | 1449                         |
| $\nu_{13}$ | CH <sub>3</sub> anti-symmetric deformation | 1449                         |
| $\nu_{14}$ | CH <sub>3</sub> symmetric deformation      | 1402                         |
| $\nu_{15}$ | CH <sub>3</sub> symmetric deformation      | 1402                         |
| $\nu_{16}$ | NH <sub>2</sub> wagging                    | 1319 <sup>a</sup>            |
| $\nu_{17}$ | Skeleton stretching                        | 1246 <sup>a</sup>            |
| $\nu_{18}$ | CH <sub>3</sub> symmetric rocking          | 1215                         |
| $\nu_{19}$ | CH <sub>3</sub> symmetric rocking          | 1144 <sup>a</sup>            |
| $\nu_{20}$ | CH <sub>3</sub> anti-symmetric rocking     | 1060                         |
| $\nu_{21}$ | CH <sub>3</sub> anti-symmetric rocking     | 1032                         |
| $\nu_{22}$ | Skeleton stretching                        | 966                          |
| $\nu_{23}$ | NH <sub>2</sub> rocking                    | 908                          |
| $\nu_{24}$ | Skeleton stretching                        | 808                          |
| $\nu_{25}$ | Skeleton bending                           | 459 <sup>a</sup>             |
| $\nu_{26}$ | Skeleton bending                           | 441 <sup>a</sup>             |
| $\nu_{27}$ | Skeleton bending                           | 411 <sup>a</sup>             |
| $\nu_{28}$ | NH <sub>2</sub> torsion <sup>b</sup>       | 295 <sup>b</sup>             |
| $\nu_{29}$ | CH <sub>3</sub> torsion <sup>b</sup>       | 282 <sup>b</sup>             |
| $\nu_{30}$ | CH <sub>3</sub> torsion <sup>b</sup>       | 269 <sup>b</sup>             |

<sup>a</sup>Denotes Raman frequency; all others are infrared.<sup>b</sup>Denotes solid infrared.

Data source: [140].

mental vibrations. Of these, 21 belong to the (CH<sub>3</sub>)<sub>2</sub>N group, three to the NH<sub>2</sub> group, and six arise from motions of these two groups in relation to each other. Only three strong bands were left unassigned. These are most likely skeletal stretching vibrations. Some assignments could be linked by similarity with bands already assigned in organic amines which also contain the dimethylamino group.

Variable temperature (168 to 123 K = -105 to -150 °C) studies of the infrared spectra (3500–400 cm<sup>-1</sup>) of UDMH in liquid krypton provided no convincing spectral evidence for the *trans* conformer, which was expected to be at least 600 cm<sup>-1</sup> less stable than the *gauche* form [142]. The structural parameters, dipole moments, conformational

stability, vibrational frequencies, and infrared and Raman intensities have been predicted using MP2/6-31G(d) *ab initio* calculations. The predicted IR and Raman spectra were compared to the experimental spectra. The adjusted  $r_0$  parameters from MP2/6-311+G(d,p) calculations were compared to those reported from an electron diffraction study. The energy differences between the *gauche* and *trans* conformers have been obtained using MP2 *ab initio* calculations and DFT by using B3LYP method calculations from a variety of basis sets. All these calculations indicated an energy difference of 650–900 cm<sup>-1</sup>, with the B3LYP calculations predicting the larger values. *Ab initio* MP2/6-31G(d) calculations predicted the barrier to internal rotation by the independent rotor model of the inner methyl group to have a value of 1812 cm<sup>-1</sup> and that of the outer one to have a value of 1662 cm<sup>-1</sup>. These values agreed well with the experimentally determined values of 1852 ± 16 and 1558 ± 12 cm<sup>-1</sup>, respectively, which were gained from a fit of the torsional transitions with the coupled rotor model.

It is very important to identify contaminants in UDMH by IR spectroscopy. Contaminants may have been introduced while making UDMH or during storage, most often by autoxidation if air has intruded into the storage container.

One of the common autoxidation products of UDMH is FDMH. Its IR spectra have been analyzed so that it can be better identified when it is encountered as a contaminant in UDMH. The IR spectrum of FDMH, (H<sub>3</sub>C)<sub>2</sub>NN=CH<sub>2</sub>, has been measured as being between 200 and 3400 cm<sup>-1</sup> in the gaseous state and between 140 and 3400 cm<sup>-1</sup> at liquid nitrogen temperatures [143]. A comparison of the vibrational spectra in the solid and fluid states indicated that the molecule exists in only one conformer in all three physical states. The Raman spectra of the gas, liquid, and solid have also been recorded. Because of the number of polarized Raman lines, the vibrational spectra have been interpreted in terms of C<sub>1</sub> symmetry and vibrational assignments were presented based upon the observed band positions, intensities, and group frequency considerations.

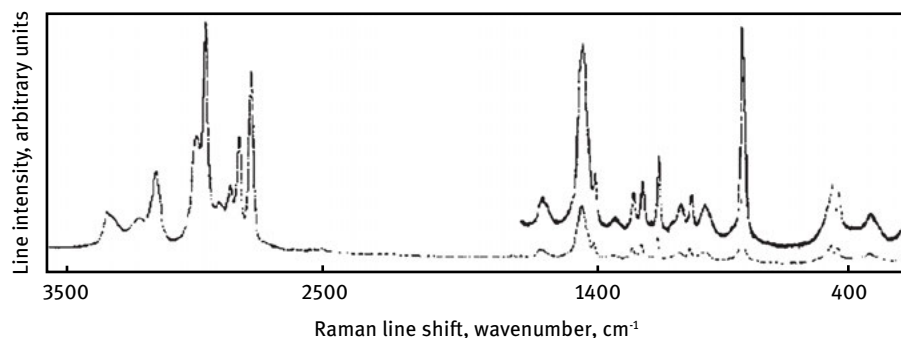
Because of the need for a controlled environment, atmospheric studies of homogeneous vapor autoxidation of UDMH in the air must be conducted in laboratory chambers with non-reactive walls. It has been noted that much of the oxidation occurs heterogeneously on the walls of these chambers and it was difficult to eliminate wall effects. The IR spectra of adsorbed UDMH on chamber materials (silica, silica-alumina, and alumina) were recorded to find inert chamber materials. Diffuse reflectance spectroscopy of hydrazines adsorbed on silica, silica-alumina, and alumina indicated that the primary surface-UDMH interaction is hydrogen bonding [144–146]. In the adsorbed methylhydrazines, the C–H stretching and methyl deformation modes were shifted to higher frequencies by 10 to 20 cm<sup>-1</sup> as a result of electron density changes on the adjacent nitrogen atom. Those weakened bonds make the molecules more susceptible to autoxidation.

The IR spectra of normal UDMH, (CH<sub>3</sub>)<sub>2</sub>NNH<sub>2</sub>, and two isotopomers, (CD<sub>3</sub>)<sub>2</sub>NNH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>NND<sub>2</sub>, have been recorded as being in the region between 100 and 600 cm<sup>-1</sup> [147]. Very rich and complex spectra were obtained and an interpretation of the spectra

arising from the two methyl torsional modes of the deuterated compound was carried out using a semi-rigid model. The resulting potential functions for the three molecules were compared to each other. *Ab initio* gradient calculations were carried out at various levels such that the structural parameters, conformational stability, and three-fold barriers to internal rotation could be determined. The *gauche* conformer was calculated to be more stable than the *trans* form by  $783\text{ cm}^{-1}$  ( $9.37\text{ kJ/mol} = 2.24\text{ kcal/mol}$ ). Isomeric 1,1- and 1,2-disubstituted hydrazines can be readily distinguished by examination of the N–H stretching frequencies in the IR spectra of their hydrochloride salts [148].

### 1.2.9.3 Raman Spectra of UDMH

Some Raman spectra data for UDMH have already been discussed in previous sections regarding the IR spectra of UDMH (see [149]). The Raman spectrum of liquid UDMH is shown in Figure 13.



**Figure 13:** Raman spectrum of liquid UDMH. (Reprinted and modified from [140], with the permission of ©1969 AIP Publishing.)

### 1.2.9.4 Index of Refraction of UDMH

The index of refraction data for UDMH is listed in Table 8.

**Table 8:** Index of refraction data for UDMH.

| Compound              | Temperature, K | $n_D$                | References |
|-----------------------|----------------|----------------------|------------|
| 1,1-Dimethylhydrazine | 298.1          | 1.4051               | [150]      |
|                       | 298.1          | 1.4055               | [151]      |
|                       | 295.4          | 1.40753 <sup>a</sup> |            |
| For comparison:       |                |                      |            |
| SDMH                  | 293            | 1.4039               | [152]      |

<sup>a</sup>Wavelength 589.3 nm

### 1.2.10 Photoelectron and XPS Spectra of UDMH

The unimolecular dissociation of UDMH ions was studied by threshold photoelectron-photoion coincidence spectroscopy [153]. Time-of-flight distributions and breakdown curves were recorded in the photon energy range of 9.5–10.4 eV. The appearance energies of the fragment ions were extracted by modeling the experimental data with a rigid activated complex theory. It was found that the data could be well-reproduced with a single transition state for each dissociation channel if two different H-loss channels were assumed; one corresponding to a C–H and the other to a N–H bond dissociation. Once the appearance energies were established, heats of formation of the fragment ions could be derived. The enthalpy of formation of the neutral molecule was computed by applying composite *ab initio* methods on a series of isodesmic reactions between methyl hydrazines and methyl-amines. The 298 K enthalpy of formation of UDMH vapor was calculated to be  $79.7 \pm 2.2$  kJ/mol, which is within the experimental error of the value of  $83.3 \pm 3.6$  kJ/mol, as reported by Donovan et al. [154]. The adiabatic ionization energy of UDMH was measured to be  $7.29 \pm 0.04$  eV.

The He I photoelectron spectra of UDMH have been measured and CNDO/2 calculations have been carried out [124]. It has been found that non-bonding splittings in the photoelectron spectra are well reproduced by CNDO/2 calculations with *gauche* forms. The results of conformation modeling were supported by published conformational studies. The first and second bands are due to the methylated and unmethylated nitrogen lone pairs, respectively. The third bands are attributed to the N–N bonding orbitals. The rest of the photoelectron spectra up to 18 eV can be explained in terms of other p-type orbitals (C–N bonding, CH<sub>3</sub> pseudo  $\pi$ , and NH<sub>2</sub> pseudo  $\pi$ ).

### 1.2.11 Thermodynamic Properties of UDMH

Thermodynamic properties of UDMH have been derived from spectroscopic or calorimetric data (see [155]).

#### 1.2.11.1 Heat Capacity of UDMH

The heat capacity data of liquid UDMH from [103] and Rocketdyne [156, 157] have been curve-fitted and may be calculated to  $\pm 1.3\%$  by

$$\begin{aligned}c_p(\text{cal g}^{-1} \text{K}^{-1}) &= 0.4071 + 8.838 \times 10^{-4} T \\c_p(\text{J g}^{-1} \text{K}^{-1}) &= 1.7033 + 3.6978 \times 10^{-3} T.\end{aligned}$$

At 298 K,  $C_p$  is  $164.0 \text{ J mol}^{-1} \text{K}^{-1}$  ( $39.2 \text{ cal mol}^{-1} \text{K}^{-1}$ ).

Other sources [108] have derived equations for the heat capacity of solid, liquid, and vapor UDMH as

$$\begin{array}{ll} \text{Solid} & c_p = 13.09 - 1.585 \times 10^{-2}T + 2.742 \times 10^{-4}T^2 \\ \text{Liquid} & c_p = 28.88 + 3.536 \times 10^{-2}T - 2.421 \times 10^{-6}T^2 \\ \text{Ideal Gas} & c_p = -0.05791 + 9.334 \times 10^{-2}T - 5.129 \times 10^{-5}T^2 \end{array}$$

where  $c_p$  is the heat capacity in  $\text{cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin.

#### 1.2.11.2 Enthalpy of Formation of UDMH

For UDMH, heats of combustion have been reported by both Aston, Rock, and Isserow 1952 [158] and Donovan, Shomate, and McBride 1960 [154]. The heat of combustion of UDMH was measured at 303 K and found to be 1980.5 kJ/mol (473.356 kcal/mol) [159] or 1977.6 kJ/mol = 472.648 kcal/mol [158]. The value by Aston et al. [158] has to be corrected to 298 K like the MMH data previously discussed in this chapter. The corrected heat of combustion at 298 K is 1982 kJ/mol = 473.701 kcal/mol. The enthalpy of formation of liquid UDMH derived from this number is  $(\Delta H)_f^{298} = +51.63 \text{ kJ/mol} = +12.339 \text{ kcal/mol}$ . The enthalpy of formation of UDMH vapor is  $+83.3 \pm 3.6 \text{ kJ/mol}$ . The heat of combustion reported by Donovan, Shomate in 1960 was  $1980.2 \pm 1.8 \text{ kJ/mol} = 473.28 \pm 0.43 \text{ kcal/mol}$  [154]. Other reported values for the heat of combustion of UDMH are 1983.7 kJ/mol (474.11 kcal/mol) [93].

#### 1.2.11.3 Enthalpy of Fusion of UDMH

The heat of fusion of UDMH, when corrected for pre-melting, was  $10.0726 \pm 0.0063 \text{ kJ/mol}$  ( $2.4074 \pm 0.0015 \text{ kcal/mol}$ ) and  $215.951 \pm 0.005 \text{ K}$  at the triple point [103, 160]. The decreasing molar heat of the fusion of methylhydrazines with progressive methylation is an indication of reduced hydrogen bonding in the series  $\text{N}_2\text{H}_4$ , MMH, and UDMH.

#### 1.2.11.4 Enthalpy of Vaporization of UDMH

The heat of vaporization of UDMH was not only derived from the vapor pressure curve; it was also directly measured [160]. The average of five determinations for UDMH gave  $(\Delta H)_{\text{vap}}^{298} \text{ UDMH} = 35.00 \pm 0.07 \text{ kJ/mol} = 8.366 \pm 0.016 \text{ kcal/mol}$  when measured [103] or  $32.8 \text{ kJ/mol} = 7.844 \text{ kcal/mol}$  when calculated [104]. From the equation

$$\log p = 6.73578 - \frac{875.89}{T} - \frac{140001.0}{T^2}$$

a heat of vaporization at the normal boiling point of  $7.797 \text{ kcal/mol} = 32.62 \text{ J/mol}$  was calculated. The Trouton constant of UDMH is 23.2.

Attempts to predict vapor pressure and enthalpy of vaporization of UDMH from theoretical computations have not always produced accurate results [127].

### 1.2.11.5 Entropy of UDMH

Aston et al. reported an ideal gas entropy of UDMH vapor at 298.16 K that was equal to  $72.82 \pm 0.20$  e.u. [103]. This was calculated using calorimetric data. A value of 70.70 e.u. was reported for the *trans* form and a value of 72.30 e.u. was reported for the *gauche* form. These were calculated using spectroscopic and molecular structure data. Since the *trans* form has higher energy than the *gauche* form, the *trans* form exists only in negligible quantities at room temperature. Therefore, the agreement between the values of entropy calculated from the two sets of data is very good. The entropy of liquid UDMH was listed as  $\Delta S_{298} = 47.86 \text{ cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$ .

### 1.2.12 Solubility of Pressurant Gases in Dimethylhydrazine

The solubility of gases in hydrazine(s) is of interest with regard to rocket propellants. In many cases, at least for small engines, the propellants are fed into the combustion chamber by a pressurant gas (usually nitrogen or helium). Unless a gas-tight, impermeable diaphragm is employed, the fuels become saturated with the pressurant gas. Heat-transfer characteristics of the gas-saturated liquids are significantly different from those of the pure liquid because dissolved gas bubbles are released prematurely, thus blocking effective heat transfer and sometimes causing the rocket chamber wall to burn out. Release of dissolved gasses and loss of thermal margin causes two-phase flow. Two-phase flow has a higher pressure drop than clean single-phase flow. Solubility-pressure relationships are governed by Henry's law

$$X = KP$$

where  $X$  is the mol fraction of dissolved gas,  $P$  is the partial pressure of the gas, and  $K$  is the solubility constant. If the pressure is entered in units of atmospheres, then the unit of  $K$  is  $\text{atm}^{-1}$ .

The solubility of common pressurant gases (nitrogen, argon, helium) in methylhydrazines has been determined by Chang, Gokcen, and Poston [161–163]. The equilibrium constant  $K_i$  for the pressurant gas equilibrium between the gas phase and the dissolved state is the mol fraction of solute  $i$  divided by its partial pressure  $P_i$  over the equilibrated solution. Its temperature dependence can be expressed by

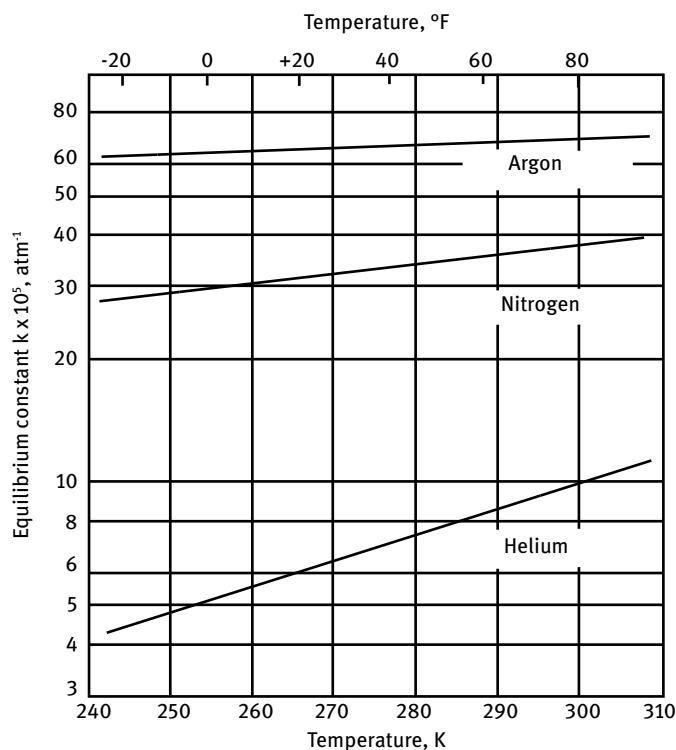
$$\log K_i = \frac{A}{T} + B$$

where  $A$  and  $B$  are constants and  $T$  is the absolute temperature. Table 9 provides a summary of  $A$  and  $B$  constants for three different gases dissolved in various hydrazines and one hydrazine blend. Figure 14 shows the same data in graphic form (see [164]).

**Table 9:** Solubility of pressurant gases in UDMH in comparison to other hydrazines.

| Gas             | Propellant                    | A    | B      | Solubility at 101 kPa, ppm by wt. |       |
|-----------------|-------------------------------|------|--------|-----------------------------------|-------|
|                 |                               |      |        | 273 K                             | 298 K |
| He              | UDMH                          | -461 | 2.3410 | 4.5                               | 6.2   |
| N <sub>2</sub>  | UDMH                          | -175 | 2.8275 | 154                               | 174   |
| Ar              | UDMH                          | -52  | 2.8351 | 440                               | 456   |
| For comparison: |                               |      |        |                                   |       |
| He              | N <sub>2</sub> H <sub>4</sub> | -275 | 0.7387 | 0.5                               | 0.6   |
| N <sub>2</sub>  | N <sub>2</sub> H <sub>4</sub> | -516 | 2.5322 | 4.4                               | 6.3   |
| Ar              | N <sub>2</sub> H <sub>4</sub> | -446 | 2.6841 | 11.3                              | 15.4  |
| He              | MMH                           | -393 | 1.6586 | 1.6                               | 2.1   |
| N <sub>2</sub>  | MMH                           | -245 | 2.5691 | 47                                | 56    |
| Ar              | MMH                           | -142 | 2.6664 | 140                               | 155   |
| He              | Aerozine-50                   | -443 | 1.8319 | 1.62                              | 2.22  |
| N <sub>2</sub>  | Aerozine-50                   | -257 | 2.5130 | 37                                | 45    |
| Ar              | Aerozine-50                   | -169 | 2.6365 | 104                               | 117   |

Data source: [162,163].

**Figure 14:** Gas solubility in liquid UDMH as a function of temperature. (Reproduced and modified from [161].)



### 1.2.13 Electrical Properties of UDMH

Electrical properties summarized in this section include electrical conductivity, dielectric constant, dipole moment, dissociation constant, and magnetic properties. Measurement of the movement and orientation of ions and dipoles in hydrazine derivatives is a fascinating field of study that compares the behavior of UDMH to that of water, hydrazine, and other non-aqueous solvents.

### 1.2.14 Dipole Moment of UDMH

Calculated dipole moments (in Debye units) were 2.93 (UDMH) and 0.06 (SDMH) [165]. Reported measured dipole moments of UDMH vapor are 1.68 D [122] or 1.72 D [166]. Dipole moment data indicated that molecules of  $R_2NNHR'$  ( $R, R' = \text{Me, H; Et, H; Et, Et; Me, Me}_2\text{CH; Me, Me}_3\text{Si; Et}_3\text{Si}$ ) possess the *gauche* conformation. In the Si-containing compounds, this conformation is stabilized by  $p\pi$ - $d\pi$  conjugation.

### 1.2.15 Critical Point Data of UDMH

Critical constants for UDMH are summarized in Table 10. Most of these data were calculated from other physical and thermodynamic properties measured under non-critical conditions. UDMH and other hydrazines are certain to decompose before critical point conditions can be achieved while heating up.

**Table 10:** Critical constants of UDMH in comparison to MMH and hydrazine.

| Compound        | Critical temperature |     | Critical pressure |      | Critical density  | References |
|-----------------|----------------------|-----|-------------------|------|-------------------|------------|
|                 | K                    | °C  | MPa               | atm  | g/cm <sup>3</sup> |            |
| UDMH            | 522                  | 249 | 6.06              | 59.8 | —                 | [103]      |
| UDMH            | 523                  | 250 | 5.4               | 53.3 | 0.275             | [102]      |
| For comparison: |                      |     |                   |      |                   |            |
| Hydrazine       | 653                  | 380 | 0.2307            | 2.28 | —                 | [167]      |
| Hydrazine       | 653                  | 380 | 1.469             | 14.5 | —                 | [168]      |
| MMH             | 567                  | 294 | 8.1               | 80   | 0.17              | [169]      |
| MMH             | 585                  | 312 | 8.21              | 81   | 0.29              | [111, 170] |
| MMH             | 530                  | 257 | 7.6               | 75   | —                 | [160]      |

### 1.2.16 Physical Properties of UDMH Salts

UDMH forms monobasic and dibasic salts with strong mineral acids. There are no industrial applications of UDMH salts. Like UDMH nitrate, they are mostly unwanted contaminants that may form in NTO/UDMH thrusters from the trickle volume of unburned propellants trapped in the injector after the engine shuts down and combustion has ceased. The physical properties of UDMH salts are summarized in Table 11.

**Table 11:** Physical properties of UDMH salts.

| Compound                                          | Gross formula                                                               | Melting point |         | References |
|---------------------------------------------------|-----------------------------------------------------------------------------|---------------|---------|------------|
|                                                   |                                                                             | °C            | K       |            |
| UDMH•H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> | C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub>                | 143           | 416     | [171]      |
| UDMH•H <sub>2</sub> SO <sub>4</sub>               | C <sub>2</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> S <sub>1</sub> | 105           | 378     | [171]      |
| UDMH•HI                                           | C <sub>2</sub> H <sub>9</sub> N <sub>2</sub> I <sub>1</sub>                 | 145–146 dec.  | 418–419 | [171]      |
| UDMH nitrate                                      | C <sub>2</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub>                 | 47            | 320     | [172]      |
| UDMH picrate                                      | C <sub>8</sub> H <sub>11</sub> N <sub>5</sub> O <sub>7</sub>                | 146–147       | 419–420 | [171]      |

### 1.3 Chemical Properties of Unsymmetrical Dimethylhydrazine

1,1-Dimethylhydrazine is a colorless and fishy-smelling liquid that can be stored indefinitely at room temperature if no ambient is allowed to leak in. UDMH is miscible in all proportions with water, hydrazine, or ammonia, however, it is not miscible with kerosene. Solutions of UDMH in water are strongly basic. If UDMH is stored in contact with air, it will both autoxidize, thus quickly leading to discoloration by becoming intensely yellow, will absorb moisture, and will also absorb carbon dioxide. Salts formed by reactions between UDMH and carbon dioxide, and their corrosion products in contact with metals, are not totally soluble in UDMH and may precipitate and clog orifices and filter screens.

#### 1.3.1 Thermal Decomposition of UDMH

The pattern of thermal decomposition of UDMH is even more complex than that of MMH or hydrazine. The thermal decomposition of UDMH has not been the focus of practical interest in the same way as MMH or hydrazine. Although UDMH has been considered a monopropellant, there is no practical way to put it to use. Gas generators in Titan-II and Russian missiles operate on fuel-rich bipropellant mixtures and the hot gas products are used to drive turbines that drive both propellant pumps. Therefore, while there is UDMH decomposition taking place, it is driven by partial combustion. The main advantage of UDMH as a monopropellant would be its low freezing point, making tank, line, and valve heaters in some satellites unnecessary. One big problem with UDMH decomposition is soot formation; this would inactivate a catalyst and plug thermal bed supports and injector orifices.

UDMH is not typically used as a monopropellant since its decomposition is very sooty and results in the formation of toxic hydrogen cyanide. Soot accumulation and cyanide adsorption would quickly foul and poison all catalyst beds. UDMH decomposition on metals is mostly of interest because unwanted, premature UDMH decomposition may occur in hot inlet sections of bipropellant thrusters using UDMH fuels or for the disposal of unwanted surplus UDMH. For bipropellant thrusters, metals found to be catalytic for UDMH decomposition should be avoided in places where the fuel might

get hot (e.g., injectors, regenerative cooling channels, heat exchangers). It appears that on one of the Apollo moon landings, UDMH decomposition from the Aerozine-50 propellant blend caused by heat soaking back from the hot engine momentarily caused a red light to flash after the lander engine was shut down.

This section on the decomposition (autodecomposition) of UDMH overlaps and somewhat duplicates information provided in a previous section in this chapter (regarding the safety properties of UDMH), however, it emphasizes the kinetics of the reaction and not just the temperature and pressure conditions under which it starts. Thermal decomposition kinetics studies were performed under both static and dynamic flow conditions.

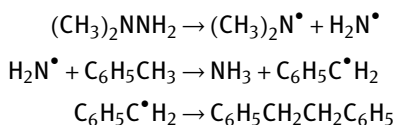
### 1.3.1.1 Thermal Decomposition of UDMH in Static and Flow Reactors

The thermal decomposition of UDMH was studied in an isothermal-flow reactor made from Pyrex tubing [173]. The decomposition started at 673 K (400 °C). The overall first-order reaction rate constant was found to be equal to

$$k = 10^{7.83 \pm 0.2} \exp\left(\frac{28680 \pm 680 \text{ cal}}{RT}\right) \text{ s}^{-1}$$

and the activation energy was 111.6 kJ/mol (28.68 kcal/mol). The products of decomposition were analyzed and found to consist mainly of methane and nitrogen with small amounts of hydrogen and traces of ammonia, dimethylamine, ethane, propane, and methylene methylamine. No cyanide was observed in this study, as opposed to results by other investigators. It was concluded that the decomposition takes place in the gas phase because it did not show a marked dependence on the surface: volume ratio of the reactor.

The thermal decomposition of hydrazine, MMH, and UDMH was studied by the toluene carrier method [174]. The homogeneous decomposition of UDMH in toluene can be accounted for by the mechanism:



with toluene acting as a scavenger for amino radicals. The fate of the dimethylamino radicals is unknown but they do not form DMA in this system. The rate constant was found to be independent of toluene pressure, contact time, reactant pressure, or surface: volume ratio:

$$\log k = 13.22 - \frac{49600}{2.3RT} \text{ s}^{-1}$$

The activation energies were assumed to be similar to the energy of the bonds that were to be broken. The heats of formation of the free radicals were calculated as

166 kJ/mol (39.8 kcal/mol) for  $\text{H}_2\text{N}^\bullet$ , 144 kJ/mol (34.5 kcal/mol) for  $\text{H}_3\text{CNH}^\bullet$ , and 123 kJ/mol (29.5 kcal/mol) for  $(\text{H}_3\text{C})_2\text{N}^\bullet$ .

The very low-pressure pyrolysis of UDMH was reinvestigated [175]. The rate constant ( $k_{\text{uni}}$ ) for the first-order disappearance of UDMH in a static reactor has been determined under very low-pressure pyrolysis conditions [176]. The  $k_{\text{uni}}$  are not the rate constants of ultimate interest since they reflect the fact that energy transfer competes with chemical decomposition. The theory allows the determination of the high-pressure rate constants ( $k_a$ ) if the mode of decomposition is known. The heats of formation of the radicals  $\bullet\text{NH}_2$ ,  $\text{CH}_3\text{N}^\bullet\text{H}$ , and  $(\text{CH}_3)_2\text{N}^\bullet$  are known. These values should be usable for the prediction of the activation energy for N—N bond homolysis in the hydrazines. Measured rate constants for UDMH and tetramethylhydrazine bear this out but the rate constant for MMH did not.

The autodecomposition and auto-ignition temperatures of UDMH in inert gases (nitrogen, helium) or air were determined by squirting 0.1 mL into a 125-mL Pyrex round flask or 0.3 mL squirted into a 1-L Pyrex round flask [177]. In nitrogen or helium, UDMH autodecomposed above 666 K (740 °F). The addition of 40% diethylenetriamine (DETA) did not significantly increase the autodecomposition temperature threshold (671 K = 748 °F). This fuel mixture is also known under the code name U-DETA. In comparison to the auto-ignition tests in air conducted in the same apparatus, the autodecomposition of UDMH was difficult to observe since there was no flame and an audible report could be heard only at the very highest temperatures tested. The criterion used to determine whether a decomposition had taken place or not was the thermocouple reading from the gas space in the flask. The static conditions chosen for this test were intended to simulate the vapor space in a mostly empty propellant tank.

No explosive decomposition was encountered in the absence of air when UDMH vapor alone was heated to 873 K at 101 kPa or 777 K at 1.38 MPa (200 psig) [178].

Decomposition of UDMH in a quartz chamber heated to up to 1273 K preceding a time-of-flight mass spectrometer showed that significant decomposition occurred only above 800 K [179]. UDMH began to decompose at temperatures between 473 and 573 K (200 and 300 °C), as evidenced by the decrease in the parent peak of mass 60. The parent peak is no longer present at 1073 K (800 °C), indicating that complete decomposition had occurred.

Other investigators measured the UDMH thermal decomposition and found that UDMH rapidly decomposes at temperatures in the range of 673 to 773 K (400 to 500 °C). The half-life time of UDMH was 2.5 minutes at 693 K (420 °C) and 1.5 minutes at 733 K (460 °C).

A model analogous to a Frank-Kamenetskii equation was developed for UDMH droplet combustion in inert atmospheres [180]. Using this theory, an inverse-C-shaped curve relating the non-dimensional vaporization rate to the ambient temperature was obtained. Another approach was based on a steady-state theory and a simplified model. This produced an explicit expression for the ignition criterion.

### 1.3.1.2 Thermal Decomposition of UDMH in Shock Tubes

The thermal decomposition rate of UDMH vapor strongly diluted by different gases (Ar, O<sub>2</sub>, N<sub>2</sub>) was studied as a function of pressure (50–250 kPa) and temperature (900–1250 K) in a shock tube, and the UDMH concentration was followed by absorption spectrometry. The rate coefficient of UDMH decomposition at low concentrations was studied behind reflected shock waves [181]. The rate of disappearance of UDMH was measured by UV absorption spectrometry at 220 or 250 nm, depending on the concentration. Products of the reaction  $\text{UDMH} \rightarrow (\text{CH}_3)_2\text{N} + \text{NH}_2$  were extracted out of the shock tube into a time-of-flight mass spectrometer and identified by their  $m/e$  ratios. Initial pressures were 55–255 kPa and peak temperatures in the shocked material were 900–1250 K. In argon, the decomposition of UDMH followed the rate equation

$$k = (2.6 \pm 1.0)10^{12} \exp\left(\frac{-20960 \pm 540}{T}\right) \text{ s}^{-1}$$

where  $T$  is entered in kelvin. The Gulati data [181] agreed quite well with the earlier Just data. In nitrogen, the rate was almost identical, but in oxygen, the rate constant was quite different:

$$k = (5.6 \pm 3.5)10^{11} \exp\left(\frac{-18550 \pm 150}{T}\right) \text{ s}^{-1}$$

The activation energy in oxygen-containing UDMH mixtures is lower than in oxygen-free mixtures. It required more than 12 mol-% oxygen to make a noticeable difference to the half-life time of UDMH. Based on these results, it was concluded that the main mode of UDMH decomposition is the direct elimination of ammonia [182, 183]. The primary stage of UDMH decomposition was first order and its rate constant was only weakly dependent on the nature of the diluent. In the presence of oxygen, the half-life decomposition time of UDMH behind the reflected shock wave was very short ahead of the self-ignition delay. A simple relationship has been established between this delay, the shock parameters, and the concentrations of O<sub>2</sub>/UDMH/Ar mixtures. The global activation energy of the explosive reaction was of the order of 108 kJ/mol. This formula made it possible to estimate the delays in a wide range of composition, pressure, and temperature. A detonation can be initiated by a shock wave in O<sub>2</sub>/UDMH mixtures that are diluted or those that have not been mixed with argon. The detonation initiation conditions, the velocity, and the characteristic size of the detonation cells were determined. Correlations between the induction distance calculated in the detonation wave and the characteristic width of the cells on the sooted plate have been proposed

The ability of decomposing UDMH to affect the ignition delay of oxygen/hydrogen/nitrogen or oxygen/methane/argon mixtures in a shock tube is linked to the species (free radicals) present while UDMH is decomposing or reacting with oxygen. Ignition delays of lean, stoichiometric, and rich mixtures of hydrogen-air over a temperature range of 800–1400 K and a pressure of 2.5 atm were experimentally determined using a shock tube [184]. Small quantities of UDMH vapor were added

to these gas mixtures and their ignition delay periods for the same test temperatures and pressure as mentioned earlier were determined. Ignition was identified by the pressure rise as well as the visible light emission using piezoelectric pressure pick-ups and photomultipliers, respectively. The delay periods of lean, stoichiometric, and rich mixtures of hydrogen and air decreased with the addition of small quantities (less than 1%) of UDMH vapor. When the concentration of UDMH in the mixture exceeded 3%, the delay periods were longer than those obtained when no UDMH was present.

The effect of trace quantities (4 to 15% of methane) of pure UDMH on the ignition delay of oxygen/methane diluted with argon has been studied in relation to reflected shock waves over a temperature range of 1600–2100 K, at a pressure of 3 atm, and composition range of 0.5 to 2.0 ( $\phi$ ) times the stoichiometric ratio [185]. Ignition was identified by pressure rise and by visible light emission using piezoelectric pressure and photomultiplier detection, respectively. The delay periods were found to decrease with increasing quantities of UDMH. The reduction in the delay period was found to be more for  $\phi = 0.5$ , less for  $\phi = 1.0$ , and least for  $\phi = 2.0$ .

### 1.3.1.3 Decomposition of UDMH on the Surface of Single Crystals

Decomposing UDMH has been considered as an alternative to ammonia as a source of active nitrogen for the nitriding of semiconductors containing silicon, gallium, or indium.

The surface reaction of UDMH with Si(100) has been studied using temperature-programmed desorption spectroscopy (TPD), temperature-programmed static secondary ion MS (TPSSIMS), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES) [186]. Adsorption of DMH on Si(100) at 170 K followed by annealing to 1100 K resulted in significant decomposition and went on to form surface carbide and nitride. TPD results showed that the only gas-phase desorption products were hydrogen and dimethylamine. XPS and TPSSIMS results indicated C–N bond cleavage beginning at 400 K, and by 600 K, all the C–N bonds dissociated.

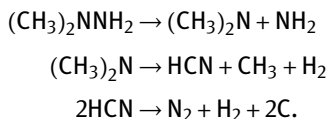
The adsorption and decomposition of UDMH on Si(100) and the low-pressure nitridation of Si(100) using UDMH were investigated using XPS and TPD [187]. UDMH dissociatively adsorbed on Si(100) at 310 K with the cleavage of both N–N and N–H bonds. TPD and XPS showed that DMA desorption resulted in the complete removal of all the carbon on the surface by ~600 K.

The pyrolysis of UDMH, which was used as an alternative for ammonia in the MOVPE growth of nitrides on gallium or indium, was investigated in a horizontal reactor using quadrupole MS [188]. The thermal decomposition rate was investigated in relation to its dependence on reactor pressure, gas-flow rate, and sampling position over the susceptor. The temperature for 50% decomposition was 673–873 K (400–600 °C), which increased with lowering the pressure irrespective of the carrier gases. The pyrolysis rate was dependent on the pressure, and higher pressures induced a more efficient decomposition of UDMH.

### 1.3.2 Catalytic Decomposition of UDMH

The catalytic decomposition of UDMH is possible, however, it is not a practical mono-propellant since the large amount of soot it produces will clog all orifices [189–191]. Catalytic decomposition of UDMH has been evaluated as a method for disposing of unwanted surplus UDMH. Investigation into this area became necessary during demilitarization in the 1990s.

During the decomposition of UDMH on a Shell 405 catalyst in a quartz chamber, the HCN peak (mass 27) rose surprisingly over the entire temperature range studied rather than rising and then falling as previously found with MMH and  $\text{CH}_3\text{ONH}_2$  under the same experimental conditions [179]. The 17/16 ratio became less than one at approximately 673 K (400 °C). The mass 15 signal rose to a peak at a temperature of about 523 K (250 °C), then rapidly declined rather than remaining constant as previously found in the absence of a catalyst. In the catalyzed experiment, the HCN kept rising and was by far the prevalent degradation product in the UDMH catalytic decomposition. The anomalous behavior of the 17:16 ratio and the mass 15 peak could not be explained without further experimental data. It appears that the predominant reactions in the catalytic decomposition of UDMH are



Adsorption of UDMH on a high surface area catalyst carrier like alumina may precede its decomposition [192]. This adsorption may also be used for the removal of UDMH from contaminated air streams or in gas masks.

UDMH decomposition on an  $\text{Ir}/\text{Al}_2\text{O}_3$  catalyst at 373–473 K is a first-order process following two parallel paths; one leading to DMA and ammonia and the other leading to methane and nitrogen [193]. The decomposition of UDMH on a catalyst containing palladium supported on silica resulted in the formation of dimethylamine, ammonia, methane, and nitrogen [194].

The surface chemistry of UDMH decomposition on polycrystalline Pt has been investigated to determine the major reaction pathways followed by this asymmetric molecule [195]. Thermal dissociation plays an important role during and/or after adsorption at 100 K. Temperature-programmed desorption spectra showed the desorption of ammonia (340 K), hydrogen (320 and 430 K), hydrogen cyanide (490 and 610 K), cyanogen (780 K), and nitrogen (855 K). Auger spectra after heating to 1000 K indicated the accumulation of surface carbon. The proposed reaction path is initiated by some N–H bond dissociation at low temperatures (<180 K) to form  $(\text{CH}_3)_2\text{NNH}$  and H. This is followed by N–N bond breaking between 250 and 300 K, forming  $-\text{NH}_x$  ( $x \leq 2$ ) and  $-\text{N}(\text{CH}_3)_2$ . These species are then involved in a series of hydrogenation and dehydrogenation reactions that lead to the observed products.

Despite the dirty exhaust, the thermal decomposition of UDMH has been used in gas generators to drive propellant pumps in Russian rockets. The reaction was initiated with a solid propellant charge.

## 1.4 UDMH Flames in Oxidizing Atmospheres

### 1.4.1 Kinetics of Oxygen/UDMH Reactions

Based on kinetic results obtained using reflected shock waves in UDMH-dioxygen-argon mixtures, a two-stage reaction for UDMH oxidation in the gas phase has been proposed [196–198]. The first rapid reaction is the unimolecular decay of UDMH. The second step, which is slower and starts only after what seems like an inhibitory delay (induction period), is the reaction between the decay products and dioxygen. The ignition delay decreases with increasing  $O_2$  content of the mixture (assuming that total pressure and temperature are the same). Furthermore, the temperature dependence of the apparent activation energy also changes with increasing oxygen concentration. This points toward a very complex reaction mechanism, where the oxygen content affects the rate of more than one reaction step.

The combustion of UDMH vapor at 5.3 kPa (40 mm Hg) in oxygen was more readily initiated, propagated faster, and was sustained over a wider range of mixture ratios than the combustion of UDMH with nitrous oxide [199]. With oxygen, the maximum flame speed was 33.2 m/s at stoichiometric mixtures (20 vol.-% UDMH) and combustion was possible from five to 45% UDMH. The slowest flame speeds were 435 cm/s in mixtures with 5% UDMH and 540 cm/s in mixtures with 45% UDMH in oxygen. With nitrous oxide, the maximum flame speed was only 13.9 m/s and the minimum observed flame speed was 3.2 m/s at 28% UDMH.

### 1.4.2 Shock Tube Studies of Oxygen/UDMH Reactions

Mixtures of dioxygen and UDMH vapor heated rapidly in a shock tube underwent rapid decomposition followed by oxidation only after an ignition delay [183]. This confirms the observations already reported by [196–198] in the previous section. The ignition delays  $\tau$  of UDMH decomposition products were measured behind a reflected shock wave in a 38-mm-I.D. shock tube at 850–1550 K, 31–212 kPa, oxidizer : fuel mol ratios from 1 to 32.3, and argon diluent mol fractions from 0.69 to 0.95. For stoichiometric  $O_2$ /UDMH mixtures (mol ratio 4:1), the critical pressure/temperature conditions under which a self-sustaining detonation wave was initiated were 27.1 kPa/806 K and 45.7 kPa/736 K. The enthalpy of reaction of this reaction that leads to water vapor is  $-1974$  kJ/mol. The apparent activation energy of the reaction was 108 kJ/mol. Detonation velocities of ternary  $O_2$ /UDMH/Ar mixtures were measured both by pressure probes and by measuring the cell size on smoked witness tubes. Measured values



(~2000 m/s without argon dilution) were below predictions from CJ calculations for such mixtures.

At an initial pressure of 190 mm Hg, dioxygen/UDMH mixtures were easily detonated [200]. Dioxygen/UDMH vapor mixtures detonate more readily than dioxygen/methane or dioxygen/hydrogen mixtures.

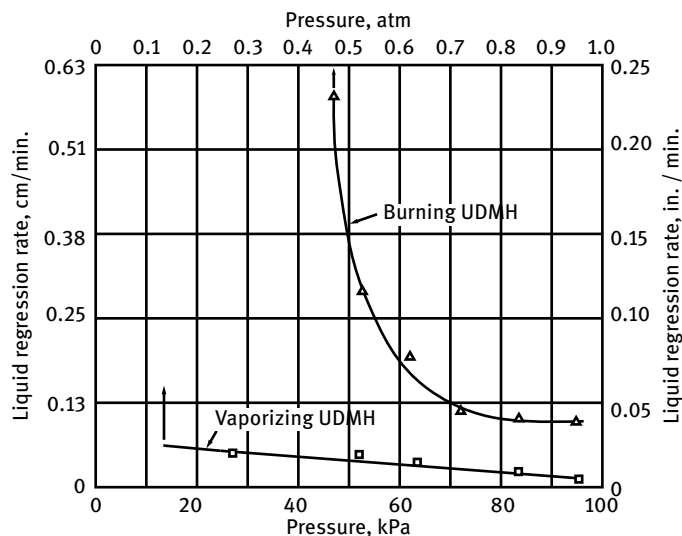
Based on shock tube studies with reflected shock waves at 1600–2100 K, 303 kPa, and  $O_2$ /fuel equivalence ratios from 0.5 to 2.0, the addition of UDMH to  $O_2/H_2$  mixtures near the second limit of explosion decreased the ignition delay [197]. In contrast, the addition of UDMH to methane-oxygen-argon mixtures increased the ignition delay [185]. UDMH and its decomposition products scavenge some of the free radicals necessary for the chain initiation of the methane-oxygen reaction.

The fundamental gas-dynamic characteristics of the detonation, instantaneous combustion (explosion) in constant volume, combustion at constant pressure, and deflagration for hydrazine, MMH, UDMH, SDMH, or trimethylhydrazine in mixtures with oxygen or air that are diluted with argon at varied initial pressure and temperature values were examined [201, 202]. Spray detonation is also potentially relevant to the study of pulse detonation engines (PDEs) and other hypersonic propulsion systems exploiting detonative reactions. The main parameters of these processes were analyzed, both in relation to gaseous propellants and heterogeneous propellants, where the propellant is a highly dispersed, sprayed-aerosol cloud in an oxidant medium. Calculations were performed using the computer code SAFETY. Calculation results agreed with experimental data. For UDMH vapor, detonation wave velocity was predicted to be  $D_0 = 1701$  m/s. For a stoichiometric mixture of UDMH vapor with oxygen, the detonation wave velocity was predicted to be  $D_0 = 2432$  m/s. For a stoichiometric mixture of UDMH vapor with air, the detonation wave velocity was predicted to be  $D_0 = 1860$  m/s. A poorly dispersed spray of liquid UDMH aerosol in oxygen in a stoichiometric proportion to oxygen was predicted to detonate with  $D_0 = 1622$  m/s.

#### 1.4.3 Open-Air UDMH Burning in Open Pans

Open-air burning tests with UDMH in pans of 30 to 150 cm diameter in pools 8 cm deep showed that the linear burning rate of UDMH (despite its higher volatility) is less than that of hexane [200, 203]. This is because the UDMH flame is not a very radiant flame. Figure 64 in chapter “Hydrogen” of *Encyclopedia of Liquid Fuels* shows the pool burning rate of UDMH in comparison to the burning rate of other fuels. The linear burning rate of UDMH in a 1-m pool was 0.3 cm/min. The total thermal output of a UDMH fire was  $9.2 \text{ kJ cm}^{-2} \text{ min}^{-1}$ ,  $2.5 \text{ kJ cm}^{-2} \text{ min}^{-1}$  of which was radiated heat.

In 1-in. diameter burning pools of UDMH at atmospheric pressure, combustion could not be sustained if the oxygen concentrations of the surrounding air-nitrogen atmospheres were less than 14 volume percent [204]. Venting a liquid pool fire to a low-pressure environment tends to increase the liquid regression rate and the flame size. The liquid regression rate of a burning pool of liquid UDMH showed a very pro-



**Figure 15:** Liquid surface regression rate of UDMH burning in air in a 1-in. diameter tray as a function of surrounding pressure. (Reproduced and modified from [204].)

nounced increase in the liquid regression rate with decreasing surrounding pressure, as demonstrated in Figure 15.

It is relatively easy to extinguish Ae-50 fires with water [205]. In similar burning tests with UDMH, DETA, and fuel mixtures of the two mixed amine fuels (MAF-1 = 41% UDMH, 50% DETA, 9% acetonitrile, MAF-3 = 20% UDMH, 80% DETA), burning rates, radiation, and flame temperatures of open pan fires were measured in comparison to gasoline and methanol [206]. For blends with constituents of widely disparate boiling points, the initial burning rate was that of the more volatile component. Toward the end of a MAF burning test in a 122-cm tray, the burning rate approached that of DETA. The maximum temperature of a UDMH flame at the flame front was about 1370 K. Infrared measurements showed that UDMH vapor absorbs a higher percentage of its flame radiation than methanol, benzene, or hydrogen (of their respective flame radiations). This may contribute to energy transfer at the phase and flame boundary. The flash-over rates of a flame spreading over a pool of UDMH, MAF-1, or MAF-3 were about the same as that of gasoline. The burning rate of open UDMH fires was 0.31 cm/min compared to 0.8, 0.7, 0.6, and 0.13 for butane, hexane, benzene, and methanol, respectively [200]. Some of the UDMH burning tests were conducted in the open (quiescent) air in pans of up to 2.4 m (8 ft.) in diameter [207].

#### 1.4.4 Droplet Burning of UDMH in Oxidizing Atmospheres

The objective of an experimental study of single-droplet burning of UDMH in relatively quiescent atmospheres of both air and 100% oxygen in comparison to droplet

burning of hydrazine and RP-1 was to obtain information that would contribute to the establishment of burning rates, evaporation constants, and droplet lifetimes. This would thus provide an index for thrust chamber performance where more complex spray burning occurs [208]. The experimental method involved fuel drops suspended on a thin quartz fiber, with the variation of diameter with time recorded photographically. Data from the experimental study were plotted in terms of droplet diameter, and the droplet diameter squared versus time. Evaporation constants were calculated for each fuel and oxygen combination from these plots. A general conclusion drawn from this study was that a thrust chamber utilizing UDMH or  $\text{N}_2\text{H}_4$  with LOX could probably be constructed with smaller  $L^*$  and that it would be lighter in weight than LOX/RP-1 chambers (provided that all other conditions of atomization, mixing, etc., were the same).

The burning of UDMH droplets in oxidizing atmospheres (other than  $\text{NO}_2$ ) was studied to separate the monopropellant decomposition and oxidizer-supported flames of UDMH combustion, and to compare this to hydrazine and MMH [209–211]. The flat-flame burner could be fed with lean fuel mixtures, generating oxygen-rich hot gases in which secondary combustion of the droplet vapor decomposition products would take place. The conditions included 1660–2530 K at ambient pressure. The tests used single droplets suspended from a 100- $\mu\text{m}$ -diameter quartz filament and porous Alundum spheres. Droplet diameter could thus be varied from 0.11 to 1.91 cm. The fuel droplets were burned in the hot gaseous combustion products of a flat-flame burner to simulate rocket engine operating conditions. The flat-flame burner could be fed with lean fuel mixtures, generating oxygen-rich hot gases in which secondary combustion of the droplet vapor decomposition products would take place. The conditions included 1660–2530 K at ambient pressure. Decomposition flames were not luminous at all, but oxidation flames of all three fuels showed two separate distinct zones of luminosity

#### 1.4.5 Burning of Gelled UDMH

A model was developed for the burning of gelled UDMH droplets [212].

#### 1.4.6 Photolysis of UDMH

Photolysis by sunlight is an important mechanism (besides autoxidation and reaction with atmospheric ozone) for UDMH decay that has been accidentally released into the atmosphere [213]. The UV absorption spectrum of dimethylhydrazine has a continuum extending from 2800 Å to beyond 2000 Å. Despite the absence of structure, the continuum is probably experimental and indicates predissociation. The photolysis, using various light sources at several pressures and wavelengths, has been studied and the overall quantum yield was 0.3. The principal initial rupture of the molecule involves the scission of a hydrogen atom. Analytically, three molecules of the hydrazine give

one molecule each of  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ , and  $(\text{CH}_3\text{N}=\text{CH}_2)_2$ . The low quantum yield was attributed to an additional reaction of dihydrogen to the free radical produced in the initial split.

The environmental fate of UDMH and the other hydrazines is determined by photolysis and autoxidation. Whereas kinetic and photolysis experiments are usually conducted with very low, and hence safe, partial pressures of UDMH, another way to study photolysis of UDMH is to operate at the brink of explosive vapor concentrations. Only minimal decomposition occurs in the vapor during the pre-irradiation period. However, the energy added by a flash of exactly-timed duration is sufficient to make the vapor explode. This mode of hydrazine, MMH, and UDMH decomposition was thoroughly investigated [214, 215]. The results were also compared to those obtained with ozone, which decomposes more readily than any of the hydrazines. For identical initial UV flash conditions, the half-life of UDMH was the shortest at  $48\mu\text{s}$  versus  $95\mu\text{s}$  for hydrazine and  $184\mu\text{s}$  for MMH.

#### 1.4.7 Radiolysis of UDMH

UDMH samples (100 mL UDMH) were irradiated with 8500000 rads of gamma rays. They generated 199 mL of radiolytic off-gas (measured at  $298\text{ K} = 25^\circ\text{C}$  and  $101\text{ kPa} = 1\text{ atm}$ ) [216, 217]. DETA, which is a component of the fuel mixture called Hydyne (consisting of 60 mass-% of UDMH and 40 mass-% of DETA), generated 101.2 mL of radiolytic off-gas. Assuming additive behavior, it was predicted that the off-gas of Hydyne would be 164.1 mL. When the samples contained 5 vol.-% of the free radical scavenger methyl methacrylate, the off-gas volumes were reduced by 18.2 and 11.0%, respectively. This prediction was confirmed in later radiolysis tests with Hydyne.

UDMH and (separately) hydrazine were radiolyzed at room temperature, exposing 1-g samples of liquid or 2-L samples of vapor to X-rays from an X-ray source operating with a tungsten target at 300 kV at intensities of 100 to 1000 roentgens per minute and total doses of  $4.1$  to  $2.3 \times 10^6$  rads [218]. The extent of decomposition was independent of dose rate and depended only on total dose absorbed. The decomposition products of UDMH were nitrogen, hydrogen, ammonia, methylamine, dimethylamine, hydrazine, and several unidentified products. Some of the products were low-volatility liquids that changed colors from blue to red to brown as they thawed in a cold trap. The G values (number of molecules decomposed per 100 eV of absorbed energy) for UDMH liquid were of the order of  $10^2$  and for UDMH vapor they were of the order of  $10^6$ , thus indicating a radical chain mechanism for decomposition. In the case of UDMH, decomposition reactions continued even after the radiation was turned off.

#### 1.4.8 Electron Impact Dissociation of UDMH

Electron impact dissociative ionization of UDMH and other methylhydrazines takes place in the inlet to most mass spectrometers. Electron impact dissociation also pro-

vides information about the bond strengths by looking at the fragments formed under those conditions. Smaller and smaller fragments are formed when the ionization chamber electrostatic potential is increased. Ionized fragments become visible in the mass spectrometer but uncharged fragments do not. Some of the work on electron impact fragmentation of methylhydrazines was already discussed in the section on MMH and, therefore, does not have to be repeated here.

The dissociation of methylated hydrazine ions was observed undergoing extensive fragmentation and rearrangement, leading to many fragments that had the same nominal mass but differed in chemical composition by an N versus  $\text{CH}_2$  moiety. Improved high-resolution quadrupole detection (0.005 amu) allowed one to distinguish ion fragments of the same nominal mass for MMH and UDMH [219]. The ratios of these close-lying fragment masses were measured for different electron impact energies and explained in terms of thermochemical thresholds and fragmentation mechanisms.

The 1,1-dimethylhydrazine ion  $(\text{CH}_3)_2\text{NNH}_2^+$  has two low-energy dissociation channels, the loss of a hydrogen atom to form the fragment ion  $m/e$  59,  $(\text{CH}_3)(\text{CH}_2)\text{NNH}_2^+$ , and the loss of a methyl radical to form the fragment ion  $m/e$  45, which is the methylhydrazyl cation,  $\text{CH}_3\text{NNH}_2^+$ . The dissociation of the 1,1-dimethylhydrazine ion has been investigated using threshold photoelectron-photoion coincidence spectroscopy in the photon energy range of 8.25–31 eV and using tandem MS [220]. Theoretical breakdown curves have been obtained from a variational transition state theory modeling of the two reaction channels and compared to those obtained from experiments. The 0 K enthalpies of formation for the two fragment ions  $m/e$  45 and  $m/e$  59 have been calculated from the 0 K activation energies obtained from the fitting procedure  $\Delta H_f^0[\text{CH}_3\text{NNH}_2^+] = 906 \pm 6 \text{ kJ/mol}$  and  $\Delta H_f^0[(\text{CH}_3)(\text{CH}_2)\text{NNH}_2^+] = 822 \pm 7 \text{ kJ/mol}$ .

#### 1.4.9 UDMH Decomposition by Neutron Beams

Sudden bursts of high-intensity neutron radiation may occur under atomic war conflict conditions, leading to rapid heating of fuels with the most efficient neutron absorption cross-section (usually hydrogen-rich fuels such as hydrazines or hydrocarbons). An analytical treatment of a cylindrical aluminum tank containing UDMH with varying ullage ratios showed that, for small ullages, the pressure rise is mostly due to the thermal expansion of the liquid, while for large ullages the increase in pressure is due to liquid evaporation and phase change [221]. Both the metallic casing and the liquid contents of a partially filled tank are subjected to heating that is uniform in time and space, although the liquid heats up at a different rate. Thermal expansion of the container walls is negligible in increasing the ullage volume. The heating due to absorption of radiation in the gas phase was neglected since its density is small in comparison to the density of the liquid. The increase in pressure is caused by two effects: **(1)** the differential expansion of the liquid and casing as the temperature increases and **(2)** the vaporization of liquid to maintain saturation vapor pressure with

an increase in temperature. Pressure increase was assumed to occur only as the result of thermal heating. Radiolysis of fuel in either the vapor or liquid phase was neglected, as was the solubility of pressurant gas in (or release of pressurant from) the propellant. Heating rates of the aluminum containers in an intense neutron beam were predicted to be so fast that the critical point of UDMH and the melting point of aluminum was reached within less than 15 s. UDMH was chosen as an example fluid but the effects of neutron beams on other hydrazine fuels would probably be similar.

#### 1.4.10 Reactions of UDMH

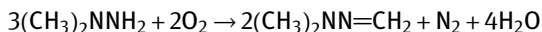
##### 1.4.10.1 Reactions of UDMH with Inorganic Compounds

The main interest in reactions with UDMH are those that might lead to its degradation as vapor in the atmosphere and reactions for the controlled destruction and decontamination of UDMH in wastewater from UDMH production and rocket tests sites. The chemical aspects of UDMH reactions are discussed here, and the application aspects will be discussed in later sections.

##### 1.4.10.2 Autoxidation of UDMH in the Air

For the study of the oxidation of liquid or dissolved UDMH by gaseous oxygen, the UDMH samples were first carefully freed from all contaminants that are commonly found in aged UDMH. All contaminants except FDMH could be removed by repeated refluxing and distilling over solid KOH. When reacting a fixed amount of oxygen in a closed vessel with UDMH in diethyl ether at 293 K (with some toluene added as an internal standard), the major products identified by GC were FDMH, methane, and nitrogen, and a trace of tetramethyl-2-tetrazene [222]. The solution did not change color at 293 K after 200 h but did do so after 24 h when kept at 298 or 303 K. In these solutions, tetramethyl-2-tetrazene, water, and *N*-nitroso-dimethylamine (NDMA, dimethylnitrosamine) could also be detected. Proton NMR of the residual liquid after evaporating the ether also revealed *sym*-hexahydro-1,4-dimethyltetrazine, the dimer of FDMH. Repeating the tests in cyclohexane instead of diethyl ether as a solvent led to similar results.

UDMH autoxidation proceeds faster in the light and metal containers (without light). Based on the results of early investigators, the autoxidation reaction was first-order in UDMH and zero-order in oxygen and was assumed to lead to formaldehyde-*N,N*-dimethylhydrazone, nitrogen, and water as the major products [223].



In another study of the gas-phase autoxidation of 1,1-dimethylhydrazine, ammonia, dimethylamine, NDMA, diazomethane, nitrous oxide, methane, carbon dioxide, and formaldehyde were detected in minor amounts [224]. The nitrous oxide yield increased if ammonia was added to the reacting mixture. Tetramethyl-2-tetrazene was not observed as a product of gas-phase oxidation of UDMH. The reaction was inhibited by

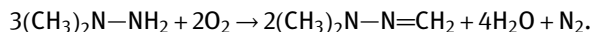
1,3-butadiene but accelerated by UV illumination. 1,1-Dimethylhydrazyl-2-hydroperoxide has been claimed as an intermediate but little proof was offered to support this hypothesis. Previous workers [225, 226] had claimed that vapor-phase oxidation of UDMH gave methyl azide but this has not been confirmed. It was later found that the IR absorption (a doublet at 4.72 and 4.78  $\mu\text{m}$ ) is due to diazomethane as an intermediate and short-lived product [224]. SDMH and trimethylhydrazine undergo rapid and complete autoxidation in the vapor phase at 298 K but tetramethylhydrazine does not react. Reaction products from SDMH autoxidation are azomethane and water. Trimethylhydrazine oxidizes to give formaldehyde *N,N*-dimethylhydrazone and water.

Preliminary investigative experiments on the UDMH-air reaction in a 20-L carboy or a 10-cm cell while monitoring the UDMH decay by recording the absorption at 908  $\text{cm}^{-1}$  revealed that the rate of oxidation is dependent on the surface : volume ratio [227]. Similar measurements had used a 44-cm short path cell and a 200-m long path cell (also with a 50-50 mixture of hydrazine and UDMH representing the Aerozine-50 propellant once used in the Titan launch vehicle) [228]. In the mixture, the hydrazines decayed (oxidized) more than ten times faster than the individual constituents by themselves. It was noted that UDMH by itself oxidizes ten times more slowly than either hydrazine or MMH under the same conditions. The data were too scattered to allow a statement on the oxidation kinetics. Additional Fourier transform infrared spectroscopy (FTIR) studies in a 60-L cell consisting of a 6-in. by 10-ft section of Pyrex pipe with an effective pathlength of 200 m revealed that the autoxidation of 6 ppm UDMH in 100% oxygen leads to FDMH as the only identifiable product [229–231].

It was difficult to study the autoxidation of hydrazines with air in Teflon-lined chambers because diffusion of UDMH vapors and the intrusion of ambient air oxygen, both through the Teflon foil, interfered with the autoxidation measurements [232]. The reaction was very slow in comparison to the other hydrazines. The half-life time of UDMH under these conditions was approximately 83.5 h.

It was shown that a 392-Pa (2.95-mm-Hg) low-pressure UDMH sample in an IR gas sample cell started to undergo pronounced changes within 49 h after the admission of air (94 kPa = 709 mm Hg) [233]. The weak combination band at 3160  $\text{cm}^{-1}$  completely disappeared and a new band formed at 3060  $\text{cm}^{-1}$ . The  $\text{CH}_3$  rocking band at 1032  $\text{cm}^{-1}$  decreased substantially and a strong new peak developed near 1010  $\text{cm}^{-1}$ . The strong  $\text{NH}_2$  rocking band at 908  $\text{cm}^{-1}$  nearly completely disappeared and a new peak formed near 885  $\text{cm}^{-1}$ . Further, the UDMH skeletal stretching band at 808  $\text{cm}^{-1}$  nearly completely disappeared and a new weak peak developed near 708  $\text{cm}^{-1}$ . Similar changes were observed in a second sample with an initial UDMH pressure of 4.2 kPa (31.9 mm Hg). The assignment of the new peaks to reaction products was not yet complete. Similarly, the UV spectrum of UDMH/dry air was scanned repeatedly for up to 73 h. A new absorption band formed at 235 nm while simultaneously UDMH absorption at 195 nm decreased. The peak at 235 nm was not NDMA (which was the main concern at the outset of this study), since NDMA absorbs at 227 nm. Instead, the spectrum of FDMH, when mixed with a fresh UDMH sample, closely resembled the spectrum of the

oxidized sample. A possible reaction would be



Kinetic analysis of the rate of UDMH disappearance indicated a first-order reaction with regard to UDMH. The half-life time under these conditions was 16 h. It has been proposed to study the progress of the reaction by MS instead of IR or UV absorption. MS would allow one to monitor the concentration of several species at the same time, even those which have no IR spectrum. Instead of constant-volume isothermal stirred reactors, shock tubes give information on kinetic rates by heating the reactants such as UDMH and oxygen very suddenly [196]. The kinetics of the oxygen/UDMH reaction were studied behind reflected shocks in a shock tube [198].

A simpler mechanism, although highly speculative and not yet supported by experimental data of its own, has been proposed [234]. This mechanism tried to account for the observed stoichiometry and changes in the order of reaction with time. It was assumed that the half-life time of UDMH in the air (or oxygen) is inversely proportional to the square root of its initial pressure. It was proposed that the initial step of the reaction is the formation (in the homogeneous gas phase) of the hydroperoxide  $(\text{CH}_3)_2\text{N}-\text{NH}-\text{OOH}$  and a free radical formed by abstracting a proton from the  $-\text{OOH}$  group. This intermediate could then bring about autocatalysis in the gas phase by chain branching. The fate of the hydroperoxide intermediate remains speculative but  $-\text{O}-\text{O}-$  splitting is likely and leads to  $\text{HO}^\bullet$  radicals forming. Similar peroxides (peracids) are formed in the autoxidation of aldehydes. Data for hydrazine and MMH autoxidation by this mechanism are not as reliable as those for UDMH. This may be caused by a greater sensitivity to surface effects in these two reactions. Difficulties in interpreting experimental results on the autoxidation of hydrazine or MMH may have been caused by the failure to recognize autocatalytic contribution by intermediates. The autoxidation of trimethylhydrazine leads to FDMH [235].

Ozone and  $\text{NO}_x$  are common atmospheric constituents and facilitate the oxidation of UDMH to nitrosamines [236]. Unoxidized UDMH was not mutagenic. However, oxidized samples suspected of containing NDMA were mutagenic [237]. In the case of *N*-aminopiperidine, both the unoxidized and the oxidized samples were mutagenic.

Earlier investigators had already hinted at the possibility of hydroperoxide intermediates in the autoxidation of UDMH. The toxicity of UDMH to bacteria may be caused by peroxide intermediates. Seven different recombinant bioluminescent strains of *escherichia coli* were used to describe the mechanism of toxicity of UDMH on bacteria, as well as to determine whether bacteria can sensitively detect the presence of this compound [238]. It was suggested that the action of UDMH on bacterial cells is determined by hydrogen peroxide, which may be formed in response to the reduction of the air oxygen level.

The autoxidation of UDMH in air is accelerated by illumination with light. The oxidation behavior of UDMH vapor was measured under different light conditions [239]. The results of GC-MS analysis showed that UDMH air oxidation produced a range



of products, including dimethylamine, partial hydrazone, *N*-nitroso dimethylamine, DMA acetonitrile, and acetaldehyde dimethyl hydrazone. With intense light, the rate of oxidation of UDMH accelerated. With the enhancement of light, oxidation products tetramethyl tetrazene, tetramethyl hydrazine, nitro dimethylamine, and dimethyl formamide were detected. In very bright light conditions, NDMA decreased significantly.

UDMH-containing wastes that were stored in contact with atmospheric oxygen contain a complicated mixture of UDMH degradation products. HPLC, high-resolution MS (HRMS), and NMR were used for the identification of highly polar and potentially toxic UDMH transformation products in this mixture [240]. Two series of triazole isomers with high ionization cross-section in electrospray ionization were isolated by repeated preparative HPLC. The structures of the isomers were established by tandem HRMS and NMR. The cytotoxicity of the isolated compounds is similar to that of UDMH or even higher.

#### 1.4.10.3 Catalytic Oxidation of UDMH

The oxidation of unwanted UDMH vapors in contaminated air can be accelerated by exposing the gas/vapor mixture to catalysts, preferably at elevated temperatures. Care must be taken to prevent flashbacks of the combustion into the feed system. Perovskites ( $\text{Ca}_{0.7}\text{Sr}_{0.3}\text{FeO}_{2.5}$  and  $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{2.5}$ ) and supported spinels (20%  $\text{Cu}_x\text{Mg}_{1-x}\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$ ) can be used as catalysts for this purpose at 423–973 K (150–700 °C) [241–244]. The catalyst  $\text{Cu}_x\text{Mg}_{1-x}\text{Cr}_2\text{O}_4/\gamma\text{-Al}_2\text{O}_3$  was found to be optimal regarding high yields of  $\text{CO}_2$  and low yields of  $\text{NO}_x$ .

The temperature dependence of the oxidation of UDMH on a Pt-containing catalyst was determined and the main intermediate and final reaction products were identified [245]. Platinum acted in the process as a multi-functional catalyst participating in dehydrogenation, hydrogenolysis, and oxidation. A new method was suggested for detecting UDMH in the air. This was based on the catalytic conversion of UDMH and the detection of the nitrogen dioxide formed with semiconductor gas sensors. The method was successfully used for detecting unsymmetrical dimethylhydrazine in the air at concentrations in the range of 0.1–10 mg/m<sup>3</sup>.

#### 1.4.10.4 Autoxidation of UDMH in the Anhydrous Liquid State

Oxygen was bubbled through pure UDMH and the vapors condensed in a cold trap at 195 K (–78 °C) [224]. Diazomethane was observed as an intermediate during UDMH autoxidation by sequential IR spectra (mainly during the initial phase of the process). If the autoxidation of UDMH was carried out in the presence of barium oxide, which would absorb water and presumably hydrogen peroxide also if any was formed, the diazomethane intermediate lifetime would be extended. So, it is possible that the diazomethane loss occurred by reaction with water that had formed as an autoxidation product, even in UDMH that initially was anhydrous. When the reaction was complete, the IR spectrum of the product closely resembled that of pure FDMH. The dark brown liquid left behind in the reaction vessel was mostly FDMH and NDMA.

#### 1.4.10.5 Autoxidation of UDMH in Solution

The autoxidation of UDMH by dissolved air in an aqueous solution is an important process if one has to determine the longevity of UDMH spills in clean surface waters without soil contact or suspended sediments. This information is needed for the design of wastewater treatment plants for wastewater drained from rocket test sites.

The rate of oxidation of UDMH (hydrazines spilled into surface water) was measured by pouring a measured amount of UDMH into 2 L of distilled air-saturated water in a glass flask and measuring pH and dissolved oxygen (D.O.) as a function of time [246]. The starting concentration of D.O. was typically above 7.5 ppm. UDMH at concentrations from 200 to 800 mg/L was studied to calculate the rate of oxidation. In some experiments, controlled amounts (0.125, 0.25, 0.5, 1.0 mg/L) of copper  $\text{Cu}^{2+}$  ion were added to test its effectiveness as a catalyst. In the sample containing the highest  $\text{Cu}^{2+}$  addition, D.O. dropped from 7 to 0.3 ppm in less than one minute. No effort was made to exclude ambient air during the experiment. However, since the experiments were short, reabsorption of oxygen from the air could be neglected. Besides, in free nature, additional oxygen from the air would also be available to aid the degradation of hydrazines in the water. The data detailing the rate of disappearance of oxygen and hydrazine were curve-fitted to a kinetic model with empirical constants of the type

$$\frac{d(DO)}{dt} = -\frac{k}{V}(DO)^n$$

where  $DO$  is D.O.,  $k/V$  is an average rate constant, and  $n$  is the average order of the reaction. Results for hydrazine, MMH, and UDMH are shown in Table 12.

**Table 12:** Autoxidation of hydrazines (in the absence of copper ions).

| Propellant      | Average order $n$ | Average rate constant, L/min |
|-----------------|-------------------|------------------------------|
| UDMH            | 0.540             | 1.6895                       |
| For comparison: |                   |                              |
| Hydrazine       | 0.985             | 4.0245                       |
| MMH             | 1.025             | 3.3296                       |

Data source: [246].

In a study of the rate of oxidation of UDMH as affected by pH and  $\text{Cu}^{2+}$  concentration, the authors concluded that for most real-life spill surface water conditions, UDMH would not persist for longer than a day or two in the absence of highly acidic conditions [247]. The kinetics of oxidation of MMH by D.O. in water has been measured at various acidities as a function of catalyst (cupric ion) concentration. In dilute solutions, the oxidation occurs through a cupric ion catalyzed process as well as by an uncatalyzed step.

Glassware used for an environmental degradation study of hydrazines in seawater, pond water, and pure water was carefully washed with 50% nitric acid before use. This rigorous cleaning was necessary to achieve reproducible results [248, 249]. Before the environmental degradation tests in soil were started, it was necessary to know the rate of degradation in surface waters without the effect of soil. In the absence of soil or catalysts, aqueous half-lives were 6–13 d for UDMH. Additional half-life data are summarized in Table 13.

**Table 13:** Half-life time of UDMH in natural waters.

| Fuel            | Initial concentration, mmol/L | Pond water, d  | Seawater, d    |
|-----------------|-------------------------------|----------------|----------------|
| UDMH            | 13.1                          | $22.2 \pm 6.9$ | $12.6 \pm 2.8$ |
| UDMH            | 6.5                           | $16.3 \pm 6.9$ | $12.6 \pm 1.1$ |
| UDMH            | 0.9                           | $7.3 \pm 1.0$  | —              |
| For comparison: |                               |                |                |
| MMH             | 19.0                          | $13.1 \pm 1.1$ | $13.1 \pm 2.2$ |
| MMH             | 9.5                           | $18.0 \pm 2.3$ | $24.1 \pm 8.8$ |
| Hydrazine       | 1.8                           | $8.3 \pm 0.6$  | —              |

Data source: [248,249].

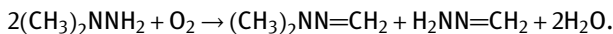
For a wastewater aeration basin with a common hydraulic detention time of 9 h, the efficiency of organics removal was seriously hampered when the UDMH concentration exceeded 5 or 8 mg/L, respectively [250]. As far as organics removal is concerned, the “no effect level” would be approximately 2 mg UDMH/L. However, even at this low level, nitrogen speciation (ammonia conversion to nitrate) was severely impeded. Inhibition of nitrification occurred at concentrations above 0.5 mg MMH/L and above 1 mg/L for the other fuels. Some UDMH was still detectable under the same conditions and the efficiency of UDMH removal was only 96%.

The autoxidation of UDMH by D.O. in an aqueous solution (homogeneous single phase, no gas bubbling) led to FDMH and formaldehyde hydrazone, nitrogen, and water as its major products. When liquid UDMH without a solvent was reacted with bubbling oxygen, the following reaction products were found just as in the previous solvent studies: nitrogen, methane, FDMH, dimethyl nitrosamine, and tetramethyl-2-tetrazene [224]. Minor products were ammonia, dimethylamine, dimethylnitrosamine, diazomethane, nitrous oxide, methane, carbon dioxide, and formaldehyde. This reaction is of the first-order in UDMH and of zero-order in oxygen. It is catalyzed by metals and metal salts, inhibited by added 1,3-butadiene, and accelerated by UV light. A free-radical chain mechanism was postulated as the rate-determining reaction sequence. The 1,1-dimethylhydrazyl-2-hydroperoxide so formed was presumed to give the products FDMH, hydrazine, and hydrogen peroxide via a rapid sequence of wall reactions. Nitrogen and most minor products were

assumed to probably result from further wall reactions of hydrogen peroxide with UDMH, FDMH, and hydrazine.

The oxidation of UDMH was investigated using atmospheric oxygen in the air and dissolved hydrogen peroxide [251]. The reactions were carried out in the presence and absence of copper catalysis and at varying pH. Reactions were also carried out in the presence of hydrazine (a constituent) and with the UDMH of the rocket fuel Aerozine-50. In the presence of copper, UDMH was degraded by air passing through the solution. The efficiency of degradation increased as the pH increased but the carcinogen NDMA was formed at neutral and alkaline pH. Oxidation did not take place in the absence of copper. The production of NDMA occurred even at copper concentrations of  $< 1$  ppm. Oxidation of UDMH with hydrogen peroxide also gave rise to NDMA. When copper was absent, degradation of UDMH did not occur at acid pH. However, when copper was present, some degradation occurred at all pH levels investigated. The unwanted production of NDMA occurred mostly at neutral and alkaline pH. In general, higher concentrations of hydrogen peroxide and copper favored the production of NDMA. Dimethylamine, methanol, FDMH, formaldehyde hydrazone, and tetramethyltetrazene were also detected. The last three compounds were tested and found to be mutagenic.

The role of copper ions as a catalyst for UDMH oxidation can be explained by the oxidation of UDMH by copper(II) salts, thus forming dimethyldiazene as an intermediate [252]. The autoxidation reaction of UDMH proceeds via dimethyldiazene  $(\text{CH}_3)_2\text{N}^+=\text{N}^-$  as an intermediate [253]:



There were no gaseous reaction products. The reaction is first order with respect to each of the two reactants and was catalyzed by an alkali. The reaction constant is a function of the  $\text{OH}^-$  ion activity. At a pH of 12.89 and in the range of 288 to 308 K, the dependence of the reaction rate on the temperature would follow the Arrhenius equation

$$k = A \exp\left(\frac{-E}{RT}\right)$$

where  $A = 4.42 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$  and  $E = 58.9 \text{ kcal/mol}$ .

The toxicity of UDMH to bacteria may be caused by peroxide intermediates [238]. The oxidation of aqueous solutions of UDMH in the presence of Cu-, Fe-, Co-, and Mn-containing catalysts of the hydroxide type supported on oxide carriers are potentially useful for the detoxification of UDMH rinse waters [254]. The Cu-containing samples proved to be the most active. The dependence of the reaction rate on the pH value, temperature, and the ratio of the catalyst sample to the solution volume was investigated in trying to achieve optimum conversion. The main products of the reaction were hydrazones and formazane. The reaction was shown to occur via different mechanisms in neutral or alkaline solutions.

Another study on the autoxidation of UDMH solutions and degradation of UDMH in the environment attempted to identify the reaction mechanism with and without the addition of a copper(II) sulfate catalyst which was dependent on pH, UDMH, or  $\text{Cu}^{2+}$  concentrations [255]. UV scanning spectroscopy demonstrated the familiar spectrum of tetramethyltetrazene with maxima at 326 and 236 nm in a pH 9.12 buffer. Acidification shifted the first maximum reversibly to 356 nm. Next, oxidation was studied by proton magnetic resonance (PMR) in  $\text{D}_2\text{O}$  as a solvent. Again, the spectrum was different for the basic and acidified condition. However, due to a lack of pure reference compounds, neither spectrum could be assigned. Most likely, the NMR spectra were those of multi-component mixtures, including unreacted UDMH. The bromination of UDMH was studied as a possible route to singly, better-defined oxidation products but with little success. The initial oxidation product of UDMH appears to be the short-lived 1,1-dimethyldiazene, which may dimerize to tetramethyltetrazene or become oxidized further. When measuring the concentration of  $\text{O}_2$  with a D.O. meter as a function of time, pseudo-first-order reaction rate constants were obtained. The data indicated that the free-base form of UDMH undergoes a reaction and that copper catalysis is not significant at concentrations less than  $10^{-6} M$  in UDMH.

Continuing the study of autoxidation kinetics of UDMH solutions, aeration of  $1 \times 10^{-4} M$  UDMH solutions in the presence of  $\text{CuSO}_4$  led to formaldehyde and 1,5,5-trimethylformazan. Aeration of more concentrated solutions ( $3\text{--}5 \times 10^{-3} M$ ) led to the formation of tetramethyltetrazene [247]. In dilute solutions, the oxidation occurred through a cupric ion catalyzed process as well as by an uncatalyzed step. The extent of the formation of NDMA depends upon the initial UDMH concentration. In dilute solutions, NDMA was not formed, but in more concentrated solutions, NDMA formation increased with increasing UDMH content; it reached a maximum at 60–80% UDMH (by volume) in water and then decreased. The NDMA yield appeared to approximately parallel the viscosity of the medium, and it was speculated that the factors which control viscosity may also be responsible for governing NDMA formation.

NDMA was not found in the dilute solution experiments within the accuracy of the detection method ( $10^{-5} M$ ). This contradicts findings reported earlier by other investigators [224]. However, when more concentrated UDMH solutions (10–90 vol.-%) were allowed to stand in contact with air, NDMA was formed to a significant extent, especially in the range of 60 to 80 vol.-% UDMH in water, and reached a maximum within 5 d. Peroxides may form in aged UDMH solutions as intermediates. It was recommended to keep UDMH dry to minimize the rate of NDMA formation during storage.

The influences of concentration of oxygen and contact with metallic materials on the rate of oxidation of UDMH during autoxidation processes were studied using GC and MS [256]. Stainless steel and aluminum can accelerate the autoxidation of UDMH and increase the concentration of DMA as an intermediate autoxidation product. Increasing the concentration of oxygen can increase the rate of oxidation of UDMH and the concentration of DMA immediately.

To explore the degradation mechanism of UDMH under conditions of actual storage, liquid-phase reaction products of the gas-liquid two-phase reaction of UDMH with  $O_2$  and air, and the change in the content of main gaseous products with time, under four sets of conditions of oxygen, oxygen/water, air, and air/water, were determined by GC-MS, and their reaction mechanisms were analyzed [257]. The results showed that there are 19 different autoxidation products of UDMH, of which NDMA, FDMH, dimethylamine, water, and *N,N*-dimethylformamide were the main products. Moreover, there were four newly-detected products: *N,N,N',N'*-tetramethylmethylenediamine, 4-methyl urazole, tris(dimethylamino)methane, and *N,N*-dimethylurea. The oxygen and oxidation of UDMH in the gas phase greatly enhances the generation of NDMA. Thirty-per-cent of the degraded UDMH was converted to NDMA and the mass fraction of NDMA in the gas phase was up to 1.3%, whereas the generation rate of NDMA in the reaction with air was about 5%.

In a UDMH autoxidation experiment, the air-flow from an air compressor was first passed through an air filter. This was then successively passed through a concentrated  $H_2SO_4$  gas-washing flask and a solid NaOH neutralizer to remove  $CO_2$ , then passed through  $CaCl_2$  drying agent. Finally, it was bubbled into the liquid UDMH sample [258]. The sample size was 700 mL and the air-flow rate was 15–25 mL/min. The exhaust air was bubbled into diluted  $KMnO_4$  solution to oxidize UDMH vapor completely before releasing the air to the atmosphere. UDMH samples, with and without a metal oxide catalyst, were oxidized by dry air for 10 h then oxidized in static air for 14 h. The samples turned yellow during the test and were then analyzed by GC/MS.

UDMH is a reducing agent and hydrogen peroxide is usually considered an oxidizing agent. Unusually, that hydrogen peroxide was detected as an intermediate and by-product of UDMH autoxidation in aqueous solutions at very small UDMH concentrations [259].

#### 1.4.10.6 Reactions of UDMH with Hydrogen Peroxide in Solution

Hydrogen peroxide is being used for wastewater treatment in many industrial applications. Therefore, it would be logical to test it as a means of destroying unwanted UDMH in solution as well.

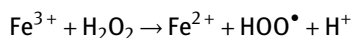
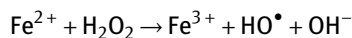
It is unlikely that anyone would want to react anhydrous UDMH with high-concentration (>70%) High Test Hydrogen Peroxide (HTP), because it is, after all, commonly known that this would lead to a hypergolic reaction and this belongs in a future *Encyclopedia of Hypergolic Bipropellant Combinations*. Therefore, if one only wants to safely destroy surplus UDMH in solution, sufficient dilution of both liquids with water is required to slow down the reaction.

It has been suggested that  $H_2O_2$  may actually be an intermediate product in the autoxidation of UDMH in solution so this is another reason to look at reactions between UDMH and  $H_2O_2$ . The use of high-resolution MS for the study of the reaction products of UDMH oxidation with hydrogen peroxide in an aqueous solution enabled the detection of hundreds of nitrogen-containing products of the CHN and CHNO types

that are formed via radical processes [260]. The vast majority of the compounds had not been previously considered as possible products of the transformation of rocket fuel. It was shown that the oxidation of UDMH proceeds in two stages with the formation of a great number of complex unstable intermediates that contain up to ten nitrogen atoms. These intermediates are subsequently converted into final reaction products with a concomitant decrease in the average molecular weight. The intermediates and final products of the oxidative transformation of UDMH were characterized based on their elemental composition. Possible compounds matching the mass-to-charge ratio ( $m/e$ ) of the most intense peaks in the mass spectra were proposed. There were indications of the presence of the following classes of heterocyclic nitrogen-containing compounds among the oxidation products: imines, piperidines, pyrrolidines, dihydropyrazoles, dihydroimidazoles, triazoles, aminotriazines, and tetrazines. The results obtained open up possibilities for the targeted search and identification of new toxic products of the degradation of UDMH and, as a result, a more adequate assessment of the ecological impact of rocket propellant spills.

A UDMH destruction method using  $\text{H}_2\text{O}_2/\text{CuSO}_4$  leads to ca. 25% NDMA, which is a toxic and unwanted end product [261]. The amount of UDMH destroyed is affected by the order of the addition of  $\text{H}_2\text{O}_2$  and  $\text{CuSO}_4$ . When the  $\text{CuSO}_4$  is added first, only ca. 65% of the UDMH is destroyed, while the reverse order of addition leads to 100% destruction of UDMH.

Fenton's reagent, a mixture of hydrogen peroxide and iron(II) salt solutions, is a known powerful oxidizer containing hydroxyl free radicals.



The free radicals generated by this process then engage in secondary reactions. For example, hydroxyl is a powerful and non-selective oxidant. Oxidation of organic compounds by Fenton's reagent is rapid and exothermic and results in the oxidation ("mineralization") of contaminants to primarily carbon dioxide and water. Fenton's reagent can be used to destroy organic compounds like UDMH. The iron ions can be either in solution or in suspension in heterogeneous systems. The iron ion can be embedded in a zeolite for maximum surface area of a heterogeneous catalyst. This is a good way to detoxify wastewaters containing UDMH. There are several more references to this process in Section 1.6.6.2.

The zeolite FeZSM-5 is active as a catalyst in the oxidation of UDMH in aqueous solutions using hydrogen peroxide [262]. The performances of heterogeneous and homogeneous Fenton systems were compared, and complete UDMH mineralization (conversion to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) was achieved. Formic and acetic acids, as well as nitromethane, were identified as oxidation by-products. Adsorption properties of FeZSM-5 with respect to hydrogen peroxide, UDMH, and NDMA, and the effects of the oxidant and

UDMH concentrations, temperature, and the pH of the aqueous solution have been studied.

Iron-containing zeolites can be activated by pre-treatment with mineral and carboxylic acids to become more active in heterogeneous Fenton reactions such as the destruction of UDMH with hydrogen peroxide [263].

UV spectroscopy was used to trace and analyze the oxidative degradation products of UDMH in wastewater under the influence of two oxidation systems:  $\text{Cu}^{2+}/\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  Fenton system [264]. The degradation products of two oxidation systems, the  $\text{Cu}^{2+}/\text{H}_2\text{O}_2$  system and the Fenton system, were analyzed. The UV peaks of UDMH and unsymmetrical dimethylhydrazone (FDMH) were at 200 and 235 nm, respectively. The two systems could effectively decontaminate UDMH wastewater, but  $\text{Cu}^{2+}/\text{H}_2\text{O}_2$  had more intermediate products and higher toxicity. The addition of  $\text{H}_2\text{O}_2$  before adding  $\text{Cu}^{2+}$  can reduce intermediates. The addition of iron powder in addition to  $\text{Fe}^{2+}$  was beneficial in decreasing toxic intermediates.

#### 1.4.10.7 Reactions of UDMH with Carbon Dioxide

Salts formed between UDMH and carbon dioxide and their corrosion products (in contact with metals) are not totally soluble in UDMH and may precipitate and clog orifices and filter screens. Similar to the formation of carbazic acid in hydrazine, the reaction of UDMH with carbon dioxide may form salts of 2,2-dimethylcarbazic acid:



This salt has been isolated, and it was noted that it sublimates at 330 K (57 °C) and thus cannot be separated from UDMH by simple distillation [265].

The stability of UDMH is greatly affected by the presence of impurities. Six new metal complexes that are likely corrosion products containing 1,1-dimethylhydrazinecarboxylate and methylhydrazinecarboxylate were prepared. The effects of these complexes on the homogeneous decomposition rates of the propellants were investigated. The Ni(II) 1,1-dimethylhydrazinecarboxylate complex has a greater effect than the Mn(II) complex on the stability of UDMH [266].

#### 1.4.10.8 Reactions of UDMH with Nitrogen Dioxide

The hypergolic reaction of UDMH with dinitrogen tetroxide (NTO) is the main reason that much UDMH has been produced and consumed over the past 70 years. The reaction between the two liquids is hypergolic. The application of the NTO/UDMH propellant combination in rocket engines will be discussed in a future *Encyclopedia of Hypergolic Bipropellant Combinations*, in the chapter titled “Hypergolic Combinations With Nitrogen Oxides.”

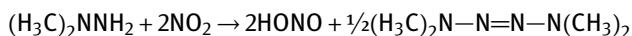
Slow and flameless reactions of UDMH with  $\text{NO}_2$  in the gas phase might occur in the vicinity of propellant storage areas where propellant has leaked, or in a rocket combustion chamber after the engine has shut down and the dribble volume slowly has emptied itself without a combustion reaction. These reactions also must be antic-



ipated if an NTO/UDMH bipropellant engine is fired for an extremely short pulse and fails to ignite.

The gas-phase reaction of UDMH with  $\text{NO}_2$  at low partial pressures was shown to produce NDMA, dimethylamine, dimethylhydrazinium nitrate, methanol, *N,N*-dimethylformamide, water, nitric oxide  $\text{NO}$ , nitrous oxide  $\text{N}_2\text{O}$ , nitrogen, and carbon dioxide [267–270]. *N,N*-Dimethylformamide was observed in significant amounts because it is not susceptible to further attacks from  $\text{N}_2\text{O}_4$ . The reaction products of the three hydrazines with NTO were analyzed by using mass spectrometry, GC, and IR spectrophotometry. Some of the GC fractograms showed as many as eight peaks, some of which still have not yet been identified.

In a study using a  $2.4 \times 2.4 \times 1.2$ -m Teflon foil-lined chamber at atmospheric pressure, concentration-time plots for reactants ( $\text{NO}_2$  and UDMH), intermediates, and products could be measured using *in-situ* FTIR spectroscopy with multiple paths of the beam running through the chamber [271, 272]. Experiments were conducted in air and nitrogen atmospheres in 3800-L and 6400-L Teflon reaction chambers. Reactant and product concentrations were measured by long pathlength (68.3–102.4 m) FTIR spectroscopy. The reaction occurred with an apparent overall reaction rate (defined in terms of UDMH decay) of  $(2.3 \pm 0.2) \times 10^{-17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The major products were nitrous acid and tetramethyltetrazene-2, according to



regardless of the initial reactant concentration or whether the reaction was carried out in nitrogen or air. There was no observable reaction of  $\text{NO}$  with UDMH in nitrogen. However, if  $\text{NO}_2$  was injected,  $\text{NO}$  would also participate. One of the unidentified intermediate reaction products was thought to be a nitrosohydrazine  $(\text{H}_3\text{C})_2\text{NNHNO}$ , which might undergo unimolecular decomposition to  $\text{N}_2\text{O}$  and dimethylamine.

NTO/UDMH is the propellant combination used by the Russian Zvezda propulsion module on the International Space Station. The Zvezda engine has to be fired periodically to maintain the space station orbit and to prevent it from falling down. There is concern that UDMH nitrate may sublime and condense on the shadow side of the station on optical surfaces or solar panels. Astronauts conducting EVA work may come into contact with the sublimate and bring it back with them into the airlock when they return. It is necessary to have detection and mitigation methods for the products of incomplete combustion. In addition to UDMH nitrate, methylammonium nitrate and dimethylammonium nitrite (which are all non-combustion reaction products of UDMH and NTO) can contaminate spacesuits during EVA operations. They can react with water on return to the International Space Station airlock to form NDMA, which is a carcinogen. Detection methods for assessing nitrite and DMA contamination were investigated [273, 274]. The methods were based on color-forming reactions in which the intensity of the color is proportional to concentration. A concept color detection kit using a commercially available criminal investigation field test for methamphetamine coupled with nitrite test strips was developed and used to detect DMA and nitrite.

In the case of launch failures of launch vehicles using storable propellants, large amounts of  $\text{N}_2\text{O}_4$  and UDMH or Aerozine-50 are released into the atmosphere. Under these conditions, only partial combustion and incomplete  $\text{NO}_2$ -UDMH reactions occur at the interphase of the oxidizer-rich and fuel-rich clouds with incomplete mixing. This depends on the catastrophic situation and the atmospheric conditions at the accident site. A large number of toxic compounds can be formed under those conditions [275].

Products of the reaction of UDMH with nitrogen dioxide in aqueous solutions were characterized by high-resolution MS with electrospray ionization [276]. It was found that more than 200 different CHO, CHN, and CHNO compounds were formed in the reaction. The main component was NDMA. Among the many products of the transformation of UDMH, *N*-nitrosodibutylamine was identified for the first time. These compounds can be found in surface and ground waters at the places of the impact of spent rocket stages containing both UDMH and NTO.

#### 1.4.10.9 Reactions of UDMH with Ozone and/or Atomic Oxygen

The reactions of UDMH with ozone are of interest for several reasons. One is the environmental fate of UDMH if it is accidentally released in the upper atmosphere where there is a prevalence of atomic oxygen. The other is the controlled use of ozone for the decontamination of wastewater from UDMH production and rocket test installations.

If UDMH is released in the upper atmosphere where it is exposed to direct incidence of sunlight, it is expected to react with ozone, atomic oxygen, and hydroxyl radicals. The reaction of atomic oxygen with UDMH may excite fluorescent emissions at characteristic wavelengths in the UV and visible range. In trying to explain high-altitude plume signature phenomena, near-UV, and visible emissions resulting from the reaction of high velocity (7 to 12 km/s)  $\text{O}^+$  ions and  $\cdot\text{O}$  atoms with UDMH were measured using a pulsed fast O-atom source [277]. The background-corrected spectrum consisted of four major bands assigned as OH(A,  $\Delta v = 0$ ), NH(A-X), CH(B-X), CN(B-X), and CH(A-X). No other major features could be seen over the range of 250–650 nm. A broad continuum extending from 350 to 750 nm, which peaked near 525 nm, was also observed. Experiments varying the  $\text{O}^+$  concentration revealed that the intensity of all of the band emissions (except OH(A)) was proportional to the square of the  $\text{O}^+$  concentration. This implied that the emissions arose primarily from ion-molecule reactions with  $\text{O}^+$  through a two-step mechanism.

Rate constants for the reactions of atomic oxygen with hydrazine, MMH, or UDMH have already been detailed in the chapter “Methylhydrazine” (within the section on MMH reactions) [278, 279].

The gas-phase kinetics of  $\text{O}(^3\text{P})$  and OH reactions with  $\text{N}_2\text{H}_4$ ,  $\text{CH}_3\text{NNH}_2$ , or  $(\text{CH}_3)_2\text{NNH}_2$  were studied in a discharge flow-tube apparatus [280, 281]. The reactions were studied in 267 Pa (2 mm Hg) of He dilution under pseudo-first-order conditions in the transient species concentration, with a known excess of hydrazines concentration. The steady-state concentration temporal profiles of the transient

species were directly monitored by fluorescence techniques to deduce the absolute second-order reaction rate coefficients. The Arrhenius expression

$$(1.96 \pm 0.29) \times 10^{-11} \exp(20 \pm 40)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

in the temperature range of 252–640 K was obtained for the reaction of  $\text{O}(^3\text{P})$  with  $(\text{CH}_3)_2\text{NNH}_2$ . The corresponding expression

$$(2.00 \pm 0.30) \times 10^{-11} \exp(330 \pm 80)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

in the range of 232 to 374 K was determined for the  $^{\bullet}\text{OH}$  reaction. Alkylation in the hydrazine molecule allows direct H-abstraction mechanisms to operate in these reaction systems. A later study [282, 283] using direct laser-induced fluorescence monitoring of the  $[\text{OH}]$  temporal profiles in a known excess of UDMH yielded the following absolute second-order OH rate coefficient expression:

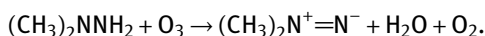
$$k_1 = (3.35 \pm 0.60) \times 10^{-11} \exp(175 \pm 25)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

for reactions with UDMH in the temperature range 232–637 K.

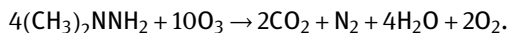
The gas-phase reaction kinetics of O atoms with UDMH was studied in a discharge flow-tube apparatus under pseudo-first-order conditions in  $[\text{O atom}]$  concentrations [282, 283]. Direct VUV CW-resonance fluorescence monitoring of the  $[\text{O atom}]$  concentration temporal profiles in a known excess of UDMH yielded the following absolute second-order O-atom rate coefficient expression in the temperature range of 232–644 K and in He pressure of 2.0 Torr:

$$K_1 = (1.94 \pm 0.34) \times 10^{-11} \exp(25 \pm 25)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The oxidation of UDMH in aqueous solution by gaseous (dissolved) ozone was characterized by the temporary appearance of red and orange colors, which was attributed to an intermediate diazolike compound [284–286] formed in the reaction



No oxidation by ozone was detected in acidic solutions. In neutral and weakly alkaline medium, analysis of gas products and the UV analysis of the liquid product suggested that the following reaction takes place:



Under the same conditions, using pure oxygen instead of ozone, produced only a complex mixture of organic compounds. If ozone or ozone-oxygen mixtures reacted directly with liquid UDMH instead of adsorbed or dissolved UDMH, up to nine products of partial oxidation were isolated and identified. However, the reaction never proceeded all the way to carbon dioxide as intended [287]. NDMA was the most stable and persistent intermediate. Other oxidation products were dimethylamine, dimethylformamide (DMF), tetramethyltetrazene, SDMH, and FDMH. Increasing the temperature from 293 to 323 K increased the rate of NDMA formation by a factor of six

but did not alter the product composition appreciably. When UDMH was adsorbed on alumina and then reacted with ozone, the colored intermediate presumed to be  $(\text{CH}_3)_2\text{N}=\text{N}$  was observed again. Half of the UDMH was oxidized to small fragments and the other half was converted to tetramethyltetrazene [288, 289]. It was suggested that the first stage of the oxidation of adsorbed UDMH is the dissociation of N—H bonds, leading to the formation of water. This is followed by the splitting of C—N bonds. The intermediate compounds can be stabilized by adsorption on alumina so that they can be studied by their IR spectra [290, 291]. The ozonization of all three hydrazines was studied in a gas bubbling column containing 30 L of solution. For runs when an ozone concentration of 13 mg/L air or less (approximately 1% by volume ozone in air) was desired, the ozonator feed gas was air. Although UDMH was reduced to approximately its detection limit after 35 minutes, 68% of the initial total organic carbon (TOC) and 40% of the initial chemical oxygen demand (COD) remained in the solution. Some of this residual organic material was determined to be methanol. Two peaks in the mass spectrum of low-concentration UDMH ozonation products were identified as NDMA and DMF. At higher UDMH concentrations, more than 15 peaks were detected and several remained unidentified. Two of the identifiable peaks were formaldehyde methylhydrazine,  $\text{CH}_3\text{NHN}=\text{CH}_2$ , and FDMH,  $(\text{CH}_3)_2\text{N}-\text{N}=\text{CH}_2$ .

Theoretical quantum mechanical calculations, used to study the reaction mechanism of UDMH with oxygen (O) atoms, predicted rate constants of the O-atom reactions with UDMH over a wide temperature range of 200–2000 K [292]. This reaction is likely to occur if UDMH diffuses to the ozone layer in the stratosphere, although it would most likely decompose before it gets there. The agreement between the theoretical predicted and experimental measured rate constants was good around room temperature. The channels of H abstraction from the  $-\text{NH}_2$  position favor temperatures below 1200 K. With increasing temperature, contributions from other channels must be considered. The reactivity of  $\text{N}_2\text{H}_4$ , MMH, and UDMH toward atomic O was compared to explore the methylation effect on hydrogen abstraction.

The formation mechanisms of NDMA from MMH, UDMH, or hydrazones during ozonation, which typically forms high NDMA conversion yields (60–90%), were investigated by using DFT computational methods [293]. Intermediates of the reactions included 1-formyl-2,2-dimethylhydrazine, FDMH, and acetone dimethylhydrazine. A new NDMA formation mechanism from hydrazines during ozonation was proposed, in which the initial step is hydrogen abstraction rather than the previously reported oxygen addition. For hydrazones, the C atom of the  $-\text{N}=\text{C}-$  moiety in hydrazones is the preferred point of attack by ozone to generate *N,N*-dimethylaminonitrene, which is an important intermediate in NDMA formation during ozonation. The reactivity order of the H atoms in hydrogen/hydride ion abstraction by ozone is  $-\text{NH}_2 > -\text{N}(\text{CH}_3)_2 > -\text{CO}-\text{NH} \sim =\text{C}(\text{CH}_3)_2 > =\text{CH}-$ . Formation pathways of some experimentally detected compounds, i.e.,  $\text{HOOH}$ ,  $\text{HOOH}$ , and  $\text{HCOH}$ , in the ozonation of hydrazines were examined.

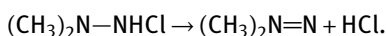
#### 1.4.10.10 Reactions of UDMH with Sulfur Dioxide

There is not much sulfur dioxide in polluted atmospheres to make reactions with SO<sub>2</sub> contribute to UDMH degradation in air. The reaction of sulfur dioxide with UDMH in trichloromethane produced 2,2-dimethylhydrazinium 2,2-dimethylhydrazinesulfate, a low-melting and readily subliming (300 K) salt [294]. Similar salts were obtained from 2-hydroxyethylhydrazine and phenylhydrazine. There do not seem to be any practical applications for such salts, so why patent them?

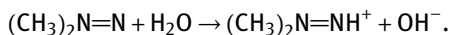
#### 1.4.10.11 Reactions of UDMH with Halogens and Hypochlorite

Hypochlorites in the form of chlorine bleach (sodium hypochlorite) or calcium hypochlorite (HTH) are frequently used for the disposal and destruction of hydrazine N<sub>2</sub>H<sub>4</sub>. In the case of hydrazine, N<sub>2</sub>H<sub>4</sub>, there would be no concern about by-products (except maybe HN<sub>3</sub>). In the case of methylhydrazines, the reaction does not always go to completion and undesirable toxic intermediates may linger around, even after the hypochlorite reaction has ceased. The oxidative destruction of unsymmetrical dimethylhydrazine (UDMH) by a molar excess of Ca(OCl)<sub>2</sub> leads mainly to FDMH and tetramethyl tetrazene but not to NDMA [261].

In the earlier experiments with UDMH and hypochlorite, GC/MS and GC/FTIR analysis of the reaction mixture revealed 90–100 different compounds [295–298]. The major reaction products were formaldehyde *N,N*-dimethylhydrazone (identified from its IR and its mass spectrum) and NDMA. Other confirmed reaction products were *N,N*-dimethyl cyanogen (relatively minor), DMF (relatively minor), and chloroform (minor). Neutralization of an acidic solution yielded many new peaks, multiply chlorinated, and all unidentifiable. No nitrosamines were found in the acidic run. In trying to explain the kinetics of this process, 1,1-dimethyl-2-chlorohydrazine may be the first product of the attack of hypochlorite on UDMH. In the next step, it is believed to lose HCl to form a reactive diazene intermediate



In an aqueous solution, the following equilibrium is also present:



During the course of the neutralization of UDMH with hypochlorite, the reaction mixture became yellow, then orange, and then red-brown. The dark red-brown color faded with further addition of hypochlorite, although gas continued to evolve. The extraction with dichloromethane yielded a yellow aqueous-phase and a dark yellow or orange organic layer. Back extraction with water also formed a yellow water layer. Hypochlorite oxidation products of UDMH were FDMH, chloroform, carbon tetrachloride, acetaldehyde ethylidene hydrazone, *N,N*-dimethylformamide, dimethylnitrosoamine, dimethyl cyanamide, 5-methyl-2,4-dihydropyrazol-3-one, isoxazolidine, and 1-methyl-1,2,4-triazole. Some of these products were formed only

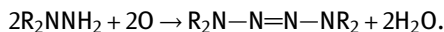
in very small quantities. Similar products were found as a result of the reaction of Aerozine-50 with hypochlorite. The reaction of iodine solution with hydrazine vapors has been used for the quantitative analysis of MMH and UDMH [299].

#### 1.4.10.12 Reactions of UDMH with Peroxydisulfate

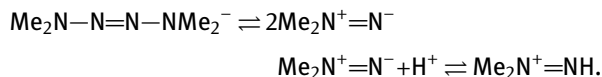
The best method of UDMH removal is complete mineralization, leaving only innocuous  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as end products. The oxidation of UDMH with peroxydisulfate in the presence of nano-iron as a catalyst was optimized for operational parameters such as iron dosage, pH, and an initial amount of peroxydisulfate [300]. The optimum conditions were pH 3.45, peroxydisulfate = 836 mg/L and nano-iron = 158 mg/L. A computer model predicted that 91% of the UDMH would be converted by mineralization at a reasonable cost compared to other treatment methods.

#### 1.4.10.13 Kinetics of Oxidation of UDMH in Solution

The use of dimethylnitrosamine (NDMA) in the manufacturing of UDMH is now largely avoided. However, there is continued concern that the oxidation of UDMH (which was made by other safer processes) released to the environment or during processes of decontamination might again form nitrosamines. The oxidation of UDMH by air, hypochlorite, bromate, iodine, or ozone has been extensively studied [284], however, the kinetics of each reaction are different and would require additional investigation. The kinetics of the oxidation of UDMH and the composition of the reaction products depend on the type of oxidant and the reaction conditions (mostly the pH). The oxidation of 1,1-dialkylhydrazines usually results in the formation of tetraalkyltetrazenes, which are intensely yellow-colored compounds



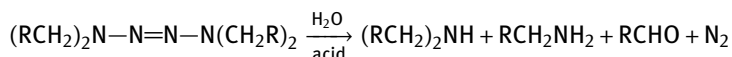
Of these, the tetramethyltetrazene has been most thoroughly investigated (see chapter “Alkylhydrazines” in *Encyclopedia of Liquid Fuels*). When measuring absorption spectra of tetramethyltetrazene as a function of pH and while looking for a method for the analysis of UDMH, it was discovered that tetramethyltetrazene dissociates to a diazene. In an acidic solution, this is stabilized as its protonated form, which is a dimethyl diazenium cation [171]:



Oxidation of UDMH in acidic solution with potassium bromate, neutralization, ether extraction, and purification by vacuum distillation produced tetramethyltetrazene in 60–90% yield [301]. Similar results were obtained with 1,1-diethylhydrazine or 1,1-di-*n*-propylhydrazine that were also converted to the corresponding tetraalkyltetrazenes. The reaction proceeds by way of  $(\text{CH}_3)_2\text{N}^+=\text{N}^-$ , which is a diazo-like compound that is

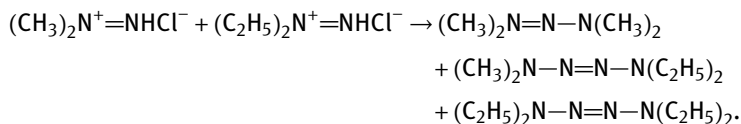
unstable and forms on decomposition of a freshly titrated UDMH-KIO<sub>3</sub> mixture, leading to additional KIO<sub>3</sub> consumption beyond the two-electron exchange stoichiometry. Spectrophotometric data support the tentative structure of R<sub>2</sub>N<sup>+</sup>=NH for the conjugate acid.

The oxidation of UDMH with iodine in neutral or weakly basic solutions, using Mg(OH)<sub>2</sub>, CaCO<sub>3</sub>, or piperidine to absorb the formed HI acid, leads to tetramethyltetrazene in at least 77% yield [171]. The decomposition of tetraalkyltetrazenes in acid solutions according to



leads to primary and secondary amines. When comparing the rates of reaction of a homologous series of tetraalkyltetrazenes, it was found that the rate of hydrolysis by acids is inversely proportional to the basicity constant [302]. The reaction proceeded as a first-order reaction until it reached at least 30% decomposition, as measured by UV absorption, nitrogen gas evolution, and NMR spectroscopy. In many cases, first-order kinetics held true up to 90% decomposition. The rate of hydrolysis remained constant at pH 1.0–5.0 but dropped sharply above pH 5.

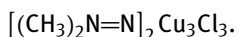
Spectrophotometric data supported the tentative conclusion of R<sub>2</sub>N<sup>+</sup>=N<sup>−</sup> and suggested the formation of an ion pair in hydrochloric acid solution [303]. When a mixture of dimethyldiazonium chloride and diethyldiazonium chloride was neutralized, three different tetraalkyltetrazenes were obtained:



This experiment indicated that the ions are freely interchangeable entities in acidic solution, which dimerize when the pH is raised. The three tetraalkyltetrazenes were separated by GC.

Radical cations of UDMH or MMH were generated by reaction of UDMH or MMH with cerium(IV) in sulfuric acid solutions in a fast-flow mixing chamber. The electron spin resonance (ESR) spectra of these short-lived intermediates were recorded and experimental nitrogen and proton coupling constants were determined [304]. Under some conditions, oxidation of UDMH led to the radical cation of tetramethyl-2-tetrazene. Molecular orbital calculations for molecules were performed and implications for reaction mechanisms for the oxidation of the hydrazines were explained.

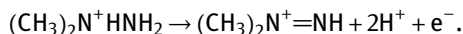
Oxidation of UDMH in aqueous solution at 273 K with copper(II)chloride forms the purple complex



This diamagnetic complex has been identified by elemental analysis, IR, and PMR spectroscopy [252, 305]. Hydrolysis of the 1,1-dimethyldiazene complex with ammonia or hydrochloric acid forms tetramethyl-2-tetrazene.

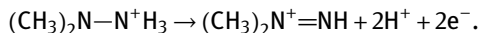
#### 1.4.10.14 Electro-Oxidation of UDMH

In addition to procedures using chemical oxidants, the oxidation of UDMH can also be achieved by electrochemical oxidation. This could serve the destruction of UDMH, act as an analytical tool, or go toward explaining the oxidation/reduction potentials of hydrazines. Controlled potential electrolysis of UDMH on smooth platinum electrodes in 1 M sulfuric acid yielded two electrons per UDMH molecule, according to the overall stoichiometry [306]:



However, the reaction proceeded after undergoing several intermediate steps. The rate-determining step was a single-electron adsorption-desorption stage, as indicated by a slope of the Tafel curve of 110 mV per current decade. The reaction orders for UDMH and  $\text{H}^+$  were 0.54 and  $-0.55$ , respectively. The diazonium salt was comparatively stable and could be identified in the solution following the test.

In a study of the anodic oxidation of UDMH on gold electrodes in 0.5–1.0 N sulfuric acid solutions, the experimental apparatus was the same as that previously used for a study on the oxidation of hydrazine [307]. Potential measurements in the range of  $-0.4$  to  $+1.0$  V (against  $\text{Hg}/\text{Hg}_2\text{SO}_4$  electrode) revealed three oxidation peaks [308]. The first peak was a well-defined irreversible oxidation threshold. A mechanism was proposed for this first step, which was most likely a two-electron transfer in acidic milieu:



This led to the diazenium cation that had already been observed in the chemical oxidation of UDMH. The remaining electrochemical oxidation steps were less well-defined than the first step. Earlier studies of the electro-oxidation of MMH had used a dropping mercury electrode in alkaline solution [309] and a gold electrode in acidic solution [310].

The electro-oxidation of UDMH on platinum has been studied in non-aqueous solvents such as dimethylsulfoxide [311] or acetonitrile [312, 313]. The latter report also included the oxidation of trimethylhydrazine. In alkaline solutions, hydrazine undergoes a quantitative four-electron oxidation process, while its methyl derivatives are oxidized quantitatively to the corresponding diimides in the same media. The anodic oxidation of MMH and UDMH on carbon fiber electrodes was studied in acetonitrile as a non-aqueous solvent [314].

Three different methods were used to study the anodic oxidation of UDMH: cyclic voltammetry, controlled potential electrolysis, and potentiostatic step measurements



[315]. The oxidation was achieved on smooth platinum electrodes in 1-*M* sulfuric acid or 2*M* perchloric acid.

#### 1.4.10.15 Reactions of UDMH with Organic Compounds

Many of the reactions, such as the reaction with acyl halides or carbonyl groups, are observed with alkylhydrazines (MMH, UDMH) and hydrazines alike. UDMH reactions and applications were summarized in a product brochure [93, 316].

Methyl groups increase the nucleophilic reactivity of the substituted position of hydrazines and reduce the nucleophilicity of the adjacent nitrogen center [317]. As a result, the tertiary nitrogen atom of 1,1-dimethylhydrazine is 3000 times more reactive than the NH<sub>2</sub> group, however, under thermodynamic control, substitution of an NH<sub>2</sub> proton can occur. The *N,N*-dimethylhydrazones of 37 carbonyl compounds were prepared and characterized by their boiling points, refractive indices, and IR spectra [318].

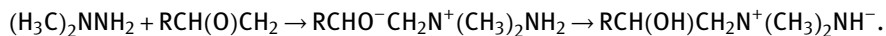
The reaction of aldehydes with excess UDMH can be used for the analysis of aldehydes by back titrating with HCl with thermometric endpoint indication [319]. Aldehydes have been used as reagents in the analysis of hydrazines but the inverse can also be the case when hydrazines are used in the analysis of aldehydes [320]. A common example is the analysis of sugars by derivatization with 2,4-dinitrohydrazine.

The melting points, decomposition temperatures, and ignition delays of 14 different solid hydrazones derived from UDMH were measured because these solid compounds were considered as fuels for hypergolic hybrid rockets [321]. Reaction of dimethylchloramine with UDMH leads to triazanum salts, which are unwanted by-products that limit the UDMH yield [49].

Amination of UDMH with NH<sub>2</sub>Cl or hydroxylamine-*O*-sulfonic acid yields 2,2-dimethyltriazanum (DMTZ) chloride and sulfate, respectively. The DMTZ cation was paired with the nitrogen-rich anions 5-aminotetrazolate, 5-nitrotetrazolate, 5,5'-azobistetrazolate, and azide, yielding a new family of energetic salts [322].

*N,N*-Dimethylhydrazones are useful intermediates in organic syntheses. Carbonyl group is often protected from unwanted side reactions by temporarily forming the dimethylhydrazone, such as during  $\alpha$ -alkylation, followed by hydrolysis of the hydrazone on silica gel [323].

Reactions of surplus UDMH with epoxides could lead to aminimines and aminimides. These can be used as intermediates for the synthesis of a number of other organic compounds



Eight saturated aliphatic aminimides with low melting points were synthesized after UDMH was alkylated, acidylated, and dehydrogenated [324]. The preparation and applications of aminimides are an effective approach to making good use of surplus UDMH [325]. In search for useful applications for surplus UDMH as part

of a demilitarization effort, it has been proposed to use UDMH for the synthesis of polyurethanes [326, 327].

#### 1.4.10.16 Alternative Uses for Surplus UDMH

Burning or spending money on aggressive chemicals capable of destroying UDMH has had mixed results and has produced a generation of unwanted and even more toxic by-products. As such, there have been numerous efforts to find alternative uses for UDMH (and  $N_2O_4$ ), with entire conferences being devoted to this topic [328]. 1,1-dimethylcarboxylic acids convert to dihydrazides. Glycidyl esters of carboxylic acids form *N*-acyl-*N'*,*N'*-dimethyl-*N'*-(2,3-dihydroxypropyl) zwitterions that rearrange to form 2,3-dihydroxypropyldimethyl amine [329]. One most unusual proposal was to react  $N_2O_4$  with agricultural waste and then react that mess with UDMH, which would result in a storable solid [330].

One of the potential uses of surplus UDMH is the synthesis of surfactants [331]. Long-chain ammonium imides derived from UDMH have surfactant and emulsifier qualities. Starting with surplus UDMH, many commercial products were synthesized successfully, including daminozide, 1,3,5-triamino-2,4,6- trinitrobenzene (TATB), heterocyclic compounds, organosilicon derivatives, and trifluoromethanesulfonic hydrazide [332].

Catalytic reduction of surplus UDMH diluted with an inert solvent (e.g., methanol) with hydrogen over Group VIII transition metal catalysts can lead to DMA and ammonia. Both of these are marketable and useful chemical raw materials that can act as reaction products [333–336].

UDMH and other energetic materials can be converted to chemicals that are useful in other synthesis reactions [337–339]. 1,1,1-Trimethylhydrazinium iodide made from UDMH is the most efficient nucleophilic aminating reagent available for the synthesis of TATB by vicarious nucleophilic substitution reactions starting with picramide. The reaction of UDMH and alkyl chlorides forms 1,1-dimethyl-1-alkylhydrazinium chlorides which are useful intermediates for the synthesis of other compounds [340] (see also [341, 342]).

#### 1.4.11 Analysis of Unsymmetrical Dimethylhydrazine

Very sensitive analytical methods for the detection and quantification of traces of UDMH in environmental samples include GC, HPLC, and ion chromatography (IC) [343].

##### 1.4.11.1 Specifications for UDMH

Procurement of UDMH was covered by MIL SPEC specification MIL-PRF-25604E [344]. MIL SPEC specification requirements for UDMH are listed in Table 14. Foreign countries have developed their own specifications for UDMH [345, 346] (see also [347]).

**Table 14:** MIL SPEC specification requirements for UDMH.

| Property                                      | Requirement    |
|-----------------------------------------------|----------------|
| UDMH assay, mass-%                            | 98.0 minimum   |
| Water, mass-%                                 | 2.0 maximum    |
| Amines, mass-%                                | 1.5 maximum    |
| NDMA, mass-%                                  | 0.01 maximum   |
| Chloride, mass-%                              | 0.003 maximum  |
| Density at 288.7 K (60 °F), g/cm <sup>3</sup> | 0.795 to 0.797 |
| Particulate, mg/L                             | 10 maximum     |

#### 1.4.11.2 Chromatographic Analysis Methods for UDMH

##### Gas Chromatographic Analysis Methods for UDMH Without Prior Derivatization

UDMH assay per MIL SPEC can be determined by GC on a 1/8 in. outer diameter (O.D.) × 6-ft packed column filled with 10% PEG400 on Fluoropack 80. NDMA content per MIL SPEC can be determined by GC in a 1/8 in. O.D. × 6-ft packed column filled with 33% Alltech AT-220 (formerly Amine 220) on 70/80 mesh silanized white diatomaceous earth.

The stability of UDMH is greatly affected by the presence of impurities. Most organic impurities are present in the propellant from when it is manufactured. To assess the likely range of impurities, a review of manufacturing methods for propellant hydrazines was undertaken. This was followed by a stability assessment and impurity survey (using GC-MS) on samples of MMH and UDMH from four different sources [266]. It was concluded that impurity profiles and stability are greatly affected by the manufacturing method.

Apparently some third world countries, in their quest for more UDMH, resorted to the direct methylation of hydrazine with dimethyl sulfate. As a result, they obtained mixtures containing four methylated derivatives of hydrazine, MMH, UDMH, SDMH, and trimethylhydrazine, with some unreacted hydrazine and water that needed to be analyzed by GC [348]. Several columns with different stationary phases under different experimental conditions (temperature ramping, carrier gas flow, split/splitless injection) were used. However, clearly resolved peaks of proper peak shape and integration could not be obtained.

A review of the existing methods for determining hydrazine and its short-alkyl and acyl derivatives with the use of different types of chromatography devoted special attention to the selectivity and sensitivity of the suggested approaches [349, 350]. Possible ways to increase the sensitivity of hydrazine determination were suggested and evaluated against real samples that were previously analyzed.

There are many types of highly sensitive chromatographic methods that can be applied to the detection of UDMH contamination in water and soil [351]. The peaks eluting from the GC were identified by mass spectrometry. Contaminants identified in UDMH included dimethylamine, FDMH, and nitrosodimethylamine. Samples containing mixtures of hydrazine, MMH, and UDMH can be separated after derivatiz-

ing the sample with acetone. Rinse waters from a test facility stored in catch tanks and not inerted with nitrogen padding (that is they were exposed to air before samples were taken) were analyzed by GC/MS. The waste products identified included acetaldehyde dimethylhydrazone, acetone dimethylhydrazone, nitrosodimethylamine, dimethylaminoacetonitrile, acetone methylhydrazone, *N,N*-dimethylformamide, acetone azine, 1-methyl-1*H*-1,2,4-triazole (MTA), guanidine, dimethyltriazole, tetramethylurea, and glyoxal bis(dimethylhydrazone).

A method for the analytical extraction of mobile species of eight main transformation products of UDMH (FDMH, acetaldehyde dimethylhydrazone, 2-furaldehyde dimethylhydrazone, 1,1,4,4-tetramethyl-2-tetrazene, *N,N*-dimethylformamide, NDMA, MTA, and 1-formyl-2,2-dimethylhydrazine) from soils using sub-critical acetonitrile at a pressure of 100 bar had recoveries of analytes that were better than 70% at an extraction time of no more than 30 minutes [352]. The effects of temperature, number of extraction cycles, and the moisture content of soil samples on the recovery of analytes were studied. It was found that, for soils with high concentrations of lignin humic substances, efficient extraction can be attained with an addition of significant amounts of alkali to the soil (2.5 g/g). A combination of the proposed sample preparation/extraction approach with analysis by GC-MS/MS ensured the accurate determination of the products of UDMH transformation in complex matrixes, such as soils with high contents of organic substances, with detection limits from 1.8 to 15 µg/kg using the direct injection of the extract into the GC system.

GC/MS analysis of UDMH and initial autoxidation products discovered that the oxidation sample contained dimethylamine, UDMH, FDMH, NDMA, acetaldehyde dimethylhydrazone, 1,1,4,4-tetramethyl-1,2-tetrazene, and dimethyldiazene with oxidation times of <100 h in air. The content of dimethylamine, FDMH, and NDMA increased in this stage but the content of DMA eventually decreased [353]. Solid-phase micro-extraction (SPME) combined with GC/MS was applied to the analysis of degradation products in water that was contaminated by UDMH [354]. The accuracy of gas chromatographic determination of UDMH can be improved by mixing UDMH with an internal standard solution [355].

### Gas Chromatographic Analysis Methods for UDMH with Prior Derivatization

Gas chromatographic analysis methods for UDMH with prior derivatization are summarized in [356]. Derivatizing reagents include 2-furaldehyde [357–359], pentanedione [360], acetone [361], 2-nitrobenzaldehyde, 4-nitrobenzaldehyde, 4-chlorobenzaldehyde, 4-cyanobenzaldehyde 4-dimethylaminobenzaldehyde, benzaldehyde, furfuraldehyde [362], salicylaldehyde [363], or alkyl isothiocyanates [351].

Analysis of a UDMH sample using GC/MS and GC/FTIR spectroscopy yielded a total-ion chromatogram with two major, three smaller, and six much smaller peaks, in addition to those due to the solvent and the UDMH itself [298]. The two major impurities were unambiguously identified as DMA from its published mass spectrum, and formaldehyde *N,N*-dimethyl hydrazone from its published IR spectrum. One of

the intermediate peaks was also unambiguously found to be chloromethane. The remaining intermediate peaks were postulated to be formaldehyde *N*-methylhydrazone and formaldehyde *N,N*-methylethylhydrazone based on their mass spectra. The remaining minor impurities could not be identified. The origin of the chloromethane is unclear. Because it was found in all the methylated fuel samples, it was presumably a residual from some common step in the manufacturing process for MMH and UDMH using the Raschig process.

The GC separation of the two isomeric dimethylhydrazines and the separation of UDMH from its oxidation products, i.e., tetramethyltetrazene and nitrosodimethylamine, can be improved by pre-treating the stationary phase with strong alkali [364].

The components of UDMH in liquid propellants were analyzed by GC/MS [365]. The retention ratios of the fractograms and the fragmentation mechanism of the mass spectra of components were studied for each component. The result showed that the UDMH in liquid propellant contains impurities of water, unsymmetrical dimethylhydrazone, dimethylamine, and acetaldehyde dimethylhydrazone. Except for dimethylamine, other impurities will reduce the specific impulse of the propellant.

Carbon dioxide in UDMH or MMH can be determined by adding a solution of barium chloride. The mass ratio of sample to be analyzed and barium chloride added should be  $1:5 \times 10^{-3}$  to  $1:1.7 \times 10^{-3}$ . The mixture should be placed into a rotavapor for vacuum distillation from a water bath at 313–318 K (40–45 °C) and heated to dryness. Distilled water should then be added to the dry residue, which leads to a mixed solution. The optical density of the said solution is determined with the help of photocolourimetry procedure at  $\lambda = 400$  nm [366]. Chloride in UDMH can be analyzed by the method described in MIL-PRF-25604E by reacting the sample with mercury(II) thiocyanate and analyzing the excess thiocyanate with iron(III) ammonium sulfate spectrophotometrically [344].

#### HPLC of UDMH Without Prior Derivatization

Hydrazine, MMH, UDMH, and SDMH can be separated and determined by ion-exchange HPLC using an electrochemical detector with a glassy carbon working and auxiliary electrodes [367]. The hydrazines do not require derivatization. Urine or blood plasma samples suspected of containing these compounds may be analyzed directly without previous work-up.

Solid-phase extraction (SPE) has been used for sample pre-treatment followed by HPLC analysis of the metabolites of UDMH in the blood of Wistar rats [368]. The blood before UDMH intoxication was collected as control and treated.

A liquid chromatography/MS method was developed for determining the transformation products of UDMH in soils, including formic acid dimethylhydrazide (= 1-formyl-2,2-dimethylhydrazine, analytical range 0.01–20 mg/kg), 1-methyl-1,2,4-triazole (analytical range 0.05–100 mg/kg), 1,1-dimethylguanidine (analytical range 0.05–100 mg/kg), and DMA (analytical range 0.25–250 mg/kg) [369]. The measurements were performed in the mode of chemical ionization under atmo-

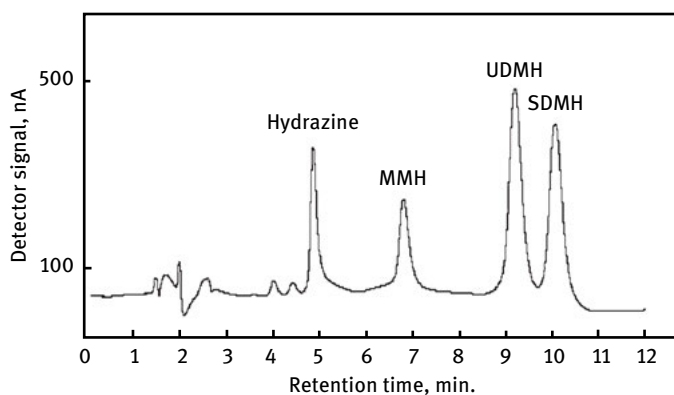
spheric pressure, followed by the registration of positive ions corresponding to the protonated forms of the components to be determined. For sample pre-treatment, the use of extraction with methanol (for 1-formyl-2,2-dimethylhydrazine) and ultrasonic extraction with a weakly alkaline buffer solution (for other substances) was proposed.

A liquid chromatography-tandem MS method for the simultaneous determination of MMH, UDMH, *N,N*-dimethylformamide, MTA, dimethylguanidine, NDMA, and 1,1,4,4-tetramethyltetrazene (all important rocket fuel pollutants of soils near rocket launch sites) used an isocratic mode on an analytical column with a Nucleosil-100-5SA sulfo cation-exchanger [370]. The mobile-phase composition was optimized to achieve effective separation of all analytes and to provide a high sensitivity of mass spectrometric detection. An ammonium acetate buffer solution (50 mM, pH 5.4) containing 25% methanol was used. Detection was performed in the positive electrospray ionization mode with multiple reaction monitoring (MRM). The parameters of an ion source, ion optics, the inlet potentials of the quadrupoles, and the collision energy for the detection of the detected product ions were optimized. Calibration curves for all compounds were linear in wide concentration ranges, covering three to four orders of magnitude. The detection limits varied from 40 pg/mL for dimethylguanidine to 18 ng/mL for MMH. No significant matrix effects were observed in the analysis of acid peaty soil extracts. The method was validated and successfully used to analyze real soil samples collected at the location of impact of the first stage of a space launch vehicle rocket.

A hydrophilic interaction liquid chromatography (HILIC) method for the simultaneous determination of hydrazine, MMH, and UDMH in natural waters and soils, based on a combination of HPLC chromatographic separation on a zwitterionic sulfobetaine stationary phase with amperometric detection, used a mixture of 78 vol. parts of acetonitrile with 22 parts of an aqueous phosphate buffer solution of pH 2.5 with an ionic strength of 20 mM as the mobile phase [371, 372]. This method allows simultaneous and rapid determination of UDMH and six major products of its transformation (methylhydrazine, NDMA, *N,N*-dimethylformamide, 1-methyl-1,2,4-1*H*-triazole, 1,1,4,4-tetramethyl-2-tetrazene, and 1,1-dimethylguanidine). Detection in the direct current mode was performed at a working electrode potential of 1.1 V. The advantages of the method are the high efficiency of separation, speed, high sensitivity, and a wide dynamic range of analyte concentrations, covering four orders of magnitude. The limits of detection were in the range of 0.07–0.13 µg/L. This was two orders of magnitude lower than those achievable in previously used methods of IC with electrochemical or mass spectrometric detection. The method was validated on samples of natural waters of different origins with added internal standards. The error of analysis did not exceed 10% for river and ground waters but increased to 20–30% for peat bog swamp waters. The utility of the method was demonstrated with samples of peat bog soils collected from places polluted by UDMH from the impact of the first stages of space launch rockets.

### IC Methods for the Analysis of Alkylhydrazines

An earlier example of separation of the three hydrazines by IC was already detailed in the chapter “Hydrazine” in *Encyclopedia of Liquid Fuels*. Analysis by IC uses equipment that is similar to HPLC. IC with amperometric detection was applied for the direct determination of UDMH, hydrazine, MMH, and SDMH in water [373]. Selectivity of two column materials, **(1)** a reversed-phase silica modified by dodecylbenzenesulfonic acid and **(2)** silica with chemically-bonded sulfonic acid, groups were investigated with conductivity detection. An example of the separation of the four hydrazines is shown in Figure 16. A detection limit with a 0.5 mL sample injection for UDMH was 2.0 ppb. The method was used for the analysis of soils contaminated by spilled UDMH from crashed Proton launch vehicles. Hydrazine and MMH were detected as decomposition products of UDMH in the soil.



**Figure 16:** Ion chromatogram of hydrazine, MMH, UDMH, and SDMH separation in water. (Reprinted and adapted from [373], with permission from ©2002 Japan Society for Analytical Chemistry)

One method for the determination of UDMH in soil samples involved the distillation of UDMH from an alkaline suspension of soil and ion chromatographic analysis of the distillate [374]. The separation was performed on a silica cation-exchanger column with an ammonium acetate buffer solution as part of the mobile phase and with amperometric detection at +1.2V. Hydrazine and MMH, which are decomposition products of UDMH, can be determined simultaneously. The limits of detection in aqueous solutions were 0.2, 0.5, and 1 µg/L for  $N_2H_4$ , MMH, and UDMH, respectively. The method was used for investigating the behavior of UDMH in spills of rocket fuels on soils. It was found that the addition of 4 kg/m<sup>2</sup> UDMH resulted in a 0.02% residue, which survived one year after the soil inoculation. The vertical migration of UDMH in soil was less than 50 cm. The ion-exchange constants for ion-chromatographic retention of 16 aliphatic amines and hydrazines on Diasorb-130-Sulfo and Nucleosil 5 SA were calculated. The selectivity of the retention of these compounds was compared

and optimum conditions of detection were determined [375]. Mass-spectrometry detection was used for compound identification after the chromatography separation and the characteristics of the mass spectra of the aliphatic amines and hydrazines were presented.

A study of the influence of eluent composition (the nature and concentration of the ion-pair reagent, medium pH, the concentration of the buffer solution, and the content of acetonitrile) on the retention of UDMH and its decomposition products on hydrophobized silica gels under the ion pair chromatography conditions was studied. This revealed that, for these sorbates, the influence of ion-pair reagents can be described correctly in terms of stoichiometric models [376].

The simultaneous determination of UDMH and its decomposition products hydrazine, methylhydrazine, NDMA, and tetramethyl-2-tetrazene with detection limits in water matrices at concentrations of 0.3, 0.7, 0.8, 7, and 1.2 µg/L, respectively (sample volume of 100 µL), is possible using ion-pair chromatography by means of sodium octylsulfate, octylsulfonate, or dodecylsulfate as an ion carrier [377]. Sodium octylsulfate was preferable as an ion-pair reagent.

There are several methods for the direct determination of hydrazines in water, including ion, ion-pair, ion-exclusion, and hydrophilic interaction chromatography [378]. The separation selectivity and sensitivity of detection for each method depend on the type of samples. Direct methods are simpler than those requiring prior derivatization of the samples, as was demonstrated with examples of hydrazine(s) determinations in real samples.

UDMH and products of its transformation in aqueous solutions can be analyzed with ion and ion-pair chromatography and mass-spectrometric detection in the electrospray ionization mode [379]. It has been shown that up to seven components may be determined within the limits of detection at the µg/L level. These methods were applied to the analysis of solutions with an initial UDMH concentration of 500 mg/L that had undergone autoxidation by atmospheric oxygen. Formic acid dimethylhydrazide, 1-methyl-1,2,4-triazole, and DMA were found among the autoxidation products [380].

Supercritical fluid extraction of UDMH from peaty soils with carbon dioxide is a rapid method of sample preparation for ion-chromatographic analysis [381].

IC with conductivity detection was used to directly analyze UDMH in wastewater, without any derivatization pre-treatment [382]. Column temperature, sample pH, different combinations of nitric acid, 2,6-pyridinedicarboxylic acid, and methanesulfonic acid on the analysis of mixed samples of UDMH and alkali metal ions were optimized. The linearity of the detected peak height (H) and peak area (A) versus UDMH concentration was studied at low, medium, and high concentrations. A good linear relationship was observed in the range of 0.5 – 1000 µg/mL. The limit of detection was 0.05 µg/mL. Actual UDMH in water samples from a rocket test site were analyzed, verifying the applicability of the method for analyzing UDMH in wastewater during the degradation process.



### HPLC of UDMH with Prior Derivatization

HPLC methods for the analysis of UDMH with prior derivatization have already been summarized in [383]. Most of the derivatizing agents described for hydrazine in this volume within the chapter “Hydrazine,” have also been examined for the presence of UDMH or MMH. Reagents used for the derivatization of UDMH included salicylaldehyde [384–386], benzaldehyde [387, 388], 2-nitrobenzaldehyde [389], 4-nitrobenzaldehyde [390], glyoxal or phenylglyoxal [391, 392], naphthalene-2,3-dialdehyde [393], and formaldehyde [394].

#### 1.4.11.3 Volumetric Methods for the Analysis of UDMH

UDMH is a weak base with a  $pK_a$  of  $8.19 \pm 0.18$ . Other sources reported it as 7.13 [249]. One will have to select the correct indicator if titrating UDMH acidimetrically.

#### Acidimetric Titration Following Reaction with Carbonyl Compounds

The  $pK$ 's of hydrazine and UDMH or MMH are too close to each other to allow simultaneous titration of mixtures of two or three bases in an aqueous solution. Following derivatization of hydrazine and UDMH, however, the acidity of the resulting azines (when titrated in non-aqueous media such as acetic acid) with perchloric acid in dioxane is distinctly different as it forms separate end points. Derivatization allows separate titration of different hydrazines and may also help in achieving sharper end points. Carbonyl compounds used to derivatize hydrazines in this application include salicylaldehyde [395–400] and acetone.

Instead of forming derivatives with salicylaldehyde, the different rate of acetylation of hydrazine and UDMH or hydrazine and MMH with acetic anhydride provides for a method to analyze binary hydrazine mixtures [401, 402]. In acetonitrile (as the solvent), both hydrazine and MMH react almost immediately, whereas the acetylation of UDMH proceeds very slowly. The total basicity of an unacetylated sample is determined by titration with standardized perchloric acid in acetic acid with quinaldine red indicator.

Hydrazine and its methylated derivatives can be differentiated, not only by reaction with acetylating agents or azine-forming reagents, but also by acidimetric titration before and after reaction of the sample with isocyanates [403, 404]. The reaction of hydrazines with alkyl or aryl isocyanates leads to semicarbazides, which are weaker bases than the parent hydrazines. In an alcoholic solution, hydrazine, MMH, and UDMH react with isocyanates at approximately the same rate to form semicarbazides. In contrast, in anhydrous acetic acid, hydrazine and MMH react rapidly but UDMH hardly reacts at all. Suitable isocyanates for masking hydrazine or MMH are phenyl isocyanate or naphthyl isocyanate.  $N_2H_4$ -UDMH and  $N_2H_4$ -MMH mixtures were titrated by this method and the error very rarely exceeded 0.5% absolute.

Formaldehyde dimethylhydrazone,  $H_2C=NN(CH_3)_2$ , FDMH, is a degradation product and contaminant of UDMH. Both UDMH and FDMH are colorless. When titrated with perchloric acid in acetic acid, both UDMH and FDMH have the same basicity.

When titrated with methanolic HCl in methanol, only UDMH acts as a base. The difference can be used for the determination of FDMH contamination in UDMH [405].

Attempts to determine total water content in UDMH by a gasometric method by reaction with calcium hydride failed because calcium hydride reacted not only with the water, but also (very slowly) with UDMH [406–408]. Gas evolution with calcium carbide has been measured as an alternate.

#### 1.4.11.4 Redox Titration Methods for UDMH

Most of the analysis methods described in older documents are now obsolete and have been replaced by more accurate instrumental methods. Attempts to apply iodine or iodate titration methods (which worked satisfactorily with hydrazine  $\text{N}_2\text{H}_4$ ) to the analysis of MMH or UDMH have not always been successful at the first attempt. Lower temperature and/or the addition of catalysts may be required to achieve sharp endpoints. Direct titration of UDMH with  $\text{KIO}_3$  is possible if one operates in concentrated HCl and a saturated solution of mercury(II) chloride is added as a catalyst [409].

Titration of hydrazines with  $\text{KIO}_3$  can lead to end points of iodine(+1) in  $\text{ICl}$  or iodine(–1) in  $\text{KI}$ , depending on the pH conditions. It is very difficult to achieve a sharp end point in these titrations [410, 411]. Acidity, sample size, temperature, amount of mercury catalyst, and time spent to reach the endpoint must be carefully controlled, with acidity maintained at above 2N HCl. The endpoint can be detected by the blue color formed by starch with the first free iodine formed from excess iodate and iodide. Potentiometric endpoint indication is also possible. The potential jump at the equivalence point is from 0.6 to 0.8 V. A dimethyldiazonium compound present in the solution at the endpoint will continue to consume iodate at a slow rate.

The potentiometric titration of hydrazine  $\text{N}_2\text{H}_4$  with iodate had previously been used only for uniform hydrazines. Also, attempts to use iodate titration for the analysis of UDMH alone has not always been successful. However, it was shown that by maintaining a high acid concentration and using potentiometric endpoint indication, it was possible not only to titrate UDMH by itself but also to determine the total number of redox equivalents (R) in  $\text{N}_2\text{H}_4/\text{H}_2\text{NN}(\text{CH}_3)_2/\text{H}_2\text{O}$  mixtures [412]. A parallel acidimetric titration gave the number of acid-base equivalents (A) in the sample. Repetitive titrations demonstrated that this method can be applied to the analysis of hydrazine-UDMH mixtures of 3% relative or better.

A Metrohm 809 automatic potentiometric titrator with potentiometric end-point indication was used to analyze UDMH [413]. The experimental results demonstrated excellent precision and accuracy and indicated that the proposed method is quite suitable for UDMH analysis. The results also were in good agreement with those using other standard methods.

#### 1.4.11.5 Electrochemical Methods for the Analysis of UDMH

Electrochemical analysis methods are becoming increasingly popular because they can be automated and will eventually interface with digital data acquisition and data reduction.

##### Coulometric Analysis Methods for UDMH

A rapid and automatic coulometric titration procedure for the determination of hydrazine and mono-substituted hydrazines with electrolytically generated bromine had a standard deviation of approximately  $\pm 1\%$  and was based on the use of the Faraday constant as a standard [414]. Samples in the 3–5-mg range could be analyzed. The use of anodically generated chlorine in place of bromine did not result in any improvements. An acetic acid/water/methanol/mercury(II)acetate/potassium bromide solvent was used for most of the compounds titrated. Other solvents tested were aqueous 0.3M hydrochloric acid with 0.1M potassium bromide and 80% acetic acid/20% water 1.0M in hydrochloric acid with potassium bromide. The choice of solvents depends on the type of hydrazine to be titrated. Unsymmetrical dimethylhydrazine consumed close to six (5.88) equivalents. The results were reproducible; SDMH, however, produced erratic results and could not be analyzed using this procedure.

A similar method in a microcell holding a small 0.5 mL sample volume has extended the range to micromol quantities of hydrazine(s) [415]. All three propellant hydrazines (hydrazine, MMH, and UDMH) from sulfuric acid-impregnated air sampling tubes or wastewater samples could be analyzed and titrated coulometrically with electrically generated chlorine or bromine, but the method did not differentiate between the three hydrazines [416]. This method is faster than many competing methods since it does not require derivatization and has no internal standards for calibration. At the lower limit of sensitivity, nanomols of hydrazines can be detected, which translates to ppb concentrations in air samples. The coulometric titration does not differentiate between hydrazines and hydrazones, which are contaminants in the sample. In samples that contain MMH and UDMH autoxidation and partial oxidation products, various amounts of formaldehyde hydrazones will be found that may also consume oxidant. Formaldehyde and its hydrazones are also oxidized by either free chlorine or bromine but the stoichiometry is different from that with pure hydrazines. In samples with large amounts of methylhydrazines and their autoxidation products, the coulometric titration results can be corrected by separately determining formaldehyde (from the hydrolysis of the methylhydrazones) colorimetrically with chromotropic acid in concentrated sulfuric acid [416].

##### Polarographic Analysis Methods for UDMH

A measurement of the half-wave potentials of hydrazine, two hydrazides, six alkylhydrazines, and phenylhydrazine in 0.1M NaOH showed that the potentials for UDMH and SDMH were essentially identical and more negative than expected for ethylhy-

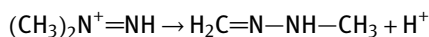
drazine [417]. The currents for these two dimethylhydrazines indicated a two-electron rather than a four-electron mechanism.

In an investigation on the polarographic determination of hydrazine derivatives with a dropping mercury electrode, anodic waves were obtained for most monoalkyl-, acyl-, dialkyl-, and acylalkyl-hydrazines in alkaline medium [418]. However, the quality and analytical usefulness of these waves varied widely. Only the unsymmetrically dialkyl-substituted hydrazines produced waves that were suitable for analytical purposes in the presence of sulfite ions. Hydrazine  $\text{N}_2\text{H}_4$  itself and MMH formed only distorted waves.

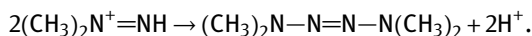
Methylamine, UDMH, and dimethylamine, which may be found in the effluent water of a UDMH production facility, can be determined simultaneously by polarography on a dropping mercury electrode in a lithium perchlorate solution/borate buffer electrolyte [419]. Oxidation of these compounds involved two electrons in all cases. The effluents may also contain formaldehyde, which is frequently an autoxidation or hydrolysis product of UDMH or tetramethyltetrazene. Formaldehyde (up to a tenfold excess) did not interfere with the analysis.

### Electro-Oxidation of UDMH in Solution

UDMH, as well as hydrazine, both show a large overpotential associated with electro-oxidation at conventional electrodes. Electrochemical analysis of hydrazines is a major challenge that calls for the development of high-performance catalysts to facilitate the oxidation process. In analogy to the studies on hydrazine, the electro-oxidation of UDMH and SDMH at a platinum electrode has been investigated using chronopotentiometry, coulometry, and product analysis [420]. The results of this study bear certain significance for the attempted polarographic analysis of these compounds. The results showed that oxidation of SDMH proceeds through an initial two-electron oxidation, followed by hydrolysis to formaldehyde and methylhydrazine. Unsymmetrical dimethylhydrazine becomes oxidized through a two-electron process to 1,1-dimethyldiazene, which undergoes a relatively slow chemical decomposition, possibly through rearrangement



forming a hydrazone. A third possible reaction involves coupling to the tetrazene:



The measurements were done with an experimental set-up that can collect, measure, and analyze gaseous electrolysis products of alkylhydrazines [421].

Three different methods were used to study the anodic oxidation of UDMH: cyclic voltammetry, controlled potential electrolysis, and potentiostatic step measurements [422]. The oxidation was achieved on smooth platinum electrodes in 1M sulfuric acid or 2M perchloric acid.

The electrocatalytic oxidation of UDMH on a prussian blue modified carbon paste electrode was studied using a cyclic voltammetry technique [423]. The results showed that prussian blue acts as a suitable modifier for electron transfer in the oxidation of UDMH. A linear range of  $3 \times 10^{-5}$  to  $1 \times 10^{-3}$  mol/L, with a limit of detection ( $3\sigma$ ) of  $1.6 \times 10^{-5}$  mol/L, was obtained using the amperometric method. The proposed sensor did not suffer from interference from hydrazine, was easy to prepare, and had good stability and repeatability. This electrode was successfully applied to the determination of UDMH in wastewater samples.

A Prussian blue/titanium dioxide nanotube composite modified carbon paste electrode for the detection of UDMH in water, based on prussian blue as the catalyst to promote oxidation of UDMH, had a linear range of 0.3–100 mg/L and a limit of detection of  $2.6 \times 10^{-5}$  g/L [424].

### Dielectric Constant Analytical Methods

If the dielectric constants of two components in binary mixtures are sufficiently disparate, and if the interference by third parties can be eliminated, measurement of the dielectric constant of liquids offers a convenient and rapid analysis method of binary mixtures. Water content in UDMH can be determined with  $\pm 0.02\%$  absolute accuracy in the 0–2%  $\text{H}_2\text{O}$  range by measuring the capacitance of a liquid-filled cell [425, 426]. Similar measurements achieved an accuracy of 0.02% for 0–5%  $\text{H}_2\text{O}$  in UDMH [265]. The interference of DMA contamination in UDMH was identified as a minor effect. Unfortunately, the dielectric constants of mixtures in the 0–100% range for both  $\text{H}_2\text{O}$ -UDMH and  $\text{H}_2\text{O}$ - $\text{N}_2\text{H}_4$  mixtures were provided only in scale units of a particular model oscillometer that the investigators happened to use. The data were not presented in terms of the more commonly used Debye units for dielectric constants.

#### 1.4.11.6 Spectrophotometric Methods for the Analysis of UDMH

##### UV-Visible Spectrophotometric Methods for the Analysis of UDMH

Many of the spectrophotometric methods operating in the visible range have the advantage that they are easy to perform, are specific for hydrazines, and do not require very costly equipment. Therefore, for the analysis of trace quantities of UDMH in air or water, spectrophotometric methods are frequently used either for routine analysis or to calibrate electronic direct-reading instruments that are based on non-spectroscopic principles. They typically involve the reaction of a sample in water or dilute acid with a color-forming reagent that is more or less specific for UDMH.

Reagents for the spectrophotometric analysis of UDMH include formaldehyde [16, 405, 409, 427, 428], salicylaldehyde [429], chromotropic acid [416, 430, 431], trisodium pentacyano ammino ferrate(II) [432–439], 5-nitro-2-furaldehyde [440], and gold nanoparticles [441].

Hydrocarbon/UDMH mixtures can be analyzed after the sample is treated with an acetic acid aqueous solution at a mass ratio of water, sample, and acetic acid =

1:(0.33–0.89):(0.10–0.33), respectively. The hydrocarbon content is determined by photometry at wavelength  $\lambda = 400$  nm [442].

A solution of 0.1% hydrochloric acid was used as the absorbent in hollow fiber (HF) membranes for the sampling of UDMH from an atmospheric standard chamber, followed by spectrophotometric detection [443]. Response surface methodology with central composite design experiment design was used to optimize the sampling parameters such as flow rate and sampling time. Several analytical parameters, including breakthrough volume, storage time, and carryover effect of the HF membrane were investigated. The optimal sampling rate was 9.90 mL/min. To validate the proposed method, it was compared with the NIOSH 3515 method [444]. Good agreement between the two methods was found. The one-step HF membrane offered a high sensitivity for the sampling of UDMH in air.

### IR and Raman Spectrophotometric Methods for the Analysis in UDMH

Water obeys Beer's law in hydrazine hydrate, MMH, or UDMH. Using the 1.9- $\mu$ m absorption band of water, an IR-spectrophotometric analysis method has been developed that is applicable to mixtures containing 0.1–15% water [445]. DMA or nitrosodimethylamine do not interfere, however, methanol or ethanol would interfere if they were present in concentrations greater than 1%. One-centimeter quartz cells were used for these tests. The results can be expressed by

$$P = a + bA,$$

where  $P$  represents weight percent of water in the mixture,  $A$  is 100 times the absorbance, and  $a$  and  $b$  are constants as follows (all data for 1-cm path length):

$$\text{MMH} \quad a = -0.0062 \quad b = 0.01958$$

$$\text{UDMH} \quad a = 0.019 \quad b = 0.01994$$

If the sample temperature differed by less than 2K from that used during calibration, only minor deviations (<1%) were encountered. Oxygen must be excluded from the solutions to prevent autoxidation and the formation of additional water.

Water in UDMH or mixtures of UDMH and DETA can be determined by a differential IR spectrophotometric method where part of the sample is first carefully dried with molecular sieves and then placed in the reference beam [408]. The absorbance of the as-received sample at 1.93  $\mu$ m is measured in silica cells (path length of only 1 cm) and calibrated through samples with known water content. The standard deviation for water content between 0.1 and 1.2% was  $\pm 0.004\%$  absolute. Similar methods were sought for determining the water content of Titan-II propellants [446].

As far as the analysis of trace UDMH and other hydrazine vapors in the air by remote sensing IR methods is concerned, some of these methods are based on a tunable

laser as the source of the IR radiation. The  $^{12}\text{C}^{16}\text{O}_2$  laser can produce over 100 different discrete wavelengths between 9.1 and 11  $\mu\text{m}$  where there is very little interference from atmospheric water or carbon dioxide. UDMH has characteristic absorption bands in this regime [447]. The absorption spectra of three hydrazines and four of their air-oxidation products were measured in the 9–12  $\mu\text{m}$  spectral region with an FTIR spectrometer with a  $0.05\text{-cm}^{-1}$  resolution to determine absorption coefficients at  $\text{CO}_2$  and tunable diode laser wavelengths. The coefficients were then used to estimate the sensitivity for remote detection of UDMH vapors using  $\text{CO}_2$  and tunable diode lasers in long-path differential absorption measurements. Far-infrared group frequencies of unsymmetrical hydrazines were measured in the range of 450 to  $75\text{ cm}^{-1}$  [448].

### Fluorescence Methods for the Analysis of UDMH

The post-chemiluminescence reaction of UDMH in potassium bromate-luminol water solution and the reaction conditions, including the concentration of potassium bromate and luminol, the length of the tube, the velocity of the solution flow, the acidity ( $\text{H}_2\text{SO}_4$ ) of the potassium bromate solution, and the alkalinity ( $\text{NaOH}$ ) of the luminol solution were investigated to develop a new method for the determination of trace UDMH in water [449]. The linear response range of this method was from  $1 \times 10^{-7}$  to  $1 \times 10^{-5}$  g/L with a detection limit of  $4 \times 10^{-8}$  g/L. The relative standard deviation for a  $5 \times 10^{-7}$  g/L UDMH solution was 2.3%.

#### 1.4.11.7 Mass Spectrometric Analysis of UDMH

Ionization potentials of UDMH fragments in a mass spectrometer have already been detailed in the chapter “Methylhydrazine” of *Encyclopedia of Liquid Fuels*. UDMH, MMH, and hydrazine in the air can be detected and identified by ion mobility spectrometry (IMS) at low concentrations, however, there can be interference from ammonia [450]. The optimum spectrometer operating conditions for the detection of hydrazine, MMH, and UDMH in the presence of ammonia were incorporated into a handheld portable instrument capable of near real-time detection. The use of ketones as dopant chemicals has been shown to be effective in the ion mobility spectrometric determination of the hydrazines.

#### 1.4.11.8 Analysis of UDMH Contamination in Water and Soil

In most cases where UDMH contamination is analyzed in water or soils, one will want to know the concentration of undecomposed UDMH and the type and amount of UDMH degradation and autoxidation products also. For a correct determination of the total concentration of UDMH in soil, it is necessary to consider the simultaneous presence of active products of its transformation that are capable of hydrolysis back to the parent compound, such as formic acid 1,1-dimethylhydrazide. A comparative study was performed exploring the methods detailed in the literature for sample preparation. This was to inform select conditions for the quantitative extraction of UDMH that was bonded by various mechanisms to organic and mineral fractions

of soil and formic acid 1,1-dimethylhydrazide (one of the most common active transformation products) [451]. It was found that the steam distillation with a 40% NaOH solution with an addition of Na<sub>2</sub>S enabled the quantitative recovery of UDMH and formic acid 1,1-dimethylhydrazide from soils of all types and the determination of the maximum original concentration of UDMH in the analysis of real samples of contaminated soils.

Testing different methods for sample extraction and chromatographic determination of mobile forms of UDMH and NDMA for the analysis of peaty boggy soils (typical for the European North of the Russian Federation where spent launch vehicle stages might have impacted the environment) showed that within a 3-d period after UDMH penetration into the soil, no more than 15% of its initial content could be extracted [452]. A large fraction of UDMH can be extracted from peat by steam distillation in the presence of a 40% solution of sodium hydroxide.

In addition to the analysis of air samples, furaldehyde derivatization has also been successfully used for the analysis of hydrazine and UDMH contamination in ground water [360]. Separation was seen on 10% OV-101 on Chromosorb WHP 80/100 mesh-packed glass columns. Detection was conducted using a thermionic specific detector (TSD) or MS detector. The detection limit was ca. 36 ppb for UDMH. This method does not apply to MMH, because of incomplete derivatization and the instability of the derivative. It is advisable to use only freshly distilled 2-furaldehyde as the reagent and prepare the dilute aqueous solution fresh daily (2 mL of redistilled furaldehyde diluted to 50 mL with 0.5 M sodium acetate solution as a buffer).

SPME was very effective in extracting UDMH transformation products from soil samples contaminated with rocket fuel. The use of SPME resulted in high sensitivity, speed, and modest labor consumption due to automation, and it was simple to use. It was shown that water addition to soil leads to a significant decrease in the recovery of almost all target transformation products of UDMH. The use of SPME for sampling and sample preparation resulted in the detection of 21 new compounds that are relevant to the UDMH transformation in soils [453].

UDMH transformation products that can be detected by GC or GC/MS include FDMH [454] and MTA [455]. A wide range of transformation products of UDMH in contaminated soil and water were analyzed and identified using gas chromatographic methods [456, 457]. A review of all data on the transformation products of UDMH, including their identification, quantitative determination, distribution, and fate in the environment, listed the analytical methods for the determination of these compounds in the environmental samples [458]. This included the results of the identification of UDMH transformation products in soil samples collected from three sites where the first stages from space launch vehicles had impacted the ground.

A highly sensitive GC-tandem MS method was developed for the simultaneous determination of eight major products of oxidative transformation of UDMH in soil and water, namely formaldehyde dimethyl-hydrazone, acetaldehyde dimethylhydrazone, 2-furaldehyde dimethylhydrazone, 1,1,4,4-tetramethyl-2-tetrazene, *N,N*-dimeth-



ylformamide, NDMA, MTA, and 1-formyl-2,2-dimethylhydrazine [459]. The detection limits were in the range of 0.3–2.3 ng/mL, which was one to two orders of magnitude lower than those for the traditional GC/MS method. The developed approaches were tested during the analysis of real samples using the surface water of a peaty swamp with high contents of organic substances. These samples were collected at places of impact during the first stages from space launch vehicles. *N,N*-dimethylformamide and MTA were predominant among the detected UDMH transformation products in natural waters.

One of the more durable UDMH degradation products is MTA, which can be analyzed by GC-MS [460]. Quantitative analysis of trace concentrations of UDMH transformation products in water requires very sensitive analytical instrumentation and tedious sample preparation. A simple and automated method for sensitive quantification of UDMH transformation products in water was developed using headspace SPME in combination with GC-MS and GC-MS/MS [461]. This method is based on the extraction of analytes from the gas phase above samples by a micro-polymer coating followed by thermal desorption of analytes in a GC inlet. Extraction by 85  $\mu$ m Carboxen/polydimethylsiloxane fiber at 323 K (50 °C) over 60 minutes provided the best combination of sensitivity and precision. Detection limits of twelve analytes using GC-MS/MS with chemical ionization were about 10 ng/L. This method is simpler, automated, provide lower detection limits, and covers more UDMH transformation products than other methods. The method was recommended for assessing the water quality in areas affected by rocket launch activities.

Micro-analysis of UDMH in water is possible using GC, HPLC, or IC [462]. A new spectrophotometric method for determining trace amounts of UDMH was developed based on UDMH possessing some retarding activity to the rate of oxidation of methyl orange by potassium bromate in an  $\text{H}_2\text{SO}_4$  medium [463]. The linear range was 0.20–0.08  $\mu\text{g/mL}$  and the detection limit was  $1.3 \times 10^{-2} \mu\text{g/mL}$ . This method was used with good results to determine trace quantities of UDMH in water samples and it offered simplicity, high sensitivity, and good stability.

#### 1.4.11.9 Analysis of NDMA in the Presence of UDMH

NDMA is an oxidation product of UDMH. It can also be an intermediate in the manufacturing of UDMH if carried over from the production process. Several extremely sensitive analysis methods have been developed to perform trace analysis on this potential carcinogen in liquid and in the air. Atmospheric sampling for NDMA performed by the Environmental Protection Agency (EPA) in Baltimore in 1975 downwind of a UDMH manufacturing plant was done using cryogenic samplers. Air samples were collected cryogenically, extracted with dichloromethane, concentrated, and then analyzed on a GC with an *N*-nitroso compound-specific thermal energy analyzer [464–466]. The NDMA levels were found to vary between 16 to 760 ng/m<sup>3</sup>. The thermal energy analyzer decomposes the *N*-nitroso compound on a catalyst into an amino radical and an NO radical. The amino radical is trapped in a cold trap at 153 K, which the nitroso

radical passes unchanged. The NO is then reacted with ozone, forming electronically excited nitrogen dioxide. The excited  $^*\text{NO}_2$  relaxes to its ground state with the emission of nearly monochromatic light in the IR region of the spectrum. The IR emission is recorded on a photomultiplier. The intensity of the emission is proportional to the number of NO radicals present. NDMA levels observed in the air of inhabited suburbs of Baltimore, MD, varied between 16 and 760 ng/m<sup>3</sup>, causing a significant amount of public concern about the potential health effects of this air pollutant. In a few instances, *N*-nitrosodiethylamine was also detected. In a simultaneous effort, two different sampling and analysis methods were used, essentially producing identical results [467]. One group sampled the air in two consecutive cold traps cooled to 195 K, extracted the traps with dichloromethane, concentrated the extracts, and injected the sample into a GC with a thermal energy analyzer. The other group concentrated organic vapors from ambient air on a pre-conditioned Tenax-GC cartridge that was then desorbed in a laboratory and analyzed using capillary GLC in conjunction with a mass spectrometer. The highest value of 32000 to 36000 ng/m<sup>3</sup> was observed adjacent to the UDMH facility. However, NDMA was also found in the air in the vicinity of a methylamine-producing plant in Belle, WV. In this instance, atmospheric nitrosation must have led to the formation of NDMA. Consequently, any fish processing plant might be a suspected source of atmospheric NDMA. By comparison, *N*-nitroso compounds were not found in the air of urban centers in Philadelphia, PA, Wilmington, DE, or Waltham, MA. In addition to the cryogenic sampling and adsorption on Tenax tubes, air samples have also been taken by bubbling the air through an impinger with dilute alkali [468, 469].

A comparison of analytical methods for the measurement of NDMA in UDMH-enriched atmospheres in animal exposure chambers included three different sampling methods: **(1)** three-stage cryogenic sampling with analysis by coupled GC-MS; **(2)** NDMA concentration on Tenax-GC cartridges with analysis by GC-MS after applying the method used by Pellizzari et al. (1976) [470], and **(3)** impinger sampling with analysis using a thermal energy analyzer (TEA) and employing a method used by Fine and Rounbehler [471].

An improved atmospheric sampling technique for NDMA and UDMH has been developed; it aspirates air through sorbent tubes filled with Tenax-GX (a 2,6-diphenyl-*p*-phenylene oxide polymer) [472]. The adsorbed contaminants were then desorbed and injected into a GC-MS data system where individual GC peaks could be identified by their MS fractionation pattern. This method can detect 0.17 µg NDMA in a 240-L air sample (21 ppb).

Astounding detection sensitivity for NDMA has been developed using a GC-MS with methane chemical ionization and single-ion ( $m/e$  75) monitoring [473, 474]. This method can detect 50 pg of NDMA per injection.

The EPA's Method 607 for the analysis of NDMA in treated UDMH wastewater was modified to meet the requirements of ambient water quality criteria (as set by the EPA), which is 0.0014 parts per billion (ppb) [475]. It was concluded that a target treatment

level of 0.0014 ppb for NDMA was realistically unachievable given the state of analytical technology available at that time. However, the technology available in the 1990s could yield reliable data in the  $10^{-4}$  to  $10^{-6}$  cancer risk factor range between 0.140 and 0.0014 ppb of NDMA.

NDMA, a degradation compound of UDMH in UDMH-containing wastewater, can be analyzed using GC/MS in the selected ion monitoring mode [476]. The wastewater sample was pre-treated using steam distillation, extraction with dichloromethane, and concentration by blowing with nitrogen. The linear relationship between the peak area and concentration of NDMA was obtained in the range of 0.31–1.54 mg/L with a detection limit of 2 µg/L. Tests for recovery and precision of this method were made by adding 2.016 µg or 10.08 µg of NDMA to 100 mL of distilled water. The recovery was 88.8 and 89.3%.

#### 1.4.11.10 Analysis of UDMH Vapors in Ambient Air

Analytical methods for detecting and quantifying UDMH vapors in the air can be either grab samples (spot analysis) or continuous direct-readout instruments with an alarm function when a certain threshold concentration is exceeded. Many different analysis methods have been developed for this purpose [477].

##### Analysis of UDMH Vapor with Grab Samples-Active Sampling

Active sampling devices require a pump and a flow meter to force the air through the absorbent material or to bubble the air through an impinger filled with dilute acid.

NDMA is either an oxidation product of UDMH or an intermediate in the manufacturing of UDMH. Several extremely sensitive analysis methods have been developed to perform trace analysis on this suspected carcinogen.

An improved atmospheric sampling technique for NDMA and UDMH aspirates air through sorbent tubes filled with Tenax-GX (a 2,6-diphenyl-*p*-phenylene oxide polymer) [472]. The adsorbed contaminants were then desorbed and injected into a GC-MS data system where individual GC peaks could be identified by their MS fractionation pattern. This method can detect 0.17 µg NDMA in a 240-L air sample (21 ppb).

##### Analysis of UDMH Vapor in Air-Passive Sampling

Passive sampling devices in the shape of lapel-worn badges like those used in radiation dosimetry can absorb UDMH vapors and either cause a color change for immediate indication or can be extracted at the end of the work shift to obtain a cumulative reading for the entire duration of exposure. The devices depend on the diffusion and natural convection of the air.

A portable system for the detection of low concentrations of UDMH in air was based upon the change of electrical resistivity of thin metal films when exposed to propellant vapors [478]. Sensitized gold metal films coated with appropriate salts were found to be optimum for UDMH. UDMH could be monitored over the range of 0.1 to 50 ppm with a standard deviation of about 20%. The effects of temperature over the

range of 323 to 363 K (50 to 90°C) and of humidity from 10 to 90% R.H. on the response characteristics of the thin film sensors were found to be significant but within the tolerance limits. A portable breadboard direct readout instrument was designed and fabricated for use with the sensors to form an integrated detection system for personal protection.

### Continuous Analysis of UDMH Vapor in Ambient Air

During the 1960s when UDMH and Aerozine-50 were introduced as fuels in various missile and launch vehicle systems, there was an acute need for air monitors that would both provide an instant readout for continuous recording and also sound an alarm if an allowable threshold concentration was exceeded. For the installation in Titan-2 missile silos, the difficulty was that the sensors had to be able to discriminate and/or operate in spite of the potential simultaneous presence of nitrogen dioxide from a leak of the oxidizer in the missile.

Infrared spectrophotometric instruments can be tuned to specific wavelengths where absorption bands for propellant vapors are known to exist. These instruments can detect more than one propellant at a time [479].

A variety of instruments were evaluated for this purpose but not all led to reliable and reproducible results [480]. Calibration and maintenance of these instruments became a time-consuming operation.

Multiple ("frustrated") internal reflection is a method to achieve very long-path-lengths in a cell with manageable (if not even portable) external dimensions. One such instrument detected UDMH at the 0.5 ppm level [481]. If UDMH vapor or vapor from other airborne hydrazines condenses on the surfaces of a cooled KRS-5 crystal in an IR spectrophotometer, multiple internal reflections allow the measurement of IR spectra of very thin films of condensate. At 12.4  $\mu\text{m}$ , UDMH has a strong and specific absorption band that is suitable for the detection of traces of UDMH (down to 5 ppm) in air [482]. There have been attempts to increase the sensitivity by coating the crystal with an absorbent film of low volatility (naphthyl isocyanate). The sensitivity was increased by two orders of magnitude; nonetheless, the signal was persistent after the first alarm and the crystal had to be cleaned and recoated to restore the stand-by operating condition.

During preliminary testing of a conductive polymer-based hydrazine sensor, the sensor showed promise as a dosimeter with the ability to detect hydrazine and UDMH at levels well below the threshold limit value (TLV) of 10 parts per billion (ppb) [483–485]. The original sensor demonstrated a minimum detectable dose of approximately one part per billion  $\times$  hour (ppb  $\times$  h) and a saturation dose of approximately 250 ppb  $\times$  h in dry conditions, offering adequate coverage of the TLV limit of 80 ppb  $\times$  h (eight hours at 10 ppb).

Electrically conductive polyaniline-coated fibers have been prepared by polymerization of aniline on surfaces of commercial polymer fibers in the presence of an oxidizing agent and used for the detection of UDMH vapors in the air [486]. The changes in

resistance of a polyaniline-coated fiber sensor were investigated and related to coating conditions. The morphology of the conducting film on the surface of the fibers was examined by SEM. The sensing behavior of a polyaniline-coated fiber sensor in the presence of other volatile organic compounds was studied experimentally. A polyaniline-coated fiber sensor demonstrated good sensitivity for UDMH and good reproducibility when re-used.

### Calibration of UDMH Vapor Detectors

Calibration of vapor detectors must be repeated frequently; the accuracy of the instruments are only as good as the accuracy of their calibration. Permeation tubes are commonly used to generate a constant flow of vapors in the air, followed by cascading dilution circuits to bring the original concentration of vapor from the temperature-controlled permeation device down to the sensitivity range of the instruments.

A study of the effect of temperature on the permeation rate for UDMH, MMH, and Hz permeation tubes showed that the variation of logarithm of permeation rate with the temperature is linear between 298 and 313 K (25–40 °C) [487]. The changes of their permeation rates were 0.65, 0.6, and 0.76% for UDMH, MMH, and Hz, respectively, when the temperature fluctuation was only 0.1 °C. The permeation rate slowly returned to the original value after brief and small temperature excursions.

A UDMH permeation tube with a permeation rate of 0.5–30.5 µg/min was prepared with high-purity UDMH as the raw material [488]. The instrument was monitored for homogeneity and stability for 13 months.

A dynamic hydrazine vapor generator, in which high-purity GN<sub>2</sub> served as the diluent gas, can develop standard hydrazine vapor concentrations using accurate amounts of hydrazine liquid injected continuously into the gas stream and an evaporator using a metering pump [489]. This equipment was able to make standard hydrazine vapor mixtures from 0.1–100 volume ppm under certain conditions.

The operating principle of UDMH vapor dynamic gas mixing equipment was examined for linearity, repeatability, and stability of the equipment [490]. The dynamic gas mixing equipment can generate hydrazine vapor mixtures of 0.1–100 ppm under carefully controlled conditions such as constant surrounding temperature, regular flow, and temperature of diluent gas.

#### 1.4.11.11 Analysis of UDMH in Food Stuff

Several decades ago, the use of succinic acid dimethylhydrazide, daminozide, and “Alar®” on apple trees in orchards and the presence of UDMH as a hydrolysis product had created a controversy between environmentalists and apple growers about the safe levels of residual daminozide and UDMH on fruit. Therefore, methods for the analysis of hydrazine residues on food crops had to be standardized. The US National Bureau of Standards has compiled a summary of recommended methods for the analysis of hydrazines on crops [491].

#### 1.4.11.12 Analysis of UDMH Decomposition Products from a Gas Generator

UDMH can be used as a monopropellant and gas generant, although the exhaust is very dirty. UDMH gas generators have been used to run turbines that drive the propellant pumps in missiles and launch vehicles that used NTO/UDMH. These gas generators usually are started with a hypergolic oxidizer and then operate extremely fuel-rich.

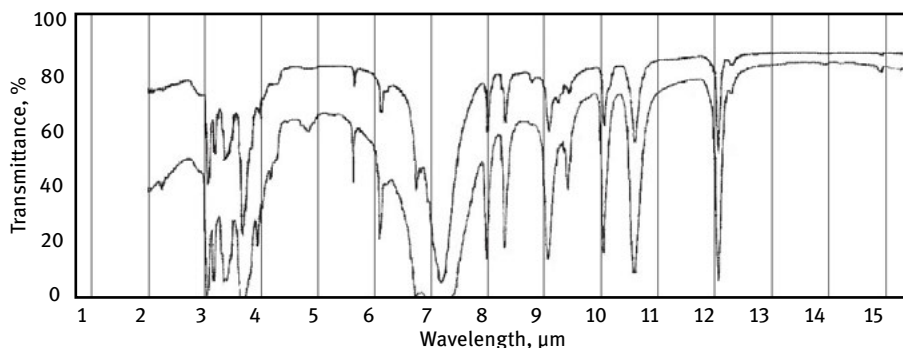
Besides the analysis of alkylhydrazines in various matrices, sometimes chemists need to analyze UDMH decomposition products consisting mostly of methane, ammonia, nitrogen, and hydrogen, depending on the degree of ammonia and methane dissociation. The ammonia dissociation is often a design variable in the design of rocket engines (see *Encyclopedia of Monopropellants*). The thermal decomposition products of UDMH in a thermal bed gas generator constitute a very unpleasant mixture of gases that are difficult to analyze. IR analysis showed the mixture to contain ammonia, methane, hydrogen cyanide, and small amounts of ethane, ethylene, and propane but no alkylamines [492]. The ammonia concentration could be calculated from the absorbances at 6.1, 10.31, and 10.7  $\mu\text{m}$ . A combination of absorptions at 3.15, 3.28, 3.34, and 10.50  $\mu\text{m}$  was used to mathematically derive the methane, ethane, ethylene, and propane concentrations. The hydrogen cyanide content was found directly from the absorption at 13.77 to 14.03  $\mu\text{m}$ .

#### 1.4.12 Salts of Unsymmetrical Dimethylhydrazine

Dimethylhydrazines form salts with strong acids. The salt of major concern is *N,N*-dimethylhydrazinium(1+) nitrate,  $[(\text{H}_3\text{C})_2\text{NHNH}_2]^+[\text{NO}_3]^-$ ,  $(\text{H}_3\text{C})_2\text{NHNH}_2\text{NO}_3$ , UDMHN,  $\text{C}_2\text{H}_5\text{N}_3\text{O}_3$ ,  $M = 123.11 \text{ g/mol}$ , 8.1228 mol/kg. This sometimes forms inadvertently from residual bipropellants in NTO/UDMH thrusters from the dribble volume after the engine has shut down. Under adverse conditions, the salt may accumulate in the engine and explode the next time the engine is operated resulting in severe pressure spikes. It may also fog up nearby solar panels or camera windows. An IR spectrum of dimethylhydrazinium(1+) nitrate is shown in Figure 17.

The heats of combustion of *N,N*-dimethylhydrazinium nitrate,  $[(\text{H}_3\text{C})_2\text{NHNH}_2][\text{NO}_3]$  were determined experimentally and calculated thermodynamically [494]. The agreement between the experimental and theoretical values (in parentheses) was very satisfactory: +1824 (+1739) kJ/mol = 14820 (14125) kJ/kg = 3542 (3376) kcal/kg.

UDMHN crystals are deliquescent and hygroscopic. Water that has been co-ordinated to the molecules cannot be removed in a vacuum, and heating under a vacuum results in decomposition. Longer storage under atmospheric conditions leads to yellow or even brown liquids. Dry 1,1-dimethylhydrazinium nitrate forms orthorhombic crystals, space group  $Pna2_1$  with the unit cell parameters of  $a = 14.0388(4) \text{ \AA}$ ,  $b = 5.6493(1) \text{ \AA}$ ,  $c = 7.6026(2) \text{ \AA}$ ,  $\beta = 90^\circ$ ,  $V = 602.96(3) \text{ \AA}^3$ ,  $Z = 4$ , and  $\rho_{\text{XRD}} = 1.35620(7) \text{ g/cm}^3$  [495]. The arrangement of dimethylhydrazinium ions and nitrate ions in the crystal lattice has been illustrated in an Oak Ridge Thermal



**Figure 17:** Infrared spectrum of dimethylhydrazinium(1+) nitrate in a KBr pellet. (Reproduced and modified from [493].)

Ellipsoid Plot (ORTEP) plot together with bond lengths. UDMHN demonstrated poor sensitivity towards shock or friction. No detonation was observed in the drop hammer impact sensitivity test. Also, no detonation was observed when grinding the compounds in a mortar. UDMHN was insensitive to an electric discharge of about 20 kV. Fast heating with a Bunsen burner resulted in melting, and at higher temperatures, in a vigorous decomposition under gas evolution. Slow heating led to a slow decomposition at temperatures higher than 333 K (60 °C).

*N,N*-Dimethylhydrazinium dicyanamidate and nitrocyanamidate ionic liquids were prepared by quaternization of UDMH with alkyl halides, followed by metathetical reactions with silver dicyanamidate or silver nitrocyanamidate [496]. These liquids are hypergolic with RFNA. Other ionic liquids were formed from UDMH and arylheteroacetic acids [497].

1,1-Dimethylhydrazinium azide,  $[(\text{H}_3\text{C})_2\text{N}^+\text{H}-\text{NH}_2][\text{N}_3]^-$ , UDMHAz, is a potential by-product of a partial reaction of UDMH with NTO. 1,1-Dimethylhydrazinium azide was prepared from UDMH and  $\text{HN}_3$  in  $\text{CH}_2\text{Cl}_2$  solution at 253 K (−20 °C). The resulting white precipitate was filtered off, dried, and stored in the freezer at 255 K (−18 °C). The crystals with a melting point of 311 K (38 °C) were characterized by elemental analysis, multi-nuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ), and vibrational spectroscopy (IR, Raman) [498]. The structure of the monoclinic crystals was determined by low-temperature (173 K) single-crystal XRD analysis and the unit cell parameters were  $a = 8.5411(2)$  Å,  $b = 7.0415(2)$  Å,  $c = 10.0878(1)$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 108.321^\circ$ , space group  $P2(1)/n$ ,  $Z = 4$ , and  $\rho_{\text{XRD}} = 1.205 \text{ g/cm}^3$ . Preliminary studies exploring the safety properties of UDMHAz revealed low impact sensitivity, electrostatic sensitivity, thermal sensitivity, and some friction sensitivity. Similar tests were performed for methylhydrazinium azide [499].

The hydrogen-bonded dimethylhydrazinium and azide ions form layers. The methyl groups of the dimethylhydrazinium ions are above and below these layers

so that two methyl groups are between each layer. Dimethylhydrazinium(1+) azide was found to have almost no sensitivity towards shock or friction. No detonation was observed after dropping a weight of 5 kg from 50 cm onto this compound, nor was any detonation observed when grinding the compound in a mortar. The  $\text{HN}_3$  salts of MMH or UDMH did not explode when heated with a heating rate of about  $10^\circ\text{C}/\text{min}$ . They sublimed away from the heat source. An explosion can only be started by a strong heat source, such as with a hot metal plate or a Bunsen burner. The more methyl groups that are attached to the hydrazinium ion, the fiercer the explosion gets. Methylhydrazinium azide and *N,N*-dimethylhydrazinium azide demonstrated the same properties, while trimethyl- and tetramethylhydrazinium azide had much bigger explosions.

Methylhydrazinium azides are all sensitive to oxidation. The oxidation is faster in compounds where more methyl groups are present. Methylhydrazinium azide is hygroscopic but can be stored in air for several minutes before a color change occurs, while the liquid  $\text{HN}_3$  salts turn brown immediately and form black residues in minutes.

Alkylhydrazinium azides were prepared by reacting the anhydrous alkylhydrazines with a solution of hydrazoic acid in ether [500, 501]. As more and more methyl groups are attached to hydrazine, the melting point of the  $\text{HN}_3$  salt decreases. Some are liquids at room temperature. The volatility of the compound also increases. With more methyl groups the elimination of  $\text{HN}_3$  from the molecule gets easier. Tetramethylhydrazinium azide will eliminate  $\text{HN}_3$  at room temperature. If a permethylated nitrogen atom is present, the molecule can no longer eliminate  $\text{HN}_3$ . Alkylhydrazinium azides with quaternized and permethylated nitrogen atoms can be synthesized via anion exchange from the corresponding alkylhydrazinium iodide with silver azide.

The reaction of 1,1-dimethylhydrazine with a solution of HCl in  $\text{Et}_2\text{O}$  results in the formation of an anhydrous salt  $(\text{H}_3\text{C})_2\text{N}(\text{H}^+)\text{NH}_2\cdot\text{Cl}^-$  in the form of needle-shaped, light orange, monoclinic crystals, space group  $P2_1/n$  [502]. The crystal structure, determined by XRD analysis, consists of two independent  $[(\text{H}_3\text{C})_2\text{NHNH}_2]^+$  cations and two  $\text{Cl}^-$  anions that are connected via hydrogen bonds. Unit cell parameters were  $a = 9.7305(9) \text{ \AA}$ ,  $b = 10.5319(10) \text{ \AA}$ ,  $c = 10.4759(10) \text{ \AA}$ ,  $T = 193 \text{ K}$ ,  $\beta = 90.475(11)^\circ$ ,  $V = 1073.54(18) \text{ \AA}^3$ ,  $Z = 8$ , and  $\rho_{\text{XRD}} = 1.195 \text{ g/cm}^3$ .

Most organic amines and hydrazines can be isolated and characterized in the form of their poorly soluble and well-crystallized picrate salts. UDMH (0.02 mol) was slowly added to a solution of picric acid (0.02 mol) in 30 mL ethanol at room temperature [503]. Single monoclinic crystals, space group  $C2/c$ , that are suitable for XRD structure analysis were obtained by slowly evaporating a distilled water solution of UDMH picrate at room temperature. The unit cell parameters were  $a = 14.2038(17) \text{ \AA}$ ,  $b = 8.1932(10) \text{ \AA}$ ,  $c = 21.233(3) \text{ \AA}$ ,  $T = 296 \text{ K}$ ,  $\beta = 98.298(2)^\circ$ ,  $V = 2445.1(5) \text{ \AA}^3$ ,  $Z = 8$ , and  $\rho_{\text{XRD}} = 1.571 \text{ g/m}^3$ .

UDMH oxalate is poorly soluble in water and well crystallized. It can be used for the separation of UDMH and for fission product separation in nuclear fuel element



reprocessing [504]. It is known that hydrazinium nitrate is used for nuclear fuel element reprocessing in the PUREX process, however, it is not known why UDMH oxalate should have an advantage over hydrazinium salts in that application. UDMH oxalate has been characterized and tested for fuel element cladding (Zr) separation from the fission products [505].

The crystal structures of 1,1-dimethylhydrazinium(1+) bromide,  $\text{C}_2\text{H}_9\text{N}_2^+ \cdot \text{Br}^-$ , (**I**), and 2,2-dimethylhydrazinium(1+) dihydrogen phosphite,  $\text{C}_2\text{H}_9\text{N}_2^+ \cdot \text{H}_2\text{PO}_3^-$ , (**II**) were determined by XRD [506]. In (**I**), the cation is protonated at the methylated N atom.  $\text{N}-\text{H} \cdots \text{Br}$  hydrogen bonds generate [010] chains in the crystal. In (**II**), the cation is protonated at the terminal N atom. The cation-to-anion  $\text{N}-\text{H} \cdots \text{O}$  and anion-to-anion  $\text{O}-\text{H}-\text{O}$  hydrogen bonds generate (001) layers.

## 1.5 Materials of Construction for Unsymmetrical Dimethylhydrazine

Experimental methods for determining the compatibility of hydrazine(s) fuels with materials of construction have already been detailed in *Encyclopedia of Liquid Fuels* within the chapter “Hydrazine.” Methods that have been successfully used for hydrazine  $\text{N}_2\text{H}_4$  can equally well be used for determining material compatibility with UDMH or MMH.

Quite often, data may be available for one of the three propellant hydrazines but not for the hydrazine of interest. To a limited extent, it is possible to extrapolate metal compatibility data from one hydrazine to another. For metallic materials, extrapolation is easier than for non-metals. Metals found to be compatible with hydrazine will most likely also be compatible with MMH and UDMH. Similarly, metals found to be compatible with MMH will most likely also be compatible with UDMH. Polymeric organic materials are more likely to swell in UDMH than in MMH or hydrazine.

### 1.5.1 UDMH Compatibility with Metals

Corrosion rate determinations were made on several metals for 28 d at 303 K (30 °C = 86 °F) or for 7 d at 436 K (63 °C = 146 °F), which is the UDMH reflux temperature [507]. The metals shown to be satisfactory in these tests were the 300-series stainless steels, CRES-416, CRES-422, CRES-A286, CRES-4130, 15-7PH, and 17-7PH. Hastelloys-B, -C, -F, and -X and commercially pure titanium. Its alloys, C120AV and B120VCA, were also acceptable. Elastomers and plastics that were compatible with UDMH included butyl rubbers, Hydropol-T, Teflon, unplasticized Kel-F, and polyethylene. Corrosion rates in all these metals were generally  $7.6 \mu\text{m/yr}$  (0.3 mil/yr) or less. Aluminum 1260-H14 was strongly attacked by UDMH-water mixtures but not by anhydrous UDMH. Components for UDMH production facilities were initially made from stainless steel. However, as time passed and more experience was gained and the Westvaco plant for the production of UDMH was enlarged, storage and shipping containers were changed

to mild steel (e.g., mild steel ICC-17C drums). Unsymmetrical dimethylhydrazine was stored without corrosion for 18–25 months in mild steel 55-gal drums in Baltimore, MD. The UDMH analyzed after this storage was still clear and colorless. Several drums were cut open and showed no internal corrosion. Both UDMH and UDMH-JP4 mixtures (JP-X and M-3) have been stored for several years in missile propellant tanks, such as aluminum 6061-T6 tanks in the BOMARC, VANGUARD-ABLE, THOR-ABLE, and NIKE-AJAX; UDMH-amine mixtures for the JUPITER-C satellite launcher were transported in Al-5052 tank cars. Aluminum-6066-T4 was used for BULLPUP, and other aluminum alloys were used for AGENA tanks. Compatibility data for UDMH or Aerozine-50 are summarized in Table 15.

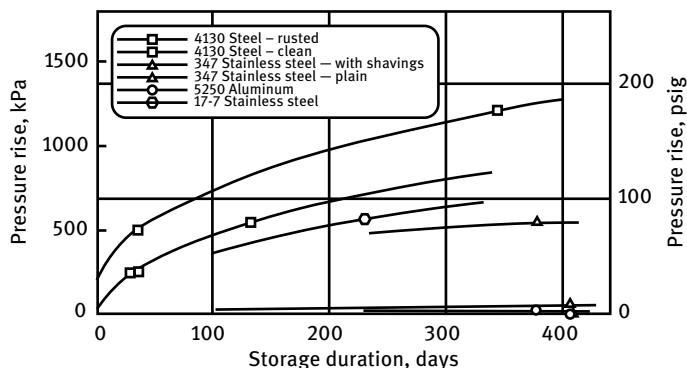
**Table 15:** Literature references regarding the compatibility of metals with UDMH and Aerozine-50.

| Material    | Gas evolution | Corrosion rates |       | Stress-corrosion fracture |                 | Weight change |
|-------------|---------------|-----------------|-------|---------------------------|-----------------|---------------|
|             | Ae-50         | UDMH            | Ae-50 | UDMH                      | Ae-50           | UDMH          |
| Al-1260-H14 | —             | [507]           | —     | —                         | —               | —             |
| Al-2014-T6  | —             | [507]           | [508] | [509]                     | —               | [508]         |
| Al-6061-T6  | —             | —               | —     | [510]                     | [510]           | —             |
| CRES-304L   | —             | [507]           | —     | [509]                     | —               | —             |
| CRES-410    | —             | —               | —     | [510]                     | [510]           | —             |
| CRES-416    | —             | [507]           | —     | —                         | —               | —             |
| CRES-422    | —             | [507]           | —     | —                         | —               | —             |
| AISI-4130   | —             | [507]           | —     | —                         | [510]           | —             |
| A-286       | —             | [507]           | —     | —                         | —               | —             |
| 15-7PH      | —             | [507]           | —     | —                         | —               | —             |
| 17-7PH      | —             | [507]           | —     | —                         | —               | —             |
| Inconel 718 | —             | —               | —     | —                         | [510]           | —             |
| Hastelloy-B | —             | [507]           | —     | —                         | —               | —             |
| Hastelloy-X | —             | [507]           | —     | —                         | —               | —             |
| Hastelloy-C | —             | [507]           | —     | —                         | —               | —             |
| Ti-6Al-4V   | [511]         | [507]           | [511] | [509, 512]                | [510, 513, 514] | —             |
| Ti-C120     | —             | [507]           | —     | —                         | —               | —             |

While searching for materials for advanced spacecraft valves, several hundred literature references on 21 different propellants that were in use as of 1967, or were anticipated to be used within the next ten years (including UDMH), were assembled [515]. However, the report by Salvinski, Howell and Lee (1967) on pages 1–24 through 1–27 only lists compatibility materials and temperatures and not the duration of immersion [515]. Similar data are on pages 3–21 through 3–25 of [516].

One indication of material incompatibility is gas evolution. There are many UDMH compatibility tests where gas evolution rates were measured. One example is shown in Figure 18, although this example, unfortunately, does not include the most common

stainless steel, CRES-304. The graph demonstrates that rusted steel is much worse than clean steel and that adding surface area in the form of shavings also increases the rate of gas evolution. Similar data are available for MMH. The source from which this second-hand information was taken failed to provide the surface:volume ratio and ullage ratio for this type of test. The original source of the data was [102]. This report was confidential and is difficult to obtain (see also [517]).



**Figure 18:** Pressure rise during UDMH storage at 344 K (71°C). (Reproduced and modified from [95].)

### 1.5.2 Stress-Corrosion Cracking in UDMH

UDMH prepared using the Raschig or chloramine process may contain varying amounts of chloride as a contaminant. Residual cleaning fluids such as Freon-TF may react with UDMH, leading to a release of chloride. Both sources of chloride may lead to stress-corrosion cracking of tankage materials holding UDMH. Stress-corrosion cracking tests of Al-2014-T6, CRES-304L, and Ti-6Al-4V in UDMH containing varying levels of chloride ion up to 100 ppm revealed that even the highest  $\text{Cl}^-$  level tested had no adverse effect on the sustained load crack growth of any of the three alloys [509]. This was of particular significance for the titanium alloy, which (in other fluids) is sensitive to chloride contaminations of the order of 1 ppm. Since no effects were observed at 100 ppm  $\text{Cl}^-$  in UDMH, a specification limit maximum of 30 ppm for  $\text{Cl}^-$  in UDMH seemed to provide a sufficient margin for safety. Part-through cracked or surface-cracked specimens loaded in uniaxial tension were used because they simulate real cracks in tanks under internal pressure load conditions. The specimens were notched in the center of each test section prior to the test. From this notch, an initial crack was started by cyclically stressing the notch in bending. Only then was the UDMH exposure commenced to study additional crack propagation.

The steel alloy AISI 4130 – a high-strength, low-alloy material – was selected as a test material because it is known to be highly susceptible to stress corrosion in several corrosive fluids [510]. Although AISI 4130 is generally not recommended for an-

hydrous hydrazine service because it rusts too easily, it is compatible with MMH and UDMH, based on static compatibility test results. In addition to 4130, for which stress corrosion in contaminated hydrazines was not unexpected, several other alloys, stainless steel 410, titanium-6Al-4V, aluminum-6061-T6, and Inconel-718 were also tested for stress-corrosion susceptibility. These alloys are more frequently used in components where they are wetted by UDMH. The metal specimens were pre-cracked by fatiguing, and then a tapered plug was inserted to load the stressed area. The plug was not immersed in the liquid. The liquid level reached only to and above the pre-cracked area. With 4130, no crack extension occurred in UDMH up to at least 2000 h. MMH caused growth after 500 h and hydrazine caused growth after about 60 h. Aerozine had about the same effect on 4130 as straight hydrazine. Methylhydrazine was more active than UDMH. The alloys mentioned can be ranked in the following order of decreasing susceptibility to stress corrosion: 4130 steel, CRES-410, Inconel-718, Ti-6Al-4V, and Al-6061-T6. In the tests conducted at NASA Ames, no crack growth was observed with Ti-6Al-4V, but other investigators using different sample geometries observed stress-corrosion cracking of this material in Aerozine-50 [513, 514].

Several high-toughness steels, including T-1, HY-140, HP-9-4-20, and 18Ni(200) maraging steel (that do stress corrode and crack in seawater), did not show stress corrosion in (presumably pure) UDMH at 322 K ( $49^{\circ}\text{C} = 120^{\circ}\text{F}$ ) [518]. Aluminum alloy LD10 double cantilever beam specimens were corroded under the conditions of UDMH,  $\text{N}_2\text{O}_4$ , or 3.5% NaCl aqueous solution immersion [519]. There were no stress-corrosion phenomena observed in UDMH.

### 1.5.3 UDMH Compatibility with Non-Metallic Materials

Polymers found to be compatible with MMH will most likely also be compatible with UDMH and hydrazine. Similarly, polymers known to be compatible with hydrazine may dissolve or swell in either MMH or UDMH.

The influence of the contact time of UDMH with styrene-butadiene rubber (SBR) on the tensile properties of SBR under certain temperature conditions was studied through immersion aging tests [520]. The results demonstrated that change rates of the tensile strength and elongation at break of SBR after soaking decrease logarithmically with prolongation of the soaking time. A major reason for the decrease of tensile properties of SBR is swelling. UDMH may leach plasticizers, such as phthalates and phosphate esters, from non-metallic materials of construction it comes into contact with [521].

### 1.5.4 Tubing for UDMH Vapor Samplers

The selection of materials for the propellant vapor manifold for remote sampling of UDMH vapors in rocket launch sites or in animal inhalation toxicity test chambers required a special study. There was not much concern about UDMH inadvertently destroying the tubing; instead, concern was raised about low vapor concentration

samples hanging up in the tubing on their way from the sampling location to a central analyzer. The plastics tested for UDMH sampling included polyethylene-lined ethyl vinyl acetate, high-density polyethylene (HDPE), polypropylene, Teflon TFE (polytetrafluoroethylene), Teflon FEP (polytetrafluoroethylene- polyhexafluoropropylene), and Teflon PFA (polytetrafluoroethylene-perfluoropropyl vinyl ether). Sample lengths of 23 and 61 m were investigated for their effect on performance [522, 523]. All tubing performed about equal with regard to sample retention, response time, and ease of cleanout with methanol. While the polyethylene-lined ethyl vinyl acetate tubing appeared most suitable for MMH, Teflon FEP, and HDPE performed best for UDMH sampling.

Unrecognized vapor loss by permeation and oxidation in incompatible plastic tubing has thrown some doubt on the validity of animal inhalation toxicity tests with hydrazine(s). These test data were later used as a reason for lowering TLV-TWA values in the 1990s without further examination of their accuracy.

### 1.5.5 Storage Tests with UDMH Blends

MAF-4 is a mixture of 60 UDMH/40 DETA. MAF-4 was previously known as “U-DETA” and “Hydyne.” The storability of MAF-4 in pre-packaged missile tanks was critically examined after an explosion caused by the adjacent IRFNA oxidizer tank when it was stored in a hot climate [524].

## 1.6 Handling of UDMH

### 1.6.1 Storage, Transportation, and Handling of UDMH

There are numerous reports and handbooks regarding the storage and handling of UDMH, usually in combination with details of using its most important propellant blend, Aerozine-50 (see also [525, 526]). Hydrazine, MMH, and UDMH were once shipped (and are sometimes still shipped) in containers of the type listed in *Encyclopedia of Liquid Fuels* within the chapter titled “Hydrazine” (Table 73). The US Army used trailer tank trucks to move UDMH and MAF fuels to the front lines to service the LANCE and BULLPUP missiles [527–529].

### 1.6.2 Leak Detection of UDMH

UDMH vapors from leaks in storage areas can be detected by the same active instruments that are also used to monitor UDMH concentrations in the air within workspaces where personnel might be exposed.

If UDMH storage systems are painted with a paint that changes color with UDMH exposure, propellant leaks can be quickly located, and corrective action can be taken. This leak detection method also works in areas where no electricity is available.

Lacquers and enamels were developed that undergo vivid color changes upon being exposed to propellants containing substituted hydrazines, nitric acids, or elemental halogens [530].

### 1.6.3 UDMH Propellant Spills

#### 1.6.3.1 Accidental UDMH Spills

Despite all the care that is devoted to planning and conducting the storage and transfer of hydrazines, occasional spills may still occur. Several reports about spills of rocket propellants and poisoning accidents in the former USSR were mostly concerned with spills of the oxidizer, dinitrogen tetroxide, judging by the red color of the clouds that are often shown in the photo/video coverage of these events.

#### 1.6.3.2 Controlled Spill Tests

As part of the Titan-II development program, the USAF performed controlled deliberate spill tests with both  $N_2O_4$  and Aerozine-50, simulating a worst-case scenario [531]. Twenty model missile spills using total propellant quantities of 50 and 300 lb and two large-scale spills using total propellant quantities up to 1600 lb were made at Haystack Butte, Edwards AFB. The Titan II propellants,  $N_2O_4$  and Ae-50, were also spilled in quantities up to 2.5 lb of total propellant in a series of small-scale tests. A biological study of the impact on surrounding biota was performed on one large-scale test.

#### 1.6.3.3 Modeling of Atmospheric Dispersion of UDMH Vapors

Chapter “Hydrazine” in this *Encyclopedia of Liquid Fuels* contains a fairly detailed summary of studies and computer models for predicting the rate of evaporation and atmospheric dispersion of UDMH spills in addition to similar studies for hydrazine itself, MMH, Ae-50, and NTO. Only a few of these models include degradation of UDMH vapors by autoxidation, photolysis, or adsorption on aerosol particles in the air.

A computerized evaporation algorithm predicts the rate of evaporation from propellant spills as a function of soil temperature, solar insolation, air temperature, wind velocity, and spill dimension [532, 533]. The model allows for the absorption of water and carbon dioxide from the atmosphere into a liquid puddle that would slow the rate of evaporation. It will also provide a calculation of the amount of water required to dilute a spill below hazardous concentrations. In some instances, such as in massive Titan-III or Titan-IV launch failures, the toxic vapor/toxic aerosol plume is a mixture of solid propellant combustion products containing hydrogen chloride and aluminum oxide with the unreacted dinitrogen tetroxide and Aerozine-50 from the liquid stages. Modeling atmospheric diffusion of plumes of this nature is a very complex task [534, 535]. Some reactions continue to occur on the aluminum oxide particles while they disperse and descend.

Sample calculations for 200-L (drum), 20000-L (trailer), and 36000-L (rail car)  $N_2H_4$ , MMH, and UDMH spills at three different ambient temperatures (273, 288, and

303 K) showed that in the case of a 36000-L spill, the hazard corridor would reach 480 m downwind for hydrazine, 1380 m for MMH, and 680 m for UDMH. The rate of evaporation from a liquid pool is

$$\dot{m} = k_m \frac{P_v M A}{R T_p}$$

where  $\dot{m}$  is the mass flow (kg/h),  $k_m$ , the mass transfer coefficient (m/h),  $P_v$ , the vapor pressure (kPa),  $A$ , the spill area (m<sup>2</sup>),  $R$ , the universal gas constant (8.314 kPa m<sup>3</sup> kg<sup>-1</sup> mol<sup>-1</sup> K<sup>-1</sup>),  $M$ , the molecular weight, and  $T_p$  = temperature of pool (K). Allowances were made for composition changes in the remaining pool due to preferential evaporation of a more volatile constituent of a mixture, absorption of water from the atmosphere, and both absorption of and reaction with carbon dioxide from the atmosphere. The evaporation rates of UDMH and MMH for similar meteorological and spill conditions are 11 and three times that of hydrazine, respectively. A comparison of predicted and experimentally observed evaporation rates revealed good agreement for the first hour of the experiment.

The launch abort problem, such as for a Titan-III or Titan-IV launch mishap, is especially difficult because there are separate initial clouds of fuel and oxidizer with regions between them where fuel and oxidizer are mixing and reacting. Attempts were made to deal with this problem using a “multi-bin” approach, which treated the fuel and oxidizer and an interface as separate bins but kept the computation tractable [536]. The computer program was based on SURFACE CHEMKIN, a standard chemical kinetic subroutine package [537]. The model results showed that the outcome is highly dependent on initial conditions. For instance, a likely scenario for a Titan-IV accident will result in 24% of the initial oxidizer remaining, of which at least half is transformed into nitric acid. Two-percent of the initial fuel is expected to remain.

The determination of a hazard corridor following a hydrazine or UDMH spill involves two separate calculations [538, 539]. First, an estimate of the evaporation rate (“source strength”) must be calculated [540]. Then an atmospheric diffusion model must be employed to predict the downwind distance required to dilute that source strength to a concentration that is considered to be tolerable. Computer models are available that will predict the concentration-time profile of the vapor plume as the function of ten input parameters. Constants that are part of the equations have been determined for UDMH, MMH, hydrazine, and H-70.

Concentrations and the dispersion of UDMH vapor clouds formed by non-burning propellant that splashed onto the ground and evaporated then diffused after a launch failure of a liquid propellant launch vehicle can be predicted using an analytical model depending on launch site environment and weather conditions [541]. Predictions from a theoretical model of liquid rocket propellant vaporization rates for the source strength were compared to experimental results of the evaporation rate of UDMH in the natural environment [542].

The rate of evaporation from a UDMH leak that formed a liquid pool on the ground was measured as a function of variables, such as pool area, wind speed, temperature, and humidity [543]. An evaporation model was developed for predicting the downwind concentration of hazardous vapors in the event of a leak.

#### 1.6.3.4 Upper Stage Venting of Unused Propellants

The evaporation of NTO or UDMH in ambient air after residual propellants were dumped overboard from an upper stage is fast enough that droplets most likely will not reach the ground [544, 545]. The aerodynamic heating during the re-entry of upper stages is sufficient to vaporize and ignite residual UDMH in the propellant tanks. The concern about spills of unused propellants from re-entering second stages persists [546]. But most of the UDMH is scattered at impact areas from spent lower stages of launch vehicles in Kazakhstan.

To reduce the creation of space debris, and to minimize the chance of residual propellant impacting the surface, the residual propellants in upper stages have to be discharged after satellite-rocket separation. An analysis revealed that the propellant jets under the discharge conditions, once it has entered space, will break up into a large number of liquid droplets [547–549]. The droplets diffuse in a high vacuum, while gaseous molecules successively evaporate from the droplet surfaces. This process yields a rarefied vapor and droplet field around the final-stage rocket. The model was applied to three-dimensional rarefied vapor and droplet plumes arising from original and new, modified methods for in-orbit discharging of the residual UDMH fuel in a CZ-4B final-stage rocket. The calculation showed that the original venting method may lead to quite large disturbance moments beyond the rocket attitude-control recovery range, whereas the new venting method induced only very small disturbance moments.

The temperature changes of UDMH droplets, ejected into the upper atmosphere after the depressurization of upper stage fuel tanks, were modeled, taking into account the temperature gradient in the air after the depressurization of the fuel tanks at high altitude [550]. Falling droplets will assume spherical shapes. The temperature of the droplets is dependent on ambient temperature, pressure, droplet size, rate of evaporation, and heat transfer coefficient. The temperature of the small size droplets will be the same as the temperature of the atmosphere at altitudes of up to 40 kilometers.

#### 1.6.3.5 UDMH Contamination at Impact Sites of Spent Stages

Residual UDMH in the fuel tanks of Proton launch vehicles in Kazakhstan has caused widespread pollution when the spent stages impact the ground and may be responsible for health problems of people living near the designated impact areas [551].

Snow pollution from residual rocket propellants, UDMH and NTO, and their transformation products ([NDMA,  $(\text{CH}_3)_2\text{NNO}$ , nitrate  $\text{NO}_3^-$ , nitrite  $\text{NO}_2^-$ , and ammonium  $\text{NH}_4^+$ ]) within the impact regions of the first and second stages of Proton-M rockets launched from the Baikonur Cosmodrome were measured [552]. At the first stage in



the impact region in Central Kazakhstan, snow with a pH range from 1.7 to 9.0 was contaminated by *N*-containing substances in concentrations up to UDMH 0.27 g/L, NDMA 0.04 g/L,  $\text{NO}_3^-$  19 g/L,  $\text{NH}_4^+$  0.04 g/L, and  $\text{NO}_2^-$  0.13 g/L. The combined pollution in snow reached 81.6 g/m<sup>2</sup>. In the second stage, toxic substances released by rockets could not be detected in the impact region in the NE Altai, and the concentrations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  corresponded to the natural background levels.

The pre-impact plant communities in the Baikonur Cosmodrome area were inventoried to estimate their chance of survival under the conditions of spent rocket impacts [553]. The potential resistance of plant communities to the impact of rocket launch activities has been estimated, and the plants were categorized in three groups: weakly resistant phytocenoses, comparatively resistant phytocenoses, and contamination-resistant plant communities.

The post-impact natural return of vegetation to the crash site of a Proton-M launch vehicle near Baikonur Cosmodrome in the Republic of Kazakhstan was investigated [554]. The crash site area was sub divided into zones defined by differences in the character and intensity of disturbance. Since a launch failure in 2013, several field trips and geobotanical assessments were carried out in 2014 and 2017. Photos taken several years apart showed the gradual return of seasonal and perennial low tundra plants and bushes to the area. The contaminated topsoil of the immediate impact area had already been removed. Only the zone of total destruction of vegetation and zone of pyrogenic transformation still showed high levels of plant community modification.

#### 1.6.3.6 Decontamination of UDMH Spills

In one of the first thorough studies on UDMH (and hydrazine) spill decontamination, 94 different chemicals were reviewed for their suitability as spill control agents [555]. Eight solids were tested as decontaminants for 96%  $\text{N}_2\text{H}_4$  by dumping 5 g of solid onto 5 g of fuel. In the case of dry HTH, the mixture promptly ignited. There is considerably less information on the chemical decontamination of MMH or UDMH spills than on the treatment of hydrazine spills. Because UDMH boils at a lower temperature, unreacted UDMH is readily emitted from reacting solutions if the spill control agent ( $\text{NaOCl}$ ,  $\text{H}_2\text{O}_2$ ) concentration is too high. Five percent  $\text{NaOCl}$  or 30%  $\text{H}_2\text{O}_2$  will cause the mixture to boil in a few seconds. Lower concentrations, at 1%  $\text{NaOCl}$  or 5%  $\text{H}_2\text{O}_2$ , should thus be used for UDMH decontamination. Other chemicals tested as spill control agents included 1%  $\text{KMnO}_4$ , 5%  $\text{H}_3\text{BO}_3$ , 9%  $\text{NaHCO}_3$ , and carbonated water. These were effective in reducing the amount of UDMH escaping as vapor from the simulated spill to less than 0.2%. Only one of seven solid agents, a hydroxyethyl cellulose material, reduced the amount of UDMH escaping to 5% of that expected without solids treatment. Foam layers can also act as a blanket on UDMH spills.

One way to absorb and immobilize UDMH is by reaction with periodate-treated lignin sulfate (sulfate kraft lignin, black liquor, a waste stream from pulp and paper mills). Black liquor is a waste stream that otherwise has only a few other uses (vanillin, recovery of sulfur by burning it). Oxidation of sulfate kraft lignin with sodium perio-

date at a temperature of 328 K (55 °C) for 20 h results in a more than two-fold increase in the content of carbonyl and quinone groups and a three-fold increase in the sorption capacity for UDMH [556]. The sorbent can bind 6.7% of UDMH. In this respect, it is substantially better than other lignin-based sorbents. It was shown that the firm chemical binding of hydrazines to carbonyl groups in oxidized lignin hinders the desorption of UDMH, while the UDMH-saturated black liquor is disposed of by other methods. The same effect can be achieved by oxidizing lignin sulfate with hydrogen peroxide instead of sodium periodate [557]. An increase in the treatment duration from 15 to 120 minutes, and an increase in the concentration of hydrogen peroxide from 6 to 30%, did not have a significant effect on the functional composition and UDMH absorption properties of lignin.

If a propellant spill occurs, it would be useful to have a supply of a chemical agent for immediate application, e.g., a layer of foam or a gelling agent that reduces vapor emissions of the puddle of liquid temporarily until a more permanent solution to the problem can be found [558]. China continues to use UDMH as fuel in the early versions of Long March satellite launchers and has developed methods for the treatment of UDMH and NTO spills [559] (see also [560]).

When selecting oxidants for the neutralization of UDMH spills, one must ensure that the oxidizer selected will not result in the inadvertent formation of NDMA (“dimethylnitrosamine”), which is a potent carcinogen. An excess of HTH resulted in the formation of FDMH and tetramethyltetrazene, however, no NDMA was found [261]. An alternate method using a mixture of copper(II) sulfate (as a catalyst) and hydrogen peroxide produced substantial amounts of nitrosodimethylamine and is, therefore, not recommended. The destruction of UDMH was more complete if the hydrogen peroxide was added first, and was followed by the copper(II) sulfate.

#### 1.6.4 Decontamination of UDMH-Contaminated Equipment

It is common practice to calibrate flowmeters for liquid propellants in closed-loop flow benches before installing them on rockets and missiles. Flowmeters and other components wetted by UDMH or Ae-50 during such tests must be thoroughly decontaminated before installing them on vehicles. Decontaminating agents must be strong enough to destroy UDMH and hydrazine but should not cause corrosion of any of the components if they are intended to be re-used. The decontamination of equipment that is intended to be destroyed as part of a demilitarization effort could use more aggressive cleaning agents since the equipment will be dismantled and scrapped anyway.

A demilitarization, decontamination, and clean-up effort of one of the many sites in the former USSR that had to go through this process are described in [561]. This presentation provided an overview of the implementation of the Heptyl Infrastructure Elimination Project in Ukraine that was a part of the Cooperative Threat Reduction (CTR) program, which was jointly led by the US Department of Defense (DoD) and the Ukrainian Ministry of Defence (MoD). It described the equipment and services re-

quired to demilitarize rocket fuel storage sites (RFSS) by neutralizing and dismantling the infrastructure, including the neutralization and incineration of contaminated soil and Heptyl and Samin rocket propellant residuals from tanks and piping.

Tank cars that have been used for transportation or storage of UDMH or Ae-50 should be rinsed with water and then decontaminated. Several such cleaning methods have even been patented [562]. The tank should first be rinsed with a fluorochlorocarbon like Freon TF. The UDMH-loaded Freon should then be washed with water to remove the UDMH from the halocarbon, and the washed Freon can be distilled and re-used. Ultimately, the tank should be rinsed with an aqueous formaldehyde solution, followed by dilute hydrochloric acid, and then with water.

Another method proposed the decontamination of polluted shaped metallic surfaces via heat treatment using a high-temperature gas jet at 1573–1653 K (1300–1380 °C) with oxygen excess [563].

### **1.6.5 Disposal of UDMH**

The easiest way for disposing of surplus UDMH would be to feed it in a controlled manner into a flare stack with sufficient oxygen from the air to achieve complete combustion. In 1994 the US DoD signed agreements with the Ukraine and the Russian Federation under which the DoD was committed to providing both former Soviet Union states with equipment and other aid for use in eliminating their strategic missiles in accordance with schedules negotiated in the Strategic Arms Reduction Treaty. One specific need consisted of process equipment to treat or destroy pure ballistic missile liquid propellant components as well as vapor or purge gases, and to rinse fluids contaminated by UDMH, RFNA, or NTO. Incineration was considered as one possible treatment process. To supply data to demonstrate that incineration is a safe and effective treatment process, a series of tests with UDMH was conducted by the US EPA's Incineration Research Facility [564].

#### **1.6.5.1 Disposal of Concentrated UDMH**

Hydrazines that must be disposed of for some reason (e.g., contamination, surplus, demilitarization) can be destroyed by burning, autoxidation, or chemical oxidation.

#### **1.6.5.2 Demilitarization of Surplus UDMH**

At the end of the Soviet era, due to missile build-up, large amounts of UMDH (“Heptyl”) and dinitrogen tetroxide (“Amyl”) and high-density RFNA (“Melanj”) had to be disposed of in a safe and environmentally acceptable manner. This was part of the Strategic Arms Reduction Talks (START) and Strategic Arms Limitation Talks (SALT) and the CTR program, [565]. The Nunn-Lugar program was assisting in the reduction of the SS-18 missile threat to the US and with the demilitarization of the propellants. This involved a chain of custody, destruction, dismantlement, and demilitarization of strategic weapons. Between 1992 and 2010, 8790 M\$ were authorized for these tasks.

Most of this went towards transportation, storage security, and the disarmament of nuclear warheads. Only a smaller portion went towards the destruction of delivery missiles (launchers) and their propellants. The US provided a substantial amount of funding to build demilitarization plants where the propellants were to be converted to other potentially useful, inert chemicals that were no longer to be used as rocket propellants. The facility to be built in Sergei Posad, some 70 km from Moscow, was to be constructed with US aid under the Nunn-Lugar technical assistance program. It appears that it intended to use a process other than burning since there were plans to use conversion products (perhaps amines?) in the manufacture of dyes. In addition to financing the plant construction, the US also supplied a fleet of railroad tank cars that were to be used for the interim storage and transportation of the chemicals to the centralized destruction plant. One project funded in this category, the construction of a plant to dispose of liquid fuel removed from Soviet ICBMs, raised concerns among some members of US Congress during the Bush Administration. The US constructed the facility at a cost of nearly \$100 million. However, before construction was completed, Russia had already used much of the fuel instead in rockets in its commercial and military space-launch program. Consequently, in 2002, Russia informed the US that it did not have any fuel for the facility. Representative Duncan Hunter stated that the episode represented an example of the potential for waste in the Cooperative Threat Reduction (CTR) program. Others, however, noted that, although unfortunate, this case was the exception in a program that has spent more than \$4 billion on threat reduction projects. As it turned out, much of that equipment was never used because the post-USSR powers-to-be sold much of the military propellants to China and/or diverted the propellants to commercial space launch vehicles.

It would be interesting to review statistical data about how much UDMH has actually been destroyed under that program and which techniques were used. A brief Internet search revealed numerous pieces of information but they could not be independently verified and the following survey may not be complete. Numerous international conferences have been devoted to the subject of cleaning up contaminated former military sites so that the areas can be returned to civilian use [566]. Most of the concern at these conferences was about spilled halogenated solvents, transformer oils, and hydrocarbon fuels that have permeated into the ground and aquifers. Some reports list UDMH alongside problems with the disposal of plutonium and chemical warfare agents. The problem with the disposal of UDMH is dwarfed by the problems associated with the disposal and accountability of these other chemicals. Only a few reports are specific for hydrazine-type missile fuels. Some discuss UDMH disposal in connection with the disposal of other liquid rocket propellants, such as Samin (a mixture of xylidine and triethylamine that is similar to the TONKA fuels used by the Germans in surface-to-air missiles toward the end of World War II) or dinitrogen tetroxide (code name: Amyl).

At least 52 heavy ICBMs of the SS-18 type were disposed of in Kazakhstan after more than 30 years in service. They were transported to the Nizhny Novgorod region

in 1995–1996 and destroyed. Approximately 6000 tons of off-loaded UDMH were available in Kazakhstan; it was transported to Russia. Approximately 130 ballistic missiles of the SS-19 type were transported from Ukraine to Russia in 1995–1996 and destroyed. The fate of the off-loaded UDMH (about 4000 metric tons) remains unknown.

The US DoD agreed in 1996 to assist Kazakhstan in the neutralization and dismantlement of missile unified fill facilities (UFFs) for SS-18s located at Derzhavinsk, Zhangis-Tobe, and Leninsk, and to provide assistance with the elimination of liquid fuel, possibly using an incinerator. Each UFF complex consisted generally of above-ground liquid ICBM fuel (heptyl) and oxidizer (amyl) storage tanks, mechanical equipment located inside buildings, earth-covered semi-buried bunkers and structures, buried distribution piping and utilities, lagoons, and communication systems. In addition to surface-launched ballistic missiles, propellant from the Northern and Pacific fleets, using two-stage, liquid propellant, submarine-launched, ballistic missiles RSM-25, RSM-40, RSM-50, and RSM-54, needed to be demilitarized. Submarines equipped with these missiles were based in three bases of the Northern fleet (Yagelnaya, Olenya, and Ostrovnoy) and two bases of the Pacific Fleet (Rybachiy and Pavlovskoye). A news item released in July 2000 quotes a Russian official stating that 2750 tons of liquid rocket propellants (that number most likely includes both oxidizer and fuel) were still stored in the province of Primorye near Vladivostock and that there was concern about corrosion and leaking of storage tanks. Thousands of SA-2 surface-to-air defense missile systems using UDMH may still be scattered in remote bases, and some are not even accounted for. The SA-2 and the SCUD tactical missile use the same propellants. This situation was substantially worse than the situation in the US during the 1970s when several hundred Nike missile sites were decommissioned, leaving cleaning solvent and propellant contamination behind.

One of the several UDMH disposal facilities was planned to be built near the Russian town of Sergiev Posad, which caused some concern in the community with regards to the safety of the installation. Estimates of how much heptyl was stored in Russia's former "closed cities," the Soviet-era secret towns like Sergiev Posad (known as Zagorsk in Soviet days), ranged from 50000 to 150000 tons. At the Scientific Research Institute of Chemical and Construction Machines (SRICCM) based in Sergei Posad, there were over 100 tons of heptyl in storage. After the new reprocessing facility was installed, at least another 10000 tons were planned to be brought there from other sites in Russia. After diluting the UDMH with copious amounts of water, the methods described in this chapter for UDMH wastewater decontamination can be used for the controlled disposal of UDMH with a minimum of toxic waste products.

In the US, demilitarization of decommissioned LANCE Intermediate Range Ballistic Missiles (IRBMs) posed a smaller problem in terms of disposing of IRFNA and UDMH propellants that had been off-loaded from missiles [567]. Some of the decommissioned LANCE missiles were later used as practice targets for anti-ballistic missile interceptor field tests.

### Disposal of UDMH by Burning and Incineration

The two-stage combustion of hypergolic rocket propellants ( $\text{N}_2\text{O}_4$  and the three hydrazine fuels) in an optimized burner was expected to lead to a minimum discharge of  $\text{NO}_x$  into the environment [568]. The first stage of combustion allowed the fuel or oxidizer to react in a respectively lean or rich flame, yielding a mixture of products including the inevitable  $\text{NO}_x$ . The second stage of combustion was supposed to achieve the reduction of  $\text{NO}_x$  as the result of the addition of  $\text{NH}_3$  or  $\text{H}_2$  (thermal  $\text{DeNO}_x$ ) or cyanuric acid. The objective was to understand and control the turbulent combustion of these propellants through the application of fluid dynamics and kinetics modeling in conjunction with optical and mass spectrometer-based flame diagnostics.

There are several incinerator-burner designs that were qualified and certified for the destruction of chemical warfare agents; these should work for the less toxic and more reactive hydrazines. A toxic waste burner has been built and evaluated for the burning of UDMH with a hot gas (pre-burner) and additional air [569]. The goal was to reduce  $\text{NO}_x$  emission in the exhaust gases down to less than 165 ppm. Initially, hydrazine and UDMH were tested in an existing air-cooled liquid incinerator with natural gas being used for ignition (in some cases, it was necessary to sustain combustion). Air was used as the oxidizer. UDMH could be destroyed by incineration down to a level below 2 ppm residual hydrazines with  $\text{NO}_x$  emissions in the discharged gas in concentrations well below 165 ppm. Incinerator dwell times were in the order of 0.1 s.

Another burner developed for the removal of liquid propellants disposed of over 453 kg/h (1000 lb<sub>m</sub>/h) of liquid propellants, including hydrazine, by burning it in the air to produce exhaust gases in the 977 K (1300 °F) range. The exhaust gases contained acceptably low levels of nitrogen oxides [570].

The US Environmental Protection Agency (EPA) Risk Reduction Engineering Laboratory conducted NTO and UDMH destruction tests in a rotary kiln incinerator with afterburner and wet scrubber [564, 571]. In the test program, the two propellant components were independently incinerated in separate sets of triplicate tests. The six UDMH destruction tests were performed at a nominal kiln exit gas temperature of 1153 K (980 °C = 1800 °F). UDMH was sprayed into the combustion chamber without any auxiliary hydrocarbon fuel. All tests were performed at a primary combustion chamber exit gas temperature of nominally 1153 K (980 °C = 1800 °F) and a secondary combustion chamber (afterburner) exit gas temperature of nominally 1363 K (1090 °C = 2000 °F). 1363 K (1090 °C = 2000 °F). The flue gas from the afterburner was passed through a wet scrubber. The test program results showed that  $\text{NO}_x$  levels were in the range of 690 to 780 ppm at 7%  $\text{O}_2$  at the primary combustion chamber exit during UDMH incineration. These were reduced to 410 to 500 ppm at 7%  $\text{O}_2$  at the secondary combustion chamber exit, largely due to the dilution that accompanies the addition of the extra fuel and air required to raise the secondary chamber's temperature. The scrubber exit levels were similar to those at the secondary chamber exit, at 440 to 500 ppm at 7%  $\text{O}_2$ . No unreacted UDMH or NDMA was detected at any flue gas location.

### Catalytic Combustion

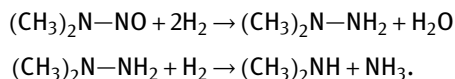
Investigators at the Russian Boreskov Institute of Catalysis proposed the destruction of UDMH in a fluidized bed catalytic combustor. A similar process had been developed for the disposal of mixed organic radioactive waste. During the low-temperature stage of the catalytic combustion process (873–1023 K), the  $\text{NO}_x$  formation is minimal. The air-to-fuel ratio will be carefully selected to minimize  $\text{NO}_x$  formation. A pilot plant with a capacity of 2 kg/h was developed. The ultimate design envisioned a plant capable of destroying 100 tons of UDMH/yr.

### UDMH Disposal by Hydrogenolysis and Reduction

To obtain products of commercial value from the disposal of UDMH, the hydrogenolysis over a supported platinum group catalyst in the presence of excess hydrogen leading to ammonia and DMA has been patented [333–336].

UDMH in aqueous solutions can be disposed of by passing the heated mixture with excess hydrogen gas through a catalytic reactor, thus forming DMA and ammonia [572, 573]. The ammonia can be dissociated, and the hydrogen thus formed is fed back into the first reactor. The apparatus can be built on skids so that it can be transported to remote sites where surplus UDMH needs to be destroyed.

Raney-nickel Al/Ni alloy in caustic 0.5-M NaOH was tested for the destruction of UDMH, NDMA, MMH, and hydrazine [574]. The following pathway for the reductive decomposition of NDMA creates UDMH as an intermediate, which ultimately is reduced to DMA and ammonia:



Besides Raney nickel, Al powder in 0.5-M NaOH, stannous chloride in methanol, and granular tin metal in concentrated hydrochloric acid were tested for the destruction of DMAZ.

### Conversion of Surplus UDMH to Other Chemicals with Commercial Value

It has been repeatedly attempted to convert UDMH and RFNA into commercially useful products. However, this is a difficult task. Even if it is technically feasible, the question remains of whether it can be done profitably [575]. Considering the problem of recycling unwanted UDMH, eight saturated aliphatic aminimides with low melting points were synthesized and the structures, melting points, and pyrolysis were determined by FTIR [324]. Some of the amines can be used in the synthesis of surfactants [331]. It has also been proposed to convert UDMH to its oxalate salt, which is relatively insoluble and stable for storage in air. UDMH oxalate can possibly be used in the PUREX process for nuclear fuel element reprocessing and radioactive isotope separation [505].

### Plasma Pyrolysis

No  $\text{NO}_x$  at all was formed when UDMH was destroyed in a steam reforming plasma burner. The plasma energy recycle and conversion (PERC<sup>TM</sup>) process for the demilitarization of propellants and explosives uses an induction-coupled plasma (ICP) torch as a heat source in a reaction chamber system to convert wastes into by-products in a safe and environmentally clean manner [576–578]. In the PERC<sup>TM</sup> process, combustion of a supplementary fuel is not necessary. The conversion process can be carried out in any reaction environment, such as an oxygen-free, reducing, steam reforming, or oxygen-rich environment. This ability to choose and control the reaction environment permits the control of the by-products formed by the process. For example, conventional destruction of UDMH in an incinerator can result in the production of  $\text{NO}_x$  as a reaction product. The PERC<sup>TM</sup> system, using the steam reforming process, will convert UDMH into carbon monoxide and hydrogen along with nitrogen gas. Destruction efficiency demonstrated in all cases was greater than 99.999%, and for certain materials, it was greater than 99.99999%. The first PERC<sup>TM</sup> system capable of processing up to 113 kg/h (250 lb/h) of liquid organic waste materials was installed in 1995.

### Hazards of Inadvertent Nitrosamine Formation During the Disposal of Alkylhydrazines

Four different methods were evaluated for the decontamination and destruction of hydrazine-based carcinogens, including a hydrazine-based pharmaceutical, in laboratory wastes: reduction with nickel/aluminum alloy in alkaline solution, oxidation with potassium permanganate in sulfuric acid solution, potassium iodate, and hypochlorite solutions [579, 580]. The reliable and environmentally-safe destruction of laboratory wastes by these four methods was verified by checking their mutagenicity before and after treatment with one of the four methods. Nitrosamines were detected when UDMH or MMH was oxidized with hypochlorites. The reductive destruction of hydrazines and nitrosamines by reaction with Raney nickel in alkaline solution was recommended several times, however, the problem with disposing of large volumes of aluminum hydroxide sludge with nickel (itself a suspect carcinogen) was not addressed [581, 582]. The incomplete reduction of NDMA would form UDMH as an unwanted intermediate, making this an undesirable option also. One group tested the reduction of ten different nitrosamines, including NDMA, with aluminum metal strips in caustic solutions. However, they failed to analyze the resulting solutions for hydrazines [583]. Nitrosamines are not truly destroyed if the waste still contains hydrazines that will readily oxidize back to nitrosamines as soon as air is admitted. We are limiting our discussion here only to the disposal of hydrazines and cannot provide a complete summary of the various methods for the destruction of nitrosamines. There are other publications that deal specifically with nitrosamines and contain chapters on nitrosamine disposal [584, 585]. Other nitrosamine environmental and toxicity discussions are detailed later in this chapter.



### 1.6.6 UDMH Wastewater Decontamination

Many different methods were tested for the decontamination of UDMH-containing wastewater, which is a more difficult task than the decontamination of either hydrazine- or MMH-contaminated waters. Although UDMH is no longer in use in the United States, the techniques described here are equally effective for decontamination of wastewater containing MMH. Several decontamination techniques were used to clean up stored process waste and tank rinse water [586]. The treatment technologies and methods UDMH wastewater decontamination included physical, biological, and chemical methods. Methods evaluated for UDMH decontamination included ozone oxidation, natural degradation, ion exchange resin, active carbon adsorption,  $\text{TiO}_2$  photo-catalytic oxidation, and biological remediation [587–589]. Many wastewater treatment techniques used for the removal of other contaminants can also be used for the treatment of MMH- or UDMH-contaminated wastewater [590].

UDMH that is being oxidized on purpose as a means of disposal and decontamination of UDMH-polluted rinse waters will rarely turn directly into carbon dioxide, nitrogen, and water, which are the desired oxidation products. Intermediate species have been analyzed by gas chromatography-mass spectrometry. The effectiveness of various chemical oxidants in respect to the main intermediates of UDMH oxidation, such as 1-formyl-2,2-dimethylhydrazine, dimethylaminoacetonitrile, NDMA, and MTA, was measured using Fenton's reagent, potassium permanganate and sodium nitrite [591]. Quantitative analysis was performed using HPLC. Oxidation products were identified by GC/MS in combination with SPME. 1-Formyl-2,2-dimethylhydrazine was completely oxidized by Fenton's reagent with the formation of formaldehyde *N*-formyl-*N*-methyl-hydrazone. 1,4-dihydro-1,4-dimethyl-5*H*-tetrazol-5-one was oxidized by the action of potassium permanganate. *N*-Methyl-*N*-nitro-methanamine was formed in the presence of sodium nitrite. Oxidation of 1-formyl-2,2-dimethylhydrazine also resulted in the formation of NDMA. Oxidation of dimethylaminoacetonitrile proceeded with the formation of hydroxyacetonitrile, DMF, and 1,2,5-trimethylpyrrole. After 30 d, dimethylaminoacetonitrile was not detected in the presence of Fenton's reagent and potassium permanganate but its concentration in samples with sodium nitrite remained 77 mg/L. In the presence of Fenton's reagent, potassium permanganate, and sodium nitrite after 30 d, NDMA concentration decreased by 85, 80, and 50%, respectively. In a control sample without nitrite, NDMA concentration decreased by 50%, indicating that sodium nitrite had no effect on NDMA decay. Only Fenton's reagent achieved the reduction of the concentration of MTA to 50% in <30 d. In the presence of other oxidants, MTA concentration decreased only by 15–20%. As a result of these experiments, Fenton's reagent turned out to be the most effective oxidant for the destruction of UDMH.

Throughout those dark ages of hydrazine chemistry when UDMH was still made by the reduction of NDMA, the removal of waste NDMA from process streams was a difficult problem. The waste stream generated in the production of UDMH contained approximately 200 mg/L of NDMA, 25% sodium hydroxide, and 5% nitrite. Various

techniques for the removal of NDMA from wastewater were tested including wet air oxidation [592]. From the limited data evaluated, it was suggested that NDMA was amenable to destruction by wet air oxidation to approximately the 1 mg/L level with relative ease. Reduction below the 1 mg/L level, however, was very difficult. The fact that some NDMA was carried out with the sparging air instead of being oxidized in solution was carelessly neglected by early investigators. The limit of NDMA detection at that time was approximately 20 µg/L. More sensitive analytical methods have become available in the interim. UDMH is now made by a different route that does not involve NDMA as an intermediate.

The US EPA at one point declared wastes generated during the manufacturing of UDMH and daminozide as hazardous wastes under the Resource Conservation and Recovery Act (RCRA) [593, 594].

The wastewater from UDMH production in the Qinghai province in China contained high concentrations of organics, ammonia, chloride ion, salinity, and highly toxic substances. A combined process of ammonia-stripping and advanced oxidation technology/activated carbon adsorption was designed to treat the sewage [595]. The capacity of this installation was 25 m<sup>3</sup>/h. An examination showed that the treatment system was stable and efficient and met wastewater discharge standards.

It is common practice to characterize various competing UDMH decontamination processes by the efficiency of the COD removal. While it is good that the COD is decreased by more than 98%, these investigations often ignored the formation of toxic by-products that do not have a COD.

Until recently, the assessment of the effectiveness of oxidative reagents for the cleanup of wastewaters and soils polluted with UDMH was mostly based on the residual content of UDMH and did not take into account the possibility of the formation of a large number of potentially dangerous, equally toxic nitrogen-containing transformation products [596]. High-resolution Orbitrap MS was used to characterize UDMH transformation products formed by the action of atmospheric oxygen and different pollution control oxidants (Fenton's reagent, KMnO<sub>4</sub>, HOCl, H<sub>2</sub>O<sub>2</sub> in the presence of Cu<sup>2+</sup> and [Fe(EDTA)] catalysts) which are typically used to detoxify spill sites. The analysis of transformation products revealed 303 compounds of various chemical structure classes. Several major products were detected that were not previously described in the literature. It was established that none of the investigated oxidative reagents ensure the complete conversion of UDMH to safe compounds. The hydrogen peroxide-based reagents, particularly the H<sub>2</sub>O<sub>2</sub> + Na[Fe(EDTA)] system often used in Kazakhstan, form the greatest number of transformation products, for many of which toxicity information was not available. The majority of the compounds found in model solutions were detected in extracts of soil from the crash site of a Proton launch vehicle that had been subjected to on-site decontamination. With each successive treatment, the number of detectable UDMH transformation products decreased. The most enduring compounds were the amines.

#### 1.6.6.1 UDMH Wastewater Decontamination by Ozone Treatment

Neither MMH nor UDMH in aqueous solution become completely oxidized to  $N_2$  and  $CO_2$  by ozonization in the dark but they can be effectively destroyed by combined UV ozonolysis [285, 286]. Mechanisms of various photolytic reactions of alkylhydrazines and nitrosamines were summarized earlier in this chapter (in Section 1.4.6.) The ozone/UV treatment can also be used for the decontamination of other hazardous waste streams [597]. One way to assure reliable, environmentally safe, and complete destruction of toxins in wastewaters by ozone is to check their mutagenicity before and after ozonation treatment [598]. Other space-faring nations like China have now also resorted to the use of UV-ozonolysis as a means of UDMH removal from wastewater [599].

The rates of oxidative destruction of hydrazine, MMH, or UDMH were investigated using ozone alone or ozone with UV [600]. All three hydrazines were oxidized rapidly with ozone or ozone/UV. The ozone was consumed as rapidly as it was introduced for as long as any hydrazine was present. The limited solubility of ozone in water is one of the rate-limiting factors. NDMA was formed as an intermediate from the methylhydrazines, but it was destroyed by continued and extended ozone treatment. Its destruction rate was significantly slower than that of the hydrazines. Contrary to the findings of other investigators, the use of UV did not appreciably enhance the destruction rate of NDMA except at high concentrations. No apparent acceleration of the ozone/UV destruction rate of NDMA was observed as the result of placing stainless steel CRES-304 panels or nichrome wire mesh into the reactor as surface catalysts. However, tungsten, both in the shape of USS No. 100 (100 mesh) powder and metal plates, accelerated the destruction of NDMA and changed the type of unwanted by-products formed. Metal catalysts accelerated the destruction of hydrazines and NDMA [601]. The tungsten plate did not lose activity after ten consecutive tests. Tungsten powder accelerated the rapid destruction of NDMA to levels below 30 ppt (detection limit). The addition of 1.2 ppm of  $Cu^{2+}$  or 15 ppm of  $Fe^{3+}$  ion to the solution surprisingly delayed the apparent NDMA destruction at concentrations below 0.1 ppm. This effect was hard to explain. It was assumed that some NDMA was complexed and protected in metal complexes and was only gradually released for photolysis. In addition to testing the metal ions by themselves, the two ions should have been tested in combination for synergistic, thus potentially accelerating effects. Starting with a mixture of 1% of each of the two methylhydrazines and in the absence of catalysts and at pH 9.5, the NDMA concentration peaked at 2000 ppm shortly after all hydrazines were consumed. NDMA destruction was reasonably fast down to a concentration of 1 ppm but became very slow at lower concentrations. If the same test was performed at pH 2.5, net NDMA production was less than observed at higher pH, and NDMA destruction rate reduced quickly down to concentrations as low as 0.01 ppm. This observed pH dependence was in contrast with results reported by other investigators [285, 286], where operation at pH 9.1 for the destruction of hydrazines was recommended (but apparently the rate of NDMA destruction was ignored). With no pH control, and starting

with typical wastewaters at pH 10, the pH dropped with progressive waste neutralization by ozone-UV. This would indicate that no pH adjustment prior to or during the process is required. The addition of acid or caustic during a test run increases the volume of the waste solution. Such additions would be done only for development tests to determine the effect of pH variation but are not needed for the actual operation of a commercial unit. The rate at which the three hydrazine fuels were destroyed was about six times slower at pH 2.5 than at 9.5. However, the concentration of NDMA at the time that the hydrazines were gone was an order of magnitude less than that during the treatment at high pH [602]. Three different methods for the treatment of hydrazine(s) wastewaters were tested at the IITRI: ozone as the primary oxidizing agent, UV light as a catalyst for the reaction between NDMA and ozone, and finally, chlorine as a final “polishing” agent following the treatment with either of the two aforementioned methods [603]. Three different reactors were used in the study: a tubular reactor containing a liquid column and a gas dispersion (sparging) element at the bottom, a UV spray chamber with two different quartz lamps (high-pressure and low-pressure mercury lamps), and a commercial UV water purifier consisting of a CRES-316 tube with a coaxial quartz tube holding the UV lamp. It was shown that chlorination, even as a “polishing” treatment, produces chlorinated hydrocarbons. Chlorination was not pursued any further because halocarbons are not permitted in the effluent of the treatment plant. The combination of ozone and UV was able to reduce the NDMA concentrations to below 20 ppt.

Tests with an ozone/UV pilot system at a flow rate of 3.78 L/min (1 gpm) and ozone pre-saturated water showed that initially the NDMA concentration was increased due to incomplete oxidation of UDMH in the raw feed water [604]. Improved destruction of NDMA was possible by injecting the ozone at the UV lamp, which emitted light at 253.7 nm. The first full-scale system was a batch operation with water recirculation, treating 3000 gal in 18 h. However, it was still too slow to keep up with demand. The reaction time of an improved system with additional UV lamps was at least eight to 10 h to achieve a residual NDMA concentration of less than 1 ppb in accordance with then-applicable regulations.

The ozonization of UDMH can be accelerated by conducting it in a suspension with catalysts [605]. The wastewater treatment by oxidation of UDMH with ozone (without UV) can be improved by iridium catalysts. The catalysts consisted of 30%, 10%, or 3% iridium on alumina. This would be a very expensive approach and may not be economically justifiable, considering the cost of iridium catalysts. It may not provide complete removal of NDMA either.

Ozonation (also referred to as ozonization and ozonolysis), in combination with UV illumination, has been used in drinking water sterilization with good success. Commercial ozonization units are available from several vendors to destroy dissolved organic contaminants present in ground water and wastewater with low levels of suspended solids [606]. The system uses a combination of UV radiation, ozone, and hydrogen peroxide to effectively oxidize most contaminants.

An ozone/UV treatment was used for the decontamination of hydrazine(s) wastewater at Rocky Mountain Arsenal [607]. The main concern was about residual NDMA left behind long after all UDMH was all gone.

NASA's White Sands Test Facility (WSTF) fabricated and tested a full-scale 85.2 m<sup>3</sup> (2250 gal) UV/ozonation hydrazine wastewater treatment system [608]. A series of 21 tests evaluated the performance of the system using synthetic mixtures of hydrazine, MMH, and UDMH at 100 and 3900 ppm concentration levels. In addition, one of these tests was performed on actual wastewater obtained from a Vandenberg Air Force Base launch site sump. The tests demonstrated that the UV ozonation system would satisfactorily reduce the hydrazine concentration to less than 5 ppb and the NDMA concentration to less than 100 ppt. The same UV-ozonolysis installation that was originally developed for hydrazine waste can also be used for the destruction of other industrial organic wastes generated during routine operations [609, 610].

A combination ozone/UV decontamination unit designed by IITRI was tested at NASA's WSTF. Once again, actual wastewaters collected from rocket test sites at WSTF and USAF VAFB were used. In 1988, the USAF Space Systems Division requested that NASA's WSTF fabricate and conduct performance evaluation tests on a full-scale prototype 8.52 m<sup>3</sup> (2250 gal) hydrazine wastewater treatment system [611]. The system consisted of three skid-mounted units, thus providing portability. The system was designed to reduce hydrazine fuel concentrations to non-detectable quantities (less than 5 ppb) and reduce NDMA to less than 100 ppt. The system uses ozone and UV light to destroy the hydrazine fuels and their by-products. Ozone concentrations of up to 5.7 mass-% O<sub>3</sub> in O<sub>2</sub> were possible. The UV lamp provided 3 kW of UV energy with 85% at the resonance line of 254 nm. To evaluate system performance under various operating conditions, tests were performed with fuel concentrations from approximately 100 to 6000 ppm, and while using various techniques for introducing the ozone into the wastewater. The system was able to reduce fuel concentrations to less than the 5 ppb detection limit and NDMA to less than 100 ppt. The system was also able to reduce the fuels in actual VAFB launch pad water that contained 300 to 400 ppm fuels to less than 5 ppb fuel and 100 ppt NDMA. The system operated as designed with one exception: the spargers used for introducing the ozone/oxygen gas stream into the water had to be altered. Examination of the gases exiting the reactor tanks vent indicated that the ozone destruct unit performed well, with no traces of ozone being emitted. Analytical testing of these exhaust gases did show low concentrations of several organic compounds. Readings taken sporadically throughout this test series with a fuel Interscan<sup>®</sup> detector indicated no traces of propellant fuel. Tungsten plates as stationary catalysts were used to catalyze the NDMA destruction.

A study of the effects of Ni/Fe catalysts on UDMH decontamination in wastewater using ozonation found that the catalysts exhibited high activities for the ozonation of UDMH [612]. The catalysts content, pH, and the initial UDMH concentration had little effect on the performance of the catalysts. The catalysts were characterized by

XRD, and the results showed that they had the spinel-type structure of magnetite and FeNi<sub>3</sub> alloy.

NDMA and UDMH can be destroyed by oxidative degradation of NDMA using conventional ozonization and an advanced oxidation process using ozone/hydrogen peroxide. The rate constants of reactions of NDMA with ozone and hydroxyl radical ( $\cdot\text{OH}$ ) were determined to be  $0.052 \pm 0.0016 \text{ mol}^{-1} \text{ s}^{-1}$  and  $(4.5 \pm 0.21) \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively [613]. The reaction with  $\cdot\text{OH}$  dominates the NDMA oxidation during ozonization. Conventional ozonization with up to  $160 \mu\text{M}$  ( $7.7 \text{ mg/L}$ ) ozone led to less than 25% NDMA oxidation in natural waters.

UDMH wastewater was treated with ozone  $\text{O}_3$ ,  $\text{O}_3/\text{UV}$ , and  $\text{O}_3/\text{VUV}$ . The most efficient process was  $\text{O}_3/\text{VUV}$ . Its rate constant was 39.8 and 65.6% higher than  $\text{O}_3/\text{UV}$  and  $\text{O}_3$  without UV, respectively [614]. The degradation intermediate formaldehyde could also be removed very quickly in the  $\text{O}_3/\text{VUV}$  process and its concentration was lowered to be undetectable within 50 minutes. The dependence of reaction efficiency on several operating parameters such as initial pH, ozone feed rate, and carbonate addition was also studied. The experimental results showed that the UDMH degraded fastest when the initial pH was nine and the corresponding rate constant reached  $0.4461 \text{ min}^{-1}$ . The rate constant increased linearly with the ozone feed rate. The apparent degradation kinetics of UDMH changed from first-order to zero-order kinetics when the initial concentration of UDMH increased from 100 to 2000 mg/L. Carbonate addition in the range of 0–2 mmol/L had little effect on UDMH degradation. The formation of inorganic nitrogen ionic compounds including  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  during reaction was identified. It was found that inorganic nitrogen that existed mostly in the form of  $\text{NH}_4^+$  only accounted for 40–60% of the total nitrogen, which implied that other nitrogen-containing organic intermediates were formed during UDMH degradation.

The NDMA formation from ozonation of six hydrazine compounds was investigated. It was found that NDMA formation yields from treatment of UDMH-contaminated groundwater (pH 7) were 7.5–89% [615]. Results in the presence of *tert*-butyl alcohol as a radical scavenger indicated that NDMA was formed by reaction with molecular ozone except for tetramethyltetrazene. From the results of effects of pH, *tert*-butyl alcohol, and water matrix (groundwater and river water), it was suggested that reactions of tetramethyltetrazene with ozone and/or hydroxyl radicals were responsible for NDMA formation. Because NDMA formation on chloramination was low, there are other NDMA precursors present during ozonation in actual water treatment.

It is surprising to find that NDMA may form during wastewater treatment with ozone, even in the absence of UDMH. There are other organic contaminants in wastewater that will be converted to NDMA. UDMH was among the several organic compounds shown to end up as NDMA as the result of ozonization [616]. Nitrosamine formation may be a significant barrier to ozonization in water re-use applications (even away from any rocket test sites), particularly for direct or indirect potable re-use since studies showed direct NDMA formation during ozonization of natural

water and treated wastewaters. Several precursor compound solutions, prepared in ultra-pure water and treated wastewater, were subjected to a 10M excess of ozone. The study discovered six new NDMA precursor compounds that had not been previously reported in the literature. The presence of bromide was important for three compounds (1,1-dimethylhydrazine, acetone dimethylhydrazone, and dimethylsulfamide) but did not enhance NDMA formation for the other precursors.

UDMH forms NDMA during ozonation but the relevant reaction chemistry was not quite understood. An investigation of the reaction kinetics and mechanisms of NDMA formation during the ozonation of UDMH and daminozide (DMZ, SADH) showed that the reaction of ozone with these NDMA precursor compounds was fast, and  $k_{O_3}$  at pH 7 was  $2 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$  for UDMH [617]. Molar NDMA yields (i.e.,  $\Delta[\text{NDMA}]/\Delta[\text{precursor}] \times 100$ ) were 84% for UDMH, as determined at the molar ozone dose ratio ( $[\text{O}_3]_0/[\text{precursor}]_0$ ) of  $\geq 4$  in the presence of *tert*-butanol as a hydroxyl free radical (OH) scavenger. The molar NDMA yields decreased significantly in the absence of *tert*-butanol, indicating  $\cdot\text{OH}$  formation. Its subsequent reaction with the parent precursors formed negligible NDMA. The  $k_{OH}$  at pH 7 was  $4.9 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$  for UDMH. Reaction mechanisms were proposed in which an ozone adduct was formed at the nitrogen next to *N,N*-dimethylamine that decomposed via homolytic and heterolytic cleavages of the  $-\text{N}^+-\text{O}-\text{O}-\text{O}^-$  bond, forming NDMA as a final product. The heterolytic cleavage pathway explains the significant OH formation via radical intermediates. Overall, significant NDMA formation was found to be unavoidable during ozonation or even during the  $\text{O}_3/\text{H}_2\text{O}_2$  treatment of waters containing UDMH due to their rapid reaction with ozone-forming NDMA with a high yield.

The majority of UDMH wastewater treatments produce lots of toxic by-products; among these, NDMA causes the most concern because it is a strong carcinogen. The compositions of the by-products are important for evaluating the treatment efficiency and understanding the UDMH degradation mechanism to achieve complete UDMH mineralization (i.e., conversion to  $\text{CO}_2$ ,  $\text{N}_2$ , and water). The intermediate and end products of UDMH treatment with different oxidants were investigated by using a simple and fast method, which was SPME in combination with GC-MS [618]. The effects of several parameters (coating fiber, salt addition, pH, sampling time, and desorption time) were studied to optimize analyte recovery. The best response can be attained by the  $65 \mu\text{m}$  PDMS/DVB fiber at pH 7 over ten minutes after desorption over one minute in the GC inlet. The intermediate and final oxidative products of UDMH wastewater treatment with different oxidants ( $\text{O}_3$ ,  $\text{Mn}^{2+}/\text{O}_3$ , or  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) were investigated. The results showed that the UDMH treatment with  $\text{O}_3$  could lead to unwanted high yields of NDMA. Metal catalytic ozonation could largely minimize the formation of NDMA. No NDMA was observed in the final decontaminated samples after treatment with Fenton's reagent,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ .

### 1.6.6.2 UDMH Wastewater Decontamination via Hydrogen Peroxide Treatment

The decontamination of wastewater containing UDMH can be achieved by catalytic oxidation, using air or  $\text{H}_2\text{O}_2$  as the oxidant [619]. With the addition of activated carbon as an adsorbent or by lengthening the time of purification, the discharge concentration of UDMH in the wastewater could be reduced to 0.5–0.8 mg/L, and that of the secondary pollutant formaldehyde could be reduced to 1.3–2.0 mg/L.

Degradation reactions of UDMH using atmospheric oxygen and hydrogen peroxide were carried out in the presence and absence of copper ion catalysis and at varying pH [251]. Reactions were also carried out in the presence of hydrazine, which is a constituent, along with UDMH, of the rocket fuel Aerozine-50. In the presence of copper, UDMH was degraded by air passed through the solution. The efficiency of degradation increased as the pH increased but the carcinogen NDMA was formed at neutral and alkaline pH. Oxidation was not seen in the absence of copper. NDMA formation occurred even at copper concentrations of <1 ppm. Oxidation of UDMH with hydrogen peroxide also gave rise to NDMA. When copper was absent, degradation of UDMH did not occur at acid pH but when copper was present with hydrogen peroxide some degradation occurred at all pH levels investigated. The production of NDMA occurred mostly at neutral and alkaline pH. In general, higher concentrations of hydrogen peroxide and copper favored the production of NDMA. DMA, methanol, FDMH, formaldehyde hydrazone, and tetramethyltetrazene were also detected. The last three compounds were tested and found to be mutagenic.

Several Cu- and Fe-hydroxide containing catalysts, supported on oxide carriers, were prepared to accelerate the removal of UDMH from aqueous solutions via oxidation by hydrogen peroxide and/or air oxygen [620]. The Cu-containing samples as well as Fe/ZSM-5 zeolites were the most active catalysts in this reaction. The reaction products were analyzed by GC and UV-visible spectroscopy. The type of oxidizer and catalyst, pH, and temperature applied had a pronounced effect on both the reaction rate and product composition.

A study of the oxidative degradation treatment of UDMH-containing wastewater using a combined UV-Fenton process revealed that the degradation rate of UDMH can reach 99% and the COD removal rate can reach 95.8% after 54 minutes at room temperature when the initial concentration of UDMH in wastewater was 400 mg/L. The added quantity of 30%  $\text{H}_2\text{O}_2$  was 102 g/L, pH value of the system was adjusted to 3.5, and 1.26 g/L of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added as the catalyst [621]. A 50% excess of hydrogen peroxide above the stoichiometrically required amount of  $\text{H}_2\text{O}_2$  was used for these experiments [622].

A Fenton's reagent process was applied to oxidize UDMH wastewater [623]. The removal efficiencies of COD in wastewater were the main indicators of reaction completion. The rate and completion of degradation of UDMH and DMA and FDMH, which were important intermediate products at different pH levels, were measured. Results showed that the degradation of UDMH and FDMH was best at pH = 3 and the removal efficiencies of COD were 91.6 and 80%, respectively. In contrast, the degradation of



DMA was best at pH = 9 and the removal efficiency of COD was 88%. The efficiency of Fenton's reagent as an oxidant can be enhanced by UV illumination, ultrasonic agitation, or microwave heating.

A potassium permanganate-hydrogen peroxide mixture has been used for the decontamination of UDMH-contaminated wastewater. The reaction products of UDMH with potassium permanganate were analyzed using GC/MS [624]. At low UDMH concentrations (<1 mg/mL), the reaction is without toxic by-products, but at high UDMH concentrations (~1 g/L), NDMA forms as a toxic by-product. The decontamination of aqueous solutions with significant UDMH concentrations (up to 1 g/L) with potassium permanganate alone or in combination with hydrogen peroxide reduced the UDMH concentration to a safe level. However, the UDMH transformation products, including the extremely toxic NDMA, accumulated in the solution.

UDMH-containing wastewater can be treated by a combined microwave-Fenton process [625]. The effects of variables such as microwave power, the dosage of the  $\text{H}_2\text{O}_2$ , the pH level, and the  $(\text{Fe}^{2+}):(\text{H}_2\text{O}_2)$  ratio on the wastewater treatment efficiency were measured. The wastewater treatment efficiency using the microwave-Fenton process was compared with efficiency when using a microwave- $\text{H}_2\text{O}_2$  method, water- $\text{H}_2\text{O}_2$  method, and water-Fenton method. The results revealed that the treatment efficiency of the microwave-Fenton process is better than the other three methods. Under the effect of microwave radiation,  $\text{H}_2\text{O}_2$  decomposes and releases  $\cdot\text{OH}$  free radicals. Thereby it can increase the efficiency of UDMH destruction by  $\text{H}_2\text{O}_2$  and reduce the negative impact of pH value on the Fenton reaction.

A special way to use hydrogen peroxide for the destruction of organic contaminants in wastewater is the Fenton's reagent, which is hydrogen peroxide with solutions of iron(II) salts. The chemistry of this reaction has already been described in this chapter. The  $\text{Fe(II)}/\text{H}_2\text{O}_2$  Fenton process was applied to oxidize UDMH in wastewater with high UDMH concentrations [626]. The results showed that when the initial pH value was 3,  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  molar ratio was 1:10, the reaction temperature was 313 K (40 °C), the degradation of UDMH in the wastewater (1000 mg/L) after 120 minutes was better than 98%, and the removal of COD was better than 96%. It was thus shown that the Fenton process was efficient in the treatment of UDMH wastewater with high concentrations.

A three-component metal catalyst was prepared and used in the process of catalytic wet peroxide oxidation (CWPO) for the decontamination of UDMH in propellant wastewater with  $\text{H}_2\text{O}_2$  [627]. The catalyst was structurally characterized using SEM, XRD, XPS, and EDAX, and its catalytic activity was evaluated using indexes such as the efficiency of UDMH degradation and COD removal and the concentrations of ammonia, formaldehyde, total nitrogen, total organic carbon, and NDMA. The reaction system was monitored using UV-Vis full wavelength scanning spectroscopy and liquid chromatography-mass spectroscopy (LC-MS). It was observed that the degradation mechanism led to  $\cdot\text{OH}$  free radicals attacking the amino group in UDMH with the simultaneous transformation of the active component  $\text{Cu(II)}/\text{Cu(I)}$ . Based on investi-

gation of the effects of reaction variables ( $\text{H}_2\text{O}_2$  dosage, temperature, catalyst dosage, pH, and the initial concentration of UDMH) on the rate of removal of NDMA, the optimal conditions for CWPO with a three-component metal catalyst were determined. The highest treatable concentration of UDMH (500 mg/L), rapid rate of UDMH removal, good reusability with a high efficiency of UDMH degradation and COD removal (99.9% in 10 minutes and 94.6% in 30 minutes, respectively), and the low concentration of NDMA by-products are all advantages of this catalyst system with  $\text{H}_2\text{O}_2$ .

A CWPO combined with a VUV irradiation process was developed for the purpose of mineralizing the UDMH in wastewater, especially to decompose all of the main by-products of UDMH decomposition, which is NDMA in this instance [628]. A CuO-NiO-MgO/ $\gamma\text{-Al}_2\text{O}_3$  catalyst was used.  $\text{H}_2\text{O}_2$  was the source of  $\cdot\text{OH}$  free radicals. UDMH degradation efficiency, COD removal efficiency, and the concentration of NDMA were measured to obtain optimal conditions, including operating parameters such as the initial UDMH concentration, catalyst dosage, initial pH,  $\text{H}_2\text{O}_2$  dosage, and temperature. The results indicated that the CWPO/ $\text{H}_2\text{O}_2$ /VUV process achieved 100% UDMH conversion efficiency, 95% COD removal efficiency, and approximately 100% UDMH removal within 30 minutes.

#### 1.6.6.3 UDMH Wastewater Decontamination Using Chlorine or Chlorine Dioxide Treatment

Chlorination of MMH or UDMH yielded significant quantities of chloromethane (methyl chloride) and small quantities of nitrogen trichloride  $\text{NCl}_3$  (it is important to note that this is a hazard if it accumulates anywhere in the system) [629, 630]. *N,N*-Dichloromethylamine, *N*-chloromethylamine, dichloromethane, and chloroform have also been detected. The potential environmental hazard of these by-products makes one-step chlorination unsuitable for the disposal of alkylhydrazines. However, chlorinolysis with simultaneous UV illumination at pH 5 is effective in destroying all types of propellant hydrazines in contaminated water [631, 632]. The ratio of UV lamp input power to reactor volume was varied from 0.1 to 0.9 W/L. Initial concentrations in the waste to be treated were 500 ppm for the three propellant hydrazines and 100 ppm for NDMA. In one series of tests in 113-L (30-gal) pilot-scale vessels it was found that UV chlorinolysis produces a much cleaner effluent than low pH chlorinolysis [633]. Excess chlorine had to be removed by treatment with sodium thiosulfate. It was also considered to keep the UV light on for several hours after the chlorine addition was stopped. This would convert some of the excess  $\text{Cl}_2$  to HCl and reduce the sodium thiosulfate requirements. Sufficient design data were obtained to scale up the process to treat 7500 L of wastewater per day.

The following products were found when treating UDMH with HTH: formaldehyde methylhydrazone, FDMH, acetaldehyde dimethylhydrazone, DMF, and tetramethyltetrazene (obviously a very complex mix of oxidation products), but no NDMA [261]. No chlorinated methanes were identified as by-products. Using more advanced GC/MS and GC/FTIR instrumentation, later investigators [295, 296] found

a mixture of 90 to 100 compounds, not all of which could be identified. FDMH was the main product. Other confirmed products were NDMA, *N,N*-dimethylcyanogen, DMF, and chloroform. In addition, acetaldehyde dimethylhydrazone and formaldehyde methylethylhydrazone were tentatively identified from their mass spectra. Since the starting products were only  $C_1$  compounds, reactions of methyl free radicals may have resulted in the formation of C—C bonds. The product distribution was very different when HTH was used. FDMH was no longer seen, but the main product tentatively identified was *sym*-1,2,3,5-tetramethyltetrazine, which is the cyclic dimer of FDMH. In continuation of that study, higher hypochlorite/hydrazine(s) ratios were applied, resulting in a lower number of reaction products and a lower concentration of the main product, FDMH. FDMH formed as an intermediate and was converted to chlorinated by-products. In one experiment, where UDMH solution was added to the sodium hypochlorite solution rather than the other way around as in most of the experiments, *N*-nitrosoethylmethylamine was found in addition to NDMA. When carbon dioxide was added to UDMH prior to the experiment, a rose color developed with the first addition of bleach, which eventually changed to yellow as the oxidation progressed. The yellow reached a maximum intensity at a point where 80% of the stoichiometric amount of hypochlorite had been added. Chloroform and NDMA were some of the more worrisome reaction products among 30 other peaks seen in the GC fractogram. In continuation of these studies, it was noted that when Aerozine-50 was treated with bleach, *N*-nitrosoethylmethylamine was prevalent, which could not be seen in identical tests with UDMH [297, 298]. It must have originated from UDMH, however, the presence of hydrazine changed the direction of the reaction. The effects of different bleach : Ae-50 ratios, lower pH (pH = 2), operating temperatures, methanol addition, and durations of standing (7 d) after bleach addition were also studied and had some impact on ultimate product compositions.

Wastewater containing UDMH was treated with chlorine dioxide and the chemical reaction mechanism was determined through analysis [634]. The wastewater was treated in a multi-stage oxidation column and an activated carbon adsorption column. Typically, the mol ratio of UDMH to chlorine dioxide was controlled between 1:9 and 1:11. Multi-stage oxidation column series were used to enhance oxidation efficiency and complete utilization of chlorine dioxide. Under the conditions of mol ratio of UDMH to  $ClO_2$  of 1:9 and an oxidation temperature of 288 K (15 °C), the treated wastewater could satisfy US local standards for wastewater discharge cleanliness.

#### 1.6.6.4 UDMH Wastewater Decontamination Using Ultrasonic Agitation

An oxidation process based on a combination of hydrodynamic cavitation and acoustic cavitation has been investigated for the decontamination of UDMH-contaminated wastewater [635]. The effects of various operating parameters such as velocity, inlet pressure, temperature, and pH on the extent of UDMH conversion have been studied with the aim of optimizing the extent of decontamination. No toxic by-products were

observed in the decontaminated samples, although the oxidation process eliminated up to 97% of UDMH. A synergistic effect has been obtained by a hybrid method of acoustic and hydrodynamic cavitation.

A pilot-scale hydrodynamic cavitation reactor, using iron metal blades as the heterogeneous catalyst, with no external source of  $\text{H}_2\text{O}_2$  was developed for the catalytic decontamination of UDMH-containing wastewater [636]. *In-situ* generation of Fenton reagents suggested an induced advanced Fenton process to explain the enhancing effect of the catalyst in the hydrodynamic cavitation process. The effects of the applied catalyst, pH of the initial solution (1.0–9.7), initial UDMH concentration (2–15 mg/L), inlet pressure (5.5–7.8 bar), and downstream pressure (2–6 bar) have been investigated. The results revealed that the highest cavitation rate of UDMH removal can be obtained at pH 3 and at initial UDMH concentrations of 10 mg/L. An increase in the inlet pressure would lead to an increase in the extent of UDMH degradation. A downstream pressure of 3 bar resulted in 98.6% degradation of UDMH after 120 minutes of processing time. Neither NDMA nor any other toxic by-product (end product) was observed in the investigated samples. Formic acid, acetic acid, and nitromethane were identified as oxidation by-products. Hydrodynamic cavitation in combination with Fenton's chemistry can be effectively used for the removal of UDMH from water.

#### 1.6.6.5 UDMH Wastewater Decontamination Using Adsorbents

Cation ion exchange fibers were used to adsorb UDMH from wastewater [637, 638]. Adsorption behaviors were studied by using static and dynamic adsorption methods. Experimental results showed that the kinetics of adsorption of the fiber was mainly controlled by a film diffusion process. Adsorption reaction rates increased with an increase in temperature. Equilibrium data for the adsorption of UDMH were correlated by a Freundlich isotherm equation. Dynamic adsorption results showed that the UDMH adsorption rate of ion exchange fibers is greater than that of granular resins, and the fiber adsorption capacity is 3.86 times larger than that of the granular resin beads. UDMH can be desorbed rapidly with sodium chloride solution.

During the investigation of the adsorption performance of strongly acidic ion-exchange fibers for UDMH, the adsorption isotherms of UDMH on ion-exchange fibers within the temperature range of 287–318 K and the concentration range of 40–190 mg/L were in accordance with the Langmuir-type and Freundlich-type isotherm equations [639]. Equilibrium adsorption isotherms at different temperatures and isosteric enthalpy of the adsorption of UDMH indicated that the process of adsorption of UDMH on ion-exchange fibers was an endothermic process. Estimations of the isosteric enthalpy of adsorption, free energy, and entropy of adsorption indicated that there were no chemical bonds formed.

The removal of UDMH from wastewater was studied using activated carbon magnetic nano-composite powders [640]. Process parameters such as pH, adsorbent

dosage, contact time, and temperature have been optimized. More than 90% UDMH removal efficiency was obtained within 30 minutes of contact time, with 20 mg of adsorbent at pH 6 at room temperature. The adsorption behavior was evaluated based on equilibrium data using both the Langmuir and Freundlich isotherm models. It was found that adsorption data were interpreted using the Freundlich model better than Langmuir model. Additionally, the adsorption data were well described by the pseudo-second-order kinetic model. The adsorption thermodynamic parameters showed that the adsorption process is endothermic with a positive standard enthalpy of 2.74 J/mol and negative standard free energy of 29.08 kJ/mol, respectively. The standard entropy changes were  $97.56 \text{ J mol}^{-1} \text{ K}^{-1}$ .

Exchange processes for different concentrations of UDMH in ion exchange resins were studied, and exchange properties could be expressed by penetration curves [641]. UDMH ion exchange properties can be expressed by a penetration and breakthrough point curve. Major factors influencing the penetration curve are concentration, velocity of flow, and type of resin. The results showed that a type 1 resin was excellent for cation exchange work and that penetration solution was in accord with the requirement to keep UDMH concentration in effluents below 0.5 mg/L. The results showed that ion exchange resins can reduce the UDMH concentration to less than 0.5 mg/L.

Carbon nanotubes (CNTs) were modified by NaOH or  $\text{H}_2\text{O}_2$  treatment and used for the removal of low concentrations of UDMH from wastewater [642]. UDMH in solution was measured using a spectrophotometric method. Scanning electron microscopy (SEM) observation and FTIR spectra showed that the as-prepared CNTs had worse dispersing properties and the tubes were longer. After treatment with NaOH, the CNTs clusters were dispersed, and after treatment with  $\text{H}_2\text{O}_2$ , the tubes were broken up and decorated with  $-\text{OH}$ ,  $\text{C}=\text{O}$ , and  $-\text{COOH}$  groups on their surface. The adsorption experiments showed that the CNTs processed by  $\text{H}_2\text{O}_2$  had the best adsorption properties for the removal of UDMH. The second best were the CNTs processed by NaOH and the worst were the as-prepared and untreated CNTs. The adsorption isotherms at 298 K and the concentration range of 40–190 mg/L all were in accordance with the Freundlich-type and Langmuir-type isotherm equations.

The UDMH adsorption performance of multi-walled carbon nanotubes (MWCNTs) modified by NaOH was in accordance with the Freundlich-type and Langmuir-type isothermal adsorption equations within the temperature range of 296–313 K and the concentration range of 44–211 mg/L [643]. Isothermal adsorption curves at different temperatures and isosteric enthalpy of adsorption of UDMH indicated that the adsorption of UDMH on MWCNTs is an endothermic process. An estimation of the enthalpy of adsorption, Gibbs free-energy, and entropy of adsorption indicated that there are no chemical bonds formed and that the adsorption behavior was reasonably well interpreted.

#### 1.6.6.6 UDMH Wastewater Decontamination via Irreversible Absorption

It was not clear if the following decontamination method was intended for UDMH solutions or UDMH vapors in the air. It might work equally well for vapor and aqueous UDMH. The absorbent (an irreversible, expendable absorbent) was oxalic-acid-modified attapulgite [644]. Attapulgite clay was modified via treatment with oxalic acid to improve its adsorption performance for UDMH. The effect of oxalic acid concentration, solid-liquid ratio, dispersant, temperature, and activation time on the adsorption performance of the attapulgite-oxalic acid was investigated and an optimal process for modifying attapulgite by using oxalic acid was selected by experiments in a test matrix. The results revealed that the UDMH absorption rate can reach 95% with attapulgite made using a saturated oxalic acid solution, a solid-liquid ratio of 1 g : 10 mL, a temperature of 303 K (30 °C), and with an immersion time of 60 minutes.

#### 1.6.6.7 UDMH Wastewater Decontamination Using Active Sludge Processes

A biodegradation technique with aerobic active sludge was used to treat UDMH-contaminated wastewater [645]. By acclimatizing cultures of bacteria to the presence of UDMH for 60 d, the removing efficiency of UDMH in the wastewater reached 98% by active sludge treatment. The pH value, sludge concentration, temperature, stirring speed, and UDMH concentration can influence biodegradation efficiency of active sludge. The optimum conditions for UDMH degradation treatment with active sludge with an incoming concentration of  $\leq 1580$  mg UDMH/L were pH 7.0–7.5, sludge mass concentration of 1.28–1.60 g/L, temperature 298–303 K (25–30 °C), and stirring speed of 80–100 RPM.

A combined process of electrolyzed oxidizing water (EOW) and membrane bioreactor (MBR) was applied to the treatment of UDMH-contaminated wastewater, and its treatment efficiency was compared with that of MBR alone [646]. The treatment efficiency of the combined process for the treatment of UDMH-contaminated wastewater was better than that of MBR alone. When the incoming COD and UDMH concentrations were 800 to 1000 mg/L and 300 mg/L, the effluent COD and UDMH concentrations were about 55 mg/L and 0.3 to 1.5 mg/L, respectively. This is close to the requirements of the allowed discharge standard of water pollutants for space propellants established by the US government. With the MBR process by itself, the effluent COD and UDMH concentrations were about 90 and 45 mg/L, respectively. These findings were worse than the results when using the combined EOW-MBR process.

An integrated MBR was used to dispose of UDMH wastewater in a laboratory test set-up [647]. The factors affecting the efficiency of UDMH removal such as hydraulic retention time (HRT), D.O., pH, and mixed liquor suspended solids (MLSS) were studied under the following test conditions: UDMH concentration 40–50 mg/L, COD 800–1000 mg/L, pH 6.5–9.0, MLSS 6–12 g/L, D.O. 0.5–3.0 mg/L, and HRT 18–24 h. The results showed that, with an HRT of 18 h, D.O. of 2.5 mg/L, pH of 8.0, and MLSS of 10 g/L, the integrated MBR had the best UDMH degradation rate. The average one-pass re-

removal efficiency of COD and UDMH removal was 95 and 99.4%, respectively. It was found that the UDMH wastewater could be purified effectively by an MBR and, therefore, the requirements of environmental protection agencies could be satisfied.

Twenty-four different strains of UDMH-degrading bacteria were isolated from acclimated activated sludge. Among them, four strains of bacteria with better degradation efficiency were selected for further testing [648]. The compound bacterial flora was built with random combinations of the four strains of bacteria. It was found that compound bacterial flora can effectively degrade UDMH. Certain combinations could achieve 72-h degradation efficiencies higher than 94% when the UDMH initial concentration was 50 mg/L. One specific combination was chosen as a highly effective compound bacterial flora for further consideration.

A combined process of EOW and MBR was applied to treat UDMH-contaminated wastewater, and its treatment efficiency was compared with that offered by MBR alone [649]. In the combined process, the treatment efficiency of UDMH wastewater was better than with the MBR alone. When the influent COD and UDMH concentrations were 800 to 1000 mg/L and 300 mg/L, the effluent COD and UDMH concentrations (after a single pass) were about 55 mg/L and 0.3 to 1.5 mg/L, respectively. This is close to the requirements of the Chinese government discharge standard of water pollutants for space propellants. In the MBR process alone, the effluent COD and residual UDMH were about 90 and 45 mg/L, respectively, which was worse than when using the combined EOW-MBR process.

On the basis of the efficiency of UDMH-degrading bacteria preserved in the laboratory, a compound flora was built with the intention to use it when UDMH leaked into water [650]. The optimal conditions for the degradation of UDMH determined by efficiency factor experiments were as follows: temperature 35 °C, medium pH 7.2, inoculation 2%, and initial UDMH concentration 50 mg/L. Under these conditions, the highest UDMH degradation efficiency was 99.10%, and UDMH residual concentration was less than 0.5 mg/L in 72 h. All indicators of water quality met the requirements of GB1473-93 emission standards.

NDMA forms naturally in many wastewater streams. Therefore, its presence does not necessarily prove that a nearby rocket test facility has contaminated the environment. Thus industrial UDMH contamination must be reviewed with consideration given to the natural concentration of NDMA found in the environment.

#### **1.6.6.8 UDMH Wastewater Decontamination via Microwave Treatment**

A combination of microwave radiation with activated carbon catalyst was used to treat UDMH-contaminated wastewater with air [651]. The effects of radiation power, exposure time, and the activated carbon amount on UDMH removal efficiency by air oxidation were studied. The results revealed that with 100 mL of 400 mg/L UDMH wastewater, radiation power 462 W, activated carbon 5.0 g, and with a reaction time of 15 minutes, the removal efficiency was only 40% under optimal conditions.

#### 1.6.6.9 UDMH Wastewater Decontamination Using Aeration

The cheapest oxidizer for the decontamination of UDMH-contaminated wastewater is air. Bubbling air through the water to maintain saturated oxygen conditions will oxidize UDMH. However, the air will also carry away some UDMH and toxic degradation products and escaped UDMH vapors may require additional secondary treatment.

The oxidation of the aqueous solutions of UDMH in the presence of Cu-, Fe-, Co-, and Mn-containing catalysts supported on oxide carriers is potentially useful as pre-treatment for the disposal of UDMH rinse waters (to conserve more expensive oxidizers needed for complete detoxification) [254]. The main products of the reaction were hydrazones and formazane, which themselves are toxic. The autoxidation of UDMH in an aqueous solution by air can be accelerated by catalysts deposited on activated charcoal [652].

An investigation into the possibility of using atmospheric oxygen as an oxidant for the full catalytic oxidative breakdown of UDMH (“heptyl”) in the natural waters of high altitude areas in the Altai/Sayan Mountains region (where the detachable portions of second-stage launchers fall down) revealed that the aerobic oxidative breakdown in the presence of copper-bearing and iron-bearing zeolite catalysts of ZSM-5 structures is an effective method for ensuring full mineralizing of UDMH, whose content in water near impact sites may be up to 1000 times the limit usually considered safe [653].

#### 1.6.6.10 UDMH Wastewater Decontamination Using Electrolyzed Oxidizing Water

Electrolyzed Oxidizing Water (EOW) can be made via electrolysis of diluted sodium chloride solutions in an electrolysis chamber with membrane separation, with free chlorine as the major oxidizing agent but also using hypochlorous acid or hypochlorite (depending on the pH level). EOW is widely used for the disinfection of food preparation equipment and even for disinfecting some food items also. EOW can be used for wastewater treatment. In addition to chlorine and hypochlorous acid, it may also contain ozone, but no hydrogen peroxide, depending on the amount of available chloride [654].

A study of the role of acidic EOW on the decontamination of UDMH-contaminated wastewater found that the UDMH removal efficiency can reach 94.8% when the volume ratio of wastewater containing an initial UDMH mass concentration of 150 mg/L to acidic EOW is 1 : 4, and when the reaction time is 1.5 minutes and the reaction temperature is  $\geq 292\text{ K}$  ( $\geq 19^\circ\text{C}$ ) [655, 656].

#### 1.6.6.11 UDMH Wastewater Decontamination via Electrolysis

Hydrazine and/or UDMH in wastewater in the concentration range of 100 to 800 ppm can be destroyed via direct electrolysis with a stainless steel cathode and a carbon, lead, or nickel anode [657]. Disodium hydrogen phosphate was added to increase conductivity and pH was adjusted with phosphoric acid.



#### 1.6.6.12 UDMH Wastewater Decontamination Using Electrodeionization (EDI)

EDI is a process that combines electrodialysis and ion exchange. An EDI device packed with strong acidic cation ion-exchange fibers was used to decontaminate simulated rocket launch site UDMH-containing wastewater under laboratory conditions [658]. The concentration of UDMH in contaminated water can reach over 3397 mg/L. The characteristic curves of voltage versus current, pH value of the water, and the effect of treating simulated water samples were studied. The results revealed that, in comparison with electro-dialysis (ED), the efficiency of water treatment using EDI was higher and the polarization of water in membrane piles mainly occurred on anion exchange membrane surfaces. The treated water after passing through the apparatus several times can reach emission standards/maximum allowable limits.

#### 1.6.6.13 UDMH Wastewater Decontamination Using Supercritical Water

The catalytic wet oxidation of UDMH in wastewater was investigated in a trickle-bed reactor system with a catalyst at 473–523 K (200–250 °C), 5.07 MPa (50 bar), and LHSV 1.8–2.3 [659]. The ratio of the oxygen-supply to COD was 2.0 and 3.0 and the initial concentration of UDMH was 0.5 to 2.0 mass-%. Experimental results showed that the UDMH concentrations could be reduced rapidly to less than 1 ppm in 26 minutes at 503 K (230 °C) or higher. A liquid-phase catalytic oxidation process was carried out continuously for 223 h and no deactivation of the catalyst was observed during this operating period.

A series of tests on the treatment of UDMH wastewater by supercritical water oxidation showed that the process with O<sub>2</sub> as the oxidant can efficiently oxidize and destroy UDMH [660]. Reaction temperature, pressure, and residence time were the main variables affecting the rate of degradation of UDMH. Increasing the reaction temperature, pressure, and prolonging the residence time can significantly augment the removal rate of UDMH. With a reaction temperature of 823 K (550 °C) at a pressure of 30 MPa and with a residence time of 90 s, the removal rate of COD was over 99.8%.

A study of supercritical water oxidation of UDMH in a tubular continuous-flow reactor system with H<sub>2</sub>O<sub>2</sub> as the oxidant, at a temperature range between 753 and 823 K (480 and 550 °C) and at a pressure of 30 MPa, revealed that the oxidative destruction of UDMH can be done quickly with a high COD removal speed up to 93.5% within 5.8 s at 823 K (550 °C) and 30 MPa on the condition that excess oxygen is available [661]. The oxidative UDMH destruction efficiency and COD removal efficiency significantly improved as reaction temperature and residence time increased. The experiments also showed that within the temperature range of 753 to 823 K (480 to 550 °C), the COD removal efficiency was strongly temperature-dependent. At 753 and 823 K (480 and 550 °C), 30 MPa, and with a 50% H<sub>2</sub>O<sub>2</sub> excess, the reaction can proceed in 1.13<sup>th</sup> order with COD and 0.29<sup>th</sup> order with oxygen. The activation energy was 44.65 kJ/mol with an Arrhenius pre-exponential factor of  $4.93 \times 10^3$ .

The catalytic oxidation of UDMH in supercritical water was investigated using  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$  as catalysts and  $\text{H}_2\text{O}_2$  as an oxidant in a packed-bed flow reactor [662]. The results indicated that  $\text{CuO}$  and  $\text{MnO}_2$  catalysts have the desired effects of accelerating the UDMH disappearance. The higher rate of UDMH removal was obtained at higher temperatures and higher pressures and had a longer residence time. A 99% removal of COD was achieved at 24–26 MPa and 673–723 K (400–450 °C) within a few seconds. The catalytic effect of the catalyst  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$  was better than that of  $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ . The final products were  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ .

Hydrothermal processing is an alternative destruction method for hazardous waste, however, the kinetics of the reactions in the high-temperature/high-pressure aqueous environment is generally unknown. The catalytic oxidation of UDMH in supercritical water was investigated over an  $\text{Mn}^{2+}$  oxidation catalyst and with  $\text{H}_2\text{O}_2$  oxidizer in a tubular continuous-flow reactor at 24–30 MPa and 673–773 K (400–500 °C) [663]. A study of the effects of temperature, pressure, residence time, and concentration of oxidant on the destruction of UDMH indicated that UDMH can be decomposed efficiently by catalytic supercritical water oxidation. The elimination efficiency of UDMH was significantly improved as reaction temperature, pressure, residence time, and oxidant/ $\text{Mn}^{2+}$  concentrations were increased. With an  $\text{Mn}^{2+}$  concentration of 30 mg/L, the destruction of UDMH was much faster than without catalyst. A 99.6% COD removal was achieved at 30 MPa, 773 K (500 °C) and with an  $\text{Mn}^{2+}$  concentration of 30 mg/L in only 3.6 s (see also [664]).

#### 1.6.6.14 UDMH Wastewater Decontamination via Reduction

Destroying UDMH by reduction instead of oxidation avoids the formation of NDMA and other unwanted oxidation products. UDMH in UDMH-contaminated wastewater can be destroyed via catalytic reduction with Raney nickel Ni/Al alloy in alkaline solution [582, 665]. This is done with >99% efficiency at pH 13 and 313 K (40 °C). All results indicated that Ni/Al hydrogenolysis of UDMH is a reliable, quantitative, and efficient degradation method.

UDMH wastewater was treated via reduction in the presence of a Raney catalyst that was made from an Al-Ni alloy. The results showed that the optimum conditions (removal of >99% of the UDMH) for the removal of UDMH is a temperature of 313 K (40 °C), a pH of 13, and a reaction time of 50 minutes [666].

Dilute aqueous solutions of UDMH, NDMA, or *N*-nitrodimethylamine (DMNM) can be decomposed by catalytic reduction with nickel-aluminum (Ni-Al) alloy under basic conditions [574, 667, 668]. Alkylhydrazines and common contaminants or partial oxidation products, including NDMA and DMNM, are reduced to ammonia and/or aliphatic amines. The reaction is based upon dissolution of Al from the Ni-Al alloy in aqueous media to form aluminum ion and hydrogen gas. The resulting finely-divided nickel catalyzes the reduction of the hydrazine, nitrosoamine, and/or nitroamine using the hydrogen produced. Greater than 99% of propellants contained

in dilute UDMH, NDMA, and DMNM aqueous solutions were decomposed when reacted with Ni-Al alloy in 0.5M sodium hydroxide. The major reaction products were simple amines. UDMH, NDMA, and DMNM were reduced to DMA and ammonia. UDMH was an intermediate in the reduction of NDMA. NDMA, and UDMH were intermediates in the reduction of DMNM. Control experiments with Al powder rather than Ni-Al alloy showed no effect on UDMH, whereas NDMA and DMNM were reduced to UDMH, which is where the reaction stopped. Spill pillows containing Ni-Al alloy and solid sodium hydroxide were also tested and found to be effective in the absorption and decomposition of UDMH. These results showed that reductive decomposition of UDMH, NDMA, and DMNM is a promising method for propellant hydrazine waste treatment and spill control.

UDMH aqueous solutions can be decontaminated by passing the heated mixture with excess hydrogen gas through a catalytic reactor, forming DMA and ammonia [572, 573]. The ammonia can then be dissociated; the hydrogen thus formed is fed back into the first reactor. The apparatus can be built on skids so that it can be transported to remote sites where surplus UDMH can be destroyed.

#### 1.6.6.15 UDMH Destruction Using an ICP Torch

An ICP torch generates extremely high temperatures that are suitable for the destruction of most hazardous chemicals, including chemical warfare agents. The PERC<sup>TM</sup> process used an ICP torch as the heat source for a reaction chamber system to convert wastes into by-products in a safe and environmentally clean manner [577, 578]. This would be an extremely energy-expensive way of getting rid of UDMH-contaminated wastewater. UDMH wastewater can be fed together with steam into the plasma discharge where they would be converted to CO and H<sub>2</sub> along with N<sub>2</sub> and a trace of NO<sub>2</sub>.

#### 1.6.6.16 Photocatalytic Decontamination of UDMH-Containing Wastewater

A study of the photocatalytic degradation of UDMH in TiO<sub>2</sub> + Cu<sup>2+</sup> suspensions with sunlight or UV-light indicated that the best performance can be achieved by using a Cu<sup>2+</sup> concentration of 40 mg/L, providing intense UV-light, adding some H<sub>2</sub>O<sub>2</sub>, and increasing the area : volume ratio of the reactor [669]. The main degradation products of UDMH can also be oxidized so that ultimately only inorganic destruction products remain.

A combination of ozone-ultraviolet-activated carbon photo-oxidative technology for sewage treatment was used for the destruction of UDMH in wastewater [670].

Pure ZnO and Nd-doped ZnO were tested as photocatalysts for the destruction of UDMH in wastewater [671, 672]. The oxide samples were characterized by means of XRD, EDAX, UV-Vis spectroscopy, and high-resolution transmission electron microscopy. The photocatalytic performance of different ZnO particles for the destruction of UDMH was studied using a 15-W UV lamp as the light source for illumination.

The effect of the amount of Nd dopant was investigated. The results indicated that Nd-doping improved the photocatalytic performance of ZnO, and that the most active  $\text{Nd}_2\text{O}_3/\text{ZnO}$  mol ratio was 0.025. At 303 K (30 °C), the degradation rate of UDMH, starting with a contaminant concentration of 0.1 g/L, could reach 92% in 100 minutes.

A combination of artificial UV and natural sunlight is effective in destroying UDMH with hydrogen peroxide, using supported  $\text{TiO}_2$  as a catalyst, and by adding  $\text{Cu}^{2+}$  and  $\text{H}_2\text{O}_2$  [673]. With UV light illuminating a 1500 mg/L UDMH solution for 0.5 h, followed by exposure to sunlight for 7 d, the degradation efficiency was 99.9%. This leads to an energy saving. Additionally, the processing period is shortened by this method compared with natural degradation using sunlight alone.

The nano-size particles of ZnO are active as catalysts for the photocatalytic degradation of UDMH in wastewater [674]. The nano-particles of ZnO used for this purpose were characterized by means of XRD and IR absorption spectroscopy, and the effects of the operating variables, including temperature, pH, and catalyst concentration on the rate of UDMH destruction in wastewater were measured.

Nano-size particles of titanium dioxide prepared by the sol-gel method are active as photocatalysts for the photocatalytic degradation of UDMH in wastewater [675].  $\text{TiO}_2/\text{glass}$  films have been prepared using a sol-gel method starting with titanium tetrabutoxide as the precursor. The films were placed in a photoreactor designed to degrade UDMH in water [676, 677]. The photodegradation followed first-order kinetics. The results indicated that the stationary film had higher catalytic activity during the photodegradation of UDMH and longer useful life in comparison to suspended  $\text{TiO}_2$  powders that were previously used.

An initial concentration of 400 mg UDMH/L in wastewater was destroyed within 30 minutes at pH 7–8 by stirring and UV illuminating with solid superacid  $\text{SO}_{2-4}/\text{TiO}_2\text{—Cu}^{2+}$  and  $\text{SO}_{2-4}/\text{TiO}_2\text{—Ag}^+$  catalysts that had been prepared by a sol-gel method. The removal efficiency was better than 96% [678].

$\text{ZnO}/\text{Pd}$  nano-particles were used in the UDMH wastewater decontamination using photocatalysis under UV-light and sunlight [679]. Results revealed that the UV absorption property was enhanced by doping with Pd; this spanned 400–800 nm in visible light. The maximum degradation rate of UDMH in contact with  $\text{ZnO}/\text{Pd}$  for 2 h was 80% in sunlight and 77% under UV-light. The disappearance of the photocatalytic intermediate product under different light sources was analyzed. It was found that the intermediate product decomposed more quickly and thoroughly under sunlight, with a COD degradation rate of 75%. This was better than under UV-light with a degradation rate of only 58%/2h.

Experiments revealed that the photocatalytic degradation efficiency using activated carbon fiber (ACF) supported solid super acid catalysts.  $\text{H}_2\text{O}_2$  were significantly superior to those using granular activated carbon (GAC) supported catalysts [680, 681].

The photocatalytic destruction of UDMH works not only in water but also with UDMH vapors in air [682]. Carbon dioxide, water, nitric acid, and nitrogen were detected as the ultimate photocatalytic oxidation products of UDMH. Adsorbed  $\text{N}_2\text{O}$  species were detected as the main surface intermediates. The formation of NDMA was not observed. Long-term experiments to determine the photocatalyst stability in photocatalytic oxidation of UDMH showed that the catalyst exhibited stable performance. The rate of deactivation was low due to the transformation of nitrogen (mainly to  $\text{N}_2$ ). Only 10% of UDMH's nitrogen was transformed to  $\text{HNO}_3$  in adsorbed form.

### 1.6.7 Filtration of UDMH-Contaminated Air

The air in UDMH vapor contaminated areas following a leak or a controlled disconnect of transfer lines may have to be filtered and purified before personnel are allowed to enter the area again without wearing whole-body personnel protection ensembles. Air filtration installation apparatus could be like over-sized personal gas masks with consumable filters that must be exchanged periodically when their absorption capacity is exhausted. Air would be recirculated through these filters by forced flow until the UDMH concentration has been lowered to a safe level. Air-oxidation of adsorbed UDMH on the surface of the absorbent in the filter would be desirable as long as it does not result in oxidation products (e.g., NDMA) that are more toxic than UDMH itself. Air filtration installations might be similar to vented gas scrubbers described in the following section.

It was not clear if the following decontamination method was intended for UDMH solutions or UDMH vapors in air. It might work equally well for vapor and aqueous UDMH. The absorbent (one that is irreversible and expendable) was oxalic-acid-modified attapulgite [644]. Attapulgite clay was modified via treatment with oxalic acid to improve its adsorption performance for UDMH. The effect of oxalic acid concentration, solid-liquid ratio, dispersant, temperature, and activation time on the adsorption performance of the attapulgite-oxalic acid was investigated, and an optimal process for modifying attapulgite by using oxalic acid was selected using an orthogonal experiment. The results revealed that the UDMH absorption rate can reach 95% with attapulgite made using saturated oxalic acid solution, a solid-liquid ratio of 1g:10mL, a temperature of 303K (30°C), and an immersion time of 60 minutes.

It is known that biodegradation of hydrazines in soil is aided by certain types of bacteria and nutrients. It has been proposed to build a stationary air filter consisting of an incubator with permeable soil where UDMH vapors would be absorbed and digested by bacteria [683].

### 1.6.8 UDMH Absorption from Vented Pressurant Gases

Transfer of small quantities of UDMH or UDMH blends is usually achieved by pressurization of the supply tank instead of pumps. After the transfer is complete, the pressurant gas, which is saturated with UDMH vapor, must be vented. In cases where the pressurant gas cannot be safely vented to the ambient atmosphere, the pressurant gas may have to be passed through a scrubber where the UDMH is adsorbed to a solid adsorbent or washed out in a spray or trickle bed tower with an absorbent liquid. The pressurant gas is an inert gas (nitrogen or helium) and some of the vapor neutralization schemes described in the previous section for the removal of UDMH vapors from the air would not work in the absence of oxygen.

### 1.6.9 Personnel Protective Equipment for the Handling of UDMH

A carefully planned approach to workplace safety is required to protect workers from the adverse effect of UDMH inhalation [684, 685]. This includes proper protective equipment, thorough personnel training, and periodical physical exams.

Mine Safety Appliance Company's Rocket Propellant Canisters, Model GMN-SSW, were tested in gas masks against  $\text{NO}_2$  and UDMH [686]. Canisters manufactured in 1967 were compared to canisters made in 1971. Results of the study indicated that there was no statistically significant difference between the absorbing capacities of the new and old canisters for both contaminants. One of the built-in safety features of the canisters was a small viewing window containing a color indicator that changed from orange to blue-green when the absorbing capacity was 50 to 75% exhausted. The concentration  $\times$  time product to cause a color change and to penetration at an inlet concentration of 1 ppm of UDMH and a flow rate of 38 L/min. was tested. It varied between 125000 and 212000 ppm  $\times$  min., but the color would change before that point. The study concluded that indicators on the new canisters were unsatisfactory for both UDMH and  $\text{NO}_2$ .

Several polymeric materials for gloves, boots, aprons, and splash shields were evaluated in permeation tests with UDMH, MMH, and IRFNA [687–689]. Of the 28 gloves tested, butyl (0.33–0.81 mm thick) and supported neoprene (1.4 mm) were found to have the lowest permeability for UDMH during a 90-minute test.

## 1.7 Safety Properties of UDMH

### 1.7.1 Flash Point and Limits of Flammability of UDMH

A very useful source for UDMH safety information and Ae-50 is the three-volume series called *Hazards of Chemical Rockets and Propellants*; a handbook published by the former Chemical Propulsion Information Agency (CPIA). Volume 1 discusses safety, health, and the environment [690]. Volume 2 discusses solid propellants (which have not yet been discussed in this publication), and Volume 3 discusses liquid propellants

[691]. NASA's WSTF has put together a very practical handbook called the *Ignition and Thermal Hazards of Selected Aerospace Fluids* (which includes UDMH and Ae-50) [692].

### 1.7.2 Flash Point of UDMH in Air

The flash point of UDMH in air is 257 K [200]. In the same report, the flash points of UDMH mixtures called MAF-1 and MAF-3 were determined to be 275 and 295 K, respectively.

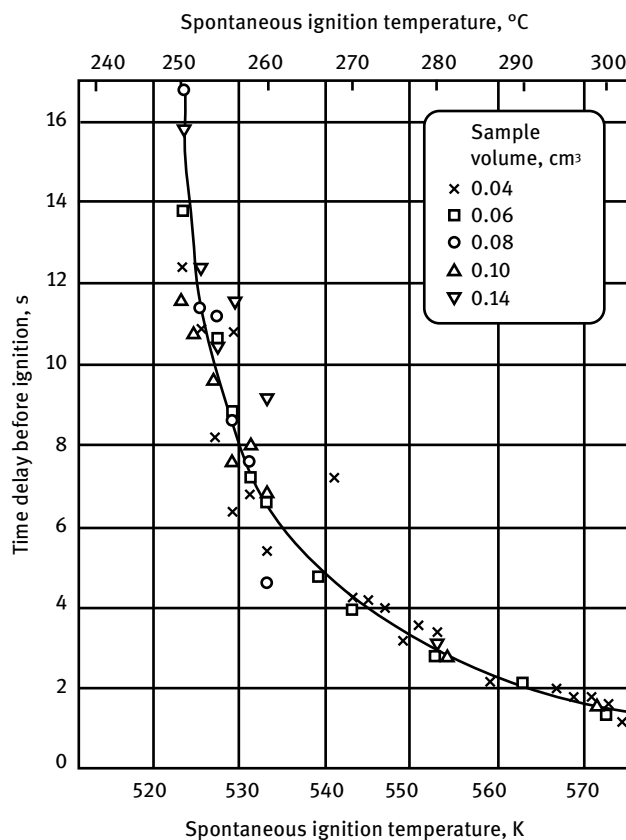
### 1.7.3 Auto-Ignition Temperature of UDMH in Air

The auto-ignition temperature of UDMH in air (0.1 mL squirted into a 125-mL Pyrex round flask or 0.3 mL squirted into a 1-L Pyrex round flask) was 507 K (454 °F) [177]. This temperature did not change much by adding 40% DETA to UDMH (516 K = 469 °F). This fuel blend is also known under the name U-DETA. Similar experiments were conducted in inert gases instead of air to determine the autodecomposition temperature of UDMH in the same apparatus.

The critical conditions of pressure and temperature and composition (critical limits) necessary for UDMH explosion have been measured and the effects of vessel surface, vessel diameter, and inert diluents on the critical limits were investigated [199]. The spontaneous ignition limit found for the decomposition of pure UDMH satisfied the criteria of a thermal explosion. The overall activation energy  $E_a = 117 \pm 4 \text{ kJ/mol} = 28 \pm 1 \text{ kcal/mol}$  derived from the measured ( $P$  versus  $T$ ) limit by the application of thermal explosion theory agreed with that derived from kinetic investigations of the slow decomposition. By contrast, spontaneous ignition in oxidative combustion is extremely complex and differs qualitatively as well as quantitatively from the superficially analogous combustion mono-, di-, and tri-methylamines. There are four distinct oxidation regimes: slow reaction, chemiluminescent oxidation, weak ignition, and strong explosion. In addition to this, multiple ignitions have been observed. The autodecomposition of UDMH in a glass vessel started at 693 K/6.4 kPa = 420 °C/48 mm Hg, 718 K/3.9 kPa = 445 °C/29 mm Hg, 758 K/1.6 kPa = 485 °C/12 mm Hg, or 787 K/0.8 kPa = 514 °C/6 mm Hg. In each case, the pressure rose to twice the initial pressure as the result of the decomposition of the UDMH vapor.

It was noted that UDMH has a lower autodecomposition temperature than hydrazine (703 versus 873 K at 8 kPa = 60 mm Hg). Additional data on the spontaneous ignition of UDMH in the air were obtained in a 350-cm<sup>3</sup> silica vessel at 6.45, 3.84, 1.65, and 0.76 kPa (48.5, 28.9, 12.4, and 5.7 mm Hg), resulting in auto-ignition temperatures of 693, 720, 757, and 787 K, respectively [693]. If the logarithm of the test pressure was plotted against the reciprocal absolute temperature of auto-ignition, a straight linear (Arrhenius-type) relationship could be observed that was suitable for data interpolation.

In another USBM spontaneous ignition test apparatus in air, UDMH ignited at 523 K (482 °F) with a delay of 12 s [178]. At an elevated pressure (1.38 MPa =



**Figure 19:** Time lag of UDMH ignition in air in a 200-mL Pyrex flask at 1 atm pressure as a function of spontaneous ignition temperature. (Reproduced and modified from [178].)

200 psig), the ignition temperature was lowered to 421 K (298 °F) and the ignition delay was markedly shorter (1 s). Figure 19 shows the time lag of UDMH ignition in air in a 200-mL Pyrex flask at 1 atm pressure as a function of spontaneous ignition temperature. The sample volume varied between 0.05 and 0.14 mL of UDMH. No ignitions were observed below 523 K (250 °C). If one plots the logarithm of ignition delay versus reciprocal absolute temperature, the slope of the curve indicates an activation energy of 88 kJ/mol (21 kcal/mol) for the temperature range 533–573 K (260–300 °C).

One can attempt to pre-mix oxidizer and fuel first, then start the heating process. However, the difficulty frequently encountered with auto-ignition temperature-testing is raising the test temperature uniformly and quickly without triggering premature slow reactions in the gas phase. Some ignition reactions also show an inhibition period, causing a delayed ignition a long time after the test temperature has been



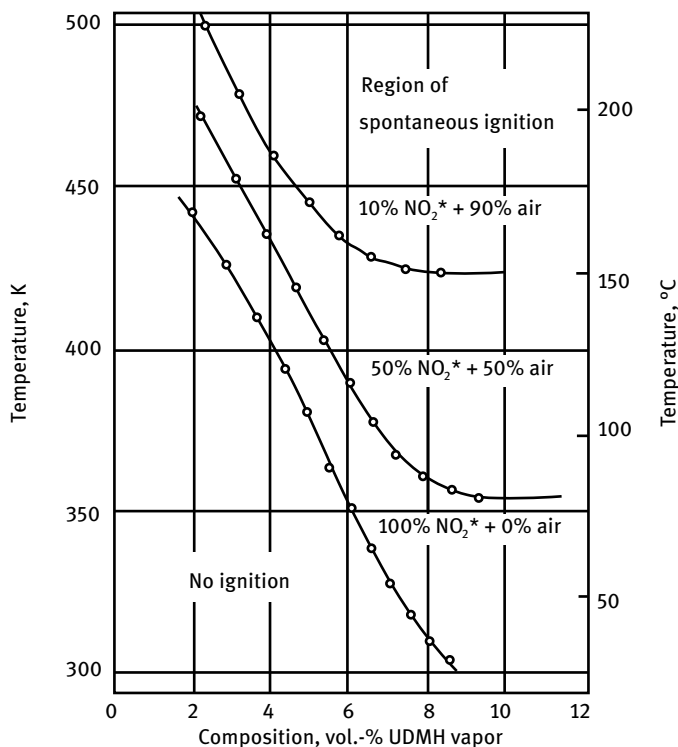
reached. This has also been observed with hydrazine and with UDMH in closed vessels at low pressures.

Minimum ignition energies measured using laser-induced breakdown in the air/UDMH mixtures were compared to those of more common flammable mixtures such as air/hydrogen and air/hexane [694]. Seeding the mixture with  $\text{CO}_2$  enhanced the absorption of radiation from the  $\text{CO}_2$  laser.

### 1.7.3.1 Auto-Ignition Temperature of UDMH in Other Atmospheres

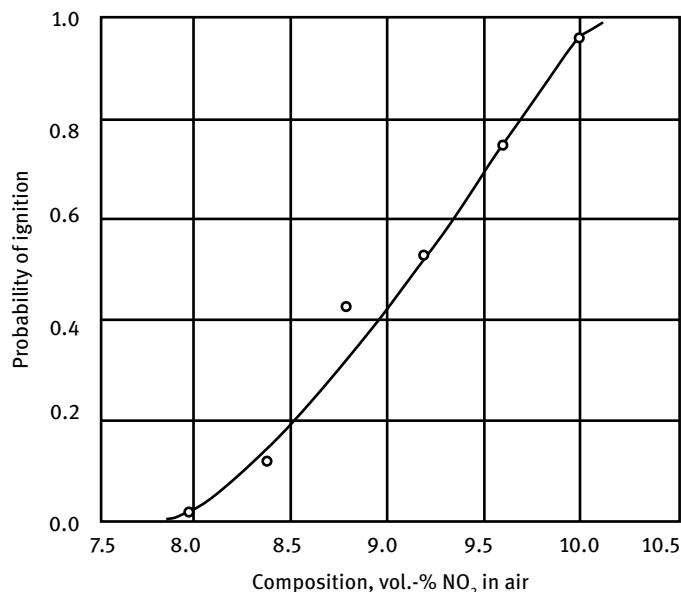
The chapter on methylhydrazine already contains discussions about the spontaneous auto-ignition of MMH in air and how that contains varying amounts of  $\text{NO}_2$ . Additionally, the conditions leading to the accidental ignition of such mixtures and tabulated spontaneous ignition data for all three hydrazines ( $\text{N}_2\text{H}_4$ , MMH, and UDMH) have already been discussed in the MMH section.

Figure 20 illustrates the spontaneous ignition temperature of UDMH vapors as a function of fuel vapor concentration in air- $\text{NO}_2$  atmospheres with varying  $\text{NO}_2$  concentrations [237].



**Figure 20:** Spontaneous ignition temperature of UDMH in  $\text{NO}_2$ /air mixtures at 298 K as a function of UDMH concentration. (Reproduced and modified from [237].)

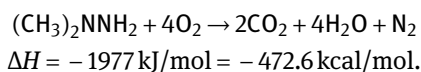
A statistical evaluation of 600 ignition tests, where liquid UDMH was injected into atmospheres containing increasing amounts of  $\text{NO}_2$  at 298 K, resulted in the probability curve shown in Figure 21.



**Figure 21:** Probability of ignition of liquid UDMH on contact with  $\text{NO}_2$ /air mixtures at 298 K as a function of  $\text{NO}_2$  concentration. (Reproduced and modified from [237].)

It is unlikely that UDMH would be in contact with pure oxygen and thus auto-ignite, except maybe at the launch sites of the Glushko RD-119 engine at one point in time. This was used in the second stage of the Russian KOSMOS launcher, and in some IRBMs and used LOX/UDMH in an O:F mass ratio of 1:5. For the laboratory study of ignition mechanisms, it is better to work with pure oxygen and to eliminate the effects of nitrogen in the air as the diluent. The critical pressure limits of the spontaneous ignition of UDMH in oxygen were determined by measuring the total pressure of the reaction mixture necessary for ignition on admission to a hot vessel [693]. Distinct modes of oxidation exist for UDMH undergoing spontaneous ignition both in decomposition and in oxidative combustion, including strong explosions, weak ignition, chemiluminescent oxidation, and slow reaction. When studying the ignition behavior of UDMH-oxygen mixtures on rapid admission to a pre-heated quartz vessel, it was found that the explosion limits of oxygen-UDMH are far more complex than those of oxygen-hydrazine. At least five different modes of reaction were observed: chemiluminescence ("cool flames"), weak ignitions, multiple ignitions, slow reaction, or vigorous explosion. The spontaneous ignition pressure limits at two different temperatures

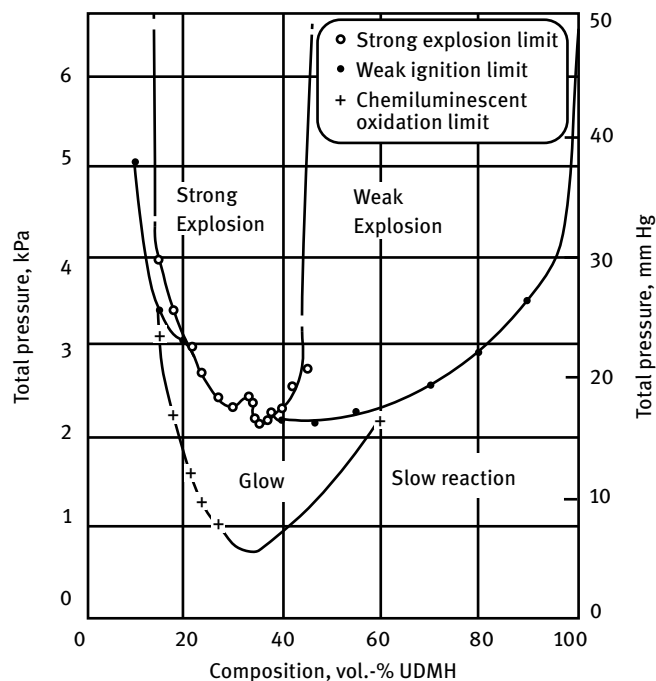
(787 and 693 K) were determined and plotted in a total pressure versus percent UDMH diagram. In this type of graphical illustration, the different regimes of ignition were separated by fairly sharp borderlines. The minimum pressure at which strong explosions could be observed (12–15 mm Hg) occurred at a composition close to  $(\text{CH}_3)_2\text{NNH}_2 + 2\text{O}_2$ . All data of pressure and temperature dependence of the explosion limit were in agreement with those expected from a thermal explosion theory. The combustion of UDMH in oxygen showed hardly any similarity with that of chemically similar looking methylamines. Qualitatively, the combustion of UDMH differed markedly from that of the superficially analogous mono-, di-, and tri-methyl-amines. Depending on the pressure, composition, and temperature, oxidation of UDMH in oxygen may be either **(1)** a slow reaction, unaccompanied by light emission, **(2)** a very feebly chemiluminescent reaction, **(3)** a weak ignition, or **(4)** a violent, audible explosion accompanied by an intense flash. Furthermore, there are possibilities of multiple ignitions with reactions **(3)** and **(4)**. Complete oxidation of UDMH with oxygen is very exothermic:



Vigorous explosions were encountered in all mixtures from 15 to 45% UDMH, with the critical pressure limit tending to be a minimum near the center of this composition range. The weak ignitions were observed in mixtures that were either too rich or too lean in UDMH for strong explosions to occur. The chemiluminescent reaction was seen (under conditions too mild for strong explosion or weak ignition) in mixtures containing from 14 to 62% UDMH. Chemiluminescence appeared not to be a precursor of ignition. The composition dependence of the pressure limits for the spontaneous ignition of  $\text{O}_2$ /UDMH mixtures at 787 or 693 K (514 or 420 °C) was found to be a minimum at ~33%, which corresponds to a stoichiometric mixture of UDMH +  $2\text{O}_2$ , as demonstrated in Figure 22.

The variation with temperature from 787 to 573 K (514 to 300 °C) of the limiting total pressure for the explosion in a mixture of  $2\text{O}_2$  + UDMH was examined. For the undiluted  $2\text{O}_2$  + UDMH mixture, ignition pressure dropped from 5.3 kPa (40 mm Hg) at 573 K (300 °C) to 1.6 kPa (12 mm Hg) at 787 K (514 °C). Diluent gases would raise the necessary pressure for ignition by 2.7–4 kPa (20–30 mm Hg). Induction periods varying from 2 s at 626 K (353 °C) to 8 s at 573 K (300 °C) were observed to occur with some explosions.

It was noted that the addition of NO made the mixture more likely to explode (with NO acting as an oxidizer). In the slow thermal hydrazine decomposition, the addition of NO reduces the reaction rate. A similar effect was observed when mixtures of UDMH vapor and NO were sparked [695]. UDMH vapor by itself would not explode at all, but mixtures with as little as 4 kPa NO and 6.66 kPa UDMH would explode above 353 K.



**Figure 22:** Spontaneous ignition of oxygen/UDMH mixtures at 693 K (420 °C). Dependence of the pressure limit on composition. (Reprinted and modified from [693], with permission from ©1963 Elsevier; permission conveyed through RightsLink.)

#### 1.7.4 Limits of Flammability of UDMH in the Air

The limits of flammability of flammable vapors can be expressed in terms of temperature limits (similar to a flash point) or in terms of percent by volume (vol.-%). The lower temperature limit of UDMH in air was found to be 258 K (5 °F) at a pressure of 98.3 kPa (740 mm Hg). The upper limit is close to the boiling point. To maintain all UDMH in the vapor phase, additional flammability tests were conducted at temperatures sufficiently high above the boiling point. At 373 K (212 °F), the flammable range of UDMH in the air was from 69 to  $92 \pm 4\%$  by volume [178]. At 473 K the flammable range was widened from  $1.8 \pm 0.1$  to  $99 \pm 1\%$  by volume UDMH. At elevated pressure (688 kPa = 100 psig) in a 5-cm (2-in.) chamber, the lower limits at 373 and 473 K were  $2.2 \pm 0.3$  and  $1.8 \pm 0.2$  vol.-%, respectively. The upper limits during the pressure tests consisted of saturated vapor mixtures with no air (Table 16). The most sensitive mixtures for the spark ignition of UDMH vapors in air occur at 8% by volume UDMH [200].

**Table 16:** Flammability limits of UDMH at elevated temperatures.

| Pressure, atm | Temperature, °C | Lower limit, Vol.-% UDMH | Upper limit, Vol.-% UDMH |
|---------------|-----------------|--------------------------|--------------------------|
| 1             | 100             | $1.9 \pm 0.1$            | $92 \pm 4$               |
| 1             | 150             | —                        | $98 \pm 2$               |
| 1             | 200             | $1.8 \pm 0.1$            | $99 \pm 1$               |
| ~7.8          | 100             | $2.2 \pm 0.3$            | 100                      |
| 7.8           | 200             | $1.8 \pm 0.2$            | 100                      |

Data source: [178].

### 1.7.5 Minimum Ignition Energy for UDMH Vapor Ignition

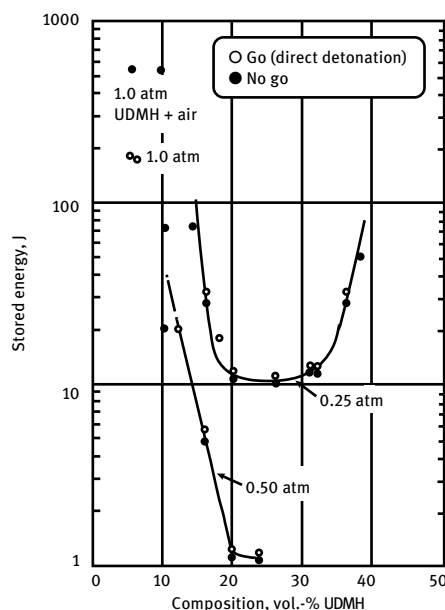
Electrostatic discharge has been the cause of numerous fire and explosion accidents. The static charge carried by a person with insulating shoe soles shuffling across a synthetic fiber carpet can reach 10 kV and  $10^{-5}$  Cb, which is sufficient to ignite UDMH vapors in the air. Designers for propellant storage and transfer facilities should adhere to the recommendations provided in NFPA 77 (*Recommended Practice on Static Electricity*) [696].

The minimum ignition energy of UDMH vapor in the air was determined in a flow-through system that was better suited to high boiling liquids than the static ASTM system. The minimum ignition energy of 4.3 vol.-% UDMH vapors in the air was 2.8–3.4 mJ for two to six positive ignition events out of six tests that were attempted [697].

Minimum ignition energies measured using laser-induced breakdown in homogeneous air/UDMH mixtures were compared to those of more common flammable mixtures such as air/hydrogen and air/hexane obtained using electric discharge ignition [694]. A model for flame initiation was based on the temporal and energy density characteristics of the energy source.

In other experiments, the minimum required energy of a spark discharge with oxygen/UDMH vapor mixtures was determined at atmospheric sea level pressure, at 0.5 atm, and at 0.25 atm pressure in the I-8 apparatus test chamber. The minimum required ignition energy as a function of UDMH concentration in oxygen is illustrated in Figure 23. Only the curve at 0.25 atm pressure shows the complete U-shape with a shallow minimum at near stoichiometric composition.

NO is not a strong oxidizer, and it is not hypergolic with UDMH. The ignition of NO/UDMH mixtures can allow some comparisons to the ignition of NO<sub>2</sub>/UDMH mixtures. Pure UDMH vapor did not explode when sparked but did ignite if NO was present [695]. A small amount of NO can affect the decomposition of a much larger amount of UDMH, with the NO acting as a sensitizer. The ignition was considerably less violent than in the case of hydrazine, and there was no appreciable emission of visible light. In the NO/UDMH mixture, there exist critical upper and lower pressure limits of explosion, the region of explosion between them being widened by an increase in the initial temperature. From the results, it was concluded that dissociation of the UDMH



**Figure 23:** Stored energy from a capacitor required for the direct detonation of oxygen/UDMH mixtures (using an exploding wire in a 1-liter bomb). (Reproduced and modified from [200].)

molecule into  $\text{Me}_2\text{N}$  and  $\text{NH}_2$  radicals is an essential step in the decomposition process. At the comparatively high temperatures reached during the ignition, the  $(\text{CH}_3)_2\text{N}$  radicals do not behave in the manner previously observed at  $100^\circ\text{C}$ ; instead, they appear mainly to react with  $\text{NO}$ .

### 1.7.6 Firefighting of UDMH Fires

The extinction of water-soluble hydrazine fires is easily compared to firefighting of other commonly used fuels (gasoline, kerosene) because hydrazine and its derivatives are miscible with water. In the event of a fire, the area is best flushed with copious amounts of water until UDMH is diluted below the fire point concentration. Open-air burning tests with hydrazine and UDMH in open pans of 28-, 315-, and 2100- $\text{cm}^2$  surface areas revealed that 4.7 L of water was consumed per L of hydrazine to extinguish a hydrazine fire. In contrast, only 1.5 L of water per L of UDMH was consumed to extinguish a UDMH fire [698–701]. Hydrazine burned an order of magnitude faster than UDMH, which was due to the ability of hydrazine to burn like a monopropellant as a decomposition flame not requiring oxygen exists close to the liquid surface. The hydrogen produced by this flame then burns with air as a diffusion flame. The addition of water to the hydrazine reduced its burning rate substantially. The slower-burning UDMH had a burning rate of the same magnitude as ethanol or gasoline. Therefore, a decomposition flame was not present. Depending on the pan size, the pool burning rate of UDMH ranged from 0.22 to 0.49 cm/min. (0.088 to 0.195 in./min.). Besides

water, including water spray, potassium bicarbonate dry chemical, carbon dioxide, Halon 1301, trichlorotrifluoroethane, and foam blankets were evaluated in relation to hydrazine fires, and plain water was found to work best [200, 203, 206, 207, 702, 703].

Two parts by weight of water per part of Aerozine-50 (Ae-50) will inert an Ae-50 spill against ignition in air [205]. In a burning Ae-50 pool, the fuel evaporation rate is approximately  $49 \text{ g s}^{-1} \text{ m}^{-2}$ . A well-dispersed flow of water at  $100 \text{ g s}^{-1} \text{ m}^{-2}$  is sufficient for extinguishing a fire. A tenfold excess of water (10 kg water per kilogram of fuel) is required to inert an Ae-50 spill against hypergolic ignition with NTO. Bromotrifluoromethane (Halon 1301) can be used to inert vapor spaces or to extinguish small fires but very high  $\text{BrCF}_3$  concentrations are required (>7% by volume) and the protection is not long-lasting.

### 1.7.7 Detonability of UDMH

#### 1.7.7.1 Detonability of UDMH Liquid

In the card gap test with a 1-in. diameter  $\times$  3-in. length aluminum tube, with donor charges of one, two, and even with three tetryl pellets with zero cards for attenuation, liquid UDMH could not be stimulated to detonate at temperatures up to 308 K (35 °C) [178]. Additional tests with UDMH samples heated to 323 K (50 °C) in a 2.5-in. diameter  $\times$  6-in. length steel tube with four tetryl pellets as a donor had the same negative result. The bulging of the tube was the same as that observed after a blank test with water. In continuation of the UDMH tests, UDMH was deliberately contaminated by soaking it with various contaminants (rust, copper, brass, copper oxide, mercury) for 24 h at room temperature. The contaminated UDMH was then tested in the 2.5-in. diameter tubes. In each case, the tube bulging of the contaminated samples was the same as that with pure UDMH. Similar tests were performed with UDMH blends such as U-DETA (which is 60% UDMH + 40% DETA) and with JP-X Type I (which is 40% UDMH and 60% JP-4). Again, the tube bulging of the contaminated samples was the same as that with pure UDMH or water. In the same test series with the same test set-up, anhydrous hydrazine or methylacetylene did not detonate, ethylene oxide had a partial detonation, and nitromethane resulted in complete fragmentation of the tube into small splinters.

#### 1.7.7.2 Detonability of UDMH Vapors

The detonation velocity of low-pressure  $\text{O}_2\text{-N}_2\text{-UDMH}$  mixtures at 5.31 and 5.58 kPa (40 and 42 mm Hg) total pressure was measured as 2100–2300 m/s, which is in close agreement with predicted velocities based on the Chapman-Jouguet calculations [196]. Mixtures of dioxygen and UDMH vapor heated rapidly in a shock tube underwent rapid decomposition followed by oxidation after an ignition delay [183, 704]. An earlier section discussing the combustion of UDMH in this chapter provided additional information on oxidation reactions in shock tubes (see also [198]).

### 1.7.7.3 Bullet Impact Sensitivity of UDMH

In one series of projectile impact tests, hydrazine or UDMH were shot at while stored in aluminum, stainless steel, or titanium tanks [705]. A stainless-steel tank was made from 89-mm (3.5-in.)-diameter tubing by welding on end caps and a similar aluminum tank was made from 102-mm (4-in.)-diameter tubing. The thickness of the end caps where the impact occurred was 0.8 mm (0.03 in.) for both tests. Steel spheres (5.6 mm = 0.219 in.) were accelerated to 1763 m/s and aimed at the end caps. UDMH in a titanium tank with 0.5-mm-thick walls was impacted by the same size steel-sphere projectile at 1763 m/s. No reaction was observed between the hydrazines and the tank wall in any of the tests, in contrast to liquid oxygen which started a violent reaction in all materials tested and was perforated by bullets.

## 1.8 Toxicity of UDMH

After the phasing out of NIKE, BULLPUP, LANCE, and TITAN missiles in the 1970s, it seemed as if the use of UDMH as a rocket propellant in the US was to become a thing of the past. The initial total reliance on the Space Shuttle as the Space Transportation System eliminated the need for any more UDMH toxicity testing, after all. This changed when, after the first Space Shuttle disaster in the 1980s, the TITANs and DELTA II upper stages re-emerged as expendable launch vehicles and UDMH (Ae-50) continued to be used as a rocket propellant in the US inventory. As of 2021, UDMH even continues to be the main fuel on the Zvezda service module on the International Space Station supplied by Russia. Even non-Russian supply ships sometimes carry UDMH fuel supplies to the International Space Station. It is hoped that there will never be any UDMH accidents. Nonetheless, it is important to include all references to UDMH toxicity in this book to serve as a source of information for hazard evaluation in the design of space station facilities and in treating of patients inadvertently exposed to UDMH vapors. Launches of DELTA II second stages with Ae-50 fuel continued into 2018 but are now a thing of the past. Residual stocks of Ae-50 had to be disposed of.

UDMH is used in the synthesis of succinic acid dimethylhydrazide which is commonly known under the tradename Alar<sup>®</sup>. It was used as a growth regulator on apples until 1989 when its use on food crops was banned by the EPA following a public controversy between apple growers and environmentalists. The hydrolysis of succinic acid dimethylhydrazide may release UDMH. Both are toxic when eaten in high doses.

A summary review of the literature on the toxicity of hydrazines, including UDMH, was compiled in 1981 [706]. The health and environmental effects profile for 1,1-dimethylhydrazine is published in a summary of literature data with 79 references on hydrazine and UDMH toxicity and a closer review of animal exposure data [707]. This EPA study was done to support listings of hazardous constituents of a wide range of waste streams under Section 3001 of the RCRA. For a  $10^{-5}$  probability of contracting cancer, the human carcinogenic potency factor ( $q_1^*$ ) of UDMH derived from a series



of animal exposure experiments was  $8.7 \text{ mg (kg body weight)}^{-1} \text{ day}^{-1}$ . However, these animals were fed hydrazinium sulfate solutions in their drinking water. As such, it is still not known whether the same carcinogenic risk numbers apply to the inhalation of UDMH vapor.

Many of the UDMH toxicity studies were done with UDMH of dubious purity. Most of the UDMH used likely contained traces of NDMA and even SDMH, both contaminants that are known to cause cancers in test animals more so than pure UDMH by itself. The investigators failed to analyze the UDMH for NDMA or SDMH before starting their experiments. As such, the experiments should be repeated with UDMH that was verified to be free from NDMA, SDMH, and FDMH.

### 1.8.1 Inhalation Toxicity of UDMH

The most likely route of accidental poisoning by UDMH is through inadvertent inhalation of UDMH vapors from a leak or a propellant spill. Inhalation toxicity of UDMH and the other hydrazines was studied over several decades in animal exposure tests. Table 17 is a comparison of LC50 data for the three hydrazines in different species of test animals. Based on these data, the acute inhalation toxicity of UDMH is between that of MMH and hydrazine.

**Table 17:** Lethality of hydrazine, UDMH, and MMH in rodents.

| Test animal species | Inhalation toxicity, LC50, ppm |           |           |
|---------------------|--------------------------------|-----------|-----------|
|                     | Hydrazine                      | UDMH      | MMH       |
| Rat                 | 570 (4 h)                      | 250 (4 h) | 74 (4 h)  |
| Mouse               | 252 (4 h)                      | 172 (4 h) | 56 (4 h)  |
| Hamster             | ND                             | 392 (4 h) | 143 (4 h) |

Data source: [708].

The most comprehensive source of information on the chemistry of hydrazines contains sections on animal inhalation toxicity tests [709].

Serious concern about the safety of previously established TLV limits for UDMH arose in 1964 when it was discovered (for the first time) that continuous 90-d exposure of animals to UDMH vapor at the then valid TLV (0.5 ppm) was lethal to one out of ten monkeys, three out of 50 rats, and six out of 100 mice [710]. Although a typical TLV load would be only 8 h/d and 40 h/wk, this test demonstrated that there was only a narrow margin for safety. It was not until 1994 that the TLV for UDMH was eventually lowered by more than one order of magnitude from 0.5 to 0.01 ppm. There were no epidemiological studies that correlated the frequency of illnesses with the period when workers might have been exposed to the full TLV concentration for UDMH when it was still 0.5 ppm.

### 1.8.2 Oral and Injection Toxicity of UDMH

The most comprehensive source of information on the chemistry of hydrazines contains sections on animal toxicity tests with UDMH, where the toxicant was administered by various routes other than by inhalation [711].

A comparison of the acute toxicities of hydrazine, MMH, and UDMH (sorted by a mode of administration) has already been provided in this volume in the chapter titled "Methylhydrazine." For other reviews and summaries on UDMH toxicity, see [712].

### 1.8.3 Blood Effects of UDMH

Blood and aqueous humor samples were obtained from anesthetized dogs after applying various single doses to a 300-cm<sup>2</sup> area on the chest [713]. The application of UDMH to the skin and the subsequent absorption of UDMH into the circulating blood did not change the thrombin, overall coagulation, syneresis, maximum amplitude, or icteric values of blood coagulation. There were no changes in any of the factors that affect blood clotting associated with either dose or time elapsed after UDMH application. Contrary to the effect of hydrazine, UDMH decreased the thromboplastin generation time after 120 minutes but the amount of the decrease was not dose-dependent.

The acute toxic effect of UDMH after intratracheal intubation in rats was studied by measuring the UDMH effect on glucose metabolism [368]. The effects of UDMH on pyruvate and  $\alpha$ -ketoglutarate metabolism in rat blood were detected by UV spectrophotometry. The level of pyruvate in rat blood had a decreasing tendency, especially at 60 and 90 minutes after UDMH administration, and the level of pyruvate decreased significantly at all dose levels. The level of  $\alpha$ -ketoglutarate also decreased under the same conditions. These results suggested that UDMH disturbs glucose metabolism and energy metabolism, following which it can cause neurotoxicity.

Hemolysis is the breaking up of red blood corpuscles (erythrocytes), rendering them ineffective for the transport of oxygen. Blood cell destruction and anemia are less frequently observed after inhalation or sc injection and are only seen in severe cases of chronic poisoning. The hemolytic action among all the alkyl hydrazines is most pronounced with MMH [714] and not with UDMH [708, 715, 716].

Three individuals out of a group of chemists working with UDMH under close medical supervision developed extremely high WBCs (white blood cell counts) above 12500 without clinical evidence of infection or hemoconcentration [717]. While initially one after the other assumed the duties of their sickened predecessors, as soon as this subacute poisoning was noted in the course of bi-weekly examinations, the individuals were assigned to other duties away from UDMH exposure. Propellant transfer personnel in a UDMH tank farm, in particular a group that had high UDMH exposure during a spill, were found to have abnormal RBC (red blood cell count), WBC, casts in the urine, and abnormally positive cephalin flocculation.

#### 1.8.4 Immune System Effects of UDMH

UDMH poisoning has adverse effects on the immune system of animals [718–720].

#### 1.8.5 Nervous System Effects of UDMH

The most comprehensive source of information on the chemistry of hydrazines contains sections on nervous system toxicity tests and effects on the brain in animals with UDMH. Comparisons to the effects caused by the other hydrazines are also provided [721]. Effects of UDMH on the brain can be caused by disturbed enzyme metabolism in the brain. Hydrazine and UDMH severely inhibited glutamate (glutamic acid) decarboxylase (GAD) activity in rat brains [722–725].

#### 1.8.6 Other Toxic Effects of UDMH

Other organs affected by UDMH toxicity are the heart [726, 727], kidney [728–730], liver [731–734], skin [713, 735–739], and eyes [713, 740].

#### 1.8.7 Therapy and Prophylaxis of UDMH Poisoning and the Treatment of Accidental Poisonings with UDMH

This section contains both the results of animal tests and the accounts of the emergency treatment of human UDMH poisoning victims. In cases of human UDMH poisoning, the first expected symptom of intoxication is emesis. If therapy is carried out immediately after this first indication of a problem, there is sufficient time to prevent convulsions.

In a series of animal tests, pyridoxine therapy constituted the first successful approach to a specific treatment that prevents convulsions and death in all species tested. The ED<sub>0</sub> (effective dose) of two vitamin B<sub>6</sub> congeners, pyridoxine hydrochloride (PIN-HCl), and pyridoxamine dihydrochloride (PAM-2HCl) was determined in mice, rats, dogs, and monkeys [741, 742]. The only manifestation that was not abolished by this therapy in dogs and monkeys was vomiting. The data were the basis for the suggested emergency treatment of severely exposed personnel, consisting of the injection of 25 mg/kg PIN-HCl. The toxicity of pyridoxine itself (without UDMH), including overall therapeutic and clinical considerations with routes of administration, dosage regimens, and other supportive measures was discussed. These experiments revealed an extremely important species difference in the protective efficacy of PIN-HCl and PAM-2HCl against UDMH toxicity in laboratory animals. It appeared that the mouse and the monkey were more easily protected by PIN-HCl than by PAM-2HCl. In contrast, PAM-2HCl was approximately ten times more effective than PIN-HCl in rats. These differences were probably caused by species differences in the metabolism of B<sub>6</sub> analogues. From a practical standpoint, both PIN-HCl and PAM-2HCl did afford protection in all species, although the dose required for protection varied with the species. After the patient displays nausea and/or vomiting,

25 mg/kg PIN-HCl should be administered. In a 70-kg person, this would amount to 1750 mg or about 8 mL. Additional measures could include hydration of the patient since 30–50% of UDMH is excreted with the urine within 5–6 h.

A dose of 100 mg/kg UDMH given to dogs *i.v.* or *i.p.* caused vomiting in 30–60 minutes and clonic-tonic convulsions in 30–120 minutes. Pentobarbital, methitural, phenobarbital, amobarbital, and diphenylhydantoin failed to control seizures or prevent death. The dose of PIN-HCl necessary to protect dogs against the consequences of a UDMH poisoning with 100 mg/kg was of the order of 100 to 150 mg/kg. A smaller protective dose of 50 mg PIN-HCl was effective in protecting a group of 19 monkeys that was exposed to the same, usually fatal dose of UDMH. A combination of two vitamin B<sub>6</sub> congeners, pyridoxine, and pyridoxamine was tested as an antidote against UDMH poisoning in rats and mice. 100 mg/kg protected rats against death from a dose of  $2 \times \text{LD}_{50}$  of UDMH. In mice, a somewhat smaller protective dose of 75 mg/kg allowed the survival of 50% of the poisoned animals. Mouse and monkeys were more easily protected by PIN-HCl than by pyridoxamine hydrochloride. Pyridoxamine hydrochloride was ten times more effective in the rat. As a result of these animal tests, an injection of 25 mg/kg of PIN-HCl is recommended as emergency treatment of personnel severely exposed to UDMH.

Eighteen different compounds were tested for their therapeutic effect against hydrazine, MMH, or UDMH poisoning (*i.p.*, mice) [726]. Of those found to be effective, arginine and ornithine provided clear-cut protection from death and convulsion caused by otherwise fatal hydrazine doses. However, the two amino acids were ineffective against MMH or UDMH. Amino-oxyacetic acid or pyridoxine provided effective protection against MMH or UDMH poisoning but were ineffective against hydrazine. Only partial protection against UDMH was offered by *p*-nitrobenzaldehyde or *p*-chlorobenzaldehyde.

There have been two cases of acute accidental hydrazine-UDMH poisonings in rocket test technicians. In these cases, the timely administration of pyridoxine•HCl brought about immediate improvement of the condition of the accident victims [743, 744]. After injecting 200 mg *i.v.* and  $2 \times 200$  mg *i.m.* PIN-HCl, all nervous disorder symptoms except chest congestion vanished within 20 minutes. Another technician caught in the same leak had hyperactive reflexes, high respiration rate, and bilateral pulmonary edema. He also was given 200 mg *i.v.* plus  $2 \times 200$  mg *i.m.* PIN-HCl. His dyspnea improved and his other symptoms abated. Follow-up studies during the next days and weeks showed no permanent ill effects in any of the two patients. In another accident at the same test installation, four workers suffered severe nausea and vomiting that possibly could have been prevented by the immediate use of pyridoxine. This drug was only later administered *i.v.* at the onset of vomiting, following which the vomiting stopped in 20 minutes.

A study of the electrolyte distribution and the effects of anti-diuretic hormones after UDMH administration showed that there was no change in electrolyte excretion in the urine of rats within 2 h following UDMH administration. Nicotine tartrate re-

duced urine excretion. It was proposed that if a diuretic could facilitate UDMH removal from the animal, some of the subsequent poisoning symptoms would be reduced. Replenishing salts after strong urine loss would restore electrolyte balance. Other protective agents tested included pyridoxine, desoxypyridoxine hydrochloride, ammonium chloride, glutamic acid hydrochloride, arginine hydrochloride, choline chloride, niacin, however, only pyridoxine showed any benefit in combating UDMH poisoning [745].

Besides amino acids and amino compounds, pyridoxine (vitamin B<sub>6</sub>, PIN), pyridoxal (PAM), and pyridoxal phosphate (PAMP) were tested as antidotes against Aerozine-50 poisonings in animals [746]. Animal tests indicated that all forms of the B<sub>6</sub> vitamers were at least partially effective against the convulsive effects of the hydrazines. This clarified, to some extent, the conflicting data on the ability of PIN (but not PAM or PAMP) to prevent convulsive seizures in UDMH-treated rats. There was a relatively narrow range of effective dosages of PAM and PAMP, with amounts above or below these ranges not being effective. Thus, findings will vary and are dependent upon the dosage used.

Other tests indicated that *i.p.* pyridoxine protects rats from UDMH toxicity, while PAM and PAMP do not. When PAM and PAMP were injected immediately after UDMH, convulsions and death occurred much sooner than with UDMH alone. Similar findings with PAM and PAMP have been reported for hydrazine and several substituted hydrazines.

Pyridoxine and phenobarbital were tested as a prophylactic treatment of Aerozine-50 poisoning [747, 748]. Aerozine-50 caused a 50% mortality in rats at a dose of 120 mg/kg. A combination of pyridoxine (0.5 mmol/kg), arginine, and L-glutamate (both at 4 mmol/kg) afforded significant protection for rats that were given 130 mg Aerozine-50/kg body weight.

Large doses of pyridoxine given either prior to or after UDMH intoxication reduced the convulsant effect of UDMH in monkeys [749].

Rats were subjected to single doses of 120 mg UDMH/kg *i.p.* (which is normally the LD<sub>100</sub>) and then treated with vitamin B<sub>6</sub> [750]. Convulsions were effectively prevented by injecting PAM, PAMP, or pyridoxine directly into the brain in order to bypass the blood-brain barrier. The treatment was more effective when it was delayed until just before the onset of convulsions. PAM and its phosphate reacted with UDMH, leaving little coenzyme available for metabolic functions at distant sites. Pyridoxine, however, provides a B<sub>6</sub> reservoir that does not form a UDMH hydrazone, allowing replenishment of active coenzyme at the site of enzymatic activity. Pyridoxine is thus the preferred prophylactic for UDMH poisoning.

Three groups made up of 20 rats in each group were treated with otherwise fatal doses (130 mg/kg) of UDMH, then treated with a combination of an anti-convulsive (5,5-diphenylhydantoin) and amino acid salts (ornithine- $\alpha$ -glutarate and arginine aspartate) [751, 752]. The mortality decreased to 53%. Other animals treated chronically with lower UDMH concentrations and afforded amino acid therapy avoided the ner-

vous disorder symptoms but not the effects on other organs. This approach is a useful complement to the more popular pyridoxine treatment.

To measure the effect of the combined use of promethazine and naloxone on the survival rate of mice intoxicated by UDMH, 80 male mice were divided randomly into four groups: control group, promethazine group, naloxone group, and combined use of promethazine and naloxone group [753]. For each group, UDMH 15.6 mg/kg was given *i.p.*, and then sodium chloride (0.9%), naloxone (0.12 mg/kg), promethazine (7.5 mg/kg), or naloxone (0.12 mg/kg) combined with promethazine (7.5 mg/kg) was given *i.p.* The symptoms and survival rates of the mice in each group suggested that the combined use of naloxone and promethazine could alleviate the symptoms and significantly postpone the mice dying from UDMH intoxication. Combined use of naloxone and promethazine was more effective in neutralizing the UDMH intoxication than using naloxone or promethazine only.

While a significant number of experimental studies were performed in the late 1950s through the mid-1960s, conflicting information exists concerning the most appropriate treatment for accidental exposures of humans to hydrazines. A cross-sectional study evaluating the most common rocket fuels (e.g., hydrazine, UDMH, MMH, and Aerozine-50) against the most commonly suggested therapies (e.g., pyridoxine, traditional anti-seizure therapies, and arginine) is needed to clarify the treatment implications for human exposure [754]. Treatments that have been useful for hyperammonemic states, such as those for urea cycle defects, have significant potential for the improvement of hydrazine(s) accidental exposure treatment (see also [755]).

The anti-oxidant properties of *salvia miltiorrhiza* have been advertised as a remedy for many ailments. Therefore, it was not surprising to learn that it can even be used as a therapeutic agent to treat UDMH and NTO poisoning. Forty-two rats were divided into three groups: the control group, the inhalation group, and the inhalation plus treatment group [756]. The latter two groups were exposed to 0.98 g UDMH/m<sup>3</sup> for ten minutes and 0.19 g N<sub>2</sub>O<sub>4</sub>/m<sup>3</sup> for ten minutes. After inhalation, the rats in one group were treated with 9 g/kg *Radix salviae miltiorrhizae* extract *i. v.* immediately and 3 g/kg *i.p.* later also. The treatment with *Radix salviae miltiorrhizae* extract appeared to attenuate the consequences of the inhalation of high-concentration UDMH and N<sub>2</sub>O<sub>4</sub>. The anti-oxidant activity of this medicine may be responsible for the protective effect.

In what appears to be a simple *in vitro* test tube experiment, the eliminating effects of vitamin B<sub>6</sub>, vitamin C, and glacial acetic acid on free UDMH were studied [757]. One (1) mg vitamin B<sub>6</sub>, 1 mg vitamin C, or 1 mg glacial acetic acid were added to 10 mL UDMH solution (1 µg/mL), respectively. The free UDMH content was determined after 30 and 60 minutes using the sodium ammino ferrocyanide (TPF) spectrophotometry method at a wavelength of 500 nm. The results revealed that vitamin B<sub>6</sub> can bind 88% UDMH in 30 minutes. Vitamin C or acetic acid had no significant removal effect on UDMH. The chemical mechanism of vitamin B<sub>6</sub> tying up UDMH is that PAM and pyridoxal 5-phosphate monohydrate (PLP) can react with UDMH to form a hydrazone.

The protective effects of curcumin, curcumin-cyclodextrin nano-particle curcumin, and nano-liposomal curcumin on *i.p.* UDMH-induced poisoning in mice were compared in a series of animal tests [758]. Each of the three chemicals reduced several of the many toxic effects of UDMH poisoning to some extent but none provided total protection against UDMH poisoning.

### 1.8.8 Metabolic Fate of UDMH

UDMH metabolizes to at least six different compounds but not all reside in every tissue sample. Based on  $^{14}\text{C}$ -labeled UDMH tests, shortly after the administration of UDMH, one finds 50–60% of the unreacted UDMH, 3–10% of the dimethylhydrazone of glucose, and 20–25% of a yet unidentified higher-molecular-weight compound in urine [433]. The metabolic fate of UDMH was studied in female rats and dogs. The metabolic pathway of UDMH in rats and dogs was studied by *i.p.* injections of  $^{14}\text{C}$ -labeled UDMH and by examining tissue samples after different elapsed times using paper chromatography and autoradiography. The radioisotope tracer technique has been used successfully for  $^{14}\text{C}$ -labeled UDMH [759]. Six radioactive UDMH-derived compounds were found, and three of these were in urine.

The absorption, distribution, and excretion of UDMH in rats, rabbits, cats, dogs, and monkeys were measured using  $^{14}\text{C}$ -tracer and colorimetric methods [760, 761]. UDMH was rapidly absorbed into the blood regardless of the route of administration. It was also quite rapidly excreted by the kidneys, as evidenced by early high concentrations in both blood and urine. UDMH at doses of 20, 40, and 60 mg/kg was rapidly metabolized by rats, as evidenced by the metabolism of UDMH- $^{14}\text{C}$  methyl groups to respiratory  $^{14}\text{CO}_2$  [762].  $^{14}\text{C}$  was also rapidly excreted into the urine after the administration of UDMH- $^{14}\text{C}$  to rats. At low levels of UDMH intoxication, the bulk of the compound was either metabolized to respiratory  $^{14}\text{CO}_2$  or excreted as either UDMH or metabolite(s) in four to six hours after *i.p.* administration of 40 mg/kg of UDMH. UDMH intoxication of rats at doses of 20, 40, and 60 mg/kg appeared to preferentially inhibit glucose catabolism to respiratory  $\text{CO}_2$  via glycolysis and the pentose phosphate pathway. A C-6 decarboxylation process, such as the glucuronate pathway, appeared to be unaffected by UDMH intoxication.

The non-enzymatic formation of methane from UDMH has been reported *in vivo* [763]. The respiratory and urinary excretion of UDMH by rats has been studied using radioactive tracer techniques [764]. Animals given a very low dose of UDMH- $^{14}\text{C}$  metabolized almost 30% of the compound to respiratory  $^{14}\text{CO}_2$  10 h. At a very low dose, almost 30% of the  $^{14}\text{C}$  from *i.p.* administered UDMH appeared as respiratory  $^{14}\text{C}$  in 10 h. At a convulsive dose, conversion of  $^{14}\text{C}$  from UDMH added up to little more than 13% within 20 h. At all doses studied, at least 50% of the radioactivity showed up in the urine (collection period 2 d).

Animals given a very low dose of  $^{14}\text{C}$ -labeled UDMH metabolized almost 30% to respiratory  $^{14}\text{CO}_2$  in 10 h [763]. At the convulsive dose level, 13% was converted to  $^{14}\text{CO}_2$

within 20 h. Rats injected *i. v.* with  $^{14}\text{C}$ -UDMH incorporated only a little radioactivity in liver ribonucleic acid (RNA) [765]. UDMH appears to be a very weak, if not even inactive, methylating agent. The PAM hydrazones of the various hydrazines form as intermediates during the metabolism of hydrazines, surprisingly with exceptionally high toxicity of their own [766]. A comparative study was conducted regarding the toxicity and convulsion activity of UDMH, MMH, and their PAM and pyridoxal-5-phosphate hydrazones. The hydrazones of UDMH were more toxic than UDMH itself when three criteria were compared: **(1)** lag-time before convulsions at various dose levels, **(2)** time of death, or **(3)** LD50. In the case of MMH, the convulsion times of hydrazones and free hydrazine are about equal while death appears earlier with the hydrazones. This work implies that PAM exacerbates rather than alleviates the convulsant activity of UDMH and MMH, and thus should not be considered an antidote. It was discovered that the PAM hydrazone of UDMH is more toxic than UDMH. With MMH and its hydrazone, the convulsion times are equal but death occurred earlier with the hydrazone.

The formation of free radicals as intermediates has been well documented in numerous biological systems, including the metabolism of known toxic drugs. Alkyl hydrazines are particularly susceptible to biological and chemical oxidation processes that lead to the sequential generation of diazene intermediates and carbon-centered free radicals. A study specifically examined the *in vitro* and *in vivo* metabolism of some model alkyl hydrazines to characterize how the nascent radical flux affects metabolite formation and the destruction of cytochrome P-450 [767]. The experimental results demonstrated that all the observed alkyl hydrazine metabolites can be rationalized by assuming the intermediacy of free radicals. The metabolism of the alkyl hydrazines under investigation lead to the loss of hepatic microsomal cytochrome P-450 in a process that was dependent on catalytic turnover. Significant production of free radicals occurs in the metabolism of alkyl hydrazines; these radicals are likely contributors to the toxic sequelae associated with the therapeutic hydrazines and hydrazides used on human patients.

The neutrophil-catalyzed metabolism of hydrazine derivatives to carbon-centered radicals was investigated by a spin-trapping technique [768]. Oxidation of MMH, UDMH, phenylethylhydrazine, or procarbazine by neutrophils led to the formation of alkyl radicals. Azide, an inhibitor of myeloperoxidase, effectively reduced the neutrophil-catalyzed radical yield from the oxidation of MMH but not UDMH. On the other hand, superoxide dismutase and catalase effectively inhibited radical formation in UDMH metabolism by PMA-activated neutrophils, in contrast to MMH metabolism. The results showed that neutrophils can metabolize hydrazine derivatives, with the pathway depending on the hydrazine substitution. Alkyl radical production during the oxidation of mono-substituted derivatives such as MMH was mediated mainly by myeloperoxidase, and that of di-substituted derivatives such as UDMH was mediated mainly by active oxygen species. Similar free radical intermediates were observed during microsomal metabolism of hydrazine.



Metabolites of UDMH in the blood of Wistar rats have been analyzed using SPE followed by HPLC analysis [368]. The blood before UDMH intoxication was collected as a control and analyzed.

#### **1.8.9 Carcinogenic Effects (Carcinogenicity and Carcinogenesis) of UDMH**

Several hydrazines have been shown to be carcinogenic in animal tests. As part of the overall effort to understand the conditions leading to the development of cancer, and to find a cure for this very complex disease, carcinogenic actions of hydrazines have been thoroughly studied. The carcinogenic activity is most pronounced with SDMH and less so with UDMH. Besides hydrazines, UDMH autoxidation products such as dimethylnitrosamine (NDMA) are listed among the most potent carcinogens known. NDMA used to be produced as an intermediate in the manufacturing of UDMH. Throughout the 1960s and 1970s, there may have been traces of residual NDMA in the UDMH that was shipped out of production facilities to the missile silos, but UDMH from the same production lots was also used by toxicity testing laboratories. Because of the increased concern about NDMA carcinogenicity, several UDMH production facilities in the US were shut down since the plants could not be modified to assure zero emissions of NDMA into the surrounding communities. Another plant had to be closed permanently when the demand for UDMH dropped off. For a limited time, in the US, UDMH was prepared using a different process that no longer involved the use of NDMA as an intermediate.

It is not known which process has been used or is currently in use in Russia and the other former countries of the USSR. Shortly after the decommissioning of Russian ICBMs, efforts to sell surplus Russian UDMH in the West have been hampered by concerns about the purity of the product. At that time ARIANE-IV was still using UH-25 as a fuel while France was producing its own UDMH.

The carcinogenic properties of methylhydrazines and NDMA are very similar, such that it was initially suspected that NDMA might be formed as an intermediate during the metabolism of methylhydrazines and might be the real cause for their carcinogenicity. Toxicity warnings about UDMH are often based on data obtained with its much more toxic isomer, SDMH. Traces of SDMH commonly present in UDMH may gravely alter the results of animal toxicity tests, but only a few researchers have verified the absence of SDMH (or NDMA) contamination before starting UDMH exposure tests with animals.

Test animals were administered UDMH by various paths of gavage and were then examined for carcinogenic effects. Summaries on the results of such animal carcinogenicity and DNA alteration tests can be found in [769].

There was a controversy over the adequacy of test methods (lack of concurrent control animals) when carcinogenicity test methods at some animal testing labs were reviewed by federal agencies [594].

1,1-Dimethylhydrazine is a probable human carcinogen that is classified as weight-of-evidence Group B2 under the EPA *Guidelines for Carcinogen Risk Assessment* [770]. Evidence on potential carcinogenicity from animal studies is sufficient, but the evidence from human studies is “No Data.” The potency factor (F) for 1,1-dimethylhydrazine was estimated to be  $82.5 \text{ (mg kg}^{-1} \text{ d}^{-1})^{-1}$  thus placing it in potency group two, according to the EPA Cancer Assessment Group methodology for evaluating potential carcinogens [771]. Combining the weight-of-evidence group and the potency group, 1,1-dimethylhydrazine was assigned a “medium” hazard ranking for the purposes of Reportable Quantity (RQ) adjustment. This potency factor (F) for UDMH,  $82.5 \text{ (mg kg}^{-1} \text{ d}^{-1})^{-1}$ , was an order of magnitude higher than the ( $q_1^*$ ) human carcinogenicity potency factor derived in another EPA study.

#### 1.8.10 Mutagenicity of UDMH

Research on mutagenicity of hydrazines, including MMH and UDMH, complement the work done on carcinogenicity. Not all mutagens are carcinogens and not all carcinogens are mutagens [772]. Because a mutagenicity test can be done quickly *in vitro* in a Petri dish and because it has fewer variables than an animal exposure test, this is usually the first test done when a new chemical is tested for toxicity before it is released to the public. Data from microbial assays with *S. typhimurium* TA98 and a DNA repair test with human embryo lung diploid WI38 suggested that UDMH is metabolically activated *in vitro* by liver microsomes to produce an intermediate that is genetically active. However, UDMH produced negative results in a dominant lethal assay with mice or rats and other animals [773–785]. Unoxidized UDMH was not mutagenic but oxidized samples suspected of containing NDMA were mutagenic [237].

#### 1.8.11 Teratogenicity of UDMH

The embryotoxicity and teratogenicity of MMH, UDMH, and SDMH were investigated with pregnant rats [786, 787]. A dose-dependent reduction in maternal weight gains occurred for all three compounds. A dose-related teratogenic effect did not occur for any of the three compounds. Embryotoxicity, manifested as reduced 20-d fetal weights, occurred only in the UDMH and SDMH high-dose treatment groups. The results indicated that none of the three methylated hydrazine derivatives were selectively embryotoxic or teratogenic in rats.

UDMH may cause disturbances in the structure of synaptonemal complexes in spermatocyte nuclei in mice [788]. Chromosomal abnormalities occurring in the pool of stem cells following a ten-day exposure period were permanently persistent.

### 1.8.12 Bacteriostatic Activity of UDMH

Data on the toxicity of UDMH to bacteria in soil have already been detailed in chapter “Methylhydrazine” in *Encyclopedia of Liquid Fuels*. Readers looking for information about UDMH may find it by reading the MMH chapter.

The toxicities of UDMH and other hydrazines were determined for mixed and unculture cultures of nitrifying bacteria, denitrifying bacteria, and anaerobic methanogenic bacteria [789–791]. MMH was more toxic than hydrazine or UDMH. The toxicity level numbers were small enough to preclude biological waste treatment of these compounds.

During a series of experiments on the death rate kinetics of hydrazine-exposed bacteria cultures, it was noted that bacteria in substrate-free media continued to grow and that metabolites derived from lysed cells were being metabolized. The effects of UDMH, MMH, or hydrazine on the utilization of arbitrarily selected saccharides and compounds involved in the intermediary metabolism were measured as a means of elucidating this mechanism of metabolism [792–795].

The toxicity of UDMH to bacteria may be caused by peroxide intermediates. Seven different recombinant bioluminescent strains of *Escherichia coli* were used to describe the mechanism of toxicity of UDMH on bacteria, as well as to determine whether bacteria can sensitively detect the presence of this compound [238]. It was suggested that the action of UDMH on bacterial cells is caused by hydrogen peroxide, which may be formed in response to the reduction of the air oxygen level.

### 1.8.13 Olfactory Threshold of UDMH

There is a wide discrepancy in reported olfactory threshold values for UDMH and the other hydrazines. Several sources agree that one should not rely on the odor of hydrazines as a warning for imminent acute or sub-acute exposure because it may cause olfactory fatigue. Also, the olfactory threshold is far above the established safe levels. A comparison table in the chapter titled “Methylhydrazine” summarizes the reported olfactory threshold of hydrazines in comparison to former and current American Conference of Governmental and Industrial Hygienists (ACGIH®) threshold limit values.

Methylhydrazines have a more distinct fishy odor than hydrazine, although it would be difficult to differentiate them from methylamine or DMA, which are common constituents of fish degradation products. A group of volunteers was exposed to UDMH vapors at concentrations of 0.2, 0.3, or 0.5 ppm [796]. The odor threshold level for UDMH has been generally quoted at 6 to 14 ppm for UDMH. The value for UDMH olfactory threshold is 12 to 28 times the threshold limit value. Seven years of field experience by personnel have indicated that the actual odor thresholds are considerably below these values. Since odor threshold levels are used by safety and operating personnel at Cape Kennedy as an indication of exposure, it was considered appropriate to evaluate this field experience. Based on these data and the results of some controlled studies, it was concluded that the actual odor

thresholds are less than 0.3 ppm for UDMH. The test objects described the odor as “fishy, unpleasant, restroom-like, ammonia-like, rotten-fish type, etc.” Back in 1959, before much was known about UDMH toxicity, one of the studies [797] suggested that “*The odor threshold of the vapor appears to offer an adequate warning of the presence of hazardous concentrations.*” Notably, this attitude has changed considerably in the 60 years since.

#### 1.8.14 Epidemiological Studies of UDMH Exposures

While epidemiological studies of workers exposed to hydrazine  $\text{N}_2\text{H}_4$  or hydrazine hydrate in the workplace have been published, no comparable studies exist for UDMH. It is difficult to estimate the number of workers exposed to UDMH over the past 60 years because UDMH was used (and is still being used) at so many different locations around the world.

The *National Occupational Exposure Survey* (1981–1983) estimated that 2917 workers were potentially exposed to UDMH [798]. This estimate was based only on observations of the actual use of the compound. The *Toxic Chemical Release Inventory* (EPA TRI) listed four industrial facilities that produced, processed, or otherwise used UDMH in 1988 [799]. In compliance with the Community Right-to-Know program in the US, the facilities reported releases of UDMH to the environment that were estimated to total 4300 lb. TRIs have been compiled every year since 1988. The reports have become more detailed and the databases more readily accessible to the public as the years have gone by. The 1979 Toxic Substances Control Act (TSCA) Inventory identified four companies that together produced 55000 lb of UDMH in 1977 [800].

Air sampling during fuel transfer operations was once done in conjunction with the evaluation of respiratory protection (gas mask canisters) for workers at Rocky Mountain Arsenal. Measurements were of the order of 2 ppm hydrazine and 3 ppm, or even up to 4.6 ppm UDMH. Air samples were taken in 1976 and 1977 during drum and truck/rail tanker filling operations [801]. The sampling methods used were sulfuric acid-coated silica gel tubes and impingers. Air samples were taken both outside and inside gas masks worn by propellant handlers. Outside air samples were typically of the order of 0.2 ppm for hydrazine and UDMH, with peak excursions of 1.66 ppm hydrazine or 1.98 ppm UDMH. The air inside the gas masks was clean. If there was any hydrazine or UDMH, it was close to the detection limit. The TLV in effect at the time was 1 ppm for hydrazine and 0.5 ppm for UDMH but lowering of the TLVs to 0.1 ppm was imminent. The odor of hydrazine and UDMH was noted when walking past the storage area, which was outside the general work area. NDMA was detected in the air in the vicinity of UDMH storage tanks. Some of the operating procedures had been improved and necessary repairs were made before the inspection team returned several months later. Shortly before the facility was shut down, air samples were taken and analyzed for NDMA in 1980 while railroad cars and tankers were cleaned and loaded [802]. NDMA was found in the entire area, using two different sor-

bent tube materials. Since there was no gas mask with proven effectiveness against NDMA, industrial hygiene staff recommended that compressed air respirators should be worn when working in the area. Another inspection two years later, after the operations were shut down, found no detectable hydrazine or UDMH in the air (D.L. of  $0.05 \mu\text{g}/\text{m}^3$   $\text{N}_2\text{H}_4$  or  $0.1 \mu\text{g}/\text{m}^3$  UDMH) but found persistent NDMA levels of typically  $2 \mu\text{g}/\text{m}^3$  (D.L.  $0.05 \mu\text{g}/\text{m}^3$ ) with excursions of  $20 \mu\text{g}/\text{m}^3$  [803]. The silica sorbent for hydrazine(s) analysis was replaced with fire brick for the later set of analyses.

It was reported that personnel exposed to UDMH suffered from aprosexia, hypomnesia, and hepatitis with increasing work duration [685]. Based on a review and risk analysis of the toxicity, toxic mechanism, and poisoning symptoms of UDMH, it was suggested that health care, nutrition care, and stricter environment inspections are effective protection measures.

Throughout the many years that ARIANE-1 through ARIANE-4 was in service as a satellite launcher, the ground personnel at the Kourou launch site observed all safety regulations. There were no serious poisoning incidents at the time because adequate safety precautions were always taken [804].

### 1.8.15 History of UDMH Accidents

Two workers who had inhaled UDMH vapor at a distance of 700 m from the source of the fumes experienced initial choking. Four hours later, both men became extremely nauseated and both vomited. Both reported the taste of UDMH being left in the mouth [717]. At the arsenal, careful pre-employment analysis of men was carried out, including cephalin flocculation and thymol turbidity tests. The observations were repeated every two weeks. Only a sub-clinical toxic state was noted in five individuals. After six months, no clinical evidence of toxicity was observed but positive cephalin flocculation was noted. Comparable results were found in another group of six men. Findings indicated that UDMH may produce pulmonary irritation, delayed gastro-intestinal irritation, haemolysis, and convulsions in humans. In another group of tank farm workers who transferred UDMH from tank cars into 55-gal drums, several individuals had abnormal RBCs, WBCs, and cephalin flocculation.

A propellant technician performing transfer of UDMH from a tanker to another container was involved first in a spill, followed by an explosion and fire with ignition of the patient's clothes, leading to them suffering severe burns (53% of upper body surface) and UDMH poisoning [805]. The patient appeared to have stabilized 40 h post-accident but complications (a drop of systolic blood pressure from 120 to 60 mm Hg) developed during anesthesia in preparation for planned surgery and skin grafting. The surgical procedure had to be abandoned. Proper antidote information was not obtained until 48 h after admission. The team then proceeded with injections of 25 mg/kg pyridoxine (25% *i.v.*, 75% *i.m.*) and ornithine ketoglutarate (35 g/24 h continuously *i.v.*). Improvement occurred within minutes of this treatment. The pyridox-

ine dose was repeated twice during the two following days. Finally, after 5 d, the patient was stabilized enough to undergo surgery for his burn wounds.

On 1 February 1988, in a railway cargo train near the city of Yaroslavl in Russia, three tank cars containing UDMH left the tracks, and approximately 740 L was spilled from one overturned tank [565]. The volume of soil that was strongly polluted (up to 20 g UDMH/kg of soil) was 150 m<sup>3</sup>. More than 1100 persons, many inadequately prepared to deal with the hazards of this chemical, participated in the clean-up effort associated with the train accident. Out of the group of 1100 participants, 58 were seriously poisoned and required hospitalization (see also [806]).

### 1.8.16 Toxicity of NTO/UDMH Reaction Products

Most of the UDMH toxicity publications deal with exposure to only the fuel vapors. In real life, however, in the case of leakage of storable propellants at a launch site (a leak not severe enough to cause instant ignition), the personnel responding to an emergency may be exposed to mixtures of UDMH and NO<sub>2</sub> vapors. This situation was simulated in a series of animal tests.

It is already extremely hazardous if living beings are exposed to UDMH by itself or NO<sub>2</sub> by itself, but the combination of the two poisons, as it may be encountered after launch vehicle failures, may aggravate the situation. The oxidative damage parameters of mice poisoned by inhaling gas mixtures containing NO<sub>2</sub> (N<sub>2</sub>O<sub>4</sub>) and UDMH were studied by randomly dividing a group of 40 mice into a control group and three experimental exposed groups [807, 808]. The mice of the three experimental groups were put into an exposure cabinet 2 h/d for four successive days. The concentrations of the mixed propellants in the cabinet were 10, 90, and 400 mg/m<sup>3</sup>, respectively. The mice were weighed and killed on the fifth day, and the content of malondialdehyde (MDA) and the activity of Total Superoxide Dismutase (T-SOD) in serum and lung tissue and content of lipofuscin in liver homogenate were measured. The weight of the mice in the 400 mg/m<sup>3</sup> group was significantly lower than that of control group (P 0.01). The serum MDA content of the 400 mg/m<sup>3</sup> group was significantly lower than that of control group (P 0.05). The lung tissue MDA contents of all three experimental groups were significantly lower than that of control group (P 0.01). The plasma T SOD activity of the animals in the 90 mg/m<sup>3</sup> group was significantly lowered (P 0.01). The T SOD activity of lung tissue in the 10 and 90 mg/m<sup>3</sup> groups was significantly lowered. Despite these changes, the variations of the oxidative damage parameters showed that there was no significant lipid peroxidation damage in the poisoned mice.

In another study of combined injury caused by blast and liquid propellant poisoning, 392 male Wistar rats were divided randomly into seven groups: blast injury group, UDMH group, N<sub>2</sub>O<sub>4</sub> intoxication group, blast injury accompanied with intoxication of UDMH group, blast injury accompanied with intoxication of N<sub>2</sub>O<sub>4</sub> group, blast injury accompanied with intoxication by UDMH and N<sub>2</sub>O<sub>4</sub> group, and a normal control group [809]. The excess pressure of the blast wave was 471 kPa and the pos-

itive pressure was sustained for 55–60 ms. To establish the blast-toxicosis combined injury model, rats were exposed to UDMH 800 ppm or/and  $\text{N}_2\text{O}_4$  43 ppm through inhalation in an intoxication tank for 15 minutes immediately after the blast injury. The clinical conditions of experimental rats were observed, and the animals were killed sequentially 3, 6, 12, 24, 48, and 72 h after injury for blood gas analysis and biochemical examination. According to the clinical observations and the results of blood gas analysis and biochemical examinations, a blast-toxicosis combined injury model was established successfully. Injury caused by the explosion of liquid hypergolic propellants can be simulated by combining the blast wave tube and the intoxication tank. The establishment of the model should be of great significance for the interpretation of actual accidents that have happened.

In a similar experiment, test animals (rats) were exposed to simulated launch mishap vapors under controlled conditions [810, 811]. Rats were exposed to combination blast effects and poison injury with  $\text{N}_2\text{O}_4$  and UDMH to study the effect of blast-poison combined injury on the blood gas analysis and pathomorphological changes. A total of 168 healthy male rats were exposed to blast waves at 471 kPa. After ten minutes of blast injury, the rats were randomly divided into three groups. The rats continuously inhaling UDMH were labeled as the BU group, the rats inhaling  $\text{N}_2\text{O}_4$  were the BN group, and the rats inhaling both UDMH and  $\text{N}_2\text{O}_4$  were the BUN group. The clinical symptoms of the rats in the BUN group were aggravated progressively, the pulmonary alveoli were diffusely filled with pink exudate and large patchy hemorrhage, and pneumorrhagia and pneumonedema were aggravated. Cloudy swelling or hyaline degeneration occurred in the cardiac muscle cells in different degrees and individual myocardial fiber was broken. The myocardial mesenchyme was loose, and hemorrhage and edema occurred. The pathologic change of the myocardium was aggravated. Dilation of the hepatic sinusoid and cloudy swelling in the hepatic cells were observed. The partial pressure of oxygen in the artery ( $P_a\text{O}_2$ ) in all three groups significantly decreased at 3–12 h after injury and reached the lowest point at 3–6 h after injury. The decreasing period of the  $P_a\text{O}_2$  in the BUN group lasted longest and it recovered more slowly than that of the other two groups. All the animals had more serious symptoms in the respiratory system with the combined exposure to blast injury and poisoning by  $\text{N}_2\text{O}_4$  and UDMH. The animals in all the three groups had pathomorphologic changes and they were the worst in the BUN group.

### 1.8.17 Maximum Allowable Exposure Levels of UDMH

The considerations in establishing maximum allowable exposure limits for hydrazines in general and UDMH in particular have already been discussed in an earlier section in this chapter while exploring the maximum allowable exposure levels of MMH.

The Committee on Toxicology of the National Research Council (NRC) published *Guides for Short-Term Exposure of the Public to Air Pollutants*, which included UDMH,

MMH, and hydrazine [812, 813]. The short-term public exposure limit (STPL) and short-term exposure limit (STEL) limits recommended by that committee are compared in Table 18 and in a similar table in the chapter on MMH.

**Table 18:** Olfactory thresholds and exposure limits for UDMH.

| Type of data <sup>a</sup> | UDMH concentration, ppm by volume | References |
|---------------------------|-----------------------------------|------------|
| Olfactory threshold       | 0.5–1.0                           | [796]      |
| Olfactory threshold       | 6–14                              | [708]      |
| ACGIH-TLV (1981)          | 0.5 (skin)                        | [814]      |
| ACGIH-STEL (1981)         | 1                                 |            |
| ACGIH-TLV (1998)          | 0.01 (skin) A3                    |            |
| NRC-EEL, 10 min           | 100                               | [815]      |
| EEL, 10 min               | 200                               | [816, 817] |
| NRC-EEL, 30 min           | 50                                | [815]      |
| EEL, 30 min               | 100                               | [816, 817] |
| NRC-EEL, 60 min           | 30                                | [815]      |
| EEL, 60 min               | 50                                | [816, 817] |
| NRC-STPL, 10 min          | 50                                | [812, 813] |
| NRC-STPL, 30 min          | 25                                |            |
| NRC-STPL, 60 min          | 15                                |            |
| NRC-PEL*, 10 min          | 100                               |            |
| NRC-PEL, 20 min           | 50                                |            |
| NRC-PEL, 30 min           | 30                                |            |

EEL = Emergency exposure limit, STEL = Short-term exposure limit, PEL = Public emergency limit

The standard operating procedure for the establishment of Acute Exposure Guideline Levels (AEGLs) is described in [818]. They list the publications that were considered in setting these limits. AEGLs are established for the general population, not just for healthy working populations covered by the TLV-TWA. AEGL-1, AEGL-2, and AEGL-3 values for UDMH are listed in Table 19.

**Table 19:** AEGL limits for UDMH.

| AEGL level             | 10 min. | 30 min.                            | 1 h                               | 4 h                                 | 8 h                                 |
|------------------------|---------|------------------------------------|-----------------------------------|-------------------------------------|-------------------------------------|
| AEGL-1 (non-disabling) | NR      | NR                                 | NR                                | NR                                  | NR                                  |
| AEGL-2 (disabling)     | 18 ppm  | 6 ppm<br>(14.7 mg/m <sup>3</sup> ) | 3 ppm<br>(7.4 mg/m <sup>3</sup> ) | 0.75 ppm<br>(2 mg/m <sup>3</sup> )  | 0.38 ppm<br>(1 mg/m <sup>3</sup> )  |
| AEGL-3 (lethal)        | 65 ppm  | 22 ppm<br>(54 mg/m <sup>3</sup> )  | 11 ppm<br>(27 mg/m <sup>3</sup> ) | 2.7 ppm<br>(6.6 mg/m <sup>3</sup> ) | 1.4 ppm<br>(3.4 mg/m <sup>3</sup> ) |

NR = not recommended

Data source: [819]



Numeric values for AEGL-1 were not recommended because of several reasons: **(1)** the lack of available data, **(2)** the data indicated that toxic effects may occur at or below the odor threshold, **(3)** the inadequate margin of safety that exists between the derived AEGL-1 and the AEGL-2, or **(4)** the derived AEGL-1 is greater than the AEGL-2. The absence of an AEGL-1 does not imply that exposure below the AEGL-2 is without adverse effects. The NRC AEGL committee treated both dimethylhydrazines together, although they acknowledged that 1,1-dimethylhydrazine may be somewhat more toxic than SDMH [820]. In a 2001 re-evaluation of AEGL data for UDMH, the ten-minute AEGL-2 level was set at 18 ppm and the ten-minute AEGL-3 level was set at 65 ppm [821]. The original (SCP) *Immediately Dangerous to Life and Health* (IDLH) concentrations of 50 ppm for UDMH were later revised to 15 ppm [822, 823] (see also [815, 824, 825]).

### 1.9 Environmental Impacts of UDMH

The US EPA has issued several *Health and Environmental Effects Profiles* for hydrazines that contain sections on environmental effects in addition to toxicity information [707]. There is substantial concern about the environmental fate of residual UDMH and NTO from the Russian launch vehicles that crash in remote corners of Kazakhstan. The descent of the first stages of Proton launch vehicles is accompanied by the spill of unburned UDMH and NTO in amounts ranging from 0.6 to 4 tons, of which 10–30 kg reach the ground and are subsequently spread over the surface.

Attempts have been made to model the spread of this contamination in the environment and to explore possible paths of degradation and adsorption to soil [781, 826, 827]. Several UDMH degradation compounds were predicted to exhibit high probabilities for potential carcinogenicity, mutagenicity, teratogenicity, and/or embryotoxicity. The compounds were ranked based on their predicted human health impact using partial order ranking methodologies that highlight which compounds on a cumulative basis should receive major attention, i.e., NDMA, 1,1,4,4-tetramethyltetrazene, trimethylhydrazine, acetaldehyde dimethylhydrazone, 1,1-formyl-2,2-dimethylhydrazine, and FDMH, respectively.

Many of the earlier publications expressing concern about the pollution of spent stage impact areas in Kazakhstan were based on assumptions and computer models. As of 2018, there is only one solid study that is based on actual field observations at the impact sites. The most comprehensive and detailed account of the environmental impact of spent launch vehicles in the first and second stages in Kazakhstan was published in 2018 [828]. During the early years of the operation of the launch vehicle model PROTON-K, residual propellants remained in the first stage after its separation from the upper stage. In most cases, it led to an explosion after hitting the ground. In the case of the more recent, improved design Proton-M, most of the first stage residual

propellants were ejected from the tanks after stage separation through a drain valve and, therefore, did not reach the ground.

The number of PROTON launches ranged from three to 11 times a year in the period 2010–2016. The leakage of UDMH from a single-stage impact incident covered an area up to 737 m<sup>2</sup>. UDMH was detected mainly in the snow of the PROTON first stage falling sites where its concentration reached up to 2200 mg/L (the most common range of concentrations was 0.1–0.2 mg/L). In sporadic soil samples, it was up to 1.5 mg/kg. UDMH was detected mainly in winter. In early spring the content of UDMH was 0.09–0.69 mg/kg in the soil, while in summer it did not exceed 0.05 mg/kg. In the N<sub>2</sub>O<sub>4</sub> leakage areas, the content of NO<sub>3</sub><sup>−</sup> increased up to 22.3 g/L in the snow and 24.8 g/kg in the soil. In the places where UDMH leakage had occurred, pH values in the snow and soil increased to 10.3 and 9.4, respectively and the background values varied from 5.1 to 7.9 and from 6.6 to 8.3, respectively. UDMH contamination occurred in only 50% of collected samples at a distance no further than five meters from the metal fragments of the stage. NDMA was detected in both snow and soil. Maximum values reached 239.9 mg/L in snow, and the most common concentrations were in the range of 0.2–0.4 mg/L. NDMA was found in only 11% of soil samples and in 46% of snow samples collected no further than 5 m from the fragments of the stage. The maximum NDMA concentration reached 13.9 mg/kg. The operation of heavy vehicles in soft soils during the recovery of fragments of the launch vehicle first stage for scrap metals recycling can expand the contaminated zone and add to the environmental damage. The Proton second stages contain less propellant and experience more aerodynamic heating during re-entry. In the impact sites of the Proton second stages, the main adverse effect was associated with the mechanical pollution of eco-systems with the fragments of fallen stages. They did not detect chemical pollution in the soil and snow surrounding second-stage fragments during three years of observation (see also [552]).

It appears that the heat from aerodynamic braking of second-stages re-entering the atmosphere at a much higher speed than the first stages causes most of the residual propellants to evaporate and disperse along the ballistic re-entry path. There are computer programs for calculating the chance of orbital debris hitting the ground (*Object Reentry Survivability Analysis Tool* and *Spacecraft Atmospheric Reentry and Aerothermal Breakup*) but they are rarely applied to the second stages of launch vehicles [829]. The launch vehicle second stages are separate from the third stages at a height of 130–160 km. Owing to aerodynamic overloads at a height of 30–50 km, the stages are destroyed and most of the second stage fragments burn out, leaving the remaining fragments to fall to the ground, scattering considerably within a range of falling sites. Residual propellants burn out and metals start melting due to the thermal heating, or they disperse in the atmosphere before reaching the Earth's surface. No more than 5% by weight of the second stages reached the ground [830].

### 1.9.1 Aquatic Toxicity of UDMH

Several data on the aquatic toxicity of UDMH on fish, algae, invertebrates, amphibians, and crustaceans in water have already been discussed in sections on the same topics when considering MMH previously. Therefore, readers looking for UDMH information may find it by scanning through these sections. The aquatic toxicity of UDMH to algae, bacteria, invertebrates, amphibians, crustaceans, and fish have already been described in detail in [831] (see also [290, 291, 832–836]).

### 1.9.2 Degradation of UDMH in the Environment

Howard's *Handbook of Environmental Degradation Rates* [837] provides data for a large number of chemicals, including UDMH, SDMH, MMH, hydrazine, and NDMA. The environmental chemistry of hydrazines continues to receive interest [838]. One of the many degradation products of UDMH is 1-formyl-2,2-dimethylhydrazine,  $(\text{H}_3\text{C})_2\text{N}-\text{NH}-\text{CHO}$ , CAS RN [3298-49-5], which was found in UDMH-contaminated water and soil samples. Under certain conditions (alkaline hydrolysis), it can hydrolyze and release UDMH back to the environment [380]. This is very similar to FDMH,  $(\text{H}_3\text{C})_2\text{NN}=\text{CH}_2$ , CAS RN [2035-89-4]. A detailed study of the environmental fate of UDMH and its by-product NDMA provided a summary of published literature on the degradation of UDMH in water, soil, and the air, and the types of follow-on products formed during this process [839].

#### 1.9.2.1 Degradation of UDMH in Water

The rate of UDMH degradation in water depends on the degree of oxygen saturation, temperature, and hardness of the water. Sunlight and dissolved transition metal salts will accelerate the process. The rate of autoxidation of UDMH in distilled water with a carefully controlled degree of oxygen saturation was already discussed in an earlier section of this chapter. Similar studies were performed for hydrazine and MMH.

Hard and soft water samples, with and without the addition of UDMH, were examined over a 96-h period for changes in alkalinity (with two different pH indicators), pH, specific conductance, ethylenediamine tetraacetic acid (EDTA) hardness, and D.O. [840]. The D.O. content changed more rapidly in hard water than in soft water.

Decomposition (degradation and autoxidation) of UDMH proceeded more rapidly in pond water than in seawater [841, 842]. After 10 d, 40% had decomposed in pond water and 30% in seawater. No change could be detected in distilled water. Half-life times of UDMH and other hydrazines have already been detailed Table 13.

Under open-air conditions, the rate of degradation of UDMH in surface water is fast, with no sharp increment of the contents of degradation products such as formaldehyde or cyano group ( $\text{CN}^-$ ) [843]. The UDMH degradation is influenced by many factors such as the hydrological conditions, daylight illumination, temperature, and acidity.

One of the autoxidation products of UDMH in water, air, or soil is NDMA. In water, it was noticed that NDMA is easily evaporated and photolyzed in aqueous solutions. The rate of evaporation is higher at alkaline pH but the rate of photolysis is greater in acidic solutions. Evaporation only converts a water pollution problem to an air pollution problem. If there is concern about the evaporation from a caustic UDMH-NDMA waste stream, it should be neutralized and acidified to enhance photolysis over evaporation.

Vacuum-assisted headspace SPME (Vac-HSSPME) followed by GC-MS was used for the quantitative analysis of UDMH transformation products in surface water samples [844]. The target transformation products were pyrazine, 1-methyl-1*H*-pyrazole, NDMA, *N,N*-dimethylformamide, 1-methyl-1-1,2,4-triazole, 1-methyl-imidazole, and 1*H*-pyrazole. For these analytes, and using shorter sampling times, Vac-HSSPME yielded detection limits (0.5–100 ng/L) that were three to ten times lower than those reported for regular HSSPME. Vac-HSSPME sampling for 30 minutes at 323 K (50 °C) yielded the best combination of analyte responses and their standard deviations (<15%). 1-Formyl-2,2-dimethylhydrazine and formamide were discarded because of poor precision and accuracy when using Vac-HSSPME. The recoveries for the rest of the analytes ranged between 80 and 119%.

### 1.9.2.2 Degradation of UDMH in Air

The rate of UDMH degradation in ambient air depends on the intensity of sunlight, relative humidity, and the presence of other air contaminants like ozone and nitrogen dioxide. The rate of autoxidation of UDMH in dry air in carefully controlled atmospheres in laboratory atmospheric research chambers has already been discussed in section “Autoxidation of UDMH in Air” above. Similar tests were conducted with hydrazine and MMH vapors.

The rate of evaporation of UDMH and the other two propellant hydrazines from a Petri dish in air was already detailed in the chapter on methylhydrazine. As stated, there is a gradual increase in the rate of evaporation and a half-life time in air or water going from hydrazine to MMH and going from MMH to UDMH.

The autoxidation of UDMH and a 50:50 mixture of UDMH and hydrazine (Ae-50 blend) was studied in a 300-mL Pyrex flask, at a partial pressure of 5 mmHg in a 44-cm path length IR spectrophotometer cell, and in a long path 55-L reaction cell constructed of a 0.152-m × 3.05-m section of Pyrex pipe [228]. With initial UDMH partial pressures of several mmHg, autoxidation proceeded too slowly to be differentiated from natural decay processes. When the initial UDMH pressure was lowered to a few ppm, the addition of oxygen caused an approximately first-order decay with a half-life of about 84 h. The main oxidation product under these conditions was FDMH. The 50-50 blend did not behave as two independent systems. Instead, there were substantial positive synergistic effects observed. At concentrations of a few mmHg of each component, the addition of oxygen resulted in a 10- to 20-fold increase

in decay rate over that shown by UDMH or hydrazine by itself. At ppm concentration levels, the situation was similar for UDMH, where a four-fold oxidation rate increase was observed when compared with a similar experiment with no hydrazine present. However, hydrazine oxidation in the 50-50 blend was somewhat slower than it was in a similar experiment with only hydrazine present.

Previous air pollution studies assumed that UDMH dumped from launch vehicles prior to re-entry was very diluted and totally evaporated as a vapor, especially at low pressures in a high atmosphere. But what happens if large quantities of liquid UDMH are suddenly released in the high atmosphere as the result of unburnt fuel re-entering with an upper stage or stage fragmentation as the result of a launch disaster? Will UDMH attach itself to water/ice in the clouds and then snow or rain onto the surroundings? In trying to find an answer to such questions, it has been attempted to model the behavior of UDMH aerosol droplets in the atmosphere [549, 845–847].

The evaporation of NTO or UDMH in ambient air after residual propellants were dumped overboard from upper stages is fast enough that droplets most likely will not reach the ground [544, 848, 849].

If the sudden atmospheric release of UDMH (Ae-50) is the result of a launch disaster of a TITAN-II, -III, or -IV launch vehicle, the toxic cloud will initially consist of a mixture of unreacted fuel and oxidizer vapor at non-hypergolic and below-flammable concentrations. The dispersion of such propellant clouds has been modeled using an atmospheric dispersion computer program [850]. The gas-phase reaction of UDMH with  $\text{NO}_2$  in the cloud of exploded propellants leads to the formation of tetramethyltetrazene-2 and NDMA [271].

Reactions of UDMH with selected species of interest that are found in the environment have been investigated [851]. Included were aqueous-phase reactions that can occur in atmospheric aerosols, raindrops, groundwater, or soils in contact with groundwater, as well as selected gas-phase reactions. Reactants include oxygen and hydrogen peroxide (both reactants in the presence and absence of catalysts), ozone, nitrous acid, sulfur dioxide, and acetone (as a model for environmental ketones and aldehydes). Rate constants for the reactions have been determined, or upper limits set. In several instances, reaction products have been identified. By far the fastest reactions measured were those involving the hydrazines and ozone with (second-order) rate constants up to  $2.4 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ .

The first and second stages of Russian expendable launch vehicles re-entering the atmosphere are said to scatter large amounts of unburnt propellants during re-entry and impact on the ground. So far, most of the interest was directed at UDMH that survived the impact, and most investigators ignored the simultaneous presence of NTO at the impact site. Because the fuel tanks are attached to the outside of the core oxidizer tank on the Proton vehicle, they may separate during re-entry and impact at different locations. Some of the NTO must be reacting with the UDMH if both are released at the same time at the same impact location. Several of the impacts have resulted in fires.

Rockets such as PROTON or DNEPR using UDMH and NTO propellants accounted for about one-third of all stratospheric rocket engine emissions, which was comparable to solid-fueled rocket emissions. Plume and global atmosphere models were developed to estimate local and global ozone depletion caused by NO and H<sub>2</sub>O emissions from the PROTON rocket, which is the largest UDMH-fueled launcher in use [852]. NO and H<sub>2</sub>O emission indices were assumed to be 20 and 350 g/kg (propellant), respectively. Predicted maximum ozone loss in the plume of a PROTON rocket would be 21% at 44 km altitude. Plume ozone loss at 20 km equals 8% just after launch. Predicted steady-state global ozone loss from ten PROTON launches annually is  $1.2 \times 10^{-4}\%$ , with nearly all the loss being due to the NO component of the emission. Normalized by stratospheric propellant consumption, the global ozone depletion efficiency of the PROTON is approximately 66–90 times less than that of solid-fueled rockets. From 2019, the PROTON was gradually phased out from service. Therefore, this problem should go away with time, although China and North Korea, and some Indian launch vehicles continue to use NTO and UDMH or NTO and UDMH fuel blends like UH-25.

### 1.9.2.3 Degradation of UDMH in Soil

Studying the degradation of alkylhydrazines in soil is a dual project. Firstly, the disappearance of hydrazines as they are digested by bacteria is measured. Secondly, the toxic effects of hydrazines that might kill the bacteria or induce irreversible mutations are measured. The fatal toxicity of alkylhydrazines to bacteria was previously detailed. Therefore, the first topic only is discussed here.

Degradation of UDMH and other hydrazines in the soil takes place via several mechanisms. The most active mechanism for the degradation and destruction of UDMH in soil is biodegradation, where UDMH and its decomposition products serve as nutrients for certain types of bacteria. In sterile soils, in the absence of bacteria, autoxidation would be the main degradation mechanism if air can freely diffuse through the soil. In wet climates, oxygen-saturated rain will carry in more oxygen and wash out and dilute the UDMH. Some of the UDMH may be firmly adsorbed to high surface area clays. Some of the UDMH may react with aldehyde and carbonyl groups in carbohydrates that are naturally present in humus-rich soil and become immobilized until its host molecule becomes consumed by another slow process. In aerated soils, the spilled UDMH will autoxidize and form NDMA. NDMA is more persistent and degrades in the soil much more slowly than UDMH [853, 854].

Both UDMH and hydrazine are strongly adsorbed or decomposed on clay particles. Montmorillonite and kaolinite clays, as well as test soils, seem to accelerate the decomposition of the UDMH and hydrazine [834].

Undiluted hydrazine, UDMH, and Aerozine-50 moved through a 50-cm (20-in.) soil column when leached with 22.8 cm (9 in.) of water [855]. Toxic concentrations of the test chemicals, as measured by the growth of rice, remained in the 30- to 50-cm (12- to 20-in.) depths after 22.8 cm (9 in.) of water had been leached through the columns.

Adsorption isotherms of UDMH vapor on peat soil were measured between 305 and 323 K using a dynamic method [856]. The differential enthalpy of adsorption was calculated from the temperature dependence of adsorption. One of the potential methods for the clean-up of UDMH-contaminated soil was thermal treatment. The desorption isotherms of UDMH from soil need to be known to optimize this process and determine how long it will take to effectively remove all UDMH contamination from soil by baking it.

Soil percolation/adsorption tests were conducted with UDMH (0.1% solutions) using four different types of soils (sand, clay, organic, and one typical for Vandenberg AFB) [248, 249]. The soil samples were mostly sandy soils with little cation exchange capacity. All soils were dried at 353 K for 24 h, which should have killed most of the soil bacteria. Yellow-colored autoxidation products interfered with colorimetric determination. GC/MS was a more reliable method in the presence of autoxidation products. Table 58 in *Encyclopedia of Liquid Fuels* in the chapter "Methylhydrazine" summarized the adsorption/extraction results obtained after soaking 3-g soil samples for 20 minutes with 30 mL of 0.002 vol.-% solutions. No fuel interaction was observed with clean sand (as in the percolation studies) but strong effects were observed in all natural soil samples. The strongest interaction was with clay-type soils. Hydrazine and MMH were more reactive than UDMH in all soils. In soil percolation tests, fuel solutions were applied to a 200-g soil sample in a column and leached with 500 mL of water. In the case of UDMH, 100% of it was leached from sand with the first 50 mL. However, in humus, a strong interaction was observed and less than 20% could be recovered after extraction with 500 mL of water.

As soon as UDMH enters the soil, some of it vaporizes, and the elevated moisture of the soil promotes an increase in the UDMH concentration at the initial moment. Then, the concentration levels off toward the end of observation. It was found that the higher the organic matter content in the soil, the higher the remaining UDMH concentration. However, at the end of the observations, on the 90<sup>th</sup> day, the total UDMH concentration did not exceed 0.5% of its initial content. To explain the UDMH behavior in soils, one must take into account the existence of different forms of this substance and the changes in their ratios with time. The main portion of UDMH retained by the soil in the free form is transformed during the first few days. HPLC and MS were used to identify the decomposition products of UDMH in soils [857–859]. Decomposition products of UDMH included DMA, FDMH, methylhydrazine, trimethylhydrazine, NDMA, 1-methyl-1,2,4-triazole, formic acid dimethylhydrazide, 1,5,5-trimethylformazane, 1-methyl-1,6-dihydro-1,2,4,5-tetrazine, *N,N*-dimethylaminoguanidine, and several other products. High-reliability structure identification was achieved using independent methods, including gas chromatography-mass spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR, and UV spectroscopy, and by measuring retention times and spectral characteristics after the synthesis of the suggested structures by other methods. Some intermediate products of the decomposition of

UDMH that are potentially capable of temporarily bonding and later releasing UDMH were characterized. Some less polar intermediates had high migration mobility in soils.

Procedures were developed based on liquid chromatography/MS for determining the transformation products of UDMH in soils, including formic acid dimethylhydrazide (identical with 1-formyl-2,2-dimethylhydrazine), 1-methyl-1,2,4-triazole, 1,1-dimethylguanidine, and DMA [369]. For sample pre-treatment, the use of extraction with methanol (for 1-formyl-2,2-dimethylhydrazine) and ultrasonic extraction with a weakly alkaline buffer solution (for other substances) was used.

One of the most stable transformation products of UDMH is MTA, which was analyzed in contaminated soils using SPME in combination with gas chromatography-MS. Quantitation of organic compounds in soil samples using SPME is complicated by a matrix effect. Thus, an isotope dilution method was chosen using deuterated analyte (1-(trideuteromethyl)-1*H*-1,2,4-triazole) for matrix effect control [460, 860] (see also [861–864]).

The effect of different soil-geochemical factors on the migration of UDMH in the landscape and the effect of organic matter, acid-base properties, particle size distribution, and mineralogy on the decrease in the concentration of UDMH in equilibrium solutions has been studied [865].

Snow cover contamination was measured in the impact areas of the first stages of the PROTON launch system in central Kazakhstan [866, 867]. It was found that the chemical effect of propellants on the snow cover is local. The increase in the content of the following toxic substances in the snow was registered: UDMH, NDMA, nitrate, and nitrite ions. Most of the pollutants were localized in the upper 5-cm snow layer. Dinitrogen tetroxide decreased the value of pH while UDMH increased it. The in-flow of calcareous soil particles from dust storms and their subsequent fallout result in the alkalization of snow and in the neutralization of acidification by dinitrogen tetroxide accompanied by the formation of the salts of nitric acid and nitrous acid (see also [552]).

UDMH behavior in soils depends on the properties of the soils, concentrations of the pollutant, and the soil's mineralogical composition. In wet soils, the UDMH concentration at the initial moment was higher than in the dry soils. However, subsequently, differences level out, and at the end of the 90-d observation, UDMH concentrations did not exceed 0.5% of the initial load regardless of the humidity. If the load of UDMH was 4 kg/m<sup>2</sup>, 2–4% of the introduced quantity was detected in the soil profile of the Luvisols, Kastanozems, and Regosols one day after the start of the experiment. After a year it disappeared to 0.02–0.1%. Clay soils absorb 70–90% of incoming UDMH and sandy soils adsorb 2–46%. The degree of UDMH desorption depends on the granulometric composition, e.g., about 2.7% of UDMH is washed away from the topsoil horizons of clay soils, and about 30% of the total amount of substances is washed away from sandy soils at the first rain [868, 869].



The penetration of UDMH, assumed to be a viscous liquid, through aerated soil was modeled to determine the penetration depth of UDMH spilled on the ground [870]. The penetration was modeled as a function of time, depth, and soil type.

During a study of the adsorption and decomposition of UDMH in red soil and yellow-brown soil, the adsorption curves and adsorption isotherms of UDMH in the two soils were obtained using an improved equilibrium method. The adsorption coefficients were calculated based on the measurement of the adsorption of UDMH in different concentrations [871]. It was found that formaldehyde was a degradation product of UDMH in the two soils. Its concentration changed with time.

Ninety-six samples of peat bog soil from the impact area of the first stage of the CYCLONE-3 launch vehicle containing unburned UDMH in the European North of Russia, near the Plesetsk Cosmodrome, were taken at different distances from the center of the impact area and from different soil horizons [872]. Samples were analyzed by HPLC with amperometric detection and gas chromatography-tandem MS. The contents of UDMH and the ten most important products of its transformations (MMH, hydrazine, 1,1,4,4-tetramethyltetrazene, formaldehyde, acetaldehyde and furaldehyde *N,N*-dimethylhydrazones, 1-formyl-2,2-dimethylhydrazine, *N,N*-dimethylformamide, NDMA, and MTA) were determined. The obtained data reflected the spatial distribution, migration, and transformation of UDMH in the impact area of rocket stages under conditions of sub-arctic climate.

Considerable amounts of UDMH and most of its transformation products were found at distances of <10 m from the center of the impact area. The maximum concentration of UDMH was found near the center where the maximal permissible concentration was exceeded 2400-fold. The worst pollution was observed in the surface soil layer, while methylhydrazine, MTA, 1-formyl-2,2-dimethylhydrazine, formaldehyde and acetaldehyde *N,N*-dimethylhydrazones, and *N,N*-dimethylformamide were the major UDMH transformation products. The composition of the transformation products changed in favor of the last three compounds with increasing distance from the center. Formaldehyde *N,N*-dimethylhydrazone and *N,N*-dimethylformamide were present in all soil samples and can be used as reliable markers of contamination with rocket fuel. The surface water of the peat bog contained four UDMH transformation products in considerable concentrations, including NDMA. The processes of migration and transformation of UDMH in peat bog soil differ considerably from those in sandy soils. This is due to the cold climate of the sub-arctic zone, the reducing environment of peat bog, and strong binding of hydrazines to the organic matter of peat which prevents the migration of pollutants and contributes to the long-term survival of high levels of soil pollution [873].

### 1.9.3 Bioremediation of UDMH Pollution in Soil

Microbial communities of soil bacteria sustainably functioned at UDMH doses of up to 20 mg/kg. When the concentration of UDMH was greater than 200 mg/kg over two weeks of incubation, bacterial activity was completely suppressed [874, 875]. UDMH concentrations of up to 10 mg/kg in soil had no notable impact on the ammonification and nitrification [876].

For bioremediation of UDMH-contaminated soil, Russian scientists decided to work with the bacteria *Rhodococcus* (also referred to as “red ball”), while their Kazakh colleagues selected *Azotobacter* as one of the most promising bacteria types. The possibility of microbiological live culture cleaning of water and soil polluted with UDMH was studied. Several isolates (bacteria, yeast, and micromycetes) capable of utilizing UDMH as the only source of nitrogen, carbon, and energy were isolated from UDMH-polluted tundra soil. Acceleration of UDMH biodegradation was achieved by using a biosorbent that involved cells of the active degrader strain immobilized on granulated activated charcoal [877]. Thus, polluted water could be recirculated through a trickle tower packed with the granulated material. Biological testing in *Escherichia coli* and cereal plants (wheat and barley) demonstrated that biodegradation significantly decreased the toxicity of solutions containing UDMH, suggesting its utility for microbiological cleaning of polluted territories.

In addition to the application of microbes for bioremediation of contaminated soil, Kazakh scientists proposed that polluted areas be planted with amaranth. According to their data, this plant possesses a definite ability to accumulate UDMH (heptyl) from the soil. The plant crop can then be simply cut and destroyed by burning.

The biodegradation rate and pathway of UDMH, when contacted with two strains of bacteria isolated from acclimated activated sludge, were investigated in solution and in soil [878]. The purpose of this study was to provide a fundamental practical way for the bioremediation of soil and water contaminated by UDMH spills at ambient temperature. The results demonstrated that *Stenotrophomonas* sp. M12 (M12) was able to degrade UDMH of 50 mg/L as the sole carbon source in an aqueous mineral salt medium (MSM) but could not degrade UDMH in soil. *Comamonas* sp. P4 (P4) barely degraded UDMH at 50 mg/L as the sole carbon source in aqueous MSM. However, the degrading capacity of P4 could be improved by the addition of an extra carbon source. Meanwhile, P4 was able to degrade UDMH at levels of 100–600 mg UDMH/kg soil. The degradation of UDMH in the soil was influenced by organic matter, autochthonous micro-organisms, and metal ions. UDMH could inhibit the metabolism of M12 and P4, and the inhibition influence was more severe in aqueous MSM than in soil. Oxygen content was important for M12 biodegrading UDMH, and co-metabolism helped P4 to self-detoxify and self-recover. The main intermediates of UDMH were identified by GC/MS, and the concentrations of UDMH and its important transformation products were determined in solution and soil.

A properly designed retaining pond and adjoining artificial wetland inoculated with active sludge sewage treatment bacteria can effectively remove UDMH and degradation products from wastewater [879].

UDMH in the air and in water can be effectively removed using a biofilter with an active bacteria culture. It was proposed to pass a UDMH-contaminated air stream through a biofilter packed with compost-scoria-sugarcane bagasse as the nutrient [683]. The filter was tested at different inlet loadings ( $0.44\text{--}2.68\text{ g m}^{-3}\text{ h}^{-1}$ ) and with various retention times (30, 60, and 90 s), bed heights, and non-ionic surfactants over 126 d. The single-pass removal efficiency was 88%. Dominant species of bacteria in the biofilter bed included *Pseudomonas*, *Acinetobacter*, and *Proteus spp* (see also [880]).

### 1.9.3.1 Degradation of NDMA in Air and in Soil

NDMA is one of the more persistent autoxidation products of UDMH. As such, it can sometimes still be found long after all UDMH and other hydrazines are gone. NDMA degradation in soil, water, and the air is an important aspect of UDMH and DMA toxicity. DMA is a natural product of decaying processes and is part of agricultural and fish industry waste. In highly polluted atmospheres, it forms NDMA during the night, but during the daytime the half-life time of NDMA in the air in full sunlight is only 0.5 h [881].

NDMA, *N*-nitrosodiethylamine, and *N*-nitrosodi-*n*-propylamine were resistant to degradation in soil, sewage, and lake water [882]. No degradation of these nitrosamines was observed in lake water over a three-and-a-half-month period. A lag of nearly 30 d occurred before their slow disappearance from soil. They disappeared slowly from sewage, but a minimum of 50% remained after 14 d. Soil samples were injected with 50 and 250 ppm NDMA and incubated for 25 d. In the first few days, NDMA content dropped rapidly (possibly due to volatilization), then only gradually for the last 20 d. Eight-day soil bacteria cultures did not show any NDMA being digested. The levels of three nitrosamines, including NDMA, decreased slowly over the course of 14 d in sewage adjusted to pH 6. Comparisons of raw versus sterilized sewage suggested some bacterial activity in the degradation of NDMA. The concentrations of three nitrosamines added to littoral water did not change during a 108-d experiment. Nitrosamines are found in cattle manure, DMA in the air surrounding sewage treatment and fish processing plants, and nitrous fumes in silage and automobile exhaust. In summary, there are many sources for the natural formation of nitrosamines. It is difficult to separate biological and physicochemical degradation mechanisms in soil.

#### 1.9.4 Effects of UDMH on Plant Growth

When the concentration of UDMH in soil reached 1.0 g/kg, the growth, development, and productivity of plants initially was stimulated. At values from 1.0 to 10 g/kg, some growth and productivity indicators decreased and the period of development increased. At values from ten to 50 g/kg, the condition of the plant significantly deteriorated. When UDMH concentration is  $\geq 100$  g/kg, the plants die [883].

Undiluted hydrazine, UDMH, or Aerozine-50 was moved through a 20-in. soil column while being leached with 9 in. of water. The soil in the column was sub-divided and each zone analyzed separately [855]. Toxic concentrations of the test chemicals, as measured by the growth of rice, remained in the 12- to 20-in. depth zones of soil even after 9 in. of water had been leached through the columns. All test compounds (at concentrations of  $>200$  ppm) were toxic to the germination and growth of rice, alfalfa, endive, or peas. Hydrazine, UDMH, and Aerozine-50 were toxic to pinto beans at concentrations  $>50$  ppm in water cultures and  $>0.3$  mg/m<sup>3</sup> as fumigants in air. In water, the 24-h median tolerance limit ( $TL_m$ ) values for goldfish, catfish, and bass ranged from 2.4 to 3.7 ppm for hydrazine, from 4.8 to 9.0 ppm for UDMH, and from 3.4 to 6.6 ppm Ae-50.

Vegetation changes at the first stage impact sites of Proton-M rocket launch vehicles were characterized during two growing seasons [884]. Spontaneous re-vegetation by ruderal plant communities occurred after the event. First stage impact sites had lower vegetation cover and species diversity. After winter rocket launches, the vegetation was less deteriorated at the impact sites than after spring and summer launches. The recovery process in plant communities was considerably faster at impact sites corresponding to winter rocket launches. The nitrate fertilizer from NTO/water reactions might help with the re-growth of plants.

### 1.9.5 History of Environmental Pollution by UDMH

#### 1.9.5.1 UDMH Pollution Sites in the US

One of the most complex environmental pollution clean-up tasks in the US was faced by the clean-up contractors for the Hydrazine Blending and Storage Facility at the Rocky Mountain Arsenal near Denver, CO. The facility was constructed in 1959 and operated for 23 years from 1959 to 1982. This facility processed an average of 900 metric tons (1.98 million lb) of Aerozine-50 per year between 1972 and 1975 [358, 359]. The primary activity at the site was the blending of hydrazine and UDMH into Aerozine-50 in support of the TITAN-II and -III programs. In early 1982, OSHA surveyed the site and detected the presence of airborne NMDA within the facility. Several clean-up contractors surveyed the site, continued to take air, soil, and groundwater samples, and proposed remedial action for the 300000 gal of contaminated rinse water still stored at the site. The mountain of paperwork generated as part of these activities is intim-

idating and overwhelming and was in fact causing issues of pollution itself due to paper pollution occurring while the propellant contamination problem was cleaned up. Instead of proceeding to solve the problem, numerous plans were published and re-published in preliminary, draft, preliminary draft, and not so preliminary draft versions. Ten years later, the site still remained on the US Superfund list.

Several decontamination techniques were used to clean up the stored process waste and tank-rinse water [586]. Significant NDMA levels persisted in the groundwater below the Rocky Mountain Arsenal for many years after the propellant mixing facility was shut down [885]. Intercept wells have been sunk to prevent the polluted groundwater from diffusing off-site. NDMA-contaminated water collected in these wells could not be cleaned by activated charcoal filters alone.

At the height of the cold war, there must have been hundreds of NIKE AJAX anti-aircraft missile sites with JP-X Type II all over the US and Europe, and apparently some were still in South Korea as of the mid-1990s. Some JP-X fuel was spilled and not properly cleaned up. Many of these former military sites have since been converted for community use, such as into parks and schools. There have been incidences where the sites were contaminated by leaked UDMH fuel and in a few instances, buried fuel canisters have been found. Unfortunately, no measurements of the persistence of UDMH or NDMA in the soil were made.

#### **1.9.5.2 Use of UDMH in the Former Soviet Union**

Production plants for UDMH in the former Soviet Union existed in Salavat (in the Bushkir Republic) and Angarsk (in the Irkutsk oblast) in the vicinity of substantial human populations. While the main concern is about Proton launches from Baikonur in Kazakhstan [886–888], similar concerns are about the impact of vehicles launched from other sites in Russia such as Plesetsk [889, 890], but not all rockets launched there carry UDMH. Estimates for the total amount of UDMH that may have been produced in the USSR at one time were provided earlier but need to be updated [891]. It was very difficult to keep track of the surplus UDMH after most of the ICBMs using it were decommissioned and demilitarized.

Table 20 is a summary of USSR launch vehicles containing UDMH. The O/F ratio may differ for the first and upper stages, but for the time being one may assume an average O/F ratio of 2.6 which corresponds to 28 mass-% of UDMH in the propellant mass. The list does not include submarine-launched missiles (e.g., SHTIL) because they are less likely to cause pollution on land. In addition, there are several third and kick stages using UDMH but they are not included in this list because they do not contain as much propellants as the first and second stages and they are less likely to impact the ground. In 2006, 16 PROTON M launches were made from the Baikonur spaceport. The first stage of the launch vehicle usually falls on the sparsely populated territory of the Ulytausky area.

**Table 20:** Propellant loads of USSR/Russian launch vehicles and missiles.

| Designation              | Number of stages | Propellant mass, metric tons |              |             | Years of operation | No. of launches                     |
|--------------------------|------------------|------------------------------|--------------|-------------|--------------------|-------------------------------------|
|                          |                  | First stage                  | Second stage | Third stage |                    |                                     |
| TSIKLON-2                | 2                | 118.7                        | 48.5         | —           | 1967–1999          | 109                                 |
| TSIKLON-3                | 3                | 118.7                        | 48.5         | 3.0         | 1977–1999          | 116                                 |
| PROTON-K                 | 4                | 419.4                        | 156.1        | 46.6        | 1967–1999          | 260                                 |
| PROTON-M                 | 4                | 428.3                        | 157.3        | 46.6        | 2000–present       | 102                                 |
| STRELA, SS19 ICBM        | 2                | ~80                          | ~14          | —           | 2003–2014          | Three as satellite launcher         |
| ROCKOT, SS19 ICBM        | 3                | ~80                          | ~14          | 4.9         | 1999–2019          | 146 + 31 as satellite launcher      |
| DNEPR, SS-18 Mod4, R-36M | 3                | —                            | —            | —           | 2000–2015          | Military + 22 as satellite launcher |
| KOSMOS 3M                | 2                | 81.9                         | 18.7         | —           | 1964–1999          | 420                                 |

Data sources: [892].

KOSMOS 3M used RFNA-27N<sub>2</sub>O<sub>4</sub>, not NTO with UDMH. That oxidizer works with a different O/F ratio. Fifty-two SS-18 missiles that were deployed for 30 years in Kazakhstan were transported to the Nizhniy Novgorod region between 1995 and 1996 where they were destroyed [565]. A total of 6000 metric tons of UDMH was transported to Russia for disposal. The US assisted in this effort by providing multimodal tank cars. During the same period, 130 SS-19 missiles were transported to Russia from the Ukraine. The fate of the UDMH contained in those missiles (about 4000 metric tons) remains unknown. Liquid propellant from decommissioned missiles was collected at special facilities located in Piban Shur (Republic Udmurtiya), Surovatikha (Nizhniy Novgorod oblast), Pashino city (Novosibirsk oblast), Krasnash (Krasnoyarsk), and Sergiev Posad (Moscow oblast).

### 1.9.5.3 UDMH Pollution Sites in Russia and Kazakhstan

In a study of populations of two villages directly under the line of flight of launched missiles and near the site of first stage impacts in the Arkhangelsk oblast, it was reported that 79–90% of inhabitants displayed pathologies. In each case, liver damage was observed in more than 50% of the surveyed inhabitants [893]. This is not a peer-reviewed publication.

Since the late 1990s, the ongoing debate about the consequences of the rocket launch activities for the health of people residing near areas of impacts of spent rockets continues [894]. Some scientists argued that the main cause of increased morbidity in those communities is the fault of spilled UDMH. However, field analyses

found UDMH only in the immediate vicinity of fallen carrier rocket fragments. More accurate data were obtained from perennial epidemiological and hygienic research [895]. A hygienic assessment of the nutritional status and health risk of people living near impact areas, and of contaminants in water, soil, and food was performed. A relationship between revealed diseases and UDMH could not be established but there was some causality due to the influence of environmental and psychological anxiety factors that were characteristic of territories and living conditions [896].

For many years, Russia has re-purposed decommissioned SS-19 ICBMs into rocket satellite launchers because it has a stockpile of SS-19s left over from the 1980s and the cold war. Using re-purposed missiles enables Russia to compete in the commercial space launch market, which yields foreign currency. The launches were marketed through Eurokot Launch Services, a joint venture of the Ariane Group and the Khrunichev Space Center. As of 2018, the company's activities were on hold until further notice. Rockets also provide low-cost launches for Russian military satellites. There was concern that residual fuel in re-entering first and second stages could survive the fiery re-entry and contaminate arctic ocean areas that are used by commercial fisheries [546]. There have not been any measurements of UDMH or NDMA residues in seawater or on drift ice in the areas where debris that survives the re-entry heat is expected to splash into the ocean.

#### 1.9.5.4 UDMH Pollution Sites in Other Countries

Most of the Chinese Long March 3 and 4 launch vehicles use NTO/UDMH but little information is available about contamination at the first and second stage impact areas.

## 2 Properties of UDMH/H<sub>2</sub>O Mixtures

Unsymmetrical dimethylhydrazine has been mixed with various other liquids, mostly other rocket fuels, to achieve desirable propellant properties such as lower freezing points, higher densities, reduced infrared emissions from UDMH flames, or improved cooling capabilities in regeneratively cooled rocket engines. One of the best performing fuel blends was a eutectic mixture of UDMH and MMH with a freezing point of 193 K (−80 °C = −112 °F) but no practical application for it has been found. The most widely used UDMH fuel blend for several decades was Aerozine-50 (Ae-50), a 50 : 50 mixture of UDMH and anhydrous hydrazine. As of 2021, Ae-50 has no remaining known uses so this chapter is mostly for historical purposes. Some applications were found for UDMH at a later stage following the first use of Ae-50, by making a fuel blend of UDMH and hydrazine hydrate called UH-25. As of 2021, the UH-25 fuel blend continues to be used in India.

## 2.1 Physical Properties of UDMH/H<sub>2</sub>O Mixtures

Unsymmetrical dimethylhydrazine mixtures with water have no rocket applications. Usually, the water content of UDMH is minimized and carefully controlled where UDMH is used as a rocket propellant. UDMH/water mixtures are encountered mostly during the production of UDMH. In one case, water was added in the form of hydrazine hydrate.

### 2.1.1 Freezing Points of UDMH/H<sub>2</sub>O Mixtures

The UDMH/water system forms two high-melting hydrates: one with 42% UDMH melting at 243.6 K (−29.5°C), and the other one containing 77% UDMH melting at 242 K (−31°C), which correspond to a pentahydrate and a nonahydrate. The UDMH/water system is one of the systems examined during studies on supercooling of strongly hydrogen-bonded binary systems. The UDMH/water solid/liquid system has been studied using thermal analysis covering the equilibrium-phase diagram and irreversible transformations that take place during warm-up of the supercooled liquid [897]. The monohydrate UDMH•H<sub>2</sub>O melts at 242.5 K. It forms a eutectic with UDMH, containing a water mol fraction of 0.125 and melting at 208.5 K. The region around 20 mol-% UDMH could not be resolved due to very slow rates of crystallization. Measurements of the activation energy and activation barriers for crystallization indicated that crystallization occurs by nucleation (if it occurs at all), and often takes place during warm-up, since the values of the entropy of the activated complex are very large and positive during this stage. A comparative study of the glass-transformation range and the viscosity of these mixtures showed a maximum in their free energies of activation at 20 mol-% UDMH. The data suggested a reaction involving a higher-order hydrate, probably a tetrahydrate UDMH•4H<sub>2</sub>O. The region from 15 to 45 mol-% UDMH in which crystallization does not proceed under ordinary conditions, requires additional investigation.

Freezing point data of UDMH/H<sub>2</sub>O mixtures over the entire range of compositions are tabulated in Table 21 and illustrated in Figure 24. The freezing points of UDMH/water mixtures are also visible along one side of the ternary fuel blend chart provided in Figure 48.

### 2.1.2 Vapor-Phase Composition of UDMH/H<sub>2</sub>O Mixtures

Measured activity coefficients of UDMH/H<sub>2</sub>O mixtures differed widely from those predicted by the Gibbs-Duhem equation [898]. The actual activity coefficient of UDMH in dilute solutions is far smaller than the equation predicts. The low degree of activity of UDMH in dilute solution explains the difficulties experienced in trying to recover it from dilute solution by distillation during UDMH production. Additional measure-



**Table 21:** Unsymmetrical dimethylhydrazine/water freezing points.

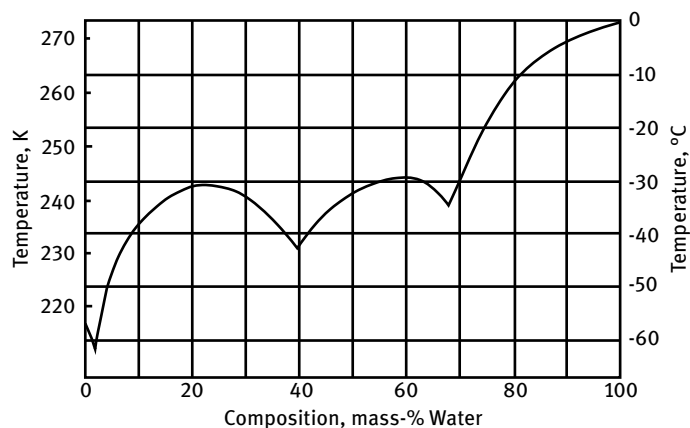
| Composition, mass-% |                  | Freezing point |       |
|---------------------|------------------|----------------|-------|
| UDMH                | H <sub>2</sub> O | K              | °C    |
| 10                  | 90               | 269.9          | -3.2  |
| 21.2                | 78.8             | 260.1          | -13   |
| 25                  | 75               | 253.6          | -19.5 |
| 26.9                | 73.1             | 249.6          | -23.5 |
| 30                  | 70               | 243.6          | -29.5 |
| 30                  | 70               | 241.6          | -31.5 |
| 31.9                | 68.1             | 238.1          | -35   |
| 36                  | 64               | 242.1          | -31   |
| 38                  | 62               | 243.3          | -29.8 |
| 40                  | 60               | 243.6          | -29.5 |
| 45.3                | 54.7             | 243.4          | -29.7 |
| 45.9                | 54.1             | 241.6          | -31.5 |
| 55                  | 45               | 237.6          | -35.5 |
| 55.3                | 44.7             | 238.1          | -35   |
| 60                  | 40               | 230.6          | -42.5 |
| 62                  | 38               | 232.1          | -41   |
| 62.5                | 37.5             | 232.4          | -40.7 |
| 64.5                | 35.5             | 234.4          | -38.7 |
| 66                  | 34               | 236.1          | -37   |
| 70                  | 30               | 239.8          | -33.3 |
| 70.4                | 29.6             | 239.6          | -33.5 |
| 77.2                | 22.8             | 242.1          | -31   |
| 79.8                | 20.2             | 241.6          | -31.5 |
| 90                  | 9.7              | 234.1          | -39   |
| 96.4                | 3.6              | 218.1          | -55   |
| 97.5                | 2.5              | 212.6          | -60.5 |
| 100                 | 0                | 216.1          | -57   |

Data source: [56].

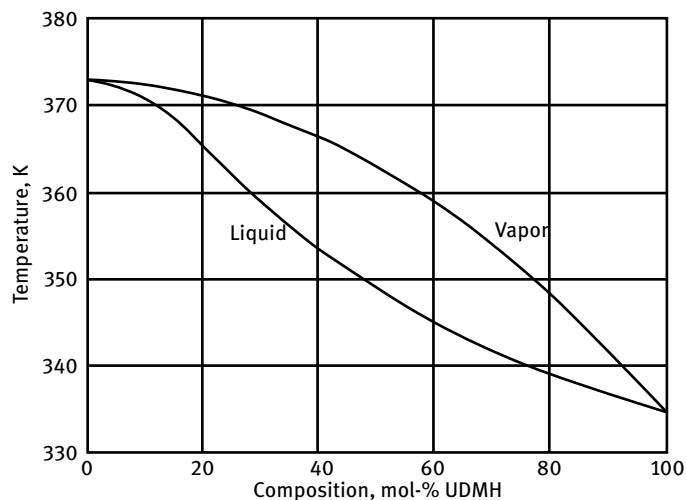
ments at reduced pressure (13.5 kPa = 102 mm Hg) of vapor-phase decomposition revealed a high-boiling azeotrope at about 6 mol% UDMH (see also [74]).

Figure 25 shows the vapor-liquid equilibrium of the UDMH/H<sub>2</sub>O system at 1 atm pressure. The azeotrope is not obvious at ambient pressure. More detailed UDMH/water vapor-phase diagrams were developed at three different pressures [109]. The vapor-phase diagram (Figure 26) shows a minimum of interaction and no azeotrope formation.

Figure 27 shows the isobaric vapor-liquid equilibrium of UDMH + water at 0.1013 MPa from experimental data, computational simulation, and the Peng-Robinson Equation of State (EOS) [127]. In contrast to other binary systems, this

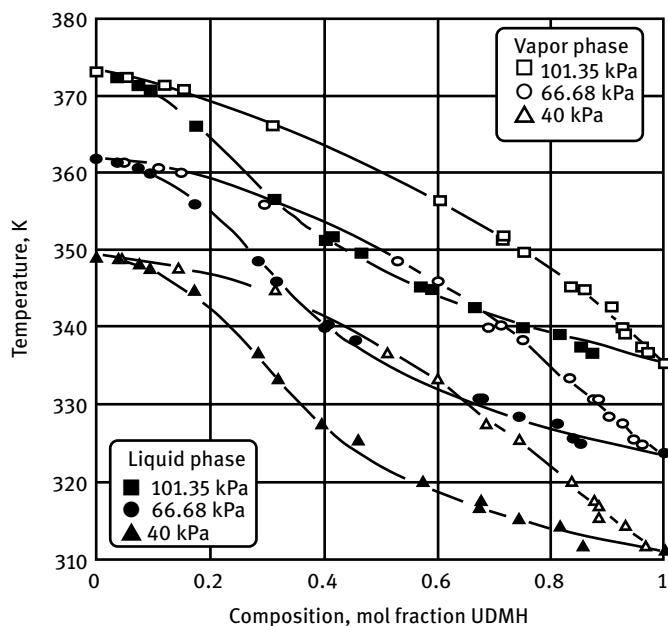


**Figure 24:** Freezing point of UDMH/H<sub>2</sub>O mixtures. (Reproduced and modified from [56].)

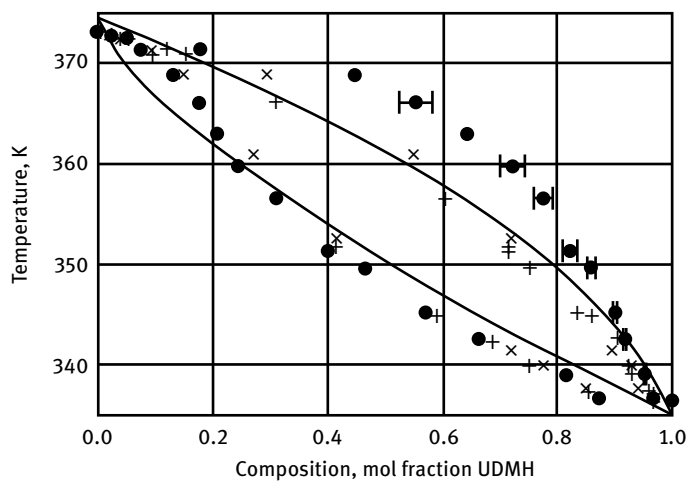


**Figure 25:** Vapor-liquid equilibrium of the UDMH/water system at 1 atm pressure. (Reprinted and modified from [898], with permission from the ©1956 American Chemical Society; permission conveyed through RightsLink.)

mixture is azeotropic. The experimental data by Carleton [898] and Ferriol et al. [109] are very similar, however, the phase envelope reported by Carleton is a little wider. The experimental vapor pressure by Ferriol et al. [109] (345.17 K and  $x_{\text{UDMH}} = 0.571$  mol/mol) was used to adjust the binary parameter of the molecular model ( $\xi = 1.3$ ) and of the Peng-Robinson EOS ( $k_{ij} = -0.285$ ). It can be seen in Figure 27 that



**Figure 26:** Vapor-liquid equilibrium of the UDMH/water system at three different pressures. (Reprinted and modified from [109], with permission from ©1993 Elsevier; permission conveyed through RightsLink.)



**Figure 27:** Isobaric vapor-liquid phase diagram of 1,1-dimethylhydrazine + water at 0.1013 MPa. (Republished and modified from [127], with permission of ©2012 Elsevier Science and Technology Journals; permission conveyed through the Copyright Clearance Center Inc.)  
 Legend: (x) experimental data by Carleton; (+) experimental data by Ferriol et al.; (•) Elts et al. simulation data with  $\xi = 1.3$ ; (—) Peng-Robinson EOS with  $k_{ij} = -0.285$ .

the results obtained by molecular simulation agreed well with the experimental results on the saturated liquid line but they overestimate the UDMH content on the saturated vapor line for intermediate compositions. In the water-rich region and in the UDMH-rich region, the narrow two-phase envelope is well predicted by simulation, whereas the Peng-Robinson EOS yields a qualitatively different form.

### 2.1.3 Density of UDMH/Water Mixtures

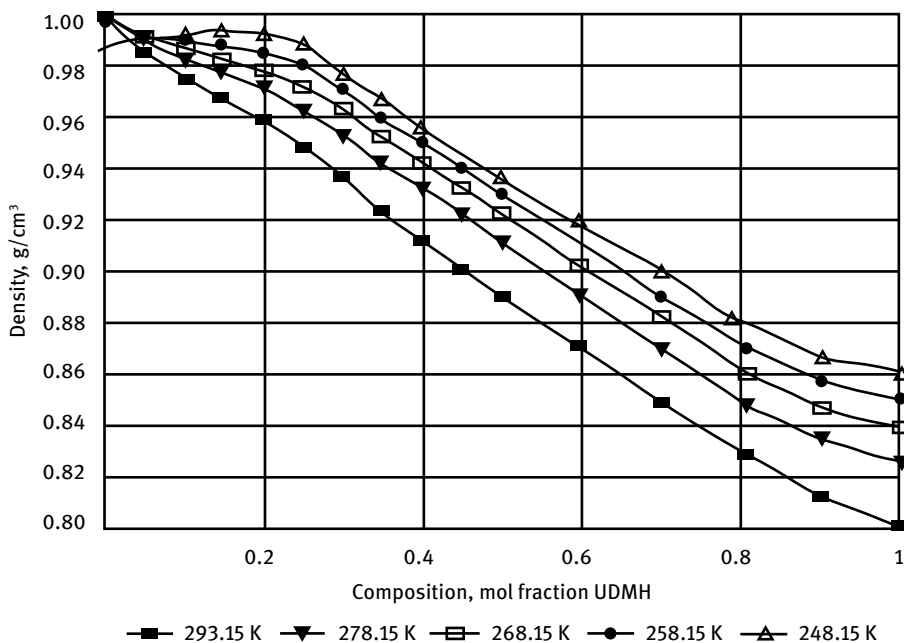
The density and viscosity of UDMH/water mixtures were measured over the entire range of compositions and between 148 and 293 K [101], as summarized in Table 22 and 23 and as illustrated in Figure 28 and 29.

Vapor pressure, density, and viscosity data applied to a chemical association model indicate that the solutions may contain a UDMH monohydrate, a trihydrate, and a UDMH dimer [105].

**Table 22:** Density of UDMH/water mixtures.

| Temperature, K    | 293.15                     | 278.15 | 268.15 | 258.15 | 248.15 |
|-------------------|----------------------------|--------|--------|--------|--------|
| Mol fraction UDMH | Density, g/cm <sup>3</sup> |        |        |        |        |
| 0.0000            | 0.9982                     | 0.9999 | 0.9993 | 0.9963 | 0.9896 |
| 0.0499            | 0.9850                     | 0.9900 | 0.9915 | 0.9920 |        |
| 0.1018            | 0.9750                     | 0.9825 | 0.9870 | 0.9900 | 0.9925 |
| 0.1471            | 0.9675                     | 0.9775 | 0.9825 | 0.9880 | 0.9940 |
| 0.2000            | 0.9590                     | 0.9715 | 0.9785 | 0.9850 | 0.9926 |
| 0.2498            | 0.9485                     | 0.9626 | 0.9720 | 0.9805 | 0.9885 |
| 0.2984            | 0.9370                     | 0.9528 | 0.9633 | 0.9710 | 0.9770 |
| 0.3466            | 0.9240                     | 0.9425 | 0.9525 | 0.9600 |        |
| 0.3473            |                            |        |        |        | 0.9675 |
| 0.3968            |                            |        |        |        | 0.9560 |
| 0.3995            | 0.9120                     | 0.9325 | 0.9424 | 0.9502 |        |
| 0.4482            | 0.9010                     | 0.9224 | 0.9325 | 0.9403 |        |
| 0.4964            |                            |        |        |        | 0.9371 |
| 0.4994            | 0.8900                     | 0.9115 | 0.9230 | 0.9298 |        |
| 0.5955            | 0.8710                     | 0.8910 | 0.9025 | 0.9117 | 0.9200 |
| 0.6986            | 0.8492                     | 0.8701 | 0.8826 | 0.8901 |        |
| 0.7001            |                            |        |        |        | 0.9003 |
| 0.7874            |                            |        |        |        | 0.8821 |
| 0.8064            | 0.8290                     | 0.8484 | 0.8605 | 0.8708 |        |
| 0.8999            | 0.8125                     | 0.8350 | 0.8475 | 0.8575 |        |
| 0.9008            |                            |        |        |        | 0.8670 |
| 1.0000            | 0.8009                     | 0.8258 | 0.8398 | 0.8507 | 0.8605 |

Data source: [101].



**Figure 28:** Density of UDMH/water mixtures. (Chart created by Schmidt 2020 based on data from [101].)

#### 2.1.4 Viscosity of UDMH/Water Mixtures

Viscosities of UDMH/water mixtures were measured over the entire range of compositions and between 148 and 293 K, as summarized in Table 23 and illustrated in Figure 29. These data are from [101].

Viscosity data indicate that the solutions may contain a UDMH monohydrate, a trihydrate, and a UDMH dimer. The viscosity of UDMH-water mixtures peaks near a UDMH mol fraction of 0.25. The peak is very pronounced at lower temperatures.

The viscosity measurements of Laachach of the UDMH/water system are very similar to earlier measurements by McMillan and Los [897] who had also studied freezing point and viscosity over a somewhat lower temperature range of 243 to 283 K and the entire range of UDMH/water ratios. We chose to display the second viscosity chart with a logarithmic viscosity scale in Figure 30, which allows better observation of the changes at low viscosities. The maximum viscosity in the older set of data (11.1 Ps at 243 K) is substantially higher than the highest viscosity measured by the French authors (0.54 Ps at 248 K).

#### 2.1.5 Electric Properties of UDMH/H<sub>2</sub>O Mixtures

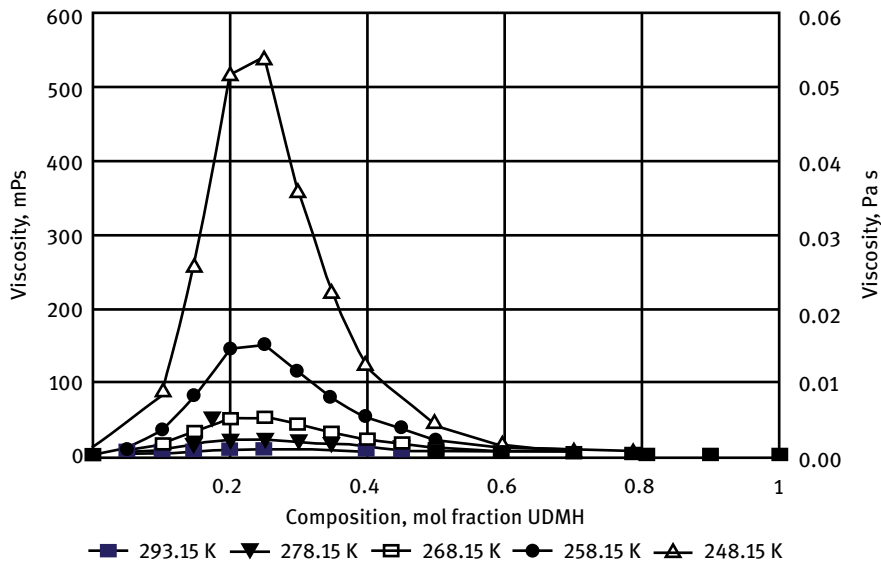
The dielectric relaxation times and static permittivity of the binary mixtures of UDMH and water were determined in supercooled conditions down to 150 K to study the

**Table 23:** Viscosity of UDMH/water mixtures.

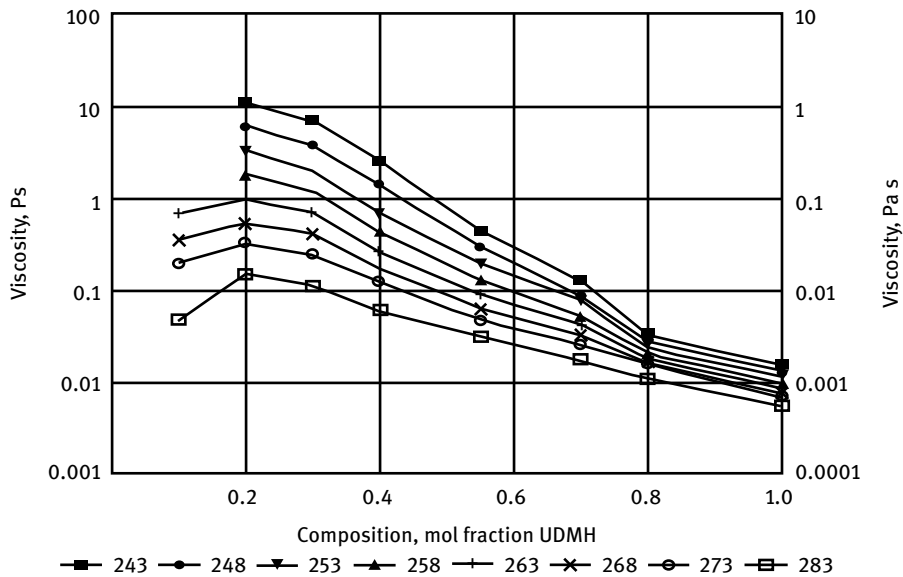
| Temperature, K    | 293.15         | 278.15 | 268.15 | 258.15 | 248.15 |
|-------------------|----------------|--------|--------|--------|--------|
| Mol fraction UDMH | Viscosity, mPs |        |        |        |        |
| 0.0000            | 1.01           | 1.53   | 2.16   | 3.34   | 6.45   |
| 0.0499            | 2.01           | 3.59   | 5.99   | 11.11  | —      |
| 0.1018            | 3.64           | 8.49   | 16.14  | 35.09  | 89.00  |
| 0.1471            | 6.22           | 15.15  | 32.87  | 80.85  | 259.57 |
| 0.2000            | 8.22           | 21.60  | 50.86  | 144.84 | 519.00 |
| 0.2498            | 8.46           | 22.32  | 53.13  | 151.47 | 541.00 |
| 0.2984            | 7.51           | 18.86  | 42.92  | 114.66 | 360.00 |
| 0.3466            | 6.25           | 14.86  | 31.59  | 79.37  | —      |
| 0.3473            | —              | —      | —      | —      | 223.30 |
| 0.3968            | —              | —      | —      | —      | 124.44 |
| 0.3995            | 4.78           | 10.74  | 21.67  | 51.42  | —      |
| 0.4482            | 4.23           | 8.81   | 16.26  | 38.35  | —      |
| 0.4964            | —              | —      | —      | —      | 45.92  |
| 0.4994            | 2.95           | 5.78   | 10.44  | 21.35  | —      |
| 0.5955            | 2.28           | 3.45   | 5.63   | 9.88   | 18.01  |
| 0.6986            | 1.27           | 1.95   | 2.92   | 4.79   | —      |
| 0.7001            | —              | —      | —      | —      | 8.19   |
| 0.7874            | —              | —      | —      | —      | 5.33   |
| 0.8064            | 0.90           | 1.34   | 1.79   | 2.59   | —      |
| 0.8999            | 0.69           | 0.97   | 1.26   | 1.69   | —      |
| 0.9008            | —              | —      | —      | —      | 2.32   |
| 1.0000            | 0.55           | 0.73   | 0.91   | 1.16   | 1.55   |

Data source: [101].

association between UDMH and water in the liquid and solid-state [899]. For each system, these properties can be modeled using chemical associations of the type  $(\text{H}_2\text{O}) \cdot (\text{RR}'\text{NNH}_2)$ , and also using self-associations for pure hydrazines. Permittivity  $\epsilon'$  and dielectric loss factor  $\epsilon''$  define the complex permittivity  $\epsilon = \epsilon' - i\epsilon''$ . Capacitance and dielectric loss factor measurements were taken for eight frequencies (2 MHz, 1 MHz, 400, 200, 100, 40, 20, and 10 kHz) on an automatic micro-processor-based LCR meter. An LCR meter is a type of electronic test equipment used to measure the inductance ( $L$ ), capacitance ( $C$ ), and resistance ( $R$ ) of an electronic component. As spontaneous crystallization occurred upon cooling in a certain range of composition, the relaxation phenomenon could be studied only for the following mol fractions  $\chi$  in UDMH:  $0.15 < \chi < 0.4$  for the UDMH/water system. Data for the temperature dependence of static permittivity were tabulated and graphed. The maximum relaxation time was located near the mol fraction  $\chi = 0.20 - 0.25$  for the UDMH/water mixtures. It was found that the associations involved are a monohydrate and a trihydrate. This behavior is closely related to that observed for viscosity [101].



**Figure 29:** Viscosity of UDMH/water mixtures. (Chart created by Schmidt 2020, based on data from [101].)



**Figure 30:** Viscosity of UDMH/water mixtures. (Chart created by Schmidt 2020, based on data from [897].)

Legend: Temperature in K.

### 3 Properties of UDMH/N<sub>2</sub>H<sub>4</sub> Mixtures

Several decades ago, the most frequently used UDMH/N<sub>2</sub>H<sub>4</sub> mixture was Aerozine-50 (Ae-50), which contained equal amounts (by mass) of UDMH and anhydrous hydrazine. With this 50:50 mix, one might argue about where it should be discussed in this book; here under UDMH or in a parallel chapter on hydrazine (chapter “Hydrazine” in *Encyclopedia of Liquid Fuels*). We chose to discuss it here because many of its properties (vapor pressure, flash point, toxicity) are dominated by its UDMH content and not by its hydrazine content.

Aerozine-50 was the main hypergolic storable fuel of a bygone era, and it is unlikely that it will ever be used again. Nevertheless, we have assembled physical properties of UDMH/hydrazine mixtures here just in case there should be a revived interest in this fuel.

#### 3.1 Physical Properties of UDMH/N<sub>2</sub>H<sub>4</sub> Mixtures

The most comprehensive summary of the physical properties of Aerozine-50 and its constituents is in a report by the Atlantic Research Corporation [108]. It contains a summary of literature data and new measurements of data in areas where some data was lacking. Many additional user manuals for Aerozine-50 developed for the Titan-II program provide a complete summary of the physical, chemical, and safety properties of Aerozine-50 that are not repeated here in detail because of the decreasing use of Ae-50 in the US [96–98, 900, 901]. The physical properties of Ae-50 are summarized in Table 24.

**Table 24:** Physical properties of Aerozine-50.

| Property                           | SI units                                | Other units                                                              |
|------------------------------------|-----------------------------------------|--------------------------------------------------------------------------|
| Molecular mass                     | 41.805 g/mol                            | 23.92 mol/kg                                                             |
| Freezing point                     | 267.6 K                                 | −5.6 °C                                                                  |
| Boiling point                      | 343 K                                   | 70 °C                                                                    |
| Density at 298 K                   | 0.8987 g/cm <sup>3</sup>                | 56.103 lb/ft <sup>3</sup>                                                |
| Sonic velocity at 298 K            | 1612 m/s                                | 5287 ft/s                                                                |
| Adiabatic compressibility at 298 K | $4.36 \times 10^{-5} \text{ atm}^{-1}$  | $2.97 \times 10^{-6} \text{ psi}^{-1}$                                   |
| Vapor pressure at 298 K            | 138.4 mm Hg                             | 2.68 psia                                                                |
| Viscosity at 298 K                 | 0.809 cPs                               | —                                                                        |
| Surface tension                    | 29.10 dyn/cm                            | $2.9 \times 10^{-3} \text{ N/m}$                                         |
| Thermal conductivity at 298 K      | $0.286 \text{ W m}^{-1} \text{ K}^{-1}$ | $6.83 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ °C}^{-1}$ |
| Heat capacity                      | $3.062 \text{ J g}^{-1} \text{ K}^{-1}$ | $0.732 \text{ cal g}^{-1} \text{ °C}^{-1}$                               |
| Enthalpy of formation              | 50.848 kJ/mol                           | 12.153 kcal/mol                                                          |
| Refractive index, $n_D^{25}$       | 1.4393                                  | —                                                                        |



More detailed summaries of the physical properties of Ae-50 are provided in the *USAF Propellant Handbooks, Hydrazine Fuels* [95], from which several of the graphs in this chapter were copied.

It is known that UDMH and hydrazine form strong associations with water and other polar fluids. As such, it was important to study the molecular associations between these [902]. Many of the physical properties of UDMH/ $\text{N}_2\text{H}_4$  mixtures are influenced by intermolecular hydrogen bonding and molecule association in the liquid and vapor phase.

### 3.1.1 Freezing Points of UDMH/Hydrazine Mixtures

Aerozine-50 (Ae-50, A-50), a 50:50 (by mass) mixture of hydrazine and UDMH, melts at 265–267 K (17.6–21.2 °F). There is a eutectic point at 214 K (−74.5 °F) that is close to the UDMH end of the system at 96.7 mass-% UDMH [903, 904]. The melting point profile



**Figure 31:** Melting temperatures of hydrazine/UDMH mixtures. (Reproduced and modified from [95] based on data from McMillan 1967.)

of the binary system N<sub>2</sub>H<sub>4</sub>/UDMH is illustrated in Figure 31. Raw data from a different source are tabulated in Table 25.

Several cases of evaporative freezing of propellant have occurred during static-test-firings of the Apollo Service Module engine (SPS) in a low-pressure environment. Although the freezing caused no apparent operational difficulties, an investigation seemed advisable to define the situation. Ae-50 that is suddenly exposed to vacuum will cool (mainly by evaporation of UDMH), and the remaining hydrazine-rich fuel will freeze at the triple point [905–908]. After freezing is complete, the residual material is nearly pure hydrazine. Similar freezing problems may be encountered with the oxidizer, dinitrogen tetroxide, which freezes at 262 K (–10 °C). Evaporation of Ae-50 in propellant valve seats or narrow passages under space vacuum conditions may clog the tubes and prevent fuel flow. Propellant valve leakage does produce system blockage and is a potential hazard to system operation [909, 910]. Although Ae-50 and MMH are very similar in performance, one advantage of MMH is that it does not freeze as easily as Ae-50 residues in a vacuum.

**Table 25:** Binary system UDMH-hydrazine freezing point data.

| Composition of mixture, Mass-% |           | Freezing point |       |
|--------------------------------|-----------|----------------|-------|
| UDMH                           | Hydrazine | K              | °C    |
| 0.0                            | 100.0     | 274.5          | +1.4  |
| 10.0                           | 90.0      | 272.6          | –0.5  |
| 20.0                           | 80.0      | 270.1          | –3.0  |
| 29.7                           | 70.3      | 268.1          | –5.0  |
| 36.0                           | 64.0      | 268.3          | –4.8  |
| 39.7                           | 60.3      | 268.1          | –5.0  |
| 40.3                           | 59.7      | 268.6          | –4.5  |
| 49.3                           | 59.7      | 267.1          | –6.0  |
| 60.0                           | 40.0      | 265.1          | –8.0  |
| 69.9                           | 30.1      | 262.6          | –10.5 |
| 80.0                           | 20.0      | 257.6          | –15.5 |
| 83.3                           | 16.7      | 253.1          | –20.0 |
| 84.1                           | 15.9      | 251.9          | –21.2 |
| 85.2                           | 14.8      | 248.6          | –24.5 |
| 92.2                           | 7.8       | 223.6          | –49.5 |
| 94.4                           | 5.6       | 225.6          | –47.5 |
| 95.0                           | 5.0       | 223.6          | –49.5 |
| 96.0                           | 4.0       | 214.6          | –58.5 |
| 96.4                           | 3.6       | 213.6          | –59.5 |
| 96.7                           | 3.3       | 214.1          | –59.0 |
| 97.9                           | 2.1       | 214.1          | –59.0 |
| 98.0                           | 2.0       | 213.6          | –59.5 |
| 100.0                          | 0.0       | 216.1          | –57.0 |

Data source: [56].

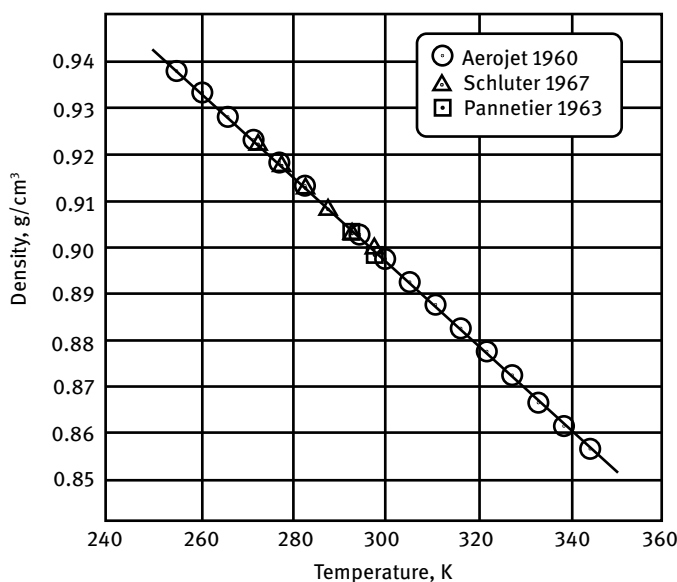
The freezing/melting points of UDMH/hydrazine mixtures are also visible along one side of the ternary fuel blend chart in Figure 48. The melting point of Aerozine-50, the most important mixture in this system, lies between 267 and 269 K (–6 and –8 °C) depending on the precise composition of the sample.

### 3.1.2 Density of UDMH/N<sub>2</sub>H<sub>4</sub> Mixtures

The density of Ae-50, a 50 : 50 mixture of hydrazine and UDMH, as a function of temperature can be expressed by

$$\rho = 1.17423 - 9.2417 \times 10^{-4} T$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $T$  is the temperature in kelvin. This equation, a composite of data from three different sources, was used to calculate the curve-fitted solid line in Figure 32.



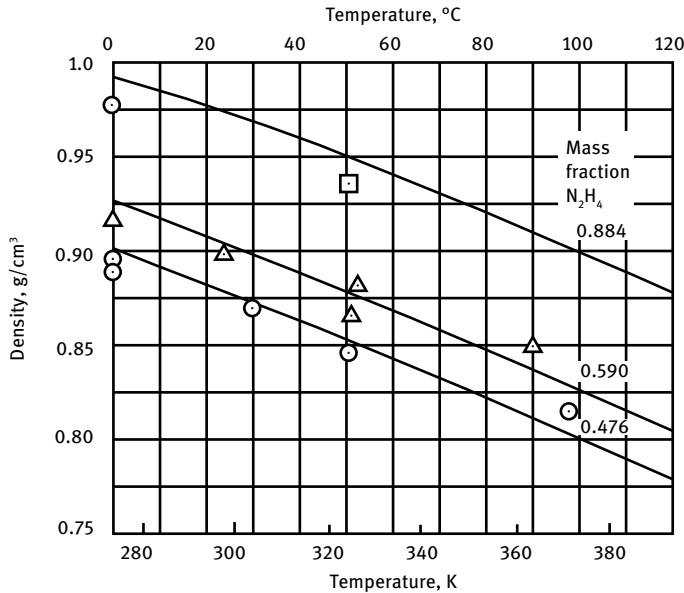
**Figure 32:** Density of Ae-50 as a function of temperature. (Reproduced and modified from [95].)

In the range of 273–313 K and 46–50% UDMH, the density of wet Ae-50 can be calculated from

$$\rho = 1.0249 - 9.550 \times 10^{-4} T - 2.165 \times 10^{-3} U + 1.715 \times 10^{-3} W$$

where  $\rho$  is the density in g/cm<sup>3</sup>,  $T$  is the temperature in °C,  $U$  is the mass-% UDMH, and  $W$  is the mass-% water [91].

Results of density measurements of three UDMH/N<sub>2</sub>H<sub>4</sub> mixtures did not exactly match the predicted density calculated, thus assuming ideal liquid behavior (calculated for ideal solutions shown as a solid line, no partial volumina considered), as illustrated in Figure 33. The densities of binary UDMH/hydrazine mixtures are also visible along one side of the ternary fuel blend chart in Figure 49.



**Figure 33:** Measured and predicted density of UDMH/N<sub>2</sub>H<sub>4</sub> mixtures. (Reproduced and modified from [108].)

### 3.1.3 Compressibility and Velocity of Sound of Aerozine-50

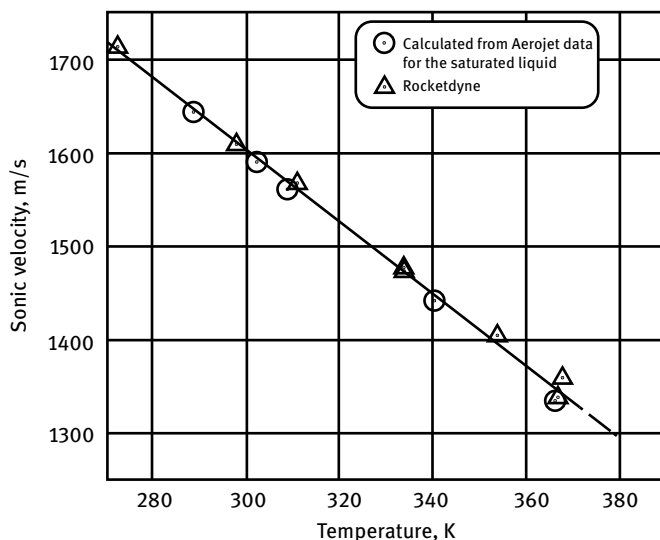
Compressibility is usually derived from velocity of sound (i.e., sonic velocity) measurements. The compressibility of a liquid propellant is an important property when evaluating cavitation in propellant pumps and pogo phenomena that may lead to unwanted resonances. The velocity of sound of Ae-50 as a function of temperature can be calculated from the linear equation

$$c = 2765.3 - 3.8695 T$$

where  $c$  is the velocity of sound in m/s and  $T$  is the temperature in kelvin. These data are illustrated in Figure 34.

The adiabatic compressibility of a liquid can be calculated from its sonic velocity and density using the equation

$$\beta_{\text{ad}} = \frac{1}{\rho c^2}$$



**Figure 34:** Sonic velocity of Ae-50 as a function of temperature. (Reproduced and modified from [95].)

where  $\beta_{\text{ad}}$  is the adiabatic compressibility,  $\rho$  is the density, and  $c$  is the sonic velocity. The adiabatic compressibility of Ae-50 as a function of temperature can be calculated from the linear equation

$$\beta_{\text{ad}} = -5.3196 \times 10^{-5} + 3.2458 \times 10^{-7} T$$

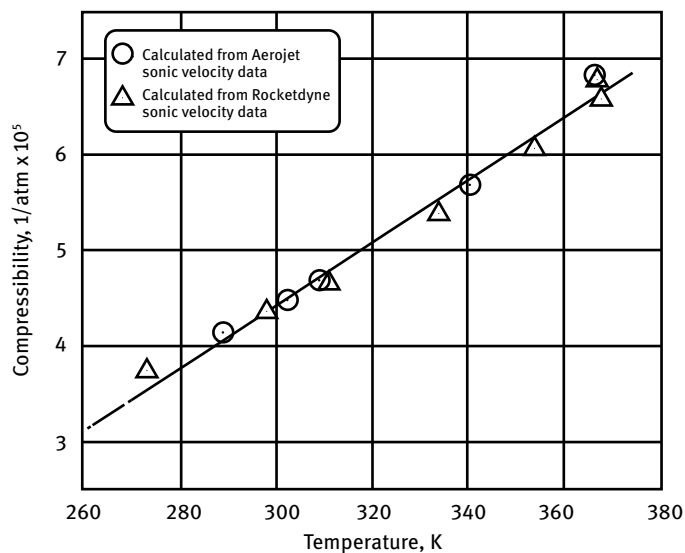
where  $\beta_{\text{ad}}$  is the adiabatic compressibility in  $\text{atm}^{-1}$  and  $T$  is the temperature in kelvin. Data calculated from this equation forms the solid line in Figure 35, and is demonstrated in comparison to data points calculated from the sonic velocity and density of Ae-50.

### 3.1.4 Vapor Pressure of UDMH/Hydrazine Mixtures

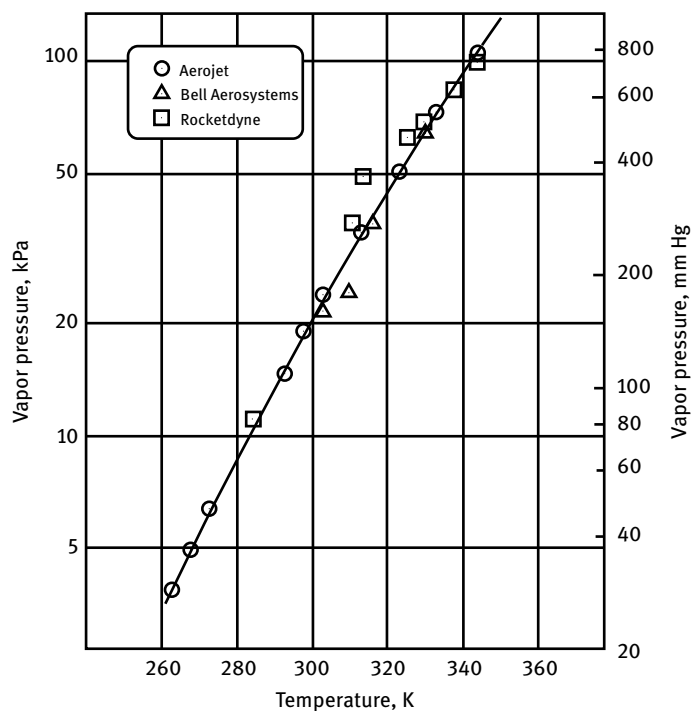
The condensation and boiling point curves show that the two compounds do not form an azeotrope. Thus, it should be easy to separate the two compounds by distillation. This task may arise in the recovery and recycling of surplus or contaminated Aerozine-50. The vapor pressure of a nominal 50 : 50 blend (actual composition was 51.0 mass% hydrazine, 48.2% UDMH, 0.5% water) as a function of temperature can be expressed by

$$\log p = 9.55828 - \frac{2820.587}{T} + \frac{181627.9}{T^2}$$

where  $p$  is in mm Hg and  $T$  is in K. The low-temperature data for the temperature range 263–344 K (–10 to 71 °C) derived from this equation are shown in Figure 36. The vapor



**Figure 35:** Adiabatic compressibility of Ae-50 as a function of temperature. (Reproduced and modified from [95].)



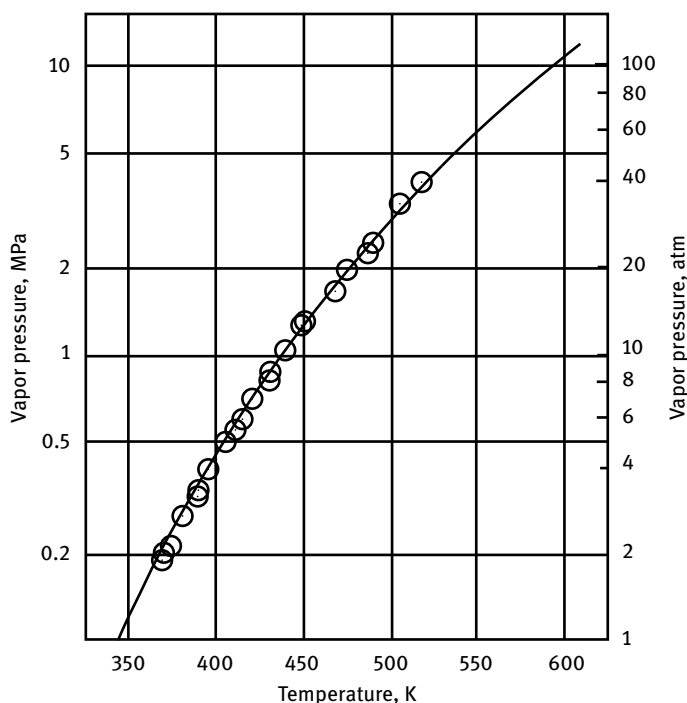
**Figure 36:** Vapor pressure of Ae-50 at moderate temperatures. (Reproduced and modified from [95].)

pressure will depend on the amount of ullage in the system because, inevitably, some evaporation occurs that changes the composition of the remaining liquid.

For higher temperatures, between 350 and 550 K, the following curve fit is a better representation of experimental data, which was extended to the critical point:

$$\log P = 5.2379 - \frac{2086.62}{T} + \frac{99387.3}{T^2}$$

where  $P$  is in atm and  $T$  is in K. The high-temperature vapor pressure data calculated from this equation are shown in Figure 37.

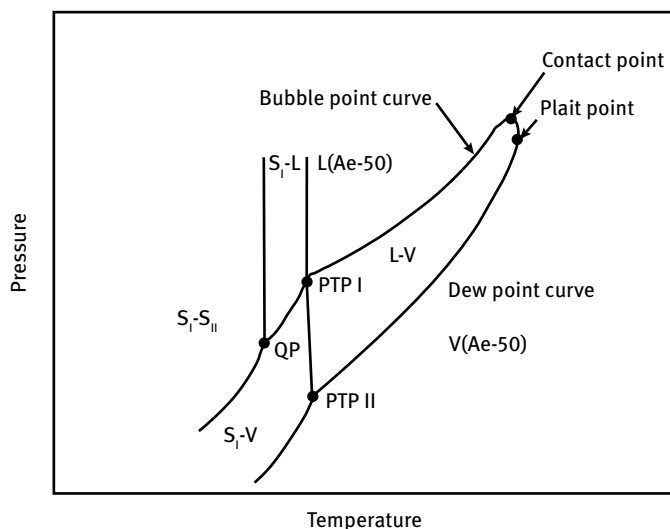


**Figure 37:** Vapor pressure of Ae-50 at elevated temperatures. (Reproduced and modified from [95].)

### 3.1.5 Vapor-Phase Composition of Hydrazine/UDMH Mixtures

Figure 38 is a schematic pressure-temperature diagram for the system Ae-50 taken from Figure 3.1 in [108]. Similar diagrams apply to other miscible two-liquid systems. The diagram in Figure 38 consists of six single- or multi-phase regions but does not have numbers associated with the temperature and pressure scales.

The condensed phases are separated from the vapor phase by a two-phase region bounded by bubble-point and dew-point curves. The reason for this is that a two-



**Figure 38:** Schematic pressure – temperature-phase diagram of the UDMH/ $\text{N}_2\text{H}_4$  system.

(Reproduced and modified from [108].)

Legend: V – Vapor; L – Liquid;  $S_I$  – Solid Hydrazine;  $S_{II}$  – Eutectic (approximately 97% UDMH);

PTPI – Pseudo Triple Point I; PTPII – Pseudo Triple Point II; QP – Quadruple Point.

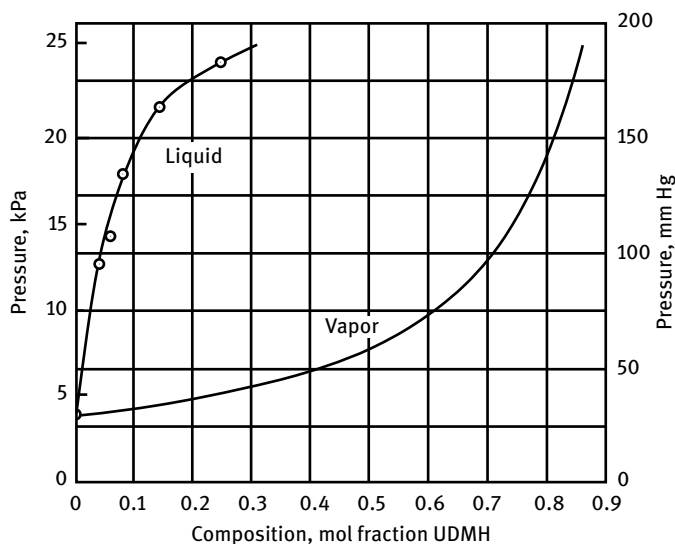
component system generally does not vaporize congruently. Thus, vapor in equilibrium (at the bubble point) with liquid Ae-50 does not have the same composition as the liquid but will have a higher concentration of the more volatile component, UDMH. Similarly, the liquid in equilibrium (at the dew point) with the vapor of Ae-50 composition is richer in the less volatile component, hydrazine. In between the bubble point and dew-point curves, the liquid phase has compositions progressing from Ae-50 to that in equilibrium with gaseous Ae-50. An analogous statement holds for the compositions of the vapor. In between the bubble- and dew-point curves the liquid has compositions progressing from Ae-50 to that in equilibrium with gaseous Ae-50. An analogous statement holds for the compositions of the vapor.

At high temperatures and pressures, the bubble-point and dew-point curves bend over towards each other and meet, forming a loop. The top of this loop corresponds to or replaces the critical point of one-component systems. However, the maximum temperature and maximum pressure for the existence of distinct vapor and liquid phases occur at separate points, the plait point and contact point, respectively. Analogous to the condition at the critical point of a single-component system, the enthalpy of vaporization (heat of vaporization) at the contact point is zero. Fundamental thermodynamics were used in the report to derive an EOS for Ae-50.



The solid phase in region  $S_1$  in Figure 38 is solid hydrazine. Because of the low pressure being considered, the composition of the liquid phase may be assumed to depend on temperature alone.

Figure 39 is an isothermal vapor-phase composition diagram of the UDMH/ $N_2H_4$  system at 311 K. Similar diagrams are available for other temperatures.



**Figure 39:** Liquid-vapor equilibria of UDMH/ $N_2H_4$  at 311 K. (Reproduced and modified from [108].)

The same source contains two more diagrams, one for 353 K and another one for 390 K. Liquid-phase activity coefficients and excess free energies of mixing were calculated for all three temperatures and the entire range of compositions. Temperature-entropy and temperature-enthalpy charts for the binary mixture complemented the set of thermodynamic data calculated for the UDMH/ $N_2H_4$  system.

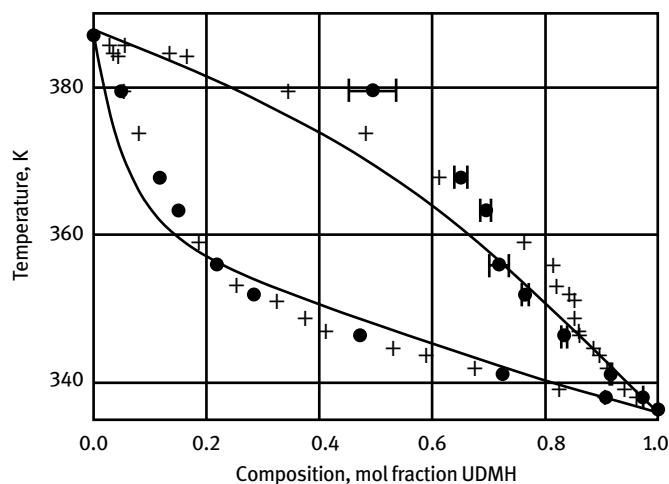
Isobaric data for liquid-vapor phase equilibria of UDMH/ $N_2H_4$  mixtures were measured in the pressure range of 33 to 101 kPa (250 to 760 mm Hg) [107, 912]. Phase compositions were determined from measurements of the refractive index. The temperature range corresponding to these data was approximately 308 to 385 K (35 to 112 °C).

Vapor pressures, phase equilibria, and equilibrium liquid-vapor-phase compositions in the hydrazine/UDMH system were measured. This allowed one to calculate the enthalpy and entropy of vaporization of Ae-50 [104].

Occasionally, if one is burdened with large quantities of waste or surplus Ae-50 and there is a good use for hydrazine, one may want to separate the two hydrazines by distillation [913] instead of disposing of the propellant by incineration. Because

the two boiling points are so far apart and they do not form an azeotrope, this is a relatively easy distillation task but will require a multi-theoretical-plate distillation column. A distillation curve of Ae-50 in a simple still showed that at 10% the distillate was 86% UDMH, at 50% the distillate was 79% UDMH and at 80% the distillate was 100%  $\text{N}_2\text{H}_4$  [900]. During the distillation the boiling point increased gradually from 338 to 388 K (149 to 239 °F).

New molecular models for hydrazine, MMH, and UDMH were proposed to study the fluid-phase behavior of these compounds. A parameterization of the classical molecular interaction models was carried out by using quantum chemical calculations and subsequent fitting to experimental vapor pressure and saturated liquid density data. To validate the molecular models, vapor-liquid equilibria for binary hydrazine mixtures with UDMH were calculated and compared with experimental data [127]. The vapor/liquid equilibrium of UDMH + hydrazine  $\text{N}_2\text{H}_4$  at ambient pressure is presented in Figure 40. This system is zeotropic (i.e., not azeotropic). The experimental vapor pressure by Pannetier and Mignotte [107] at 346.35 K and  $\chi_{\text{UDMH}} = 0.4717$  mol/mol was used to adjust the binary parameter of the molecular model ( $\xi = 1.01$ ) and the Peng-Robinson EOS ( $k_{ij} = -0.1$ ). It should be noted that the description of the interactions between the Lennard-Jones sites of unlike molecules was, in this case, very close to the standard Lorentz-Berthelot combining rules. Simulation results matched almost perfectly with the experimental data on the saturated liquid



**Figure 40:** Isobaric vapor-liquid-phase diagram of the 1,1-dimethylhydrazine/hydrazine system. (Republished and modified from [127], with permission of ©2012 Elsevier Science and Technology Journals; permission conveyed through Copyright Clearance Center Inc.)  
 Legend: + Hydrazine at 0.1013 Mpa: (+) experimental data by Pannetier and Mignotte; (•) Elts et al. 2012 simulation data with  $\xi = 1.01$ ; (—) Peng-Robinson EOS with  $k_{ij} = -0.1$ .

line. On the saturated vapor line, the experimental data and the simulation results exhibited some scatter but the agreement was reasonable. The Peng-Robinson EOS would yield a qualitatively different form.

Out of the three propellant hydrazines, UDMH is the least sensitive to accidents caused by adiabatic compression of vapor bubbles. Nonetheless, the isentropic compression of UDMH and Ae-50 vapors was examined using real gas behavior and equations of state fitted for UDMH for the appropriate real fluid thermodynamic analysis of compression heating and fuel venting [914]. Similar calculations had been performed earlier for hydrazine and MMH. Propellant grade UDMH may contain 98.0 mass-% UDMH, 0.3% H<sub>2</sub>O, and the remainder related amines, which were mathematically treated as similar to hydrazine. UDMH and Ae-50 are usually stored or transported under a blanket of inert gas (either helium or nitrogen). As such, the fuel mixture would also be saturated with blanket gas. Many operations occur in aerospace applications where this fuel mixture undergoes near adiabatic compression or expansion resulting in greatly differing temperatures of the fuel mixture. To predict peak temperatures under those conditions, the Peng-Robinson EOS was validated for pure UDMH. Following this, the UDMH vapor-phase constant-pressure heat capacity was estimated and compared to other hydrazine family heat capacities. Thermodynamic properties were calculated for UDMH. Mixing rules were identified and the non-ideality of the UDMH-hydrazine mixture in Ae-50 was represented by fitting a temperature-dependent interaction coefficient for the UDMH-hydrazine interaction. Isentropic calculations were then made for a mixture corresponding to Ae-50. For these calculations, the following physical properties of UDMH were adopted:

$T_c = 523 \text{ K}$ ;  $P_c = 59 \text{ atm}$ ; acentric factor  $\omega = 0.361$ . The vapor pressure was calculated from

$$\log p = 6.73578 - 875.89/T - 140001.0/T^2$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in K. For higher temperatures, the vapor pressure was calculated from

$$\log P = 4.9439 - 1659.84/T$$

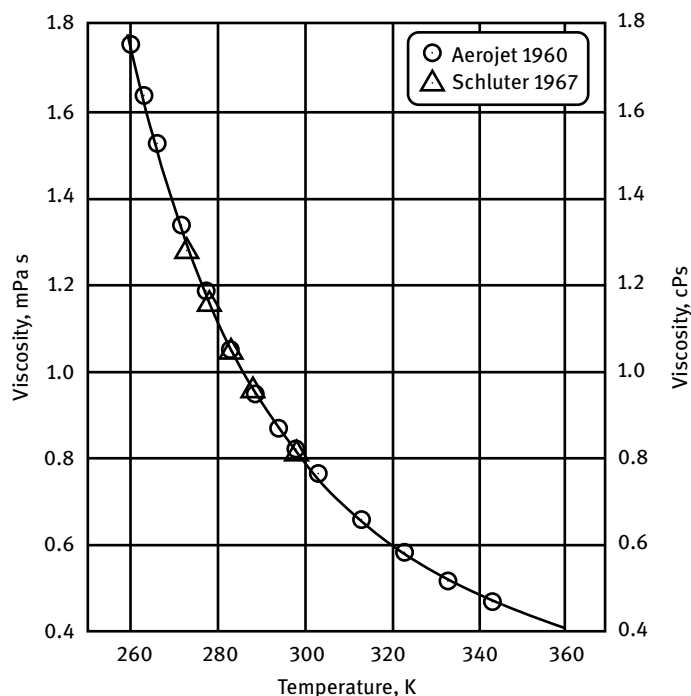
where  $P$  is the vapor pressure in atm and  $T$  is the temperature in K. The peak temperatures for isentropic compression of Ae-50 vapor or the vapor space above Ae-50 with 3% He were calculated for pressure ratios from 10 to 10000. The peak temperatures for a pressure ratio of 100 were 486 and 491 K, respectively, for the real fluid behavior.

### 3.1.6 Viscosity of Aerozine-50

The viscosity of Ae-50 as a function of temperature in the temperature range 273 to 343 K (0 to 70 °C) can be expressed by the equation

$$\log \mu = -0.28445 - \frac{501.489}{T} + \frac{166602.5}{T^2}$$

where  $\mu$  is the viscosity in cPs and  $T$  is the temperature in kelvin. A curve calculated from this formula is illustrated in Figure 41.



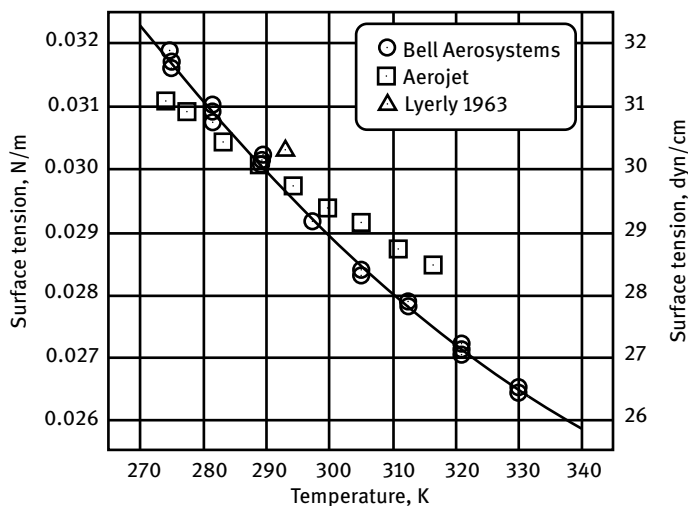
**Figure 41:** Viscosity of Ae-50 as a function of temperature. (Reproduced and modified from [95].)

### 3.1.7 Surface Tension of Aerozine-50

The surface tension of Ae-50 can be calculated from the polynomial equation

$$\sigma = 105.960 - 0.41606 T + 5.3088 \times 10^{-4} T^2$$

where  $\sigma$  is the surface tension in dyn/cm and  $T$  is the temperature in kelvin. The surface tension curve in Figure 42 was derived using this equation. To convert the units from dyn/cm to N/m, multiply the numbers by 0.001.



**Figure 42:** Surface tension of Ae-50 as a function of temperature. (Reproduced and modified from [95].)

### 3.1.8 Thermal Conductivity of Aerozine-50

The following polynomial equation represents the thermal conductivity of liquid Ae-50 over the temperature range of 383 to 425 (10 to 152°C) [95]:

$$\lambda = 7.1983 \times 10^{-4} + 3.7467 \times 10^{-7} T - 1.6736 \times 10^{-9} T^2$$

where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{K}^{-1} \text{s}^{-1}$  and  $T$  is the temperature in kelvin. The same data in SI units gives the equation

$$\lambda = 0.30118 \times 10^{-1} + 1.5676 \times 10^{-4} T - 7.0023 \times 10^{-7} T^2$$

where  $\lambda$  is the thermal conductivity in  $\text{W m}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. These data are illustrated in Figure 43. To convert units from  $\text{cal cm}^{-1} \text{K}^{-1} \text{s}^{-1}$  to  $\text{W K}^{-1} \text{m}^{-1}$  multiply the numbers by 418.4.

### 3.1.9 Heat-Transfer Coefficient of Aerozine-50

The process for determining the upper limit for the nucleate boiling of hydrazine  $\text{N}_2\text{H}_4$  in heated tubes was dangerous, and even catastrophic, at times. Adding UDMH to hydrazine, as was done in the Ae-50 fuel blend, significantly reduced the explosion hazard. As such, the heat flux for the surface nucleate boiling of Ae-50 at the upper limit could be safely determined (Table 26).

The heat flux at the upper limit of nucleate boiling was determined for two hydrazine-UDMH mixtures containing 50 and 77% hydrazine, respectively [917]. Nominal test conditions for the 50:50 mix ranged from 3.78 to 7.57 MPa fluid static

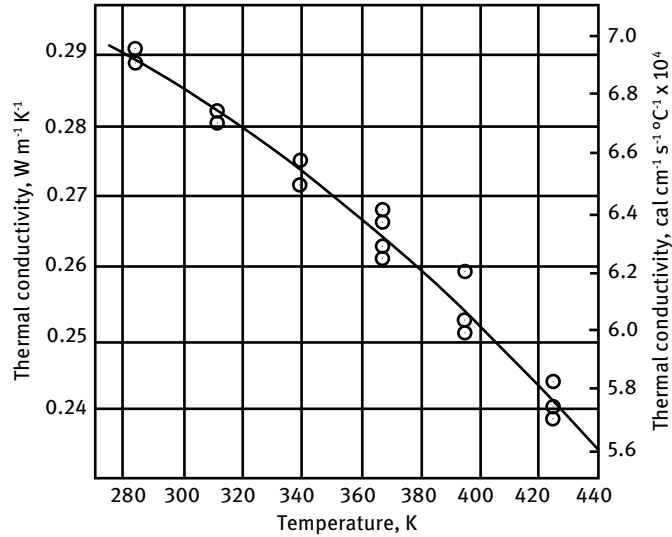


Figure 43: Thermal conductivity of Ae-50. (Reproduced and modified from [95])

Table 26: Heat flux for surface nucleate boiling of Ae-50 at the upper limit.

| Propellant                    | Pressure |      | Bulk temperature |     | Velocity |      | (q/A) <sub>ul</sub>                   |                   |
|-------------------------------|----------|------|------------------|-----|----------|------|---------------------------------------|-------------------|
|                               | Mpa      | psia | K                | °F  | m/s      | ft/s | BTU in. <sup>-2</sup> s <sup>-1</sup> | W/cm <sup>2</sup> |
| Ae-50                         | 4.128    | 600  | 339              | 150 | 9.12     | 30   | 7.8                                   | 1275              |
| Ae-50                         | 4.128    | 600  | 339              | 150 | 27.36    | 90   | 15.9                                  | 2598              |
| For comparison:               |          |      |                  |     |          |      |                                       |                   |
| N <sub>2</sub> H <sub>4</sub> | 4.128    | 600  | 339              | 150 | 9.12     | 30   | 12.2                                  | 1994              |
| N <sub>2</sub> H <sub>4</sub> | 4.128    | 600  | 339              | 150 | 18.24    | 60   | 16                                    | 2165              |
| N <sub>2</sub> H <sub>4</sub> | 4.128    | 600  | 339              | 150 | 27.36    | 90   | 22                                    | 3595              |
| NH <sub>3</sub>               | 3.440    | 500  | 333              | 140 | 9.12     | 30   | 5.3                                   | 866               |
| NH <sub>3</sub>               | 3.440    | 500  | 333              | 140 | 18.24    | 60   | 7.9                                   | 1291              |

Data source: [915,916].

pressure, 9.1–27 m/s fluid velocity, and 311–366 K liquid bulk temperature. The other mix was investigated only over a narrower range from 3.78 to 6.19 MPa and at two bulk temperatures, 333 and 366 K. Testing was done in an electrically heated CRES-347 tube with 6.3 mm outer diameter and 0.22-mm walls. The heated section was 75 mm long. The transition from nucleate to film boiling manifested itself experimentally by a sudden large increase of tube-wall temperature. In most cases, the temperature rise resulted in the loss of tube-wall strength, and the test section would rupture before

heater power could be turned off. The  $q_{ul}$  of the 50:50 mix was typically 65% of that previously determined for pure hydrazine at similar conditions. The  $q_{ul}$  ranged from 229 to 638 cal cm<sup>-2</sup> s<sup>-1</sup> (5.85 to 16.33 BTU in.<sup>-2</sup> s<sup>-1</sup>). The numerical data can be approximated using the equation

$$q_{ul} = 7.86 - 4.93 \times 10^{-3}(p - 1100) + 0.1343(V - 50) - 1.20 \times 10^{-2}(T_L - 160)$$

where  $q_{ul}$  is the upper limit of nucleate boiling in BTU in.<sup>-2</sup> s<sup>-1</sup>,  $p$  the static fluid pressure in psia,  $V$  the fluid velocity in ft/s, and  $T_L$  is the bulk temperature in °F. Ninety-five percent of the test data were within  $\pm 15\%$  of the  $q_{ul}$  dependence calculated using this equation. The mixture containing 77% hydrazine and 23% UDMH had upper limits at 77% of those of hydrazine. Demonstrated upper-limit heat fluxes ranged from  $1.31 \times 10^7$  to  $3.06 \times 10^7$  W/m<sup>2</sup> ( $312\text{--}732$  cal cm<sup>-2</sup> s<sup>-1</sup> =  $8\text{--}18.7$  BTU in.<sup>-2</sup> s<sup>-1</sup>) (see also [918, 919]).

### 3.1.10 Pressurant Gas Solubility in Aerozine-50

Solubility of pressurant gases in Ae-50 in comparison to other hydrazines was already detailed in Table 9.

An analysis of dissolved gases using mass spectrometer resulted in another set of gas solubility data. Helium solubility in Ae-50 can be calculated from a linear regression analysis of NASA data [920]

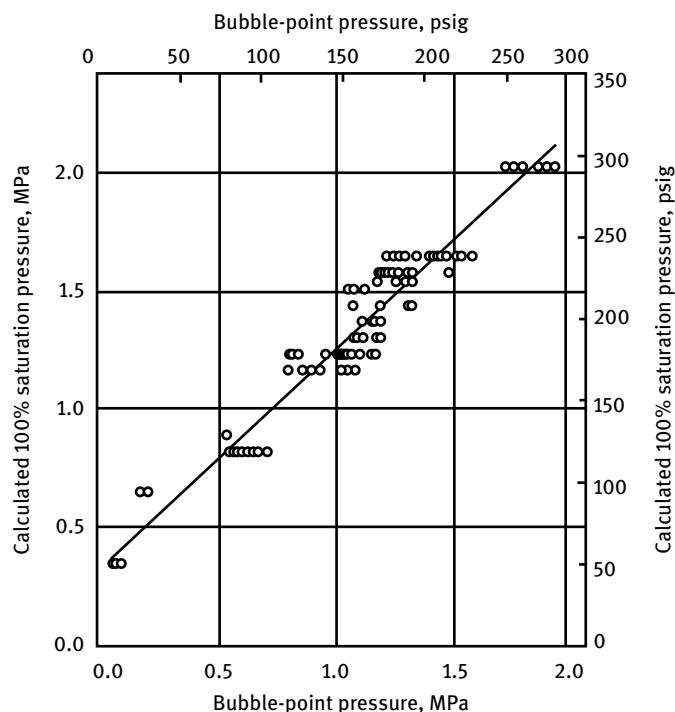
$$\alpha = -0.0257 + 2.75 \times 10^{-4}p + 8.69 \times 10^{-4}t$$

where  $\alpha$  is the solubility in cm<sup>3</sup> He STP/g Ae-50,  $p$  is the pressure in psig, and  $t$  is the temperature in °F. Converting to SI units would result in the following equation:

$$\alpha = -0.0257 + 3.997 \times 10^{-5}P + 8.69 \times 10^{-4}[(T - 273.15)1.8 + 32]$$

where  $\alpha$  is the solubility in cm<sup>3</sup> He STP/g Ae-50,  $P$  is the pressure in kPa, and  $T$  is the temperature in K. Figure 44 is a plot of Ae-50 bubble-point pressure as a function of 100% helium saturation pressure. However, Figure 44 does not show separate plots for different Ae-50 temperatures. Because the total gas content of the Ae-50 is very low, the apparent effect of temperature on the Aerozine-50 is not as pronounced as the apparent effect of temperature on the N<sub>2</sub>O<sub>4</sub>. Since the temperature effect on the Aerozine-50 bubble point was smaller than the variations encountered when Ae-50 bubble-point readings were repeated, the variations due to the temperature effect could not be accurately determined. The average error for all the Aerozine-50 bubble-point pressure data is  $\pm 6.3\%$ .

Nitrogen gas solubility in Ae-50 measurements was conducted on this hydrazine-UDMH fuel blend (composition 50.9 mass-% N<sub>2</sub>H<sub>4</sub>, 48.6 mass-% UDMH, 0.3 mass-% H<sub>2</sub>O, and 0.2% other soluble impurities) over the temperature range of 300 to 331 K (80.6 to 136.0 °F = 27.0 to 57.8 °C) [911]. The raw and reduced data are listed in Table 27.



**Figure 44:** Ae-50 bubble-point pressure as a function of calculated 100% helium saturation pressure. (Reproduced and modified from [920].)

**Table 27:** Gas solubility of nitrogen in Ae-50.

| Temperature |      | Nitrogen partial pressure |      | Experimental specific gas solubility         | Calculated specific gas solubility           |                                              |
|-------------|------|---------------------------|------|----------------------------------------------|----------------------------------------------|----------------------------------------------|
| °F          | °C   | psia                      | atm  | cm <sup>3</sup> N <sub>2</sub> (STP)/g Ae-50 | cm <sup>3</sup> N <sub>2</sub> (STP)/g Ae-50 | 10 <sup>-4</sup> lb N <sub>2</sub> /lb Ae-50 |
| 80.6        | 27.0 | 284                       | 19.3 | 0.551                                        | 0.552                                        | 6.9                                          |
| 82.0        | 27.8 | 585                       | 39.8 | 1.042                                        | 1.032                                        | 12.9                                         |
| 83.1        | 28.4 | 983                       | 66.9 | 1.609                                        | 1.607                                        | 20.1                                         |
| 95.4        | 35.2 | 286                       | 19.5 | 0.612                                        | 0.616                                        | 7.7                                          |
| 95.0        | 35.0 | 586                       | 39.9 | 1.122                                        | 1.132                                        | 14.1                                         |
| 95.0        | 35.0 | 986                       | 67.1 | 1.753                                        | 1.754                                        | 21.9                                         |
| 113.2       | 45.1 | 237                       | 16.1 | 0.589                                        | 0.587                                        | 7.3                                          |
| 113.4       | 45.2 | 483                       | 32.9 | 1.083                                        | 1.077                                        | 13.5                                         |
| 113.5       | 45.3 | 741                       | 50.4 | 1.550                                        | 1.554                                        | 19.4                                         |
| 113.5       | 45.3 | 989                       | 67.3 | 1.977                                        | 1.981                                        | 24.8                                         |
| 135.7       | 57.6 | 279                       | 19.0 | 0.765                                        | 0.765                                        | 9.6                                          |
| 136.0       | 57.8 | 578                       | 39.3 | 1.425                                        | 1.426                                        | 17.8                                         |
| 136.0       | 57.8 | 975                       | 66.3 | 2.230                                        | 2.225                                        | 27.8                                         |

Data source: [911].



From these data, the following correlation was developed for the gas solubility as a function of temperature and nitrogen partial pressure:

$$\alpha = 1.0264 \times 10^{-3} p + 1.7413 \times 10^{-5} t p + 4.464 \times 10^{-3} p^{1/2} + 1.416 t p^{1/2} - 1.594 p^2$$

where  $\alpha$  is the solubility in  $\text{cm}^3 \text{ n}_2/\text{g Ae-50}$ ,  $t$  is the temperature in  $^\circ\text{C}$ , and  $p$  is the pressure in psia. It has also been attempted to derive gas solubility for binary mixtures of hydrazine and UDMH from statistical thermodynamic considerations [921].

The rate of solution of a gas in a liquid is highly dependent upon the extent of agitation and mixing. Gas diffusion through an immobile liquid can take months to equilibrate. The rate of helium absorption into static Ae-50 can be predicted [922].

### 3.1.11 Thermodynamic Properties of UDMH/ $\text{N}_2\text{H}_4$ Mixtures

Next to hydrazine hydrate, the most widely used hydrazine mixture was (for a long period) the 1:1 mixture of hydrazine with UDMH. The thermodynamic properties of this fuel have been thoroughly investigated as a potential fuel in rocket propellant combinations [104, 108, 150]. The heat capacity of this mixture can be calculated from

$$\begin{aligned} c_p(\text{cal g}^{-1} \text{K}^{-1}) &= 0.51241 + 7.3624 \times 10^{-4} T \\ c_p(\text{J g}^{-1} \text{K}^{-1}) &= 2.14392 + 3.0804 \times 10^{-3} T, \quad T \text{ in K.} \end{aligned}$$

The heat of mixing the equal weight proportions of hydrazine and UDMH at 298 K has been estimated to be  $-15.69 \text{ J/g} = -3.75 \text{ cal/g}$ . This amount must be deducted from the theoretical enthalpy of formation of Aerozine-50 before the number can be used for accurate rocket performance calculations. The heat of mixing as a function of the mol fraction and temperature has been derived from sets of data obtained by two different laboratories using a batch adiabatic calorimeter method, as summarized in Table 28 [923]. The experimental values can be expressed by a polynomial curve fit

$$H = x(1-x)(1288.7 + 3.01 T) + 1966.6 x^2(1-x) - 1297.0 x^3(1-x)$$

where  $H$  is the heat of mixing in  $\text{J/mol}$ ,  $x$  is the mol fraction of hydrazine, and  $T$  is the temperature in kelvin. As shown in the last two rows of Table 28, the polynomial equation represents the experimental values reasonably well. Similar data are available for 308 and 323 K, and can be approximated by the equation

$$H = x(1-x)[2800 + 3(T - 273.15) - 400(1-2x)]$$

where  $H$  is the heat of mixing in  $\text{J/mol}$ ,  $x$  is the mol fraction of hydrazine, and  $T$  is the temperature in kelvin. The heat of mixing of UDMH and hydrazine hydrate, as in UH-25, is  $-206.6 \text{ J/mol}$  for an HH100 mol fraction of 0.2933 [924].

**Table 28:** Enthalpy of mixing of UDMH with hydrazine – measured versus curve-fitted smoothed values.

|                                   | Mol fraction N <sub>2</sub> H <sub>4</sub> |       |       |       |       |       |       |       |       |
|-----------------------------------|--------------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
|                                   | 0.1                                        | 0.2   | 0.3   | 0.4   | 0.5   | 0.6   | 0.7   | 0.8   | 0.9   |
| Temperature, K                    | Enthalpy of mixing, J/mol                  |       |       |       |       |       |       |       |       |
| <i>Measured data</i>              |                                            |       |       |       |       |       |       |       |       |
| 273.15                            | 205.0                                      | 393.3 | 543.9 | 644.3 | 694.5 | 677.8 | 598.3 | 456.1 | 255.2 |
| 293.15                            | 213.4                                      | 405.8 | 560.7 | 665.3 | 711.3 | 694.5 | 615.0 | 468.6 | 263.6 |
| <i>Curve-fitted smoothed data</i> |                                            |       |       |       |       |       |       |       |       |
| 273.15                            | 206.5                                      | 392.4 | 542.7 | 645.6 | 692.5 | 677.7 | 598.9 | 456.6 | 254.7 |
| 293.15                            | 211.9                                      | 402.0 | 555.3 | 660.0 | 707.5 | 692.2 | 611.5 | 466.3 | 260.1 |

Data source: [150, 923, 925].

### 3.1.12 Optical Properties of UDMH/N<sub>2</sub>H<sub>4</sub> Mixtures

The index of refraction of binary hydrazine mixtures can be used as a method of quick quantitative analysis. A calibration curve must be prepared first. A refractometric method of analysis of binary hydrazine-water or hydrazine/UDMH mixtures has been described by Pannetier and Mignotte [151, 926]. Data were measured at two temperatures, 293.15 and 298.15 K, over the entire range of compositions. Only the 298.15 K data has been reproduced here (Figure 45).

The refractive index of N<sub>2</sub>H<sub>4</sub>/UDMH mixtures as a function of composition can be expressed by the following equation:

$$n_D^{20^\circ\text{C}} = 1.4683 - 0.09806X + 0.04685X^2 - 0.0119X^3$$

where  $X$  is the mol fraction UDMH.

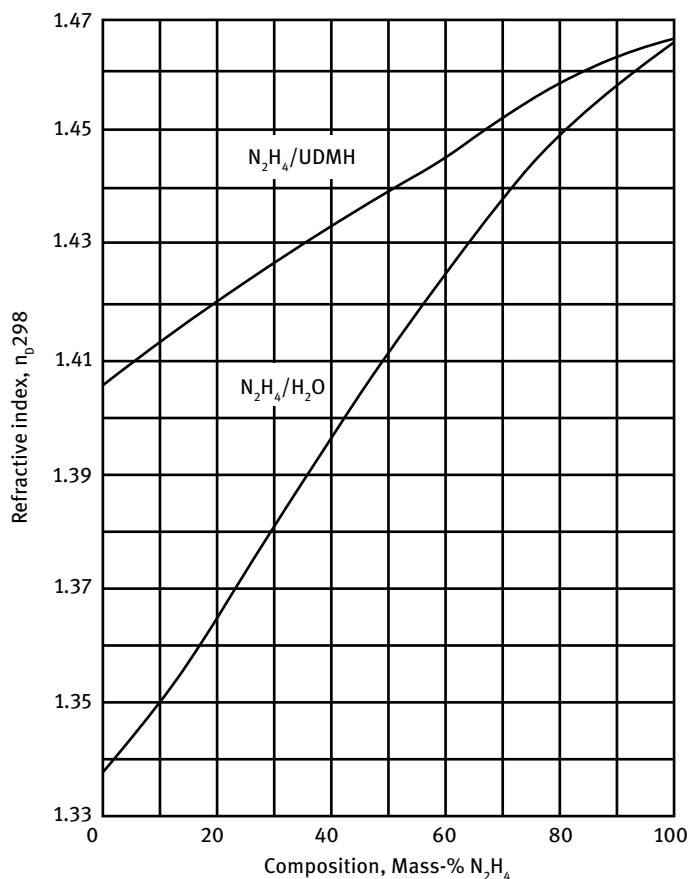
## 3.2 Chemistry of UDMH/N<sub>2</sub>H<sub>4</sub> Mixtures

### 3.2.1 Storage Stability of Aerozine-50

Missiles fueled with Ae-50 were designed to remain in service in silos for several decades. It was not planned to exchange propellants periodically. The fuel had to be able to remain in storage without degradation of performance for a long period [927].

### 3.2.2 Radiolysis of UDMH/N<sub>2</sub>H<sub>4</sub> Mixtures

Radiation effects on UDMH and N<sub>2</sub>H<sub>4</sub> mixture propellants were studied by exposing the propellant to integrated gamma ray doses of  $10^7 r$  and  $10^{15} n_f vt = 5 \times 10^{15} n/cm^2$  total integrated flux of fast neutrons [928]. The most significant radiation effect was the formation of a small amount of off-gas from the UDMH/N<sub>2</sub>H<sub>4</sub> fuel mixture that appeared



**Figure 45:** Refractive index of hydrazine mixtures at 298 K. (Reprinted and modified from [151].)

to be a linear function of the total radiation dose. The oxidizer  $N_2O_4$ , which was tested in the same way, was not affected by the radiation.

### 3.2.3 Specifications for UDMH/ $N_2H_4$ Mixtures

The specification requirements for the 50-50 mixture of UDMH and hydrazine per MIL-PRF-27402D are listed in Table 29. The older MIL-STD-1775, *Military Standard, Propellant, Hydrazine-Uns-Dimethylhydrazine 50-50 Blend* (4 Jun 1982) is no longer in effect.

### 3.2.4 Analysis of UDMH/ $N_2H_4$ Mixtures

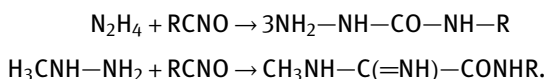
#### 3.2.4.1 Titrimetric Analysis in Non-Aqueous Solutions

In previous papers [396, 399, 929], Malone presented non-aqueous methods for the determination of  $N_2H_4$  in admixtures with UDMH and secondary amines. These meth-

**Table 29:** Specification requirements for the 50-50 mixture of UDMH and hydrazine per MIL-PRF-27402D.

| Properties                                      | Limits           |
|-------------------------------------------------|------------------|
| Hydrazine (% by weight)                         | 51 ± 0.8 minimum |
| UDMH (% by weight)                              | 47 minimum       |
| Water (% by weight)                             | 1.8 maximum      |
| Total hydrazine, UDMH, and amines (% by weight) | 98.2 minimum     |
| Particulate (mg/L)                              | 10 maximum       |

ods were based on the acid-base titration of the UDMH and amines, using perchloric acid as titrant, after the N<sub>2</sub>H<sub>4</sub> had been rendered neutral with either salicylaldehyde or acetic anhydride [402]. This was a rapid chemical method based on the differential reaction rate method of UDMH/hydrazine (N<sub>2</sub>H<sub>4</sub>), or of MMH/N<sub>2</sub>H<sub>4</sub> with either phenyl isocyanate or naphthyl isocyanate. In alcoholic solution, with ethanolic hydrochloric acid as titrant, N<sub>2</sub>H<sub>4</sub>, MMH, and UDMH all react with isocyanates at about the same rate to form semicarbazides. In anhydrous acetic acid, however, N<sub>2</sub>H<sub>4</sub> and MMH react rapidly (MMH slightly slower than N<sub>2</sub>H<sub>4</sub>) with isocyanates, but UDMH does not react appreciably in less than 2h at room temperature. In an acid medium, phenyl and naphthyl isocyanate react with N<sub>2</sub>H<sub>4</sub>, MMH, and UDMH to form semicarbazide



Under the conditions of the experiment, only the N<sub>2</sub>H<sub>4</sub> and MMH react completely. The UDMH reaction rate is very slow.

Mixed hydrazine or UDMH fuels can be analyzed using GC or conductometric methods in the field [930]. Other field test methods were developed for the determination of N<sub>2</sub>H<sub>4</sub>, UDMH, water, and particulate matter in Ae-50, for the determination of water and particulates in nitrogen tetroxide oxidizers and for NO in 90/10 N<sub>2</sub>O<sub>4</sub>/N<sub>2</sub>O<sub>3</sub> oxidizer.

#### 3.2.4.2 Gas Chromatographic Analysis Methods for UDMH/N<sub>2</sub>H<sub>4</sub> Mixtures

Polyethylene glycol (PEG) 400, 600, and 1000 and a nonylphenol-glycidol ether adduct (NPG-10) on Column Pak T or Anakrom AB were tested as column packing for the separation of Ae-50 constituents and ammonia, water, and DMA contaminants [931]. Thirty percent of PEG-400 on Column Pak T formed more symmetrical and better-resolved peaks than NPG-10. The method recommended in an early MIL SPEC for analysis of hydrazine-UDMH mixtures at one time used a 6-mm × 1-m column packed with 33% PEG (Carbowax 400) on 90–100-mesh AnaKrom B [932].

The most recent revision of this spec now recommends a 60-m × 0.53mm, 1.00μm film thickness Agilent DB-Wax capillary column, a thermal conductivity

detector (TCD) with a split injector, and a glass wool packed split liner [933]. Response factors ("normalization factors") must be determined first by analyzing a mixture of known composition. The retention volumes of hydrazine, MMH, UDMH, SDMH, trimethylhydrazine, and 1-aminoaziridine on PEG-20000 are proportional to the base constant  $pK_a$  of these compounds [934].

A field test method was developed for determining the water content of Titan-II propellants [446]. The salicylaldehyde acidimetric titration method of Malone and Barron [399] for the analysis of mixtures of hydrazine and UDMH was found to be unsatisfactory for some purposes. Although a modification of this method gave better reproducibility, the fact that the overall determination was based on the total amine content led to the need to develop a more accurate and specific method. A gas chromatographic method gave separate numbers for ammonia,  $N_2H_4$ , UDMH, and an unidentified compound (probably methylamine or DMA) [935].

If the GC inlet is made from incompatible or catalytic metals and operated while too hot, the UDMH/hydrazine sample may decompose before it has a chance to be separated in the column and be sensed by the detector at the outlet of the column [936]. The GC method that was later adopted for the MIL SPEC was developed in a laboratory at the Olin Mathieson Chem Corp [931].

### 3.2.4.3 Analysis of UDMH Mixtures with Other Organic Fuels

Mixtures of UDMH, DETA, and water (0.15–9%  $H_2O$ ) were analyzed using a 6.35-mm  $\times$  3.65-m ( $1/4$ -in.  $\times$  12-ft.) column packed with 30% tetrahydroxyethylethylenediamine on 30–60-mesh Chromosorb W. They were also reviewed in comparison to results of a near-IR spectrometric method [408]. Synthetic mixtures with known amounts of water and *n*-butanol as an internal standard were run first to determine the response factor for water. This mixture is similar to Hydyne except that it did not contain any acetonitrile.

SDMH is much more toxic than UDMH and is an unwanted contamination in UDMH. SDMH is formed as a by-product, especially if UDMH is made by the direct alkylation of hydrazine. Alkalizing the support prior to applying the stationary phase resulted in the improved separation of alkylhydrazine mixtures [364, 937]. When the Celite C22 support was treated with KOH in methanol prior to applying Carbowax-400 in chloroform, the column filled with this material provided perfect separation of UDMH and SDMH. A similar column packing coated with KOH after the application of the Carbowax was ineffective for SDMH/UDMH separation but separated UDMH and tetramethyltetrazene (TMTZ). The alkalized column was also capable of separating SDMH, UDMH, TMTZ and NDMA. Three different stationary phases (solid paraffin wax, Silicone oil 702, and Carbowax 400) on alkalized Chromosorb *P* were evaluated for the separation of hydrazine, MMH, ethylhydrazine, propylhydrazine, UDMH, trimethylhydrazine, and tetramethylhydrazine [938]. GC separation of a homologue series of monoalkyl-hydrazines was better on paraffin or silicone oil, but separation of hydrazines with increasing degree of methylation was more effective on carbowax,

which is a more polar stationary phase. This series of tests, comparing GLC retention times to boiling points of hydrazines with various degrees of substitution, very nicely illustrate the effects of affinity between the hydrazines and the stationary phases on retention volumina and separation efficiency.

GC separation of all three propellant hydrazines and aniline (a frequent contaminant carried over in the dehydration process) is possible by using wide-bore (0.53-mm) glass capillary columns coated with cross-linked Carbowax 20M [939]. Wide-bore columns allow separations in typically half the time required for packed columns. They have better sample-size capabilities than capillary columns, which are less than 0.35 mm in diameter. Reliable separation of all four compounds, including in the presence of water and ammonia as contaminants, was achieved by splitless injection, temperature programming from 313 to 403 K at a rate of 10 K/min, with helium carrier gas. A flame ionization detector was used for the trace carbonaceous contaminants in hydrazine, which were detectable down to 10 ppm. Aniline in hydrazine cannot be analyzed very well with packed columns using Amine 220 as described in an older MIL SPEC. On the wide-bore column with cross-linked Carbowax 20M, aniline eluted within 12 minutes, and the peaks were even, very symmetrical, and easy to integrate at levels down to 10 ppm aniline. Polyimide coatings on capillary columns are usually very temperature resistant in the absence of hydrazine. However, the liner in the injection port was destroyed after several hundred injections in contact with hydrazine vapors and had to be removed.

#### 3.2.4.4 Analysis of UDMH in Wastewater and Ground Water

Mixtures of ammonia, hydrazine, UDMH, and DMA such as those typically encountered in the effluents from a Raschig process UDMH production facility can be separated on a 1-m column packed with 30% Carbowax-400 on 90/100 mesh Anakrom B support, even in the presence of water [940]. Complete separation could only be achieved by two separate injections at 333 and 398 K column temperature and isothermal operation. The constituents of the mixture eluted in the sequence ammonia, DMA, UDMH, water, MMH, hydrazine. Higher percentages of water (>90%) caused erratic results.

Hydrazine and UDMH in the wastewater from a propellant manufacturing plant can be analyzed in a packed column with Chromosorb-103 and -101 with a detection limit of 10 ng and a relative error of  $\pm 4.9\%$  [941]. Furaldehyde derivatization improved sensitivity and selectivity and allowed the analysis of traces of hydrazine and UDMH (but not MMH) contamination in ground water [360].

Some ground waters react with hydrazines. It is important to test spike recoveries with actual water samples in addition to making standards with clean, deoxygenated, distilled, or deionized water. Sulfuric acid extracts of contaminated soil were reacted with pentanedione and the derivatives so formed were analyzed by GC [942].

Quantitative analysis of trace concentrations of UDMH transformation products in water requires very sensitive analytical instrumentation and tedious sample prepara-

tion. A simple and automated method for the sensitive quantification of UDMH transformation products in water was developed using headspace SPME in combination with GC-MS and GC-MS/MS [461]. This method is based on the extraction of analytes from the gas phase above samples using SPME and applying a micro-polymer coating followed by a thermal desorption of analytes in a GC inlet. Extraction by 85  $\mu\text{m}$  Carboxen/polydimethylsiloxane fiber at 323 K (50 °C) over 60 minutes provided the best combination of sensitivity and precision. Detection limits of 12 analytes using GC-MS/MS with chemical ionization were about 10 ng/L. This method is simpler, automated, provides lower detection limits, and covers more UDMH transformation products compared to other methods. The method was recommended for assessing the water quality in areas affected by rocket launch activities.

Internal standard and standard addition calibrations were used to achieve good accuracy of the quantification of key environmental degradation and transition products of UDMH [943]. 1-Trideuteromethyl-1*D*-1,2,4-triazole (MTA-*d*3) was used as the internal standard. Internal standard calibration facilitated the control of the matrix effects during the quantification of MTA, *N,N*-dimethylformamide (DMF), and NDMA in soils with humus content <1%. Using SPME at 333 K (60 °C) for 15 minutes with 65- $\mu\text{m}$  Carboxen/polydimethylsiloxane fibers, recoveries of MTA, DMF, and NDMA for sandy and loamy soil samples were 91–117, 85–123, and 64–132%, respectively. The method accuracy could be improved, and a wider range of analytes could be detected by a combination of standard addition and internal standard calibration. The combined calibration approach provided the best accuracies for NDMA, DMF, *N*-methylformamide, formamide, 1*H*-pyrazole, 3-methyl-1*H*-pyrazole, and 1*H*-pyrazole. For the determination of 1-formyl-2,2-dimethylhydrazine, 3,5-dimethylpyrazole, 2-ethyl-1*H*-imidazole, 1*H*-imidazole, 1*H*-1,2,4-triazole, pyrazines, and pyridines, the standard addition calibration method was more suitable.

### 3.3 Handling of Aerozine-50

Several handbooks describe safe handling practices for Ae-50. Most of those handbooks were developed for the TITAN-II missile program [96–98, 944, 945]. This is now only of historical interest.

#### 3.3.1 Transportation of Aerozine-50

During the period when Titan-II missiles were deployed, and for a short while after they were decommissioned, NTO and Ae-50 had to be transported by tanker truck across the US. Similarly, when TITAN-III and TITAN-IV were used to launch satellites, the propellants had to be delivered to Cape Canaveral AFS and Vandenberg AFB. The tanker trucks were accompanied by hazardous materials response teams. All these propellant movements were achieved without any serious accidents or spills. Nev-

ertheless, in order to be prepared for all eventualities, the agencies responsible for the safe transport of hazardous propellants prepared training material, driver certification regulations, and response guidelines for “what if” scenarios. This included the development of a computerized emergency response protocol system for releases of hypergolic propellants, modeling atmospheric dispersion in a computerized hazard response protocol system, and a transportation accident response co-ordination guide.

### 3.3.2 Aerozine-50 Spill Treatment

The rate of evaporation of Ae-50 from shallow pools divided by the pool radius is a linear function of the wind speed [703]. Ammonium carbonate (carbamate) was tested as a spill control to reduce the fire hazard. Although ammonia is evolved, ammonia is less of a fire hazard than UDMH vapor. An aqueous acetate-acetic acid buffer solution with a gelling agent was tested as a spill control and fire extinguishing agent against small spills or fires of Ae-50 and/or dinitrogen tetroxide [946].

A vapor cloud caused by either vaporization or reaction of hydrazine and/or UDMH with NTO, as it was used on the Apollo spacecraft, was analyzed to determine the generation and concentration of toxic products and the safe toxic distances in the case of a spill [947]. It was predicted that the process of vaporization of propellant without reaction creates the largest quantity of toxic products. Assuming that the total quantity of fuel or oxidizer aboard the Apollo spacecraft would be spilled in sand and vaporized during unfavorable atmospheric conditions, it would have resulted in a maximum safe toxic distance of 5.5 km (3.4 miles). This safe toxic distance was considered to be the worst case as the cooling effect of vaporization tends to reduce the actual rate of vaporization. The reaction of hydrazine/UDMH mixtures with NTO will produce a smaller quantity of toxic products, thus reducing the toxicity hazard. When formed and above ambient temperature, these hot products will rise and expand, thus creating a faster rate of product dilution (see also [948–952]).

### 3.3.3 Firefighting of Aerozine-50 Fires

The recommended methods for firefighting of Ae-50 fires are similar to those practiced for the extinguishment of UDMH fires [200, 207, 698, 700, 701]. Halon 1301 (Freon 13B1), carbon dioxide, and water were tested as fire extinguishing agents on Ae-50 or MMH fires. The effectiveness of a Halon 1301 system for inerting the atmosphere of an Apollo spacecraft was tested. The conclusion was that Halon 1301 could provide some protection as an inerting agent for spills of Ae-50, and that it could serve well to extinguish secondary fires of many flight vehicle combustibles. However, it was ineffective in combatting an established fire of Ae-50 and led to toxic combustion products and to visibility-limiting smoke [205, 703]. Two parts by weight of water per part of Ae-50 will inert an Ae-50 spill against ignition in air. In a burning Ae-50 pool, the fuel evaporation rate is approximately  $49 \text{ g s}^{-1} \text{ m}^{-2}$  ( $0.6 \text{ lb min}^{-1} \text{ ft}^{-2}$ ). A well-dispersed flow of water at



$100 \text{ g s}^{-1} \text{ m}^{-2}$  is sufficient for extinguishing a fire. A ten-fold excess of water (10 kg water per kilogram of fuel) is required to inert an Ae-50 spill against hypergolic ignition with NTO. Bromotrifluoromethane (Halon 1301) can be used to inert vapor spaces or to extinguish small fires, however, very high  $\text{BrCF}_3$  concentrations are required (>7% by volume) and the protection is not long-lasting (see also [203, 206, 698, 702]) for open-pan burning tests with UDMH in comparison to fires with other more common hydrocarbon fuels. Foams for firefighting and spill control must be compatible with a wide range of propellants [11].

Although carbon dioxide is ordinarily considered a good fire extinguishant and an inert vapor, it formed a solid when it came into contact with Ae-50 or UDMH. It formed syrupy liquids when it came into contact with hydrazine or MMH. Heat was evolved in each case.

### 3.4 Materials Compatibility with UDMH/ $\text{N}_2\text{H}_4$ Mixtures

In view of the widespread use of Ae-50 during the Titan, DELTA second stage, and Apollo programs, there exists a substantial amount of information on materials compatibility with this propellant [953]. It would require a sizable database to collect all this information and present it in a usable format. The same would also be useful for other UDMH-based propellant blends. Unfortunately, this was not possible during the preparation of this book.

#### 3.4.1 Aerozine-50 Compatibility with Metals

It would be difficult to extrapolate from known materials compatibility information for hydrazine  $\text{N}_2\text{H}_4$  and UDMH to the materials compatibility with Ae-50. In most cases where reliable information was required to make well-informed decisions about the long-term storage of missiles in missile silos, the materials compatibility had to be determined with the actual propellant blend and under conditions at the upper-temperature limit of the operating conditions.

In looking for materials for advanced spacecraft valves, several hundred literature references on 21 different propellants that were in use as of 1967, or were anticipated to be used within the next ten years (including Ae-50) were assembled. However, the reports on pages 1–28 through 1–33 lists only materials and temperatures for compatibility and not the duration of immersion [515]. Similar data were on pages 3–26 through 3–31 of [516].

It is not possible to list all references discussing the materials compatibility of Ae-50; therefore, just a few key references are listed here [900, 944, 954–956]. A hydrazine fuels materials compatibility database would be useful to organize this information in a user-friendly way.

### 3.4.1.1 Brazing Alloys for Aerozine-50

Hydrazine and Ae-50 decomposition caused by brazing alloys and their constituents were measured by capturing and analyzing the ammonia formed [957]. The compatibility of hydrazine or Ae-50 with either the 82Au-18Ni alloy or the pure metals (Au or Ni) was equally poor as soon as the temperature exceeded 430 K (156 °C = 314 °F). The amount of ammonia evolved was taken as the indication of hydrazine decomposition at 330 K. It would have been better to use the amount of nitrogen formed because some of the ammonia may remain dissolved in the propellant.

The heat exchanger used to heat helium with Ae-50 in the propulsion system of the Apollo Lunar Module was constructed of CRES-347 stainless-steel. The nickel-based alloy originally used in the fabrication of this unit was found to be unsuitable, and the gold-based alloys, Palniro 7 and Nioro, were selected as appropriate replacements from a structural standpoint. Palniro 7 and Nioro are trade names of braze alloys of the following composition:

Palniro 7    70% gold, 22% nickel, 8% palladium

Nioro        82% gold, 18% nickel

Exposure of gold-based brazing alloys to Ae-50 and to Ae-50 doped with 0.05% chloride or 0.5% ammonia at 339 K (150 °F) for 48 h did not result in leaching of excessive amounts of gold, nickel, or palladium. Neither gold nor palladium was present in detectable amounts in any of the fuel samples. Nickel was found in detectable amounts in all the fuel samples, including those not exposed to the alloys (blank controls).

Very little (unmeasurable) quantity of gas was evolved with Palniro 7 but a substantial amount of gas was evolved with Nioro [958]. The pressure rise in a manometric vessel was not excessive, even in samples that were deliberately contaminated with 0.5 mass-% chloride ion or 0.5% ammonia.

### 3.4.1.2 Stress-Corrosion Cracking in Aerozine-50

Stress-corrosion cracking has been observed in tanks intended to hold NTO or Ae-50. While NTO is an active contributor to stress-crack propagation, Ae-50 is not. Problems with stress corrosion in Ae-50 tanks were mostly caused by residual cleaning fluids (halogenated solvents) or residual methanol once used as an Ae-50 substitute during dynamic and acoustic testing of propulsion systems in space simulation chambers.

A more detailed investigation has shown that some metals are indeed susceptible to stress-corrosion crack growth in liquid hydrazines. Stainless-steel 410, used as a tankage material in the DELTA 89 vehicle, showed stress-corrosion susceptibility with Ae-50 that was most likely contaminated with carbazic acid by absorption of atmospheric carbon dioxide. However, in tests at the Aerospace Corporation, several high-strength steels, including T-1, HY-140, HP-9-4-20, and 18Ni(200) maraging steels that do stress-corrode in seawater did not show stress corrosion in (presumably pure) UDMH [518].

While pressure testing with methanol in 1966, two Apollo Spacecraft Propulsion System (SPS) fuel tanks failed, prompting the NASA Manned Spacecraft Center to initiate a study aimed at obtaining laboratory verification of the cause of the tank failures. The study included obtaining a quantitative evaluation of the expected performance of the other various Apollo tanks in their test and wetted service environments. As part of this study, NASA issued contracts to perform an investigation of the flaw growth characteristics of the Ti-6Al-4V tankage material [514]. Plane-strain cyclic and sustained load flaw growth characteristics were evaluated for Ti-6Al-4V forgings and weldment heat-affected zones (HAZ) at temperatures ranging from 291 to 316 K (65 to 110 °F) in Ae-50, MMH, and NTO inhibited with 0.49% NO, methanol, Freon MF, and distilled water (with and without sodium chromate additions). The basis for the evaluation was the determination of the threshold stress intensity values (the value below which sustained load flaw growth could not occur) in the various liquid environments. The results showed that sustained load threshold values (in terms of initial-to-critical stress intensity ratios) were relatively high, exceeding 75%, with the exception of three environments: methanol, Freon MF, and (at test temperatures exceeding 302 K [85 °F]), dinitrogen tetroxide. Little or no difference in sustained load behavior was observed between base metal and weld HAZ except in the environment of Freon MF. In this case, the flaw growth was significantly more pronounced in the HAZ than in the base metal. At stress intensity levels below the sustained load threshold value, cyclic load flaw growth rates were quite low and were not considered to be a serious problem. In the case of methanol, the base metal threshold value was 24% of the critical stress intensity. With regard to the failed Apollo SPS fuel tanks, this value indicated that initial flaws as small as about 0.003 in. deep could have grown and caused the failure to occur when exposed to methanol at maximum operating stress.

Despite the known stress-corrosion cracking problem with methanol, methanol has been recommended as flushing fluid for the decontamination of Apollo Service Module Ae-50 tanks (it is assumed that systems thus decontaminated were not expected to fly anymore because there may be residual methanol after flushing and drying) [959, 960].

### **3.4.2 Aerozine-50 Compatibility with Non-Metallic Materials**

There are numerous literature summaries on elastomeric materials compatibility with Ae-50 and other propellants [961]. These are needed for gaskets, O-rings, expulsion bladders, and personnel protection equipment.

Molded parts made from thermoplastic resins can be manufactured in the near-net-shape ultimate dimensions, which require no further machines, thus leading to cost savings. The trouble was that, until recently, very little was known about the compatibility of thermoplastic resins with rocket propellants because many of these materials became available only within the past two decades. Ten engineering ther-

moplastics were tested in anhydrous hydrazine for suitability in an Ae-50 application [962].

#### 3.4.2.1 Propellant Expulsion Diaphragms and Bladders for Aerozine-50

For a propellant expulsion bladder or diaphragm, it is important that the material is strong and flexible, remains flexible under conditions of propellant exposure and radiation exposure, has low permeability to propellant liquid, propellant vapors, and pressurant gases, and does not leach any contaminants into the propellant.

Bladders intended for Ae-50 were initially made of multiple sprayed layers of tetrafluoroethylene (TFE) and fluoroethylene propylene (FEP). TFE was manufactured like a sintered powder metallurgical part by compressing the powder. FEP was similar in character to a true thermoplastic material. The major problem was bladder tearing during 3-axis vibration, especially at the lower temperature range [963, 964].

In the early days of hydrazine flight system development, hydrazine stability in elastomer expulsion devices was measured only in weeks [965–967]. For instance, a butyl rubber expulsion bladder was used on the Ranger-3 spacecraft where storability was proven to be better than nine to thirteen weeks. Although EPR-5 demonstrated no measurable Ae-50 permeation, Butyl-7 allowed 0.7% of the propellant to escape after only 7 d. Among six candidate formulations based on *cis*-1,4-polybutadiene, Butyl-218, Hydropol, or ethylene-propylene rubber (EPR), the latter showed the lowest swelling (16%) after immersion in Ae-50 at 344 K (160 °F) for 30 d. In MMH, *cis*-1,4-polybutadiene swelled 10%, EPR swelled 18%, and butyl rubber swelled 26%.

#### 3.4.2.2 Lubricants for Aerozine-50 Service

Many seals and moving parts (pump bearings) must be lubricated to avoid fretting and reduce friction. Greases qualified for hydrazine and UDMH service can be used for Ae-50 as well.

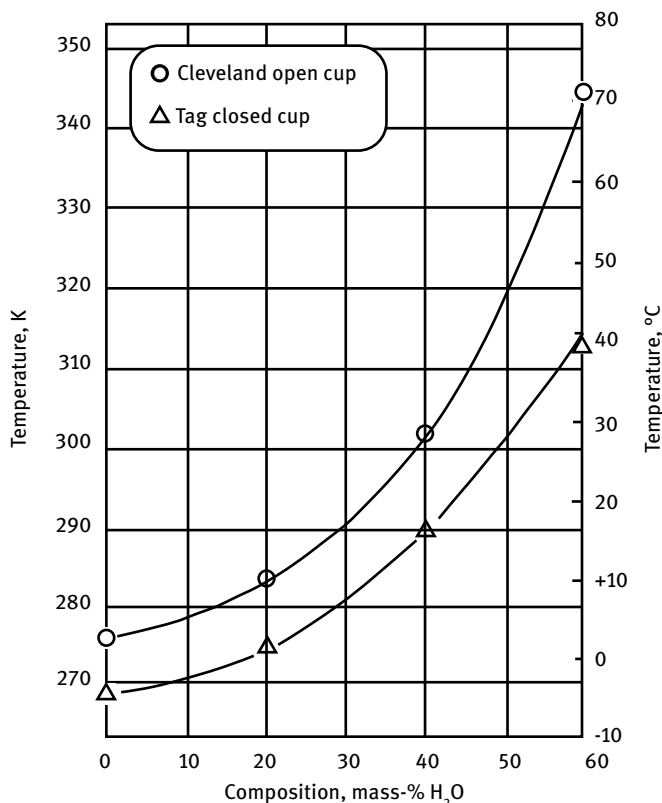
There was one incident of Ae-50 contamination by leaked hydraulic fluid that was similar to incidents that took place many years later in the hydrazine auxiliary power unit (APU) for Space Shuttle Space Transportation System (STS). In the earlier case, solid contaminants found deposited in the cavity between the fuel pump and the gear box of TITAN boosters were analyzed and identified to be composed primarily of aze-laic acid dihydrazide [968]. This product was shown to have resulted from the interaction of Ae-50 and the hydraulic fluid (MIL-L-7808D1 oil) from the gear box. Its structure was conclusively established by independent synthesis of an authentic sample (see also [969, 970]).

### 3.5 Safety Properties of Aerozine-50

#### 3.5.1 Flash Point of Aerozine-50 in Air

At 1 atm pressure, an Ae-50/water mixture must contain at least 37 mass-% water to produce non-flammable vapors in a Cleveland Open Cup apparatus at 298 K (25 °C), and 48 mass-% water in a Tag Closed Cup tester under the same conditions [703]. Unfortunately, heat is evolved when water is added to Ae-50 so that the liquid temperature increases above that of the surroundings. For this reason, more water is needed initially to produce a non-flammable mixture (because of the elevated liquid temperature). A 2:1 water dilution ratio (i.e., 2 kg of water per kg of Ae-50) was considered adequate to prevent the formation of a flammable mixture following an Ae-50 spill.

The flash point of Ae-50 in the air at atmospheric pressure is 276 K (+3 °C) with the Cleveland Open Cup method and 268 K (−5 °C) with the Tag Closed Cup method. The effect of water dilution on the flash point(s) of Ae-50 is shown in Figure 46. A similar



**Figure 46:** Flash points of Ae-50/water mixtures at atmospheric pressure. (Reproduced and modified from [703].)

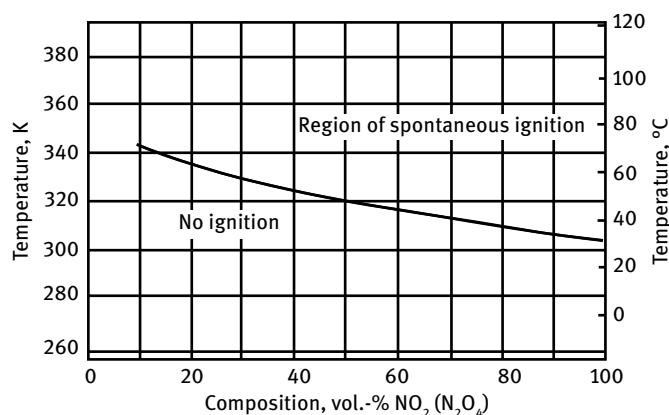
chart exists for MMH. For comparison, the Cleveland Open Cup flash point of undiluted UDMH is 257 K (−16 °C).

### 3.5.2 Flammability Limits of Aerozine-50 in Air

The flammability of Ae-50 in the air is mostly dictated by its UDMH component. The lower limit of flammability at 101 kPa and 311 K was observed at 3.0% by volume [971]. The upper limit of flammability at 101 kPa and 366.5 K was found at 98.5% by volume. The minimum ignition pressure was at 4 kPa with an Aerozine-50 concentration of 7.6% by volume (complete evaporation of both fuel components).

### 3.5.3 Auto-Ignition of Aerozine-50 Vapors

When Ae-50 vapors come in contact with N<sub>2</sub>O<sub>4</sub> (NO<sub>2</sub>) vapors in the air, they may ignite spontaneously. In Figure 47, the limits of ignition of Ae-50 vapors under those conditions are shown as a function of the NO<sub>2</sub> concentration in the air it comes in contact with.



**Figure 47:** Vapor-liquid equilibrium temperatures of 50-50 fuel blend required for the spontaneous ignition of the resulting vapors in contact with N<sub>2</sub>O<sub>4</sub>-air mixtures. (Reproduced and modified from [900].)

### 3.5.4 Accident History of Aerozine-50

#### 3.5.4.1 Aerozine-50 Exposure

A rocket test stand supervisor had detected an Ae-50 leak, initially escaped the hazard area to don an acid suit and a gas mask, but then returned to the area to check for other leaks [743, 744]. He later had a strong odor of Ae-50 still adhering to his clothes when he reported to the dispensary. He complained of headache, nausea, and a shaky feeling. His exhaled breath smelled strongly of hydrazines even 2h after the expo-

sure. He exhibited twitching of the extremities and clonic movements. Reflexes were hyperactive. After injecting 200 mg *i. v.* and  $2 \times 200$  mg intramuscularly (*i. m.*) pyridoxine•hydrochloride (PIN-HCl), all symptoms except chest congestion vanished within 20 minutes. He still developed bilateral pulmonary edema in the form of wet rales and tachypnea. Oxygen and isuprel inhalation were given to alleviate this problem. Another technician caught in the same leak event had inhaled excessive amounts of Ae-50 vapor before he was able to put on an air supply. He tried to return to the leak area to offer assistance but was overcome by dyspnea, trembling, and weakness. He developed hyperactive reflexes, high respiration rate, and bilateral pulmonary edema. He also was given 200 mg *i. v.* plus  $2 \times 200$  mg *i. m.* PIN-HCl. His dyspnea improved and his other symptoms abated. The use of acute therapeutic doses of PIN-HCl greatly improved the rate of recovery of the accident victims. Follow-up studies during the next days and weeks showed no permanent ill effects in either of the two patients. In another accident at the same test installation, four workers had to control an Ae-50 leak. Wearing acid suits and gas masks prevented them from suffering pulmonary edema but they still suffered severe nausea and vomiting, which possibly could have been prevented by the immediate use of pyridoxine. This drug was administered later *i. v.* at the onset of vomiting, and the vomiting stopped in 20 minutes.

### 3.5.4.2 Titan-II Missile in a Silo Explosion

The accident with the worst potential consequences was caused by a 9-lb wrench socket dropped accidentally into a missile silo while performing maintenance (to restore nitrogen pressure in the second stage oxidizer tank) in September 1980 near Damascus, Arkansas, where it fell several stories deep, puncturing the fuel tank of the first stage and causing Ae-50 to leak out under pressure [972]. The leaked propellant fumes eventually ignited and the missile exploded as soon as all four of the tanks in both stages were crushed. Oxidizer and fuel came in contact with each other, lifting the 740-ton heavy concrete lid off the silo and throwing it several hundred feet into the air. The nuclear warhead was thrown out as well and later recovered. Fortunately, it did not explode.

## 3.6 Environmental Impact of Aerozine-50

### 3.6.1 Flash Evaporation of Aerozine-50 in Vacuum

If an Ae-50 tank is suddenly vented or breached in a vacuum, the UDMH evaporates first, leaving a cloud of frozen hydrazine snow behind. If both Ae-50 and NTO are released at the same time, the two clouds may ignite as soon as they come in contact with each other and depending on the ambient pressure. To study the reactivity and expansion characteristics of Ae-50 and dinitrogen tetroxide released instantaneously in bulk quantities into low-pressure environments ranging from 0.00001 to 1 atm, experiments were performed in a large vacuum chamber by simultaneously breaking

thin-walled glass spheres, each containing 300 mL of Ae-50 or NTO [973]. Following the breakage of the spheres, high-speed motion pictures and pressure measurements by piezoelectric transducers showed that the liquids dispersed by boiling at the exposed surface, and the resulting cloud of vapor and drops expanded symmetrically. At ambient pressures of 0.1 atm and above, the hypergolically ignited combustion or mild explosion occurred approximately 5 ms after the release (the spheres were 0.5 in. apart). At ambient pressures below 0.01 atm, normal hypergolic ignition did not occur. Instead, a mist of an unknown compound formed and detonated 70 to 180 ms after the release. The detonation occurred when the pressure was a few mm Hg above the original ambient level and apparently was initiated by one of the warm metal surfaces of the steam-ejector pumping system.

### 3.7 Properties of UDMH/N<sub>2</sub>H<sub>5</sub>OH Mixtures

#### 3.7.1 Physical Properties of UDMH/N<sub>2</sub>H<sub>5</sub>OH Mixtures

##### 3.7.1.1 Ternary UDMH/Hydrazine/Water Mixtures

Ternary hydrazine mixtures are made up of constituents that are all liquids at ambient temperature. Such mixtures may occasionally be formed to obtain blends with properties not otherwise achievable with binary mixtures. The UDMH/N<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>O mixtures listed in Table 30 have been formulated to provide one oxygen for every carbon when these mixtures were used as monopropellants.

**Table 30:** Freezing points of ternary UDMH/water mixtures with hydrazine.

| Composition, mass-% |                               |                  | Freezing range, K |
|---------------------|-------------------------------|------------------|-------------------|
| UDMH                | N <sub>2</sub> H <sub>4</sub> | H <sub>2</sub> O |                   |
| 37.5                | 40.0                          | 22.5             | 227–218           |
| 26.8                | 57.1                          | 16.1             | 242               |
| 20.3                | 67.6                          | 12.1             | 252               |
| 17.9                | 71.4                          | 10.7             | 255               |

Data source: [974].

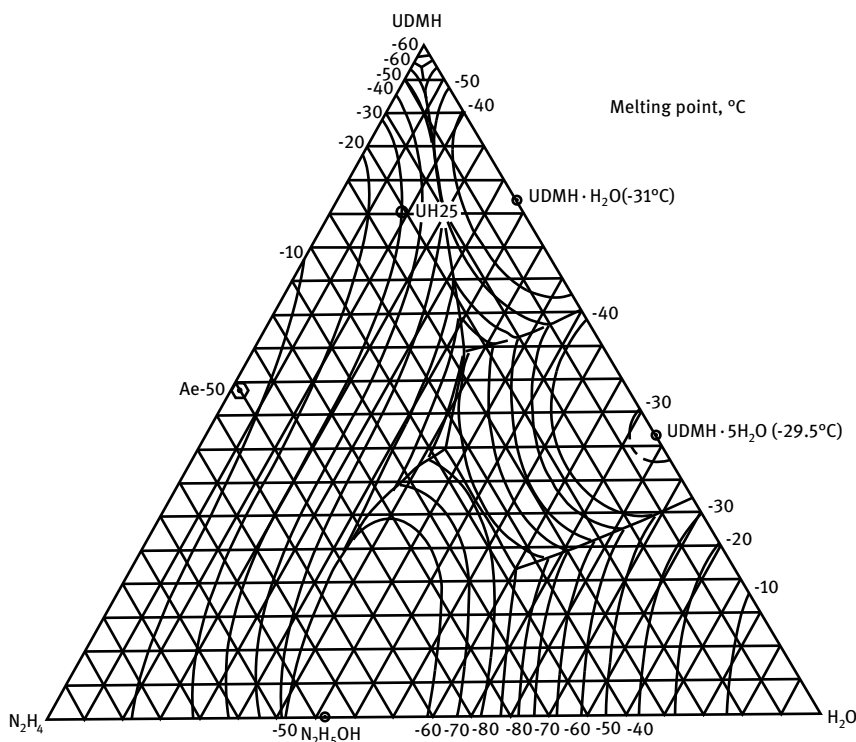
It was hoped that the preferential formation of carbon monoxide would avoid the formation of soot. At the lower temperatures, the mixtures exhibited extensive supercooling, and only a freezing range rather than a freezing point could be determined.

At one point, the European ARIANE-3/-4 rocket switched from pure UDMH as a rocket fuel to a mixture consisting of 75% UDMH and 25% hydrazine hydrate. This mixture is called UH-25 and freezes at 243 K (–30 °C). As of 2021, the Indian Geosynchronous Satellite Launch Vehicle (GSLV) and Polar Satellite Launch Vehicle (PSLV) still use UH-25.



### 3.7.1.2 Freezing/Melting Point of UDMH/ $\text{N}_2\text{H}_5\text{OH}$ Mixtures

The freezing/melting point isotherms in the ternary system of UDMH/hydrazine/water are illustrated in Figure 48. The lowest freezing points are encountered along a line connecting the composition of hydrazine hydrate (64%  $\text{N}_2\text{H}_4$ ) with the UDMH corner on top of the triangle.



**Figure 48:** Melting point isotherms in the ternary system of UDMH/hydrazine/water. (Reproduced and modified from [95].)

### 3.7.1.3 Density of UDMH/ $\text{N}_2\text{H}_4$ / $\text{H}_2\text{O}$ Mixtures

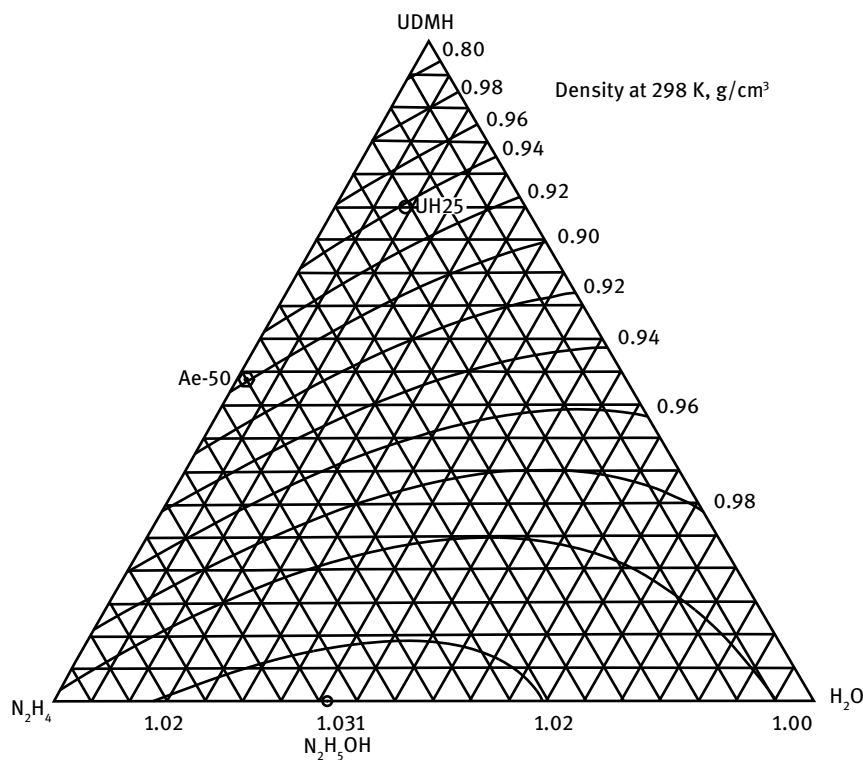
The densities of ternary UDMH/ $\text{N}_2\text{H}_4$ / $\text{H}_2\text{O}$  mixtures are illustrated in Figure 49. The highest densities are encountered near the composition of hydrazine hydrate ( $\text{N}_2\text{H}_5\text{OH} = 64\% \text{N}_2\text{H}_4$ ).

### 3.7.1.4 Vapor Pressure of UDMH/ $\text{N}_2\text{H}_5\text{OH}$ Mixtures

The vapor pressure of UH-25 was measured between 293 and 390 K; the data can be expressed using the following equation [975]:

$$\ln P = 9.6838 - 2661.1/T - 224330/T^2$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.



**Figure 49:** Densities of ternary UDMH/ $\text{N}_2\text{H}_4$ / $\text{H}_2\text{O}$  mixtures. (Reproduced and modified from [95].)

The heat of vaporization of UH-25 calculated from this vapor pressure equation is 34.7 kJ/mol, while the additive behavior of an ideal solution would expect it to be 36.5 kJ/mol.

### 3.7.2 Chemical Properties of UDMH/ $\text{N}_2\text{H}_5\text{OH}$ Mixtures

#### 3.7.2.1 Thermal Decomposition of UDMH/ $\text{N}_2\text{H}_5\text{OH}$ Mixtures

The pressure rise rate in a closed bomb at temperatures between 391 and 525 K was measured for hydrazine hydrate, UDMH, and UH-25. The logarithm of the pressure rise rate plotted versus the reciprocal temperature formed an Arrhenius plot and the energy of activation could be derived from the slope of the curve. The energies of activation of the decomposition of UDMH, hydrazine hydrate, and UH-25 were 83.2, 99.7, and 100.2 kJ/mol, respectively [975].

#### 3.7.2.2 Analysis of UDMH/ $\text{N}_2\text{H}_5\text{OH}$ Mixtures

The French satellite launch vehicle Ariane-4 used UH-25, which can be analyzed using GC, IR, and iodometric methods [976].

## 4 UDMH/Organic Amines Mixtures

Alkylamines are cheaper than UDMH yet have similar hypergolic fuel properties. It would therefore be advantageous to mix alkylamines with UDMH to make hypergolic fuel mixtures. The preferred amine to mix UDMH with when making mixed amine fuels is diethylenetriamine, DETA,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ . Several of these mixtures have been assigned names in the Mixed Amine Fuel (MAF) series. Table 31 is a summary of the compositions of MAF fuels. More detailed physical properties of MAF fuels are available in the *USAF Propellant Handbooks, Hydrazine Fuels* (Units eight to 12) [95]. Diethylene triamine has a higher density than UDMH ( $0.9525\text{ g/cm}^3$  compared to  $0.7861\text{ g/cm}^3$ ), therefore the mixtures too have higher densities than UDMH and can replace it in a launch vehicle design, and provide higher total impulse for the same tankage volume. This was a substantial advantage when the Jupiter-C carrying the first US satellite into space changed its fuel choice from ethanol to U-DETA.

**Table 31:** Compositions of MAF fuels.

| MAF   | UDMH | DETA | $\text{H}_3\text{CC}\equiv\text{N}$ | Other amines | $\text{H}_2\text{O}$ |
|-------|------|------|-------------------------------------|--------------|----------------------|
| MAF-1 | 50   | 39   | 10                                  | —            | <1                   |
| MAF-2 | —    | —    | —                                   | 100          | —                    |
| MAF-3 | 20   | 80   | —                                   | —            | <1                   |
| MAF-4 | 60   | 40   | —                                   | —            | —                    |
| MAF-5 | 29.5 | 50.5 | 20.0                                | —            | —                    |

A MAF fuel blend was once used as the fuel in the LR-44-RM-2/SPARROW III AIM-7E, a pre-packaged air-to-air missile with IRFNA as the oxidizer [977]. The fuel consisted of 40.5% UDMH, 50.5% DETA, and 9% acetonitrile. At that time, the solid propellant motors in use in SPARROW I and SPARROW II were outdated, and more advanced solid propellant units were experiencing difficulty at the ambient temperatures expected when carrying the missiles under the wings at high Mach numbers. Solid propellants at that time could not survive a 6-h soak at 366 K (200 °F) before firing.

The composition and properties of MAF-3 were specified by MIL-P-23686A (dated 18 April 1964) and Amendment I (dated 15 March 1965), which allowed a maximum of 1%  $\text{H}_2\text{O}$ .

MAF-4 was alternately known as “U-DETA” and “Hydyne”; it was used in the North American/Rocketdyne LR64-NA-4 target drone engine and in the Army Jupiter-C satellite launch vehicle. The properties and methods of analysis for MAF-4 were specified in MIL-P-23686A.

The only operational use of MAF-1 as a propellant has been as the fuel in the ASM-N7 A and B (GAM•S3) BULLPUP missiles that were produced in large numbers (close to 20000 missiles for the BULLPUP A version). One version of Bullpup A used the LR58-

RM-2 (later LR58-RM-4) propulsion unit from RMD-Thiokol. The Bullpup B missile, which carried a 1000-lb warhead, was based on the LR62-RM-2 propulsion unit and was approximately three times the weight of the BULLPUP A but was controlled in a similar manner with many common components. Seventeen thousand units of the heavier B version were produced during the 1970s.

Procurement of MAF 1 was covered by MIL-P-23741 A (3), dated 15 April 1964, and included Revision I, dated 15 March 1965. The effect of Revision 1 was to relax the lower limit on density at 25 °C from 0.863 to 0.861 g/mL. One of the advantages of the visual-guided liquid-propelled BULLPUP over solid-propelled missiles was the cleanliness of the exhaust, which made seeing the target possible without obstruction by smoke. The smokeless exhaust of a liquid unit would improve visibility during the firing stage and facilitate visual guidance. It was hoped that a pre-packaged liquid propulsion unit would give substantially increased total impulse and thus improve the missile stand-off distance.

MAF-2 was a rarely used hypergolic fuel mixture consisting of 42.6% propargyldiglycidylamine, (PRODGA),  $\text{HC}\equiv\text{CCH}_2\text{N}(\text{CH}_2\text{OCHCH}_2)_2$ , 48.3% dipropargylglycidylamine, (DIPG A),  $(\text{HC}\equiv\text{CCH}_2)_2\text{N}(\text{CH}_2\text{OCHCH}_2)$ , and 9.1% tripropargylamine (TRIPRAM),  $(\text{HC}\equiv\text{CCH}_2)_3\text{N}$ . The acetylenic triple bond and the oxiridine ring tension added energy to those fuels. The disadvantages of MAF-2 were high viscosity and poor ignition with RFNA. MAF-2 did not contain any UDMH at all. It just happens to be part of the MAF family. Mixed hydrazine or UDMH fuels can be analyzed in the field using GC or conductometric methods [930].

#### 4.1 UDMH/DETA Mixtures

DETA is a high-density, low-volatility amine. It is readily available in industrial quantities. Ten tons of AZ-11, a blend of 89% diethylenetriamine and 11% UDMH, were used during development of the AL SAMUD missile in Iraq during 1998–2002 [978].

##### 4.1.1 Physical Properties of UDMH/DETA Mixtures

The physical properties of U-DETA are summarized in Table 32.

##### 4.1.2 Materials Compatibility with UDMH/DETA Mixtures

Materials compatibility for U-DETA mixtures is essentially the same as for UDMH [979, 980]. Thousands of BULLPUP missiles using MAF-1 as the fuel had been fielded during the 1960s, and several were examined for corrosion after they were decommissioned and unloaded after ten to twelve years in the field. No leakage of the missile tanks was found to have occurred in the ten-year storage period. The degree of corrosion that did occur was considered insignificant and would not affect the functional capability of the missile system. Propellant tanks in BULLPUP missiles were examined

**Table 32:** Physical properties of U-DETA (MAF-4).

| Property                        | SI units                   | Other units |          |
|---------------------------------|----------------------------|-------------|----------|
| Freezing point                  | <189 K                     | <-84 °C     | <-120 °F |
| Boiling point                   | 345 K                      | 71.7 °C     | 161 °F   |
| Vapor pressure at 289 K (60 °F) | 9.06 kPa                   | 68 mm Hg    | 1.3 psia |
| Density at 289 K (60 °F)        | 0.858 g/cm <sup>3</sup>    | —           | —        |
| Viscosity at 298 K (60 °F)      | 0.0196 N s m <sup>-2</sup> | 196 cPs     | —        |
| Flash point                     | 281 K                      | 7.8 °C      | 46 °F    |
| Refractive index $n_D^{25}$     | 1.438                      | —           | —        |

Data source: [178,979].

after extended storage tests [981]. The tightly adherent film observed on the fuel tank interior and propellant exposed component surfaces were analyzed and found to be  $\beta$ -aluminum hydroxide.

#### 4.1.3 Toxicity of Mixed Amine Fuels

Toxicity tests of mixed amine fuel, MAF-1, composed of UDMH 50.5%, DETA 40.5%, and acetonitrile 9.0% were initiated to determine and compare the toxicity of the fuel with those of the separate components [982, 983].

#### 4.1.4 Pool Burning of Mixed Amine Fuels

Pool burning and fire extinguishing tests were conducted with MAF-1 and MAF-3, and their constituents, UDMH and DETA [206, 702]. The major components of MAF-1 and MAF-3 differ very widely in their volatility: UDMH boils at 336 K (63 °C) and DETA at 480 K (207 °C). For the 76 and 122 cm diameter trays, predicted pool-burning rate values exceeded observed averages for the middle half of the burning time by about 15% for MAF-1 and about 50% for MAF-3. Once diluted with water, the puddles were more difficult to ignite. The fire point of MAF-1 at 307 K (34 °C) was 64 vol.-% fuel and the fire point of MAF-3 at 298 K (25 °C) was 63 vol.-% fuel.

#### 4.1.5 Detonability of Mixed Amine Fuels

Hydine is non-detonable. It is insensitive to initiation by booster charges consisting of 50 to 100 g tetryl [178].

#### 4.1.6 UDMH/Silicone Oil Mixtures

A desirable heat flux reduction in regeneratively cooled engines is possible by adding up to 3% silicone oil to the hydrazine-type fuel. As the result of silicone oil combustion, the fire side of the combustion chamber becomes coated with a lining of sili-

con dioxide, which reduces heat transfer [984]. Solubility screening tests of 132 compounds showed that UDMH was the best solvent for silicones, MMH was intermediate, and Aerozine-50 was the worst solvent for silicone [985, 986]. Fuel blends containing 3 mass-% of silicone were subjected to 48 h temperature stability tests and 30 d storage tests. Analytical methods for the high-density acid/UDMH/silicone oil propellant that was at one time used in the Agena upper stage are described in [987].

## 5 UDMH/Kerosene Mixtures

Unsymmetrical dimethylhydrazine had been evaluated as a hypergolizing additive to kerosene JP-4 to render it hypergolic with RFNA or WFNA. There were two types of UDMH/JP-4 blends; one with 17% UDMH and one with 40% UDMH, as specified by Specification MIL-P-26694B. JP-X Type I is a mixture of 60% JP-4 and 40% UDMH and was used in the BOMARC booster [988] and early NIKE anti-aircraft rockets [507]. The later NIKE AJAX missile fuel was JP-X Type II with 17% UDMH in JP-4 [989]. The problem was that small quantities of water absorbed from the air caused the binary solution to break into two phases (similar phase separation problems are encountered with Gasohol in automobiles). The phase diagrams for the ternary system UDMH/JP-4/H<sub>2</sub>O were determined at 251 and 298 K for three different grades of JP-4 [990]. The phase diagrams for ternary systems containing mixtures of UDMH, water, and JP-4 were determined at 250 and 298 K (−9 and 77 °F) for three grades of JP-4 (0, 15, and 27% aromatics). The phase diagrams for UDMH, water, and toluene were determined at 250, 298, and 331 K (−9, 77, and 136 °F). The diagrams showed the amount of water required for the undesirable formation of two phases in any combination of UDMH and JP-4 or toluene. For a mixture containing 17% UDMH in JP-4, only 0.2% water will cause phase separation at 233 K. When the mixture contains 40% UDMH, it will tolerate 1% water at 233 K [991, 992]. The mixture containing 40 mass-% UDMH and 60 mass-% JP-4 had the designation JP-X Type I.

### 5.1 Chemical Properties of UDMH/Kerosene Mixtures

#### 5.1.1 Analysis of UDMH/Kerosene Mixtures

Data presented showed that it is possible to procure JP-4 and UDMH, with both complying with their respective specifications. When blended, however, the mixture fails to comply with the limits of specification MIL-P-26694 [993]. Recommended changes for the 10, 35, and 50% distillation points were 341, 350, and 422 K (155, 170, and 300 °F), respectively.

A rapid manometric procedure was developed for the determination of water and UDMH in rocket fuel mixtures of JP-4 and UDMH [407]. These procedures were specif-

ically designed for use in the field by non-technical personnel and were to be used for surveillance checking of Nike fuels. Water content was determined by measuring the hydrogen pressure developed from the reaction of the water with calcium hydride. UDMH in the sustainer fuel mixtures was determined by measuring the gaseous pressure developed by reaction with nitrous acid.

### 5.1.2 Specifications for UDMH/Kerosene Mixtures

The compositions of JP-X mixtures are specified by Military Specification MIL-P-26694B - Propellant, JP-X (JP-4 + UDMH) [994]. These specifications cover three types of JP-X. The nominal composition limits and purity requirements of these three types of JP-X are listed in Table 33.

**Table 33:** Composition limits and purity requirements of hypergolized kerosene per MIL-P-26694B.

| Constituent            | Distillation limit | Unit              | Type I          | Type II         | Type III      | Analytical method          |
|------------------------|--------------------|-------------------|-----------------|-----------------|---------------|----------------------------|
| JP-4 per MIL-T-5624    |                    | Mass-%            | 40 ± 1          | 17.0<br>± 0.3   | 50.0 ± 2.0    |                            |
| UDMH per MIL-P-25604   |                    | Mass-%            | 59 min.         | 83.0<br>± 0.3   | 48 min.       | Potassium iodate titration |
| Distillation           | 10% point          | °F                | 155 max.        | 245 max.        | Not specified |                            |
|                        | 35% point          | °F                | 170 max.        |                 |               |                            |
|                        | 50% point          | °F                | 300 max.        | 340 max.        |               |                            |
|                        | 70% point          | °F                | 370 max.        |                 |               |                            |
|                        | 90% point          | °F                | 470 max.        | 466 max.        |               |                            |
| Density at 298 K       |                    | g/cm <sup>3</sup> | 0.746–<br>0.788 | 0.749–<br>0.792 | 0.746–0.786   | ASTM D941-55               |
| No phase separation at |                    | °F                | –65 max.        |                 | –65 max.      |                            |
| Particulate            |                    | mg/L              | 10 max.         | 10 max.         | 10 max.       | ASTM D-2276-65T            |

The ignition properties of this fuel with hypergolic oxidizers will be described in a future *Encyclopedia of Hypergolic Bipropellant Combinations*, in the chapter “Hypergolic Combinations With Nitric Acid.” Even smaller additions of UDMH to kerosenes (insufficient to achieve hypergolic ignition) improve the stability of combustion of kerosenes with WFNA or RFNA [995].

## 6 Other UDMH Mixtures

Ammonia/UDMH mixtures are hypergolic with WFNA, RFNA, and NTO, but the mixture  $\text{NH}_3$ /UDMH required at least 25% UDMH to be hypergolic with NTO.

### 6.1 Vapor-Phase Composition of UDMH/FDMH and FDMH/Water Mixtures

Formaldehyde dimethylhydrazone,  $\text{HC}=\text{N}-\text{N}(\text{CH}_3)_2$ , FDMH, is an intermediate in some UDMH manufacturing processes, a by-product in others, and in all cases a degradation product of UDMH and a potential environmental pollutant. It is therefore of interest to separate FDMH from UDMH and water. Measurements of the equilibrium liquid and vapor compositions versus temperatures at 101 kPa (1 atm) total pressure for the non-ideal system of UDMH/FDMH and FDMH/ $\text{H}_2\text{O}$  showed rather large deviations from ideal liquid-vapor solution behavior [105, 996, 997]. The solution model attributes the non-ideality to the formation of chemical association species which obey Henry's law in terms of actual solution equilibrium mol fractions. For the FDMH(=A)/ $\text{H}_2\text{O}$ (=B) and FDMH(=A)/UDMH(=B) systems, associates of the formula  $\text{AB}_2$  as well as  $\text{A}_2\text{B}$  were identified as likely species, as well as an  $\text{A}_2$  dimer of FDMH. The FDMH/ $\text{H}_2\text{O}$  system shows a minimum boiling azeotrope and a large positive deviation in the excess Gibbs-free energy of mixing.

### 6.2 UDMH/Hydroxyethylhydrazine Mixtures

2-Hydroxyethylhydrazine, hydrazinoethanol, HEH, is a hydrazine derivative that, up to now, had not been used as a rocket propellant. *Encyclopedia of Monopropellants* will present a new application for the nitrate salt of HEH, which is abbreviated as HEHN, when it is used as a monopropellant ingredient in combination with hydroxylammonium nitrate, HAN, as the oxidizer. HEH has a much lower vapor pressure but a much higher viscosity than UDMH or ethylhydrazine. Table 34 shows a comparison of the properties of HEH and UDMH. Thus, it would be desirable to use HEH/UDMH mixtures to lower the vapor pressure of UDMH and to lower the viscosity of HEH.

#### 6.2.1 Physical Properties of UDMH/HEH Mixtures

Physical properties of UDMH/HEH mixtures have been determined for mixtures containing 0–50 mass-% HEH [998].



**Table 34:** Comparison of physical properties of UDMH and HEH.

| Property                                      | UDMH                                 | HEH                                                           |
|-----------------------------------------------|--------------------------------------|---------------------------------------------------------------|
| Molecular formula                             | $(\text{H}_3\text{C})_2\text{NNH}_2$ | $\text{HOCH}_2\text{CH}_2\text{NNH}_2$                        |
| Molecular mass, g/mol                         | 60.10                                | 76.10                                                         |
| Liquid density at 298 K, g/cm <sup>3</sup>    | 0.786                                | 1.123                                                         |
| Boiling point, °C                             | 62.3 at 760 mm Hg                    | 155–160 at 32 mm Hg<br>148–152 at 30 mm Hg<br>127 at 17 mm Hg |
| Freezing point, °C                            | –57.2                                | –70                                                           |
| Flash point, °C                               | –15                                  | 74                                                            |
| Refractive index ( $n_D^{25}$ )               | 1.4053                               | 1.4885                                                        |
| Liquid viscosity at 25°C, cPs                 | 0.492                                | 147                                                           |
| Vapor pressure, mm Hg                         | 167.25 at 25 °C                      | <1 at 25 °C<br>4 at 110 °C                                    |
| Heat of vaporization at boiling point, kJ/mol | 32.623                               | 76.384                                                        |

### 6.2.2 Density of UDMH/HEH Mixtures

The measured density of UDMH/HEH mixtures at 293 K, as illustrated in Figure 50, can be expressed by the linear equation

$$\rho_{\text{meas}} = 2.97 \times 10^{-3} C_{\text{H}} + 0.79$$

while theoretical mixture densities assuming ideal solution behavior would be calculated by

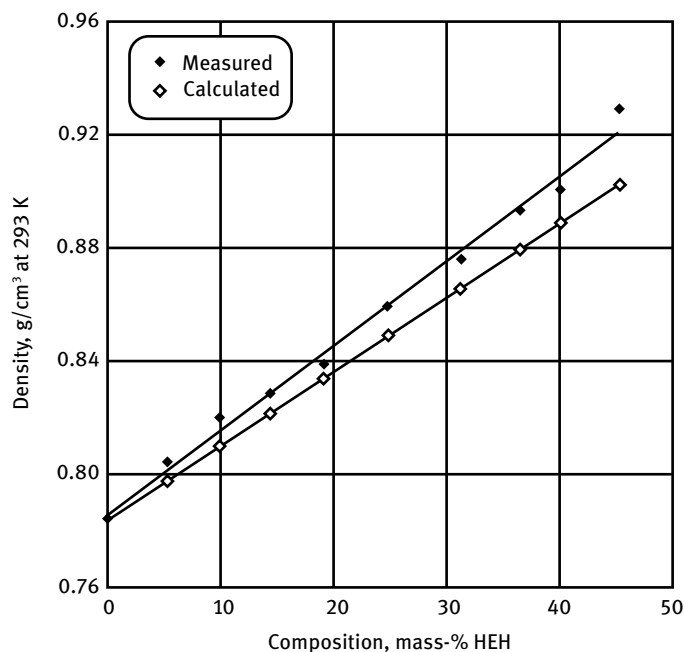
$$\rho_{\text{theor}} = 2.60 \times 10^{-3} C_{\text{H}} + 0.78$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $C_{\text{H}}$  is the concentration of HEH in mass-%. The measured density is higher than the predicted density, which is a deviation in the desirable direction.

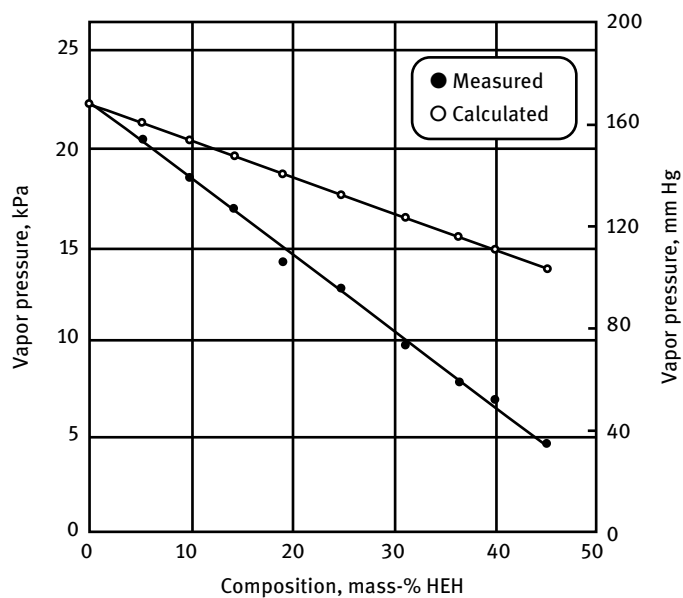
### 6.2.3 Vapor Pressure of UDMH/HEH Mixtures

Appreciable lowering vapor pressures of binary mixtures of UDMH/HEH can be expected via the addition of HEH to UDMH because the difference between the vapor pressures of the two components at room temperature is substantial. Reducing vapor pressure of UDMH through the addition of HEH permits not only easier handling of the propellants but also provides a more effective pump design in applications where the propellant is pumped because it is less likely to suffer from cavitation.

Vapor pressures of binary mixtures of UDMH and HEH at 298 K (25 °C) were determined indirectly by the Clausius-Clapeyron equation and mixing rule. The interaction parameter of enthalpy of vaporization for a binary mixture of UDMH/HEH can be obtained from the geometric mean of both components. Figure 51 shows the changes of vapor pressures for both ideal (Raoult's law) and real solutions at 298 K (25 °C) as



**Figure 50:** Measured and predicted density of UDMH/HEH mixtures at 293 K. (Reprinted and modified from [998], with permission from ©2011 Taylor & Francis Ltd, [www.tandfonline.com](http://www.tandfonline.com).)



**Figure 51:** Measured and predicted vapor pressure of UDMH/HEH mixtures at 298 K. (Reprinted and modified from [998], with permission from ©2011 Taylor & Francis Ltd, [www.tandfonline.com](http://www.tandfonline.com).)

a function of HEH content. Measured and calculated vapor pressure as a function of HEH content can be expressed by the equations

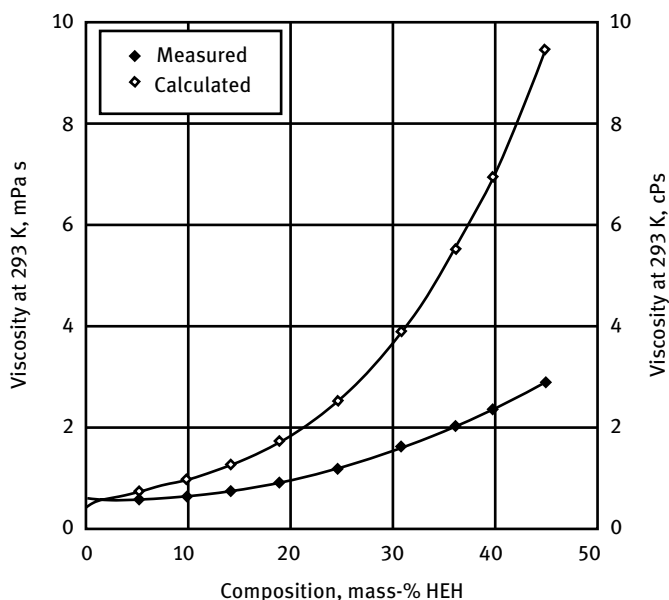
$$p_{\text{meas}} = 168.5 - 299.9 \times 10^{-2} C_H$$

$$p_{\text{theor}} = 167.6 - 143.9 \times 10^{-2} C_H$$

where  $p$  is the vapor pressure in mm Hg and  $C_H$  is the concentration of HEH in mass-%. The measured vapor pressure is lower than the predicted vapor pressure, which is favorable (Figure 51). The deviation is an indication of intense hydrogen bonding between the two molecules in the liquid phase.

#### 6.2.4 Viscosity of UDMH/HEH Mixtures

HEH is extremely viscous, which is a disadvantage for liquid propellants that need to flow through narrow valve and injector passages. UDMH/HEH mixtures have a lower viscosity than HEH that makes the fuel more pumpable and flowable. The curve fitting equations of the measured and calculated viscosity data for UDMH/HEH mixtures shown on page 54 of [998] do not match the data shown in the accompanying graph. The measured viscosity was lower than the predicted viscosity. The deviation is an indication of intense hydrogen bonding between the two molecules in the liquid phase.



**Figure 52:** Measured and predicted viscosity of liquid UDMH/HEH mixtures at 293 K. (Reprinted and modified from [998], with permission from ©2011 Taylor & Francis Ltd, [www.tandfonline.com](http://www.tandfonline.com).)

The viscosity of the mixtures does not increase much until the HEH content exceeds 30% (Figure 52). Deviations of the measured values from predicted results become more pronounced by increasing the mass percentage of HEH, which may be attributed to the non-ideality of the system which can be interpreted as hydrogen bonding between two adjacent molecules in the liquid state. The UDMH/HEH blend has been tested as a hypergolic fuel with NTO and RFNA [999].

### 6.3 UDMH/Hydrazinium Salt Solutions

Instead of water, an oxidizing hydrazinium salt like HN can be added to UDMH/ $\text{N}_2\text{H}_4$  mixtures to lower the freezing point and improve the performance. Some examples are listed in Table 35.

**Table 35:** Freezing points of UDMH-hydrazine-HN mixtures.

| Composition, mass-% |                        |      | Freezing point, K |
|---------------------|------------------------|------|-------------------|
| UDMH                | $\text{N}_2\text{H}_4$ | HN   |                   |
| 37.2                | 23.5                   | 39.2 | 219.3             |
| 33.3                | 31.5                   | 35.2 | 223.2             |
| 30.2                | 37.9                   | 31.9 | 237               |
| 27.6                | 43.3                   | 29.1 | 240.4             |
| 25.4                | 47.8                   | 26.8 | 248.2             |

Data source: [974].

A rarely referenced, mostly forgotten ternary UDMH fuel mixture is MHF-2, consisting of 36.5 mass-% UDMH, 40.2% HN, and 23.3%  $\text{N}_2\text{H}_4$ ; it freezes at 219.3 K ( $-59.9^\circ\text{C}$ ). It was intended as a low-freezing point fuel but was very viscous and lacked thermal stability in comparison to similar blends with MMH instead of UDMH [1000]. The density of MHF-2 in the range of 218 to 333 K ( $-55$  to  $+60^\circ\text{C}$ ) can be calculated from

$$\rho = 1.3201 - 7.552 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin. The viscosity of MHF-2 at 298 K was 6.467 cPs.

## 7 Gelled and Metalized UDMH

The performance of UDMH as a fuel for bipropellant combination can be enhanced by suspending finely distributed metal powders, preferably aluminum or beryllium. To prevent the metal powder from settling during storage, the mixture has to be gelled. The amount of metal that can be added is limited by the increasing viscosity of these blends, which makes them hard to pump and inject into a combustion chamber.

There are numerous patents and reports about gelled MMH. Gelling agents that have been proven to work with MMH may also work satisfactorily with UDMH, but the selection of gelling agents for UDMH and hydrazine  $N_2H_4$  follows different guidelines.

Fumed silica Cab-O-Sil, ethylcellulose, methylcellulose, agar agar, polypropylene glycol, hydroxymethyl cellulose, carboxymethyl cellulose, and clay were tested as gelling agents for UDMH and kerosene [1001]. Agar agar formed only partial gelation at 12% in UDMH. Ethyl cellulose at 17% gelling agent formed only a very thin gel. Carboxymethyl cellulose did not gel. Methylcellulose formed a good gel that could be loaded with 30% 15-micron size Al powder. Lecithin was added as a homogenizer. Thermal stability tests done in sealed glass containers for 90 minutes at 281, 293, 303, 313, and 323 K (8, 20, 30, 40, and 50 °C) did not show any separation, demonstrating its stability over a wide temperature range. But such short laboratory tests are meaningless when the gelled fuel needs to be stored for years.

Experimental studies on UDMH gelation using propellant grade (15  $\mu$ m) and pyrotechnic grade (1.5  $\mu$ m) Al powder at the 500-g batch level showed that gellant (methyl cellulose) concentration could be reduced by 50% using pyrotechnic grade Al [1002]. Methyl cellulose (MC) gellant was added pinch by pinch under mechanical agitation. This was followed by the addition of surfactant (silicone oil) and stepwise addition of Al powder. The pseudoplastic and thixotropic behavior of the gels was studied using a Brookfield viscometer at different rpm. Time intervals and flow rates through capillary die holes, burst pressure tests, and bulk density were measured. UDMH gels loaded with 25–30% Al with both grades of Al were stable, pseudoplastic (shear thinning), and thixotropic (time-dependent shear thinning), but their flow pattern through die holes differed in nature.

Thixotropic gels of UDMH have been prepared using methylcellulose (4.48 mass-%) and agar-agar (0.64 mass-%) chemical gelling agents [1003]. Red fuming nitric acid has been gelled by using sodium silicate (4.25 mass-%). The effect of various parameters like the size of the container, particle size of gellants, and temperature on gelation time of UDMH gelled system has been investigated. The gelation time of UDMH gel was found to increase with the increase in the internal diameter of the container. Gelation time was found to show direct proportionality with the particle size when MC was used as the gellant. In the case of MC, the gelation occurred quickly at higher temperature, whereas the reverse trend was observed when agar-agar gellant was used. To boost the performance of liquid propellants,

metalized gels of UDMH containing Al (10–40 mass-%) or Mg (10–25 mass-%) metal powders have been prepared. The density measurements of virgin and metalized gels revealed that there is a maximum increase of 47% and 19% over virgin gels upon the incorporation of Al or Mg powders, respectively.

Efforts have been made to understand the process of gelation using optical and photomicrographic techniques. Rheological studies on UDMH-methylcellulose gelled systems have been conducted under varying shear rates to measure their flow characteristics [1004]. The gel was found to behave as a pseudo-plastic thixotrope. The viscosity build-up as a function of time has been traced to the point of reaching a firm set gel. The viscosity increased with time rapidly in the beginning and only minor changes were observed thereafter. The effect of temperature and metal (Al or Mg) loading on apparent viscosity of the gelled system has been investigated. Both the apparent viscosity and thixotropic character of the unloaded gel were found to decrease with an increase in temperature. An increase in shear rate decreased the apparent viscosity significantly. The thixotropic character of the metalized gelled systems increased with metal content and they exhibited a shear thinning behavior. Polynomial curve fitting was applied to assess the variation of pseudo-plastic index  $n$  and consistency index  $K$  with temperature and metallization. The results revealed that  $n$  increased with temperature and decreased with metal loading whereas  $K$  showed an opposite trend. The yield value of gelled systems decreased with temperature and increased with metal loading.

Preparation of a gelled UDMH fuel metalized with nano-aluminum was done in two steps [1005, 1006]. First, nano-aluminum was suspended in UDMH using ultrasonic-magnetic agitation. Following this, gelling agent was added under mechanical-magnetic agitation. Tween-80 as a surfactant was added to the fuel to better distribute nano-Al particles in the gel media. Experimental study showed that adding 3% Tween-80 to the gel mixture led to better distribution of nano-particles in the gel, improved homogeneity and stability, and decreased syneresis of the liquid UDMH fuel from the network of the gel. Increasing the surfactant concentration from 1 to 3% reduced the vaporization mass loss during centrifuging tests from 14 to 11%.

Gelling agents that have been shown to be useful for the gelling of ethanol as a rocket propellant can also be used for gelling of UDMH. An experimental comparative investigation on the rheological properties of ethanol and UDMH gels using MC as the gelling agent showed that the gelled fuels were thixotropic in nature [1007]. Gelling agent concentrations of 4.5 mass-% were used for the gelation of ethanol and UDMH. Their apparent viscosity values drastically decreased with shear rate and at higher ambient temperatures. The up-and-down shear rate curves for both gels formed an hysteresis loop that showed no significant change with variations in temperature. The UDMH-MC gel had a very high initial viscosity at lower temperatures (283.5 K) that decreased at higher temperature in the shear rate range covered. The gels started flowing at a nominal shear rate range of 1 to 20  $\text{s}^{-1}$ .

UDMH-based shear-thinning (thixotropic) gelled fuel systems and their rheologic-flow properties, mechanism of formation, metallization using nanometer/micron-size metal powders, performance characteristics, ignition, and combustion behavior were tested, but storage life was not determined. Some of the purported advantages of gelled UDMH fuels were advertised with unsubstantiated claims [1008]. If all those unproven claims were true, gelled UDMH would already have been flying in the armament inventory several decades ago (see also [1009]).

The unsteady combustion of organic gel droplets is different from the quasi-steady combustion of conventional liquid droplets and has a significant influence on the spray combustion-flow field of gel fuel liquid rocket engines and on how to optimize engine design. Based on the unsteady evaporation characteristics inside UDMH organic gel droplets and the micro-molecule structure of organic gel propellants, three types of liquid-phase evaporation models were proposed: the unsteady multi-component evaporation model, the interface tracking multi-phase flow evaporation model, and the discrete element multi-phase flow evaporation model [212]. The unsteady multi-component evaporation model regards the gel droplet as a binary multi-component droplet, in which the gellant inside the gel droplet is equivalent to a species with low volatility and high boiling temperature. In order to depict the shape and location variety of vapor bubbles inside the gel droplets more precisely, the interface tracking multi-phase flow evaporation model regards the gel droplet and the vapor bubble inside it as a single fluid, and uses a level set function to track the interface location of vapor bubbles. In view of mixing and combustion process of the gas-phase surrounding the UDMH organic gel droplets, it was proposed that the finite rate chemical reaction model and the flamelet model should be used for the stagnation ambient and convective ambient condition, respectively.

Bipropellant applications of gelled UDMH with IRFNA or NTO as the oxidizer will be discussed in a future publication, *Encyclopedia of Hypergolic Bipropellant Combinations*, in the chapter on “Hypergolic Combinations With Nitric Acid.”

## 8 Symmetrical Dimethylhydrazine (SDMH)

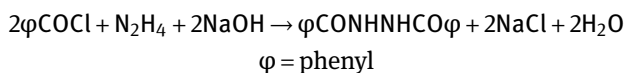
Symmetrical dimethylhydrazine, SDMH, *N,N'*-dimethylhydrazine,  $\text{H}_3\text{CNHNHCH}_3$ ,  $\text{C}_2\text{H}_8\text{N}_2$ , SDMH, CAS RN [540-73-8], an isomer of UDMH, is **NOT** used as a rocket propellant and its formation as an unwanted, more toxic by-product during production, degradation, and disposal of MMH or UDMH must be avoided. The presence of traces of SDMH as a contaminant in UDMH had been ignored in many UDMH toxicity studies. SDMH is a much more potent carcinogen than UDMH and its unrecognized presence may invalidate the published results of some UDMH toxicity tests. Some of

the animal exposure toxicity tests should be repeated with SDMH-free and NDMA-free UDMH.

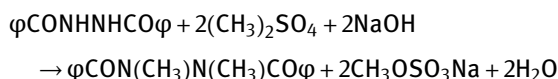
SDMH may be needed as a reference compound when analyzing MMH or UDMH rocket propellants for SDMH contamination. This is the only reason why some information on the preparation and properties of SDMH is listed here; otherwise, it would be omitted from this book altogether. However, the vast amount of information on the toxicity of SDMH that is available in the literature is not included here. One of the only scientific applications of SDMH is the deliberate and reproducible induction of cancer in test animals to allow for the effectiveness of anti-cancer treatments to be evaluated.

### 8.1 Preparation of Symmetrical Dimethylhydrazine

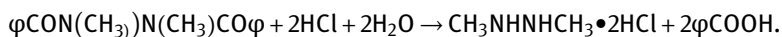
The synthesis of SDMH and its dichloride is so fundamental that it has even been included as an educational exercise in organic syntheses [1010]. The method described in that book blocks one position on each nitrogen atom of hydrazine by benzoylation:



followed by methylation with dimethyl sulfate:



and hydrolysis to release the SDMH dichloride:



There are many more methods for the preparation of SDMH described in the hydrazine literature [67].

Aliphatic Schiff's bases and *N*-chloro-alkylamines RNHCl react to form intermediate *N,N'*-dialkyl-diaziridines. This can be hydrolyzed with aqueous hydrochloric acid to form the chlorides of *N,N'*-dialkylhydrazines [1011].

### 8.2 Physical Properties of SDMH

The physical properties of SDMH are summarized in Table 36. SDMH is a slightly stronger base than UDMH, with a  $\text{p}K_a$  of  $9.29 \pm 0.70$ .



**Table 36:** Physical properties of SDMH.

|                                | SI units                 | Other units                 |
|--------------------------------|--------------------------|-----------------------------|
| Molecular mass                 | 60.10 g/mol              | 16.64 mol/kg                |
| Melting point                  | 264.3 K                  | $-8.88 \pm 0.04$ °C         |
| Boiling point                  | 354.6                    | 81.5 °C at 753 mm Hg        |
| Density (at 293 K)             | 0.8274 g/cm <sup>3</sup> | 0.052 lb/ft <sup>3</sup>    |
| Vapor pressure at 298 K        | 9.32 kPa                 | 69.9 mm Hg                  |
| Critical temperature           | 530 K                    | 257 °C                      |
| Critical pressure              | 9.12 MPa                 | 90 at                       |
| Enthalpy of formation, liquid  | +50.6 kJ/mol             | +12.1 kcal/mol              |
| Enthalpy of formation, vapor   | +90 kJ/mol               | +21.5 kcal/mol              |
| Heat of fusion                 | 13.788 $\pm$ 0.02 kJ/mol | 3.2955 $\pm$ 0.005 kcal/mol |
| Heat of evaporation at 298 K   | 39.3 $\pm$ 0.06 kJ/mol   | 9.400 $\pm$ 0.015 kcal/mol  |
| Heat of combustion             | 1981 kJ/mol              | 473.5 kcal/mol              |
| Index of refraction $n_D^{20}$ | 1.4039                   | —                           |

### 8.3 Optical Properties of SDMH

Knowledge of the IR spectra of SDMH will help to identify it as a troublesome contaminant in rocket propellants. The IR spectra of gaseous, liquid, and polycrystalline solid symmetrical dimethylhydrazine and its deuterium analogs have been recorded from 70–4000 cm<sup>-1</sup> [1012]. A comparison of the infrared and Raman spectra of the respective compounds indicated that the liquid phase consists of approximately a 69:31% mixture of *gauche* conformers. An assignment of the observed frequencies based on band positions, relative intensities, and isotopic shifts was presented for both molecular conformations. Although the torsional fundamentals were observed for the molecules in both the gaseous and crystalline states, the bands observed for the solids were more clearly defined and were thus employed for barrier height calculations. The three-fold methyl rotational barrier was calculated to be approximately 13.8 kJ/mol (3.3 kcal/mol), whereas the magnitude of the barrier hindering internal rotation about the N–N bond was estimated to be 20.9 kJ/mol (5.0 kcal/mol). The Raman spectrum of SDMH is quite different from that of UDMH [149, 1013].

### 8.4 Thermodynamic Properties of Symmetrical Dimethylhydrazine

Symmetrical dimethylhydrazine is **not** used as a rocket propellant, so physical property data shown here are mostly for comparison with UDMH and for theoretical studies. The heat of combustion of SDMH was measured at 303.15 K and found to be 1981 kJ/mol = 473.454 kcal/mol, which is very similar to that of UDMH [158]. The heat of vaporization of SDMH is 39.33  $\pm$  0.14 kJ/mol (9.400  $\pm$  0.015 kcal/mol).

## 8.5 Chemistry of SDMH

Oxidation of SDMH leads to azomethane, which is potentially detonable. Energetic, nonvolatile salts of SDMH can be used as propellant ingredients, toxicity notwithstanding [1014]. The thermal decomposition of SDMH is quite different from that of UDMH [1015].

## 8.6 Toxicity of SDMH

There are thousands of publications on toxicity, especially the carcinogenicity of SDMH. On more than one occasion, the results of these studies have been confused with results from UDMH toxicity studies. In many instances, people doing toxicity studies with UDMH failed to verify the absence of SDMH as a contaminant in UDMH that was fed to the biota. In this book, we have not covered studies that dealt exclusively with SDMH. In several of the publications referenced throughout this publication, SDMH happened to be included in studies that dealt with all methylhydrazines (mostly UDMH). As such, SDMH was only included for comparison purposes.

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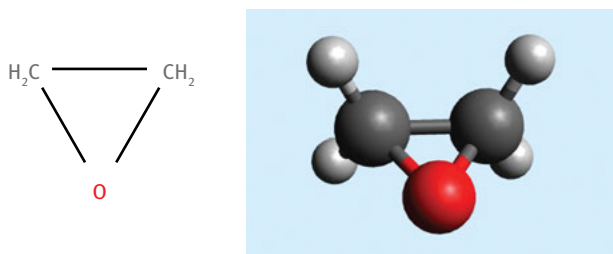
# Ethers

## Ethers

This chapter contains sections on alkyl ethers as rocket fuels. Alcohols and ethers share one element, both possess an oxygen atom in the molecule, and ethers can be made by dehydration of alcohols. Ethers contain an oxygen bridge between two organic groups, typically alkyl groups. Ethers are derived by combining two alkyl groups with an —O— bridge, or by dehydrating two mols of alcohol by removing one mol of water. The oxygen balance of ethers is more negative than that of alcohols, so they should make better fuels. Ethers are only partially miscible with water. Ethers have been tested as rocket propellants but do not offer any advantages over alcohols. Ethers that have been tested as rocket propellants include a cyclic ether, ethylene oxide (oxirane), in monopropellants and vinyl alkyl ethers in hypergolic bipropellants.

### 1 Ethylene Oxide

Ethylene oxide, also known as  $C_2H_4O$ , oxirane, epoxyethane, oxacyclopropane, 1,2-epoxyethane, EtO, CAS RN [75-21-8],  $M = 44.0526$  g/mol, is a heterocyclic aliphatic ether. Its molecular structure is shown in Figure 1.



**Figure 1:** Molecular structure of ethylene oxide

The strained ring structure is the main reason for the high enthalpy of formation and the ease of thermal decomposition of this compound, which is why it was once considered as a monopropellant; see the chapter “Organic Monopropellants” in *Encyclopedia of Monopropellants*. Here, we only summarize its physical and chemical properties and a few academic studies of its decomposition kinetics. Ethylene oxide decomposition gas generators were once tested as turbine drives to drive the oxidizer and fuel pumps in large rockets. It would have been a replacement for hydrogen perox-

ide, which is usually used to generate the hot steam needed to drive these propellant pumps. Ethylene oxide is not commonly used as a rocket fuel.

Ethylene oxide vapor is widely used for the sterilization of medical equipment and for the fumigation of grain in storage silos. It was estimated that the total world consumption in 2002 was  $14.7 \times 10^6$  metric tons, about 73% of which went into the production of ethylene glycol. Other derivatives of ethylene oxide include glycol ethers, ethanolamines, and surfactants. Ethylene glycol for polyester production is still a firm market. Additional information on ethylene oxide can be found in common reference encyclopedias [1, 2].

### 1.1 Production of Ethylene Oxide

Ethylene oxide is made by direct oxidation of ethylene using a silver catalyst. Historically, ethylene oxide was first made from chlorohydrin with alkali, but this process is no longer used. Ethylene oxide is an important intermediate in the syntheses of many industrial chemical compounds, mostly glycols and other polyols [3]. As of 1983, 12 companies produced ethylene oxide in the United States and Puerto Rico using four different technologies at 15 different locations.

### 1.2 Physical Properties of Ethylene Oxide

The physical properties of ethylene oxide are summarized in Table 1. At room temperature, EtO is a colorless gas. It condenses at  $283.8\text{ K} = 10.7^\circ\text{C}$  into a colorless liquid. The liquid can be stored at room temperature under its own vapor pressure, but it is usually stabilized by addition of carbon disulfide or pyrogallol to prevent unwanted polymerization.

An empirical fundamental equation of state correlation was developed for ethylene oxide [5]. The correlation is explicit in terms of the Helmholtz energy and can be used to calculate all thermodynamic properties. The underlying dataset consisted of experimental and molecular simulation data. The experimental data almost exclusively covered the gaseous phase and were available for temperatures from the triple point up to the critical point. Molecular simulation data were used to extend the validity to the liquid state and up to a maximum temperature of 1000 K and a maximum pressure of 700 MPa.

The vapor pressure of ethylene oxide can be calculated from the Antoine equation

$$\log P = A - [B/(T + C)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin. Values for the constants  $A$ ,  $B$ , and  $C$  are available for two different temperature ranges, as shown in Table 2.

**Table 1:** Physical properties of ethylene oxide.

| Property                                                 | SI units                                 | Other units   |
|----------------------------------------------------------|------------------------------------------|---------------|
| Molecular mass                                           | 44.0526 g/mol                            | 22.700 mol/kg |
| Freezing point                                           | 160.6 K                                  | −112.5 °C     |
|                                                          | 160.55 K                                 | −112.6 °C     |
| Boiling point                                            | 283.8 K                                  | 10.7 °C       |
| Density (at 293 K)                                       | 0.8711 g/cm <sup>3</sup>                 | —             |
| Coefficient of thermal expansion (at 328 K = 55 °C)      | 0.00161/°C                               | —             |
| Vapor pressure (at 293 K = 20 °C)                        | 146 kPa                                  | 1095 mm Hg    |
| Dynamic viscosity (at 273 K = 0 °C)                      | $3.2 \times 10^{-4}$ N s m <sup>−2</sup> | 0.32 cPs      |
| Dynamic viscosity at boiling point                       | $2.8 \times 10^{-4}$ N s m <sup>−2</sup> | 0.28 cPs      |
| Surface tension (at 293 K = 20 °C under pressure)        | $2.43 \times 10^{-4}$ N/cm               | 24.3 dyn/cm   |
| Refractive index ( $n_D^{20}$ ), liquid, at 280 K = 7 °C | 1.3597                                   | —             |
| Dielectric constant (at 272 K = −1 °C)                   | 13.9                                     | —             |
| Critical temperature                                     | 468.9 K                                  | 195.8 °C      |
| Critical pressure                                        | 7.23 MPa                                 | 72.33 bar     |

Data sources: [3, 4]

**Table 2:** Values for the constants in the vapor pressure equation for ethylene oxide.

| Temperature range, K | A       | B       | C       | References |
|----------------------|---------|---------|---------|------------|
| 182.59–283.59        | 4.386   | 1115.1  | −29.015 | [6]        |
| 273.4–304.9          | 5.84696 | 2022.83 | 62.656  | [7]        |

Another vapor pressure equation for ethylene oxide for the range 199.3–469 K (−73.8 to +196 °C) used four coefficients and the equation

$$\log p_V = A + \frac{B}{T} + C \log T + DT$$

where  $p_V$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The correlation constants are  $A = 40.723$ ,  $B = -2372.6$ ,  $C = -12.865$ , and  $D = 7.3243 \times 10^{-3}$ . For a temperature of 298 K, this equation gives a vapor pressure of 1297 mm Hg [8].

The dynamic viscosity of liquid ethylene oxide in the range 223–273 K can be calculated from the following equation:

$$\mu = 4.189 \times 10^6 T^{-2.923}$$

where  $\mu$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The viscosity at 273 K is 0.320 cPs [9].

The dynamic viscosity of liquid ethylene oxide in the range 160–468 K (–113 to +195 °C) can be calculated from the following equation:

$$\log \eta = A + \frac{B}{T} + CT + DT^2$$

where  $\eta$  is the viscosity in cPs and  $T$  is the temperature in kelvin. The coefficients for this equation are  $A = -1.678$ ,  $B = 312.4$ ,  $C = 0.03232 \times 10^{-2}$ , and  $D = -0.7838 \times 10^{-6}$ . For example, the viscosity from this equation at 298 K is 0.25 cPs [8].

The surface tension of ethylene oxide at 243.2 K is 32.65 dyn/cm and at 298 K (under pressure) it is 23.21 dyn/cm.

The thermal conductivity of ethylene oxide as a saturated liquid can be calculated from the equation

$$\lambda = A + BT + CT^2$$

where  $\lambda$  is the thermal conductivity in  $\mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin. The correlation constants for ethylene oxide in the temperature range 160–453 K (–113 to +180 °C) are  $A = 626.62$ ,  $B = -79.51 \times 10^{-2}$ , and  $C = -2.85 \times 10^{-4}$  [10]. At 293 K (+20 °C), the thermal conductivity of liquid ethylene oxide under pressure is  $369 \mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$ .

The thermal conductivity of ethylene oxide vapor can be calculated from the polynomial equation

$$\lambda_G = A + BT + CT^2 + DT^3$$

where  $\lambda_G$  is the thermal conductivity of ethylene oxide vapor at low pressure (approx. atmospheric pressure) in  $\mu\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin. The correlation constants for ethylene oxide in the temperature range 273–1273 K (0 to 1000 °C) are  $A = -34.84$ ,  $B = 12.96 \times 10^{-2}$ ,  $C = 3.63 \times 10^{-4}$ , and  $D = -18.26 \times 10^{-8}$  [8].

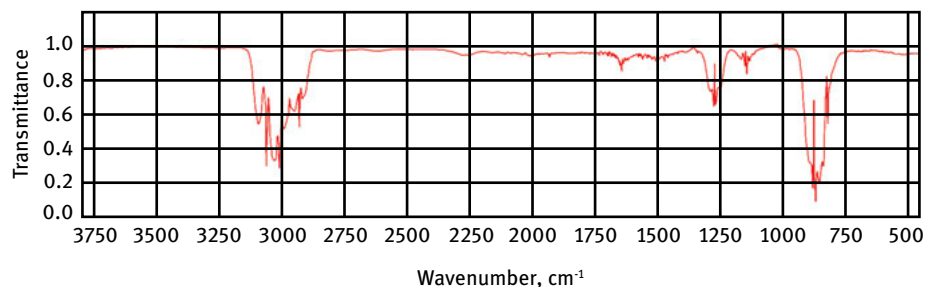
### 1.2.1 Molecular Structure of Ethylene Oxide

The atom distances in the ethylene oxide molecule are C–C = 0.1466 Å, C–H = 0.1085 Å, and C–O = 0.1431 Å. The H–C–H bond angle is 116.6° and the C–O–C bond angle is 61.64°.

The potential energy hypersurface for two interacting rigid ethylene oxide molecules was created by computing the second virial coefficient, shear viscosity, and thermal conductivity of the gas [11]. The values of these properties were substantiated by the best experimental data as they tended to fall within the uncertainty intervals and obeyed the experimental temperature functions, except for viscosity, where experimental data were insufficient. Due to the lack of reliable data, especially for the transport properties, calculated values were the most accurate estimates for these properties of ethylene oxide available at that time.

### 1.2.2 Infrared Spectrum of Ethylene Oxide

The IR spectrum of ethylene oxide is shown in Figure 2.



**Figure 2:** Infrared spectrum of ethylene oxide. (Reproduced and modified with permission from [12])

### 1.2.3 Thermodynamic Properties and Thermal Properties of Ethylene Oxide

Thermodynamic properties of ethylene oxide are summarized in Table 3.

**Table 3:** Thermodynamic properties of ethylene oxide.

| Property                                                               | SI units                                     | Other units                                             | References |
|------------------------------------------------------------------------|----------------------------------------------|---------------------------------------------------------|------------|
| Heat capacity (liquid)                                                 | $1.88 \text{ J g}^{-1} \text{ K}^{-1}$       | $0.45 \text{ cal g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ |            |
| Enthalpy of formation, vapor ( $\Delta H_f^{298}$ )                    | $-52.64 \text{ kJ/mol}$                      | $-12.58 \text{ kcal/mol}$                               | [13]       |
| Enthalpy of formation, liquid ( $\Delta H_f^{298}$ )                   | $-97.5 \text{ kJ/mol}$                       | $-23.3 \text{ kcal/mol}$                                | [3]        |
|                                                                        | $-95.7 \pm 1.3 \text{ kJ/mol}$               | $-22.87 \pm 0.3 \text{ kcal/mol}$                       | [13]       |
| Heat of fusion                                                         | $5.17 \text{ kJ/mol}$                        | $1.2364 \text{ kcal/mol}$                               | [3]        |
|                                                                        | $5.1731 \text{ kJ/mol at } 160.65 \text{ K}$ | $1.2364 \text{ kcal/mol at } -112.5^{\circ}\text{C}$    | [13]       |
| Heat of vaporization                                                   | $25.5 \pm 0.02 \text{ kJ/mol}$               | $6.101 \pm 0.006 \text{ kcal/mol}$                      | [3]        |
|                                                                        | $25.527 \text{ kJ/mol at } 283.66 \text{ K}$ | $6.101 \text{ kcal/mol at } 10.51^{\circ}\text{C}$      | [13]       |
| Heat of solution in water at constant pressure at $18^{\circ}\text{C}$ | $+6.3 \text{ kJ/mol}$                        | $+1.5 \text{ kcal/mol}$                                 | [3, 7]     |
| Heat of combustion, gaseous, 298 K, 101 kPa                            | $1307.7 \pm 0.8 \text{ kJ/mol}$              | $312.55 \pm 0.20 \text{ kcal/mol}$                      | [3]        |
|                                                                        | $1306.0 \pm 0.59 \text{ kJ/mol}$             | $312.14 \text{ kcal/mol}$                               | [13]       |

For additional information on thermodynamic properties of EtO, see [4, 14, 15].



### 1.2.3.1 Heat Capacity of Ethylene Oxide

The heat capacity of gaseous ethylene oxide can be calculated from the Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$ , A, B, C, D, and E are constants, and  $\tau$  is the absolute temperature in kelvin divided by 1000. The coefficients are listed in Table 4. The same coefficients (and others) are used for formulas expressing the standard enthalpy of formation and the standard entropy of the vapor. These equations were obtained by curve fitting data covering the ranges 298–1200 and 1200–6000 K.

**Table 4:** Constants for thermodynamic properties of ethylene oxide vapor.

| Temperature range, K | 298–1200  | 1200–6000 |
|----------------------|-----------|-----------|
| A                    | −23.25802 | 131.3483  |
| B                    | 275.6997  | 13.80594  |
| C                    | −188.9729 | −2.645062 |
| D                    | 51.03350  | 0.175820  |
| E                    | 0.386930  | −30.03639 |
| F                    | −55.09156 | −158.3795 |
| H                    | −52.63514 | −52.63514 |

Data source: [13, 16]

Enthalpy data were determined calorimetrically for both vapor and liquid ethylene oxide from 322 to 422 K (120–300 °F) and 0.345 to 3.723 MPa (50–540 psi) with an estimated accuracy of 2% [17]. Entropy values were derived from the experimental data, and the results were presented in table format and on a  $p$ – $\Delta H$  diagram. Vapor pressures evaluated from the experimental data from 322 to 422 K (120–300 °F) were in reasonably good agreement with values predicted by extrapolating previously published information applicable to lower temperatures.

Another source of data gives the heat capacity of ethylene oxide vapor assuming ideal gas behavior from the polynomial equation [18]:

$$C_p = -7.520 + 2.2206 \times 10^{-1}T - 1.2560 \times 10^{-4}T^2 + 2.5918 \times 10^{-8}T^3$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin.

The heat capacity of liquid ethylene oxide between 161 and 314 K can be calculated from the equation

$$C_p = 79.81 - 2.751244 \times 10^{-2}T + 1.822322 \times 10^{-4}T^2$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin [19]. A similar but older polynomial gives the heat capacity of liquid ethylene oxide between 160.6 and 453 K ( $-112.5$  and  $+180^\circ\text{C}$ ) as

$$c_p = 0.2839 + 2.347 \times 10^{-3} T - 11.66 \times 10^{-6} T^2 + 20.04 \times 10^{-9} T^3$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} ^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin [10]. The heat capacity of liquid ethylene oxide at 283 K is  $0.47 \text{ cal g}^{-1} ^\circ\text{C}^{-1}$ .

### 1.2.3.2 Enthalpy of Formation and Heat of Combustion of Ethylene Oxide

The vapor-phase excess enthalpy above the standard enthalpy of formation  $\Delta H^\circ_{f,298}$  of EtO can be calculated from the Shomate equation:

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{\tau} + F - H$$

where A, B, C, D, E, F and H are constants and  $\tau$  is the absolute temperature in K divided by 1000. The coefficients are the same as those listed in Table 4. The same coefficients (and others) were used for a formula expressing the heat capacity of the vapor (see above). These equations were obtained by curve fitting data covering the range from 298 to 6000 K. The heat of combustion is  $1306.0 \pm 0.59 \text{ kJ/mol}$  for EtO vapor and  $1262.9 \pm 1.3 \text{ kJ/mol}$  for EtO liquid.

## 1.3 Chemical Properties of Ethylene Oxide

Ethylene oxide is miscible with water over the entire range of mixture ratios. It forms a clathrate with water. It will react with water at higher temperatures and hydrolyze to form ethylene glycol, which is an industrial process for making ethylene glycol, most of which is used as an antifreeze in automobiles. Polymerization of ethylene oxide leads to poly(ethylene glycol). Ethylene oxide is a very good solvent for most polar organic compounds, similar to diethyl ether or dioxane. Lower alkanes do not dissolve very well in EtO; only butane dissolves appreciably.

Once upon a time (long, long ago), when the US Air Force was still considering and testing the use of ethylene oxide as a monopropellant to drive auxiliary power units, the procurement of ethylene oxide was governed by *Military Specification MIL-P-8845 – Propellant, Ethylene Oxide*, which established the contaminant limits listed in Table 5. No document has superseded this specification.

**Table 5:** Contaminant limits in ethylene oxide per MIL-P-8845A.

| Constituent  | Maximum concentration | Method                        |
|--------------|-----------------------|-------------------------------|
| Free acidity | 0.005 mass-%          | Acidimetric titration         |
| Water        | 0.03 mass-%           | Karl Fischer titration        |
| Total iron   | 0.1 mg/L              | Colorimetry                   |
| Aldehydes    | 0.3 mass-%            | Iodine titration              |
| Chloride     | 0.2 mass-%            | AgNO <sub>3</sub> colorimetry |

### 1.3.1 Analysis of Ethylene Oxide

The concentration of EtO vapor in air can be measured using IR spectrophotometric methods [20]. The easiest method of performing occasional spot checks of ethylene oxide concentration in the air in the workplace is to use gas detection tubes containing an indicator (supported on a granular material) that changes color when exposed to ammonia. Such tubes are available from Draeger, MSA, Kitagawa, and others. Gas detection tubes are sensitive to as little as 1 ppm C<sub>2</sub>H<sub>4</sub>O and can measure up to 500 ppm C<sub>2</sub>H<sub>4</sub>O with ten strokes. Draeger ethylene oxide gas detection tubes are available for two ranges of concentrations (Table 6).

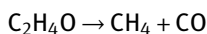
**Table 6:** Draeger ethylene oxide gas detection tubes.

| Tube designation       | Concentration range | Draeger part number |
|------------------------|---------------------|---------------------|
| Ethylene Oxide 1/a (5) | 1–15 ppm            | 67 28 961           |
| Ethylene Oxide 25/a    | 25–500 ppm          | 67 28 241           |

Data source: [21]

### 1.3.2 Thermal Decomposition of Ethylene Oxide

The exothermic homogeneous gas-phase decomposition of EtO in the absence of catalysts or contaminants:



starts at 843 K = 570 °C and leads mostly to methane and carbon monoxide in addition to other decomposition byproducts (ethane, ethylene, soot, hydrogen). In the presence of catalysts (Fe<sub>2</sub>O<sub>3</sub>, Raney nickel, unidentified contaminants), the reaction starts at 400 K = 127 °C. The exothermic decomposition of EtO makes this chemical useful as a monopropellant, but it has also been the cause of numerous industrial accidents. Most studies on the decomposition of ethylene oxide have been motivated by the desire to prevent future industrial accidents and not so much by the need to understand the decomposition of ethylene oxide if it is used as a gas generant or a rocket propel-

lant. The equation shown here is only an oversimplified representation of the more complex actual decomposition reaction. The applications of ethylene oxide as a rocket propellant and gas generant are discussed in more detail in a later section on monopropellants (see the chapter “Organic Monopropellants” in *Encyclopedia of Monopropellants*).

### 1.3.2.1 Ethylene Oxide Decomposition Mechanisms and Kinetics

The decomposition kinetics of ethylene oxide are difficult to investigate because the reaction products are not a homogeneous gas mixture, but a two-phase mixture of gases and solid carbon.

The homogeneous unimolecular gas-phase decomposition of ethylene oxide vapor in a Pyrex glass vessel was studied, attempting to avoid wall effects and catalysts [22]. In that work, the slow decomposition of ethylene oxide between 653 and 717 K (380–444 °C) in a Pyrex chamber was studied by measuring the total pressure as a function of time. The reaction was found to be first order and homogeneous, with  $\text{CH}_4$ , CO, and  $\text{H}_2$  as products. The reaction exhibited a considerable induction period that ranged from 1 to 0.5 min at 717 K (444 °C) to 30 min at 653 K (380 °C). The effects of eleven diluents were studied. Ten of them, e.g., carbon dioxide, carbon monoxide, nitrogen, and neon, depressed the rate, but hydrogen increased it considerably.

The thermal decomposition of ethylene oxide exhibited an induction period and was inhibited by the addition of inert gases [23]. Two assumptions – that ethylene oxide mainly isomerizes to acetaldehyde but at the same time produces free radicals that induce chain decomposition of the acetaldehyde, and that the recombination of methyl radicals requires a third body – led to expressions for the length of the induction period and the pressure change during the decomposition experiment that were in qualitative agreement with results from previous investigators.

The rate of EtO decomposition was measured in a Pyrex vessel between 708 and 778 K (435–505 °C) using methods generally similar to those used by Heckert and Mack, and the results agreed quite well with previous data [24, 25]. It was noticed, however, that the total pressure increase for complete reaction fell below 100% at greater temperatures or pressures, with the minimum value being slightly less 80% at 778 K (505 °C). This was explained as being the result of a polymerization process occurring simultaneously with the decomposition. A solid product was formed at high temperatures that subsequently decomposed slowly. See also [26, 27].

The rate of disappearance of EtO and the rate of formation of decomposition products can be monitored by IR absorption spectrophotometry [28].

The thermal decomposition of ethylene oxide in a stream of helium was analyzed by a mass spectrometer [29]. The decomposition of 1 mol of ethylene oxide created 0.6 mol of methyl free radicals.

The thermal decomposition of ethylene oxide vapor was studied in the temperature range from 623 to 713 K (350–440 °C) and at pressures from 24 to 58 kPa (180–440 mm Hg) [30–32]. The disappearance of ethylene oxide was determined by analyzing the unreacted ethylene oxide. In agreement with previous investigations, the experiments indicated that the reaction is approximately first order. The rate at 673 K (400 °C) was reduced to 46% of its normal value by the addition of propylene, which acted as a free-radical scavenger. The reaction in the presence of propylene was first order. The activation energies for the reactions with and without added propylene were 240 and 220 kJ/mol (57.4 and 52.7 kcal/mol), respectively. Formaldehyde, acetaldehyde, and acrolein were detected in small quantities in the reaction products. When the surface:volume ratio in the reactor vessel was increased, the reaction mechanism remained unchanged.

In a flow reactor designed for the study of reaction kinetics at high temperatures, the rates of decomposition of ethylene oxide were measured up to temperatures approaching its adiabatic decomposition temperature (~1200 K) [33–36]. The reaction process was followed not by the freezing (quenching) technique usually employed in flow systems, but by tracing the temperature history of the reaction. The ethylene oxide decomposition study showed that the kinetics followed a first-order mechanism overall, and the overall activation energy was  $176 \pm 8$  kJ/mol ( $42 \pm 2$  kcal/mol). The results were independent of the amount of fuel injected, the velocity of the inert carrier gas, and the inert gas itself. A free-radical decomposition mechanism consistent with the experimental results was postulated.

It was postulated that the pyrolysis of EtO proceeds via internal isomerization (similar to that of isoelectronic cyclopropane) to form an excited  $(\text{CH}_3\text{CHO})^*$  molecule [37]. It was estimated that the excess energy of this molecule is about 356 kJ (85 kcal), which is about 29 kJ (7 kcal) in excess of the C–C bond dissociation energy in an unstrained molecule such as  $\text{CH}_3\text{CHO}$ . The lifetime of  $(\text{CH}_3\text{CHO})^*$  for bond fission is very short, so it is predominantly quenched at  $P \geq 26.7$  kPa (200 mm Hg). Analysis of the chain mechanism indicated a chain length of between one and two with the production of a “hot”  $\cdot\text{CH}_2\text{CHO}$  radical formed by exothermic ring opening of EtO. This is likely to be quenched but may decompose spontaneously to  $\text{H}_2\text{C}=\text{CO} + \cdot\text{H}$ . Published data on high-temperature reactions (1100 K) give absolute rates in reasonable accord with the 700 K reaction. The lower values of  $E_{\text{act}}$  found at the higher temperatures may not be reliable. Data on the pyrolysis of a similar oxirane, propylene oxide, were in good agreement with this model.

The homogeneous decomposition of EtO was studied in a steady-flow microreactor constructed of gold and operated differentially at atmospheric pressure and from 763 to 963 K (490–690 °C) [38]. The reactant was diluted with more than 70% helium to prevent runaway reactions. The conversion of EtO was kept to below 10%. Space velocities were varied from 0.7 to  $23 \text{ s}^{-1}$ , and EtO partial pressures were varied from 2.27 to 94 kPa (17–705 mm Hg). Decomposition products included acetaldehyde, CO,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{H}_2$ , and traces of  $\text{C}_3\text{H}_8$ . The pre-exponential factor of  $2.4 \times 10^{13} \text{ s}^{-1}$  is what

one would expect for a unimolecular reaction. The activation energy of 226 kJ/mol (54 kcal/mol) is consistent with isomerization of EtO to an excited acetaldehyde fragment  $\text{CH}_3\text{CHO}^*$ , which either decomposes unimolecularly to methyl and formyl radicals or collides with the wall and rids itself of excess energy to become acetaldehyde, which decomposes further. The activation energy for ring opening of EtO is 218 kJ/mol (52 kcal/mol).

Decomposition waves in liquid ethylene oxide were investigated both theoretically and experimentally with an emphasis on near-critical conditions, where the liquid surface within the wave approaches its thermodynamic critical point [39]. Wave velocities, temperature distributions, and sample conditions required for ignition were measured for pressures of 2.4–24 MPa. Predictions were made of flame properties, liquid surface conditions, and critical combustion conditions. Laminar waves were observed for pressures of 6–16 MPa, and turbulent waves were observed at higher pressures. In the laminar regime, wave velocity was a linear function of pressure, indicating a global second-order reaction. Heated or fused wires were used as ignitors since ignition energies were in excess of 8 J. Film boiling occurred along the wires prior to ignition for subcritical conditions. Both predictions and measurements indicated that critical liquid-phase combustion occurs at pressures of 12–16 MPa, which also corresponds to the pressure range where that sample temperatures required to initiate decomposition abruptly decrease. Reduced convective heat loss from the ignitor in the near-critical region was suggested as the mechanism for this behavior.

### Computational Chemistry Studies of Ethylene Oxide Decomposition

The unimolecular decomposition of ethylene oxide (oxirane) and the oxiranyl radical was examined by molecular orbital calculations and detailed kinetic modeling of ethylene oxide pyrolysis in a single-pulse shock tube [40]. It was found that the largest energy barrier to the decomposition of ethylene oxide lies in its initial isomerization to form acetaldehyde, and, in agreement with previous studies, the isomerization was found to proceed through the  $\cdot\text{CH}_2\text{CH}_2\text{O}\cdot$  biradical. Because of the biradical nature of the transition states and intermediate, the energy barriers for the initial C–O rupture in ethylene oxide and the subsequent 1,2-H shift remain highly uncertain. An overall isomerization energy barrier of  $247 \pm 8$  kJ/mol ( $59 \pm 2$  kcal/mol) was found to satisfactorily explain the available single-pulse shock tube data. This barrier height is in line with the estimates made from an approximate spin-corrected procedure. The dominant channel for the unimolecular decomposition of ethylene oxide was found to form  $\cdot\text{CH}_3 + \text{HC}\cdot\text{O}$  at around the ambient pressure. This accounts for >90% of the total rate constant for  $T > 800$  K. The high-pressure limit rate constant for the unimolecular decomposition of ethylene oxide was calculated as

$$k_{1,\infty} = (3.74 \times 10^{10}) T^{1.298} e^{(-29990/T)} \quad \text{s}^{-1}$$

for  $600 < T < 2000$  K.

### 1.3.2.2 Effects of Contaminants on Decomposition of Ethylene Oxide

Catalysts and contaminants (alkaline substances, acids, Lewis acids, anhydrous  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{SnCl}_4$ ) catalyze the spontaneous decomposition and exothermic polycondensation of EtO. Accidental contact of liquid EtO with such substances must be avoided because it could cause explosive rupture of the storage vessel [41].

Rust is everywhere, so the chances are that rust will accidentally find its way into any ethylene oxide system. Samples of various iron oxides suspended above ethylene oxide in an adiabatic calorimeter exhibited exothermic activity at temperatures as low as room temperature [42]. A  $\gamma\text{-Fe}_2\text{O}_3$  sample was found to show the highest reactivity with ethylene oxide. When in contact with most of the iron oxide fines tested, ethylene oxide displayed exothermic activity below 373 K (100 °C). Self-heating rates near 2000 °C/min were observed for the  $\gamma\text{-Fe}_2\text{O}_3$  fines, while rates in excess of 100 °C/min were found for other fines ( $\alpha\text{-Fe}_2\text{O}_3$  and hydrated  $\alpha\text{-Fe}_2\text{O}_3$ ). In two cases ( $\alpha\text{-Fe}_3\text{O}_4$  and  $\alpha\text{-Fe}_2\text{O}_3$ ), pressurization rates were above 1000 psi/min. Some of these iron oxides might be useful as catalysts for ethylene oxide decomposition reactors in gas generators or rocket engines.

The reactivity of ethylene oxide (EtO) with contaminants such as potassium hydroxide (KOH), sodium hydroxide (NaOH), and ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was measured using an automatic pressure tracking adiabatic calorimeter (APTAC) [43, 44]. Each contaminant was investigated using three different concentration levels of around 0.10, 0.50, and 1.0 g in roughly 14 g EtO. KOH, NaOH, and  $\text{NH}_4\text{OH}$  had significant effects on EtO thermal stability. Lowering of the onset temperature was observed as the contaminant concentrations were increased.  $\text{NH}_4\text{OH}$  caused the highest reactivity compared to the other contaminants. KOH reduced the onset temperature of pure EtO to near room temperature, even at a low concentration.

An investigation of the reactivity of EtO with various contaminants, including water, different kinds of iron oxides, and alkalis, showed that pure EtO is not prone to initiating a runaway reaction below 473 K (200 °C) under adiabatic conditions, that the possibility that an EtO aqueous solution will experience an exothermic reaction depends strongly on the EtO concentration, and that the onset temperature could be predicted by a fourth-order reaction rate model [45]. EtO exhibited different sensitivities to various kinds of iron oxides. Although  $\gamma\text{-Fe}_2\text{O}_3$  was the most active iron oxide in contact with EtO, its runaway reaction consequence was less severe. The order of reactivity of EtO with iron oxides was  $\gamma\text{-Fe}_2\text{O}_3 > \alpha\text{-Fe}_3\text{O}_4 > \text{hydrated } \alpha\text{-Fe}_2\text{O}_3 > \alpha\text{-Fe}_2\text{O}_3$ . Alkaline materials at sufficient concentrations reduced the initial reaction temperature of EtO to room temperature, and the order of hazard potential for alkalis was:  $\text{NH}_4\text{OH} > \text{KOH} > \text{NaOH}$ .

The unwanted polymerization of EtO can be retarded or prevented by antioxidants [46].

### 1.3.2.3 Catalytic Decomposition of Ethylene Oxide

For the frequently proposed but rarely observed application of ethylene oxide as a monopropellant gas generant or rocket propellant, it would be very useful to have a catalyst that enhances the decomposition of ethylene oxide or even initiates the decomposition at room temperature. Unfortunately, no such catalyst has been identified up to now. The majority of publications on EtO decomposition deal only with homogeneous gas-phase decomposition in the absence of catalysts.

Where ethylene oxide is used for sterilization of medical equipment, the gases leaving the sterilization chambers and vented above the roof have to pass through a catalytic incinerator, where ethylene oxide is destroyed by reaction with excess air. Catalytic incinerators have been the source of ignitions and have caused numerous accidents where combustion has propagated upstream into the sterilization chambers. Catalysts for ethylene oxide incineration with an excess of oxygen in air are different from catalysts aimed at decomposition of EtO as a monopropellant.

Nickel (supported on amorphous Raney nickel or as a single crystal) can decompose ethylene oxide. The adsorption and decomposition of ethylene oxide on single crystals with Ni(110) surfaces at 95–350 K was investigated by LEED and X-ray and UV photoelectron spectroscopy [47]. Thermal as well as photon-induced decomposition was discovered, with X-rays being about ten times more efficient than UV photons under the chosen experimental conditions. A possible reaction pathway involves intermediates, such as methoxy,  $\text{CH}_x$ , and the final (at  $>300\text{ K}$ ) species, CO and carbon. A further possible intermediate, adsorbed acetaldehyde, appeared to be short-lived on Ni(110).

### 1.3.2.4 Suitable Materials of Construction for Ethylene Oxide Systems

Most metals that are commonly used in construction, except copper, silver, magnesium, and their alloys, are suitable for use in equipment in contact with liquid or gaseous EtO. If hardenable steels and other ferrous alloys are used, one must be very careful to remove all traces of rust before the equipment is put in service. The use of stainless steels and pure aluminum ( $>99.6\%$  Al) is preferred.

Gaskets, flex hoses, valve stem packings, and similar applications will use Teflon, Kel-F, nylon, or polyethylene. Copolymers of polyethylene and polypropylene have shown very good compatibility with EtO. Common hydrocarbon-based lubricants are useless because they dissolve readily in liquid EtO. The verdict about the suitability of perfluorinated halocarbon lubricants is not unanimous. Some rate them as permissible, whereas others warn against the use of Kel-F [48].

Liquid ethylene oxide with carbon disulfide as a stabilizer may corrode the aluminum alloy 61S, which is welded and heat-treated to the T-6 condition, differently from pure EtO [49].

For additional information about elastomeric materials of construction that are suitable for use with EtO, see [50].



## 1.4 Handling of Ethylene Oxide

The safe handling of EtO requires special precautions. The handling of EtO is complicated by a combination of a high vapor pressure at room temperature, a wide range of flammability, low initiation energy, autodecomposition, and toxicity.

Ethylene oxide is used in huge quantities as an intermediate in the chemical process industry, so there is a good experience base upon which recommendations for safe handling of EtO can be based.

Ethylene oxide was once evaluated as a monopropellant for auxiliary power gas generators, and the experience from that experiment was documented to help others understand the hazards of working with this chemical [51]. See also [52].

### 1.4.1 Ethylene Oxide Spill Neutralization

Ethylene oxide spills can be dissolved with lots of cold water. Ethylene oxide vapor clouds can be washed out with water spray. If ethylene oxide is spilled into water in aquatic media, ethylene oxide will degrade by hydrolysis with a half-life of ~12–14 d. Evaporation from aquatic media will also be a significant loss process.

### 1.4.2 Fighting of Ethylene Oxide Fires

Ethylene oxide fires can be extinguished with water, carbon dioxide, or bicarbonate powder fire extinguishers. Water is favorable in that the burning puddle of liquid will soon be diluted below the flash point and will quit burning. A volume of water 22 times the volume of the spilled fuel is needed to dilute the fuel below the flash point. Halon 1301, which is often used for fighting fires in electrical and high-value installations, is not as effective as sodium bicarbonate dry chemical extinguishers, but it is still better than carbon dioxide. Fire-fighting personnel must wear respiratory protection to prevent inhalation of unburnt vapors of EtO.

## 1.5 Safety Properties of Ethylene Oxide

Liquid ethylene oxide is insensitive to initiation by a detonator (blasting cap). Ethylene oxide vapor will detonate when initiated by a detonator, a hot wire, or an electric spark. The limits of flammability in air range from 3 to 100 vol.-% ethylene oxide for upward propagation.

In the absence of air, EtO vapor will decompose exothermally. It has been recommended that EtO containers should be purged with inert gas to prevent the formation of explosive air/EtO mixtures. The inert gas is nitrogen or argon or carbon dioxide.

### 1.5.1 Ignition Energy and Limits of Flammability of Ethylene Oxide in the Absence of Air

Depending on the vessel geometry, the explosive limits in the absence of air will be narrowed by diluent gases. The lower limits of autodecomposition of ethylene oxide initiated by a platinum glow wire in the presence of various diluent gases are summarized in Table 7. The diluent gas should not be very soluble in liquid EtO if the gas is to be used as an inert gas pad on top of the liquid EtO storage container to improve storage safety.

**Table 7:** Lower limits of explosion of ethylene oxide in diluent gases and the solubilities of diluent gases in liquid ethylene oxide.

| Diluent gas    | Limit, vol.-% C <sub>2</sub> H <sub>4</sub> O |                          | Solubility at 202 kPa |
|----------------|-----------------------------------------------|--------------------------|-----------------------|
|                | Lower limit of explosion                      | Upper limit of explosion | Mass%                 |
| Hydrogen       | 25                                            | 100                      | —                     |
| Nitrogen       | 25                                            | 100                      | 0.02                  |
| Carbon dioxide | 18                                            | 100                      | 2.8                   |
| Methane        | 15                                            | 100                      | 0.02                  |

The ignition of EtO decomposition flames in the absence of air was investigated by spark and hot wire ignition techniques [53]. Below a limiting pressure and in narrow tubes, the ethylene oxide decomposition flame fails to propagate. The critical diameter below which the flame extinguishes can be expressed as a function of operating pressure by the following equation:

$$d_q = \frac{10}{p}$$

where  $d_q$  is the critical diameter of extinguishment in mm and  $p$  is the pressure in atm. At atmospheric pressure, the critical diameter is 10 mm. For comparison, the critical diameter of air/methane flames is 1 mm. The minimum spark ignition energy required for EtO decomposition flames is four orders of magnitude higher than that for air/EtO flames. There are several different theoretical methods for predicting the flame speed, flame temperature, and exhaust composition, and some of the results agree quite well with experimental measurements. The theoretical flame temperature is 1600 K. The electrostatic discharge energy required to initiate the monopropellant decomposition of EtO (in the absence of air) is 10000 times greater than the energy required to ignite a stoichiometric air/EtO mix at 1 atm and 298 K.

The explosion limits of EtO/GN<sub>2</sub> mixtures under pressure and preheated to the point of ignition at 723–833 K (450–560 °C) in a pressure bomb were measured as a function of EtO content, temperature, and pressure [54]. The activation energy

was not very dependent on EtO concentration. The induction period was  $< 10$  s and decreased with increasing temperature and EtO content.

When studying the ignition properties of EtO at high pressure, the ignition of EtO was examined near heated vertical surfaces under natural convection conditions, where the materials were heated in excess of the thermodynamic critical pressure [55].

At very high pressures, many materials become detonable that ordinarily are considered safe to handle. Decomposition waves in liquid EtO were investigated both theoretically and experimentally with an emphasis on near-critical conditions, where the liquid surface within the wave approaches its thermodynamic critical point [39]. Wave velocities, temperature distributions, and sample conditions required for ignition were measured for pressures up to 24 MPa. Laminar waves were observed for pressures of 6–16 MPa, and turbulent waves were observed at higher pressures. In the laminar regime, wave velocity was a linear function of pressure, indicating a global second-order reaction. Heated or fused wires were used as ignitors since ignition energies were in excess of 8 J. Under subcritical conditions, film boiling occurred along the wires prior to ignition. Measurements confirmed predictions that critical combustion occurs at pressures of 12–16 MPa.

In an effort to obtain data on explosive limits for EtO/nitrogen explosions beyond the published data range, additional tests were conducted at temperatures from 333 to 463 K (60–190 °C) and pressures in the range 69–551 kPa (10–80 psig) [56]. Initial measurements showed that the limits for the EtO/GN<sub>2</sub> system are very dependent on the type of ignition source. Hot wire ignition gave very erratic responses. Induction coil sparks were not satisfactory due to inadequate energy and uncertain gap breakdown at elevated pressure. High-energy capacitive discharges across an exploding bridge element gave responses that were reproducible and judged to be true and conservative. A graphite fiber was used as the exploding bridge “wire” to avoid metal contamination of the test mixture. Metals are catalysts, but carbon is a product of EtO decomposition anyway. The data showed that the EtO explosive range becomes wider with increasing pressure at the low end of the temperature range. At modest pressures, the directly measured limits at elevated temperature agreed with extrapolations of earlier reported data.

A mathematical equation was developed that expressed the decomposition explosion limits applicable to liquid ethylene oxide storage conditions [57]. This equation can be used to maintain safe operating limits of EtO storage tanks.

An experimental and theoretical investigation of explosive decomposition of EtO at fixed initial experimental parameters ( $T = 373$  K = 100 °C,  $P = 400$  kPa = 4 bar) in a 20-L sphere measured safety-related parameters, namely the maximum explosion pressure, the maximum rate of pressure rise, ignition energy, and the  $K_d$  values for pure EtO and EtO diluted with GN<sub>2</sub> [58]. All these dependencies were quantified in empirical formulas. Additionally, the effect of turbulence on explosive decomposition of EtO was investigated. In contrast to previous studies, it was found that turbulence significantly influences the explosion severity parameters, mostly the rate of pressure

rise. Thermodynamic models were used to calculate the maximum explosion pressures of pure and of nitrogen-diluted EtO at different initial temperatures. There was a relation between the amount of soot formed and the explosion pressure.

Explosive limits of the decomposition reactions of mixtures of ethylene oxide, propylene oxide, and nitrogen at temperatures from 373 to 473 K (100–200 °C) and pressures from 100 to 600 kPa (1.0–6.0 bar) were determined by experiment [59]. A comparison with literature data indicated that the results are also applicable to larger vessels and ignition sources with intermediate energy.

Gas phases of EtO and propylene oxide, commonly used for large-scale industrial alkoxylation reactions, can decompose explosively with enormous temperature and pressure rises, even without the presence of air. To estimate the consequences of such runaway reactions, explosion peak pressures and rates of pressure rise of EtO and certain mixtures of EtO and propylene oxide at temperatures between 373 and 473 K (100–200 °C) and pressures between 100 and 1000 kPa (1–10 bar) were determined experimentally using vessels with volumes of 3 L (3 dm<sup>3</sup>) and 100 L (100 dm<sup>3</sup>) [60]. See also [61].

Carbon dioxide is most frequently used to inert ethylene oxide and ethylene oxide/air mixtures, but large amounts of carbon dioxide are required to render such gas mixtures non-flammable and non-detonable. The limits of flammability of the ternary system air/ethylene oxide/carbon dioxide were determined by experiment [62].

### 1.5.2 Autoignition Temperature of Ethylene Oxide in Air

The very low ignition energy of EtO in air makes mixtures prone to electrostatic discharge ignition. Its large burning velocity and flammable range make flame acceleration likely under conditions of confinement or in the presence of obstacles. Acceleration is not seen in free-air deflagration. The autoignition temperature (AIT) depends on the vessel volume and surfaces. Using the ASTM method, EtO has an AIT of 718 K (445 °C). Acetaldehyde, an isomer of EtO, has an AIT of 468 K (195 °C). The presence of acetaldehyde is important for lowering the ignition temperature. Acetaldehyde may be catalytically produced by isomerization from EtO on surfaces. Rust may form hotspots for ignition.

### 1.5.3 Explosive Limits of Ethylene Oxide Decomposition in the Absence of Air

The explosive decomposition of EtO when ignited by a melting, exploding 31-gauge Nichrome wire was studied as a function of the diluent gas and pressure [63]. The cylindrical stainless steel explosion vessel used in this investigation had an internal diameter of 11.4 cm (4.5 in.) and an internal volume of 2.44 L (148.9 in.<sup>3</sup>). It was designed for a maximum dynamic pressure of 10.34 MPa (1500 psig). The use of an inert gas to maintain a non-explosive vapor-phase mixture is the only reliable method of preventing an EtO explosion from ignition sources within a vessel. Although propane and butane were most effective in suppressing the explosive decomposition of EtO,

in practice their use is restricted because of their solubility in liquid EtO. The proportion of nitrogen needed to suppress the explosibility of EtO at a partial pressure of 827 kPa (120 psia) and 398 K (125 °C) is 65 vol.-%. However, a small amount of oxygen or an increase in the partial pressure of EtO vapor will raise this figure; hence, in practice it might be necessary to increase the proportion of nitrogen to ~75 vol-% N<sub>2</sub> to cover these contingencies. This procedure necessitates designing a vessel to withstand a working pressure about four times the initial partial pressure of the EtO vapor. Ammonia, steam, propylene oxide, carbon dioxide, and methanol were also tested as explosion suppressants [64].

The boundaries for explosive decomposition of EtO and EtO/GN<sub>2</sub> mixtures in a cylindrical 1.4-L pressure bomb were determined as a function of pressure, temperature, and vapor composition [65]. See also [66–68].

Some studies have indicated that ethylene oxide explosions may propagate through vapor/liquid mixtures. The thermal decomposition limits, autoignition temperatures, and minimum ignition energies of liquid and gaseous EtO were measured under a variety of realistic conditions in equipment simulating pipes in a chemical factory subjected to heating by external fires [69, 70]. This was the most comprehensive examination of conditions leading to EtO accidents. It was shown that flame propagation through liquid-filled lines may occur via decomposition of vapor pockets. The following was concluded as the result of a very detailed experimental test program. In the case of EtO vapor deflagration, the deflagration produces a maximum pressure ratio of about 12:1. The pressure ratio decreases with increased initial temperature and surface-to-volume ratio of the container. It increases with increased initial pressure. The pressure ratio can be greatly increased in the presence of EtO mist or spray. A flame above condensed liquid may cause some liquid decomposition. At certain elevated temperature and pressure combinations, the flame will propagate directly into the liquid phase (!). Tubular bundle flame arrestors can be effective in quenching decomposition flames. In the absence of air, EtO has a relatively high autodecomposition temperature (ADT) of about 723 K (450 °C) in small equipment such as pipes with diameters of less than 4 in. High nitrogen dilution has little effect on the ADT. However, proper inerting will prevent flame propagation from the initiation site. Decomposition is difficult to initiate from point sources under normal storage or handling conditions. EtO is not prone to static ignition or steel–steel impact sparks of short duration. Decomposition may be initiated by reactive hotspots such as rust at temperatures well below the ADT. The mechanism may involve either polymerization or isomerization. For EtO liquid deflagration, point source ignition requires severe temperature and pressure combinations. Under fire exposure conditions, establishment of a vapor decomposition zone in a pipeline may allow flame propagation in a liquid-filled line. If a high pressure is generated, then a transition to a true liquid decomposition may occur. Based on tests in an accelerating rate calorimeter in a titanium bomblet, pure EtO requires about 473 K (200 °C) to initiate a runaway reaction under adiabatic conditions. The reaction

involves isomerization and aldol condensation reactions. The runaway reaction threshold temperature is greatly reduced by water and miscellaneous initiators. Solid catalysts that facilitate ignition include iron oxide, aluminum oxide, and various types of insulation, particularly asbestos and calcium silicates.

Undiluted EtO vapor may propagate decomposition flames through a pipe above certain minimum conditions of temperature, pressure, and pipe diameter. Flame propagation was studied in both closed and vented 5-cm (2-in.) diameter pipe and closed 30-cm (12-in.) diameter pipe [71]. Flame progression in a closed pipe was irregular and proceeded in pulsed stages. A possible mechanism involves preferential flame propagation at the pipe roof accompanied by periodic autodecomposition of EtO that accumulates in hot products behind the flame front, with the accumulation probably augmented by liquid EtO that has condensed on the pipe walls ahead of the expanding flame system. Flames propagated 15 m (50 ft) through a horizontal 5-cm pipe at 323 K (70 °C) and at initial pressures  $\geq 4.3$  bar (62 psia). In a series of 30-cm pipe tests employing low-energy ignition and otherwise increasingly severe conditions, a deflagration-to-detonation transition (DDT) occurred, partially destroying the test equipment. Two EtO detonations at 2.9 bar and one at 3.5 bar were directly initiated via strong shocks from hydrogen–oxygen detonations used as a donor section.

#### 1.5.4 Adiabatic Compression Sensitivity of Liquid Ethylene Oxide

Whereas other organic monopropellants, e.g., propyl nitrate or acetylene, are susceptible to detonation initiated by adiabatic compression or local cavitation in turbulent flow at sharp corners, liquid EtO is stable even if rapidly compressed at 1362 atm/s (20000 psi/s) or in turbulent flow in sharp-edged orifices [72]. Even in the presence of small inert gas bubbles, it cannot be initiated by adiabatic compression. The sample holder cell had a diameter of 12.2 mm and held 2 mL of sample liquid.

When tested in stainless steel tubes with 63 mm (2.5 in.) O.D., 13.3 mm (0.52 in.) wall thickness, and 16.5 cm (6.5 in.) length with a 100-g tetryl charge as the donor, liquid ethylene oxide at 276 K (3 °C) was partially detonable (incomplete propagation), and it was suspected that at higher temperatures the detonation might have propagated the entire length of the tube [73].

#### 1.5.5 Adiabatic Compression Sensitivity of Ethylene Oxide Vapor

Conditions leading to spontaneous ignition of ethylene oxide vapor were explored in circumstances where the vapor was subjected to rapid compression and heating due to adiabatic compression [74]. Experiments were carried out using a rapid compression apparatus on dilute mixtures of ethylene oxide in argon, and on systems containing varying amounts of added oxygen. The total initial pressure was varied from 13 to 50 kPa and the compression ratio from ca. 10:1 to ca. 12:1. Pressure–time histories were measured, and gas temperatures were derived from them. Emitted light intensities were recorded and overall compositions were measured by mass spectrom-

etry. Decomposition occurred rapidly at temperatures of about 850 K and the exothermicity exceeded 100 kJ/mol. Ignition of ethylene oxide was possible in the mixture of  $1\text{C}_2\text{H}_4\text{O} + 20\text{Ar}$  when compression was more than 11-fold. A typical ignition delay was 5 ms. Trace amounts of added oxygen enhanced the reaction rate and the extent of self-heating. With roughly equal amounts of ethylene oxide and oxygen, ignition occurred in circumstances where none would be possible in the absence of oxygen, and the delay was very short ( $< 2$  ms). The results showed that small amounts of ethylene oxide ( $< 1$  vol-%) in air are a potential explosion hazard if modest but rapid compression occurs.

Compressing ethylene oxide vapor mechanically by a mechanical piston apparatus is a slow process compared to compression of ethylene oxide vapor in a shock tube. Shock tube compression is a useful method to measure decomposition kinetics because the temperature can be increased quickly to a pre-set value. The decay of the reactants is then measured spectroscopically. The pyrolysis of ethylene oxide highly diluted in argon was studied behind reflected shocks in a single-pulse shock tube at 830–1200 K, and total pressures behind the shocks varied between 1.5 and 10 atm [75]. The rate of production of the various reaction products varied by up to four orders of magnitude over this temperature range. The concentrations of  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_3\text{H}_8$ ,  $\text{CH}_3\text{CHO}$ , and  $\text{H}_2$  were determined as a function of temperature, total density, and initial ethylene oxide concentration. It was shown that the main channel for pyrolysis is ethylene oxide–acetaldehyde isomerization, yielding methyl and formyl radicals as well as methane and carbon monoxide upon decomposition. The formation of ethylene and acetylene could not be explained on the basis of the isomerization channel. Rupture of the C–O bond in ethylene oxide by H-atom substitution was suggested to account for the production of these products.

Ignition delay times in ethylene oxide/oxygen/argon mixtures behind a reflected shock were measured in a 24.3-mm diameter shock tube [76]. The shock-tube driver section gas was pure helium. Nine different test gas mixtures with various concentrations of argon were prepared so that its effect on the reaction rate of the ignition could be evaluated. In all of the experimental runs, the initial pressure of the test mixture in the driven section was 13.3 kPa (100 mm Hg), except for mixtures with high concentrations of EtO, where the initial pressure was fixed at 7.5 kPa (56 mm Hg).

## 1.6 Accident History of Ethylene Oxide

Numerous accidents have occurred during the use of EtO. The chemical industry and their insurance companies have combined their efforts to prevent future accidents of this type [77].

The occasional occurrence of EtO explosions during the fumigation of dried fruit led to detailed studies of the combustion characteristics of the vapor [78]. The spontaneous ignition temperature is similar to that of acetaldehyde. Cool flames can be ini-

tiated in air/EtO mixtures in the neighborhood of 603 K (330 °C) at atmospheric pressure.

In the literature there are many more descriptions of industrial accidents with ethylene oxide [79]. The most serious accident, which occurred on 24 June 1997 at Accra Pac, an ethylene oxide re-packager in Elkhart, IN, killed one worker and injured 69 others.

Ethylene oxide is widely used as a sterilizing agent for medical and food applications and products. However, due to its broad range of flammability in air, this gas presents a particularly serious explosion hazard, which is compounded by extremely stringent and ever-increasing requirements for pollution control equipment. Many pollution control devices contain potential ignition sources, such as open flames or hot catalysts, that could trigger an explosion. An explosion that caused extensive damage at a sterilization facility in the United States in August 2004 occurred as workers were attempting to troubleshoot one of their sterilization chambers and consequently bypassed safety interlocks while evacuating the gas [80, 81]. This allowed a flammable mixture to enter an ethylene oxide incineration unit that utilized an open flame to pre-heat waste gases before they passed through a catalytic oxidizer bed. The resulting deflagration propagated through the ductwork and back into the sterilization chamber, which exploded. Alert notices and safeguard instructions have been issued to prevent any further accidents of this type [82].

## 1.7 Toxicity of Ethylene Oxide

At low concentrations, the odor of ethylene oxide is similar to that of ether, but at higher concentrations it will irritate the mucous membranes and the respiratory tract [51]. The threshold for the onset of irritation is 50 ppm by volume (90 mg/m<sup>3</sup>).

Long-term inhalation of EtO below the irritation threshold causes headache, nausea, and vomiting. Generally, these symptoms subside within 24–36 h after the victim is moved to fresh air. The sensitivity of victims to renewed exposure is increased in the case of recurring exposure to vapors of this propellant. Repeated exposure to lower concentrations can cause chronic respiratory irritation, anemia, and some damage to the liver and kidneys. Inhaled ethylene oxide induced pre-neoplastic foci in rat liver [83].

In acute studies in laboratory animals, the LC<sub>50</sub> values for inhalation exposure (rats, mice, and dogs) ranged from 835 to 5000 ppm for a 4-h exposure, and the oral LD<sub>50</sub> value (rabbits, guinea pigs, and rats) ranged from 100 to 631 mg/kg body weight.

Inhalation of 5–10 vol.-% EtO in air was fatal to guinea pigs within a few minutes. Liquid EtO spilled on skin can cause serious skin burns if the chemical is not immediately washed off with lots of water. Aqueous solutions of EtO are highly irritating to the skin and may sensitize it to future exposures.



### 1.7.1 Ethylene Oxide Permissible Exposure Limits in Air

Conversion factor: 1 ppm = 1.80 mg/m<sup>3</sup> at 25 °C and 1 atm.

NIOSH IDLH: 800 ppm

OSHA PEL: 1 ppm/5 ppm (15 min excursion)

TWA, cancer hazard, suspected human carcinogen [84]

NIOSH REL: 0.1 ppm = 0.18 mg/m<sup>3</sup>

TWA: 5 ppm = 9 mg/m<sup>3</sup> (<10 min/day) ceiling concentration

Potential carcinogen. Limit exposure to lowest feasible level, see *NIOSH Pocket Guide*, Appendix A [85].

ACGIH TLV: 1 ppm = 1.8 mg/m<sup>3</sup>

Protective Action Criteria (PAC)

TEEL-0: 1 ppm

PAC-1: 5 ppm

PAC-2: 45 ppm

PAC-3: 200 ppm

The chosen IDLH of 800 ppm was based on the observation that the estimated LC50 for a 4-h exposure was approximately 800–1500 ppm, depending on the species. It was stated that for humans, 500 ppm is probably safe for single exposures (no more than once per week) of 1 h duration [86, 87].

### 1.7.2 Harmful Effects and Symptoms of Ethylene Oxide Exposure

**Short-Term Inhalation Exposure:** Signs and symptoms of acute exposure to ethylene oxide may be severe and include dyspnea (shortness of breath), cough, pulmonary edema, pneumonia, and respiratory failure. Lethargy, headache, dizziness, twitching, convulsions, paralysis, and coma may be observed. Cardiac arrhythmias and cardiovascular collapse may also occur. Gastrointestinal effects of acute exposure may include nausea, vomiting, and abdominal pain. Ethylene oxide irritates the eyes, skin, and respiratory tract. Very high exposures can cause pulmonary edema, a medical emergency that can remain unrecognized for several hours.

**Inhalation:** Acute exposure to EtO gas may result in respiratory irritation and lung injury, headache, nausea, vomiting, diarrhea, shortness of breath, and cyanosis. Chronic exposure has been associated with the occurrence of cancer, reproductive effects, mutagenic changes, neurotoxicity, and sensitization. Exposure to 500–700 ppm for 2–3 min resulted in nausea, vomiting, headache, disorientation, fluid in the lungs, followed by seizures. Human volunteers breathing a concentration of about 2500 ppm experienced slight irritation of the respiratory tract; breathing in 12500 ppm led to definite respiratory tract irritation within 10 s. Symptoms may not occur for hours after exposure.

**Skin:** The pure liquid may cause frostbite. A 1% water solution can cause irritation and redness. A 40–80% water solution may cause extensive blister formation. Ethylene oxide may severely irritate or burn mucous membranes and moist skin.

**Eyes:** May cause irritation and severe burns. May affect the eyes, causing delayed development of cataract. Eye contact may result in conjunctivitis (red, inflamed eyes) and erosion of the cornea.

**Ingestion:** May cause gastric irritation and liver injury.

**Long-Term Exposure:** Repeated or prolonged contact with skin may cause a skin allergy. EtO may affect the nervous system, kidneys, adrenal glands, skeletal muscles, and cause reproductive effects. It may be carcinogenic to humans. Exposure to low concentrations of gaseous EtO may cause irritation to the respiratory tract and eyes, loss of sense of smell, and nausea and vomiting. Repeated skin exposure can cause scaling, cracking, and redness. Exposure to 5–10 ppm for 11 years or to 1 ppm for 15 years has caused blood changes. EtO has caused cancer in several species of laboratory animals. It has also caused changes in genetic material and reproductive problems in laboratory animals. EtO may damage the developing fetus. It may cause inheritable genetic damage in humans. There is an increased incidence of gynecological disorders and spontaneous abortions among workers in ethylene oxide production.

Case reports of workers exposed repeatedly to ethylene oxide indicated the occurrence of neurotoxicity consistent with sensorimotor neuropathy. Some signs of neuropathy appeared to persist even after cessation of exposure. In occupational epidemiology studies, the non-neoplastic results were reported to be an increase in lymphocyte count, a decrease in hemoglobin value (levels of exposure were not reported), and an increased incidence of deaths resulting from diseases of the circulatory system (exposure level < 50 mg/m<sup>3</sup>).

Ethylene oxide has been shown to induce gene mutations in bacteria, fungi, higher plants, *Drosophila*, and cultured mammalian cells in tests conducted without the use of exogenous hepatic metabolic activation systems. On the basis of the human, animal, and mutagenic data, ethylene oxide is classified as being “probably carcinogenic to humans” and belonging in EPA Group B1. See also [88–90].

## 1.8 Other Applications of Ethylene Oxide

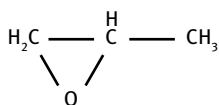
Ethylene oxide is used in the synthesis of hydroxyethylamines and hydroxyethylhydrazine by reaction with ammonia or hydrazine. Trihydroxyethylammonium nitrate (TEAN) was used as a fuel in liquid gun propellants LP-1845 and LP-1846. It is a candidate fuel for hydroxylammonium nitrate-derived monopropellants in rockets, as is hydroxyethylhydrazinium nitrate, which can be made from ethylene oxide and hydrazine hydrate and is used in AF-M315E.

Ethylene oxide is widely used for the sterilization of surgical equipment. Unfortunately, several explosions have occurred in sterilization facilities because the hazardous properties of EtO were not totally understood or the facility was not operated correctly.

For many years, ethylene oxide diluted with carbon dioxide (Oardox) was used for killing insects in grain silos. At the concentrations used, it was also toxic to rats and mice. Per 10CFR § 185, the FDA has only approved ethylene oxide fumigation for raw spices, dehydrated vegetables, and spice blends that do not contain salt.

## 2 Propylene Oxide

Propylene oxide, also known as 1,2-propylene oxide, 2-methyloxirane, 1,2-epoxypropane,  $C_3H_6O$ , CAS RN [75-56-9],  $MW = 58.079$  g/mol, is a homologue of ethylene oxide with similar chemical properties. The oxirane ring adds energy to the propane molecule.



Propylene oxide

A good overview of the production and industrial uses of propylene glycol is published in the encyclopedic literature [91]. Propylene oxide may be co-polymerized with ethylene oxide or tetrahydrofuran to form polyether polymers that are useful as binders in solid propellants. Polyol pre-polymers may consist of propylene oxide oligomers with only a dozen ether linkages. In the chemical industry, most propylene oxide is hydrolyzed to propylene glycol, which is used as an antifreeze and as the starting product for synthesis of propylene glycol dinitrate (see the chapter “Nitrate Esters” in *Encyclopedia of Oxidizers*). It can also be converted to glycerol. Propylene oxide can be reacted with cellulose to make hydroxypropylcellulose. Hydroxypropylcellulose is a gelling agent for hydrazine, MMH, and other hypergolic fuels.

Propylene oxide is the parent compound for glycidyl azide, which, in the polymerized form, is a high-energy binder for solid propellants. Propylene oxide is more thermally stable than ethylene oxide [92].

Because of their reliable ignition and instant detonation, air/propylene oxide mixtures have been used in the donor section of a shock tube for studying DDT detonation transitions in air/isopropyl nitrate mixtures [85].

Propylene oxide is used in fuel-air explosive (FAE) bombs. The flammable range of propylene oxide in air is 2.8–37 vol.-%. Other sources have reported a flammable range of 2.3–36 vol.-% in air. There is no MIL SPEC for propylene oxide. Propylene oxide

could be used as a fuel for bipropellant, pulsed detonation, or rotating detonation engines. Although the combustion [93] and detonation [94] of oxygen/propylene oxide mixtures have been studied, there are no indications that such mixtures have already been used in rocket engines.

As far as the toxicity of propylene oxide is concerned, the OSHA PEL TWA is 100 ppm, and the original NIOSH IDLH of 2000 ppm was lowered to 400 ppm. The reported dog 4-h LC<sub>50</sub> was 2005 ppm and the mouse 4-h LC<sub>50</sub> was 1740 ppm, as cited by NIOSH [87].

### 3 Oxetane Derivatives

Oxacyclobutane, oxetane, is a cyclic ether and is the parent for a number of derivatives of interest as rocket propellant ingredients. Oxetanes are four-membered rings containing one oxygen atom. The simplest oxetane is 1-oxacyclobutane. The energetic groups are usually attached at the 3-position of the oxetane ring. One or two groups can replace the hydrogen(s) at the 3-position. The energetic binders derived from azido oxetane derivatives are called azidated oxetanic polymers.

Oxetane and its derivatives can be polymerized to form polyethers. Lewis acids act as catalysts for this ring-opening reaction. Widely used energetic polymers are formed from 3-nitratomethyl-3-methyloxetane (polyNiMMO), 3,3-bis(azidomethyl) oxetane (BAMO), and azidomethyl methyloxetane (polyAMMO). There will be several sections on these energetic polymeric binders in planned future volumes on solid propellants in the *Encyclopedia of Rocket Propellants*. Energetic polyoxetanes based on BAMO and AMMO were discovered in 1982 [95].

#### 3.1 Nitrooxetanes

3-Nitrooxetane was made by oxidation of 3-aminooxetane. It boils at 350 K (77 °C) at reduced pressures of 0.5–1.0 mm Hg. 3,3-Dinitrooxetane can be made by reaction of the sodium salt of 3-nitrooxetane with silver nitrate or by nitration with tetranitromethane [96]. 3,3-Dinitrooxetane melts at 343–344 K (70–71 °C).

#### 3.2 Azidooxetanes

3-Azidooxetane (AZOX) can be made by reaction of 3-oxetyl tosylate with sodium azide [96]. Distillation of 3-azidooxetane begins at 363 K (90 °C). The polymerization of 3-azidooxetane has given potentially useful difunctional oligomers.

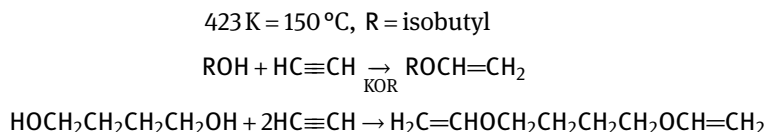
## 4 Other Ethers

### 4.1 Vinyl Alkyl Ethers

Vinyl isobutyl ether, and vinyl ethyl ether, also known by the code name Visol, were used in Germany during WWII as hypergolic fuels with WFNA or RFNA in the WASSERFALL and TAIFUN anti-aircraft missiles. The radar-guided WASSERFALL was a precursor to the American NIKE anti-aircraft missile. HERMES, one of the first liquid-propelled missiles developed by the US Army after WWII, had a striking external similarity to the WASSERFALL. It is unlikely that vinyl ethers will ever again be used as hypergolic fuels, but, in order to provide a complete history of rocket propellants, the production and physical properties of vinyl ethers are discussed here.

#### 4.1.1 Production of Vinyl Alkyl Ethers

Vinyl alkyl ethers can be made from acetylene and alkanols by the Reppe synthesis [97]. Visol-1 (isobutylvinyl ether) and Visol-4 (butanediol-1,4-divinyl ether) were prepared from alcohols and diols via the Reppe technique by reaction with acetylene under high pressure:



The acetylene has to be diluted with nitrogen to prevent explosions at high pressures [98, 99]. Various types of alkyl vinyl ethers can be synthesized by the reaction of alcohols with vinyl acetate under the influence of a catalytic amount of an iridium catalyst combined with  $\text{Na}_2\text{CO}_3$  [100].

#### 4.1.2 Properties of Vinyl Alkyl Ethers

Table 8 shows the properties of two vinyl alkyl ethers that have been used as rocket propellants. Vinyl ethers can be stored at room temperature for only a few months, even when water and acids are carefully excluded. *N,N*-Diethylaniline can be added as a stabilizer.

#### 4.1.3 Applications of Vinyl Alkyl Ethers

Vinyl ethers were used as rocket fuels in Germany during the years 1940–1945. The code name Visol-1 was given to *n*-butylvinyl ether (b.p. at 750 mm Hg: 355 K = 82°C), the code name Visol-2 or -3 was given to isobutylvinyl ether, and the code name Visol-4 was given to butanediol-1,4-divinyl ether (b.p. at 20 mm Hg: 333–338 K =

**Table 8:** Properties of vinyl alkyl ethers.

| Property                                         | Ethyl vinyl ether                                     | Isobutyl vinyl ether                                    |
|--------------------------------------------------|-------------------------------------------------------|---------------------------------------------------------|
| Formula                                          | $\text{C}_2\text{H}_5-\text{O}-\text{CH}=\text{CH}_2$ | $\text{i-C}_4\text{H}_9-\text{O}-\text{CH}=\text{CH}_2$ |
| CAS RN                                           | [109-92-2]                                            | [109-53-5]                                              |
| Freezing point                                   | 158 K = $-115^\circ\text{C}$                          | 161 K = $-112^\circ\text{C}$                            |
| Boiling point                                    | 309 K = $36^\circ\text{C}$                            | 356 K = $83^\circ\text{C}$                              |
| Density at $20^\circ\text{C}$                    | 0.754 g/cm <sup>3</sup>                               | 0.769 g/cm <sup>3</sup>                                 |
| Refractive index ( $n_D^{20}$ )                  | 1.3767                                                | 1.3965                                                  |
| Heat of vaporization ( $\Delta H_{\text{vap}}$ ) | 379 kJ/kg                                             | 332 kJ/kg                                               |
| Flash point in air                               | 228 K = $-45^\circ\text{C}$                           | 258 K = $-15^\circ\text{C}$                             |

Data source: [97]

60–65°C) [101]. Visol-6 was the code name for vinyl ethyl ether. Visols are hypergolic with WFNA and burn softly (no chamber pressure oscillations), similar to turpentine. They can also be mixed with amines to obtain shorter ignition delays.

Visol-1 was used with WFNA in the German WASSERFALL anti-aircraft rocket during WWII. Isobutylvinylether has a boiling point of 355 K ( $82^\circ\text{C}$ ) at 750 mm Hg, and butanediol-1,4-divinyl ether has a boiling point of 333–338 K = 60–65°C at 20 mm Hg. The Visol that was used in the small TAIFUN rocket was incorrectly described as a “mixture of hydrocarbons” [102].

## 4.2 Triethylene Glycol Dimethyl Ether

The Gelled Propellants Laboratory at Purdue University has tested the ignition of HTP with  $\text{NaBH}_4$ /triglyme (triethylene glycol dimethyl ether) as fuel, so one can assume that  $\text{NaBH}_4$ /triglyme is one of the fuel A or fuel B combinations quoted by other Purdue researchers [103].

Triglyme, triethylene glycol dimethyl ether,  $\text{C}_8\text{H}_{18}\text{O}_4$ , 2,5,8,11-tetraoxadodecane, 1,2-bis(2-methoxyethoxy)ethane, dimethyltriglycol, CAS RN [112-49-2], is a clear liquid with a density of 0.986 g/cm<sup>3</sup>, a freezing point of 227 K ( $-46^\circ\text{C}$  =  $-51^\circ\text{F}$ ), and a boiling point of 489 K ( $216^\circ\text{C}$  =  $421^\circ\text{F}$ ) at atmospheric pressure.

## 4.3 Methyl *tert*-Butyl Ether

In the 1990 Clean Air Act Amendments, Congress mandated the addition of oxygenated fuels to gasoline to reduce toxic emissions and improve air quality in urban areas. Besides ethanol, the main oxygenated fuel additive was methyl *tert*-butyl ether, which has the advantage that it also improves the octane rating of gasoline and can be made in refineries instead of corn fermentation plants. Methanol and

isobutylene can be reacted over catalysts to produce methyl *tert*-butyl ether, MTBE. MTBE was used as a gasoline additive (anti-knock enhancer) but ended up polluting the groundwater. MTBE was introduced to reduce air pollution, but its use has created another environmental problem: contamination of groundwater and drinking water wells. Many states have banned the use of MTBE in gasoline, pointing out that the same reduction in automobile emissions can be achieved with ethanol as the oxygenate. Because MTBE is readily available, and because it is a good solvent for hypergolizing additives, it could be used as a rocket fuel.

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# Heterocyclic and Heterocycloaliphatic Amines

## Introduction

*Encyclopedia of Liquid Fuels* contains three chapters on amines: “Aliphatic Amines,” “Aromatic Amines,” and “Heterocyclic and Heterocycloaliphatic Amines.” The current chapter on Heterocyclic and Heterocycloaliphatic Amines is the largest of the three. Amines are used as rocket fuels and as raw materials for the synthesis of other fuels and energetic compounds. A different type of amine are the nitramines described in the chapter “Nitramines.”

## 1 Heterocyclic and Heterocycloaliphatic Amines

There are several reasons behind the widespread interest in the diverse chemistry of heterocyclic compounds, with focus especially being on potential rocket propellants, gas generants, and explosive applications. Initially, the interest lay mostly in high-nitrogen compounds for gas generants such as that in airbag inflators, with 5-aminotetrazole being the leading candidate in this application.. The search for less sensitive replacements for 1,3,5-trinitro-1,3,5-hexahydrotriazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) (themselves heterocyclic compounds) has driven many investigations into other nitrogen-containing ring systems. Many of the **High-Energy-Density Material** (HEDM) compounds listed in this chapter on heterocyclic compounds predominantly behave as explosives. Nonetheless, they are listed in this book on rocket propellants because, while they are detonable in their pure state, they can be incorporated in rocket propellant formulations similar to nitramine propellant formulations based on RDX. RDX is an explosive but many nitramine solid propellants safely incorporate a limited amount of RDX in their formulations. A similar approach is possible by using many of the energetic compounds described in this chapter in place of, or in addition to, RDX.

If the title of this book could be expanded, it would read “Encyclopedia of Liquid Fuels, Rocket Propellants, and Other Energetic Materials” since much of the information on other energetic materials is provided in this chapter. Although most of the HEDM energetic materials that will be discussed do not qualify as rocket propellants, we have attempted to include them here nevertheless to demonstrate the relationships between chemical structures, energy content, and sensitivity. The boundaries between a less sensitive and poor explosive and an excessively sensitive but overly energetic rocket propellant are not well defined. Many rocket propellant chemists, in the search for more energetic rocket propellants, unwittingly ended up with an explosive instead. We therefore will venture into this area, always keeping safety in mind.

Of the hundreds of chemical compounds listed in this chapter, only very few will ever advance to the level of industrial production and widespread applications in rocket propellants. The process of developing, characterizing, and eventually selecting a few outstanding performers in this group of chemicals for rocket propellant applications has kept chemists busy for half a century and promises to do so for a few more years to come.

Most of the compounds described in this chapter are solids; this chapter, therefore, is rather misplaced where it is currently located (in *Encyclopedia of Liquid Fuels*). However, as most heterocyclic energetic compounds do not qualify as solid binders for solid propellants, they would be misplaced within a volume on solid propellant binders (fuels) too.

The parent compounds of families of energetic materials (the heterocyclic amines described at the entrance of each section) are not used as rocket propellants as such. They only serve as the skeleton to which functional groups are attached in an effort to obtain energetic materials or ionic liquids suitable as rocket propellants.

Only during the past 25 years has the search for ionic liquids added a new twist to heterocyclic chemistry. Ionic liquids (ILs) can be used as monopropellants by themselves, as fuels for monopropellants with other oxidizers (e.g., hydroxylammonium nitrate, HAN) and as fuels for hypergolic bipropellant combinations in an effort to find a non-volatile replacement for methylhydrazine (MMH). A separate chapter describes the chemistry and applications of ionic liquids (*Encyclopedia of Liquid Fuels*, “Ionic Liquids” chapter), although there is some overlap between the former and the chapter at hand.

While much work with solid heterocyclic compounds was directed at less sensitive, thermally more stable energetic materials, other efforts aimed in the opposite direction, looking for replacements for lead azide as a primer explosive. The first stab-sensitive heterocyclic compound in this category was tetrazene (tetracene), however, several other primary explosive compounds have been discovered since then, including some in the form of metal (non-toxic, non-lead) salts of heterocyclic compounds. These can serve as non-toxic replacements for lead azide and mercury fulminate.

Although the unsubstituted heterocyclic parent compounds are not very useful as propellant ingredients, we have included them in this book to better understand the effects of substitution on the rings on thermal stability, chemical reactivity, and enthalpy of formation of these molecules. The substituents most often attached to heterocyclic rings are nitro, nitramino, azido, hydrazino, difluoroamino, and amino groups (preferably explosophoric groups). Hopefully, with this fundamental understanding, we are becoming more knowledgeable in this area. Moreover, with continuing advances in computational chemistry, one will be able to create “designer explosives” or “designer energetic materials” as rocket propellant ingredients. It may be as simple as clicking on a computer screen before going to the laboratory and mixing the relevant ingredients in an attempt to accomplish the hands-on synthesis of energetic ingredients.

Heterocyclic compounds with nitro, nitramino, difluoroamino, trinitromethyl, or oxo groups as substituents are candidates for explosives. Other heterocyclic compounds with amino, hydrazino, cyano, azido or alkyl groups are candidates as high-nitrogen compounds and fuels. There are a few good summaries available regarding the use of heterocyclic compounds as propellant ingredients [1–3]. These will need to be updated frequently and continuously to keep up with the progress of developments in this area.

This chapter on heterocyclic amines is one of the most complex in this book due to the inclusion of a very large number of different chemical compounds. It is difficult to organize this amount of information in a systematic manner. While other chapters on energetic compounds in this book were arranged by the increasing number of carbon atoms in the molecule, we chose the total number of atoms in the heterocyclic ring and the increasing number of nitrogen and oxygen heteroatoms as the ordering system for the following sections on heterocyclic compounds. This sorting scheme lists the number of carbon atoms in decreasing order as more and more carbon atoms in the ring structure are replaced by nitrogen (or oxygen in a few cases). The increased nitrogen content makes the compounds more energetic and more suitable as ingredients in gas generants, e.g., in airbag inflator gas generators.

Many heterocyclic compounds occur naturally in alkaloids, medicinal herbs, and amino acids, and coal tar also. Consequently, the main applications of heterocyclic compounds are in pharmaceutical products and in synthetic dyes. Many heterocyclic compounds have aromatic resonance structures similar to benzene. The most common heterocyclic amine is pyridine, often found as a contaminant in benzene derived from coal tar. Heterocycloaliphatic amines do not have resonance structures; they are cycloalkanes, which is when one or more carbon atom has been replaced by nitrogen. They often are obtained via the gentle reduction (without ring splitting) of related heterocyclic compounds, e.g., the reduction of pyridine leads to piperidine = hexahydropyridine.

The chemistry of heterocyclic compounds is already very thoroughly investigated and summarized in a series of encyclopedic books. Current research on heterocyclic compounds is published in several scientific journals and books that are exclusively devoted to this area, e.g., *Journal of Heterocyclic Chemistry* [4], *Advances in Heterocyclic Chemistry* [5], *Chemistry of Heterocyclic Compounds* [6], and *Heterocyclic Communications* [7]. While these traditional sources all provide information about the synthesis, physical, and chemical properties of heterocyclic compounds, they contain little information on the energy content, explosive properties, and sensitivity of these compounds. This is why we have attempted to collect some of the relevant information that would be of interest to a rocket propellant chemist.

High-nitrogen compounds are a sub-class of heterocyclic compounds in general. Most heterocyclic compounds contain nitrogen. There are very few heterocyclic compounds that contain only one heteroelement other than nitrogen. The chemistry of heterocyclic compounds is a domain in its own right, as evident from the existing lit-



erature in this area, which contains a lot of useful information for propellant and gas generant formulators (albeit it is hard to find). The following sources of literature on heterocyclic compounds, in general, are worth reviewing.

*Comprehensive Heterocyclic Chemistry III (CHEC-III)* is a 15-volume reference work that should be treated as the first point of call for all scientists interested in heterocyclic ring systems [8, 9]. Since its publication in 1984, it has become the standard reference point on the subject, indispensable to all serious readers in the interdisciplinary areas where heterocycles are employed. *CHEC-III* builds on and complements the material in *CHEC* and *CHEC-II* and is designed to be used both alone and in conjunction with these two works. Volumes 1 and 2 cover three- and four-membered heterocycles, together with all fused systems containing a three- or four-membered heterocyclic ring. Volume 3 covers five-membered rings with one heteroatom together with their benzo- and other carbocyclic-fused derivatives. Volumes 4, 5, and 6 cover five-membered rings with two heteroatoms, three or more heteroatoms. Volumes 7, 8, and 9 cover six-membered rings with one, two, and more than two heteroatoms, respectively. Volumes 10, 11, and 12 cover systems containing at least two directly fused heterocyclic five- and/or six-membered rings. Volumes 13 and 14 cover seven-membered and larger heterocyclic rings, including all their fused derivatives.

A few excellent summaries of current research on high-nitrogen HEDMs based on heterocyclic ring structures have been published while the work is still actively continuing and more publications continue to appear every month. As such, it is difficult to keep track of all new developments in this area. A summary by Singh et al. contains chapters on triazolium-based, tetrazolium-based, tetrazine-based, azetidinium-based, and imidazolium-based high-nitrogen heterocyclic compounds, and is supported by a long list of 126 relevant literature references [2]. For many of the compounds, the melting points, densities, and enthalpies of formation of their various salts formed with nitric acid, perchloric acid, or dinitramidic acid were tabulated. This is an excellent resource for further in-depth studies on this subject. These types of HEDMs derive their energy from a large number of N—N and C—N bonds and their intrinsic energy content rather than a high heat of combustion. Heterocyclic ring compounds typically have higher heats of formation (HOFs) than their isocyclic (alicyclic, cycloaliphatic) analogs. Many heterocyclic high-nitrogen compounds have a positive enthalpy of formation, which makes them attractive options for the production of explosives and propellants. The reactions of heterocyclic rings containing either ring-bound or attached amino groups with nitric acid, dinitramidic, or perchloric acid form highly energetic salts that can find applications in explosives and rocket propellants. Special interest is devoted to salts in which both the cation and the anion are formed from a high-nitrogen compound. Examples in this category are the azolium azolate salts such as triazolium nitrotetrazolate salts, which sport both high energy and a high nitrogen content [10].

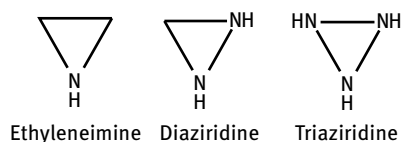
Another summary dealing with furazans, triazoles, triazines, tetrazoles, tetrazines, polycyclic cages, and all-nitrogen compounds is [11]. The favorable

properties and disadvantages of these materials are described and possible solutions for these problems are also provided.

Although much of the information on the use of heterocyclic amines as rocket propellants and explosives deals with the amines in the form of their water-soluble salts, the following chapters contain fundamental information on the parent, unprotonated heterocyclic amines. This information is sometimes needed when calculating the properties of the energetic salts derived from the amines by reacting them with strong acids (for monopropellant applications, preferably oxidizing strong acids). The following information on heterocyclic amines and their salts is subdivided into chapters by the number of members in the core ring, most of them being derived from five-membered rings, and a few being derived from six-membered rings. Single-ring systems are discussed first, followed by multiple ring systems, bridged ring systems, and fused-ring systems.

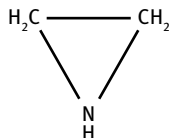
## 2 Three-Membered Ring Amines

Including one or two nitrogens in highly strained three-membered and four-membered ring amines promised to lead to highly energetic fuels and building blocks for other high-energy compounds. There are three saturated three-membered ring cyclic amines with one, two, or three nitrogen atoms in the ring: ethyleneimine (aziridine, azirine; *1H*-azirine, dihydro-; dihydro-*1H*-azirine; dihydroazirine), diaziridine, and triaziridine.



### 2.1 Ethyleneimine

Aziridines are three-membered organic heterocycles that contain one nitrogen atom in the ring.



All commercially available aziridine derivatives are made from ethyleneimine (aziridine) and propyleneimine (2-methylaziridine). Ethyleneimine, aziridine, C<sub>2</sub>H<sub>5</sub>N<sub>1</sub>,

CAS RN [151-56-4], is a colorless liquid that boils at 328.9 K (55.8°C). Polymers of ethyleneimine are usually available as 50% aqueous solutions. An entire book has been devoted to ethyleneimine and other aziridines [12]. A summary of aziridines, describing their preparation, properties, and applications is available in [13]. Various substituted ethyleneimine derivatives have been evaluated as rocket fuels.

### 2.1.1 Preparation of Ethyleneimine

Ethyleneimine can be produced industrially using the  $\beta$ -chloroethylamine process, the Dow process, the BASF-Wenker process, and the catalytic 2-aminoethanol dehydration process. Aziridines, polyethylenimines, and aziridine-modified polymers are used primarily in the coating, paper, water treatment, textile, and petroleum industries.

Until 1963 ethyleneimine was produced commercially by the reaction of 2-chloroethylamine hydrochloride with sodium hydroxide. Dow Chemical once produced ethyleneimine by a reaction of 1,2-dichloroethane with excess ammonia but stopped production in 1978. Badische Anilin und Soda Fabrik (BASF) produced ethyleneimine by reaction of 2-aminoethanol with sulfuric acid to make 2-aminoethyl hydrogensulfate, which was then cyclicized with aqueous sodium hydroxide to produce ethyleneimine. The most economical process is the catalytic dehydration of aminoethanol.

### 2.1.2 Physical Properties of Ethyleneimine

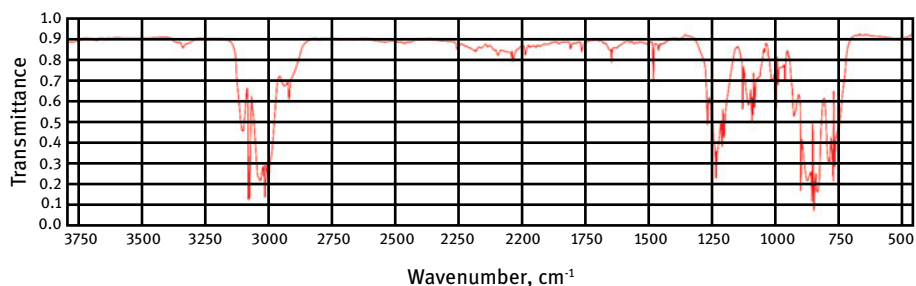
The physical properties of ethyleneimine are listed in Table 1.

**Table 1:** Physical properties of ethyleneimine.

| Property                                                       | SI Units                       | Non-SI units                      | References |
|----------------------------------------------------------------|--------------------------------|-----------------------------------|------------|
| Molecular mass                                                 | 43.0678 g/mol                  | 23.219 mol/kg                     | [14]       |
| Freezing point                                                 | 199 K                          | -74 °C                            |            |
|                                                                | 195 K                          | -78 °C                            | [14]       |
| Boiling point                                                  | 328.9 K                        | 55.8 °C                           | [15]       |
|                                                                | 328.65                         | 55.5 °C                           | [14]       |
| Vapor pressure                                                 | 8.13 kPa at 273 K              | 61 mm Hg at 0 °C                  | [15]       |
| Density                                                        | 837 kg/m <sup>3</sup> at 298 K | 0.8371 g/cm <sup>3</sup> at 25 °C | [15]       |
| Viscosity                                                      | 0.418 mPa s at 298 K           | 0.418 cPs at 25 °C                |            |
| Refractive index, $n_D^{20}$                                   | 1.413                          | 1.413                             | [15]       |
| Standard enthalpy of formation ( $\Delta H_f$ ) <sup>298</sup> | +90.67 kJ/mol                  | +21.67 kcal/mol                   | [15]       |
|                                                                | +91.88 kJ/mol                  | +21.96 kcal/mol                   | [16, 17]   |
|                                                                | +91.90 $\pm$ 0.59 kJ/mol       | +21.96 kcal/mol                   | [14]       |
| Heat of vaporization                                           | 33.83 kJ/mol                   | 8.086 kcal/mol                    | [15]       |
| Heat of combustion                                             | 1591.36 kJ/mol                 | 380.3 kcal/mol                    | [14]       |

Ethylene imine is miscible with water in all ratios. Traces of acidity (e.g., already weak acid such as carbonic acid from the air) will cause it to polymerize quickly. The polymerization reaction is exothermic and can lead to the explosion of the storage vessel (a similar polymerization hazard exists with ethylene oxide). For this reason, ethylene imine is usually stored on alkali metal hydroxides, which act as stabilizers and prevent polymerization.

The infrared (IR) spectrum of aziridine vapor is shown in Figure 1.



**Figure 1:** Infrared spectrum of aziridine vapor. (Reproduced and modified with permission from [18].)

### 2.1.3 Reactions of Ethyleneimine

Aziridines can undergo polymerization reactions, i.e., homopolymerization to form polyethyleneimines, or graft and co-polymerization reactions to give aziridine-modified polymers. Polyfunctional aziridines can be obtained by reaction of ethylenimine and propyleneimine and trifunctional acrylates. Ethylenimine and propyleneimine react with amines in ring-opening reactions and with oxiranes and isocyanates under preservation of the aziridine ring.

Ethylene imine can be polymerized, which forms polyethyleneimine, a long-chain secondary aliphatic polyamine that can form salts with a variety of acids. The perchlorate salt of polyethyleneimine is of interest as a coating for AP and other oxidizers. Commercial ethyleneimine usually contains inhibitors to prevent polymerization.

It may be possible to attach fluorine atoms to diazirine  $F_2CN=N$  rings. The cyclic structure of  $F_2CN_2$  has been confirmed by electron diffraction of the vapor [19]. Perfluorodiazirine has  $C_2$  symmetry (planes of  $CF_2$  and  $CN_2$  are mutually perpendicular) with  $C-F = 1.315 \pm 0.004 \text{ \AA}$ ,  $C-N = 1.426 \pm 0.004 \text{ \AA}$ ,  $N=N = 1.293 \pm 0.009 \text{ \AA}$ ,  $\angle FCF = 111.84 \pm 0.52^\circ$ , and  $\angle NCN = 53.95 \pm 0.36^\circ$ . A comparison of the metrics of perfluorodiazirine with  $H_2$  diazirine showed that the  $C-N$  distance was shorter, and the  $N=N$  distance was longer in the former than in the latter by about  $0.06 \text{ \AA}$ .

In air, the flammability limits are: Upper Flammability Limit (UFL): 54.8 vol.-%, Lower Flammability Limit (LFL): 3.3 vol.-%. The flash point (closed cup) is at 262K ( $-11^\circ\text{C}$ ).

Various substituted ethyleneimine derivatives have been evaluated as rocket fuels. The reaction of cyanogen azide with ethylene at 273–303 K (0–30 °C) gives mixtures containing *N*-cyanoaziridine [20].

Ethyleneimine mixtures with ammonia, ethanol, diethylamine, aniline, or hydrocarbons have been patented as hypergolic fuels [16, 17, 21]. It was claimed that adding five to 50 mass-% ethyleneimine to hydrocarbons, alcohols, other amines, ammonia, alkyl hydrazines, hydrazine, and ethers can improve the specific impulse of these fuels.

A mixture of ethylene imine with pyrrole was patented as hypergolic fuel [22]. The suggested mixture ratios range from 10 to 97 vol.-% pyrrole and 13 to 19 vol.-% ethylene imine. A mixture of 80% pyrrole and 20% ethylene imine has a melting point of 223 K (–50 °C) and has an ignition delay of only 7 ms with white fuming nitric acid (WFNA) at 297 K (24 °C) and an ignition delay of 11 ms at 233 K (–40 °C).

#### 2.1.4 Toxicity of Ethyleneimine

Aziridines are highly toxic, which can likely be attributed to the alteration of nucleic acids, proteins, and other vital biochemicals by alkylation. Substances derived from aziridines but no longer containing the aziridine ring (e.g., polyethyleneimines) are normally of low toxicity.

The handling of ethylene imine requires special safety precautions. Ethyleneimine spilled on unprotected skin causes severe chemical burns with long-lasting burn scars. Inhalation of ethyleneimine vapors causes vomiting with nausea continuing for hours afterward. The compound is a potent carcinogen. It is classified as an A2 proved animal carcinogen and suspected human carcinogen. Ethyleneimine is a mutagen that has a positive Ames test [23].

The conversion factor for permissible exposure limits in air is 1 ppm = 1.76 mg/m<sup>3</sup> at 25 °C and 1 atm. The American Conference of Governmental Industrial Hygienists (ACGIH) at one time recommended a threshold limit value (TLV) of 0.5 ppm (0.09 mg/m<sup>3</sup>) and a time-weighted average (TWA) of 0.1 ppm (0.18 mg/m<sup>3</sup>), with skin contact to be always avoided. Nonetheless, exposure of this chemical to workers should be controlled through the required use of best possible engineering controls, careful work practices, and personal protective equipment, including respirators. Protective Action Criteria (PAC) are Temporary Emergency Exposure Limit (TEEL-0): 0.05 ppm; PAC-1: 0.1 ppm; PAC-2: 4.6 ppm; PAC-3: 9.9 ppm. Worker exposure must be limited to the lowest feasible concentration. The National Institute for Occupational Safety & Health (NIOSH) Immediately Dangerous to Life or Health (IDLH) concentration is 100 ppm. In acute toxicity tests with test animals, the lethal dose LD50 (oral, rat) was 14 mg/kg, LD50 (skin, rabbit) was 13 mg/kg, and lethal concentration LC50 (10-min. inhalation, mouse) was 2236 ppm.

Ethyleneimine is one of the 13 Occupational Safety and Health Administration (OSHA)-regulated carcinogens, as listed in NIOSH Pocket Guide to Chemical Hazards [24].

### 2.1.5 Fire Hazard Properties of Ethyleneimine

The flammable range of ethyleneimine in air is from 3.6 to 46 vol.-%. The auto-ignition temperature is 593 K (320 °C).

## 2.2 Diaziridine

Diaziridine, a cyclic hydrazine, is hydrogenated diazomethane (diazirine), which is extremely hazardous in its explosive and toxic properties. It is usually only prepared in solutions. Diaziridine is unstable and not suitable as a rocket propellant. Alkyl-diaziridines are somewhat more stable [25].

## 2.3 Triaziridine

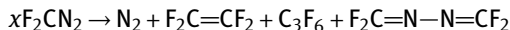
Triaziridine, cyclotriazane,  $N_3H_3$ , has not yet been synthesized in the pure state. It was found as an inclusion in a silver zeolite treated with ammonia. It is a very energetic molecule like hydrazine.

The molecular structure of a series of nitro-triaziridines was studied as high-energy-density compounds using a density functional theory (DFT) method [26]. The HOFs, bond dissociation energies (BDE), and detonation performance were calculated. It was found that all nitro-triaziridines have highly positive  $\Delta H_f$ 's, and the electron-withdrawing action of nitro groups, the steric hindrance, and N—N bonds have a positive effect on increasing values of  $\Delta H_f$ . The thermodynamic stability was estimated by BDE and available free space per molecule in a unit cell.

The unsubstituted parent compound remains elusive, however, the *cis*- and *trans*-2,3-dialkyl-substituted triaziridines were reported. *Ab initio* quantum chemical computations of substituent effects, including stabilization by participation in aromatic rings, were performed on triaziridine strain energy and HOF in the hope of predicting more stable derivatives of this compound [27]. It may be possible to stabilize  $N_3H_3$  by sandwiching it with a triangular boron hydride and forming an  $N_3(BH_2)_3$  adduct.

Cyclotriazane exists only when stabilized in a lattice of silver zeolite [28] but its existence has been questioned [29]. The potential energy surface of the  $N_3H_3$  molecule was examined by *ab initio* calculations and five stable isomers of  $N_3H_3$  were identified. It may be possible to stabilize triazirine in low-temperature argon matrices.

The gas-phase thermal decomposition of difluorodiazirine according to the reaction



has been studied in a static system in the temperature range of 396–443 K (123–170 °C) and a pressure range of 13–106 kPa (100–800 mm Hg) [30]. The primary decomposition, yielding nitrogen and difluorocarbene, appeared to be unimolecular and homogeneous. The rate constant was pressure dependent in the pressure range studied. At a total pressure of 27 kPa (200 mm Hg), the first-order rate constants would fit the Arrhenius equation

$$k = 0.68k_\infty = 1013.1 \pm 0.4 \exp\left(\frac{-32200 \pm 700}{RT}\right) \text{ s}^{-1}.$$

The activation energy calculated from extrapolated values of  $k_\infty$  at 396 and 443 K (123 and 170 °C) agreed within limits of experimental error with that obtained from values of  $k$  at 27 kPa (200 mm Hg).

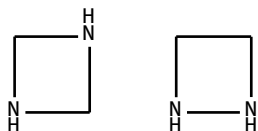
### 3 Four-Membered Ring Amines

Propyleneimine, also known as trimethyleneimine, azacyclobutane, azetidine, aze-tane, and CAS RN [503-29-7] is miscible with water, boils at 334–335 K (61–62 °C), and has a density of 0.847 g/cm<sup>3</sup> at 298 K (25 °C). Azetidine is rarely used in the chemical industry. We were tempted to skip the discussion of four-membered ring amines at this point because azetidine itself is not easily obtained. There are several azetidine derivatives of interest as rocket fuels and explosives, so let us continue.

The enthalpy of formation of azetidine was predicted by *ab initio* calculations [31].

The most important azetidine derivative is 1,3,3-trinitroazetidine, also known as C<sub>3</sub>H<sub>4</sub>N<sub>4</sub>O<sub>6</sub>, TNAZ, CAS RN [97645-24-4] which has been thoroughly investigated as a new HEDM with improved sensitivity characteristics (improved over RDX). The properties of TNAZ and its salts are discussed here.

Inserting more than one nitrogen atom into a four-membered saturated ring leads to structural isomers, one is a bifunctional ring-closed symmetrical secondary amine and the other with vicinal nitrogen atoms is a ring-closed hydrazine:



1,3-diazetidine    1,2-diazetidine

1,2-Dimethyldiazetidine has been proposed as a rocket fuel [32]. 1,2-Dimethyldiazetidine can be prepared from symmetrical dimethylhydrazine (SDMH) and ethylene bromide. It freezes at 183 K ( $-90^{\circ}\text{C}$ ) and boils at 343 K ( $+70^{\circ}\text{C}$ ), has a density of  $0.8099\text{ g/cm}^3$ , and has a refractive index  $n_D^{25} = 1.4130$ .

Inserting one or more nitrogen atoms into a four-membered unsaturated ring (cyclobutadiene) leads to structural isomers, the predicted stability of which decreases in the order cyclobutadiene > 1,3-diazete > azete (azacyclobutadiene) > 1,2-diazete > triazete > tetraazete [33]:



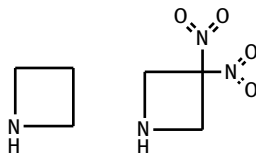
cyclobutadiene > azete (azacyclobutadiene) > 1,2-diazete > triazete > tetraazete

With successive aza-substitution, the difference in the energies of the substituted cyclobutadienes and the corresponding aza-substituted tetrahydrofurans decreases. 1,3-Diazete is a theoretical dimer of hydrocyanic acid but has not been found via this route. Polyheteroatomic rings consisting only of nitrogen or phosphorus atoms can be stabilized by the introduction of acceptors of the unshared electron pair of the heteroatom, particularly oxygen atoms, with the formation of oxo compounds [34].

Tetraazetetrahedrane,  $\text{N}_4$ , is 11.3 kJ/mol lower in energy than tetrazete, in contrast to its hydrocarbon analogue, tetrahedrane, which has 108.9 kJ/mol higher energy than that of cyclobutadiene. The open-chain  $C_s$  structure of tetranitrogen (having the triplet ground state) is predicted to be the most stable isomer of  $\text{N}_4$ . Its energy is 62.0 kJ/mol lower than that of tetrazete. The predicted enthalpies of formation,  $\Delta H_{298}^f$ , of tetraazetetrahedrane, tetrazete, and the open-chain tetranitrogen are  $732.5 \pm 8.0$  kJ/mol,  $746.5 \pm 7.6$  kJ/mol, and  $686.6 \pm 7.6$  kJ/mol, respectively [35]. Tetraazetetrahedrane has yet to be synthesized and stabilized.

### 3.1 3,3-Dinitroazetidine

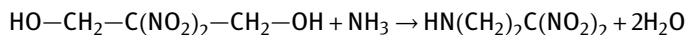
The two hydrogens in the 3,3-position on the carbon atom in azetidine can be substituted with geminal nitro groups, which interestingly somewhat stabilizes the strained ring.



Azetidine    3,3-Dinitroazetidine



One wonders about the huge amount of attention devoted to TNAZ when its lesser nitro analog 3,3-dinitroazetidine (also called propanedinitroimine) can be prepared with much less effort [36]:

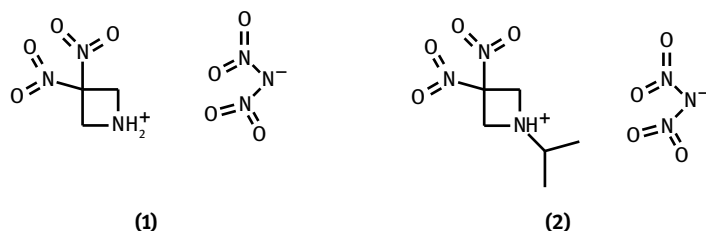


(see also [37] and [38]). 3,3-Dinitroazetidine should be evaluated further as a propellant ingredient.

### 3.1.1 Salts of 3,3-Dinitroazetidine

3,3-Dinitroazetidine is an explosive in its own right. Its explosive power and oxygen balance can be improved by forming the dinitramide salt of the amine, called dinitroazetidinium dinitramide [39]. 3,3-Dinitroazetidine contains only two nitro groups instead of three. This compound has a secondary amine  $-\text{NH}-$  group instead of a nitramine group and behaves like an amine. It forms salts with strong acids. Salts with oxidizing acids are of interest as energetic additives.

The pressure-temperature phase diagram for 3,3-dinitroazetidinium dinitramide (DNAZ-DN) has been measured using a high-pressure diamond anvil cell with Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and optical polarizing light microscopy [40]. The phase diagram was determined between ambient pressure and 10.0 GPa over the temperature range from 198 K ( $-75^\circ\text{C}$ ) to decomposition temperatures above 423 K ( $150^\circ\text{C}$ ). The phase diagram delineates the melt curve for  $\alpha$ -DNAZ-DN, a reversible, pressure-induced phase transformation in  $\alpha$ -DNAZ-DN forming a new high-pressure polymorph called  $\beta$ -DNAZ-DN. Additional measurements provided the pressure and temperature conditions for solid-state decomposition of  $\beta$ -DNAZ-DN. FTIR and Raman spectra were obtained for both the  $\alpha$  and  $\beta$  phases as a function of pressure at room temperature. The new high-pressure  $\beta$ -polymorph could not be retrieved after lowering the pressure to ambient conditions.  $\alpha$ -DNAZ-DN is orthorhombic with  $C_{m21}$  symmetry and has a density of  $1.791\text{ g/cm}^3$ . The polymorphs' stability fields are as follows: **(1)** the orthorhombic phase,  $\alpha$ -phase, is stable between atmospheric pressure and 1.05 GPa from 198 to 409 K ( $-75$  to  $+136^\circ\text{C}$ ); **(2)** the liquidus phase is stable from atmospheric pressure to 1.0 GPa between 409 to 419 K ( $136$  to  $146^\circ\text{C}$ ); **(3)** the high-pressure polymorph,  $\beta$ -phase is stable above 1.0 GPa between 223 K ( $-50^\circ\text{C}$ ) and up to incipient decomposition temperatures. Between 1.1 and 10.0 GPa and 198 and 423 K ( $-75$  and  $+150^\circ\text{C}$ ),  $\beta$ -DNAZ-DN is the stable phase. A similar paper by the same authors on ammonium dinitramide (ADN) has previously been published. The crystal structures of 3,3-dinitroazetidinium dinitramide **(1)**, and 1-*iso*-propyl-3,3-dinitroazetidinium dinitramide **(2)**, have been determined [41].



3,3-Dinitroazetidinium dinitramide **(1)** crystallizes in the orthorhombic space group  $C_{mc}2_1$  with unit cell dimensions  $a = 9.932(1) \text{ \AA}$ ,  $b = 8.545(1) \text{ \AA}$ ,  $c = 11.107(1) \text{ \AA}$ , while **(2)** crystallizes in the orthorhombic space group  $Pbca$  with cell dimensions  $a = 11.464(2) \text{ \AA}$ ,  $b = 11.657(2) \text{ \AA}$ ,  $c = 17.916(4) \text{ \AA}$ . Compound **(2)** formed spontaneously from **(1)** by reacting with the solvent, acetone, during attempts to recrystallize it.

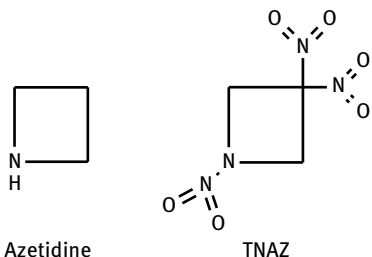
$^2\text{H}$ -,  $^{13}\text{C}$ -, and  $^{15}\text{N}$ -labeled isomers of 1,3,3-trinitroazetidine and 3,3-dinitroazetidinium nitrate were synthesized by using appropriately labeled starting materials and characterized by nuclear magnetic resonance (NMR) and mass spectral analysis [42]. Unequivocal assignments of all NMR chemical shifts of the unlabelled title compounds and their intermediate precursors were facilitated by the NMR spectra of the labeled compounds along with carbon-hydrogen correlation experiments.

The 3,3-dinitroazetidinium (DNAZ) salt of perchloric acid ( $\text{DNAZ} \cdot \text{HClO}_4$ ) was characterized by elemental analysis, IR, NMR, and X-ray diffraction (XRD) [43]. The thermal decomposition of  $\text{DNAZ} \cdot \text{HClO}_4$  was investigated with constant heating rates by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)/differential thermogravimetry (DTG). The results showed that the thermal decomposition process of  $\text{DNAZ} \cdot \text{HClO}_4$  is a two-stage process. The apparent activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) of the exothermic decomposition reaction of  $\text{DNAZ} \cdot \text{HClO}_4$  were  $156.47 \text{ kJ/mol}$ , and  $10^{15.12} \text{ s}^{-1}$ , respectively. The critical temperature of the thermal explosion is  $461.6 \text{ K} = 188.5^\circ\text{C}$ . The values of  $\Delta S$ ,  $\Delta H$ , and  $\Delta G$  of this reaction are  $42.26 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $154.44 \text{ kJ mol}^{-1}$ , and  $135.42 \text{ kJ mol}^{-1}$ , respectively.

### 3.2 1,3,3-Trinitroazetidine

1,3,3-Trinitroazetidine, also known as TNAZ,  $\text{C}(\text{NO}_2)_2(\text{CH}_2)_2\text{NNO}_2$ ,  $\text{C}_3\text{H}_4\text{N}_4\text{O}_6$ , CAS RN [97645-24-4],  $M = 192.088 \text{ g/mol}$ , with a four-membered ring, is a very energetic additive and has been investigated as an explosive in its own right. The oxygen balance of TNAZ is  $-16.66\%$  and the nitrogen content is  $29.2 \text{ mass-\% N}$ . TNAZ was first synthesized in 1983 and has received a very thorough examination in the interim. Here we are mostly interested in evaluating it as an energetic additive to rocket propellants. It remains to be seen if replacing RDX in nitramine propellants with TNAZ brings any benefit to propellant properties and can be justified given the increased costs. The de-

velopment of TNAZ as an explosive may continue but it is unlikely to become a major achievement for propellant formulations. Over time, interest in TNAZ has been lost because of some drawbacks such as the high cost of the product and high volatility.



1,3,3-Trinitroazetidine is both a nitro compound and a nitramine and the ring structure is a heterocyclic amine. Therefore, one must decide if it should be discussed here, under heterocyclic amines within the chapter dealing with its parent molecule, azetidine, or in the chapter on nitramines. We opted to place it here under heterocyclic amines, the parent structure of TNAZ.

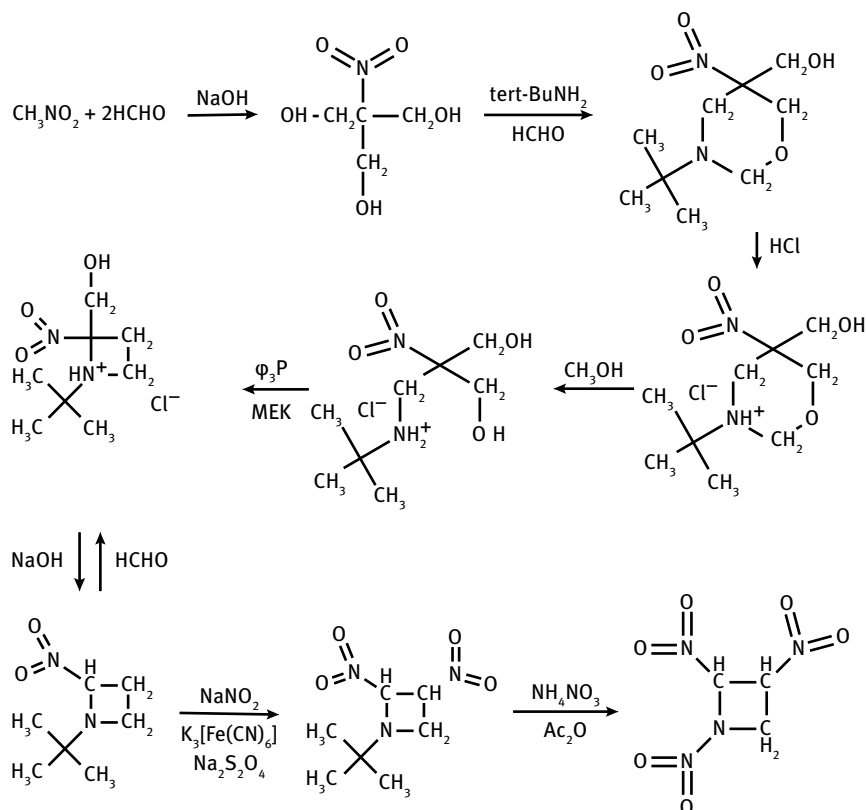
TNAZ has a melting point of 374 K (101 °C), a crystal density of 1.84 g/cm<sup>3</sup>, and good thermal stability up to 513 K (240 °C). It has a slightly negative oxygen balance for complete combustion to CO<sub>2</sub>, -16.7%. It is only half as sensitive to impact as HMX (with twice the drop height required to set it off). Its disadvantage is high production costs and slight volatility.

### 3.2.1 Preparation of TNAZ

When TNAZ was first synthesized in 1983, it was the result of a multi-step synthesis and the yield was only 5% [44, 45]. One of the first processes used for the synthesis of TNAZ started with epichlorohydrin and *tert*-butylamine. Direct nitrolysis of 3-substituted azetidinium hydrochlorides with acetyl nitrate produces cyclic nitramines. In the meantime, several other synthesis methods have been developed and the price has dropped somewhat. TNAZ was manufactured on a pilot plant scale at Thiokol and its cost continues to drop. Until 1991, TNAZ had only been prepared in laboratories in half-pound batches. As a next step, a process demonstration module facility was completed at Picatinny Arsenal to prepare it in multi-pound batches [46].

1,3,3-Trinitroazetidine can be prepared by reacting 1,3,5-trialkyl hexahydrotriazine and tris(hydroxymethyl)nitromethane, and after following several intermediate steps by converting 1-alkyl-3,3-dinitroazetidine into 1,3,3-trinitroazetidine [47]. Another 8-step synthesis of TNAZ involved the condensation of tris-(hydroxymethyl)-nitromethane with *tert*-butylamine and formaldehyde to yield 3-*tert*-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine [38]. This was treated with methanolic HCl to yield 2-*tert*-butylaminomethyl-2-nitro-1,3-propane diol hydrochloride. The cyclized azetidine ring was achieved with excellent reproducibility

by the effect of diisopropyl azodicarboxylate (DIAD), which was subsequently treated with NaOH and oxidatively nitrated to yield 1-*tert*-butyl-3,3-dinitroazetidine (BDNA). The nitrolysis of BDNA with  $\text{NH}_4\text{NO}_3$  and  $\text{Ac}_2\text{O}$  yielded TNAZ in 57% overall yield.



(See also [48].) The electrophilic addition of  $\text{NO}^+\text{NO}_2^-$  across the highly stressed C—N bond of 1-aza-bicyclo[0,1,1]butane eventually leads to TNAZ [49]. A group of chemists in China described a method also starting with epichlorohydrin and *tert*-butylamine [50].

The group at Fraunhofer Institute of Chemical Technology (ICT) perfected the Hiskey method for the synthesis of TNAZ [51]. The overall yield of the five-step procedure was 15–20%.

A review of more than 16 routes for TNAZ synthesis revealed that the total yield of the most technologically successful of these synthesis routes does not exceed 30% of theory [52]. It was stated that TNAZ is a highly energetic material, more powerful than RDX, and which may be less vulnerable than most other nitramines. This makes it suitable for applications as a castable explosive as well as a plasticizer. However, a relatively high vapor pressure, volume contraction, and formation of shrinkage cavities in the solidification of its melt can be a minor disadvantage of TNAZ.

When the original synthesis method of TNAZ was scaled up to produce several hundred kg of TNAZ for evaluation by the DoD, it produced significant amounts of chemical waste (over 1200 kg waste per kg of TNAZ), including large quantities of halogenated solvents. An alternate synthesis method, which gave much higher yields of TNAZ and left less waste than generated by the original process, was developed at the Los Alamos National Laboratory and transferred to Aerojet, Sacramento, where it was scaled up to production-plant quantities to give TNAZ in 57% overall yield [53]. The new process produced only about 10% of the waste produced in the original process without recycling solvents or reagents.

Other methods are described for synthesizing 1,3,3 trinitroazetidine [54]. Another synthesis method for TNAZ starts with nitromethane and formaldehyde, cheap raw materials, via a five-step process [55]. The overall yield was above 40%. A review of routes for TNAZ synthesis developed since 1990 was presented in [56] (see also [57]).

The most popular route to TNAZ now seems to be one where the first step is to make 3-*tert*-butyl-5-hydroxymethyl-5-nitrotetrahydroxy-1,3-oxazine by reacting a solution of paraformaldehyde, NaOH, nitromethane, and *tert*-butylamine [58]. This eventually leads to TNAZ using the scheme demonstrated earlier. It was shown that TNAZ was significantly more sensitive to mechanical stimuli than 2,4,6-trinitrotoluene (TNT).

1,3,3-Trinitroazetidine was synthesized using an alternative approach based on the transformation of 3-oximino-1-(*p*-toluenesulfonyl)azetidine in the reaction with nitric acid through an intermediate pseudonitrol [59]. Nitrolysis of *N-tert*-butyl-3,3-dinitroazetidinium nitrate with  $\text{NH}_4\text{NO}_3/\text{Ac}_2\text{O}$  at a reaction temperature of 353 K (80 °C) gives TNAZ with a yield of 83.1% [60].

### 3.2.2 Physical Properties of TNAZ

The physical properties of TNAZ are summarized in Table 2.

**Table 2:** Physical properties of TNAZ.

| Property                                      | S.I. Units             | Other units                    | References |
|-----------------------------------------------|------------------------|--------------------------------|------------|
| Molecular mass                                | 192.0871 g/mol         | 5.206 mol/kg                   | [14]       |
| Melting point                                 | 373.8 K                | 100.7 °C                       |            |
| Density                                       | 1.84 g/cm <sup>3</sup> |                                |            |
| Enthalpy of formation                         | +36.17 kJ/mol          | +8.644 kcal/mol<br>= +45 cal/g | [61]       |
|                                               | +189.50 kJ/kg          | +45.29 kcal/kg                 | [62]       |
| Heat of fusion                                | 29 kJ/mol              | 6.93 kcal/mol                  | [63]       |
| Heat of vaporization (from the melt at 393 K) | 66.8 kJ/mol            | 15.96 kcal/mol                 | [63]       |
| Heat of sublimation (at 373 K)                | 95.3 kJ/mol            | 22.8 kcal/mol                  | [63]       |

Enthalpy of formation data reported in existing literature varies widely from +8.79 to +457.7 kJ/mol, thus making it difficult to find an accurate number. See also [64–67].

### 3.2.2.1 Melting Point and Phase Diagrams of TNAZ

The peak temperature of the melting endotherm of TNAZ was 375.69 K (102.54 °C) and the enthalpy of melting was  $30.31 \pm 0.30$  kJ/mol ( $7.24 \pm 0.07$  kcal/mol) [68].

The phase diagrams of TNAZ in mixtures with other energetic materials have been investigated to see if the properties (as melt-castable explosives in particular) could be improved by adding another component. Components analyzed in TNAZ mixtures included HMX [69], 1,3-dinitro-3-(1',3'-dinitroazetidin-3'-yl)azetidine (TNDAZ) [70], *N*-acetyl-3,3-dinitroazetidine (ADNAZ) [71], and *N*-nitroso-3,3-dinitroazetidine [72].

1,3,3-Trinitroazetidine and TNT form a eutectic mixture with a melting temperature of 60.6 °C containing 35.3 mol-% TNAZ [73]. The binary system 1,3,3-trinitroazetidine (TNAZ)/1,3,5-trinitrobenzene (TNB) had an area with at least three eutectic points from different phase modifications of TNB and/or TNAZ at 341.5 K (68.4 °C) with 53.4% TNAZ, at 336.7 K (63.6 °C) with 47.8% TNAZ, and at 335.1 K (62.0 °C) with 45.6% TNAZ [74].

Another energetic azetidine derivative is 3-azido-1,3-dinitroazetidine (AzDNAZ). Melting point measurements of TNAZ/AzDNAZ mixtures with different TNAZ contents revealed a eutectic composition TNAZ/35/65 with a melting point of 334 K (61 °C) [75]. Combined introduction of nitro- and azido groups followed by nitration of tBuDNAZ/tBuAzNAZ mixtures in  $\text{N}_2\text{O}_5/\text{CH}_3\text{CN}$  or  $\text{NH}_4\text{NO}_3/(\text{CH}_3\text{CO})_2\text{O}$  systems opens up the possibility of synthesis TNAZ/AzDNAZ mixtures.

### 3.2.2.2 Vapor Pressure of TNAZ

One disadvantage of TNAZ is its high volatility. The vapor pressure can be calculated in the widened temperature interval (373–773 K = 100–500 °C):

$$\ln p = -7591/(T - 11.33)$$

where  $p$  is the pressure in MPa and  $T$  is the temperature in kelvin. The dependence detailed yields a TNAZ boiling point at an atmospheric pressure of 548 K (275 °C) and heat of evaporation of 63.1 kJ/mol [76].

### 3.2.2.3 Solubility of TNAZ

Solubility information can be useful for purifying and recrystallizing energetic materials. The solubility of TNAZ in ethanol-water binary solvent mixtures was determined from 293 to 323 K [77]. The results revealed that the solubility of TNAZ in ethanol-water binary solvent mixtures increased with an increase in temperature. In the pure ethanol solvent, the solubility increased from 0.01349 to 0.03935 mol/mol with a temperature increase from 293 to 323 K.

### 3.2.2.4 Thermal Conductivity of TNAZ

The heat capacity, thermal conductivity, and thermal diffusivity of a range of other oxidizers, binders, and rocket propellants were determined and compared to data in existing literature [78]. The thermal diffusivity  $\alpha$  of TNAZ for the range from 293 to 361 K (20 to 88 °C) can be described by the linear equation

$$\alpha = 1.51 \times 10^{-3} - 3.36 \times 10^{-6}t$$

where  $\alpha$  is the thermal diffusivity in  $\text{cm}^2/\text{s}$  and  $t$  is the temperature in °C. The thermal conductivity  $\lambda$  of TNAZ in the range from 293 to 361 K (20 to 88 °C) can be described by the linear equation

$$\lambda = 0.841 \times 10^{-3} - 25.7 \times 10^{-7}t$$

where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$  and  $t$  is the temperature in °C.

### 3.2.2.5 Thermodynamic Properties and Thermal Properties of TNAZ

#### Heat Capacity of TNAZ

The heat capacity of TNAZ near room temperature is  $1.372 \text{ J g}^{-1} \text{ K}^{-1}$  ( $0.328 \text{ cal g}^{-1} \text{°C}^{-1}$ ) [78].

#### HOF and Heat of Combustion of TNAZ

The standard enthalpy of formation of TNAZ is  $\Delta H_f +36.4 \text{ kJ/mol} = +189.50 \text{ kJ/kg} = 8.70 \text{ kcal/mol} = +45.29 \text{ cal/g}$  [62]. Other sources gave a  $\Delta H_f$  of  $280 \text{ kJ/kg}$  [51].

#### Heat of Fusion and Solid-State Phase Transitions of TNAZ

The heat of fusion of TNAZ at 372–375 K (99–102 °C) was  $30.31 \pm 0.30 \text{ kJ/mol}$  [68]. Other sources have reported a heat of fusion of  $29.45 \text{ kJ/mol}$  ( $6.93 \text{ kcal/mol}$ ) [63, 79].

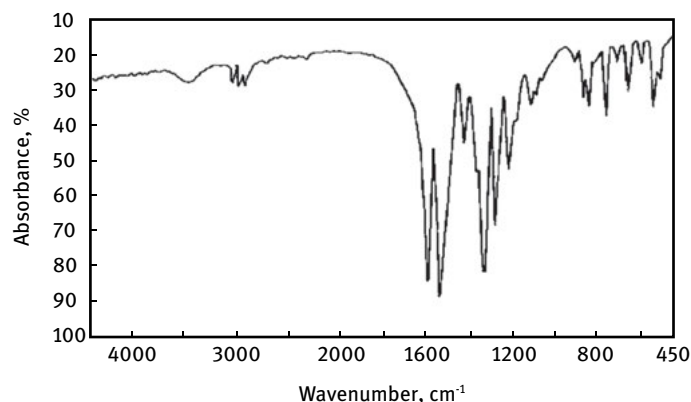
### 3.2.2.6 Molecular Structure of TNAZ

TNAZ crystallizes with unit cell parameters of  $a = 5.7580(6) \text{ Å}$ ,  $b = 11.1309(12) \text{ Å}$ ,  $c = 21.524 \text{ Å}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1379.5 \text{ Å}^3$ , and  $Z = 8$ ,  $\rho_{\text{XRD}} = 1.850 \text{ g/cm}^3$  [58, 70]. This thermal data supported the existence of more than one polymorph for TNDZ and for TNAZ. A structural relative of TNAZ is 1,3-dinitro-1,3-diazetidine, DNAD, CAS RN [78246-06-7], which is also an explosive substance.

### 3.2.2.7 Optical, Electrical, and Magnetic Properties of TNAZ

#### Absorption Spectra of TNAZ

The IR spectrum of TNAZ with absorption peaks at 3036, 1596, 1540, 1332, 1278, 1016, 842, 762, and  $665 \text{ cm}^{-1}$  is shown in Figure 2. Infrared spectra were obtained and normal co-ordinate calculations were made for TNAZ and *N*-acetyl-3,3-dinitroazetidine (ADNAZ) to learn more about the conformational behavior of these compounds and to make assignments of the IR bands to the appropriate normal modes of vibration



**Figure 2:** IR spectrum of TNAZ in a KBr pellet. (Reprinted and modified from [58], with permission from ©2004 Elsevier; permission conveyed through RightsLink.)

[80]. Semi-empirical molecular orbital (MO) calculations were then made to obtain additional information about the molecular structures.

### 3.2.3 Chemistry of TNAZ

#### 3.2.3.1 Salt Forming Reactions with TNAZ

TNAZ is a base with a  $pK_a = 6.5$  and forms salts with strong acids. Salts formed with strongly oxidizing anions and highly energetic anions are of prime interest as propellant and explosive ingredients. The properties of TNAZ salts are summarized in Table 3. A unique combination is the salt formed from TNAZ base and NTO acid. Both of these parent compounds are new HEDMs developed during the early 1990s.

**Table 3:** Physical properties of trinitroazetidinium salts.

| Compound                                                | Gross formula                                                | Molecular mass<br>g/mol | Melting point |     | Density<br>g/cm <sup>3</sup> | Enthalpy of formation |              |
|---------------------------------------------------------|--------------------------------------------------------------|-------------------------|---------------|-----|------------------------------|-----------------------|--------------|
|                                                         |                                                              |                         | K             | °C  |                              | kJ/mol                | kcal/mol     |
| 1,3,3-Trinitroazetidinium nitrate                       | C <sub>3</sub> H <sub>4</sub> N <sub>5</sub> O <sub>9</sub>  | 254.09                  | 415           | 142 | 1.76                         | -260 ± 8              | -62.1 ± 1.9  |
| 1,3,3-Trinitroazetidinium dinitramide                   | C <sub>3</sub> H <sub>4</sub> N <sub>7</sub> O <sub>10</sub> | 298.1                   | 412           | 139 | 1.79                         | -34 ± 16              | -8.13 ± 3.82 |
| 1,3,3-Trinitroazetidinium 5-nitro-1,2,4-triazol-3-onate | C <sub>5</sub> H <sub>6</sub> N <sub>8</sub> O <sub>9</sub>  | 322.15                  | 434           | 161 | 1.76                         | -201 ± 4              | -48.0 ± 0.9  |



### 3.2.3.2 Thermal Stability of TNAZ

#### Experimental Studies of Slow Thermal Decomposition of TNAZ

Photofragmentation translational spectroscopy was used to study fragments shed during the incipient decomposition of TNAZ. This was carried out to try and identify the weakest link in the molecule, the one that breaks first [81]. In this method, vapors of the molecule of interest are expanded from a nozzle into a vacuum. The expansion is then collimated to form a molecular beam. The molecular beam is crossed with the output of a pulsed CO<sub>2</sub> laser which excites the molecule of interest above the dissociation threshold, relying on infrared multi-photon excitation to induce decomposition. To dissociate, a molecule must absorb approximately 20 infrared photons. TNAZ easily fragments upon ionization. All time-of-flight (TOF) mass spectra were consistent with the sequential loss of two NO<sub>2</sub> groups. Following this loss, the remaining fragment decomposes into C<sub>3</sub>H<sub>4</sub> and N<sub>2</sub>O<sub>2</sub>.

The mechanism and reaction kinetics of the thermal decomposition of TNAZ and (separately) its key decomposition intermediate, 1-nitroso-3, 3-dinitroazetidine (NDNAZ), were studied at varying temperatures and at a range of isothermal temperatures at 10 °C intervals from 393–433 K (120–160 °C) for NDNAZ and 433–483 K (160–210 °C) for TNAZ using a simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS) [82]. TNAZ decomposed via four separate routes, one of which led to NDNAZ, which subsequently decomposed via at least two distinct routes.

The apparent activation energy of TNAZ decomposition was 133 kJ/mol and the pre-exponential constant was 10<sup>9.8</sup> s<sup>-1</sup>. For comparison, the activation energy of RDX decomposition was 134.7 kJ/mol and for HMX it was 380.9 kJ/mol. The critical temperature of the thermal explosion was calculated as 511–523 K [68]. The thermal stability of TNAZ and that of six other explosives was measured by a thermogravimetric analysis-mass spectrometry (TGA-MS) combination (STMBMS). The results were compared to develop a kinetic model and to identify the rate-determining steps [83, 84].

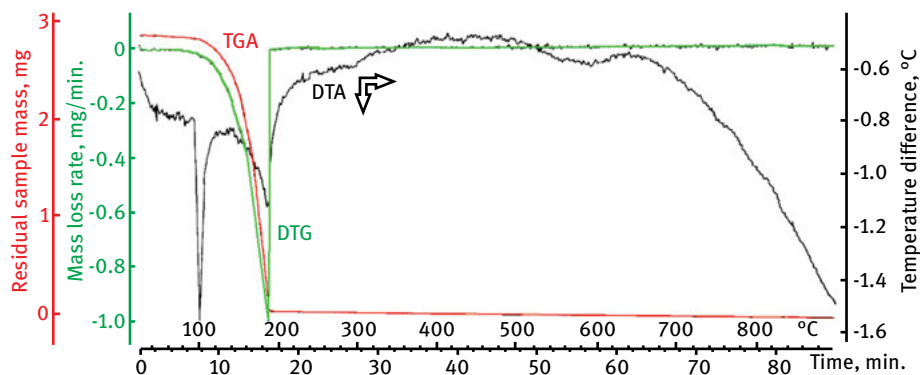
A fused-silica capillary column with a narrow internal diameter and a stationary phase was used for the simultaneous gas chromatography-mass spectrometry (GC-MS) determination of N<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, NO, NO<sub>2</sub>, (CN)<sub>2</sub>, and H<sub>2</sub>O from the thermal decomposition of TNAZ [85]. The detection of hydrogen cyanide and cyanogen gases as products of TNAZ thermal decomposition was reported for the first time.

The thermal behavior of TNAZ was studied by using DSC, differential thermal analysis (DTA), and TGA [79]. Data indicated that TNAZ is thermally more stable than RDX but less stable than HMX and TNT. The reaction of intense thermal decomposition started at 456–503 K (183–230 °C) (depending on the heating rate) while the first exothermic reaction was observed at 451 K (178 °C) at a heating rate of 1 °C/min. By applying multiple heating rate DSC measurements and Ozawa's method, the activation energy of 161.3 kJ/mol, and a pre-exponential factor of 8.27 × 10<sup>13</sup> 1/s were calculated from the DSC peak maximum temperature-heating rate relationship.

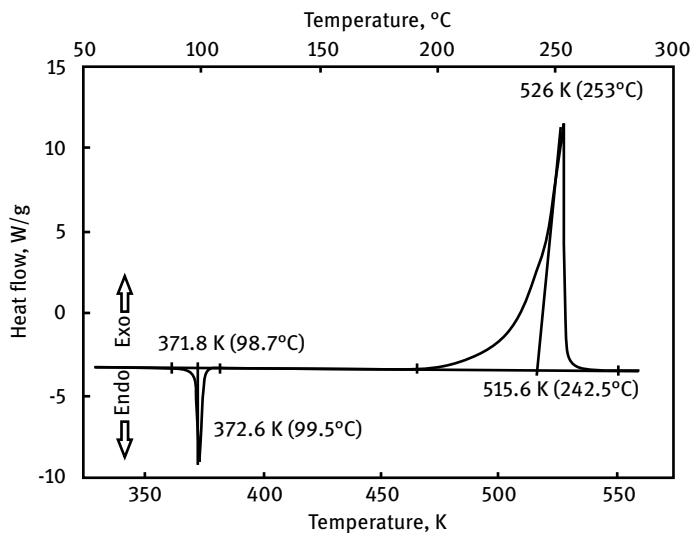
The thermal decomposition kinetics of TNAZ have been measured using non-isothermal DSC [86]. Samples of TNAZ in open pans and pierced pans underwent mainly melting ( $\Delta H_{\text{fus}} = 27 \pm 3 \text{ kJ/mol}$ ) and vaporization ( $\Delta H_{\text{vap}} = 74 \pm 10 \text{ kJ/mol}$ ) during heating. However, when confined in sealed high-pressure crucibles, exothermic thermal decomposition was observed. The activation energy for thermal decomposition of  $184 \text{ kJ/mol}$  at the start of the reaction decreased to  $38 \text{ kJ/mol}$  near the end of the reaction. The rates clearly exhibit acceleratory behavior that was ascribed to autocatalysis. The measured heat release of thermal decomposition ( $Q = 640 \pm 150 \text{ kJ/mol}$ ) was independent of the heating rate and the sample mass.

Based on computer models, two pathways can be initiated by the fission of the  $\text{N}-\text{NO}_2$  and  $\text{C}-\text{NO}_2$  bonds to yield radical intermediates, while the other two pathways involve the molecular elimination of  $\text{HONO}$  [87]. Energy profiles for the pathways and possible routes to some of the experimentally observed species of TNAZ decomposition were calculated. The energy required to initiate the  $\text{NO}_2$  bond fission pathways is  $4\text{--}8 \text{ kcal/mol}$  lower than the  $\text{HONO}$  elimination pathways. In the gas phase, the  $\text{NO}_2$  elimination pathways were predicted to be the dominant routes for TNAZ decomposition. In the condensed phase, however, this trend may be reversed.

The DSC, TGA, and DTG curves of TNAZ demonstrated in Figure 3 show an endothermic melting peak at  $373 \text{ K}$  ( $100^\circ\text{C}$ ) accompanied by steady evaporation TGA weight loss [58]. The DTA baseline decreased steadily between approximately  $393$  and  $453 \text{ K}$  ( $120$  and  $180^\circ\text{C}$ ), thus reflecting the endothermic nature of TNAZ evaporation. The curve revealed decomposition of TNAZ at  $378\text{--}407 \text{ K}$  ( $105\text{--}134^\circ\text{C}$ ) with a weight loss of  $10\%$ . The complete loss of sample was observed due to evaporation/decomposition over the temperature range  $376\text{--}467 \text{ K}$  ( $103\text{--}194^\circ\text{C}$ ), and the onset of exotherm was at  $453 \text{ K}$  ( $180^\circ\text{C}$ ).



**Figure 3:** DSC, TGA, and DTG curves of TNAZ. (Reprinted and modified from [58], with permission from ©2004 Elsevier; permission conveyed through RightsLink.)



**Figure 4:** DSC thermogram of TNAZ. (Republished and modified from [88], with the permission of ©2005 John Wiley & Sons – Books; permission conveyed through Copyright Clearance Center, Inc.)

In the DSC, the melting endotherm of TNAZ started at 371.8 K (98.7°C) and maxed at 372.6 K (99.5°C). The decomposition exotherm started at 473 K (200°C) and maxed at 526 K (253°C), as demonstrated in Figure 4 [88].

The thermal decomposition of TNAZ in the gas phase, and in the molten state in dilution with *m*-dinitrobenzene in a wide concentration range (5–80%), was studied by manometry, volumetry, thermogravimetry, IR, and MS [59, 89]. The gas-phase reaction at 443–493 K (170–220 °C) followed first order of kinetics and obeyed Arrhenius equation with an activation energy of 169 kJ/mol (40.5 kcal/mol) and a logarithm of pre-exponential factor of 15.6. The complete TNAZ decomposition at 493 K (220 °C) resulted in the formation of nitrogen, nitrogen dioxide, carbon dioxide, nitroacetaldehyde, and traces of CO and NO. The rate-determining step of the process is the homolytic cleavage of the N–NO<sub>2</sub> bond in the TNAZ molecule. In a melt at 443–483 K (170–210 °C), the thermal decomposition proceeded with a pronounced self-acceleration and the maximum reaction rates were observed at conversions of 53.9–67.4%. The solid decomposition products auto-accelerated the reaction. It is most likely that the autocatalysis of TNAZ decomposition in the liquid phase is due to the autocatalytic decomposition of 1-nitroso-3,3-dinitroazetidine, which is formed by the thermal decomposition of TNAZ. In *m*-dinitrobenzene solution, TNAZ also decomposed with self-acceleration. It was found that the higher the concentration in the solution, the more pronounced the self-acceleration.

Based on the initial temperature at which DSC curves deviate from the baseline and the onset temperature and maximum peak temperature from the non-isothermal

DSC curves of TNAZ at different heating rates, the thermal decomposition activation energy and pre-exponential constant were obtained. Kissinger's method and Ozawa's method, were employed to facilitate this and also the values of heat capacity were obtained by microcalorimetry [90]. The thermal explosion temperature, adiabatic time-to-explosion, 50% drop height (H50) of impact sensitivity, and the critical temperature of hot-spot initiation of TNAZ were calculated. The data showed that **(1)** TNAZ is thermally stable; **(2)** its impact sensitivity is better than that of cyclotrimethylene trinitramine (RDX); **(3)** the critical temperature of hot-spot initiation is higher than that of RDX and between those of triaminotrinitrobenzene (TATB) and hexanitrostilbene (HNS).

If TNAZ is used in solid propellant combinations, it may come in contact with other energetic materials and ballistic modifiers. The compatibility of TNAZ with some common energetic materials such as HMX, RDX, nitrocellulose (NC), and nitroglycerine (NG) was tested by DSC [91]. DSC data indicated that the compatibility of TNAZ with HMX or RDX is good. However, with NC or NG it is worse than that of RDX.

### Experimental Studies of Rapid Thermal Decomposition of TNAZ

Vapors of TNAZ were pyrolyzed in a single-pulse shock tube under high dilution in Ar and over the temperature range of 750–1100 K (reflected shocks) [92]. The decay of TNAZ and the appearance of the reactive intermediate, NO<sub>2</sub>, were followed spectrophotometrically at 271 and 405 nm, respectively, in real-time via a multiple-pass quartz extension of the shock tube terminus. Major products that were generated during 1.5 ms residence time and wave quenched were identified and quantitated by gas chromatography (GC) and FTIR. The unimolecular rate constant (high-pressure limit) for the dissociation of TNAZ under these experimental conditions was

$$k_{\text{uni}} = 10^{13.96 \pm 0.63} \exp[(-19900 \pm 1190)/T] \text{ s}^{-1}.$$

Successive fissions of NO<sub>2</sub> groups were indicated by the time-dependent absorption levels at 405 nm. A gas-phase FTIR spectrum of TNAZ recorded at ~110 °C provided the missing data for computing the thermochemical parameters for this compound. The observed product distributions differed markedly from those calculated, indicating that the overall reaction was kinetically limited. A reaction mechanism consisting of 46 chemical reaction steps was proposed. Simulations based on this mechanism agreed reasonably well with the experimental results.

The initial decomposition products of laser-pyrolyzed TNAZ that were irradiated with 248 nm laser pulses were characterized using TOF mass spectrometry [93]. Products released to the gas phase were ionized by a pulse of 118 nm light, and the ions were detected using a TOF mass spectrometer. An analysis of the temperature dependence of the relative product yields showed that two reactions were important in the initial decomposition of TNAZ: unimolecular nitro-nitrite rearrangement followed by loss of NO and a bimolecular reaction generating nitrosodinitroazetidine (NDNAZ). Loss of NO<sub>2</sub> appears to be an early but not initial decomposition step. Experiments

with isotopically labeled TNAZ showed that the nitro-nitrite rearrangement occurred on the nitramine group and that  $\text{NO}_2$  was lost from both the nitroalkyl and nitramine groups.

Thin layers of solid TNAZ (initially at room temperature) were impacted by shock-waves, in an Ar or Ar/ $\text{O}_2$  medium [94]. The step functions of the pressure/temperature increments had rise-times well below microseconds. The pressure jumps ranged from 2–10 atm and the associated temperature jumps varied from 550 to 2500 K. In all these tests the elevated pressure/temperature conditions lasted for 1.5 ms.

The thermal behavior of TNAZ was studied using high-pressure DSC, which is a combination technique of *in-situ* thermolysis cell with rapid-scan FTIR and fast thermolysis probe with rapid-scan FTIR [95]. The thermal decomposition mechanism showed that the decomposition temperature of TNAZ at 1 MPa is 537.8 K (264.7 °C). Both the C– $\text{NO}_2$  and N– $\text{NO}_2$  bonds and all the other C–N, C–C, and C–H bonds of the four-membered ring of TNAZ were simultaneously broken with an increase in temperature. The gas products detected during the thermal decomposition of TNAZ consisted of  $\text{CO}_2$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , and NO.

### Computational Studies of Thermal Decomposition of TNAZ

It was attempted to match experimental data to a computer model of TNAZ thermal decomposition [96, 97]. DFT and *ab initio* calculations were conducted to predict decomposition pathways of TNAZ initiated by unimolecular loss of  $\text{NO}_2$  or HONO [98]. The energies for  $\text{NO}_2$  elimination by N–N and C–N bond fission was 43.21 and 50.46 kcal/mol, respectively. The decomposition initiated by trans-HONO elimination can occur by a concerted H-atom and nitramine  $\text{NO}_2$  group elimination or by a concerted H-atom and nitroalkyl  $\text{NO}_2$  group elimination via barriers of 197 kJ/mol (47 kcal/mol) and 202 kJ/mol (48.27 kcal/mol), respectively. The ranking of these four decomposition steps from energetically most favored to least favored was:  $\text{NO}_2$  elimination by N–N bond fission, HONO elimination involving the nitramine  $\text{NO}_2$  group, HONO elimination involving a nitroalkyl  $\text{NO}_2$  group, and finally  $\text{NO}_2$  elimination by C–N bond fission.

The thermal decomposition of TNAZ crystals at high temperatures was modeled by molecular dynamics (MDs) simulations [99]. The change in the potential energy of TNAZ, the formation of small-molecule products and clusters during decomposition, and the initial reaction path of TNAZ were analyzed. The kinetic parameters of different reaction stages in TNAZ thermal decomposition could be obtained. The primary thermal decomposition reaction path of TNAZ was predicted to be as follows: N– $\text{NO}_2$  and C– $\text{NO}_2$  bonds broke first, then an H atom on the quaternary ring was transferred to the nitro group, and finally the C– $\text{HNO}_2$  and N– $\text{HNO}_2$  bonds broke. The main decomposition products of TNAZ were thus  $\text{NO}_2$ , NO,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{HNO}_2$ , as well as some macromolecular clusters. The size of the cluster structure was related to the reaction temperature, decreasing in size with an increase of temperature.

### 3.2.3.3 Electron Bombardment Fission of TNAZ

TNAZ easily fragments upon electron bombardment and ionization. A study of the electron-impact (EI) fragmentation pathways of TNAZ,  $^{15}\text{N}$ , and  $^2\text{H}$  isotopically labeled compounds allowed the determination of most of the major fragmentation peaks [100]. It was found that the major pathway involves the loss of  $\text{NO}_2$  or  $\text{HNO}_2$  from the dinitroalkyl group followed by a loss of  $\text{NO}_2$  or  $\text{NO}$  from the nitramine group. The peak at  $m/e$  46,  $[\text{NO}_2]^+$ , which is the base peak, resulted primarily from N–N bond scission, while the peak at  $m/e$  30,  $[\text{NO}]^+$ , was equally likely to come from any  $\text{NO}_2$  bond. The fragmentation pathway of TNAZ showed similarities with other nitramine and nitrocarbon explosives.

### 3.2.4 Strand Burning of TNAZ

Strand burning of TNAZ, 3-azido-1-nitroazetidine (AzNAZ), and 3-azido-1,3-dinitroazetidine (AzDNAZ) in a constant-pressure bomb in the pressure range of 0.1–30 MPa and flame temperature profiles of TNAZ, AzDNAZ, and AzNAZ were measured using thin tungsten-rhenium thermocouples [76, 101]. TNAZ in the form of pressed strands of 4 mm diameter started burning at 0.4 MPa with a rate of 0.7 mm/s. Burning proceeded with a bright luminous flame, with no appreciable amount of soot and other condensed products released during combustion. The burning rate of TNAZ at 10 MPa was 17.5 mm/s, which was close to the burning rates of HMX and RDX. In the interval of 0.4–12 MPa, the burning rate law for TNAZ can be expressed as

$$r_b = 1.757p^{0.99}$$

where  $r_b$  is the burning rate in mm/s. The pressure exponent is almost equal to unity and, in combination with high volatility of TNAZ, it may be evidence of the leading role of the gas-phase chemistry in combustion.

### 3.2.5 Explosive Sensitivity of TNAZ

The shock sensitivity of pressed solid TNAZ was determined using the embedded manganin pressure gauge technique [102]. At an initial pressure of 1.3 GPa, pressure buildup (exothermic reaction) was observed after ten  $\mu\text{s}$ . At 2 GPa, TNAZ reacted rapidly and transitioned to detonation in approximately 13 mm. At 3.6 GPa, detonation occurred in less than 6 mm of shock propagation. Thus, pure TNAZ is more shock sensitive than HMX-based explosives but less shock sensitive than pentaerythritol tetranitrate (PETN) based explosives.

A 60:40 mixture of RDX/TNAZ, designated ARX-4007, had high volatility and rapidly evaporated from the liquid phase ( $>101^\circ\text{C}$ ) [103]. Hazards assessment revealed TNAZ to have an increased sensitiveness compared to TNT, while ARX-4007 was found to have sensitiveness levels that were similar to pentolite. Performance assessment of ARX-4007 as a general-purpose metal accelerating explosive gave excellent VoD (8660 m/s) and  $P_{\text{CJ}}$  (33.0 GPa) and represented substantial improvements over Composition B (7860 m/s and 29.5 GPa). TNAZ was ranked unsuitable as a TNT replacement in melt-cast systems.

TNAZ was tested as an explosive in comparison to 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX112) and 2,4-dinitroimidazole (2,4-DNI) [104]. TNAZ is useful for its performance and castability. The shock sensitivity of TNAZ was between that of pressed PETN and PBX-9501 (PBX-9501 = HMX/estane/DNPAF 95/2.5/2.5).

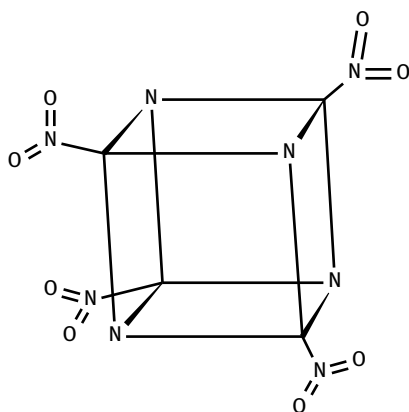
### 3.2.6 Toxicity of TNAZ

Genetic toxicity studies with TNAZ were initiated based on the possibility that it might convert or metabolize to a carcinogenic or mutagenic nitroso derivative [105, 106]. The following assays, capable of detecting mutations at the gene level, were employed: a bacterial (Ames Salmonella) test, an *in vitro* forward mutation assay at the hypoxanthine-guanine phosphoribosyl-transferase locus in Chinese hamster ovary (CHO) cells, and an *in vivo* cytogenetic (mouse bone marrow erythrocyte micro-nucleus) test. The results of the genetic toxicity studies indicated that TNAZ was negative in all three test systems. Thus, TNAZ was negative for the gene mutations in bacterial and mammalian cells and chromosomal mutations of mouse bone marrow erythrocytes.

## 4 Bridged, Caged, Fused, and Annulated Heterocyclic Compounds from Four-Membered Rings

The most unusual molecule that can be built from four-membered rings is cubane. Various cubane derivatives, such as nitrocubanes and aminocubanes, have already been discussed in previous sections. If one or more carbons in the cubane cube are replaced by nitrogen, and four hydrogens are replaced by nitro groups, one obtains a new class of energetic compounds, which are tetranitrotetraazacubanes.

Studies have suggested that octanitrocubane (ONC) is one of the most powerful HEDMs currently known. 2,4,6,8-Tetranitro-1,3,5,7-tetraazacubane (TNTAC) may be an even better HEDM due to its high nitrogen content and crystal density.



DFT and molecular mechanics methods were used to study the crystal structure, IR spectrum, electronic structure, thermodynamic properties, gas-phase, and condensed-phase HOF, detonation performance, and pyrolysis mechanism of TNTAC [107]. TNTAC has a predicted density of about  $2.12 \text{ g/cm}^3$ . Its predicted detonation velocity ( $10.42 \text{ km/s}$ ) and detonation pressure ( $52.82 \text{ GPa}$ ) are higher than that of ONC. The space group is  $P2_12_12_1$ , and the unit cell parameters are  $a = 8.87 \text{ \AA}$ ,  $b = 8.87 \text{ \AA}$ ,  $c = 11.47 \text{ \AA}$ ,  $Z = 4$ .

Another unusual four-membered heterocyclic ring structure was theorized but has not yet been synthesized. It consists of a central carbon atom in a spiro configuration with two rings formed by  $\text{—O—N—O—}$  atoms on either side. 2,6-Diaza-1,3,5,7-tetraoxaspiro[3,3]heptane and its dinitramine derivative, 2,6-dinitro-2,6-diaza-1,3,5,7-tetraoxaspiro[3,3]heptane, were predicted to have explosive performances that are similar to TNT or RDX [108].

## 5 Five-Membered Rings

It is interesting to follow the trend of the enthalpy of formation of cyclopentanes where one or more carbons are sequentially replaced by nitrogen. In the sequence from imidazole ( $\Delta H_{298}^f(\text{S}) = +58.5 \text{ kJ/mol}$ ) to 1,2,4-triazole ( $\Delta H_{298}^f(\text{S}) = +109 \text{ kJ/mol}$ ) to tetrazole ( $\Delta H_{298}^f(\text{S}) = +237.2 \text{ kJ/mol}$ ), the trend in the variation of their HOFs in the crystalline state is increasingly positive. The same trend is observed with their salts (their amino- and nitro-derivatives). With increasing enthalpies of formation, these compounds become more interesting as rocket propellants and explosives.

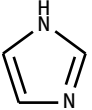
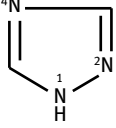
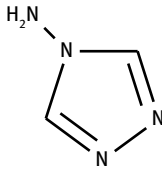
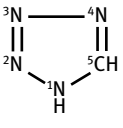
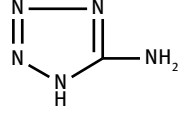
The enthalpies of formation of several imidazolium-, 1,2,4-triazolium-, and tetrazolium-based energetic salts were repeatedly calculated theoretically using different computational methods. The advances of computational chemistry have been tested in this area. At this time, there are many more computed data for the enthalpies of formation of these energetic salts than experimental measurements of the heats of combustion. The results are summarized in Tables 9 and 18, which can be found in the section on imidazolium-, 1,2,4-triazolium-, and tetrazolium-based energetic salts.

It is interesting to compare the changes in enthalpy of formation and thermal stability when one progressively replaces one carbon atom after another in a five-membered ring molecule (Table 4). From imidazole ( $\Delta H_f = +58.5 \text{ kJ/mol}$ ) to 1,2,4-triazole ( $\Delta H_f = +109.0 \text{ kJ/mol}$ ) to tetrazole ( $\Delta H_f = +237.2 \text{ kJ/mol}$ ), the enthalpies of formation get increasingly positive. Slightly different  $\Delta H_f$  numbers are shown in Table 4.

A very comprehensive 60-page summary with 387 references of azoles as energetic materials was compiled by Gao and Shreeve [109]. This is an excellent compilation of information and literature references on all kinds of energetic compounds based on nitrogen-containing five-membered heterocyclic rings. Another good source of information on azole-based energetic compounds is a dissertation [110].



**Table 4:** Effect of carbon substitution by nitrogen in five-membered ring molecules.

| Compound name                 | Imidazole                                                                         | 1,2,4-Triazole                                                                    | 4-Amino-1,2,4-triazole                                                            | Tetrazole                                                                         | 5-Aminotetrazole                                                                   |
|-------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
|                               |  |  |  |  |  |
| Enthalpy of formation, kJ/mol | +49.8                                                                             | +108.7                                                                            | +318.0                                                                            | +236.0                                                                            | +209.2                                                                             |
| Oxygen balance, %             | -188.0                                                                            | -127.4                                                                            | -114.2                                                                            | -68.5                                                                             | -65.8                                                                              |
| Decomposition temperature, °C | >257 (b.p.)                                                                       | >260 (b.p.)                                                                       | 270                                                                               | 188                                                                               | ≥206                                                                               |
| Decomposition temperature, K  | >530 (b.p.)                                                                       | >533 (b.p.)                                                                       | 543                                                                               | 461                                                                               | ≥479                                                                               |

The structure of heterocyclic five-membered rings of pyrrole, imidazole, 1,3,4-triazole, and tetrazole and some of their salts was examined based on their IR spectra [111]. The HOFs ( $\Delta H_f^\circ$ ) for azoles can be calculated using a semi-empirical MO theory. Sealed cell-DSC (SC-DSC) measurements for some azoles have been conducted and heats of reaction obtained by DSC have reflected the calculated  $\Delta H_f^\circ$  [112]. By combining heats of sublimation obtained by the additivity rule with  $\Delta H_f^\circ$  in the gas phase, which was obtained by using Parametric Method 3 (PM3),  $\Delta H_f^\circ$  of azoles in the solid phase have been estimated to within about  $\pm 10$  kcal/mol of observed values.

## 6 Pyrrole and Pyrrolidine

### 6.1 Pyrrole

Pyrrole (also called pyrrol),  $C_4H_5N$ , CAS RN [109-97-7], is a colorless, combustible fluid. It has a freezing point of m.p. 249 K =  $-24^\circ\text{C}$ , a boiling point of b.p. 403 K =  $130^\circ\text{C}$ , and a density of  $\rho = 0.9691\text{ g/cm}^3$  (Table 5). It discolors quickly when exposed to air, where it turns yellow and polymerizes to a brown resin. It is very sensitive to acids which turn it into a mix of red-colored polymers. The name is derived from its red discoloration. It has no value as a rocket propellant. Each of us carries pyrrole derivatives in our blood, as do the trees (in their leaves). Hemoglobin and chlorophyll are pyrrole derivatives [113]. The perhydrogenated pyrrole is pyrrolidine. Some energetic compounds are derived from it.



Pyrrole



Pyrrolidine

Pyrrole has a very low basicity compared to aliphatic amines. The decreased basicity is attributed to the delocalization of the lone pair of electrons of the nitrogen atom in the aromatic ring. Pyrrole is a very weak base with a  $pK$  of about  $-4$ . Pyrrole belongs to the heterocyclic compounds but its chemical behavior, evidenced by the ease of polymerization in the presence of traces of acids, is more that of a diene than that of an aromatic heterocyclic compound. The tendency toward resin formation makes it difficult to use pyrrole as a rocket fuel.

The addition of hydrazine is supposed to prevent resin formation by either pyrrole or *N*-methylpyrrole [114]. Similarly, the addition of hydrazine is supposed to reduce the resin formation during storage of furfuryl alcohol. Pyrrole stabilized by the addition of 3% hydrazine was reported to have a substantially reduced rate of resin formation, forming only 9.2 mg resin per 100 mL pyrrole within 60 d at 323 K ( $+60^\circ\text{C}$ ) compared to 418 mg resin formed in an untreated control sample. A parallel test with *N*-methyl pyrrole showed that the resin formation within 60 d was reduced from 471 to 17.8 mg by adding 3% hydrazine. The hydrazine addition not only improved the storability but also improved the ignition delay in a hypergolic bipropellant rocket engine. The phase diagram of the binary system pyrrole/hydrazine has two eutectic points: one at 11%  $\text{N}_2\text{H}_4$  melting at 233 K ( $-40^\circ\text{C}$ ) and the other at 49%  $\text{N}_2\text{H}_4$  melting at 236 K ( $-37^\circ\text{C}$ ).

Another patent describes fuel mixtures from pyrrole and ethylene imine which were already mentioned earlier in the ethylene imine chapter [22]. The suggested mixture ratios range from 10 to 97 vol.-% pyrrole and 13 to 19 vol.-% ethylene imine. A mixture of 80% pyrrole and 20% ethylene imine has a melting point of 223 K ( $-50^\circ\text{C}$ ) and has an ignition delay of only 7 ms with WFNA at 297 K ( $24^\circ\text{C}$ ) and an ignition delay of 11 ms at 233 K ( $-40^\circ\text{C}$ ).

**Table 5:** Physical properties of pyrrole.

| Property                                              | SI units                                   | Non-SI units                                       | References |
|-------------------------------------------------------|--------------------------------------------|----------------------------------------------------|------------|
| Molar mass                                            | 67.0892 g/mol                              | 14.906 mol/kg                                      | [14]       |
| Density                                               | 967 kg/m <sup>3</sup>                      | 0.967 g/cm <sup>3</sup>                            |            |
| Freezing point                                        | 250 K                                      | $-23^\circ\text{C}$                                |            |
| Boiling point                                         | 402–404 K                                  | 129–131 $^\circ\text{C}$                           |            |
| Heat capacity, liquid, at 298 K                       | 127.74 J mol <sup>-1</sup> K <sup>-1</sup> | 30.53 kcal mol <sup>-1</sup> $^\circ\text{C}^{-1}$ | [14]       |
| Enthalpy of formation, liquid                         | $+63.1 \pm 0.4$ kJ/mol                     | +15.08 kcal/mol                                    | [14]       |
| Heat of evaporation, at normal boiling point (n.b.p.) | 38.75 kJ/mol                               | 9.26 kcal/mol                                      | [14]       |
| Heat of fusion, at 250 K                              | 7.9078 kJ/mol                              | 1.89 kcal/mol                                      | [14]       |

Pyrrole, pyrrolidine, and alkylpyrroles, by themselves or in mixtures with mercaptans, were patented as hypergolic fuels [115]. Nitropyrroles, nitropyrazoles, and nitroimidazoles are intermediates in the synthesis of other energetic compounds. 2-Nitropyrrole melts at 337–338 K (64–65 °C) and 3-nitro pyrrole melts at 373–374 K (100–101 °C) [116]. A study of the kinetics of thermal decomposition of pyrrole nitro derivatives with activation energies in the 35–57 kcal/mol range suggested that the decomposition of 2-nitro and 2,5-dinitropyrroles follows a molecular mechanism [117]. The decomposition of nitropyrroles substituted at the heterocyclic ring nitrogen atom follows a radical mechanism. The thermal stability of the pyrrole nitro derivatives increased on carrying the nitro group from the  $\alpha$  to the  $\beta$  position and rose when the NH group hydrogen was replaced by a methyl group.

## 6.2 Pyrrolidine

The fully hydrogenated pyrrole is pyrrolidine, also known as tetrahydropyrrole, azolidine, tetramethylene imine,  $C_4H_9N$ , CAS RN [123-75-1], molecular mass 71.121 g/mol, m.p. 213 K = –60 °C, b.p. 361 K = 88 °C,  $\rho$  = 0.8520 g/cm<sup>3</sup>. It is a fishy-smelling liquid, miscible with water and a strong base that forms stable salts with a range of mineral acids. There are no known uses of pyrrolidine as rocket fuel. Pyrrolidinium salts have been evaluated as ionic liquids.

### 6.2.1 Pyrrolidinium Salts

Pyrrolidinium nitrate,  $C_4H_{10}N_2O_3$ , CAS RN [129228-91-7],  $M$  = 134.13, is a low-melting IL. The melting point of pyrrolidinium nitrate is 258 K (–15 °C) and its freezing point is 246 K (–27 °C) [118]. Decomposition in a DSC started at 431 K (158 °C). The heat capacity at room temperature is 228 J mol<sup>–1</sup> K<sup>–1</sup>, the refractive index is 1.3955, and the density is 1.1675 g/cm<sup>3</sup> [119]. Density, electrical conductivity, and viscosity of pyrrolidinium nitrate (including in mixtures with inert diluents) were determined as being between 283 and 353 K [120]. The data are summarized in Table 6.

A batch of the protic IL pyrrolidinium nitrate exploded during drying under reduced pressure at 383 K (110 °C) using a rotary evaporator with a silicone oil bath [121]. Therefore, caution is necessary when working with any amine nitrate or perchlorate.

The heat of combustion of 1-butyl-1-methylpyrrolidinium dicyanamidate,  $[C_4H_8N(CH_3)C_4H_9]^+[N(CN)_2]^-$ ,  $C_{11}H_{20}N_4$ , CAS RN [370865-80-8] is  $7244.8 \pm 2.3$  kJ/mol, and the standard molar enthalpy of formation  $\Delta H_f^{298}$  (L) is  $+57.9 \pm 2.8$  kJ/mol and  $\Delta H_{melt}$  is  $161.0 \pm 2.0$  kJ/mol [122].

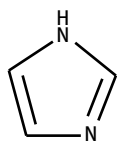
**Table 6:** Physical properties of pyrrolidinium nitrate.

| Temperature<br>K | Density<br>kg/m <sup>3</sup> | Viscosity<br>Pa s |
|------------------|------------------------------|-------------------|
| 283.15           | 1235 ± 2.8                   | 0.0589 ± 0.0059   |
| 293.15           | 1228 ± 2.7                   | 0.0403 ± 0.004    |
| 303.15           | 1220.4 ± 2.7                 | 0.0288 ± 0.0029   |
| 313.15           | 1213.1 ± 2.7                 | 0.0209 ± 0.0021   |
| 323.15           | 1205.5 ± 2.7                 | 0.0167 ± 0.0017   |
| 333.15           | 1197.2 ± 2.7                 | 0.0133 ± 0.0013   |
| 343.15           | 1190.2 ± 2.6                 | 0.0112 ± 0.0011   |
| 353.15           | 1182 ± 2.6                   | 0.00928 ± 0.00093 |

Data source: [120].

## 7 Imidazoles and Pyrazoles

Imidazole (1*H*-imidazole, 1,3-diazole, 1,3-diazacyclopentene, glyoxaline (archaic), 1,3-diazacyclopenta-2,4-diene, C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>, CAS RN [288-32-4]) is a stable heterocyclic amine. It forms colorless crystals (m.p. 363–364 K = 90–91 °C, b.p. 530 K = 257 °C,  $\rho = 1.030 \text{ g/cm}^3$ ,  $\Delta H_{298}^f(\text{S}) = +58.5 \text{ kJ/mol}$ ) and is soluble in water or alcohol. It is a weak base. Imidazole is used as an intermediate for the synthesis of many pharmaceutical drugs [123]. Imidazole and its hydrogenated members (imidazoline) are naturally occurring as building blocks in amino acids (histidine, histamine), peptides, and alkaloids. Imidazole itself is not useful as a rocket propellant. The interest in imidazole(s) as a rocket propellant ingredient stems mostly from the low melting point of the imidazolium salts, which places them into the category of “ionic liquids.” The most commonly shown structural formula is 1*H*-1,3-imidazole,

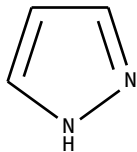


Imidazole

although compounds derived from other imidazoles (2*H*-imidazole, 4*H*-imidazole) are known. In searching for the ideal ionic liquid, the effect of substitution on the heterocyclic ring on the physical properties of the resulting salts has been thoroughly investigated.

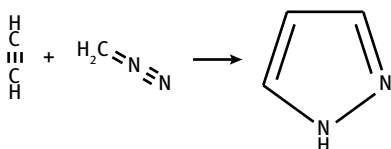
Pyrazole, also known as 1*H*-pyrazole, 1,2-diazole, 1,2-diazacyclopentene, C<sub>3</sub>H<sub>4</sub>N<sub>2</sub>, CAS RN [288-13-1], is a stable heterocyclic amine and an isomer of imidazole. It forms soft, wax-like crystals that melt at 339–343 K = 66–70 °C and boil at 459–461 K = 186–

188°C. Pyrazole is the parent compound of a large number of energetic substances which are created by attaching explosophoric groups to the heterocyclic ring.

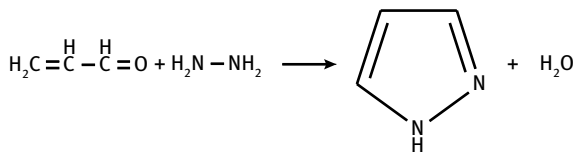


Pyrazole

Using a method first developed by von Pechmann in 1898, it was found that pyrazole can be synthesized from acetylene and diazomethane [124].



An easier method for the production of pyrazoles is the reaction of  $\alpha,\beta$ -unsaturated aldehydes with hydrazine and subsequent dehydrogenation:



## 7.1 Mono-Substituted Imidazoles

### 7.1.1 Nitroimidazole

The antibiotic azomycin is 2-nitroimidazole, which has many other uses in medical imaging. Depending on the strength of the nitrating agent and the operating conditions, the nitration of imidazole will yield mono-, di-, or tri-nitroimidazole [125].

The molecular structure and bond energies in nitroimidazoles, polynitroimidazoles, and their methyl derivatives were investigated using DFT methods [126]. The homolytic BDE corresponding to  $\text{—NO}_2$  group removal from carbon or nitrogen sites on the imidazole ring was calculated and the weakest bond was determined. A correlation was developed between impact sensitivity and the ratio (BDE/ $E$ ) of the weakest bond BDE to the total energy  $E$ . If one extrapolates this relationship, one can predict the impact sensitivities for compounds where experiments are not available. It was found that most of the nitroimidazoles were insensitive towards impact stimuli, with their 50% point being larger than 60 cm. HOFs for 21 nitroimidazoles at 298 K

in the gas phase were calculated using isodesmic work reactions. The calculated BDEs and HOFs consistently indicated that C-nitro-substituted imidazoles were more stable than the corresponding *N*-substituted ones. The introduction of methyl on C increased the stability whereas methyl groups attached to the N atom decreased the stability.

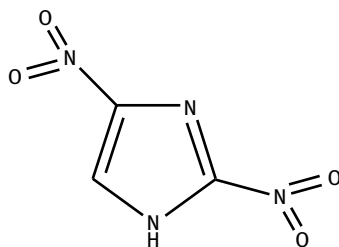
An *N*-functionalized strategy, including *N*-amination and *N*-trinitroethylamination, was utilized for the synthesis of nitroimidazole-based energetic materials, leading to a family of highly insensitive energetic *N*-aminonitroimidazoles and oxygen-rich *N*-trinitroethylaminonitroimidazoles with good safety properties [127]. The materials were characterized by IR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR, elemental analysis, and XRD. *N*-trinitroethylaminoimidazoles have favorable densities (1.75–1.84 g/cm<sup>3</sup>), good detonation properties ( $P_{\text{det}}$  27.6–35.9 GPa;  $v_{\text{det}}$  7815–8659 m/s), and moderate thermal stabilities (409–445 K = 136–172°C). These properties are better than those of some known energetic compounds, such as TNT or TATB.

4-Nitroimidazole,  $\text{C}_3\text{H}_3\text{N}_3\text{O}_2$ , molecular mass 113.07 g/mol, CAS RN [3034-38-6], melts at 576 K (303°C) (dec.) and is available commercially. It can be used as a building block for other energetic chemicals.

## 7.2 Di-Substituted Imidazoles

### 7.2.1 2,4-Dinitroimidazole

2,4-Dinitroimidazole; 1*H*-imidazole, 2,4-dinitro-; 2,4-DNI,  $\text{C}_2\text{H}_2\text{N}_4\text{O}_4$ , CAS RN [5213-49-0],  $M = 146.06$  g/mol, has a melting point of 537–540 K (264–267°C) and has moderate performance as an explosive that is expected to be 60% greater than TNT. However, it is less shock sensitive.



2,4-Dinitroimidazole

2,4-Dinitroimidazole (2,4-DNI) was synthesized by thermal rearrangement of 1,4-dinitroimidazole. 2,4-DNI is of interest mostly as an explosive where its performance is expected to be 60% better than TNT, however, it does not have any advantages as a rocket propellant [128]. The specific impulse is below that of HMX or TNAZ. It is also used as an intermediate in the synthesis of antibacterial pharmaceutical

drugs. 2,4-DNI crystallized in the orthorhombic space group, *Pbca* (with unit-cell dimensions  $a = 10.127(2) \text{ \AA}$ ,  $b = 18.497(2) \text{ \AA}$ ,  $c = 6.3337(2) \text{ \AA}$  and  $Z = 8$ ) and has an XRD density of  $1.770 \text{ g/cm}^3$  [129, 130].

Imidazole derivatives with more than two nitro groups are expected to be potential energetic ingredients for insensitive explosive or propellant formulations [131, 132]. The shock sensitivity of pressed solid 2,4-DNI was determined [133]. At an initial shock pressure of 2 GPa, several microseconds were required before any exothermic reaction was observed. At 4 GPa, 2,4-DNI reacted more rapidly but did not transition to detonation at the 12 mm deep gauge position. At 6 GPa, detonation occurred in less than 6 mm of shock propagation. Thus, 2,4-DNI is more shock sensitive than TATB-based explosives but is considerably less shock sensitive than HMX-based explosives.

The crystal structure of an isomeric dinitroimidazole, 4,5-dinitroimidazole was determined and compared to those of the 1,4- and 2,4-isomers [134]. The crystal structure of 4,5-dinitroimidazole was monoclinic, space group *P2<sub>1</sub>/n*,  $a = 11.5360$ ,  $b = 9.07$ ,  $c = 11.822$ ,  $\rho = 1.781 \text{ g/cm}^3$ . Both 4,5-dinitroimidazole and 5-nitrotetrazole, with electron-withdrawing nitro-substituents on the ring, are strong NH acids ( $\text{p}K_a = 0.8$  for 5-nitro-tetrazole).

Nitroimidazoles are amphoteric and can form salts with strong acids or strong bases. The molecular structure can be modeled to predict proton affinity. The protonation and deprotonation energies for all the nitro substituted imidazoles were computed [135]. This is a measure of the acid/base strengths of these compounds.

Thermal decomposition of 2,4-DNI was compared to that of HMX between 448 and 473 K (175 and 200 °C) using the STMBMS with a focus on the initial stages of the decomposition [136]. The early 2,4-DNI thermal decomposition is characterized by an initial decomposition, an apparent induction period, then an initial acceleratory period. The main gaseous products are NO, CO<sub>2</sub>, HNCO, H<sub>2</sub>O, N<sub>2</sub>, CO, HCN, and C<sub>2</sub>N<sub>2</sub>. The presence of adsorbed and occluded H<sub>2</sub>O is a possible cause for the early decomposition. The solid-phase thermal decomposition of 2,4-DNI was studied utilizing STMBMS between 473 and 520 K (200 and 247 °C) [137–140]. Arrhenius parameters for the induction period are  $E_a = 46.9 \pm 0.7 \text{ kcal/mol}$  and  $\log(A) = 16.3 \pm 0.3$ . The pyrolysis products were identified using perdeuterated and <sup>15</sup>N-labeled isotopomers. The products consisted of low molecular-weight gases and a thermally stable solid residue that was polyurea- and polycarbamate-like in nature.

A study of the thermal decomposition of 2,4-dinitroimidazole and 1,4-dinitroimidazole provided experimental evidence of an N–NO<sub>2</sub> bond scission reaction step in the nitramine functional group of 1,4-DNI under high heating rates [141]. No corresponding mechanism was found in 2,4-DNI, which has no N–N bonds and no nitramine functional groups. Under slow heating conditions, the main reaction channel was the conversion of 1,4-DNI to 2,4-DNI and subsequent decomposition to form CO<sub>2</sub>, N<sub>2</sub>O, NO, HCN, and other minor products. Attempts to isolate the initial reaction products were unsuccessful. There was no evidence for the formation of NO

at any stage in the reaction of 2,4-DNI. Therefore, C—NO bond scission is unlikely to play a major role in the decomposition mechanism of 2,4-DNI.

A physicochemical and mathematical model of the decomposition of 2,4-DNI was developed and applied to the experimental results [142]. The first generation of this model revealed differences between theoretical and experimental data collected under different conditions.

The thermal stability of 2,4-DNI and that of six other explosives was measured by using STMBMS. The results were compared to develop a kinetic model and identify the rate-determining steps [84]. The crystal structure of 2,4-DNI has been resolved by using neutron scattering spectroscopy and compared to a predicted structure calculated by using DFT methods [143].

The synthesis of 2,4-dinitroimidazole (2,4-DNI) by rearrangement of 1,4-dinitroimidazole (1,4-DNI) can be achieved by microwave heating instead of conventional heating [144]. This method improved the yield of the product and shortened the reaction time from 4–50 h to 10 min with the yield of 2,4-DNI up to 95% with a melting point of 538–541 K (265–268 °C) (decomposition). Direct nitration of imidazole with a mixture of concentrated nitric acid and concentrated sulfuric acid gives 4,5-dinitroimidazole, which can be converted to its ammonium salt [145].

Amino-2,4-dinitroimidazole (ADNI) was synthesized by amination of 2,4-dinitroimidazole with 2,4,6-trimethylbenzenesulfonic hydroxylamine in a total yield of 57.8% [146]. The structure of ADNI was characterized by IR, <sup>1</sup>H NMR, LC-MS, and single-crystal XRD. Results showed that ADNI belongs to an orthorhombic system, space group *Pca*2<sub>1</sub> with *a* = 10.0626(14) Å, *b* = 55.684(8) Å, *c* = 11.5639(15) Å, *Z* = 4, *D*<sub>c</sub> = 1.774 g/cm<sup>3</sup>. DSC test results revealed that ADNI has good thermal stability.

2,4-Dinitroimidazole was synthesized by nitrating 2-nitroimidazole and a thermal rearrangement of 1,4-dinitroimidazole and characterized by thermal decomposition, crystallization characteristics, explosion performance, friction sensitivity, and impact sensitivity [147]. 2,4-Dinitroimidazole was tested as an explosive in comparison to LAX112 and TNAZ [104].

The impact sensitivity of polynitroimidazoles, polynitropyrazoles, and similar nitroheterocyclic compounds can be predicted by interpolating between known data and applying structural adjustment factors [148, 149].

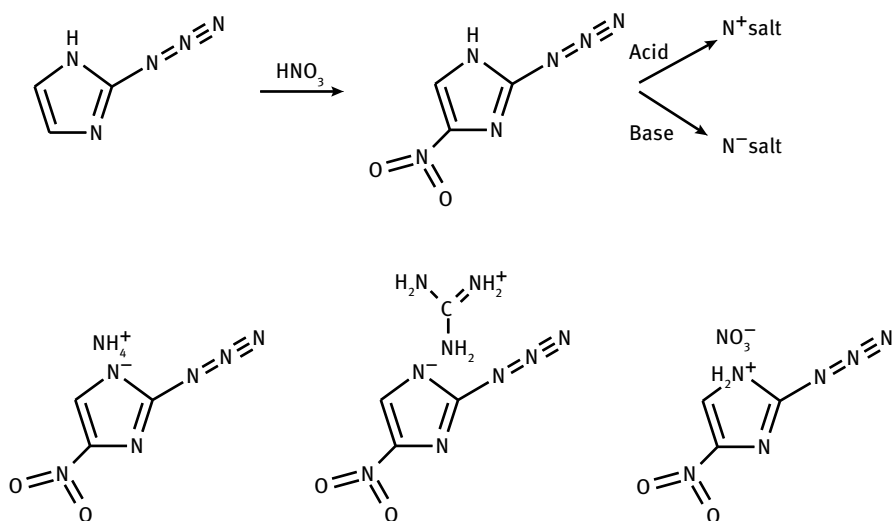
### 7.2.2 2-Azido-4-nitroimidazole

2-Azido-4-nitroimidazole and several of its derivatives have been synthesized for energetic material applications [150]. The calculated densities of the compounds ranged between 1.71 and 1.92 g/cm<sup>3</sup>. The calculated detonation pressures for these derivatives were in the range from 25.17 to 32.62 GPa and the detonation velocities were in the range from 7.65 to 8.55 km/s.

2-Azido-4-nitroimidazole was synthesized using 2-amino-4-nitroimidazole or 2-azidoimidazole as raw materials with yields of 87 or 78%, respectively, and its



structure was confirmed by MS, IR, and  $^1\text{H}$  NMR [151]. The calculated detonation velocity and detonation pressures were 7.59 km/s and 24.39 GPa, respectively. 2-Azido-4-nitroimidazole is tautomeric and can act either as an acid or as a base. The structures of salts formed from nitrogen-rich bases and 2-azido-4-nitroimidazole were determined by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and elemental analysis [152]. These salts exhibited high positive enthalpies of formation, high nitrogen content, and moderate detonation properties.



## 7.3 Tri-Substituted Imidazoles

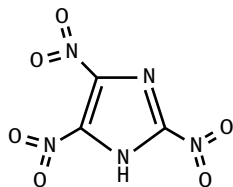
### 7.3.1 1-Nitramino-2,4-dinitroimidazole

New energetic salts based on 1-nitramino-2,4-dinitroimidazole were synthesized and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR spectroscopy, DSC, and elemental analyses [153]. The salts were found to have good physical and detonation properties. The crystal structure of guanidinium 1-nitramino-2,4-dinitroimidazolate was further confirmed by single-crystal XRD. The densities of the energetic salts ranged between 1.70 and 1.93  $\text{g}/\text{cm}^3$  as measured by a gas pycnometer. The detonation pressures and detonation velocities calculated by the EXPLO5 code ranged between 29.3–40.5 GPa and 8370–9209 m/s, respectively.

### 7.3.2 2,4,5-Trinitroimidazole

2,4,5-Trinitroimidazole, 2,4,5-trinitro-1*H*-imidazole,  $\text{C}_3\text{H}_2\text{N}_5\text{O}_6$ ,  $M = 203.070$  g/mol, CAS RN [24079-73-0], is an explosive energetic material with an acidic character. 2,4,5-Trinitroimidazolate (TNI) salts with “high-nitrogen” cations tend to be highly

hydrogen-bonded and have extremely positive enthalpies of formation ranging up to 616 kJ/mol [154]. The enthalpy of formation of 2,4,5-trinitroimidazole is +201 kJ/mol (+48.1 kcal/mol).



2,4,5-Trinitroimidazole

1-Methyl-2,4,5-trinitroimidazole can be synthesized with 1-methylimidazole as an initial material via a two-step nitration reaction [155]. Its structure was characterized by IR,  $^1\text{H}$  NMR, and elemental analysis.

#### 7.4 Tetra-Substituted Imidazoles

HOFs ( $\Delta H_f^\circ$ ) in the gas phase of substituted imidazole-based energetic materials were theoretically investigated by employing DFT and isodesmic reactions [156]. The BDEs corresponding to  $\text{NO}_2$ ,  $\text{NH}_2$ ,  $\text{CH}_3$ , and Cl removal from carbon or nitrogen positions of the azole ring were calculated. The substituent effect of electron-withdrawing ( $\text{NO}_2$ , Cl) and electron-donating ( $\text{NH}_2$ ,  $\text{CH}_3$ ) groups affects the  $\Delta H_f^\circ$ , BDE, stability, and acidity/basicity of these molecules. One of the most promising energetic compounds, which have potentially good energetic performance and low sensitivity, was 1-amino-2,4,5-trinitroimidazole.

#### 7.5 Other Nitroimidazoles

Various nitroimidazole derivatives including 2,4-dinitroimidazole, 4,5-dinitroimidazole, 2,4,5-trinitroimidazole, 1,2,4,5-tetranitroimidazole, and 1-methyl-2,4,5-trinitroimidazole have been investigated experimentally and theoretically [157]. The structure of 1,2,4,5-tetranitroimidazole has been investigated theoretically by using various levels of theories [158].

4,4',5,5'-Tetranitro-2,2'-bi-1*H*-imidazole (TNBI) has been synthesized by treating 2,2'-bi-1*H*-imidazole with an excess of sodium nitrate. Unfortunately, despite their importance in the development of new energetic materials, few studies are found in the literature concerning the thermodynamic properties of the imidazole derivatives in detail. The enthalpies of formation have been calculated for several imidazole deriva-

tives, with a focus on a particular group of picryl-substituted imidazoles using DFT methods [159]. The computed condensed phase HOFs are listed in Table 7.

**Table 7:** Predicted condensed phase HOFs of imidazole derivatives.

| Compound name                 | Gross formula     | $\Delta H_f$ condensed |          |
|-------------------------------|-------------------|------------------------|----------|
|                               |                   | kJ/mol                 | kcal/mol |
| 1-Picrylimidazole             | $C_9H_5N_5O_6$    | +296                   | +70.8    |
| 2-Nitro-1-picrylimidazole     | $C_9H_4N_6O_8$    | +295                   | +70.4    |
| 4-Nitro-1-picrylimidazole     | $C_9H_4N_6O_8$    | +295                   | +70.4    |
| 2,4-Nitro-1-picrylimidazole   | $C_9H_3N_7O_{10}$ | +293                   | +70.0    |
| 2,4-Dinitroimidazole          | $C_3H_2N_4O_4$    | +247                   | +59.0    |
| 2,4,5-Trinitroimidazole       | $C_3HN_5O_6$      | +245                   | +58.6    |
| 4,4',5,5'-Tetranitroimidazole | $C_6H_2N_8O_8$    | +558                   | +133.3   |

Data source: [159].

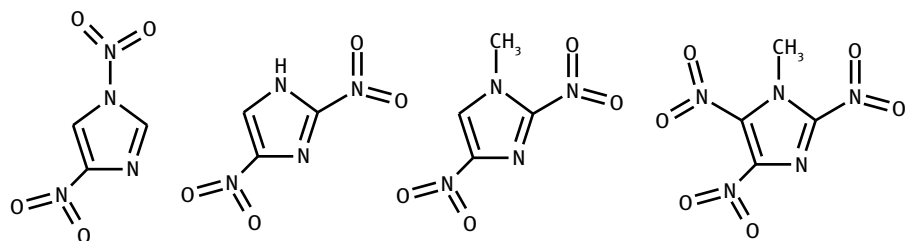
Table 8 is a summary of the predicted heat of detonation, molar volume, density, detonation velocity  $D$ , and Chapman-Jouguet ( $C-J$ ) pressure  $P$  of substituted nitro-imidazole compounds. Reviewing the direct imidazole and 1-picrylimidazole derivatives, it is noted that the values of  $D$  and  $P$  gradually increase when the number of  $-NO_2$  groups increases.

**Table 8:** Predicted densities and detonation properties of substituted nitroimidazole compounds.

| Compound                      | $Q$   | $V$                  | $\rho$            | $D$   | $P$   |
|-------------------------------|-------|----------------------|-------------------|-------|-------|
|                               | kJ/g  | cm <sup>3</sup> /mol | g/cm <sup>3</sup> | km/s  | GPa   |
| 1-Picrylimidazole             | 5.466 | 147.22               | 1.90              | 10.78 | 53.64 |
| 2-Nitro-1-picrylimidazole     | 5.82  | 175.33               | 1.85              | 11.14 | 56.36 |
| 4-Nitro-1-picrylimidazole     | 5.82  | 175.33               | 1.85              | 11.14 | 56.36 |
| 2,4-Nitro-1-picrylimidazole   | 6.087 | 202.65               | 1.82              | 11.49 | 58.99 |
| 2,4-Dinitroimidazole          | 5.847 | 92.55                | 1.71              | 11.38 | 55.73 |
| 2,4,5-Trinitroimidazole       | 6.566 | 114.86               | 1.78              | 12.31 | 66.73 |
| 4,4',5,5'-Tetranitroimidazole | 6.600 | 169.82               | 1.85              | 12.28 | 68.02 |

Data source: [159].

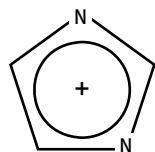
The thermal stability of four imidazole-based energetic molecules (1,4-dinitroimidazole, 2,4-dinitroimidazole, 1-methyl-2,4-dinitroimidazole, and 1-methyl-2,4,5-trinitroimidazole)



was studied both experimentally and theoretically [160]. Different from PETN, HMX, and RDX, the thermal dissociation process (ground electronic state decomposition from the Franck-Condon equilibrium point) of multi-nitroimidazoles was predicted to be a competition between  $\text{NO}_2$  elimination and nitro-nitrite isomerization followed by  $\text{NO}$  elimination for all multi-nitroimidazoles except 1,4-dinitroimidazole. In the latter instance,  $\text{N}-\text{NO}_2$  homolysis became the dominant decomposition channel on the ground electronic state, as found for HMX and RDX. Energetic materials with  $\text{C}-\text{NO}_2$  are usually more thermally stable and impact/shock insensitive than other energetic materials are with  $\text{N}-\text{NO}_2$  and  $\text{O}-\text{NO}_2$  moieties. The imidazole aromatic ring also plays an important role in improving the stability of these energetic materials. Thus, multi-nitroimidazoles energetic materials can be of significant potential for both civilian and military applications.

## 7.6 Imidazolium Salts

The nomenclature for these compounds is not very strict. They could be called imidazole salts or imidazolium salts. After the imidazole is protonated, the location of the positive charge cannot be fixed and a resonance process (which is very stable like a benzene ring) distributes the positive charge over the entire ring structure.



This enhances the stability of the ion(s). The physical properties of imidazolium salts are summarized in Table 9. The picrate salts melt at substantially higher temperatures than the nitrate salts and they are not considered ionic liquids. An excellent summary review of azole (azolium, azolate, imidazole, triazole, and tetrazole) salts with 387 references is provided in [109].

**Table 9:** Physical properties of imidazolium salts.

| Compound name                                        | Glass point |     | Onset of decomposition |      | Melting point |      | Density at 298 K<br>g/cm <sup>3</sup> | Enthalpy of formation <sup>a</sup> |          | References |
|------------------------------------------------------|-------------|-----|------------------------|------|---------------|------|---------------------------------------|------------------------------------|----------|------------|
|                                                      | K           | °C  | K                      | °C   | K             | °C   |                                       | kJ/mol                             | kcal/mol |            |
| 1-Methyl-3- <i>H</i> -imidazolium nitrate            | —           | —   | —                      | —    | 338.9         | 65.8 | —                                     | —                                  | —        | [161]      |
| 1,2-Dimethyl-3- <i>H</i> -imidazolium nitrate        | —           | —   | —                      | —    | 357.5         | 84.4 | —                                     | —                                  | —        | [161]      |
| 1,3-Dimethylimidazolium picrate                      | —           | —   | —                      | —    | 422           | 149  | —                                     | —                                  | —        | [161]      |
| 1-Butyl-3-methylimidazolium azide                    | 199         | −74 | 495                    | +222 | 309           | +36  | —                                     | +305                               | +73      | [162, 163] |
| 1-Hydroxyethyl-3-methylimidazolium azide             | 270         | −3  | 487                    | +214 | 309           | +36  | —                                     | +167                               | +40      | [162, 163] |
| 1-Allyl-3-methylimidazolium azide                    | 196         | −77 | 423                    | +150 | 292           | +19  | —                                     | +448                               | +107     | [162, 163] |
| 1- <i>n</i> -Butyl-3-methylimidazolium dicyanamidate | 183         | −90 | —                      | —    | 267           | −6   | 1.0580                                | —                                  | —        | [164]      |

<sup>a</sup> Estimated for solid phase.

Several imidazolium-based ionic liquid azides with saturated and unsaturated side chains were prepared and their physical and structural properties were investigated [162, 165]. The hypergolic ignition reactivity of these new and some previously reported ionic liquid azides with N<sub>2</sub>O<sub>4</sub> and inhibited red fuming nitric acid (IRFNA) was studied. With IRFNA and N<sub>2</sub>O<sub>4</sub>, all compounds reacted vigorously with copious production of red fumes but without ignition. The initial heat release during these reactions did not result in hypergolic ignition of the material under the tested conditions.

Thermophysical properties of imidazole-derivative 13 ILs were determined by using DSC, but only one of the ILs investigated would be of interest as a rocket propellant: 1-*n*-butyl-3-methylimidazolium dicyanamidate, CAS RN [44824-52-1]. This is a potential fuel for bipropellant engines [164]. Its density at 297 K (24 °C) is 1.0580 g/cm<sup>3</sup> and at 355.8 K (82.7 °C) is 1.0258 g/cm<sup>3</sup>. It has a glass transition temperature of 183 K (−90 °C) and a melting point of 267 K (−6 °C). The heat capacity at 298 K is 364.6 J mol<sup>−1</sup> K<sup>−1</sup> and the heat capacity function is  $C_p = 0.197T + 305.81$  J mol<sup>−1</sup> K<sup>−1</sup>.

Atomistic molecular dynamics (MDs) simulations were performed on the ionic liquids 1-butyl-3-methylimidazolium azide [bmim][N<sub>3</sub>], 1-butyl-2,3-dimethylimidazolium azide [bmmim][N<sub>3</sub>], and 1-butylnyl-3-methylimidazolium azide [bumim][N<sub>3</sub>]

[166]. Good agreement between the experimentally determined and simulated crystal structure of [bumim][N<sub>3</sub>] as well as the liquid-state density and ionic conductivity of [bmmim][N<sub>3</sub>] was achieved. Methylation of bmim (yielding bmmim) resulted in dramatic changes in the ion structuring within the liquid and slowing of ion motion. Conversely, replacing the butyl group of bmim with the smaller 2-butylnyl group resulted in an increase of ion dynamics.

There has been a great deal of interest in energetic materials based on ionic salts containing heterocyclic rings derived from 1*H*-imidazole, 1*H*-1,2,4-triazole, 1*H*-1,2,3-triazole, and 1*H*-tetrazole, which all have a high nitrogen content. These materials derive their energetic qualities from their high enthalpies of formation ( $\Delta H_f^\circ$ 's) due to the large number of C—N and N—N bonds and the more compact nature of the heterocyclic ring systems, which add density to the materials. The crystalline enthalpies of formation increase from 58.6 to 109.2 to 237 kJ/mol (14.0 to 26.1 to 56.7 kcal/mol) for 1*H*-imidazole, 1*H*-1,2,4-triazole, and 1*H*-tetrazole, respectively. The following paper [167] is referenced at all three locations at imidazolium, triazolium, and tetrazolium salts. Here is the first location where it is referenced and this is where we discuss it in detail. Reliable  $\Delta H_f^\circ$ 's for energetic precursor molecules and ions were used as a starting point for a computational approach to the prediction of the HOFs of solid-state energetic salts from electronic structure and volume-based thermodynamic (VBT) calculations [167]. The  $\Delta H_f^\circ$ 's of more complex energetics species such as substituted imidazole, 1,2,4-triazole, and tetrazole molecules and ions containing amino, azido, and nitro (including methyl) substituents were calculated using an isodesmic approach. Based on comparisons to experimental data for neutral analogues, this isodesmic approach was accurate to <3 kcal/mol for the predicted cation and anion  $\Delta H_f^\circ$ 's. The  $\Delta H_f^\circ$ 's of the energetic salts in the solid state were derived from lattice energy ( $U_L$ ) calculations using a VBT approach. Improved values for the  $\alpha$  and  $\beta$  parameters of 19.9 (kcal nm)/mol and 157 kJ/mol (37.6 kcal/mol) for the  $U_L$  equation were obtained on the basis of comparisons to experimental  $U_L$ 's for a series of 23 salts containing ammonium, alkylammonium, and hydrazinium cations. The total volumes were adjusted to account for differences between predicted and experimental total volumes due to the different shapes of the ions (flat vs. spherical). The predicted  $\Delta H_f^\circ$ 's of the energetic salts were estimated to have error bars of 25–29 kJ/mol (6–7 kcal/mol), on the basis of comparisons to established experimental  $\Delta H_f^\circ$ 's of a subset of the salts studied. Energetic salts with the highest positive  $\Delta H_f^\circ$ 's were predicted for azido-containing cations, coupled with heterocyclic anions containing nitro substituents. The substitution of functional groups on carbon versus nitrogen atoms of the heterocyclic cations had interesting stabilization and destabilization effects.

Using the experimental (or calculated) values for densities, a combination of theoretical and empirical calculations was used to predict the HOFs of energetic salts [168]. The HOFs of cations and anions and the lattice energies of 119 energetic salts were cal-

culated separately based on Born-Haber energy cycles. The HOFs coupled with densities can be used further for predicting the detonation pressures and velocities and specific impulses of energetic salts. This is a straightforward and inexpensive route to screen large numbers of energetic salts.

One of the anions which imidazolium cations can be combined with is *N,N'*-dinitrourea. The crystal structure and vibrational spectrum of imidazolium *N,N'*-dinitrourea were investigated in detail [169]. *In-situ* IR analysis, mass spectral fragmentation, and bond dissociation enthalpy calculations revealed that the initial decomposition step of imidazolium *N,N'*-dinitrourea was the breakage of the N–N bond in the anion. The *in-situ* IR of gaseous phase products and mass spectral fragmentation indicated that the main final products of decomposition were N<sub>2</sub>O and imidazole.

A series of dicationic fluoro-substituted alkylimidazolium salts have been synthesized and characterized [170]. The properties of these salts, including density, transition and decomposition temperatures, indicated that their performance was strongly dependent on the positions of the fluoro substituents, the number of carbon atoms in the alkyl group, and the anion they were partnered with.

### 7.6.1 Imidazolium Nitrate

Imidazolium nitrate, C<sub>3</sub>H<sub>5</sub>N<sub>3</sub>O<sub>3</sub>, is a potential rocket propellant ingredient. In addition to unsubstituted imidazolium nitrate, the nitrates of mono- and di-methyl substituted imidazoles have been characterized [161]. They have somewhat higher melting points, but the melting points are still below 373 K (100 °C). Therefore, they fall under the category of ionic liquids.

The synthesis of ten *N*-alkyl-*N*-cyanoalkyl-functionalized imidazolium (*N*-methyl- and *N*-butyl-*N*-((CH<sub>2</sub>)<sub>*n*</sub>CN)imidazolium; *n* = 1–4) nitrate and eleven *N*-alkyl-*N*-cyanoalkyl-functionalized imidazolium (*N*-methyl-*N*-((CH<sub>2</sub>)<sub>*n*</sub>CN)imidazolium; *n* = 1–6, *N*-(2-cyanoethyl)-*N*-((CH<sub>2</sub>)<sub>*n*</sub>CN)imidazolium; *n* = 1, 3–6) dicyanamidate salts was achieved via *N*-alkylation of substituted imidazoles with haloalkylnitriles followed by anion exchange [171]. Based on their observed melting points, all dicyanamide salts and all but one nitrate salt (1-cyanomethyl-3-methylimidazolium nitrate) had melting points of <373 K (<100 °C). DSC data indicated that melting points can be decreased by increasing the *N*-alkyl or *N*-cyanoalkyl chain length or by exchanging with the dicyanamide anion, which produced the lowest melting points in comparison to analogous halide or nitrate salts. Thermogravimetric analyses indicated that thermal stability increased for longer *N*-cyanoalkyl substituent lengths. However, it decreased significantly for nitrates and more so for dicyanamides bearing short-chain *N*-cyanoalkyl substituents [e.g., *N*-cyanomethyl, *N*-(1-cyanoethyl), and *N*-(2-cyanoethyl)] in comparison to halide precursors.

### 7.6.2 Imidazolium Perchlorate

Imidazole•imidazolium perchlorate, which is imidazolium perchlorate with an additional imidazole molecule attached, crystallizes as colorless plates that are exceedingly sensitive to moisture. XRD spectra indicated that the crystal lattice is monoclinic,  $a = 5.0994(3) \text{ \AA}$ ,  $b = 8.7333(5) \text{ \AA}$ ,  $c = 11.8228(5) \text{ \AA}$ ,  $\beta = 98.691(5)^\circ$ ,  $Z = 2$ ,  $\rho_{\text{XRD}} = 1.51 \text{ g/cm}^3$ , space group  $P2_1$ . The proton is shared between the two rings by hydrogen bonding with a hydrogen bond length of  $2.73 \text{ \AA}$  [172]. Imidazolium perchlorate is a ferroelectric substance.

Structural, dielectric, and optical properties of the imidazolium perchlorate crystal have been studied via XRD, dielectric, and birefringence measurements [173]. On cooling, structural phase transitions occurring at  $373 \text{ K}$  ( $T_{c1}$ ) and  $210 \text{ K}$  ( $T_{c2}$ ) are of second and first order, respectively. The crystal is destroyed below  $T_{c2}$  by a large structure deformation.

Imidazolium perchlorate has been synthesized and studied over a wide range of temperatures by DSC, XRD, proton NMR, optical observation, and dielectric spectroscopy [174]. Polymorphic solid-solid phase transitions were taking place at  $487$ ,  $373$ , and  $247 \text{ K}$ . The crystal structure at  $298 \text{ K}$  has been determined as trigonal, space group  $R3m$ ,  $Z = 1$  with  $a = 5.484(1) \text{ \AA}$  and  $\alpha = 95.18(2)^\circ$ . At  $385 \text{ K}$  the crystal structure remained trigonal, space group  $R\bar{3}m$ ,  $a = 5.554(1) \text{ \AA}$  and  $\alpha = 95.30(2)^\circ$ . Dielectric measurements revealed the crystal as a new ferroelectric compound with a Curie point of  $373 \text{ K}$ .

Precise measurements of specific heat changes have been performed for imidazolium perchlorate crystals using an AC calorimeter [175]. Phase transitions took place at about  $373$  and  $219 \text{ K}$ , with the continuous second-order phase transition at  $373 \text{ K}$  going to the ferroelectric phase. Excess enthalpy,  $\Delta H$ , and the excess entropy,  $\Delta S$ , of the continuous transition were estimated.

### 7.6.3 Other Imidazolium Salts

Imidazolium picrate  $[\text{C}_3\text{N}_2\text{H}_5^+][\text{C}_6\text{N}_3\text{O}_7\text{H}_2^-]$  was prepared by mixing an imidazole ethanol solution and picric acid ethanol solution [176]. Single crystals suitable for XRD measurement were cultured at room temperature. The crystal is a rhombic system, space group  $Pbca$  with crystal parameters of  $a = 0.8950 \text{ nm}$ ,  $b = 1.3474(3) \text{ nm}$ ,  $c = 2.0164 \text{ nm}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 2.4317(3) \text{ nm}^3$ ,  $D_c = 1.624 \text{ g/cm}^3$ ,  $Z = 8$ . A theoretical investigation of imidazolium picrate structure was carried out by computational chemistry methods and the atomic net charges and the electron population density were calculated.

### 7.6.4 Mono-Substituted Imidazolium and Imidazolate Salts

A computational approach to the prediction of the HOFs ( $\Delta H_f^\circ$ 's) of solid-state energetic salts from electronic structure and VBT calculations used as its starting point reliable  $\Delta H_f^\circ$ 's for energetic precursor molecules and ions [167, 177]. The  $\Delta H_f^\circ$ 's of more



**Table 10:** Theoretical and measured enthalpies of formation of azolium and azolate ions.

|                                 | $\Delta H_f^\circ$ calculated at 298 K |          | $\Delta H_f^\circ$ measured at 298 K |                 |
|---------------------------------|----------------------------------------|----------|--------------------------------------|-----------------|
|                                 | kJ/mol                                 | kcal/mol | kJ/mol                               | kcal/mol        |
| <b>Cations</b>                  |                                        |          |                                      |                 |
| 1,3- <i>H</i> -Imidazolium      | +718.0                                 | +171.6   | +720.5 $\pm$ 8.368                   | +172.2 $\pm$ 2  |
| 1,4- <i>H</i> -1,2,4-Triazolium | +836.0                                 | +199.8   | +836.8 $\pm$ 8.368                   | +200 $\pm$ 2    |
| 1,3- <i>H</i> -Tetrazolium      | +1026.8                                | +245.4   | —                                    | —               |
| 1,4- <i>H</i> -Tetrazolium      | +1022.2                                | +244.3   | —                                    | —               |
| <b>Anions</b>                   |                                        |          |                                      |                 |
| NO <sub>3</sub> <sup>−</sup>    | −302.9                                 | −72.4    | −306.7 $\pm$ 1.2552                  | −73.3 $\pm$ 0.3 |
| ClO <sub>4</sub> <sup>−</sup>   | −276.1                                 | −66      | −331.4 $\pm$ >58                     | −79.2 $\pm$ >14 |
| Imidazolate                     | +66.9                                  | +16      | +67.8 $\pm$ 9.2048                   | +16.2 $\pm$ 2.2 |
| 1,2,4-Triazolate                | +105.0                                 | +25.1    | +102.9 $\pm$ 9.6232                  | +24.6 $\pm$ 2.3 |
| Tetrazolate                     | +187.4                                 | +44.8    | +200.4 $\pm$ 12.9704                 | +47.9 $\pm$ 3.1 |

Data source: [167].

complex energetic species such as substituted imidazole, 1,2,4-triazole, and tetrazole molecules and ions were calculated in this way and compared to experimental data (Table 10).

Based on comparisons to experimental data for neutral analogues, this isodesmic approach was accurate to <3 kcal/mol for the predicted cation and anion  $\Delta H_f^\circ$ . The  $\Delta H_f^\circ$  data of the energetic salts in the solid state were derived from lattice energy calculations using a valence bond theory approach. The predicted  $\Delta H_f^\circ$  of the energetic salts were estimated to have error bars of 25–29 kJ/mol (6–7 kcal/mol), based on comparisons to established experimental  $\Delta H_f^\circ$  of a subset of the salts studied. Energetic salts with the highest positive  $\Delta H_f^\circ$  were predicted for azido-containing cations, coupled with heterocyclic anions containing nitro substituents. The substitution of functional groups on carbon versus nitrogen atoms of the heterocyclic cations can have stabilizing or destabilizing effects.

The initial melting point analysis revealed that generally, due to the size and shape of the anion, the nitrate salts exhibited significantly lower melting points than their picrate equivalents [177, 178]. TGA of nitro-substituted and non-substituted protonated imidazolium salts revealed that thermal stabilities range from 343–473 K (70–200 °C), with picrate salts exhibiting higher stabilities (by 40 K = 40 °C) than nitrate salts. Disappointingly, however, the thermal stabilities of these protonated salts were significantly lower than those of alkylated derivatives.

Three organic imidazolium-based perchlorate salts ILs have been synthesized by simple, inexpensive, and non-hazardous methods, using ammonium perchlorate (AP) as the perchlorate source [179]. By selecting the appropriate cation, perchlorate can be incorporated into an ionic liquid which serves as its own electrolyte for the electrochemical reduction of the perchlorate anion, using an ionic liquid as both reagent

and electrolyte. This is a continuous perchlorate removal/remediation process for converting sometimes unwanted perchlorate to chloride. Instead of using  $\text{HClO}_4$  (which is dangerous when mixed with organics),  $\text{LiClO}_4$ , or  $\text{AgClO}_4$  (which has a higher cost) it is more economical to utilize AP (even recycled AP) in the synthesis of perchlorate-based ILs. Three potential routes to incorporate the perchlorate anion into potentially energetic 1-methylimidazolium, using AP as the perchlorate source, are: **(1)** the reaction of a neutral amine (1-methylimidazole) with AP in aqueous solution, resulting in the formation of a protonated imidazolium perchlorate and liberating ammonia gas; **(2)** decarboxylation of 1,3-dimethylimidazolium-2-carboxylate<sup>13</sup> by reaction with AP to form 1,3-dimethylimidazolium perchlorate,  $\text{NH}_3$ , and  $\text{CO}_2$ ; and **(3)** metathesis of 1-butyl-3-methylimidazolium chloride with AP in water, forming the insoluble 1-butyl-3-methylimidazolium perchlorate and water-soluble  $\text{NH}_4\text{Cl}$ .

A series of functionalized imidazolium and 1,2,4-triazolium salts with cyanomethyl, vinyl, and propargyl substituents coupled with energetic anions (such as perchlorate, nitrate, dicyanamidate, and dinitramidate) were prepared and characterized by NMR and IR spectroscopy and elemental analyses [180, 181]. Since some of these salts melt  $<373\text{ K}$  ( $<100^\circ\text{C}$ ), they can be classified as ionic liquids. Their densities ranged between 1.25 and  $1.76\text{ g/cm}^3$ . The standard enthalpies of formation of the salts were calculated and ranged from  $\Delta H^\circ_f = -56$  to  $+851\text{ kJ/mol}$ . Of all the salts synthesized, the dicyanamidates exhibited the highest positive HOFs but also the lowest densities.

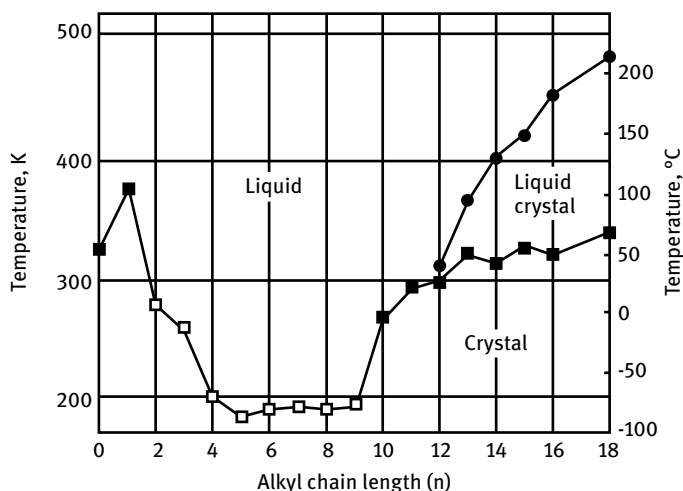
The dinitromethanide  $(\text{NO}_2)_2\text{CH}^-$  anion proved to be a useful component of room temperature ILs with substituted imidazolium cations [182]. Delocalization of both the  $(\text{NO}_2)_2\text{CH}^-$  anion and dimethylimidazolium cation was found from single-crystal structure data. Their impact sensitivities were determined, and they were found to be insensitive ( $>40\text{ J}$ ).

Although the following paper deals only with ionic liquids with non-energetic anions, the insight gained about the thermal stability of the cations is useful for developing other (energetic) ionic liquids. The thermal decomposition of a series of imidazolium-type IL samples was studied using pyrolysis-gas chromatography at  $823\text{ K}$  ( $550^\circ\text{C}$ ) [183]. As for the imidazolium halides, haloalkanes and 1-alkylimidazoles corresponding to the alkyl substituents were mainly formed through the nucleophilic attacks of halide ions to the alkyl groups. This was followed by C—N bond cleavage along with a minor amount of alkenes. Meanwhile, in the case of the ionic liquids with  $\text{BF}_4$ ,  $\text{PF}_6$ , and  $\text{CF}_3\text{SO}_3$  anions, corresponding alkenes were predominantly produced along with 1-alkylimidazoles rather than haloalkanes. As for the samples with longer alkyl groups, the pyrolyzates reflecting the C—C bond scissions in the alkyl groups were also formed to some extent. Imidazole rings did not split under the experimental conditions at around  $823\text{ K}$  ( $550^\circ\text{C}$ ).

## 7.6.5 Di-Substituted Imidazolium and Imidazolate Salts

### 7.6.5.1 Di-Substituted Imidazolium Salts

The melting points of organic salts are influenced by the symmetry of the molecule, the flexibility of the alkyl or aryl substituents, and the accessibility of the charges. An interesting graph in the ionic liquids literature, which is provided in Figure 5, demonstrates the plot of the melting point of an ionic liquid as a function of structure modification [184]. This graph shows the tremendous effect of modest structural changes on physical properties. A similar trend is observed when the melting point is plotted versus the counter anion structure. This illustrates one of the greatest advantages of ionic liquids, their tunable physical properties.



**Figure 5:** Melting point versus alkyl chain length of 1-alkyl-3-methylimidazolium tetrafluoroborates. (Modified from [184] with permission obtained from Dr. Joshua Aronson, 30 June 2020.)

The influence of the substituents on both formation and thermal properties of ionic liquids, the salts of 1,3-dimethyl-4-nitroimidazolium, 1-ethyl-3-methyl-4-nitroimidazolium, 1,2,3-trimethyl-4-nitroimidazolium, 1,3-dimethyl-2-nitroimidazolium, and 1-ethyl-3-methyl-2-nitroimidazolium has been determined by DSC, TGA, and single-crystal XRD. It was shown that an electron-withdrawing nitro substituent can be successfully appended and has a similar influence on the melting behavior as that of corresponding methyl group substitution. In the solid state, the nitro group has a suggestive effect, beyond the steric contribution, on the crystal packing. Twelve 1,3-dialkylimidazolium salts containing strong electron-withdrawing groups (EWG) nitro- and cyano-functionalities directly appended to the cationic heterocyclic rings have been synthesized. However, the anions (methylsulfonate, triflate, bis(triflyl)-imides) were less suitable as energetic salts [185]. The goal was to develop synthetic

and predictive strategies for the introduction of energetic functions and components into ionic liquid systems, as well as to understand how to engineer low melting or specific activity ILs.

Twenty-eight energetic salts with tetramethyl-, tetraethyl-, and tetrabutylammonium and 1-butyl-3-methylimidazolium cations paired with 3,5-dinitro-1,2,4-triazolate, 4-nitro-1,2,3-triazolate, 2,4-dinitroimidazolate, 4,5-dinitroimidazolate, 4,5-dicyanoimidazolate, 4-nitroimidazolate, and tetrazolate anions have been prepared and characterized by using DSC, TGA, and single-crystal XRD in order to study the effects of cation and anion type on the physicochemical properties of the resulting crystalline salts or ionic liquids [186]. Ionic liquids (defined as having m.p.  $<373\text{ K} = <100^\circ\text{C}$ ) were obtained with all combinations of the 1-butyl-3-methylimidazolium cation ( $[\text{C4mim}]^+$ ) and the heterocyclic azolate anions studied. Ionic liquids were also obtained with several combinations of tetraethyl or tetrabutylammonium cations and the azolate anions. The  $[\text{C4mim}]^+$  azolates were liquids at room temperature where they exhibited wide liquid ranges and formed glasses on cooling. Glass-transition temperatures were in the range of 220 to 191 K ( $-53$  to  $-82^\circ\text{C}$ ), except for the 3,5-dinitro-1,2,4-triazolate salt with m.p.  $306\text{ K} = 33^\circ\text{C}$ .

Rapid-scan FTIR spectroscopy and TOF mass spectrometry were used to study the thermal decomposition of three imidazolium-based ionic liquids, with 1-ethyl-3-methyl-imidazolium (emim) as the cation and  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  as the anions at heating rates of  $2000\text{ K/s}$  and temperatures to  $435^\circ\text{C}$  in an ambient inert gas at 1 atm [187]. The evolution of gas-phase species indicated that the most probable sites for proton transfer and subsequent secondary reactions were primarily the methyl group and, secondarily, the ethyl group. The ring appeared to remain intact, as there was no evidence of the formation of HCN, imines, or related products. The nitrate group in  $[\text{emim}]\text{NO}_3$  served as a strong oxidizer and reacted strongly with the methyl/ethyl groups at elevated temperatures to produce combustion products.

The molar enthalpy of formation of the liquid 1-butyl-3-methylimidazolium dicyanamide was measured using a combustion calorimetry and found to be  $206.2 \pm 2.5\text{ kJ/mol}$ . The molar enthalpy of vaporization was obtained from the temperature dependence of the vapor pressure measured using the transpiration method and was found to be  $157.2 \pm 1.1\text{ kJ/mol}$  [188]. The enthalpy of formation of gaseous 1-butyl-3-methylimidazolium dicyanamide was  $363.4 \pm 2.7\text{ kJ/mol}$ .

Thirty-one salts were synthesized by pairing diverse cations (1-butyl-3-methylimidazolium, tetramethyl-, tetraethyl-, and tetrabutylammonium) with azolate anions (5-nitrobenzimidazolate, 5-nitrobenzotriazolate, 3,5-dinitro-1,2,4-triazolate, 2,4-dinitroimidazolate, 4-nitro-1,2,3-triazolate, 4,5-dinitroimidazolate, 4,5-dicyanoimidazolate, 4-nitroimidazolate, and tetrazolate) [189]. These salts were characterized by DSC, TGA, and single-crystal XRD. The azolates in general were surprisingly stable in the systems explored. Ionic liquids were obtained with all combinations of the 1-butyl-3-methylimidazolium cation and the heterocyclic azolate anions studied, and with several combinations of tetraethyl- or tetrabutylammonium cations and the

**Table 11:** Properties of 1-ethyl-3-methyl-*H*-imidazolium perchlorate.

| Compound                         | Property                                  | Physical state | SI units                                         | Other units                                      |
|----------------------------------|-------------------------------------------|----------------|--------------------------------------------------|--------------------------------------------------|
| [emim][ClO <sub>4</sub> ]        | lattice energy $U_{\text{TOT}}$           | solid          | $+515 \pm 67$ kJ/mol                             | $+123 \pm 16$ kcal/mol                           |
| [emim] <sup>+</sup>              | enthalpy of formation $\Delta H_f^\circ$  | gaseous cation | $+603$ kJ/mol                                    | $+144.2$ kcal/mol                                |
| [ClO <sub>4</sub> ] <sup>−</sup> | enthalpy of formation $\Delta H_f^\circ$  | gaseous anion  | $-277$ kJ/mol                                    | $-66.1$ kcal/mol                                 |
| [emim][ClO <sub>4</sub> ](S)     | enthalpy of formation $\Delta H_f^\circ$  | solid          | $-230 \pm 67$ kJ/mol                             | $-55 \pm 16$ kcal/mol                            |
| [emim][ClO <sub>4</sub> ](L)     | enthalpy of formation $\Delta H_f^\circ$  | liquid         | $-218 \pm 67$ kJ/mol                             | $-52 \pm 16$ kcal/mol                            |
| [emim][ClO <sub>4</sub> ](S)     | Gibbs energy $\Delta G_f^\circ$           | solid          | $+121 \pm 67$ kJ/mol                             | $+29 \pm 16$ kcal/mol                            |
| [emim][ClO <sub>4</sub> ](L)     | Gibbs energy $\Delta G_f^\circ$           | liquid         | $+100 \pm 67$ kJ/mol                             | $+24 \pm 16$ kcal/mol                            |
| [emim][ClO <sub>4</sub> ](S)     | standard absolute entropy $S^\circ_{298}$ | solid          | $347 \pm 17$ J K <sup>−1</sup> mol <sup>−1</sup> | $83 \pm 4$ cal K <sup>−1</sup> mol <sup>−1</sup> |
| [emim][ClO <sub>4</sub> ](L)     | specific impulse                          | liquid         | 2237 m/s                                         | 228 s                                            |
| [emim][ClO <sub>4</sub> ](L)     | detonation velocity                       | liquid         | 5466 m/s                                         | —                                                |
| [emim][ClO <sub>4</sub> ](L)     | detonation pressure $p_{\text{CJ}}$       | liquid         | 99 kbar                                          | —                                                |
| [emim][ClO <sub>4</sub> ](L)     | explosion temperature                     | liquid         | 2842 K                                           | 2569 °C                                          |

Data source: [191]

azolate anions. Favorable structure-property relationships were most often achieved when changing from 4- and 4,5-disubstituted anions to 3,5- and 2,4-disubstituted anions. The most promising anion for use in energetic ionic liquids (EILs) of those studied for this publication was 3,5-dinitro-1,2,4-triazolate. This is based on its contributions to the entire set of desired properties.

Thermal stability and thermal decomposition kinetics of 1-butyl-3-methylimidazolium dicyanamidate ([bmin<sup>+</sup>][N(CN)<sub>2</sub><sup>−</sup>]) were investigated using both isothermal and non-isothermal TGA under high pure nitrogen as carrier gas [190]. The long-term thermogravimetric studies revealed that the highest storage temperature should be 383 K = 110 °C. At this temperature [bmin<sup>+</sup>][N(CN)<sub>2</sub><sup>−</sup>] lost less than 10% by mass in 10 h. The non-isothermal activation energy was  $147 \pm 2$  kJ/mol.

Thermochemical and detonation parameters were calculated for the ionic liquid, 1-ethyl-3-methyl-*H*-imidazolium perchlorate, [emim][ClO<sub>4</sub>] and its associated solid (Table 11) [191]. The effect of azolate anion structure on the physical properties of four ionic liquids, specifically on their glassy dynamics and ion interactions was studied utilizing rheology, X-ray scattering, UV/vis absorption, and *ab initio* calculations [192]. The study used four ionic liquids, three of which shared the same 1-butyl-3-methylimidazolium cation. The anions were tetrafluoroborate, 1-butyl-3-methylimidazolium 4-nitroimidazolate, and 1-butyl-3-methylimidazolium 5-aminotetrazolate. The peculiar rheological behavior for these ionic liquids, which

deviates from the one expected for molecular glass-formers, included high elasticity in the low-frequency zone and failure of time-temperature superposition. These peculiarities were attributed to specific interactions in the nitrogen-rich planar rings of azolate ionic liquids. X-ray scattering measurements revealed a nanometer-ordered organization in azolium azolates due to hydrogen bond interactions. This conclusion was also supported by *ab initio* calculations.

MDs simulation calculations of ionic liquids containing 1-butyl-3-methylimidazolium [bmim] cation and nitrate, azide, or dicyanamidate anions were conducted. A comparison of thermodynamic properties such as densities, enthalpies of vaporization, and ion binding energies, as well as structural correlations obtained from simulations at atmospheric pressure and over the temperature range 298–393 K demonstrated that ionic liquids with the  $\text{N}(\text{CN})_2$  anion showed significantly different characteristics compared to ionic liquids with the  $\text{N}_3$  and  $\text{NO}_3$  anions [193]. This trend was further manifested in dynamical properties characterized by self-diffusion coefficients and molecular rotational relaxation times. For [bmim][ $\text{NO}_3$ ], the simulations gave a value for  $\Delta H_{\text{vap}}$  of 145.8 kJ/mol, which was in good agreement with prior experiments (162.4 kJ/mol). The experimental value of  $\Delta H_{\text{vap}}$  for [bmim][ $\text{N}_3$ ] was very similar to the value of 152.5 kJ/mol predicted from simulations at 298 K. The predicted  $\Delta H_{\text{vap}}$  for [bmim][ $\text{N}(\text{CN})_2$ ] was 195.3 kJ/mol.

Density, viscosity, and surface tension data sets of 13 ionic liquids formed by imidazolium, pyridinium, or pyrrolidinium cations paired with dicyanamidate (dca), tetrafluoroborate, thiocyanate, methylsulfate, and trifluoroacetate anions were measured at temperatures between 293 and 363 K [194]. The effect of the ionic-liquid-forming anion and cation on the physical properties was analyzed systematically. A longer alkyl chain in imidazolium-based ionic liquids was associated with lower density, higher viscosity, and lower surface tension. Density of 1-butyl-3-methylimidazolium dicyanamidate [C4mim][dca]  $\text{C}_{10}\text{H}_{15}\text{N}_5$  at 293.15 K and 100 kPa was  $1.064.4 \pm 0.008 \text{ g/cm}^3$  and viscosity was  $0.0332 \pm 0.0009 \text{ Pa}\cdot\text{s}$ . Additional data can be found in [195–197].

Eight 5-aminotetrazolate (5-AT) salts based on the 1,2,3-trimethylimidazolium (**1**), 1,3-dimethylimidazolium (**2**), 1-ethyl-3-methylimidazolium (**3**), 1-butyl-3-methylimidazolium (**4**), 1-isobutyl-3-methylimidazolium (**5**), 1-(3'-methylbutyl)-3-methylimidazolium (**6**), 1-hexyl-3-methylimidazolium (**7**), and 1-methyl-3-octylimidazolium (**8**) cations have been synthesized and characterized by IR and NMR spectroscopy and elemental analysis [198]. DSC/TGA measured the thermal stabilities of the 5-AT salts. These salts decomposed within the temperature range 296–535 K (230–262°C). Salts **3–8** were very fluent room-temperature ionic liquids, whose glass transition temperatures were quite low. Their viscosities at 303 K (30°C) were in the range from 92 to 208 cPs. Salt (**2**) with the 1,3-dimethylimidazolium cation had the highest positive enthalpy of formation. These 5-AT salts were insensitive to impact (>40 J) and friction (>360 N). Hypergolic reactions of these 5-AT salts with 100%  $\text{HNO}_3$  were also examined but only few ignited.

The imidazole ring already has a good amount of internal energy that is available for forming energetic salts. The energy of imidazolium salts was further increased by first combining two methylimidazole rings with an acetylene molecule to form a di-(methylimidazolyl)acetylene and then replacing the chloride counter ions with either dodecaboranate  $[(B_{12}H_{12})^{2-}]$  or perchlorate anions to gain even more energetic salts [199]. These compounds were characterized by NMR, MS, TGA, and elemental analyses. The enthalpy of formation and heat of explosion of all the compounds were experimentally determined via the enthalpy of combustion. Based on the properties of these compounds, they could be used as insensitive energetic materials in rocket propellants and burn rate accelerators.

*N,N*-Bis(1*H*-tetrazol-5-yl)amine anions (HBTA<sup>-</sup> and BTA<sup>2-</sup>) were used as nitrogen-rich components for the construction of EILs. Seven ionic liquids, namely, 1,3-dimethylimidazolium (1), [C1mim]HBTA, 1-ethyl-3-methylimidazolium (2), [C2mim]HBTA, 1-butyl-3-methylimidazolium (3), [C4mim]HBTA, 1-hexyl-3-methylimidazolium (4), [C6mim]HBTA, 1-methyl-3-octylimidazolium (5), [C8mim]HBTA, and 1,2,3-trimethylimidazolium (6), [C1mmim]HBTA cations with the HBTA<sup>-</sup> anion, and di-1,2,3-trimethylimidazolium *N,N*-bis(1*H*-tetrazol-5-yl)amine (7), [C1mmim]2BTA were synthesized and characterized by IR and NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry [200]. The crystal structures of (1) and (7) were determined by single-crystal XRD (1): monoclinic,  $P2_1/n$ ,  $a = 14.0653(4) \text{ \AA}$ ,  $b = 6.9507(2) \text{ \AA}$ ,  $c = 22.4699(7) \text{ \AA}$ ,  $\beta = 93.996(3)^\circ$ ,  $V = 2191.38(12) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho = 1.511 \text{ g/cm}^3$ ; (7) monoclinic,  $P2_1/c$ ,  $a = 17.5869(3) \text{ \AA}$ ,  $b = 12.8757(2) \text{ \AA}$ ,  $c = 21.9203(6) \text{ \AA}$ ,  $\beta = 125.0580(10)^\circ$ ,  $V = 4063.15(15) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho = 1.221 \text{ g/cm}^3$ . The ionic liquids 1–7 were thermally stable up to 493 K (220 °C) and 2–5 were room-temperature ionic liquids. The HOFs of 1–7 obtained by both experimental and theoretical methods were all positive. The ionic liquids 1–7 were insensitive towards impact (>40 J) and friction (>360 N). They could be ignited in air. These new EILs contain only C, H, and N and are of interest as potential propellants with high energy, high thermal stability, low sensitivity to impact and friction, and environmentally friendly decomposition products.

### 7.6.5.2 Multi-Substituted Imidazolium and Imidazolate Salts

1,3-Dimethyl-4-nitroimidazolium nitrate can be prepared by adding silver nitrate to a magnetically stirred solution of 1,3-dimethyl-4-nitroimidazolium iodide in water. After 2 h at room temperature, silver iodide was removed by filtration. The filtrate was dried in vacuo at 333 K (60 °C) to produce colorless needles in 98% yield, m.p. 435–436 K (162–163 °C) [201].

The HOFs were determined for seven of the multi-substituted imidazolium salts [202]. Interestingly, while the 5-nitro perchlorate and nitrate salts had a quite high negative  $\Delta H_f$ 's, the 2-azido salts had modestly high positive  $\Delta H_f$ 's but rather high  $T_m$  values. For example, 2-azidoimidazolium perchlorate had a melting point of 389 K (116 °C), started to decompose at 405 K (132 °C), and had a density of  $1.73 \text{ g/cm}^3$ .

2-azidoimidazolium nitrate had a melting point of 397 K (124 °C), started to decompose at 397 K (124 °C), and had a density of 1.89 g/cm<sup>3</sup>. 1,2,3-trimethyl-5-nitroimidazolium perchlorate had a melting point of 459 K (186 °C), started to decompose at 580 K (307 °C), and had a density of 1.65 g/cm<sup>3</sup>. 1,2,3-trimethyl-5-nitroimidazolium nitrate had a melting point of 434 K (161 °C), started to decompose at 439 K (166 °C), and had a density of 1.52 g/cm<sup>3</sup>.

Ammonium 2,4,5-trinitroimidazolate can be readily prepared by treating an ether solution of 2,4,5-trinitroimidazole with anhydrous ammonia [203]. It is thermally more stable than RDX, melts at 521 K (248 °C), is stable up to 521 K (248 °C), has a density of 1.835 g/cm<sup>3</sup>, an enthalpy of formation of −86.02 kJ/mol, a detonation velocity of 8560 m/s, and a drop weight sensitivity of 50.3 cm with an Explosives Research Laboratory of the National Defense Research Committee (ERL) Type 12 tool [204].

Energetic salts comprising of an energetic 1,2-dimethyl-3-(2-nitrooxyethyl)-imidazolium cation and energetic anions such as nitrate, 3,5-dinitro-1,2,4-triazolate, picrate, 3-nitro-5-oxo-1,2,4-triazolate, dinitromethanide, dinitramide, and 5-nitrotriazolate were easily synthesized via quaternization, nitration, and metathesis and characterized by FTIR, UV-Vis spectroscopy, electrospray ionization mass spectrometry (ESI-MS), NMR, TGA, DSC, and elemental analysis [205]. The salts are typical ionic liquids with glass transition temperatures of 215 to 251 K (−58 to −22 °C) and a melting point below 373 K (100 °C).

## 7.7 Other Imidazole Derivatives

Different amino- and methyl-trinitrodiazoles have been considered as potential candidates for high explosives and their predicted properties were calculated by quantum chemical methods [206]. Geometric and electronic structures, band gap, thermodynamic properties, crystal density, and detonation properties were studied using DFT methods. Presumably, the relative positions of methyl or amino group and nitro groups in the trinitrodiazole would determine the stability, sensitivity, and crystal density and thus detonation performance as an explosive. The chemical energy of explosion (1.35 to 1.47 kcal/g), density (1.93 g/cm<sup>3</sup>), detonation velocity (9.0 to 9.3 km/s), and detonation pressure (38 to 40 GPa) of aminotrinitrodiazoles are comparable to those of RDX and HMX.

### 7.7.1 Biimidazolate Salts

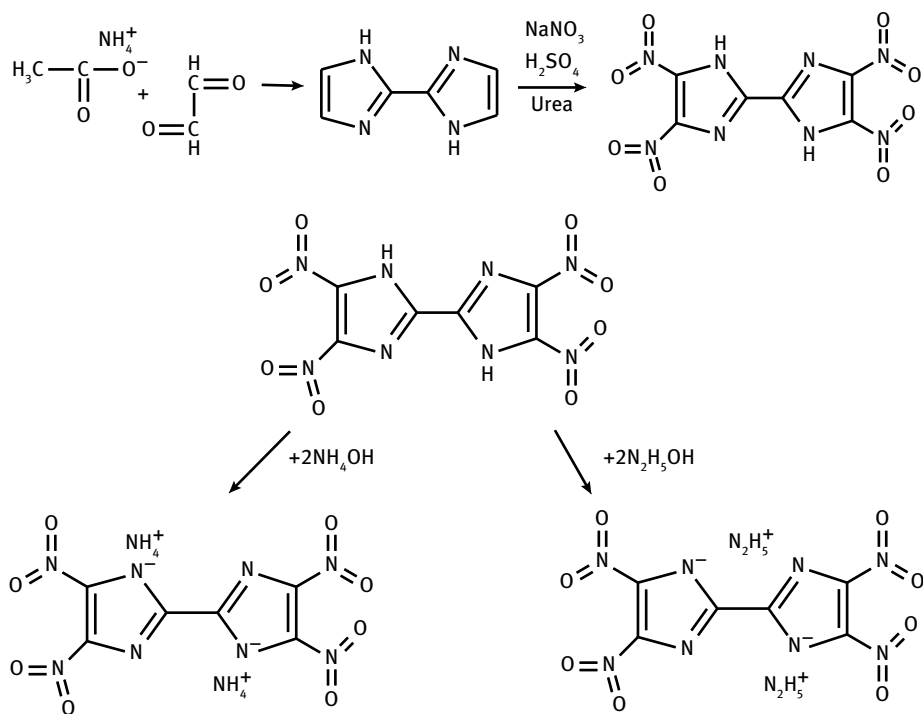
Several salts of 4,4',5,5'-tetranitro-2,2'-biimidazolate were synthesized and characterized [207]. Each of the salts was characterized chemically, thermally, morphologically, as well as with external stimuli (impact, friction, thermal, electrostatic discharge [ESD]). The bis-triaminoguanidinium salt of 4,4',5,5'-tetranitro-2,2'-biimidazole dis-



played a fast-burning rate and had the lowest pressure dependence exponent yet measured for any triaminoguanidinium salt.

Nucleophilic addition reactions of the diammonium salt of 4,4',5,5'-tetranitro-1,1'-biimidazole can form 1,1'-dimethyl-4,4',5,5'-tetranitro-2,2'-biimidazole, 1,1'-diamino-4,4',5,5'-tetranitro-2,2'-biimidazole, or ammonium 1-amino-4,4',5,5'-tetranitro-2,2'-biimidazolate [208].

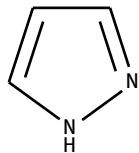
The diammonium and dihydrazinium salts of 4,4',5,5'-tetranitro-2,2'-biimidazolate (TNBI) were synthesized and characterized [209]. These dianionic salts were easily formed in good yields by the reaction of TNBI with aqueous solutions of the cationic species. TNBI can be synthesized from 2,2'-biimidazole, which can be synthesized via the condensation of aqueous glyoxal with ammonium acetate. The compounds were characterized by density, NMR, FTIR, Raman spectroscopy, elemental analysis, thermal analysis (DSC, vacuum thermal stability [VTS], and calorimetry), and small-scale safety testing (impact, friction, ESD).



*N,N*-Dinitramino imidazole was paired with nitrogen-rich bases, resulting in versatile ionic derivatives which were fully characterized by IR, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and elemental analysis [210].

## 7.8 Pyrazole Derivatives

Pyrazole, 1*H*-pyrazole,  $C_3H_4N_2$ , is a five-membered ring with two vicinal nitrogen atoms



Pyrazole

### 7.8.1 Mono-Substituted Pyrazole Derivatives

Substituents can be added to the pyrazole ring in either the 1, 3, or 4-position (the 5-position would be identical to the 3-position). Nitration in the 1-position would create a cyclic nitramine.

To synthesize the salts of 3-nitropyrazole, *N*-nitropyrazole was first synthesized with pyrazole as raw material and  $HNO_3$ - $Ac_2O$ - $HAc$  as a nitration agent [211]. *N*-nitropyrazole at high temperature was rearranged as 3-nitropyrazole. The structures of products were characterized by melting point, IR, NMR, and elemental analysis. The optimum reaction yield was 85.5% for nitration, 92.8% for rearrangement reaction, and 79.3% for total yield. The copper and lead salts were synthesized by the reaction of 3-nitropyrazole with some inorganic copper and lead salts. The structures of the products were characterized by melting point, IR, NMR, and elemental analysis

The molecular and crystal structure of 3-nitropyrazole was determined by XRD [212]. The triclinic unit cell contains 12 molecules, which form four hydrogen-bonded ( $N-H\cdots N$ ) trimers. Each trimer comprises of a pseudo-ring in a flattened envelope that was distorted towards a chair conformation. *Ab initio* calculations were performed on 3(5)-nitro- and 4-nitropyrazole, and their corresponding protonated forms, to explain the cause for the difference in basicities between the two nitropyrazoles.

*N*-Nitropyrazole is a nitramine; it crystallizes in space group  $P2_1/e$ , monoclinic, with cell parameters of  $a = 7.337(1) \text{ \AA}$ ,  $b = 10.032(1) \text{ \AA}$ ,  $c = 7.199(1) \text{ \AA}$ ,  $\beta = 116.6(2)^\circ$ ,  $M_r = 113.1$ ,  $Z = 4$ ,  $D_{XRD} = 1.585 \text{ g/cm}^3$ . The molecule is planar and the  $\angle O-N-O$  angle,  $128.5(2)^\circ$ , is slightly larger than in other  $N-NO_2$  fragments [213].  $^{14}N$  nuclear quadrupole resonance data for several pyrazoles and 1,2,4-triazoles are listed in [213]. *N*-Nitropyrazole can be prepared by treating pyrazole nitrate with acetic anhydride. The compound is stable and melts at 366 K ( $93^\circ C$ ) without decomposition.

A time-resolved pulsed photoacoustic spectroscopy technique powered by a Nd:YAG laser at the second harmonic, i.e.,  $\lambda = 532 \text{ nm}$ , 7 ns pulse width at 10 Hz repetition rate was used to study the thermal decomposition of 3(5)-nitropyrazole, 4-nitropyrazole, and 1-nitropyrazole [214], examining the effect of pressure, tem-

perature, and incident laser energy on the thermal decomposition mechanism of nitropyrazoles.

### 7.8.2 Di-Substituted Pyrazole Derivatives

Theoretically, six different structural isomers of di-substituted pyrazoles are possible: 1,3-, 1,4-, 1,5-, 3,4-, 3,5-, and 4,5-disubstituted pyrazoles. 3,4-Dinitropyrazole and 4,5-dinitropyrazoles are tautomers, and in solution, they exist as equilibrium mixtures.

A very comprehensive overview of dinitropyrazoles has been compiled, including methods of synthesis and many derivatives that carry other substituents in addition to or in place of nitro groups and chemical reactivities. This is supported by 163 references in the existing literature but these lack a good summary of simple physical properties like melting points and densities [215]. The energies of pyrazoles substituted in the 3- or 5-position are very similar. Pyrazoles that carry nitro groups in the 1- and/or the 3-positions are nitramines. They are more energetic than their C—NO<sub>2</sub> counterparts. Thermal rearrangement of nitro groups in dinitropyrazoles is common. Starting with 1,3-dinitropyrazole or 1,4-dinitropyrazole by simple heating in a solvent like nitrobenzene, one usually ends up with 3,5-dinitropyrazole which is the thermally most stable. Treatment of 1,3-dinitropyrazole with secondary amines results in denitration of the more reactive —NO<sub>2</sub> group from the 1-position. Treatment of 1,4-dinitropyrazole with primary amines results in ring opening. 1,3-Dinitropyrazoles are low-melting (<373 K = <100 °C) oily substances. 2,3-Dinitropyrazoles are better crystallized and melt at higher temperatures (403–473 K = 130–200 °C). 3,4-Dinitropyrazole ( $pK_a = 5.48$ ) and 3,5-dinitropyrazole ( $pK_a = 3.14$ ) are weak acids.

The heats of combustion of 1,2,4-triazole, tetrazole, benzofurazan, 2-nitropyrrole, 4-nitroimidazole, 4-nitropyrazole, 3-nitro-1,2,4-triazole, nitrotetrazole, 3-methyl-4-nitrofuroxan, 5-nitrobenzofurazan, and 5-nitrobenzofuroxan were measured by precision bomb calorimetry. The standard enthalpies of formation were calculated for azoles, oxadiazoles, and the mononitro derivatives [216]. The energetic effect of the introduction of the nitro group into azole heterocyclic compounds on the enthalpy of formation increased in the order pyrrole < imidazole < pyrazole < triazole < tetrazole. The effect was defined as the enthalpy of formation of the nitro derivative minus the enthalpy of formation of the unsubstituted parent amine.

The specific enthalpy of formation of a pyrazole (1702 kJ/kg = 406.9 kcal/kg) is a little higher than that of 1,2,4-triazole (1593 kJ/kg = 380.7 kcal/kg). In the group of azoles, the pyrazole occupies an intermediate position between the high-enthalpy tetrazole (3372 kJ/kg = 806.0 kcal/kg) and low-enthalpy imidazole (859 kJ/kg = 205.2 kcal/kg). The energies of combustion were measured in a calorimeter and the standard enthalpies of formation for a group of derivatives of nitropyrazole were calculated [217] (Table 12). The influence of the number and location of substitution of amino and nitro groups attached to the pyrazole ring on the thermochemical and physicochemical properties of the compounds was analyzed.

**Table 12:** Effect of nitro, amino, and nitramino substituents on the enthalpy of formation of pyrazole compounds.

| Compound                        | Enthalpy of formation |          | Density           |
|---------------------------------|-----------------------|----------|-------------------|
|                                 | kJ/mol                | kcal/mol | g/cm <sup>3</sup> |
| 3-Nitropyrazole                 | +71.5                 | +17.1    | —                 |
| 4-Nitropyrazole                 | +67.8                 | +16.2    | —                 |
| 3,4-Dinitropyrazole             | +120.1                | +28.7    | 1.81              |
| 3,5-Dinitropyrazole             | +93.7                 | +22.4    | 1.8               |
| 1-Methyl-3,4-dinitropyrazole    | +105.4                | +25.2    | —                 |
| 4-Amino-5-nitropyrazole         | +15.1                 | +3.6     | 1.67              |
| 3-Nitramino-4,5-dinitropyrazole | +124.7                | +29.8    | 1.97              |
| 3-Amino-4,5-dinitropyrazole     | +60.2                 | +14.4    | 1.9               |
| 4-Amino-3,5-dinitropyrazole     | −0.8                  | −0.2     | 1.93              |
| 1-Amino-3,4-dinitropyrazole     | +173.6                | +41.5    | 1.76              |
| 1,4-Dinitropyrazole             | +176.6                | +42.2    | —                 |

Data source: [217].

Using the experimental values of enthalpies of formation and the calculated densities, the heat of explosion and the detonation velocity of the investigated derivative nitropyrazoles were calculated.

3,4-Dinitropyrazole, 3,4-DNP,  $C_3H_2N_4O_4$ ,  $M = 158.07$  g/mol, CAS RN [38858-92-3], has a density of  $1.81$  g/cm<sup>3</sup> and melts at  $359$  K ( $86^\circ\text{C}$ ). 3,4-Dinitropyrazole was synthesized and characterized by IR, elemental analysis, mass spectrometry, and NMR spectroscopy [218]. Its thermal decomposition and phase change were also analyzed with DSC. Its melting point was  $358$ – $360$  K ( $85$ – $87^\circ\text{C}$ ).

A candidate for TNT replacement, 3,4-dinitropyrazole was synthesized from pyrazole via a three-step reaction sequence of nitration, rearrangement, and nitration [219]. The reaction conditions of the third step were optimized to achieve a yield of 41%. The structure was confirmed by  $^1\text{H}$  NMR and IR (see also [220]).

4-Amino-3,5-dinitro-1*H*-pyrazole (LLM-116) was synthesized by a vicarious nucleophilic substitution reaction. Its structure was characterized by NMR, IR, and elemental analysis [221]. The thermal decomposition kinetics and mechanisms were studied using DSC, thermolysis *in-situ* rapid-scan FTIR, and simultaneous TGA-MS analysis. The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction of LLM-116, obtained by the Kissinger method, were  $107$  kJ/mol,  $10^{10}$  s<sup>−1</sup> in the first decomposition stage, and  $139$  kJ/mol,  $10^{12}$  s<sup>−1</sup> in the second decomposition stage. The decomposition of LLM-116 begins with one molecular water lost by  $-\text{NO}_2$  and  $-\text{NH}_2$ , forming a furazan in the LLM-116 structure.

The decomposition of 3,4-dinitropyrazole (DNP) and two model molecules (4-nitropyrazole and 1-nitropyrazole) was investigated both theoretically and experimentally [222]. The initial decomposition mechanisms for these three nitropyrazoles were explored with computational methods. The NO molecule was observed as an initial

decomposition product from all three materials after UV excitation. The theoretically predicted mechanism was consistent with experimental results; DNP decomposed in a lower electronic state than the model systems did. Thus the vibrational energy in the NO product from DNP should be hotter than from the model systems. The observed rotational energy distributions for NO were consistent with the final structures of the respective transition states for each molecule.

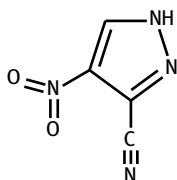
The thermal decomposition under non-isothermal and isothermal conditions, burning behavior, and flame structure of dinitropyrazoles, such as 3,4-dinitro-1*H*-pyrazole (3,4-DNP), *N*-(3,5-dinitro-1*H*-pyrazol-4-yl)-[1,2,4]triazolo[3,4-*b*][1,2,4,5]tetrazin-6-amine (ADNPTrTz), and 3,3',4,4'-tetranitro-1,1'*H*-bipyrazole-5,5' (TNBP) in the liquid phase lies between the stability of nitramines RDX and HMX [223]. The decomposition of dinitropyrazole moiety in 3,4-DNP and TNBP starts from a nitro group loss. If the nitropyrazole molecule contains an amino group, the thermal decomposition may begin with an NO<sub>2</sub> group isomerization, followed by decomposition of either the pyrazole ring or formed furazan ring. The pyrazole moiety is resistant to oxidation by NO<sub>2</sub>, leading to a low heat effect at the initial decomposition stages. This results in difficulties with determining real kinetics from DSC experiments. The activation energy of decomposition of 4-amino-3,5-dinitro-1*H*-pyrazole appeared to be rather low (108.8 kJ/mol). This might be indicative of a possible hazard in handling this compound even though its onset of decomposition temperature was high enough. 4-Amino-3,5-dinitropyrazole (ADNP) and 3,4-dinitro-1*H*-pyrazole (3,4-DNP), *N*-(3,5-dinitro-1*H*-pyrazol-4-yl)-[1,2,4]triazolo[3,4-*b*][1,2,4,5]tetrazin-6-amine burned only with combustion instability at low pressures and TNBP did not burn at pressures below 15 MPa.

A comparative study of the thermal stability and combustion parameters of three dinitropyrazole isomers showed that the rate-limiting stage of the decomposition of 1,3-dinitropyrazole (1,3-DNP) and 1,4-dinitropyrazole (1,4-DNP) – both having the *N*-bounded nitro group – is the N C migration of the nitro group rather than its elimination, followed by secondary decomposition reactions of the non-aromatic 3*H*-pyrazole [224]. In the case of 3,4-dinitropyrazole (3,4-DNP), the rate-limiting stage was assumed to be the nitro group elimination. The burning rate versus pressure dependences of all the studied pyrazole isomers were similar to each other, despite significant differences in the thermal stability and volatility.

A study of the thermal decomposition, burning behavior, and flame structure of low-melting oxygen-rich energetic *N*-trinitromethyl-3,4-dinitropyrazole (**1**), *N*-trinitromethyl-3,5-dinitropyrazole (**2**), *N*-fluorodinitromethyl-3,5-dinitropyrazole (**3**), and *N*-[(difluoroamino)dinitromethyl]-3,5-dinitropyrazole (**4**) showed that the stability of *N*-trinitromethyl azoles is higher than the stability of similar *C*-trinitromethyl heterocycles [225]. Replacing one nitro group in the trinitromethyl moiety with fluorine or difluoroamine group changed the C–NO<sub>2</sub> bond length and the thermal stability. However, there was no linear correlation between the rate constants and the C–NO<sub>2</sub> bond length. This indicated the presence of other factors affecting

the stability of trinitro- and substituted dinitromethylpyrazole derivatives. The burning rates of the nitropyrazoles varied from 26.8 mm/s (for **1**) to 77.5 mm/s (for **4**) at 10 MPa. The increased thermal stability of the fluorodinitromethyl compound (**3**) caused a decrease in its decomposition in the melt and shifted the main reaction of its combustion into the gas phase. A two-stage decomposition mechanism was indicated by different thermal stabilities of the substituent and the dinitropyrazole fragment.

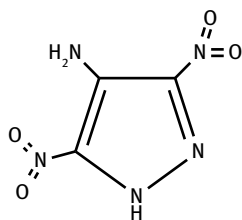
The synthesis and characterization of 1*H*,4*H*-3,6-dinitropyrazolo[3,4-*c*]pyrazole amine salts opened a new path to energetic salts [226]. 3-Cyano-4-nitropyrazole, 4-nitro-1*H*-pyrazole-3-carbonitrile; 1*H*-pyrazole-3-carbonitrile, 4-nitro-;  $C_4H_2N_4O_2$ ,  $M = 138.09$  g/mol, CAS RN [61241-07-4] (also recognized under the code name of LLM-162) has been evaluated as a burning rate modifier. It melts at 426 K (153 °C) and has a density of 1.659 g/cm<sup>3</sup>.



3-Cyano-4-nitropyrazole

### 7.8.3 Tri-Substituted Pyrazole Derivatives

4-Amino-3,5-dinitropyrazole, also known as 3,5-dinitro-1*H*-pyrazol-4-amine,  $C_3H_3N_5O_4$ , ADNP, HANP,  $M = 173.09$  g/mol, CAS RN [152678-73-4], LLM-116, was synthesized in 70% yield from 3,5-dinitropyrazole via treatment with 1,1,1-trimethylhydrazinium iodide in dimethylsulfoxide (DMSO) in the presence of two equivalents of potassium 1-butoxide [227, 228].



4-Amino-3,5-dinitropyrazole (LLM-116)

LLM-116 has a density of 1.90 g/cm<sup>3</sup>, an onset of decomposition point of 451 K (178 °C), and has an impact sensitivity of 50% at a drop height of 165 cm with a 2.5-kg drop mass. LLM-116 is predicted to have 90% of the power of HMX.

High-density energetic salts from nitrogen-rich cations and the 3,4,5-trinitropyrazolate anion were synthesized by neutralization or metathesis reactions and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, DSC, and elemental analysis [229, 230]. The structures of the 3,5-diaminotriazolium and triaminoguanidinium 3,4,5-trinitropyrazolates were determined by single-crystal XRD. Based on the measured densities and calculated HOFs, the detonation performances of the 3,4,5-trinitropyrazolate salts were comparable with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Impact sensitivities were determined to be no less than 35 J by drop weight impact tests, which places these salts in the insensitive class.

3,4,5-Trinitropyrazole can be made by nitrating 3,5-dinitropyrazole with nitric acid in oleum [231]. It is a strong acid and forms energetic salts with a variety of bases. The nitro group in the 4-position of 3,4,5-trinitro-1*H*-pyrazole is easily replaced by nucleophilic reagents [232]. The crystal structure of 3,4,5-trinitro-1*H*-pyrazole was initially assigned to space group  $C2/c$  but a critical investigation revealed that it should be  $P2_1/c$  [233]. The crystal unit cell parameters are  $a = 15.0080(5) \text{ \AA}$ ,  $b = 8.1732(3) \text{ \AA}$ ,  $c = 17.1160(5) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 92.2510(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $Z = 3$ .

The thermal decomposition of 3,4,5-1*H*-trinitropyrazole (TNP), 1-methyl-3,4,5-1*H*-trinitropyrazole (MTNP), and ammonium 3,4,5-1*H*-TNP has been studied experimentally by TGA and DSC at four different heating rates (1, 2, 5, and 10 K/min) [234]. At a heating rate of 2 K/min, the onset of exotherm of TNP was 456 K (183 °C) and the maximum peak temperature was 487 K (214.2 °C). At a heating rate of 5 K/min, the onset was at 457.7 K (184.6 °C) and the max was at 501.4 K (228.3 °C). The ammonium salt of TNP was thermally more stable than its parent acid. At a heating rate of 2 K/min, the onset of exotherm was at 469 K (195.9 °C) and the peak max was at 471.7 K (198.6 °C). At a heating rate of 5 K/min, the onset was at 479 K (205.9 °C) and the peak max was at 481.6 K (208.5 °C). The activation energy of TNP decomposition was  $E_a = 127.3 \text{ kJ/mol}$  and the activation energy of the decomposition of its ammonium salt was 231.9 kJ/mol, again showing that the ammonium salt is more stable than its parent acid. Ammonium 3,4,5-trinitropyrazolate,  $\text{C}_3\text{H}_4\text{N}_6\text{O}_6$ ,  $[\text{NH}_4^+][\text{C}_3\text{N}_5\text{O}_6^-]$ ,  $M = 220.1 \text{ g/mol}$  (which is also referred to as its code name of LLM-165) has a density of  $1.729 \text{ g/cm}^3$  and decomposes at 469–472 K (196–199 °C) without prior melting.

3,4,5-Trinitropyrazole-1-ol and its nitrogen-rich ammonium and triazolium salts were synthesized and well-characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR spectroscopy, elemental analysis, and XRD [230, 235]. 3,4,5-trinitropyrazole-1-ol and its salts have densities from  $1.72$  to  $1.90 \text{ g/cm}^3$ , the onset of thermal decomposition  $T_{\text{dec}}$  from 391 to 459 K = 118 to 186 °C, detonation pressures of 28.77 to 36.40 GPa, detonation velocities of 8175 to 8676 m/s, and impact sensitivities of 1 to 40 J.

4-Amino-3,5-dinitropyrazole (HANP) can be prepared by nitration of pyrazole with fuming nitric acid, followed by the thermal rearrangement of *N*-nitropyrazole in benzonitrile and amination with 1,1,1-trimethylhydrazinium iodide. Reactions of the acidic HANP with bases such as ammonia, hydrazine, guanidinium carbonate, aminoguanidinium bicarbonate, triazole, 3-aminotriazole, 4-aminotriazole, 3,5-di-

**Table 13:** Properties of 4-amino-3,5-dinitropyrazolate salts.

| Com-pound No.   | Compound name                                      | $T_m$ |     | $T_{dec}$ |     | $\rho$ | $\Delta H_f$ salt |        | $P_{det}$ | $v_{det}$ | $I_{sp}$ at 6.8 MPa |
|-----------------|----------------------------------------------------|-------|-----|-----------|-----|--------|-------------------|--------|-----------|-----------|---------------------|
|                 |                                                    | K     | °C  | K         | °C  |        | g/cm <sup>3</sup> | kJ/mol |           |           |                     |
| 1               | Ammonium 4-amino-3,5-dinitropyrazolate monohydrate | —     | —   | 548       | 275 | 1.63   | +64.8             | +0.34  | 26.27     | 8139      | 230.9               |
| 2               | Hydrazinium 4-amino-3,5-dinitropyrazolate          | —     | —   | 494       | 221 | 1.64   | +222.6            | +1.09  | 26.44     | 8193      | 245.2               |
| 3               | Hydrazinium 4-amino-3,5-dinitropyrazolate          | —     | —   | 576       | 303 | 1.63   | +36.1             | +0.16  | 21.62     | 7717      | 205.5               |
| 4               | Aminoguanidinium 4-amino-3,5-dinitropyrazolate     | 496   | 223 | 496       | 223 | 1.69   | +140.1            | +0.57  | 25.23     | 8244      | 212.5               |
| 10              | Diaminoguanidinium 4-amino-3,5-dinitropyrazolate   | 474   | 201 | 474       | 201 | 1.67   | +250.5            | +0.96  | 25.85     | 8351      | 219.6               |
| 11              | Triaminoguanidinium 4-amino-3,5-dinitropyrazolate  | —     | —   | 502       | 229 | 1.71   | +356.9            | +1.29  | 28.85     | 8751      | 225.6               |
| For comparison: |                                                    |       |     |           |     |        |                   |        |           |           |                     |
| TNT             | 2,4,6-Trinitrotoluene                              | 353   | 80  | 568       | 295 | 1.65   | +67               | +0.29  | 19.5      | 6881      | —                   |
| TATB            | 1,3,5-Triamino-2,4,6-trinitrobenzene               | 597   | 324 | 597       | 324 | 1.93   | +140              | +0.54  | 31.15     | 8114      | —                   |

Data source: [229,236].

aminotriazole, and carbohydrazide resulted in the formation of salts. 4-amino-3,5-dinitropyrazole with a crystal density of 1.90 g/cm<sup>3</sup> has a structure similar to TATB and is easily deprotonated to form a 4-amino-3,5-dinitropyrazolate anion. Fifteen nitrogen-rich 4-amino-3,5-dinitropyrazolate energetic salts were prepared and characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR, IR spectroscopy, DSC, elemental analysis, and drop weight impact tests [236]. The properties of a select group of six of the 15 salts are shown in Table 13 as examples.

Some salts decomposed without melting while others melted with decomposition. The HOF was measured or calculated. With one exception, all HOFs were positive with the highest value at +1.64 kJ/g. As highly insensitive energetic materials, the performance of some of the salts was comparable with that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, 31.15 GPa and 8114 m/s).

#### 7.8.4 Tetra-Substituted Pyrazole Derivatives

There are only four positions on the pyrazole ring that can be substituted with ligands other than hydrogen. Ideally, if all four hydrogens could be replaced with nitro groups, the result would be an explosive with a positive oxygen balance (+12.9%).

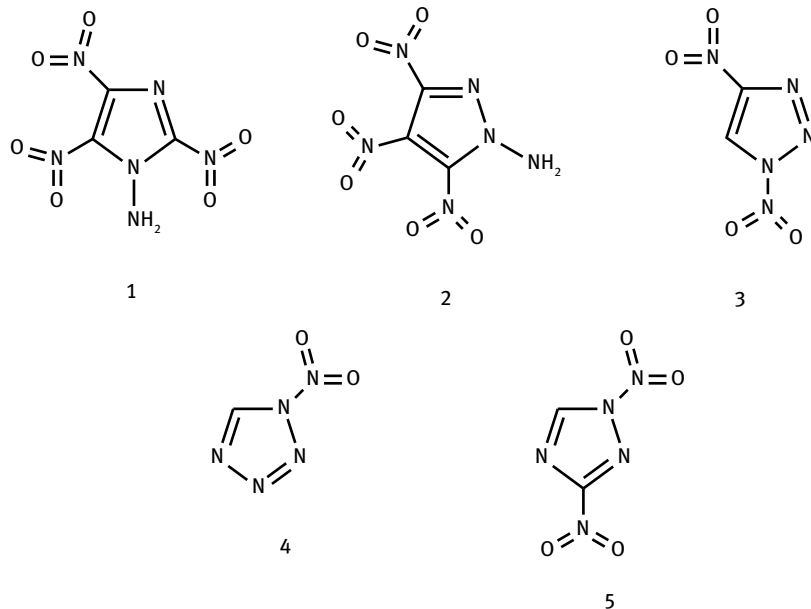


The molecular structures of 3,4,5-trinitro-1*H*-pyrazole, 3,4,5-trinitro-1*H*-pyrazol-1-amine, 1-methyl-3,4,5-trinitro-1*H*-pyrazole, and 1,3,4,5-tetranitro-1*H*-pyrazole have been calculated by quantum chemical MO methods [237]. The geometric and electronic structures, band gap, thermodynamic properties, crystal density, and detonation properties were studied using DFT methods. The calculated energy of explosion, density, and detonation performance of model compounds are comparable to RDX and HMX. It is important to understand the nature of intra-molecular interactions and the strength of trigger bonds.

*Ab initio* MO calculations have been carried out to explore the structure, stability, sensitivity, and band gap of nitropyrazoles [238]. Kamlet and Jacobs equations were used to calculate the detonation velocity and detonation pressure of the paper-designed compounds. The explosive properties of polynitropyrazole-*N*-oxides appeared to be more attractive compared to those of ONC and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane. The sensitivity, heat of explosion, density, detonation velocity, and detonation pressure are presumably related to the number and the relative positions of NO<sub>2</sub> groups on the pyrazole ring.

MO calculations were performed for the geometric and electronic structures, band gap, thermodynamic properties, density, detonation velocity, detonation pressure, stability, and sensitivity of 1,3,4,5-tetranitropyrazole (R23) [239]. The calculated density (approx. 2.06 g/cm<sup>3</sup>), detonation velocity (approx. 9242 m/s), and detonation pressure (approx. 41.30 GPa) of the model compound are promising compared to RDX or HMX.

Enthalpies of formation ( $\Delta H_f^\circ$ ) in the gas phase of a group of five substituted imidazole, pyrazole, 1,2,3-triazole-, 1,2,4-triazole-, and tetrazole-based energetic materials were theoretically investigated by employing DFT and isodesmic reaction calculations [156]. The BDEs corresponding to NO<sub>2</sub>, NH<sub>2</sub>, CH<sub>3</sub>, and Cl removal from carbon or nitrogen positions of the azole ring were calculated. The substituent effect of electron-withdrawing (NO<sub>2</sub>, Cl) and electron-donating (NH<sub>2</sub>, CH<sub>3</sub>) groups affects the  $\Delta H_f^\circ$ , BDE, stability, and acidity/basicity of these molecules. Both EWG and electron-donating groups (except the CH<sub>3</sub> group) increased the  $\Delta H_f^\circ$  of these energetic materials when the substituent was at an N position on the azole ring. For substitution at a C atom on the azole ring, electron-withdrawing and electron-donating groups had different effects on the  $\Delta H_f^\circ$  for different azole compounds. A correlation was developed for this series of energetics between impact sensitivity  $h_{50\%}$  and the defined sensitivity index. Based on this empirical relationship and its extrapolation, the impact sensitivities of compounds for which experiments were not available were extrapolated. Five different compounds were identified as the most promising energetic compounds, which have potentially good energetic performance and low sensitivity: 1-amino-2,4,5-trinitroimidazole (**1**), 1-amino-3,4,5-trinitropyrazole (**2**), 1,4-dinitro-1,2,3-triazole (**3**), 1-nitrotetrazole (**4**), and 1,3-dinitro-1,2,4-triazole (**5**).



### 7.8.5 Pyrazolium Salts and Pyrazolate Salts

Pyrazolium nitrate can be prepared by first drying pyrazole under vacuum for 30 min., cooling in an ice bath, and adding trifluoroacetic anhydride (TFAA) through a septum, then very slowly adding 70% nitric acid [201]. After the complete addition of nitric acid, the mixture should then be left to stir at room temperature for 12 h. 4-Nitropyrazole and 4-nitropyrazolium nitrate is a byproduct of this process. The solvent should then be removed under vacuum, following which recrystallization of the crude product from ethyl acetate produces pyrazolium nitrate as white needles in 65% yield, m.p. 420–421 K (147–148 °C). Pyrazolium nitrate crystallizes from ethyl acetate as thin needles in the monoclinic space group  $P2_1/c$ . The onset of exotherm in the DTA is at 393 K (120 °C).

Unfortunately, it was found that 4-nitroamino-3,5-dinitropyrazole itself was unstable at room temperature. 4-Nitramino-3,5-dinitropyrazole was prepared by nitrating 4-amino-3,5-dinitropyrazole with mixed acid and stabilized through the formation of its ammonium salt. With selected cations, 14 nitrogen-rich energetic salts were synthesized by metathetical reactions replacing the ammonium and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, and elemental analysis [240]. The resulting energetic salts showed acceptable thermal stability, detonation performance, and impact sensitivity. The structures of the ammonium, 3,4,5-triaminotriazolium, and biguanidinium salts were determined by single-crystal XRD. Based on experimental and calculated values, the 4-nitramino-3,5-dinitropyrazolate salts revealed properties

such as decomposition temperatures, detonation pressures and velocities, and impact sensitivities that place them in line with energetics such as RDX and TATB. The properties of a distinct group of five salts selected from the list of 14 salts are summarized in Table 14.

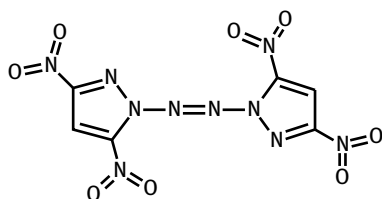
**Table 14:** Properties of 4-nitramino-3,5-dinitropyrazolate salts.

| Compound No.    | Compound name                                                  | $T_{\text{dec}}$ |     | $\rho$ | $\Delta H_f$ salt |       | $P_{\text{det}}$ | $v_{\text{det}}$ |
|-----------------|----------------------------------------------------------------|------------------|-----|--------|-------------------|-------|------------------|------------------|
|                 |                                                                | K                | °C  |        | kJ/mol            | kJ/g  | GPa              | m/s              |
| 2               | Ammonium 4-nitramino-3,5-dinitropyrazolate hemihydrate         | 443              | 170 | 1.74   | −77.3             | −0.31 | 30.95            | 8511             |
| 4               | Hydroxylammonium 4-nitramino-3,5-dinitropyrazolate hemihydrate | 420              | 147 | 1.80   | +54.2             | +0.19 | 37.42            | 9013             |
| 5               | Hydrazinium 4-nitramino-3,5-dinitropyrazolate                  | 444              | 171 | 1.75   | +274.7            | +0.97 | 33.84            | 8917             |
| 11              | Guanidinium 4-nitramino-3,5-dinitropyrazolate                  | 502              | 229 | 1.66   | −0.8              | −0.01 | 24.33            | 7920             |
| 14              | Triaminoguanidinium 4-nitramino-3,5-dinitropyrazolate          | 445              | 172 | 1.65   | +701.5            | +1.65 | 28.88            | 8581             |
| For comparison: |                                                                |                  |     |        |                   |       |                  |                  |
| TNT             | 2,4,6-Trinitrotoluene                                          | 568              | 295 | 1.65   | +67               | +0.29 | 19.5             | 6881             |
| TATB            | 1,3,5-Triamino-2,4,6-trinitrobenzene                           | 597              | 324 | 1.93   | +140              | +0.54 | 31.15            | 8114             |

Data source: [240].

### 7.8.6 Azopyrazole Derivatives

A nitrogen-rich polynitro energetic compound with an  $-\text{N}=\text{N}-$  azo linkage, 1,1'-azobis(3,5-dinitropyrazole), (ABDNP), bis(3,5-dinitropyrazol-1-yl)diazene, was synthesized using 3,5-dinitropyrazole (DNP) as starting material via neutralization, *N*-amination, and oxidative coupling reaction. Its structure was characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS, and elemental analysis [241].

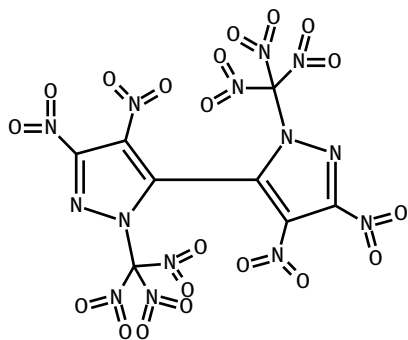


1,1'-Azobis(3,5-dinitropyrazole)

The effects of oxidizing agents on the coupling reaction were investigated. Results showed that *tert*-butyl hypochlorite (*t*-BuOCl) was a better oxidizing agent with a yield of ABDNP up to 43.5%. At a packing density of 1.94 g/cm<sup>3</sup>, the predicted detonation velocity was 9309 m/s. Detonation pressure was 42.2 GPa, which is better than that of RDX.

### 7.8.7 Bipyrazole Derivatives

4,4',5,5'-Tetranitro-2,2'-bis(trinitromethyl)-3,3'-bipyrazole, also known as 5-[4,5-dinitro-2-(trinitromethyl)pyrazol-3-yl]-3,4-dinitro-1-(trinitromethyl)pyrazole, was obtained by *N*-alkylation of 4,4',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole with bromoacetone and subsequent nitration [242].

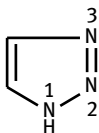


X-ray single-crystal diffraction confirmed its structure and revealed a unique high crystal density of 2.021 g/cm<sup>3</sup> at room temperature, introducing it into the group of top three of the densest CHNO compounds known. This high-density material has an attractive positive oxygen balance, acceptable sensitivity, and enthalpy of formation (on a unit of weight) similar to 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20). With calculated specific and effective impulses exceeding those of AP and ADN, it makes it a competitive replacement for AP as a green energetic oxidizer for solid propellants.

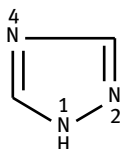
## 8 Triazoles

Triazoles are five-membered ring-shaped molecules that contain three nitrogen atoms at either the 1,2,3 or 1,2,4-positions in the ring. In the five-membered ring of triazoles, the three nitrogens can be either in vicinal (adjacent) positions (1,2,3-triazole, CAS RN [288-36-8]) or separated by a carbon atom (1,2,4-triazole, CAS RN [288-88-0]) [243].

Note that sometimes authors omit the “a” in triazole and call these compounds **trizole** instead (in analogy to tetrazole and pentazole).



1,2,3-Triazole



1,2,4-Triazole

Sometimes the structure is made more specific by adding the location of the hydrogen atom, e.g., in *1H*-1,2,3-triazole [244, 245]. The physical properties of triazoles are summarized in Table 15.

Triazoles are amphoteric. There is a substantial amount of interest in salts formed by either triazolium cations or triazolate anions. These salts are formed mostly with substituted triazoles and only occasionally with the unsubstituted parent triazole itself. The properties of the neutral triazole compounds are summarized here and are followed by several chapters on triazolium and triazolate salts. There is some overlap between these three sections. The *pK* of 1,2,4-triazole is 10.04 and that of 1,2,3-triazole is 8.2. Triazoles mostly act as a base when reacted with strong acids [246].

**Table 15:** Physical properties of triazoles.

| Property                                 | 1 <i>H</i> -1,2,3-Triazole | 1 <i>H</i> -1,2,4-Triazole | 4-Amino-1,2,4-triazole, 4 <i>H</i> -1,2,4-triazol-4-amine | 3,4,5-Triamino-1,2,4-triazole; 4 <i>H</i> -1,2,4-triazole-3,4,5-triamine, guanazine |
|------------------------------------------|----------------------------|----------------------------|-----------------------------------------------------------|-------------------------------------------------------------------------------------|
| Molecular mass                           | 69.09                      | 69.09                      | —                                                         | 114.11                                                                              |
| CAS RN                                   | 288-36-8                   | 288-88-0                   | 584-13-4                                                  | 473-96-1                                                                            |
| Nitrogen content, mass-%                 |                            |                            |                                                           |                                                                                     |
| Melting point, °C                        | 23                         | 121                        | 87; 82–83                                                 | 257                                                                                 |
| Melting point, K                         | 296                        | 394                        | 360; 355–356                                              | —                                                                                   |
| Boiling point, °C                        | 204                        | 260                        | 267 (extrapolated)                                        | —                                                                                   |
| Density, g/cm <sup>3</sup>               | 1.1861                     | 1.132                      | 1.59                                                      | 2.45 (predicted)                                                                    |
| Standard enthalpy of formation, kcal/mol | +65 (calculated)           | +47 (calculated)           | +76 (calculated)                                          | +56 (calculated)                                                                    |
| Standard enthalpy of formation, kcal/mol | —                          | +26 (measured)             | —                                                         | —                                                                                   |
| Standard enthalpy of formation, kJ/mol   | +272 (calculated)          | +109 (measured)            | +318                                                      | +234 (calculated)                                                                   |

There are now many synthetic methods that lead to triazoles and triazole derivatives [247]. There are many applications for 1,2,4-triazoles other than as rocket propellants. 1,2,4-Triazole and 1,2,4-triazole derivatives can be prepared by **(1)** cyclizations to form a triazole ring, **(2)** transformations of heterocyclic compounds to construct a triazole ring, **(3)** substitutions on a 1,2,4-triazole ring, and **(4)** structural modifications in side chains of 1,2,4-triazole rings [248].

## 8.1 Physical and Chemical Properties of Triazole and Triazole Derivatives

The physical properties of triazoles and two triazole derivatives are summarized in Table 15. Both triazoles are commercially available.

Other sources give the enthalpies of formation of 1,2,4-triazole and 1,2,3-triazole as +109 and +272 kJ/mol, respectively. The heats of combustion of a wide range of triazole and tetrazole derivatives have been determined and the enthalpies of formation can be derived from these numbers [249, 250]. The following sections detail the properties of neutral molecule (not a salt) triazoles. Sections on triazolium and triazolate salts are further down in this chapter.

## 8.2 Mono-Substituted 1,2,3-Triazole Derivatives

1-Amino-1,2,3-triazole is identical with 3-amino-1,2,3-triazole. 1,2,3-Triazoles with a phenyl ring attached in the 1-position were synthesized by cycloaddition reactions between phenyl azides and alkynes, followed by nitration [251]. The phenyl ring could carry a nitro group or a methoxy group in the 2-, 3-, or 4-position to start with. Additional nitro groups could be introduced once the aryltriazole has been formed. The additional nitration may also place a nitro group on the triazole ring in the 4-position. Most of the polynitro-bearing triazole derivatives decomposed within the range 415–592 K (142–319 °C). Their HOFs and crystal densities and detonation velocities and pressures were calculated. Most of these compounds exhibited high positive HOFs, good thermal stabilities, reasonable densities, and acceptable detonation properties that were comparable to those of TNT. Similar compounds, for instance, a pyridine with two triazole rings attached, were obtained by reacting pyridyl (di)azide with alkynes.

The explosive power of 1,2,3-triazole increases if one or more nitro groups are introduced into the molecule, such as in 4-nitro-2*H*-1,2,3-triazole or 4,5-dinitro-2*H*-1,2,3-triazole [252]. The reaction of 3-amino-1-nitroguanidine with tri-Et orthoformate leads to the formation of 3-nitramino triazole [253].

### 8.3 Di-Substituted 1,2,3-Triazole Derivatives

One example for an energetic di-substituted 1,2,3-triazole derivative is 4-azido-5-nitro-2*H*-1,2,3-triazole,  $C_2H_1N_7O_2$ ,  $M = 155.08$  g/mol. It has a density of  $1.777$  g/cm<sup>3</sup> and is also known by the code name LLM-134. The condensation of ethyl 2,2-dinitroacetate with acetaldehyde in the presence of  $NaN_3$  gave 4-methyl-5-nitro-1,2,3-triazole, which was converted to 4-amino-5-nitro-1,2,3-triazole [254]. Their structures were confirmed by IR, NMR, DSC, and elemental analysis. 4-Amino-5-nitro-1,2,3-triazole; 1*H*-1,2,3-triazol-4-amine, 5-nitro-;  $C_2H_3N_5O_2$ , ANTZ, CAS RN [145769-58-0],  $M = 129.08$  g/mol, melts at  $570$  K ( $297^\circ\text{C}$ ) and has a density of  $1.835$  g/cm<sup>3</sup>. 4,5-Dinitro-1,2,3-triazole forms an ammonium salt that is relatively stable and would make a good propellant ingredient. Ammonium 4,5-dinitro-1,2,3-triazolate; 4,5-dinitro-1,2,3-triazole, ammonium salt; ADNTr,  $C_2H_4N_6O_4$ ,  $M = 176.09$  g/mol, melts at  $441$  K ( $168^\circ\text{C}$ ) (decomposition) and has a density of  $1.716$  g/cm<sup>3</sup>.

### 8.4 Other Di-Substituted 1,2,3-Triazole Derivatives

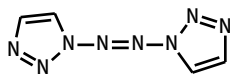
Attaching two tetrazole rings to 1,2,3-triazole in the 4- and 5-positions creates a compound with an extremely high nitrogen content that would be a good ingredient for gas generator formulations. 4,5-Di(tetrazol-5-yl)-1,2,3-triazole; 2*H*-tetrazole, 5-[4-(2*H*-tetrazol-5-yl)-1*H*-1,2,3-triazol-5-yl]-;  $C_4H_3N_{11}$ , LLM-137, CAS RN [869060-66-2],  $M = 205.14$  g/mol, has a predicted density of  $\rho = 2.035$  g/cm<sup>3</sup>. This compound is made by reaction of 4,5-dicyano-1,2,3-triazole with hydrogen azide [255, 256]. This compound is slightly acidic (predicted  $pK_a = -0.15 \pm 0.10$ ) and can form salts with a variety of bases.

### 8.5 Tri-Substituted 1,2,3-Triazole Derivatives

Energetic derivatives of 5-nitro-1,2,3-2*H*-triazole, which include 2-(methyl or amino)-4-(nitramino, azido, or nitro)-5-nitro-1,2,3-2*H*-triazoles, were prepared and characterized by NMR, IR, DSC, densities, detonation pressures and velocities, impact sensitivities, and elemental analysis [257]. Among the several new derivatives, 2-amino-4,5-dinitro-1,2,3-2*H*-triazole exhibited favorable properties ( $T_m = 367$  K =  $94^\circ\text{C}$ ;  $T_{dec} = 463$  K =  $190^\circ\text{C}$ ;  $\rho = 1.83$  g/cm<sup>3</sup>;  $P_{det} = 36.2$  GPa,  $v_{det} = 8843$  m/s, impact sensitivity 24 J) that was comparable with RDX.

## 8.6 Azo-1,2,3-Triazole Compounds

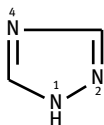
The construction of a catenated nitrogen chain of eight nitrogen atoms was achieved through oxidative azo coupling of the  $\text{N}-\text{NH}_2$  moiety, where the amino group attached to a triazole ring was first transformed into a diazonium ion under acidic conditions. A subsequent nucleophilic attack of the amino group of the 1-amino-1,2,3-triazole on this diazonium cation produced an unusual structure containing eight catenated nitrogen atoms: 1,1'-azobis-1,2,3-triazole (1,1'-azo-1,2,3-triazole, bis(triazol-1-yl)diazene) has a nitrogen content of 68.27% [258]. This N8 compound is thermally stable up to 466 K (193 °C) and has a relatively high enthalpy of formation of +962 kJ/mol.



1,1'-Azo-1,2,3-triazole

## 8.7 Physical and Chemical Properties of 1,2,4-triazole

The physical properties of 1,2,4-triazole have already been summarized in Table 15.



1,2,4-Triazole

The thermal decomposition behavior of 1H-1,2,4-triazole at low and high temperatures was studied by product-gas-analysis using flash pyrolysis [259]. In the case of low-temperature decomposition, hydrogen cyanide and ammonia were detected as decomposition product gases, and hydrogen cyanide and methane were detected in high-temperature decomposition products. It was supposed that the decomposition mechanism is different below and above 873–973 K (600–700 °C). One theory is that singlet nitrilimine decomposed to form hydrogen cyanide and NH. Conversely, triplet nitrilimine could have formed methane; the reaction path to form methane would be similar to the decomposition of 1H-tetrazole. However, triazole decomposition generated no acetylene while tetrazole released acetylene and methane. The difference could be explained in terms of the HOF of triazole and tetrazole.

Because 1,2,4-triazole is readily available and can be made in high purity, it has been considered a reference material (similar to benzoic acid) with a known heat of combustion for calibrating the combustion calorimetry of nitrogen-containing organic compounds [260].



## 8.8 Mono-Substituted 1,2,4-Triazole Derivatives

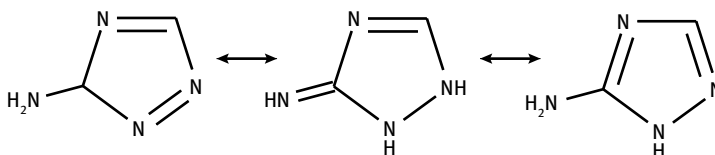
The 1,2,4-triazole ring can carry substituents in various positions, preferably on the carbon atom in positions three and five. But 1,2,4-triazole derivatives where a side group has been attached in the 1-position on the nitrogen atom are also known [261, 262]. Highly energetic compounds can be obtained by attaching 1,2,4-triazole rings (with or without substituents on the triazole ring) to tetrazole rings in the 5-position of the tetrazole ring [263].

### 8.8.1 1-Amino-1,2,4-triazole

*N*-substituted triazoles can be prepared either by direct synthesis during ring closure or by alkylation of 1,2,4-triazole [264]. The isomer 1-amino- $\alpha$ -vic-triazole or 1-amino-1*H*-1,2,3-triazole melts at 324 K (51°C) and explodes soon after this temperature is exceeded. It contains four connected nitrogen atoms. Additional substitution with methyl groups stabilizes the molecule somewhat.

### 8.8.2 3-Amino-1,2,4-triazole

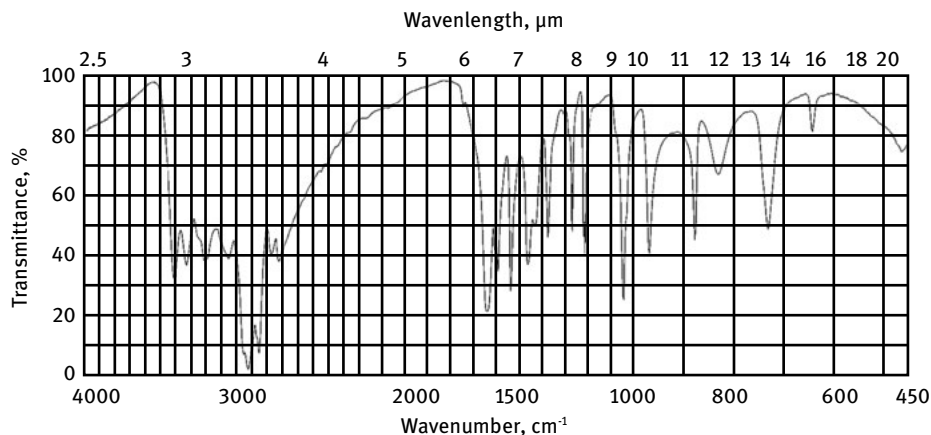
The pendant amino group can be attached to either a carbon or a nitrogen atom in the triazole ring. 3-Amino- $\alpha$ -sym-triazole, 3-amino-1*H*-1,2,4-triazole, 1*H*-1,2,4-triazolyl-3-amine, amitrole, 1,2,4-triazol-3-amine, aminotriazole,  $C_2H_4N_4$ , 3-AT, CAS RN [61-82-5] may also be called 5-amino-1,3,4-triazole. It forms yellow crystals, has a melting point of 432 K (159°C), and sublimes and partially decomposes at higher temperatures. Its density is 1.138 g/cm<sup>3</sup>. It can exist in several tautomeric structures:



Tautomeric forms of 3-amino-1*H*-1,2,4-triazole

3-Amino-1*H*-1,2,4-triazole is commercially available and is widely used as an herbicide and cotton defoliant. 3-AT is a non-selective systemic herbicide used on non-food croplands to control annual grasses, broadleaf, and aquatic weeds. It is not used on food crops because of its carcinogenic properties. As an herbicide, it is known as aminotriazole, amitrole, or amitrol. It is very soluble in water (280 g/L). The IR spectrum of 3-amino-1*H*-1,2,4-triazole is shown in Figure 6.

Its nitrate salt, 3-amino-1*H*-1,2,4-triazolium nitrate,  $C_2H_5N_5O_3$ , has an oxygen balance of -38.1%, a nitrogen content of 47.61%, and melts at 453.6–454.6 K (180.5–181.5°C) with incipient decomposition. The standard enthalpy of formation of



**Figure 6:** IR spectrum of 3-amino-1*H*-1,2,4-triazole. (Reproduced and modified from Sigma-Aldrich.)

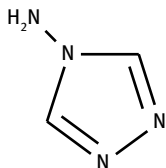
3-amino-1*H*-1,2,4-triazole is +76.8 kJ/mol (+18.36 kcal/mol) and the standard enthalpy of formation of its nitrate salt is −589 kJ/mol (−140.89 kcal/mol) [250].

The pendant amino group can be attached to either a carbon or a nitrogen atom in the triazole ring. 1-Amino-1,2,3-triazole is a hydrazine derivative with four catenated nitrogen atoms.

A new preparation method of 1-amino-1,2,3-triazole has been developed [265]. Glyoxal bishydrazone, which was synthesized from glyoxal and aqueous hydrazine, was oxidized with manganese(IV) dioxide to give 1-amino-1,2,3-triazole with the yield of 78.30%. The structure of 1-amino-1,2,3-triazole was confirmed by IR, NMR, MS, and elemental analysis. 1-amino-1,2,3-triazole with high purity (96%) can be obtained by crystallization from acetonitrile.

### 8.8.3 4-Amino-1,2,4-triazole

The pendant amino group can be attached to either a carbon or a nitrogen atom in the triazole ring. The most common aminotriazole is 4-amino-4*H*-1,2,4-triazole, 4-amino-1,2,4-triazole, 1,2,4-triazol-4-amine, ATA, C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>, CAS RN [584-13-4], where the amino group is attached to a nitrogen atom.



4-Amino-1,2,4-triazole

The amino group in 4-amino-1,2,4-triazole is attached to a nitrogen atom in the 4-position. The N—N bond indicates that its synthesis starts with hydrazine. 4-amino-1,2,4-triazole can be readily synthesized from formic acid and hydrazine in the presence of catalysts. Formylhydrazine is an intermediate in this reaction but it does not have to be isolated if the aminotriazole is the desired product. 4-Amino-1,2,4-triazole forms hygroscopic needles that melt at 355–356 K (82–83 °C) and are readily soluble in water or hydrochloric acid. The enthalpy of formation of 4-amino-1,2,4-triazole is +318 kJ/mol. 4-Amino-1,2,4-triazole is available commercially (this is not to be confused with 3-amino-1,2,4-triazole, which is produced in larger quantities).

The enthalpy of formation of 4-amino-1,2,4-triazole, which is commonly referenced in the literature as +318.0 kJ/mol, appears to be too high. More recently a new value was published ( $+222.8 \pm 1.8$  kJ/mol), which is in good agreement with the theoretical prediction. Calorimetric bomb work resulted in an enthalpy of formation of  $+223.5 \pm 2$  kJ/mol [266, 267].

$\mu$ -Tris(4-amino-1,2,4-triazole)copper(II) diperchlorate  $[\text{Cu}(\text{C}_2\text{H}_4\text{N}_4)_3][\text{ClO}_4]_2$  is a primary explosive detonator with performance close to that of lead azide. However, it is also quite a stable compound that shows moderate sensitivity to thermal and mechanical stimuli [268]. The thermal decomposition kinetics was studied and detonation and explosion parameters (detonation heat and velocity, acceleration ability, water shock wave overpressure, and energy) were measured and/or calculated. 4-Amino-1,2,4-triazole as a ligand forms coordination compounds with metal salts [269].

Twelve salts formed by the reaction of the bases 4-amino-1,2,4-triazole (**A**), 1-amino-1,2,4-triazole (**B**), and 5-aminotetrazole (**C**) upon reaction with the acids  $\text{HNO}_3$ ,  $\text{HN}(\text{NO}_2)_2$ ,  $\text{HClO}_4$ , and  $\text{HC}(\text{NO}_2)_3$  were studied using DFT calculations [270]. For the reactions with the same base, those of  $\text{HClO}_4$  were the most exothermic and had the highest decomposition temperature of the resulting salt. The ability of anions and cations to form hydrogen bonds decreased in the order  $\text{NO}_3^- > \text{N}(\text{NO}_2)_2^- > \text{ClO}_4^- > \text{C}(\text{NO}_2)_3^-$  and  $\text{C}^+ > \text{B}^+ > \text{A}^+$ . For the salts with the same anion, the larger total hydrogen-bond energy leads to a higher melting point. For the production of energetic salts, 5-aminotetrazole and  $\text{HClO}_4$  were identified as the preferred base and acid, respectively.

The single-crystal structure of the salt formed by the reaction of 4-amino-1,2,4-triazole with 3-nitro-1,2,4-triazole-5-one (NTO) was determined by XRD [271]. The results showed that the crystal is monoclinic, belonging to space group  $P21/c$  with main crystallography parameters  $a = 7.071(2)$  Å,  $b = 6.361(3)$  Å,  $c = 18.792(7)$  Å,  $\beta = 96.43(3)^\circ$ ,  $V = 839.9(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.694$  g/cm<sup>3</sup>. The standard volume of gas evolved in the vacuum stability test (VST) at 100 °C during 48 h was 0.28 mL/g. The 50% drop height of impact sensitivity was 124.7 cm. The ESD 50% fire voltage was 12.841 kV and 2.515 J, respectively. This indicated that (AT)(NTO) is thermally stable and relatively insensitive to impact, friction, and spark.

#### 8.8.4 3-Azido-1,2,4-triazole

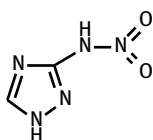
3-Azido-1,2,4-triazole, CAS RN [35038-46-1] reacts with electrophiles [272]. Syntheses of five different azido-1,2,4-triazole derivatives were carried out starting with triaminoguanidinium chloride and a carboxylic acid (formic, acetic, 2,2,2-trifluoroacetic, 2-benzylacetic, monochloroacetic acid) via a three-step synthetic route [273]. The thermal decomposition of five different azido-1,2,4-triazoles was studied theoretically by using CHETAH and T1 software, and experimentally by using DSC to obtain kinetic data. Numerical modeling and mass spectrometry were also performed to estimate the nature of the intrinsic molecular reactivity and the possible early stages of a self-heating process.

Silver, copper(I), copper(II), potassium, cesium, ammonium, hydrazinium, guanidinium, and aminoguanidinium salts of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)-tetrazol-1-ol were prepared and characterized by IR and multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ) NMR spectroscopy, mass spectrometry, and DSC [274]. The metal salts were very sensitive while the nitrogen-rich salts were mostly insensitive. The metal salts were tested for their suitability as primary explosives.

3-Azido-1,2,4-triazole can be used as a starting product for the synthesis of other energetic materials and can be alkylated, halogenated, and complexed with metals, and converted to salts [275]. The azido group can also be carried at the end of an ethyl group instead of being directly attached to the ring [276].

#### 8.8.5 3-Nitramino-1,2,4-triazole

3-Nitramino-1,2,4-triazole, *N*-(1*H*-1,2,4-triazol-3-yl)nitramide,  $\text{C}_2\text{H}_3\text{N}_5\text{O}_2$ , CAS RN [34815-01-5],  $M = 129.084 \text{ g/mol}$ , is an energetic compound capable of forming salts. The enthalpy of formation of 3-nitramino-1,2,4-triazole is  $+112 \text{ kJ/mol}$  ( $+26.87 \text{ kcal/mol}$ ) [250].



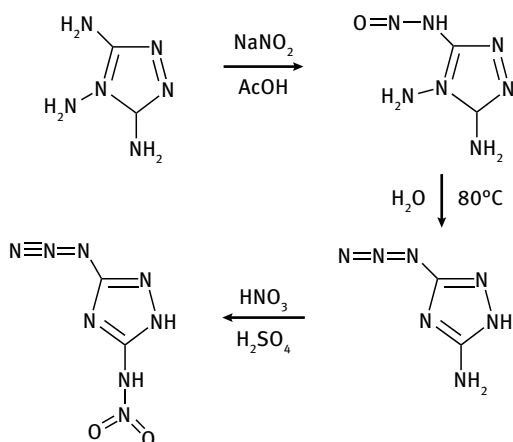
3-Nitramino-1,2,4-triazole

The thermal destruction of *C*- and *N*-nitramino-substituted polynitrogen heterocycles, which are capable of tautomeric conversion, proceeds most likely through the thermochemically least stable nitramine form, as predicted by DFT calculations [277]. It was determined that the thermal destruction of *C*- and *N*-nitramino-substituted polynitrogen heterocycles, which are capable of tautomeric conversion, was most likely through the thermochemically least stable nitro- or nitramine form. Thermal decomposition of the considered tautomers is preferred at the  $\text{NNO}_2$  fragment and not at the triazole ring. The direction of the structural stabilization of the investigated

compounds has been clarified by comparison of the geometric, electronic, and thermochemical characteristics of C—NNO<sub>2</sub>- and N—NNO<sub>2</sub>-substituted 1,2,4-triazoles.

3-Nitramino-1,2,4-triazole (as the hydrate) was one of the many energetic compounds synthesized and used to make metal salts that are potentially useful as coloring agents in pyrotechnic formulations, replacing the environmentally damaging use of chlorates or perchlorates [278]. 3-Nitramino-1,2,4-triazole monohydrate, C<sub>2</sub>H<sub>5</sub>N<sub>5</sub>O<sub>3</sub>, with a molecular mass of 147.093 g/mol and an oxygen balance of −38.1%, melted at 365 K (92 °C) with loss of water and started to decompose at 488 K (215 °C). The anhydrous 3-nitramino-1,2,4-triazole, C<sub>2</sub>H<sub>3</sub>N<sub>5</sub>O<sub>2</sub> with a molecular mass of 129.078 g/mol and an oxygen balance of −43.1%, melted at 491 (218 °C). The heat of combustion was 2565 cal/g.

Triazolium or triazolate salts that contain both nitroamino and azido groups had not been well investigated until 2011. 3-Azido-*N*-nitro-1*H*-1,2,4-triazol-5-amine (which could also be called 3-azido-5-nitramino-1*H*-1,2,4-triazole or *N*-(3-azido-1*H*-1,2,4-triazol-5-yl)nitramide) was prepared by the selective nitration of guanazine, followed by heating at approximately 373 K (100 °C) for 1 h.



It decomposes at 416 K (143 °C), has a density of 1.79 g/cm<sup>3</sup>, and has an enthalpy of formation of 637 kJ/mol. 3-Azido-*N*-nitro-1*H*-1,2,4-triazole-5-amine was selected as the parent compound to become the anion in a series of salts that were prepared and examined. The proton on the nitramino N-atom is acidic. Twelve energetic nitrogen-rich salts based on 3-azido-*N*-nitro-1*H*-1,2,4-triazol-5-amine were prepared and characterized by <sup>1</sup>H, <sup>13</sup>C NMR, IR, DSC, and elemental analysis [279]. The crystal structures of the neutral compound 3-azido-*N*-nitro-1*H*-1,2,4-triazole-5-amine and its triaminoguanidinium salt were determined by single-crystal XRD.

1-Nitroamino-1,2,3-triazole was synthesized and its zwitterionic structure was established using single-crystal XRD [280]. The calculated detonation properties for 4-nitroamino-1,2,4-triazole (*P*<sub>det</sub> = 33.4 GPa, *v*<sub>det</sub> = 8793 m/s) and 1-nitroamino-1,2,3-tri-

azole ( $P_{\text{det}} = 33.0 \text{ GPa}$ ,  $v_{\text{det}} = 8743 \text{ m/s}$ ) were comparable with RDX. A series of energetic salts based on either the 1-nitroamino-1,2,3-triazolate or the 4-nitroamino-1,2,4-triazolate anion were prepared and characterized by IR, NMR, elemental analyses, density, TGA, and DSC. The HOFs and detonation properties for these stable salts were calculated using Gaussian 03 and Cheetah 4.0. Comparison of the properties of the 1,2,3- and 1,2,4-triazolate salts indicated that while the 1,2,4-derivatives were more stable thermally, the 1,2,3-analogs invariably had higher HOFs. In contrast to its salts, 1-nitroamino-1,2,3-triazole is extremely shock-sensitive with an impact sensitivity of  $<1 \text{ J}$ . In addition to 4-nitroamino-1,2,4-triazole, there is also a 1,2,4-triazole that contains two nitramino groups instead of only one. It forms triazolate salts with many inorganic (hydrazine) or organic amine bases.

Hydrazinium 3,5-dinitroamino-1,2,4-triazolate (HDNAT) was synthesized via condensation, nitrification, and hydrazinolysis reactions with a total yield of 63% [281]. Its structure was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR, and elemental analysis. Its density is  $1.89 \text{ g/cm}^3$ , it has a melting point of  $467\text{--}469 \text{ K}$  ( $194\text{--}196^\circ\text{C}$ ), friction sensitivity of 92%, impact sensitivity of  $\text{H50 } 26.8 \text{ cm}$ , detonation velocity of  $9000 \text{ m/s}$  ( $\rho = 1.80 \text{ g/cm}^3$ ), and a detonation pressure of  $36 \text{ GPa}$ .

The 1-amino-2-nitroguanidinium 4-nitroamino-1,2,4-triazolate salt was synthesized using 1-amino-2-nitroguanidine and 4-nitroamino-1,2,4-triazole as the starting materials and its preparation reaction conditions were optimized [282]. The thermal decomposition behavior was investigated by TGA-DSC and its detonation properties were predicted using the Kamlet-Jacobs (K-J) equation. The yield of 1-amino-2-nitroguanidinium 4-nitroamino-1,2,4-triazolate salt was 86.5% under the optimum synthetic conditions (with a reaction time of 4 h and a reaction temperature of  $323 \text{ K} = 50^\circ\text{C}$ ). The compound decomposed sharply around  $448 \text{ K} = 175^\circ\text{C}$ . The HOF of the compound obtained by the Born-Haber cycle was  $551.3 \text{ kJ/mol}$ . The density is  $1.59 \text{ g/cm}^3$ . Based on the HOF and density obtained, the predicted detonation velocity and detonation pressure of the compound are  $8.05 \text{ km/s}$  and  $26.6 \text{ GPa}$ , respectively.

### 8.8.6 Nitro-1,2,4-triazoles

The nitro group can be attached to the 1,2,4-triazole ring either in the 2, (=4) or 3 (=5) position. In the 3- or 5-position, the molecule would contain a  $\text{C}-\text{NO}_2$  group. In the 2- or 4-position it would be a cyclic nitramine. Already small structural differences may affect the explosive properties of energetic materials to a great extent. This was demonstrated in the case of a series of 19 related compounds which all belonged to the group of nitrotriazoles and exhibited more or less distinctly different explosive properties [283]. Seven of these had been synthesized for the first time and are described in this publication. All compounds were characterized by IR, NMR, impact sensitivity, and friction sensitivity. Properties of several of these compounds are summarized in Table 16.

A summary of various methods for the properties and synthesis of nitro-1,2,3-triazoles is provided in [284]. The nitroazole derivatives discussed up to here are only

**Table 16:** Properties of nitrotriazole derivatives.

| Compound name                                                      | Density           | Enthalpy<br>of<br>formation | Explosion<br>temperature |      | Friction<br>sensitivity |      | Drop<br>weight<br>sensitivity |
|--------------------------------------------------------------------|-------------------|-----------------------------|--------------------------|------|-------------------------|------|-------------------------------|
|                                                                    | g/cm <sup>3</sup> | kJ/mol                      | K                        | °C   | kp = kg <sub>f</sub>    | N    | J                             |
| 3-Nitro-1,2,4-triazole                                             | 1.72              | +97.9                       | 491                      | 218  | >6                      | >59  | >25                           |
| 4-Nitro-1,2,4-triazole                                             | 1.73              | +167.0                      | 491                      | 218  | 29                      | 284  | 4.5                           |
| 3-Nitro-5-amino-1,2,4-triazole<br>(ANTA)                           | 1.82              | +70.1                       | 527                      | 254  | >36                     | >353 | >25                           |
| Nitrobi-1,2,4-triazole                                             | —                 | —                           | 540                      | 267  | >36                     | >353 | >25                           |
| C,N-Dinitrobitriazole                                              | 1.82              | +515.6                      | 531                      | 258  | <8.4                    | <82  | 1.5                           |
| 3-Nitramino-1,2,4-triazole<br>(NITRA)                              | 1.83              | +93.9                       | 499                      | 226  | 19                      | 186  | 6.5                           |
| 3-Nitro-triazol-5-one (NTO)                                        | 1.91              | −59.9                       | 509                      | 236  | >36                     | >353 | 25                            |
| C,C-Dinitrobitriazole                                              | 1.89              | +189.9                      | 544                      | 271  | >36                     | >353 | 4                             |
| N-Dinitrophenyl-nitrobitriazole                                    | —                 | —                           | >523                     | >350 | >36                     | >353 | >25                           |
| 2-Dinitrophenyl-4-nitrotriazole                                    | —                 | —                           | 519                      | 246  | >36                     | >353 | >25                           |
| 1-Dinitrophenyl-4-nitrotriazole                                    | —                 | —                           | 520                      | 247  | 19                      | 186  | 2.0                           |
| 2-Picryl-4-nitrotriazole                                           | 1.83              | —                           | 545                      | 272  | >36                     | >353 | 5.5                           |
| 1-Dinitrophenyl-3-nitrotriazole                                    | —                 | —                           | 631                      | 358  | >36                     | >353 | >25                           |
| Bis(4-nitrotriazolyl)-<br>nitropyrimidine                          | —                 | —                           | 480                      | 207  | <0.5                    | <4.9 | <1.5                          |
| 2,4-Bis(5-amino-3-nitro-1,2,4-<br>triazole-1-yl)-5-nitropyrimidine | —                 | —                           | 611                      | 338  | 36                      | 353  | 25                            |
| Nitro-(1,2,3-triazolyl)-1,2,3-<br>triazole                         | —                 | —                           | 531                      | 258  | —                       | —    | 22.5                          |
| For comparison:                                                    |                   |                             |                          |      |                         |      |                               |
| RDX                                                                | 1.82              | +66.9                       | 503                      | 230  | 12                      | 118  | 4.5                           |
| PETN                                                               | 1.77              | −538.8                      | 475                      | 202  | 6                       | 59   | 3.0                           |

Data source: [283].

a small sample of the many nitroazole compounds that have found industrial applications. An entire book has been devoted to nitrotriazoles, their synthesis, structures, and applications [285]. This monograph gives an exhaustive and systematic description of the methods of synthesis, application, structure, and properties of nitroazoles as components of high-energy materials and other applications. All five-membered ring nitro derivatives of azoles (pyrazoles, imidazoles, triazoles, tetrazoles, oxazoles, isoxazoles, oxadiazoles, thiazoles, isothiazoles, and thiadiazoles) were included, as were their benzanalogs (indazoles, benzimidazoles, benzoxazoles, benzisoxazoles, benzoxadiazoles, benzothiazoles, benzoisothiazoles, benzothiadiazoles, and benzo-triazoles). Several of these compounds are used for medicinal purposes.

Quantum chemical calculations were used to predict the BDE of seven nitrotriazole derivatives [286]. It was noted that the BDE of the initial scission step is be-

tween 184 and 293 kJ/mol (44 and 70 kcal/mol), which are larger than those of piperidine and diazocine compounds and polynitro benzoate molecules. Substituent groups greatly affected the BDE of these compounds. The HOFs for seven energetic materials were calculated via designed isodesmic reactions. It was noted that substituent groups strongly affect the HOFs. It was demonstrated that the HOF of compounds substituted by a five-membered ring is larger than those substituted by a six-membered ring for 1,2,4-triazole.

*N*-Trinitroethylamino energetic derivatives were obtained by carbon and nitrogen functionalization of nitropyrazoles and nitrotriazoles with nitroalkyl groups [287]. *N*-Trinitroethylamino nitroazoles and *N*-amino nitroazoles were characterized by IR, NMR, XRD, and elemental analyses. *N*-Functionalized nitroazoles have moderate to excellent thermal stabilities with good densities. Data based on impact and friction tests showed that these compounds ranged from very sensitive to insensitive and have good to excellent detonation pressures and velocities.

3-Nitro-1,2,4-triazole, with a well-known crystal structure [288], was one of the many energetic compounds synthesized and used to make metal salts that are potentially useful for colored pyrotechnic formulations, replacing the historical use of chlorates or perchlorates [278]. 3-Nitro-1,2,4-triazole, Compound No. (**12**),  $C_2H_2N_4O_2$ , which has a molecular mass of 114.063 g/mol and an oxygen balance of  $-42.1\%$ , melted at 488 K (215 °C), and started to decompose at 567 K (294 °C). The heat of combustion was 2388 cal/g.

Different nitroazole isomers based on five-membered heterocyclics were designed and investigated using computational chemistry to explore the relationships between the structure and performance of such high-nitrogen compounds [289]. Electronic structures of the molecules have been calculated using DFT and the HOF has been calculated using an isodesmic reaction approach. All designed compounds showed high positive HOF due to the high nitrogen content and energetic nitro groups. The crystal densities of these energetic azoles have been predicted with different force fields. All the energetic azoles had densities higher than 1.87 g/cm<sup>3</sup>. Detonation properties of energetic azoles were evaluated by using the K-J equation based on the calculated densities and HOFs. The energetic nitroazoles had a predicted detonation velocity of about 9.0 km/s and a detonation pressure of 40 GPa. The stability of the designed compounds was predicted by evaluating the BDE of the weakest C–NO<sub>2</sub> bond.

## 8.9 Di-Substituted 1,2,4-Triazole Derivatives

The HOFs ( $\Delta H_f^\circ$ ) in the gas phase of 1,4-dinitro-1,2,3-triazole and 1,3-dinitro-1,2,4-triazole were theoretically investigated by employing DFT and isodesmic reactions [156]. A correlation was developed between impact sensitivity h50% and the defined



sensitivity index. Based on this empirical relationship the impact sensitivities of new compounds, for which experiments were not available, were extrapolated.

### 8.9.1 3,5-Diamino-1,2,4-triazole

3,5-Diamino-1,2,4-triazole, 1*H*-1,2,4-triazole-3,5-diamine,  $C_2H_5N_5$ , CAS RN [1455-77-2] (also referred to as guanazole or guanozole), is a useful ingredient in gas generants and ionic liquids and is commercially available. 3,5-Diamino-1,2,4-triazole has a molecular mass of 99.09 g/mol and melts at 478 K (205 °C) (decomp.). The density of 3,5-diamino-1,2,4-triazole was predicted to be  $1.686 \pm 0.06$  g/cm<sup>3</sup>. It forms complexes with many transition metal salts.

The mid and far FTIR and FT-Raman spectra of 3,5-diamino-1,2,4-triazole were measured in the condensed state and compared to predicted spectra calculated using quantum chemical calculations [290]. The fundamental vibrational frequencies were calculated under different possible symmetries by a DFT method. The results of the calculations obtained (assuming *C*<sub>2</sub> symmetry) produced a global minimum on the potential energy surface. The vibrational spectra were interpreted with the aid of normal co-ordinate analysis based on scaled density functional force field theory. Alkylation of 3,5-diamino-1,2,4-triazole can occur either on the ring or on the amino groups [291].

The oxidation of 3,5-diamino-1,2,4-triazole occurs in two steps, with substantial differences in the rates of the first and second stages of oxidation yielding 5-amino-3-nitro- and 3,5-dinitro-1,2,4-triazole and allows isolation of the intermediate in up to 60% yield [292].

### 8.9.2 3,5-Dinitro-1,2,4-triazole

3,5-Dinitro-1,2,4-triazole, 3,5-dinitro-1*H*-1,2,4-triazole, DNTz,  $C_2H_1N_5O_4$ , CAS RN [26621-32-9], *M* = 159.06 g/mol, has a density of 2.042 g/cm<sup>3</sup> and an enthalpy of formation of +167 kJ/mol (+40.0 kcal/mol = +251 cal/g).

3,5-Dinitro-1,2,4-triazole can be prepared from 3,5-diamino-1,2,4-triazole (guanazole, DAT), with sulfuric acid and excess sodium nitrite [293]. The ammonium salt of 3,5-dinitro-1,2,4-triazole (ADNT) is an explosive with interesting properties. It is quite soluble in water (28 g/100 mL), has a calculated *P*<sub>CJ</sub> of 262 kbars at its crystal density of 1.632 g/cm<sup>3</sup>, melts with loss of ammonia at 443 K (170 °C), and has ERL Type 12/12B drop-weight impact sensitivities of 59/80 cm. It can be separated from the reaction mixture by solvent extraction [294].

3,5-Diamino-1,2,4-triazole was converted into 3,5-dinitro-1,2,4-triazole by diazotization with excess sodium nitrite. An alternate procedure was proposed for preparing 3,5-dinitro-1,2,4-triazole from dicyanodiamide and hydrazine without isolation of 3,5-diamino-1,2,4-triazole intermediate [295].

A pulsed laser-based photoacoustic pyrolysis technique using a Q-switched Nd:YAG laser at 532 nm with 7 ns duration pulses at 10 Hz repetition rate was used to

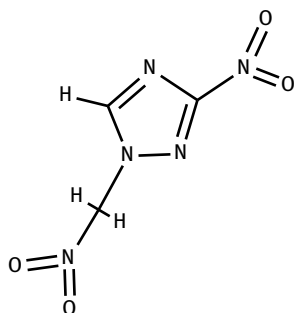
study the thermal stability of 1*H*-1,2,3-triazole derivatives with one to several nitro groups in the range 303–523 K (30–350 °C) [296].

The structural-kinetic laws of thermal decomposition in the solid phase of 3-nitro-1,2,4-triazole, bis(3-nitro-1,2,4-triazole-5-yl), and bis(3-nitro-1,2,4-triazole-5-yl)methane with melting points of 484.6, 510.6, and 581 K (211.5, 237.5, and 308 °C), respectively, were studied to reveal the influence of the 5-functional substituent on the rate and activation parameters of these compounds. The study also provided definitions of an eventual retarding effect of a crystal lattice (the ratio of decomposition rate constants in the liquid and the solid phase) [289, 297]. The gaseous decomposition products were analyzed by GC and MS. The condensed residue after decomposition was analyzed by IR. Thermal decomposition of these compounds in a temperature range 293–773 K (20–500 °C) proceeded in three stages. This was irrespective of the structure of the substance, where the exothermicities for first two compounds were thermoneutral. For the third compound, a heat emission was observed by DTA already at the first stage, accompanied by a smooth increase of an exothermic peak with a maximum at 551 K (278 °C).

3,5-Dinitro-1,2,4-triazole has a  $pK_a$  of  $-0.6$ , which indicates that it is a strong acid and thus it forms stable salts with many nitrogen bases. The CAS RN of the ammonium salt is [76556-13-3]. The assay of 1-ammonium-3,5-dinitro-1,2,4-triazole and its mixtures with ammonium nitrate (AN) can be determined by titration with cetylpyridinium chloride [298, 299].

### 8.9.3 3-Amino-5-nitro-1,2,4-triazole

3-Amino-5-nitro-1,2,4-triazole, 5-amino-3-nitro-1,2,4-triazole, 3-nitro-1*H*-1,2,4-triazol-5-amine, ANTA,  $M = 129.08$  g/mol,  $C_2H_3N_5O_2$ , CAS RN [58794-77-7] or [218787-12-3], can be prepared by an improved sequence where the dinitrotriazole salt is reduced with hydrazine, producing an almost quantitative conversion [300, 301]. ANTA melts at 513 K (240 °C) and has a density of  $1.820$  g/cm<sup>3</sup>.



3-Nitro-1-nitromethyl-1*H*-1,2,4-triazole

ANTA is very insensitive to impact and is moderately sensitive to thermal stimuli. Performance was found to be inferior to TATB. One of the best synthesis methods of ANTA is a three-step route using commercially available 3,5-diamino-1,2,4-triazole [302]. ANTA is being tested because it is an insensitive energetic material. The substituent combination of amino and nitro groups provides the inter- and intra-molecular hydrogen bonding that may stabilize the molecule and increase its density (see TATB). The heterocyclic structure is capable of adding density compared to the corresponding carbocyclic materials and in many cases contributes more to a positive HOF.

Nitrotriazoles are multi-purpose energetic materials. In this group, there are examples for all classes of explosives: primary explosives, insensitive high explosives (IHE), and gas generants. 3-amino-5-nitro-1,2,4-triazole (ANTA) can be converted into a new explosive with theoretically improved performance, a bitriazolyl compound [303]. Physical data and small-scale explosive properties of the new substances were summarized in this publication.

5-Amino-3-nitro-1*H*-triazole (ANTA) is a molecule with high thermal stability. Aside from being an IHE, it is also used as a synthon for other potential new energetic materials. The crystal structure of ANTA was resolved by XRD crystallography and two isomorphous crystal forms were found [304]. When ANTA was recrystallized from 2-butanone, crystals with molecular packing characterized by extended planar sheets were obtained ( $\beta$ -ANTA). The crystal density of  $\beta$ -ANTA is 1.73 g/cm<sup>3</sup>, which is less dense than that of  $\alpha$ -ANTA ( $\rho$  = 1.82 g/cm<sup>3</sup>). The crystal structure of  $\beta$ -ANTA, C<sub>2</sub>H<sub>3</sub>N<sub>5</sub>O<sub>2</sub>,  $M$  = 129.1 g/mol, was monoclinic with space group  $P2_1/n$ , and the unit cell parameters of  $a$  = 6.517(1) Å,  $b$  = 9.691(1) Å,  $c$  = 8.410(1) Å,  $\beta$  = 111.1°,  $V$  = 495.5(1) Å<sup>3</sup>,  $Z$  = 4, 1.730 g/cm<sup>3</sup>.

ANTA has more energy than NTO. It has a crystal density of 1.82 g/cm<sup>3</sup>, a positive HOF ( $\Delta H_f$ ) of +87.9 kJ/mol (+21.0 kcal/mol), and is thermally stable up to its melting point of 511 K (238 °C). The detonation velocity of ANTA was calculated at a crystal density higher than that of TATB and was predicted to be 8460 m/s, which is 7% higher than TATB.

The thermal stability of ANTA and that of six other explosives was measured by a TGA-MS combination using STMBMS. The results were compared to develop a kinetic model and to identify rate-determining steps [84].

The structure, tautomerism, and vibrational spectra of 3-amino-5-nitro-1,2,4-triazole molecule were studied by *ab initio* MO and DFT calculations, both in the gas phase and in solution [305]. It was found that in the gas phase, the most stable tautomer is 2*H*-ANTA (3-amino-5-nitro-1,2,4-2*H*-triazole) at one level, while at other levels the most stable tautomer is 1*H*-ANTA (3-amino-5-nitro-1,2,4-1*H*-triazole). For the 2*H*-ANTA tautomer, the calculated structures agreed well with the experimental X-ray structures. However, twisting of the nitro and amino groups were found to be much larger than in the solid state. The predicted IR spectra were given for all tautomers.

The results obtained for the dielectric constants  $\epsilon = 4.8, 18.5$ , and  $78.4$  suggested that, in a polar solvent, the most stable tautomer is *2H*-ANTA. This is in agreement with the existing experimental studies.

3-Amino-5-nitro-1,2,4-triazole and one of its derivatives have been prepared in order to carry out systematic studies on structural aspects, explosive performance, and thermal stability [306]. Thermal stability studies were carried out for ANTA and 4,6-bis-(3-amino-5-nitro-1*H*-1,2,4-triazole-1-yl)-5-nitropyrimidine (DANTNP) by TGA, DTA, DSC, and manometric thermal analysis. The results showed that DANTNP is thermally more stable than ANTA when compared in terms of activation energy.

5-Amino-3-nitro-1,2,4-triazole can be prepared by nitration of 5-acetamido-1,2,4-triazole, diazotization of 3-acetamido-5-amino-1,2,4-triazole, oxidation of guanazole and *N*-acylguanazole, or reduction of 3,5-dinitro-1,2,4-triazole [307]. Inelastic neutron scattering (INS) spectra were used to clarify the molecular and crystal structure of 3-amino-5-nitro-1,2,4-*2H*-triazole [308]. The experimental results were then compared to results from theoretical DFT calculations.

The thermal decomposition of 3-amino-5-nitro-1,2,4-triazole was examined using TGA-DTG-DTA and DSC techniques in the  $N_2$  atmosphere [309]. In the TGA, ANTA was found to decompose in two steps. The first step of mass loss was  $\sim 38\%$ , which corresponds to the removal of a  $NO_2$  group. The second step of thermolysis was due to the slow thermolysis of the residue, which can also be seen by the presence of two DTG peaks. Both DTA and DSC curves clearly indicated the exothermic nature of the first step of decomposition as there was an exothermic peak. The maximum of the DTA peak was at  $531\text{ K}$  ( $258^\circ\text{C}$ ) and the maximum of the DSC peak was at  $524\text{ K}$  ( $251^\circ\text{C}$ ). The second step of mass loss was slow and seemed to be somewhat exothermic. Just before the first exothermic peak, there was an endothermic peak in both the DTA (both under  $N_2$  as well as in air atmospheres) and DSC, which is due to the melting of ANTA (m.p.  $511\text{ K} = 238^\circ\text{C}$ ). Soon after melting, the compound decomposed, exothermically suffering a sudden weight loss. It was evident from simultaneous TGA-DTG-DTA plots that the compound suffered approximately  $95\%$  mass loss and only a very small amount ( $\sim 4.5\%$ ) of residue was left. The Arrhenius parameters of the isothermal decomposition were derived by 14 different methods and the activation energy ranged from  $53$  to  $62\text{ kJ/mol}$  with  $\ln$  of pre-exponential factors ranging from  $-6.6$  to  $-9.2$ . The activation energy derived from the time to explosion was  $48\text{ kJ/mol}$ .

ANTA forms a salt with hydrazine, which would also make a good propellant ingredient [310]. The compound forms orthorhombic crystals, space group *Pbca* with crystal lattice parameters of  $a = 5.392(2)\text{ \AA}$ ,  $b = c = 18.483(6)\text{ \AA}$ ,  $\rho = 1.612\text{ g/cm}^3$ ,  $V = 1327.1(7)\text{ \AA}^3$ ,  $Z = 8$ .

#### 8.9.4 3-Azido-5-amino-1,2,4-triazole

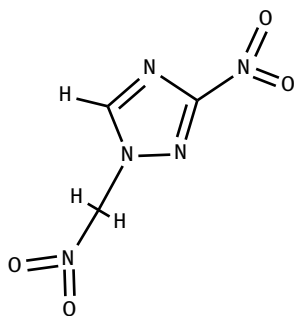
3-Azido-5-amino-1,2,4-triazole was obtained from 3,5-diamino-1,2,4-triazole in two ways. The first was by partial diazotization-substitution directly in the substrate or during its primary nitrosation. The second was with the use of direct or indirect protection of an amino group with subsequent conversion into an azido compound followed by deprotection [311].

#### 8.9.5 3-Hydrazino-4-amino-1,2,4-triazole

3-Hydrazino-4-amino-1,2,4-triazole (HATr) is a high-nitrogen compound (73.65% N) with good thermal stability. Its dihydrochloride can be prepared by reaction of tri-aminoguanidinium chloride with formic acid and with hydrochloric acid as catalyst under reflux conditions. Lithium hydroxide can then be used to neutralize the salt to obtain the free 3-hydrazino-4-amino-1,2,4-triazole [273]. It forms salts even with weak acids such as picric acid or 2,4,6-trinitroresorcinol [312]. From the DSC thermogram, the activation energy and the critical temperature for a thermal explosion for the two salts were calculated. The critical temperature for the thermal explosion of the picrate was 485 K and the critical temperature for the thermal explosion of the 2,4,6-trinitroresorcinol salt was 479 K.

#### 8.9.6 3-Nitro-1-nitromethyl-1H-1,2,4-triazole

3-Nitro-1-nitromethyl-1H-1,2,4-triazole,  $C_3H_3N_5O_4$ ,  $M = 173.10$  g/mol, crystallized in monoclinic, colorless plate crystal shapes, space group  $P2_1/c$ , and with the unit cell parameters of  $a = 6.6305(4)$  Å,  $b = 9.2888(3)$  Å,  $c = 10.9828(6)$  Å,  $\beta = 104.837(5)^\circ$ ,  $V = 653.87(6)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{XRD} = 1.758$  g/cm<sup>3</sup> at  $T = 293$  K [313]. The structure of 3-nitro-1-nitromethyl-1H-1,2,4-triazole is illustrated in Figure 7.



Molecular conformation analysis showed that the first stage of thermal decomposition is a breakage of the  $H_2C-NO_2$  bond. Activation parameters of the process were  $E_a = 172.6$  kJ/mol,  $\log A = 14.25$  [314].

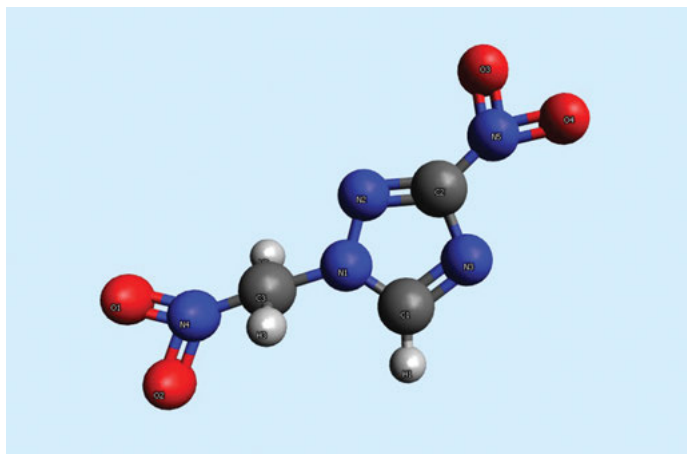


Figure 7: 3-Nitro-1-nitromethyl-1*H*-1,2,4-triazole.

### 8.10 Tri-Substituted 1,2,4-Triazole Derivatives

One of the most frequently used tri-substituted triazoles serving as the starting point for the synthesis of energetic salts is 3,4,5-triamino-1,2,4-triazole (guanazine) [315]. Triaminotriazole is sensitive to air oxidation, which results in red-colored polyazoles.

4-Amino-3,5-dimethyl-4*H*-1,2,4-triazole or 3,5-dimethyl-4-amino-1,2,4-triazole can be prepared by reaction of acetonitrile with hydrazine hydrate. It crystallizes in prisms that melt at 469–472 K (196–199 °C). It is an intermediate in the synthesis of energetic compounds and ionic liquids.

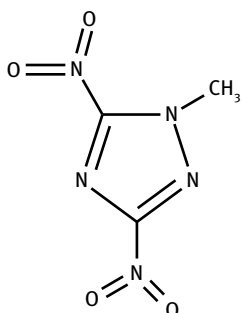
1-Amino-3,5-dinitro-1,2,4-triazole (ADNT) can be made by amination of the sodium salt of 3,5-diamino-1,2,4-triazole (DNT- $\text{Na}^+$ ) with mesitylene sulfonyl hydroxylamine with a yield of 66% [316]. The DNT- $\text{Na}^+$  was obtained from 3,5-diamino-1,2,4-triazole. The structure of ADNT was characterized by IR, MS,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and elemental analysis, and the thermal stability was studied by DSC. The melting and decomposition temperatures are 401.8 and 498.9 K (128.7 and 225.8 °C), respectively. The impact sensitivity (H50) with a 2-kg drop weigh is beyond 112 cm. This revealed that ADNT is an insensitive explosive with good performance. 4-Amino-3,5-dimethyl-1,2,4-triazole can be synthesized starting with hydrazinium hydrazinecarboxylate [317].

1-Amino-3,4-dinitro-1,2,4-triazole (ADNT) can be prepared by the amination of the parent anion with *O*-tosylhydroxylamine [318]. The prepared materials have been characterized chemically (XRD, NMR, IR, Raman) and as explosives (mechanical and electrostatic sensitivity). Their explosive performances can be calculated using the EXPLO5 computer code. Other 3,4,5-trisubstituted 1,2,4-triazoles can be prepared via *N*-acylamidrazone intermediates such as *N'*-acetyl-*N,N*-dimethylhydrazonamide or oxadiazole precursors [319].

The nitrate, perchlorate, dinitramide, azide, and 5-nitrotetrazolate salts of methylated 3,4,5-triamino-1,2,4-triazole-, 5-amino-1*H*-tetrazole-, 2-tetrazene-, and 1,1-dimethylhydrazine bases were prepared and their densities, melting points, onsets of exothermic decomposition, and heats of combustion were measured [320]. These energetic salts were prepared from the iodides by metathetical reactions with silver salts of the energetic anions. The insoluble silver iodide always precipitated. The enthalpies of formation of the energetic salts were calculated from the heats of combustion. Methylation decreased the sensitivities towards mechanical stimuli and increased the thermal and chemical stabilities of these salts.

#### 8.10.1 1-Methyl-3,5-dinitro-1,2,4-triazole (DNMT)

1-Methyl-3,5-dinitro-1,2,4-triazole,  $C_3H_3N_5O_4$ , CAS RN [1199-63-9], DNMT, MDNT, has been evaluated as a melt-cast binder, which is relative to TNT. It is an ideal “next generation” candidate, which would offer significantly improved performance and insensitivity over existing melt-cast binders [321]. Based on the melting point, calculated density, and perceived ease of preparation, DNMT is a good candidate for an insensitive explosive.



1-Methyl-3,5-dinitro-1,2,4-triazole

About 25 grams of the compound were prepared for characterization and small-scale safety evaluation. Based upon those results, the next phase envisioned a scale-up of up to 250 grams of material, with an eye toward optimization of the syntheses, obtaining sufficient material for Interim Hazard Classification (IHC), and Explosive (EX) classification tests, and somewhat larger scale safety and performance testing. In the

DSC, DNMT melted at 95 °C and began to decompose at 210 °C. Table 17 shows the impact sensitivity, friction sensitivity, and ESD test results of DNMT and RDX. The data reveals that DNMT is much less sensitive than RDX in these tests. The measured detonation velocity is 7850 m/s. This is nearly 99% that of Comp B but the C-J pressure is only 85% that of Comp B.

**Table 17:** Safety properties of DNMT in comparison to RDX.

| Compound abbreviation | ERL impact, cm | BAM friction, N | ESD, J |
|-----------------------|----------------|-----------------|--------|
| DNMT                  | >100           | >252            | >0.25  |
| RDX                   | 25.4           | >144            | >0.25  |

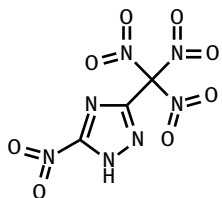
Data source: [321]

A high-performance liquid chromatography (HPLC) method was developed to analyze 1-methyl-3,5-dinitro-1*H*-1,2,4-triazole and the main impurity, 1-methyl-3-nitro-1*H*-1,2,4-triazol-5-amine [322]. 1-Methyl-3,5-dinitro-1*H*-1,2,4-triazole was detected by a UV-visible detector at 240 nm. The detection limits for 1-methyl-3,5-dinitro-1*H*-1,2,4-triazole and 1-methyl-3-nitro-1*H*-1,2,4-triazol-5-amine were 0.6 and 0.31 mg/mL, respectively. The method was shown to have a wide linear range, high sensitivity, and good reproducibility.

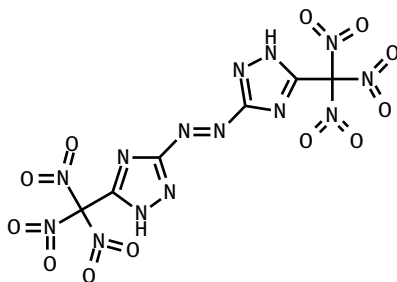
### 8.10.2 Polynitrotriazoles

1,2,4-Triazoles and azotriazoles containing one or two trinitromethyl groups were synthesized and characterized using IR and NMR spectroscopy, elemental analysis, DSC, and XRD [323]. The enthalpies of formation were calculated with Gaussian 03 and then combined with experimentally determined densities to calculate predicted detonation pressures and velocities of the energetic materials (Cheetah 5.0). They exhibited high density, good thermal stability, acceptable oxygen balance, positive HOF, and excellent detonation properties which were superior to those of TNT, RDX, and HMX in some instances. Examples of these are 5-nitro-3-(trinitromethyl)-1*H*-1,2,4-triazole,  $C_3HN_7O_8$ , and 5,5'-bis(trinitromethyl)-3,3'-azo-1*H*-1,2,4-triazole, (E)-bis[5-(trinitromethyl)-1*H*-1,2,4-triazol-3-yl]diazene, 3,3'-[(E)-1,2-Diazenediyl]bis-[5-(trinitromethyl)-1*H*-1,2,4-triazole],  $C_6H_2N_{14}O_{12}$ . The lone hydrogen on the triazole ring is acidic and allows the formation of salts with many bases.





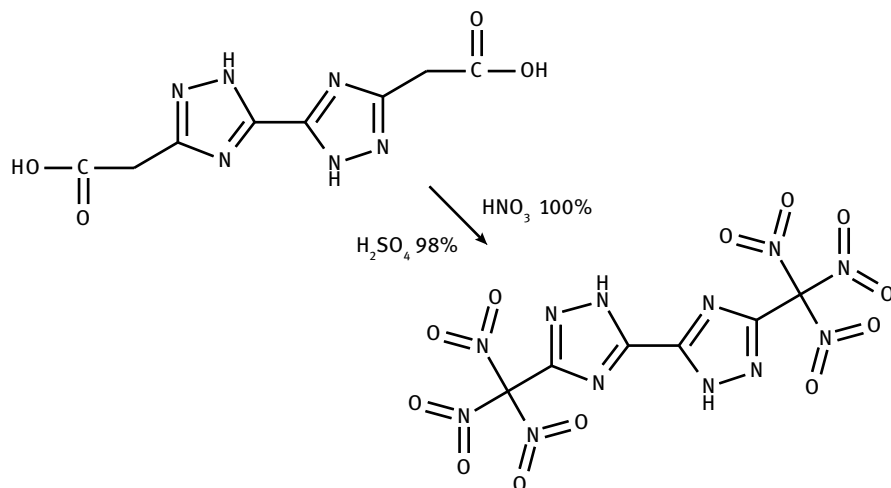
3-Trinitromethyl-5-nitro-1,2,4-triazole



5,5'-Bis(trinitromethyl)-3,3'-azo-1H-1,2,4-triazole

Salts of trinitromethyl-substituted triazoles, 5-nitro-3-trinitromethyl-1H-1,2,4-triazole, and 5,5'-bis(trinitromethyl)-3,3'-azo-1H-1,2,4-triazole were synthesized and characterized using IR, NMR, elemental analysis, and DSC [230, 324]. Based on the HOFs calculated with Gaussian 03 and combined with experimentally determined densities, detonation properties of the energetic materials obtained with the EXPLO5 program identified them as potentially explosive compounds. They exhibited high density, moderate to good thermal stability, acceptable oxygen balance, reasonable HOF, and excellent detonation properties which were superior to those of RDX in some instances.

Three examples of 1,2,4-triazole and bi-1,2,4-triazole with trinitromethyl substitution were synthesized and characterized [325] including 3,3'-bistrinitromethyl-5,5'-bi-1H-1,2,4-triazole, which forms a solvate with diethyl ether:



Another compound synthesized was 5-nitro-3-trinitromethyl-1H-1,2,4-triazole. This compound had a density of 1.950 g/cm<sup>3</sup> and melted at 385.7 K (112.6 °C), followed immediately by a strong, exothermic decomposition. A trinitromethyl analog to NTO, where the nitro group has been replaced by a trinitromethyl group, gave an energetic compound with properties similar to NTO and improved oxygen balance. However, it had poor thermal stability. 3-trinitromethyl-1,2,4-triazol-5-one had a density of 1.885 g/cm<sup>3</sup> at 150 K and a very low onset of decomposition at 343 K (70 °C).

DFT methods were used to study the HOFs, electronic structure, energetic properties and pyrolysis mechanism of a series of trinitromethyl-substituted heterocyclic compounds, including triazole, tetrazole, furazan, tetrazine, and fused heterocycles [326]. It was found that the fused ring, tetrazine, and the tetrazole ring structures are effective structural units for increasing the HOFs of energetic materials. The substitution of the combination of nitro and trinitromethyl is very useful for improving their HOFs. The calculated energetic properties indicated that the combination of the nitro and trinitromethyl is very helpful for improving their detonation properties and oxygen balances. Most of the compounds studied in this work had a good oxygen balance above zero. An analysis of the BDE for several relatively weak bonds suggests that the N—O bond in the ring is a trigger bond for decomposition and the ring —NO<sub>2</sub> and (NO<sub>2</sub>)<sub>2</sub>C—NO<sub>2</sub> bond cleavage is likely to happen in thermal decomposition for other compounds.

The HOFs ( $\Delta H_f$ ) of various nitro-substituted azoles were predicted by orbital mechanics quantum chemical methods [327]. The overall mean absolute deviations and root-mean-square deviations of the predicted numbers were 2.0 and 2.6 kcal/mol, respectively, on the predictions of 48 known molecules. Overall, each additional nitrogen in the azole ring increased  $\Delta H_f$  by 10–30 kcal/mol. While the effect of the NO<sub>2</sub> substitution to carbon (C—NO<sub>2</sub>) was minor, that to nitrogen (N—NO<sub>2</sub>) increased  $\Delta H_f$

by 15–32 kcal/mol. Second-neighbor contribution can be significant for non-bonding interactions between NO<sub>2</sub> groups, which may increase  $\Delta H_f$  by 3–4 kcal/mol.

## 8.11 Other Triazole Compounds

### 8.11.1 Other Multi-Substituted Triazole Compounds

If the hydrogen atoms in triazoles or tetrazoles are replaced with nitrogen-containing energetic functional groups like the azido group or difluoroamino group, the enthalpy of formation of these compounds can be increased further. For example, the standard enthalpy of formation of 1,2,4-triazole increases from +109 to +458 kJ/mol if an azido group is introduced at the 3-position. The azidotriazole (and azidotetrazole) can form highly energetic salts with nitrate, perchlorate, 4,5-dinitro-imidazolate, or 5-nitrotetrazolate anions [328]. Quaternization of azidoalkyl-substituted 1,2,4-triazoles with 4,5-dinitroimidazole or 5-nitrotetrazole results in room-temperature liquids that may be useful in energetic materials/propellant applications [329, 330]. Similar salts are obtained from triazoles that carry both a methyl group and an azido group or triazoles that are substituted with an azidoethyl group.

Energetic salts were synthesized via the quaternization of azido or nitro derivatives of 1,2,4-triazole and substituted derivatives of tetrazole with nitric acid or perchloric acid or iodomethane. The first step reactions were followed by metathesis reaction with AgNO<sub>3</sub> or AgClO<sub>4</sub> to produce 1-(2-azidoethyl)-1,2,4-triazolium-5-nitrotetrazolate, 1-(2-azidoethyl)-3-azido-1,2,4-triazolium 5-nitrotetrazolate, 1-(2-azidoethyl)-4-amino-1,2,4-triazolium perchlorate and 1-(2-azidoethyl)-1,2,4-triazole [276]. These ionic liquid salts exhibited good thermal stabilities, low vapor pressure, high HOF, and high densities. Constant volume combustion energies and structures were determined experimentally using oxygen bomb calorimeter, DSC, and <sup>1</sup>H and <sup>13</sup>C NMR.

The nitrogen-rich energetic material 3,4,5-triamino-1-tetrazolyl-1,2,4-triazole (TATT) was synthesized from diaminoguanidine using a straightforward method [331]. The assumption that a 1,2,4-triazole ring is an intermediate in the one-pot reaction was supported by the synthesis of TATT from an analogous reaction of 3,4,5-triamino-1,2,4-triazole with cyanogen azide. TATT•HNO<sub>3</sub> crystallizes in the monoclinic system *P*2<sub>1</sub>/*c*. TATT has excellent thermal stability which resembles that of triaminotrinitrobenzene (TATB), but with a higher positive HOF and greater impact insensitivity.

### 8.11.2 Polymeric 1,2,4-Triazole Compounds

Energetic polymer salts from 1-vinyl-1,2,4-triazole derivatives have been synthesized via free radical polymerization of 1-vinyl-1,2,4-triazolium monomer salts or by protonation of poly(1-vinyl-1,2,4-triazole) with inorganic or organic acids [332]. Standard

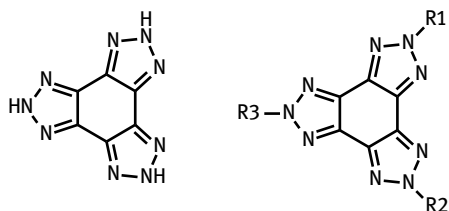
enthalpies of formation of the monomer salts were calculated. Compared with the monomer salts, the polymer salts have good thermal properties with high densities  $\rho > 1.5 \text{ g/cm}^3$ .

Triazole and/or tetrazole-containing polymers would be of interest for solid rocket propellants. Interaction of cyanuric chloride and its mono- and di-chloro derivatives with ammonium or sodium 4-nitro-1,2,3-triazolates and polymer-analogous transformations of tetrazole-containing polymers were used to synthesize polynuclear systems and macromolecular compounds with heterocyclic structures bearing explosophoric groups [333].

1,2,3-Triazole crosslinked polymers were synthesized as a new binder for solid rocket propellant systems by reacting the azide groups of the polymer with the ethynyl groups of a dipolarophile curing agent [334]. The prepolymer mixtures were cured in an oven at 325 K (52°C) for 7 d. The progress of the curing reaction was monitored using an FTIR spectrometer. The carbonyl group adjacent to the  $\text{C}\equiv\text{C}$  triple bond, which acts as an EWG, considerably accelerated the 1,3-dipolar cycloaddition reaction between the azide and ethynyl functional groups, producing rubbery materials. The modulus of the polymers increased whereas the elongation at the break decreased with the increasing ratio of the crosslinker to the prepolymer, resulting in highly crosslinked polymers.

### 8.11.3 Fused Triazolo Ring Compounds

A benzene ring can carry up to three attached 1,2,3-triazole rings, forming a four-ring system called tris(1,2,3-triazolo)benzene or 5,8-dihydro-2*H*-bis[1,2,3]triazolo[4,5-*e*:4',5'-*g*]benzotriazole.



Tris(1,2,3-triazolo)benzene

Tris(triazolo)benzene was synthesized via 1,3,5-triaminobenzene and converted to its trinitro and trichloro derivatives ( $\text{R}=\text{NO}_2$ ,  $\text{Cl}$ ) [335]. The HOFs of these high-nitrogen compounds were calculated and combined with experimentally determined densities to establish detonation pressures and velocities. They exhibited high density, good thermal stability, high HOFs, and moderate to good detonation properties. Trinitrotris-(triazolo)benzene is not stable at room temperature and starts decomposing at 311 K (38°C). Its density is  $1.82 \text{ g/cm}^3$ , its HOF is  $+710 \text{ kJ/g}$ , the predicted detonation pressure

is 31.20 GPa, the detonation velocity is 8376 m/s, and its drop weight impact sensitivity is 3.0 J. As far as drop weight sensitivity is concerned, this was the most sensitive compound of the entire group investigated. The hydrogens on the triazole rings are acidic and can form ammonium salts.

#### 8.11.4 Bi-1,2,4-triazole Compounds

These compounds are commonly called bis-triazole although a more appropriate name would be bi-triazole. For instance, the compound formed by connecting two benzene rings is correctly called *biphenyl* and not *bisphenyl*. If two triazole rings are connected at the 4-position, the resulting bi-triazole (or bis-triazole) is a very energetic compound that can also form salts with strong acids [202, 336]. The melting points of these salts have already been stated in Table 76. A starting reactant for the synthesis of many other bitriazole derivatives is 3,3'-diamino-5,5'-bi-1,2,4-triazole. This can be made by reaction of oxalic acid and aminoguanidinium bicarbonate in concentrated hydrochloric acid at 343 K (70 °C) followed by isolation of the intermediate product by filtration. While heating to reflux in basic media, the molecule undergoes cyclization, which leads to the formation of 5,5'-diamino-bi-1,2,4-triazole.

Bi-1,2,4-triazoles connected through a C—C bond are expected to demonstrate similar energetic properties in comparison to azo-bridged 1,2,4-triazole compounds, also when comparing them to the outstanding properties of 5,5'-bitetrazoles. 5,5'-dinitro-3,3'-bi-1,2,4-triazole (DNBT) is a HEDM. The thermal stability of DNBT and that of six other explosives was measured by a TGA-MS combination using STMBMS. The results were compared to develop a kinetic model and were used to identify the rate-determining steps [84].

Bi-1,2,4-triazole was synthesized from *N,N*-dimethylformamide azine dihydrochloride and 4-amino-1,2,4-triazole in toluene as solvent [337]. The structure of bi-1,2,4-triazole was characterized by <sup>1</sup>H NMR, IR, MS, and elemental analysis. A single crystal of bis-1,2,4-triazole was also cultivated successfully and its crystal structure was determined by XRD. The crystal was an orthorhombic system, space group *Pnma* with crystal parameters of  $a = 0.69712(14)$  nm,  $b = 0.74045(15)$  nm,  $c = 1.1156(2)$  nm,  $V = 0.5759(2)$  nm<sup>3</sup>,  $Z = 4$ , and  $D_{\text{XRD}} = 1.570$  g/cm<sup>3</sup>. The two triazole rings in bis-1,2,4-triazole are oriented vertically to each other. This should be beneficial to the stability of the molecule due to the least steric hindrance.

There are substantially more publications on bistetrazoles and azotetrazoles than on bistriazoles and azotriazoles. Nevertheless, these compounds have been explored but they do not seem to offer any advantages over their tetrazole relatives.

The synthesis and full structural and spectroscopic characterization by XRD, IR, Raman, and multi-nuclear NMR spectroscopy of three asymmetrically substituted bi-1,2,4-triazoles, along with different energetic moieties like amino, nitro, nitrimino, and azido moieties, was done to study the influence of these energetic moieties on structural and energetic properties [263, 338]. A calculation of the standard enthalpies

of formation revealed highly positive HOFs and good detonation properties for all compounds. The measured sensitivities to mechanical stimuli and decomposition temperatures strongly depended on the energetic moiety of the triazole ring. The ionic derivatives were found to be thermally stable and insensitive compounds.

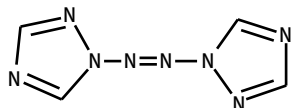
Substituents like nitroimino groups on both rings of bitriazole will increase the energy content of the molecule [339]. Bis[3-(5-nitroimino-1,2,4-triazolate)]-based energetic salts exhibited low solubility in available solvents, high hydrolytic stability, excellent thermal stability, high density, positive HOF, low shock sensitivity, and excellent detonation properties. The physical and energetic properties of some salts are similar and even superior to those of RDX.

Five symmetrical bi-1,2,4-triazoles, where both rings were carrying energetic substituents like amino, nitro, nitrimino, azido, and dinitromethylene groups, were synthesized and characterized [340]. The main objective was a comparative study on the influence of those energetic substituents on the structural and energetic properties of the resulting compound. A complete characterization included XRD, IR, Raman, and NMR spectroscopy of all compounds. The standard enthalpies of formation were calculated and the predicted detonation parameters were computed using the EXPLO5.05 program. The impact, friction, and ESD sensitivities were determined experimentally. The molar enthalpy of formation of 3,3'-dinitro-5,5'-bi(1*H*-1,2,4-triazole) is +285 kJ/mol, and that of 3,3'-diazido-5,5'-bi(1*H*-1,2,4-triazole) (DNBT) is +971 kJ/mol. The onset of decomposition of 3,3'-dinitro-5,5'-bi(1*H*-1,2,4-triazole) is 524 K (251 °C) and that of 3,3'-diazido-5,5'-bi(1*H*-1,2,4-triazole) is 474 K (201 °C). DNBT may also be described as 5,5'-dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole, where the location of the hydrogen atoms is identified. It has a very high density (1.903 g/cm<sup>3</sup>) and can form stable salts, preferably with nitrogen-rich bases. Highly nitrogen-rich salts of DNBT formed from ammonium, hydroxylammonium, hydrazinium, guanidinium, aminoguanidinium, and triaminoguanidinium cations were prepared and fully characterized by IR, Raman, NMR, DSC, and XRD [341]. The standard enthalpies of formation were calculated for selected compounds and the predicted detonation parameters were calculated. The impact, friction, and ESD sensitivity were also determined. One cannot help but wonder if “triazolide” anion should not be referred to as “triazolate” anion instead. Or is the anion ending with “ate” reserved only for oxygen-containing anions?

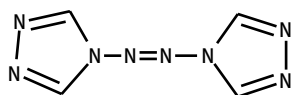
### 8.11.5 Azo-1,2,4-triazole Compounds

Two triazole rings can be connected either directly via a C—C bond as in bitriazole or via an azo —N=N— group (as in azotriazole). The conjugation of the electron cloud extends from one ring to the other, thus stabilizing the molecule. Azo-bridged triazoles (mainly 1,2,4-triazoles) are high nitrogen compounds as well as HEDM [342]. Azotriazole can form azotriazolium salts. Instead of being connected directly by a C—C or N—N bond, the two triazole rings in azotriazole are connected via an azo —N=N—bridge.

This actively participates in the resonance structure of the aromatic system. The connection to the ring can be at the 1-, 3- or 4-position. Azotriazoles are also called azobistriazoles but the *bis* prefix is unnecessary. Azobenzene does not use the *bis* prefix either.



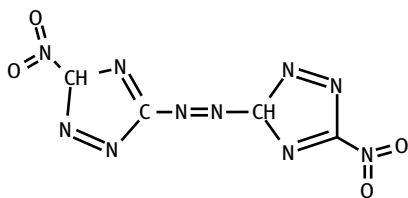
1,1'-Azo-1,2,4-triazole



4,4'-Azo-1,2,4-triazole

1,1'-Azo-1,2,4-triazole contains a chain of six nitrogen atoms and is unsymmetrical while 4,4'-azo-1,2,4-triazole has only four nitrogen atoms in line and is symmetrical along the N=N axis of the azo group.

5,5'-Dinitro-3,3'-azo-1,2,4-triazole, 3,3'-dinitro-5,5'-azo-1*H*-1,2,4-triazole, 3,3'-azobis(5-nitro-1*H*-1,2,4-triazole),  $C_4H_2N_{10}O_4$ , DNAT, CAS RN [140218-61-7],  $M = 254.13$  g/mol, has a density of  $1.88$  g/cm<sup>3</sup> and has a HOF of  $+406$  kJ/mol ( $+97$  kcal/mol). DNAT is a strong acid and forms salts with many bases. Based on XRD crystallography data, 1,1'-dinitro-3,3'-azo-1,2,4-triazole (N-DNAT) exists in two polymorphic forms [343]. The yellow color polymorph has a crystal density of  $1.701$  g/cm<sup>3</sup>, while the density of the orange crystal is  $1.831$  g/cm<sup>3</sup>.

3,3'-Dinitro-5,5'-azo-1*H*-1,2,4-triazole (DNAT)

The high-nitrogen molecule, 5,5'-dinitro-3,3'-azo-1,2,4-triazole, (3-nitro-3*H*-1,2,4-triazol-5-yl)-(5-nitro-3*H*-1,2,4-triazol-3-yl)diazene, DNAT, was calculated to have a high density and a positive enthalpy of formation [304]. In an attempt to prepare DNAT via the oxidation of ANTA with different oxidizers, it was found that DNAT was the reaction product when the potassium salt of ANTA was oxidized with potassium permanganate. However, when ANTA was oxidized with ammonium persulfate in an aqueous medium, one of the reaction products obtained was the azoxy molecule of DNAT (DNATzT). It was not possible to determine the crystal densities of either

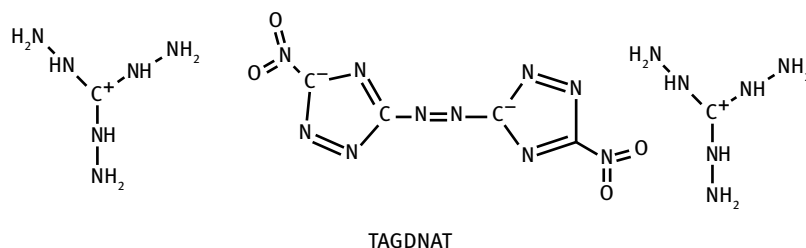
DNAT or DNAzT because the crystals obtained were solvated with the crystallization solvents.

The solid-state structure of 4,4'-azobis(1,2,4-triazole) was determined by XRD [344]. The experimentally determined density and enthalpy of formation matched with theoretically computed values based on the B3LYP method. Based on DSC results, 4,4'-azobis(1,2,4-triazole) decomposed at a relatively high temperature (586 K = 313 °C). By comparison with 3,3'-azobis(1,2,4-triazole), which contains a C=N=N-C'-azo linkage, the N,N'-azo linkage was found to provide compounds with a relatively high density and high energy.

3,3'-Dinitro-5,5'-azo-1*H*-1,2,4-triazole (DNAT) was synthesized by the oxidative coupling of 5-amino-5-nitro-1,2,4-triazole (ANTA) as raw material [345]. Its structure was characterized by IR, NMR, and elemental analyses.

The drop weight impact sensitivity  $H_{50}$  of DNAT was 17.08 cm (drop-hammer mass 5 kg) and the friction sensitivity of 60% initiation was 3.92 MPa pressure at a pendulum angle of 90°. Single crystals of DNAT•4H<sub>2</sub>O were grown from solutions, and the crystal structure was determined by XRD to be monoclinic with space group  $P_2(1)/n$  and a density of = 1.550 g/cm<sup>3</sup>.

DNAT and its triaminoguanidinium salt were characterized for thermal stability and detonation and strand burning behavior [346–349]. The triaminoguanidinium salt of DNAT, TAGDNAT, can be easily synthesized through neutralization by treatment of DNAT with sodium hydroxide, followed by cation metathesis with triaminoguanidinium chloride.



The reaction was performed in water and the product was isolated in excellent yield as a yellow crystalline solid. The material was found to have a thermal decomposition onset temperature of 478 K (205 °C), using a 10 °C/min heating ramp rate. The energy released upon decomposition was 1681 J/g. The HOF of TAGDNAT was measured using combustion calorimetry. Based on the values for the heat of combustion for TAGDNAT, a HOF of +711 kJ/mol was determined. In comparison, the HOF of DNAT itself was reported to be 406 kJ/mol. Similar reactions were performed with the *N*-oxide of DNAT. TAGDNAT was formulated with 5% KEL-F binder and pressed into cylindrical pellets (1.27 × 1.27 cm) of 94% theoretical maximum density and tested for detonation velocity and constant-pressure strand burn rates. The measured detonation velocity and



estimated detonation pressure of TAGDNAT pellets were compared with and closely matched the predicted values calculated using the Cheetah 5.0 code. The burning rate function was  $r_b = 0.799p^{0.507}$ . Additional information on TAGDNAT may be found in the section on TAG salts (*Encyclopedia of Liquid Fuels*, chapter “Amides and Imides”).

1,1'-Azobis-1,2,4-triazole, 1,1'-azobis-(3-nitro-1,2,4-triazole), or 1,1'-azobis-(3,5-dinitro-1,2,4-triazole) can be prepared by oxidizing the corresponding amine with *tert*-butyl hypochlorite [350]. Azo-bridged azole derivatives were designed and investigated to find a comprehensive relationship between the structure and performance of nitrogen-rich energetic compounds [351]. DFT calculations were used to predict optimized structures, HOF, and detonation properties. The nitroazoles showed higher densities than amino and azido derivatives and hence better detonation performance. Thermal stability was analyzed using BDE of C—NO<sub>2</sub>, C—NH<sub>2</sub>, and C—N<sub>3</sub> bonds. The amino derivatives were found to be more stable and less sensitive than the nitro or azido compounds.

A new family of high-nitrogen compounds – that is, polyazido- and polyamino-substituted *N,N'*-azo-1,2,4-triazoles – were synthesized and fully characterized [352]. The structures of 3,3',5,5'-tetra(azido)-4,4'-azo-1,2,4-triazole and 3,3',5,5'-tetraamino-4,4'-azo-1,2,4-triazole were confirmed by XRD and thermal stability was determined by DSC. Their HOF and density, which were calculated by using a Gaussian 03 method, were used to predict the detonation performances of the related compounds using EXPLO 5.05. The HOFs of the polyazido compounds were also derived by using an additive method. 3,3',5,5'-tetra(azido)-4,4'-azo-1,2,4-triazole had the highest HOF (6933 kJ/kg) reported so far for energetic compounds and a detonation performance that is comparable to that of HMX, while 3,3',5,5'-tetra(amino)-4,4'-azo-1,2,4-triazole had a predicted onset of decomposition temperature of up to 563 K (290 °C).

*N*-diazo-bridged azoles were synthesized based on oxidative coupling of *N*-aminoazoles [353]. The incorporation of extended catenated nitrogen-atom chains with nitro groups led to compounds with favorable functional compatibilities. This combination was the basis for a series of high-density energetic materials (HEDMs) with high HOFs, enhanced densities, positive oxygen balances, and good detonation properties while retaining excellent thermal stabilities and relatively low impact sensitivities. Calculated and experimental studies showed the delicate balance between the length of the nitrogen atom chain and the energetic performance and stability, thus providing a promising strategy for designing advanced energetic materials.

A series of derivatives of *N,N'*-azobis(1,2,4-triazole) substituted by —N<sub>3</sub>, —NO<sub>2</sub>, —NF<sub>2</sub>, and —NH<sub>2</sub> groups was studied using the DFT method [354]. Strong  $p-\pi$  and  $\pi-\pi$  conjugation interactions exist in these molecules. Substituent effects on the geometrical and electronic structures, the aromaticity of the triazole ring, electronic sensitivity, impact sensitivity, thermal stability, density, solid-state HOF, detonation velocity, detonation pressure, and specific impulse were investigated. Substituent groups had significant and differing effects on performance: —N<sub>3</sub>, —NF<sub>2</sub>, and —NO<sub>2</sub> groups are

very helpful for enhancing explosive performance but the opposite occurs for the  $\text{—NH}_2$  group. The order of the contribution of various groups to explosive performance was  $\text{—NF}_2 > \text{—NO}_2 > \text{—N}_3 > \text{—NH}_2$ .  $\text{—NO}_2$  results in the second-highest explosive performance and the best electronic stability.  $\text{—N}_3$  gives relatively low explosive performance and stability but the highest  $\Delta H_f$  and specific impulse.  $\text{—NH}_2$  leads to the lowest explosive performance while providing the best impact and thermal stability.

Nitrogen-rich energetic salts based on 3,3'-diamino-4,4'-azo-1,2,4-triazole containing an N,N'-azo linkage have been synthesized and fully characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, elemental analysis, DSC and sensitivities toward impact, and friction and electrostatic discharge [355]. The crystal structures of the chloride, nitrate, and perchlorate salts have been determined by single-crystal XRD. All the salts exhibited high thermal stabilities with decomposition temperatures over 473 K (200 °C) except for the nitroformate salt. The densities of the salts were in the range of 1.71 to 1.99 g/cm<sup>3</sup>.

Azo-bis-1,2,4-triazole acts as an excellent backbone for the synthesis of energetic compounds owing to its characteristics such as high enthalpy of formation, high nitrogen content, and plane structure [356].

## 8.12 Triazolium and Triazolate Salts

The pK of an amine base is usually a good indication of how easily the amine can be protonated. The pK of 4-amino-1,2,4-triazole is 2.25, that of 1,2,4-triazole is 10.04, and that of 1,2,3-triazole is 8.2. All three triazoles form salts with mineral acids that have interesting properties as ionic liquids. In particular, the salts with oxidizing mineral acids such as nitric, perchloric, and dinitramidic acid are of interest as potential rocket propellants. The melting points of 1,2,3-triazolium salts are lower than those of their 1,2,4-triazolium isomers. Even lower melting points can be achieved with highly unsymmetrical mono- or poly-substituted triazolium salts. The physical properties of triazolium salts are summarized in Table 18. The perchlorates are the most stable and the dinitramides are the least stable triazolium salts. All are potentially explosive and some are very friction sensitive [357–360]. The IR, Raman, and NMR spectra of the various salts were measured. Only the 1,2,4-triazolium perchlorate was crystallized well enough that a single crystal could be used for the determination of its crystal structure by XRD.

The EILs formed by the 1,2,4-triazolium cation family and dinitramide anion were investigated by *ab initio* quantum chemistry calculations. This was to address the following questions: How does the substitution at the triazolium ring's nitrogen atoms affect its HOF and its charge delocalization? What kind of ion dimer structures might exist? And, do deprotonation reactions occur, as a possible first step in the decomposition of these materials [361]? (see also [328]).

**Table 18:** Physical properties of unsubstituted and substituted 1,2,3- and 1,2,4-triazolium salts.

| Parent amine                  | Anion                                         | Melting point    |                  | Decomposition temperature |         | Density<br>g/cm <sup>3</sup> | Standard enthalpy of formation (calculated) |          | Impact sensitivity, kg-cm (2-kg weight) |
|-------------------------------|-----------------------------------------------|------------------|------------------|---------------------------|---------|------------------------------|---------------------------------------------|----------|-----------------------------------------|
|                               |                                               | K                | °C               | K                         | °C      |                              | kJ/mol                                      | kcal/mol |                                         |
| 1,2,4-Triazole                |                                               |                  |                  |                           |         |                              |                                             |          |                                         |
|                               | NO <sub>3</sub> <sup>−</sup>                  | 410              | 137              | 433–455                   | 160–182 | 1.64                         | −42.7                                       | −10.2    | >200                                    |
|                               | ClO <sub>4</sub> <sup>−</sup>                 | 362              | 89               | 558                       | 285     | 1.96                         | −1.3                                        | −0.31    | 114                                     |
|                               | N(NO <sub>2</sub> ) <sub>2</sub> <sup>−</sup> | 348              | 75               | 393                       | 120     | 1.66                         | +149.9                                      | +35.8    | 98                                      |
| 1,2,3-Triazole                |                                               |                  |                  |                           |         |                              |                                             |          |                                         |
|                               | NO <sub>3</sub> <sup>−</sup>                  | 341              | 68               | 398                       | 125     | 1.57                         | +42.9                                       | +10.2    | >200                                    |
|                               | ClO <sub>4</sub> <sup>−</sup>                 | 346              | 73               | 473                       | 200     | 1.79                         | +90.4                                       | +21.6    | <5                                      |
|                               | N(NO <sub>2</sub> ) <sub>2</sub> <sup>−</sup> | 334              | 61               | 353                       | 80      | 1.66                         | +228.2                                      | +54.5    | Not done                                |
| 4-Amino-1,2,4-triazole        |                                               |                  |                  |                           |         |                              |                                             |          |                                         |
|                               | NO <sub>3</sub> <sup>−</sup>                  | 342              | 69               | 438–453                   | 165–180 | 1.6                          | +77.1                                       | +18.4    | >200                                    |
|                               | ClO <sub>4</sub> <sup>−</sup>                 | 346–357          | 73–84            | 483                       | 210     | 1.81                         | +117.2                                      | +28.0    | 30                                      |
|                               | N(NO <sub>2</sub> ) <sub>2</sub> <sup>−</sup> |                  | oil, <20         | 418–423                   | 145–150 | —                            | +273.6                                      | +65.4    | <5                                      |
| 1,5-Diamino-1,2,4-triazole    |                                               |                  |                  |                           |         |                              |                                             |          |                                         |
|                               | NO <sub>3</sub> <sup>−</sup>                  | 432              | 159              | 422                       | 149     | 1.65                         | +196.2                                      | +46.9    |                                         |
|                               | ClO <sub>4</sub> <sup>−</sup>                 | 411              | 138              | —                         | —       | 1.83                         | +240.9                                      | +57.6    |                                         |
|                               | ClO <sub>4</sub> <sup>−</sup>                 |                  |                  |                           |         | 1.74                         |                                             |          | Det. vel.<br>8300 m/s                   |
| 3,4,5-Triamino-1,2,4-triazole |                                               |                  |                  |                           |         |                              |                                             |          |                                         |
|                               | NO <sub>3</sub> <sup>−</sup>                  | 478              | 205              | 523                       | 250     |                              |                                             |          |                                         |
|                               | NO <sub>3</sub> <sup>−</sup>                  | 498              | 225              |                           |         |                              |                                             |          | 200; Friction<br>16 kg <sub>f</sub>     |
|                               | ClO <sub>4</sub> <sup>−</sup>                 | 469              | 196              | >573                      | >300    |                              |                                             |          |                                         |
|                               | ClO <sub>4</sub> <sup>−</sup>                 | 488              | 215              |                           |         |                              |                                             |          | 50, Friction<br>15.2 kg <sub>f</sub>    |
|                               | N(NO <sub>2</sub> ) <sub>2</sub>              | 418              | 145              | ~423                      | ~150    |                              |                                             |          |                                         |
|                               | N(NO <sub>2</sub> ) <sub>2</sub>              | 418              | 145              |                           |         |                              |                                             |          | 196, Friction<br>15.2 kg <sub>f</sub>   |
| 1-Methyl-1,2,4-triazole       |                                               |                  |                  |                           |         |                              |                                             |          |                                         |
|                               | NO <sub>3</sub> <sup>−</sup>                  | 514<br>(decomp.) | 241<br>(decomp.) | >514                      | >241    | 1.581                        |                                             |          |                                         |

Data sources: [2, 201, 325, 359, 362].

Ionic liquids are discussed in this volume in the chapter “Ionic Liquids.” Similar properties can be observed with aminotriazoles where the amino group can be attached to a nitrogen or a carbon atom in the ring. The most common aminotriazole is the 4-amino-1,2,4-triazole.

1,2,3-Triazolium salts have been known for a long time. However, their potential as ionic liquids and catalysts was recognized only two decades ago. 1,2,3-Triazolium ionic liquids can serve as solvents, catalysts, hosts in anion recognition, and as energetic materials [363]. One application involves tethering catalytically active species such as (S)-proline with triazolium ionic liquids and using this as an anion-recognizing organocatalyst. Such catalysts are interesting not only due to their recyclability but also because of their outstanding tunable properties. They can have a wide liquid range, thermal stability, tunable polarity, low flammability, tunable solubility, and low vapor pressure along with ease of separation. The syntheses of 1,2,3-triazolium salts are mainly based on the copper-catalyzed azide-alkyne cycloaddition as the most practical click reaction and subsequent *N*-alkylation of the resulting 1,2,3-triazoles. This synthetic route has the advantage of having four structural units, i.e., the alkyne, the azide, the alkylating agent, and the counter anion that can be varied in order to tune the properties of the resulting ionic liquid. Unlike the imidazolium ionic liquids, 1,2,3-triazolium salts do not have an acidic proton at position two, which could make them inappropriate for reactions under basic conditions. The low acidity of 1,2,3-triazolium salts in position four can be exploited in the formation of 1,2,3-triazol-4-ylidene metal complexes with marked catalytic properties (see also [364]).

### 8.12.1 Physical and Chemical Properties of 1,2,4-Triazolium Salts

The nitrate, perchlorate, and dinitramidate salts of 1*H*-1,2,4-triazole, 4-amino-1,2,4-triazole, 3,4,5-triamino-1,2,4-triazole (“guanazine”), and 1*H*-1,2,3-triazole were synthesized and characterized for their sensitivity [357, 365]. XRD study of 1,2,4-triazolium perchlorate showed significant hydrogen bonding between the perchlorate anion and the triazolium ring, which contributes to its relatively high density of 1.96 g/cm<sup>3</sup>. The nitrate salt of 3,4,5-triamino-1,2,4-triazole melted at 478 K (205 °C), the perchlorate salt at 469 K (196 °C), and the dinitramidate salt at 418 K (145 °C). The onset of exotherm in the DSC was 523 K (250 °C) for the nitrate, above 573 K (300 °C) for the perchlorate, and 423 K (150 °C) for the dinitramidate salt. In the thermal stability test at 348 K (75 °C), the mass loss rate was less than 1%/day for several days. The friction and impact sensitivity was less than that of HMX. Two of the salts of 4-amino-1,2,4-triazole, m.p. 394 K (121 °C) had melting points lower than the parent amine. The melting points were 410 K (137 °C), 362 K (89 °C), and 348 K (75 °C) for the nitrate, perchlorate, and dinitramidate, respectively. 1*H*-1,2,3-triazole is a liquid at room temperature, but its salts were melting higher than the parent amine. The nitrate salt melted at 383 K (110 °C) with a DSC exotherm onset at 398 K (125 °C). The perchlorate salt melted at 346 K (73 °C) with an exotherm onset at 493 K (220 °C). The dinitramidate salt melted at 334 K (61 °C) with an

exotherm onset at 353 K (80 °C). When stored at 348 K (75 °C) for several days, only the perchlorate had a mass loss rate of less than 1%/d.

Many of these lower melting salts are ionic liquids [359, 362, 366, 367]. Additional information on ionic liquids can be found in *Encyclopedia of Liquid Fuels*, chapter “Ionic Liquids.”

The densities and enthalpies of formation of triazolium salts can be predicted using computational chemistry methods [368]. While it is relatively easy to predict enthalpies of formation of gaseous molecules, it is more difficult for crystalline or molten substances. A method has been derived from empirical density data to predict the cohesive energy from the molecular structure of ionic compounds [369]. Table 19 is a sample of energetic compounds for which densities were known.

Table 20 is a summary of properties of 1,2,4- and 1,2,3-triazolium nitrates, perchlorates, and dinitramides. 1*H*-1,2,4-triazole-copper complexes are of interest as gas generants. The thermal stability and ignition temperature of such complexes can be modified by substituting a ring hydrogen with an electrophilic or nucleophilic group.

**Table 19:** Properties of triazolium salts.

| Compound                                | Density at<br>348 K (75 °C) | Decomposition<br>temperature |     | Melting point |     | Impact<br>sensitivity |
|-----------------------------------------|-----------------------------|------------------------------|-----|---------------|-----|-----------------------|
|                                         | g/cm <sup>3</sup>           | K                            | °C  | K             | °C  | kg cm                 |
| 4-Amino-1,2,4-triazolium<br>nitrate     | 1.6                         | 453                          | 180 | 342           | 69  | >200                  |
| 1,2,4-Triazolium nitrate                | 1.64                        | 455                          | 182 | 410           | 137 | >200                  |
| 1,2,3-Triazolium nitrate                | 1.57                        | 383                          | 110 | 383           | 110 | >200                  |
| 4-Amino-1,2,4-triazolium<br>dinitramide | —                           | 253                          | −20 | 419           | 146 | <5                    |
| 1,2,4-Triazolium dinitramide            | 1.66                        | 348                          | 75  | 285           | 12  | 98                    |
| 1,2,3-Triazolium dinitramide            | 1.66                        | 334                          | 61  | 353           | 80  | —                     |

Data source: [369].

**Table 20:** Properties of 1,2,4- and 1,2,3-triazolium nitrates, perchlorates, and dinitramides.

| Compound                     | $T_{\text{melt}}$ |     | $T_{\text{dec}}$ |     | Density,<br>meas. | Density, calc.<br>from XRD |
|------------------------------|-------------------|-----|------------------|-----|-------------------|----------------------------|
|                              | K                 | °C  | K                | °C  | g/cm <sup>3</sup> | g/cm <sup>3</sup>          |
| 1,2,4-Triazolium nitrate     | 410               | 137 | 455              | 182 | 1.64              | 1.55                       |
| 1,2,4-Triazolium perchlorate | 362               | 89  | 558              | 285 | 1.96              | 1.75                       |
| 1,2,4-Triazolium dinitramide | 348               | 75  | 393              | 120 | 1.66              | 1.64                       |
| 1,2,3-Triazolium nitrate     | 341               | 68  | 398              | 125 | 1.57              | 1.55                       |
| 1,2,3-Triazolium perchlorate | 346               | 73  | 473              | 200 | 1.79              | 1.77                       |
| 1,2,3-Triazolium dinitramide | 334               | 61  | 353              | 80  | 1.66              | 1.64                       |

Data source: [309].

The effects of a given substituent, its ability to supply/withdraw electrons to/from the reaction site on the properties of 1*H*-1,2,4-triazole-copper complexes were investigated [370]. The substituents were selected based on their Hammett constant value. Nitro group ( $-\text{NO}_2$ ), chloro group ( $-\text{Cl}$ ), and an amino group ( $-\text{NH}_2$ ) were selected as substituents, and 1*H*-1,2,4-triazole-copper complex, nitro-1*H*-1,2,4-triazole-copper complex, amino-1*H*-1,2,4-triazole-copper complex, and chloro-1*H*-1,2,4-triazole-copper complexes were synthesized and their thermal decomposition behaviors were investigated. According to SC-DSC measurements, the substituents can be used to control the thermal stability of 1*H*-1,2,4-triazole-copper complexes based on their electron donor/acceptor nature and their Hammett constant value.

Triazolyl-functionalized monocationic energetic salts were prepared through reactions of 1-(chloromethyl)-1*H*-1,2,4-triazole with 1-methylimidazole, 1-methyl-1,2,4-triazole, or 4-amino-4*H*-1,2,4-triazole in the presence of NaI, followed by metathetical reactions with equivalent silver salts [371]. Subsequent protonation with corresponding acids gave rise to triazolium-functionalized dicationic salts. Direct treatment of neutral 1-(1*H*-imidazole-1-yl)methylene-1*H*-1,2,4-triazole gave rise to the corresponding dicationic energetic salts. These were prepared by reaction of 1-(chloromethyl)-1*H*-1,2,4-triazole with imidazole in the presence of a base, with acids in methanol or metathesis with silver salts after quaternization with methyl iodide. All of the energetic salts were characterized by DSC, TGA, and density determinations. The majority exhibited good thermal stability and relatively high density. The synergistic effect of two energetic rings in cations and the effect of anions on their preparation and physicochemical properties were examined. The densities, standard enthalpies of formation, detonation pressures, detonation velocities, and specific impulse values for these unsymmetrical dicationic energetic salts were then calculated.

A series of functionalized imidazolium and 1,2,4-triazolium salts with cyanomethyl, vinyl, and propargyl substituents coupled with energetic anions such as perchlorate, nitrate, dicyanamide, and dinitramide were prepared and characterized by NMR, IR spectroscopy, and elemental analyses [181]. Since some of these salts melt  $<100^\circ\text{C}$ , they can be classified as ionic liquids. Their densities ranged between 1.25 and 1.76 g/cm<sup>3</sup>. The standard enthalpies of formation of the salts were calculated and ranged from  $\Delta H^\circ_f = -56$  to  $+851$  kJ/mol. Of all the salts synthesized, the dicyanamides exhibited the highest positive HOFs but also the lowest densities.

Joining a 1,2,4-triazole ring with a tetrazole ring such as in 1-(1*H*-1,2,4-triazol-3-yl)-1*H*-tetrazole gives a wide range of high-nitrogen compounds that can form salts with nitrogen-rich cations. The energetic salts of 1-(1*H*-1,2,4-triazol-3-yl)-1*H*-tetrazole, 5-(1*H*-tetrazol-1-yl)-1*H*-1,2,4-triazol-3-amine, 1-(3-azido-1*H*-1,2,4-triazol-5-yl)-1*H*-tetrazole, and 3-azido-1*H*-1,2,4-triazol-5-amine with various cationic moieties were prepared and their densities, HOFs, chemical energy of detonation, detonation velocities and pressures were calculated [372]. All of the compounds possessed high positive HOFs due to high energy contribution from the molecular backbone of the

corresponding compounds. Substitution with nitro, amino, and azido groups can improve their performance and/or stability.

Any combination of nitrogen-rich 1,2,4-triazole (**1**) and 1,2,3-triazole (**2**) bases with oxygen-rich acids  $\text{HNO}_3$  (a),  $\text{HN}(\text{NO}_2)_2$  (b), or  $\text{HClO}_4$  (c) produces energetic salts (1a, 1b, and 1c and 2a, 2b, and 2c, respectively). These are useful for composite explosives and propellants. The enthalpies of formation of these salts were studied with the dispersion-corrected DFT [373]. For the isomers such as 1a and 2a, the more negative  $\Delta G$  of the formation reaction leads to a thermally more stable salt. The ability to form intramolecular hydrogen bonds predicted with the quantum theory of atoms in molecules has the order of  $2 > 1$ . Different hydrogen bonds result in different second-order perturbation energies, redshifts in IR, and electron density differences. The charge transfer, binding energy, dispersion energy, lattice energy, and energy gap between frontier orbitals in the salts of (**1**) are larger than those of (**2**). This helps stabilize the former, with (**1**) being more stable than (**2**) via the formation of salts. 1,2,4-Triazole is preferred as a base over 1,2,3-triazole in terms of forming stable salts.

Table 21 is a summary of the predicted enthalpies of formation of triazolium salts. The estimates from two different sources, [167] and [374], are included in the table.

**Table 21:** Predicted enthalpies of formation of triazolium salts.

| Compound                                    | Enthalpy of formation |          | References |
|---------------------------------------------|-----------------------|----------|------------|
|                                             | kJ/mol                | kcal/mol |            |
| 5-Azido-1,2,4-triazolium nitrate            | +218.8                | +52.3    | [374]      |
|                                             | +252                  | +60.3    | [167]      |
| 1,2,4-Triazolium 5-nitrotetrazolate         | +409.6                | +97.9    | [374]      |
|                                             | +353                  | +84.3    | [167]      |
| 1-Amino-1,2,4-triazolium nitrate            | +34.7                 | +8.3     | [374]      |
|                                             | −25.5                 | −6.1     | [167]      |
| 3-Amino-1,2,4-triazolium nitrate            | −171.1                | −40.9    | [374]      |
| 4-Amino-1,2,4-triazolium nitrate            | −4.1                  | −1.0     | [167]      |
|                                             | −109.6                | −26.2    | [374]      |
| 4-Amino-1,2,4-triazolium 5-nitrotetrazolate | +702.1                | +168     | [374]      |
|                                             | +467                  | +111.6   | [167]      |

### 8.12.2 1,2,4-Triazolium Nitrate and 1,2,3-Triazolium Nitrate

1,2,4-Triazolium nitrate (1,2,4-triazole nitrate) is a high-nitrogen additive and has been repeatedly proposed for gas generant applications. It is soluble in water and is a potential fuel for HAN-based monopropellants.

*In vitro* rat hepatocyte toxicity and bacteria (*Salmonella*) genotoxicity assays were performed on thirteen high-energy chemicals that are candidates for potential

replacement monopropellants for hydrazine [375]. The chemicals were mostly hydrazine derivatives and amino compounds in the form of their nitrate salts. The results in hepatocytes showed a dose-dependent decrease in mitochondrial activity (MTT) and an increase in lactate dehydrogenase (LDH) leakage. 1,2,4-Triazolium nitrate was one of the least toxic compounds tested in this group.

1,2,4-Triazolium nitrate can be prepared by adding concentrated nitric acid dropwise to a solution of 1,2,4-triazole in dry methanol under nitrogen flow at room temperature [201]. In one study, the colorless and homogenous reaction mixture was stirred for 1 h at ambient temperature. After this time, the stirring bar was removed and the solvent was evaporated under a high vacuum to give 1,2,4-triazolium nitrate as white micro-crystals in 93% yield, m.p. 410 K (137 °C) [359, 376, 377].

The thermal decomposition of 1,2,3-triazolium nitrate was studied at four different heating rates [378]. The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction were 134 kJ/mol and  $10^{14.58} \text{ s}^{-1}$ , respectively. The critical temperature of the thermal explosion was 375 K = 102 °C. The entropy ( $\Delta S$ ) and enthalpy ( $\Delta H$ ) of activation and the free energy of activation ( $\Delta G$ ) of the decomposition reaction were 23.88 J mol<sup>-1</sup> K<sup>-1</sup>, 131, and 121 kJ/mol, respectively. The self-accelerating decomposition temperature ( $T_{\text{SADT}}$ ) was 368.6 K = 95.5 °C. The specific heat capacity equation is

$$C_p = -42.6218 + 0.6807T \text{ (for the temperature range } 283.1 < T < 353.2 \text{ K)},$$

where  $C_p$  is the heat capacity in J mol<sup>-1</sup> K<sup>-1</sup> and  $T$  is the temperature in kelvin. The critical temperature of hot-spot initiation was 637 K = 364 °C and the drop height of impact sensitivity (H 50) was 9.16 cm.

The properties of dissolution in different solvents, the specific heat capacity, and the thermal decomposition process under the non-isothermal conditions for energetic triazole ionic salts 1,2,4-triazolium nitrate (**1a**), 1,2,3-triazolium nitrate (**1b**), 3,4,5-triamino-1,2,4-triazolium nitrate (**2a**), and 3,4,5-triamino-1,2,4-triazolium dinitramide (**2b**) were measured using a Calvet Microcalorimeter [379]. The thermochemical equilibrium equation, differential enthalpies of dissolution, standard molar enthalpies of dissolution, apparent activation energy, pre-exponential constant, kinetic equation, linear relationship of specific heat capacity with temperature over the temperature range of 283 to 353 K, standard molar heat capacity and enthalpy, entropy and Gibbs free-energy of 283 to 353 K (taking 298.15 K as the benchmark for compounds **1a**, **1b**, **2a**, and **2b**) were obtained based on experimental data and theoretical calculation methods. In addition, the kinetic and thermodynamic parameters of the thermal decomposition reaction, the critical temperature of thermal explosion, the self-accelerating decomposition temperature, and the adiabatic time-to-explosion of compounds **1a**, **1b**, **2a**, and **2b** were calculated.

An MDs study was performed where several triazolium-based cations (1,2,4-triazolium, 1,2,3-triazolium, 4-amino-1,2,4-triazolium, and 1-methyl-4-amino-1,2,4-triazolium) were paired with nitrate or perchlorate anions [380]. Properties of the more



common ionic liquid, 1-*n*-butyl-3-methylimidazolium nitrate, were also computed and compared with the properties of the triazolium-based compounds. A molecular mechanic force field was developed for these materials using a mix of *ab initio* calculations and parameter fitting, using the molecular compound 1*H*-1,2,4-triazole as a basis for the triazolium cations. Liquid-phase properties that were computed included heat capacities, cohesive energy densities, gravimetric densities/molar volumes as a function of temperature and pressure, self-diffusivities, rotational time constants, and various pair correlation functions. Heat capacities and lattice parameters were computed for the solid phase. Of all of these properties, only lattice parameters have been measured experimentally (and only for four of the triazolium compounds). The agreement with the experimental crystal structures was good. When compared with that of the imidazolium-based ionic liquid, the triazolium-based materials have much smaller molar volumes, higher cohesive energy densities, and larger specific heat capacities. They also tended to be less compressible, have a higher gravimetric density, and have faster rotational dynamics but similar translational dynamics.

### 8.12.3 1,2,4-Triazolium Azides and 1,2,3-Triazolium Azides

Ionic liquid azides from azidoethyl, alkyl, and alkenyl substituted derivatives of 1,2,4- and 1,2,3-amino-triazoles were prepared and their structural and physical properties were determined (Table 22) [163]. All salts possessed melting points below 373K

**Table 22:** Physical properties of di-substituted triazolium azides.

| Compound name                                     | Melting or glass transition point |             | Decomposition onset |      | Calculated $\Delta H_f^{298}(S)$ |          | Impact sensitivity |
|---------------------------------------------------|-----------------------------------|-------------|---------------------|------|----------------------------------|----------|--------------------|
|                                                   | K                                 | °C          | K                   | °C   | kJ/mol                           | kcal/mol | kg cm              |
| 1-Methyl-4-amino-1,2,4-triazolium azide           | 316                               | +43         | 402                 | +129 | +569                             | +136     | >200               |
| 1-Amino-3-methyl-1,2,3-triazolium azide           | 323                               | +50         | 429                 | +156 | +623                             | +149     | >200               |
| 1-(2-Hydroxyethyl)-4-amino-1,2,4-triazolium azide | $T_g = 223$                       | $T_g = -50$ | 402                 | +129 | +389                             | +93      | 176                |
| 1-Allyl-4-amino-1,2,4-triazolium azide            | $T_g = 216$                       | $T_g = -57$ | 382                 | +109 | +674                             | +161     | 132                |
| 1-Amino-3-allyl-1,2,3-triazolium azide            | $T_g = 211$                       | $T_g = -62$ | 387                 | +114 | +733                             | +173     | <60                |
| 1-(2-Azidoethyl)-4-amino-1,2,4-triazolium azide   |                                   | liquid      | 379                 | +106 | +933                             | +223     | 150–200            |

Data source: [163].

(100 °C). The unique character of these ionic liquid azides is based upon the fact that these molecules are not simple protonated salts like previously reported substituted hydrazinium azides. The presence of quaternary nitrogen seems to confer both thermal stability and reduced volatility.

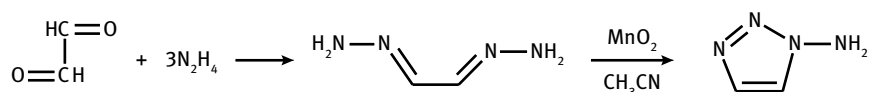
#### 8.12.4 Other Unsubstituted 1,2,4-Triazolium, 1,2,4-Triazolate, and 1,2,3-Triazolium Salts

Special interest has been devoted to azolium azolate salts such as triazolium nitrotriazolate salts, which sport both a high energy and a high nitrogen content. Energetic salts containing substituted imidazolium and 1,2,4-triazolium cations and 4,5-dinitro-imidazolate and 5-nitrotetrazolate anions were synthesized and characterized [10]. Based on experimentally obtained heats of combustion, the calculated HOFs ranged from  $\Delta H_f^\circ = +80$  to  $+1071$  kJ/mol. Imidazolate salts are denser but have lower HOFs than their tetrazolate analogues. Several salts had melting points  $<100^\circ\text{C}$ . 1,2,4-triazolium perchlorate undergoes a large endothermic crystalline phase change at 362 K (89 °C) and starts to decompose at 548 K (275 °C), as determined by DSC [359, 376, 377]. Triazolium dinitromethanide salts can be very insensitive to impact [381].

#### 8.12.5 Mono-Substituted 1,2,3-Triazolium and 1,2,3-Triazolate Salts

Direct alkylation of 1(H)-1,2,3-triazoles usually forms mixtures of one- and two-substituted 1,2,3-triazoles, which are often difficult to separate. Once formed, they often undergo isomerization equilibria in solution.

1-Amino-1,2,3-triazole, triazol-1-amine, 3-amino-1,2,3-triazole,  $\text{C}_2\text{H}_4\text{N}_4$ , CAS RN [155-25-9], can be synthesized from glyoxal and hydrazine followed by oxidation with manganese(IV)dioxide:



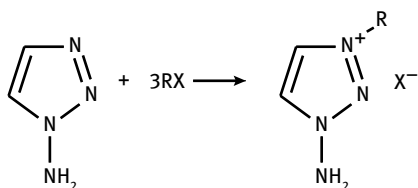
4-Amino-1,2,4-triazolium nitrate melts at 342 K (69 °C) and 4-amino-1,2,4-triazolium perchlorate melts at 357 K (84 °C) [359, 376, 377]. High-density energetic salts that contained the 1-amino-1,2,3-triazole (ATZ) or 3-methyl-1-amino-1,2,3-triazole (MAT) cation and nitrogen-rich anions were synthesized and characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, DSC, and impact sensitivity [382]. 1-Amino-1,2,3-triazolium 5-nitrotetrazolate, 3-methyl-1-amino-1,2,3-triazolium 5-nitrotetrazolate, and 3-methyl-1-amino-1,2,3-triazolium azotetrazolate crystallize in the triclinic space group  $P\bar{1}$ . Their densities were 1.688, 1.588, and  $1.550\text{ g/cm}^3$ , respectively. The measured densities of the other organic energetic salts ranged between 1.56 and  $1.86\text{ g/cm}^3$ . The detonation pressures

calculated for these salts ranged from 21.2 to 37.3 GPa, and the detonation velocities ranged from 7239 to 9082 m/s.

The thermal decomposition kinetics of 1-amino-1,2,3-triazolium nitrate were investigated by non-isothermal TG-DTG at various heating rates (2, 5, 10, 15, and 20 °C/min) [383, 384]. The results showed that the thermal decomposition of 1-amino-1,2,3-triazolium nitrate consisted of two mass-loss stages. At a heating rate of 2 °C/min, two mass-loss stages appeared in the TGA-DTG curve within the ranges 372–434 K (99–161 °C) and 434–460 K (161–187 °C), respectively. The first mass-loss stage corresponded to the loss of nitrate anion and the substituent group, while the second stage corresponded to the splitting of the triazole ring. The apparent activation energies and pre-exponential factors  $\log A$  values for the first decomposition stage were  $E = 128.97$  kJ/mol and  $\log A = 13.78$  s<sup>-1</sup>. Those for the second stage were  $E = 117.37$  kJ/mol and  $\log A = 10.93$  s<sup>-1</sup>, respectively

#### 8.12.6 Di-Substituted 1,2,3-Triazolium and 1,2,3-Triazolate Salts

Quaternization of 1-amino-1,2,3-triazole with alkyl iodide gives quaternary triazolium halogenide salts. However, they have high melting points and do not qualify as ionic liquids [385].



$\text{X} = \text{I}^-$ ,  $\text{R} = \text{CH}_3$ ;  $\text{X} = \text{Br}^-$ ,  $\text{R} = \text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ,  $\text{C}_4\text{H}_9$

Quaternary salts based upon 3-alkyl substituted 1-amino-1,2,3-triazolium cations (alkyl = methyl, ethyl, *n*-propyl, 2-propenyl, and *n*-butyl) have been synthesized and characterized by vibrational spectra, multi-nuclear NMR, elemental analysis, and DSC studies. Subsequent diazotization of these salts resulted in the exclusive formation of 1-alkyl-1,2,3-triazoles. Single-crystal X-ray studies were carried out for 1-amino-3-methyl-1,2,3-triazolium iodide, 1-amino-3-ethyl-1,2,3-triazolium bromide, 1-amino-3-*n*-propyl-1,2,3-triazolium bromide, and 1-amino-3-*n*-butyl-1,2,3-triazolium bromide as well as for the starting heterocycle and 1-amino-1,2,3-triazole itself. The quaternary triazolium halogenides can be reacted with silver nitrate in a metathetical reaction to form the nitrates which are of more interest as rocket propellants [386, 387]. The melting points of five of the nitrate salts are summarized in Table 23. One of the salts with a short alkyl group, 1-amino-3-methyl-1,2,3-triazole nitrate (1-AMTN), was identified as a viable candidate as a TNT replacement due to its relatively high melting point of 361 K (88 °C).

**Table 23:** Melting points of 1-amino-3-alkyl-1,2,3-triazolium nitrates.

| Compound name                             | Gross formula                                                | Molecular mass | Melting Point |    |
|-------------------------------------------|--------------------------------------------------------------|----------------|---------------|----|
|                                           |                                                              | g/mol          | K             | °C |
| 1-Amino-3-methyl-1,2,3-triazolium nitrate | C <sub>3</sub> H <sub>7</sub> N <sub>5</sub> O <sub>3</sub>  | 161.12         | 359           | 86 |
| 1-Amino-3-ethyl-1,2,3-triazolium nitrate  | C <sub>4</sub> H <sub>9</sub> N <sub>5</sub> O <sub>3</sub>  | 175.15         | 303           | 30 |
| 1-Amino-3-propyl-1,2,3-triazolium nitrate | C <sub>5</sub> H <sub>11</sub> N <sub>5</sub> O <sub>3</sub> | 189.18         | 306           | 33 |
| 1-Amino-3-allyl-1,2,3-triazolium nitrate  | C <sub>5</sub> H <sub>9</sub> N <sub>5</sub> O <sub>3</sub>  | 187.16         | 281           | 8  |
| 1-Amino-3-butyl-1,2,3-triazolium nitrate  | C <sub>6</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub> | 203.2          | 225           | 48 |

Data source: [386].

1-Amino-3-methyl-1,2,3-triazolium nitrate (1-AMTN) was synthesized using glyoxal and hydrazine hydrate as starting materials in three steps, i.e., addition-elimination, cyclization, methylation, and replacement reaction [388]. The overall yield was 71.8% (based on glyoxal). The structure of products was confirmed by IR, MS, NMR, and elemental analysis. The properties of 1-AMTN were estimated as follows: density 1.63 g/cm<sup>3</sup>, enthalpy of formation 84 kJ/mol, and detonation velocity 8115 m/s. Other sources gave the HOF of 1-AMTN as +83.7 kJ/mol (+20 kcal/mol) (estimated) [365]. The onset of decomposition of 1-AMTN in the DSC was at 530 K (257 °C), so it is relatively stable.

Traditionally, the conversion from quaternized alkyl-amino-triazolium halogenides to the desired and more energetic nitrates has been accomplished via a metathetical reaction with silver nitrate, which is expensive. A more economical and cleaner method of conversion, which leads to obtaining a product free of metal salts, is the reaction of triazolium halogenides with dinitrogen tetroxide [389, 390]. Three 1-alkyl-4-amino-1,2,4-triazolium bromides (alkyl = hydroxyethyl, propionitrile, acetonitrile) and 1-amino-3-propyl-1,2,3-triazolium bromide were chosen as typical examples of the process.

MD simulations based on both electronically non-polarizable and polarizable models have been carried out to investigate the ionic liquid 1-hydroxyethyl-4-amino-1,2,4-triazolium nitrate [391]. The intention was to not only provide simulation data but also to provide insight into the relationship between molecular structure, dynamics, and other useful physical properties for this class of ionic liquids. Replacing the ethyl group in 1-ethyl-4-methyl-1,4-imidazolium nitrate by a 2-hydroxyethyl group created an ionic liquid with an interwoven network of hydrogen bonds. This was simulated by MD calculations and the predicted glass transition temperature closely matched that measured by experiments.

The 1,3-diamino-1,2,3-triazolium cation can be prepared by the amination of 1-amino-1,2,3-triazole with *O*-tosylhydroxylamine [392]. The cation was then paired with the energetic anions nitrate, nitrotetrazolate-2-oxide, 5,5'-bis(1-oxidotetrazolate), 5,5'-azobis(1-oxidotetrazolate), and nitriminotetrazolate. The resulting salts were

characterized. The HOFs and detonation properties were calculated and the impact, friction, and electrical spark sensitivities of the 1,3-diamino-1,2,3-triazolium salts were measured. These salts were easily initiated energetic materials.

The energetic ionic liquid 4-amino-1-butyl-1,2,4-triazolium nitrate (C4N) can be prepared via a one-step metal-free route using butyl nitrate [393]. C4N offers promising properties like very low vapor pressure combined with good insensitivity. The potential use as an energetic additive to improve the rheological properties of glycidyl azide polymer-based (GAP-based) energetic polymers has been studied, resulting in an almost four times lower viscosity at 15 mass-% C4N content. As an additive to a nitromethane-based monopropellant, C4N works as a burning rate modifier. This reduces the propellant sensitivity.

### 8.12.7 Mono-Substituted 1,2,4-Triazolium and 1,2,4-Triazolate Salts

#### 4-Amino-1,2,4-triazolium and 1,2,4-Triazolate Salts

4-Amino-1,2,4-triazole forms stable salts with most mineral acids and nitroform. It also forms quaternary salts with methyl iodide [328].

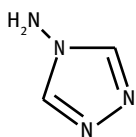
#### 4-Amino-1,2,4-triazolium Salts

4-Amino-1,2,4-triazolium nitrate (4-amino-1,2,4-triazole nitrate) is a high-nitrogen additive and has been repeatedly proposed for use in gas generant applications. It is also soluble in water and is a potential fuel for HAN-based monopropellants.

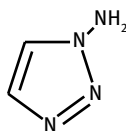
4-Amino-1,2,4-triazolium nitrate can be prepared by adding concentrated nitric acid dropwise to a solution of 4-amino-1,2,4-triazole in dry methanol under nitrogen flow at room temperature [201]. The colorless and homogeneous reaction mixture was stirred for 1 h at ambient temperature. After 1 h, the stirring bar was removed and the solvent was evaporated under a high vacuum. This produced 4-amino-1,2,4-triazolium nitrate as colorless crystal prisms in 89% yield, m.p. 342 K (69 °C).

*In vitro* rat hepatocyte toxicity and bacteria (*Salmonella*) genotoxicity assays were performed on 13 high-energy chemicals that are candidates for potential replacement monopropellants for hydrazine [375]. The chemicals were mostly hydrazine derivatives and amino compounds in the form of their nitrate salts. The results in hepatocytes revealed a dose-dependent decrease in MTT and an increase in LDH leakage. 4-Amino-1,2,4-triazolium nitrate was one of the least toxic compounds tested in this group.

The amino group can be attached to either the 3-position or in the 4-position in 1,2,4-triazole or in the 1-position in 1,2,3-triazole.



4-Amino-1,2,4-triazole



1-Amino-1,2,3-triazole

The 4-amino-1,2,4-triazole is the more commonly synthesized compound. However, the oxidizing anion salts of 3-alkyl-substituted 1-amino-1,2,3-triazoles have also been investigated [362]. The melting points of several 4-amino-1,2,4-triazolium salts are summarized in Table 18. 1,2,3-Triazole derivatives generally have higher melting points and glass transition temperatures than the corresponding 1,2,4-triazole isomers. Properties of amino-1,2,4-triazolium salts are summarized in Table 24.

**Table 24:** Properties of aminotriazolium salts.

| Compound                                              | $T_{\text{melt}}(T_{\text{glass}})$ |     | $T_{\text{dec}}$ |     | Density, meas.    | Density, calc. from XRD |
|-------------------------------------------------------|-------------------------------------|-----|------------------|-----|-------------------|-------------------------|
|                                                       | K                                   | °C  | K                | °C  | g/cm <sup>3</sup> | g/cm <sup>3</sup>       |
| 4-Amino-1,2,4-triazolium nitrate                      | 342                                 | 69  | 453              | 180 | 1.6               | 1.58                    |
| 4-Amino-1,2,4-triazolium perchlorate                  | 357                                 | 84  | 483              | 210 | 1.81              | 1.78                    |
| 4-Amino-1,2,4-triazolium dinitramide                  | 293                                 | 20  | 419              | 146 | —                 | 1.66                    |
| 1-Amino-1,2,4-triazolium nitrate                      | 394                                 | 121 | 422              | 149 | 1.69              | 1.75                    |
| 1-Amino-1,2,4-triazolium perchlorate                  | 364                                 | 91  | 508              | 235 | 1.8               | 1.92                    |
| <i>N</i> -Methyl-1-amino-1,2,4-triazolium nitrate     | 335                                 | 62  | 490              | 217 | 1.51              | 1.6                     |
| <i>N</i> -Methyl-1-amino-1,2,4-triazolium perchlorate | 364                                 | 91  | 508              | 235 | 1.66              | 1.77                    |
| 1-Methyl-4-amino-1,2,4-triazolium nitrate             | 333                                 | 60  | 494              | 221 | 1.55              | 1.6                     |
| 1-Methyl-4-amino-1,2,4-triazolium perchlorate         | 359                                 | 86  | 532              | 259 | 1.8               | 1.92                    |
| 1,5-Diamino-1,2,4-triazolium nitrate                  | 432                                 | 159 | 422              | 149 | 1.65              | 1.76                    |
| 1,5-Diamino-1,2,4-triazolium perchlorate              | 411                                 | 138 | —                | —   | 1.83              | 1.93                    |

Data source: [309].

The initiation of the decomposition of several EILs, including 4-amino-1,2,4-triazolium nitrate, was studied using confined rapid thermolysis (CRT). Rapid-scan FTIR spectroscopy and TOF mass spectrometry were utilized to identify the products evolved from sub-milligram quantities that were subjected to heating rates of about 2000 K/s [394]. 4-amino-1,2,4-triazolium nitrate is a crystalline white solid under standard conditions. 4-amino-1,2,4-triazolium nitrate was found to undergo thermolysis through a proton transfer involving (primarily) the amino group to form HNO<sub>3</sub>. Subsequent reactions led to the formation of 1*H*-1,2,4-triazole. The highly energetic nitrate salt formed copious amounts of H<sub>2</sub>O and N<sub>2</sub>O through multiple secondary reaction channels.

The thermal decomposition of two EILs, formed by pairing the 4-amino-1,2,4-triazolium cation with chloride (4ATCl), and nitrate (4ATN) anions, was studied by CRT [395]. A combination of rapid-scan FTIR spectroscopy and TOF mass spectrometry was used to identify the products of decomposition at heating rates of 2000 K/s and temperatures of up to 340 °C in an ambient inert gas at 1 atm. Whereas a proton transfer

from the N1 position primarily initiated decomposition in 4ATCl, the amino group was found to primarily participate in the initiation reaction in the case of 4ATN. The parent molecule, 1*H*-1,2,4-triazole, was detected during subsequent reactions. Ring fracture was also evident from the presence of HCN. The highly energetic nitrate salt formed copious amounts of H<sub>2</sub>O and N<sub>2</sub>O through multiple secondary reaction channels.

The behavior of an ionic liquid, 1*H*-4-amino-1,2,4-triazolium nitrate, during thermal decomposition driven by an IR laser (10.6  $\mu\text{m}$ ) with a laser heat flux of 100 W/cm<sup>2</sup> in helium at 1 atm was examined in comparison to three other materials: 4-amino-1,2,4-triazolium hydrochloride, 4-amino-1,2,4-triazole, and 1*H*-1,2,4-triazole [396]. The focus was to understand the initial decomposition reaction steps and subsequent reactions that lead to ring decomposition and, eventually, to ignition. A triple quadrupole mass spectrometer with molecular beam sampling was used to obtain gaseous decomposition products of the sample. The results showed that the most probable route to initiate the decomposition of the 1*H*-4-amino-1,2,4-triazolium nitrate is through proton transfer from an N1 site to the nitrate, thus forming a neutral pair of nitric acid and amino-triazole. Subsequent reactions involve the decomposition of the neutral pair and their interactions.

Energetic nitroformate salts that contain high-nitrogen cations were synthesized and characterized by elemental, spectral, and thermal analyses [397]. Single-crystal XRD of 4-amino-1,2,4-triazolium nitroformate revealed that it is a co-crystal of a neutral 4-amino-1,2,4-triazole molecule with the 4-amino-1,2,4-triazolium nitroformate ion pair. The presence of the neutral molecule appears to lend stability to the salt. The structure of 3,6-diguanidino-1,2,4,5-tetrazinium nitroformate was confirmed by single-crystal XRD. Theoretical performance calculations indicated that these materials have properties that compare favorably with hydrazinium nitroformate, TNT, and tetryl, suggesting potential applications as eco-friendly oxidizers.

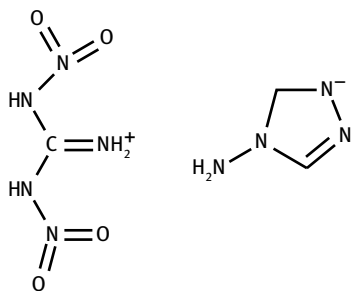
The rates of decomposition of 4-amino-1,2,4-triazolium nitrate (4ATN) were measured by CRT. Arrhenius-type reaction rate parameters for the initiation reactions governing the thermal decomposition were determined by numerical techniques [398]. The reaction rate parameters were obtained by an algorithm that compared the difference between the experimental and simulated species evolution profiles from the decomposition process. The decomposition process was simulated by applying conservation and equilibrium equations to the condensed and gas phases individually. The processes governing the decomposition of these energetic compounds were found to be autocatalytic in nature. The autocatalytic agents were the strong acids generated by the initial decomposition step. The activation energy  $E_{\text{act}}$  and pre-exponential factor  $A$  for the unimolecular decomposition step for 4ATN was 167 kJ/mol and 10<sup>16</sup> s<sup>-1</sup>, respectively. This is similar to previously determined values for AN.

An ionic compound (3-ATz)<sup>+</sup> (NTO)<sup>-</sup> was synthesized by the reaction of 3-amino-1,2,4-triazole (3-ATz) with 3-nitro-1,2,4-triazol-5-one (NTO) in ethanol [399]. Single crystals suitable for XRD were obtained by crystallization at room temperature. The crystal is monoclinic, space group  $P2_1/c$  with crystal parameters of  $a = 0.6519(2)$  nm,

$b = 1.9075(7)$  nm,  $c = 0.6766(2)$  nm, and  $\beta = 94.236(4)^\circ$ . The self-accelerating thermal decomposition temperature was 505 K and the critical temperature of thermal explosion was 525 K.

3-Amino-1,2,4-triazolium dinitramide was synthesized through the combination of 3-amino-1,2,4-triazole cation and oxygen-rich dinitramide anion. Its structure was confirmed by single-crystal XRD, elemental analysis, FTIR, UV-Vis spectrometry, and NMR [400]. The thermal stability was studied using DSC, TGA, and TGA tandem IR. Results indicated that this salt was thermally stable up to 439 K. The activation energy of the decomposition reaction was  $E_a = 281.9$  kJ/mol. The structure of a salt prepared via a neutralization reaction using 4-amino-1,2,4-triazol and dinitroguanidine as raw materials was characterized by IR and thermodynamic parameters (specific heat capacity, enthalpy, and entropy of formation). The relation between these parameters and the temperature of the energetic ionic salt was calculated using a DFT method [401]. The theoretical density, enthalpy of formation, detonation velocity, and detonation pressure of the ionic salt were estimated using a Monte-Carlo method, Born-Haber cycle, and K-J formulae, respectively. The results showed that the theoretical density, enthalpy of formation, detonation velocity, and detonation pressure of the ionic salt were  $1.72$  g/cm<sup>3</sup>,  $+313.92$  kJ/mol,  $8.15$  km/s, and  $28.53$  GPa, respectively.

The critical temperature of the thermal explosion of the dinitroguanidinium 4-amino-1,2,4-triazolate salt is  $459$  K =  $186^\circ\text{C}$  [402]. The entropy of activation, enthalpy of activation, and free energy of activation of the decomposition reaction are  $\Delta S = 60.22$  J mol<sup>-1</sup> K<sup>-1</sup>,  $\Delta H = 143.24$  kJ/mol, and  $\Delta G = 116.34$  kJ/mol, respectively. The predicted detonation pressure is  $P_{\text{CJ}} = 29.78$  GPa and detonation velocity is  $V_{\text{det}} = 8.28$  km/s. The material was not very sensitive, with the impact sensitivity being  $h_{50} = 135$  cm.



Dinitroguanidinium 4-amino-1,2,4-triazolate

3-Azido-1,2,4-triazolium 5,5'-azotetrazolate is a very sensitive explosive [403]. This salt was characterized by NMR, IR, XRD, and DSC. The sensitivity to mechanical stimuli was also determined by small-scale sensitivity testing, small-scale shock reactivity testing, and small-scale internal blast testing.



### 8.12.8 Di-Substituted 1,2,4-Triazolium and 1,2,4-Triazolate Salts

In this heading, “di-substituted” refers to the sum of functional and alkyl groups.

#### Diamino-1,2,4-triazolium Salts

1,5-Diamino-1,2,4-triazolium nitrate and perchlorate are stable salts prepared directly from the amine and the acid in aqueous solutions [404]. Several energetic salts were synthesized via the quaternization of azido or nitro derivatives of imidazole, 1,2,4-triazole, and substituted derivatives of tetrazole with nitric or perchloric acid or with iodomethane followed by metathesis reaction with silver nitrate or silver perchlorate [328]. The structures of 1,4-dimethyl-3-azido-1,2,4-triazolium nitrate, 3-azido-1,2,4-triazolium nitrate, 1-methyl-4-amino-1,2,4-triazolium perchlorate, and 1,4-dimethyl-2-*H*-1,2,4-triazolium triiodide were confirmed by single-crystal XRD. Most of the salts exhibited good thermal stabilities and low melting points. By using constant volume combustion energies that were determined experimentally using an oxygen bomb calorimeter, the standard molar enthalpies of formation were derived based on designed Hess thermochemical cycles.

EILs based on anionic lanthanide nitrate complexes  $\text{Cat}^{+3}[\text{Ln}(\text{NO}_3)_6]^{3-}$ , where  $\text{Cat}^+$  is guanidinium, 4-aminotriazolium, 4-amino-1-methyltriazolium, 4-amino-1-ethyltriazolium, 4-amino-1-butyltriazolium, 1,5-diaminotetrazolium, and 1,5-diamino-4-methyltetrazolium were prepared and characterized [405]. The hexanitratolanthanate (-cerate) salts with the last two cations, which are the first CO-balanced EILs that are stable to hydrolysis and air, have impact sensitivities of about 27 J. These ionic liquids were obtained by an environmentally friendly and simple method using nitrate-containing precursors. All salts were fully characterized by IR and NMR spectroscopy, elemental analysis, and through the determination of thermal stability, phase behavior, density, and water content. Theoretical thermodynamic equilibrium calculations showed that these new compounds have potential as rocket propellants.

1,5-Diamino-1,2,4-triazolium nitrate and perchlorate and 3,5-diamino-1,2,4-triazolium nitrate and perchlorate are isomers with very similar properties. 3,5-Diamino-1,2,4-triazole was protonated with diluted hydrochloric acid and nitric acid as well as perchloric acid, forming 3,5-diamino-1,2,4-triazolium chloride hemihydrate, 3,5-diamino-1,2,4-triazolium nitrate, and 3,5-diamino-1,2,4-triazolium perchlorate, respectively [406]. As a second reaction step 3,5-diamino-1,2,4-triazolium perchlorate can be made to react with potassium dinitramide, forming 3,5-diamino-1,2,4-triazolium dinitramide and low solubility potassium perchlorate. These compounds were characterized by low-temperature single-crystal XRD, IR, and Raman spectroscopy, as well as multi-nuclear NMR spectroscopy, mass spectrometry, and DSC. The HOFs were calculated by the CBS-4M method, as summarized in Table 25.

**Table 25:** Properties of 3,5-diamino-1,2,4-triazolium salts.

| Compound                                          | Enthalpy of formation, kJ/mol |
|---------------------------------------------------|-------------------------------|
| 3,5-Diamino-1,2,4-triazole                        | +81.1                         |
| 3,5-Diamino-1,2,4-triazolium chloride hemihydrate | +124.7                        |
| 3,5-Diamino-1,2,4-triazolium nitrate              | −76.1                         |
| 3,5-Diamino-1,2,4-triazolium perchlorate          | −25.2                         |
| 3,5-Diamino-1,2,4-triazolium dinitramide          | +138.7                        |

Data source: [406].

With these values and the X-ray densities too, several detonation parameters were calculated using the computer codes EXPLO5.03 and EXPLO5.04. In addition to this, the sensitivities of all compounds were determined by a BAM drop-hammer and a friction tester, as well as a small-scale ESD sensitivity test device.

Energetic salts of 3,4-diamino-triazole such as nitrate and picrate were characterized by FTIR, elemental analysis, DSC, and XRD [407]. Predicted detonation properties were 21.5–32.8 GPa and 7017–8620 m/s, which were much higher than those of TNT.

Several energetic mono- and dicationic 3,4-diaminotriazolium salts were prepared by combining stoichiometric amounts (1:1 or 2:1 molar ratio) of 3,4-diaminotriazole with various oxygen-containing tetrazolates and the structures were confirmed by single-crystal XRD [408]. All structures are dominated by a strong hydrogen-bond network owing to both the amino groups and the oxygen in the molecule. Most salts exhibited excellent thermal stabilities, with decomposition temperatures above 473 K (200 °C) and predicted detonation pressures (20.3–33.9 GPa) and velocities (7095–8642 m/s) above those of conventional explosives.

#### 4-Amino-1-methyl-1,2,4-triazolium Salts

The synthesis methods and some properties of 4-amino-1-methyl-1,2,4-triazolium nitrate (AMTN) were described in [266, 267, 409]. AMTN has a glass transition point of 218 K (−55 °C) and shows good thermal stability. The synthesis of 4-amino-1-methyl-1,2,4-triazolium nitrate via alkylation of 4-amino-1,2,4-triazole with iodomethane and subsequent anion metathesis with silver nitrate lead to an ionic liquid that had a glass transition point of 218 K (−55 °C) and showed low sensitivity against impact (15 Nm) and friction (160 N). Burning tests performed on 4-amino-1-methyl-1,2,4-triazolium nitrate have led to a flame temperature of 2200 K [409]. Combustion experiments of 4-amino-1-methyl-1,2,4-triazolium nitrate and one equimolar liquid mixture of 4-amino-1-methyl-1,2,4-triazole and 4-amino-1-methyl-1,2,4-triazolium nitrate were performed in a pressurized window bomb at room temperature and pressure up to 13 MPa. The samples all showed low-pressure dependence and even slightly decreasing burn rates at higher pressures.

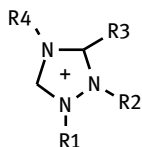
The synthesis of EILs on the base of 4-amino-1,2,4-triazole with nitrate as an anion where the substituents at N1 were methyl, cyanomethyl, and cyanoethyl, resulted in 4-amino-1-methyl-1,2,4-triazolium nitrate, 4-amino-1-(cyanomethyl)-1,2,4-triazolium nitrate and 4-amino-1-(cyanoethyl)-1,2,4-triazolium nitrate. 4-Amino-1-methyl-1,2,4-triazolium nitrate is a room temperature EIL but 4-amino-1-(cyanomethyl)-1,2,4-triazolium nitrate and 4-amino-1-(cyanoethyl)-1,2,4-triazolium nitrate are solids at room temperature [410].

Values for the published enthalpy of formation of AMTN vary substantially. However, none of the three different values can be viewed as reliable until the numbers have been confirmed experimentally:  $-187$  kJ/mol [404],  $+58$  kJ/mol [202], and a theoretical value of  $-27.6$  kJ/mol [167].

4-Amino-1,2,4-triazolium perchlorate (4-ATP), 1-methyl-4-amino-1,2,4-triazolium perchlorate (MATP), and 1-amino-3-methyl-1,2,3-triazolium nitrate (1-AMTN) were evaluated as candidates to replace TNT [411].

### Other Di-Substituted 1,2,4-Triazolium Salts

Heterocyclic rings (containing amino, nitro, or azido substituents) were paired with nitrate, perchlorate, dinitramidate, or picrate anions to form highly energetic salts, which may be more environmentally acceptable as propellants and explosives (perchlorate excepted) [202]. Additionally, high-energy salts in which both the cation and anion are high-nitrogen species, e.g., azolium, substituted azolium, guanidinium, bridged imidazolium, triazolium, and urotropinium cations, etc. coupled with azolates, substituted azolates, azotetrazolate, bis(5,5'-tetrazolates), and iminobis(5-tetrazolate) were synthesized. All have been thoroughly characterized via NMR and mass spectral analyses, melting point, thermal stability, density, and elemental analyses. Computational chemistry methods gave theoretical HOFs and detonation pressure/velocity and specific impulse. In addition to this, an accurate empirical method for the estimation of crystal densities of energetic compounds was developed. Substituted imidazolium, triazolium, and tetrazolium cations were combined with nitrodicyanomethanide and dinitrocyanomethanide anions to produce a new class of ionic liquids. 1,2,4-Triazolium cations with  $-\text{CH}_3$ ,  $-\text{NH}_2$ , or  $-\text{N}_3$  substituents on the rings were combined with 4,5-dinitroimidazolate or 5-nitrotetrazolate anions to form a wide array of salts and a few ionic liquids. Table 26 is a summary of the properties of these energetic compounds.



Amino- and/or methyl-substituted imidazolium, triazolium, and tetrazolium cations were combined with nitrodicyanomethanide and dinitrocyanomethanide anions to

**Table 26:** Properties of 1,2,4-triazolium 4,5-dinitroimidazoles or 5-nitrotetrazolates.

| R1                            | R2              | R3              | R4              | X <sup>-</sup>    | <i>T<sub>m</sub></i> ( <i>T<sub>g</sub></i> )<br>K | <i>T<sub>m</sub></i> ( <i>T<sub>g</sub></i> )<br>°C | <i>T<sub>dec</sub></i><br>K | <i>T<sub>dec</sub></i><br>°C | $\rho$<br>g/cm <sup>3</sup> | $\Delta H_f$<br>kJ/mol | $\Delta H_f$<br>kcal/mol |
|-------------------------------|-----------------|-----------------|-----------------|-------------------|----------------------------------------------------|-----------------------------------------------------|-----------------------------|------------------------------|-----------------------------|------------------------|--------------------------|
| —                             | —               | —               | —               | Nlmi <sup>a</sup> | 400                                                | 127                                                 | 400                         | 127                          | 1.64                        | +499.5                 | +119.4                   |
| H                             | —               | H               | H               | Nlmi              | 429                                                | 156                                                 | 438                         | 165                          | 1.73                        | +238.3                 | +57.0                    |
| CH <sub>3</sub>               | —               | H               | H               | Nlmi              | 375                                                | 102                                                 | 423                         | 150                          | 1.66                        | +206.8                 | +49.4                    |
| H                             | —               | N <sub>3</sub>  | H               | Nlmi              | 365                                                | 92                                                  | 431                         | 158                          | 1.7                         | +599.7                 | +143.3                   |
| CH <sub>3</sub>               | —               | N <sub>3</sub>  | H               | Nlmi              | 353                                                | 80                                                  | 418                         | 145                          | 1.6                         | +566.7                 | +135.4                   |
| H                             | —               | H               | NH <sub>2</sub> | Nlmi              | 410                                                | 137                                                 | 422                         | 149                          | 1.65                        | +354.9                 | +84.8                    |
| —                             | NH <sub>2</sub> | NH <sub>2</sub> | H               | Nlmi              | 426                                                | 153                                                 | 438                         | 165                          | 1.64                        | +294.9                 | +70.5                    |
| H                             | —               | H               | NH <sub>2</sub> | NTr <sup>b</sup>  | 337                                                | 64                                                  | 471                         | 198                          | 1.5                         | +839.9                 | +200.7                   |
| —                             | —               | —               | —               | NTet <sup>c</sup> | 385                                                | 112                                                 | 410                         | 137                          | 1.51                        | +697.9                 | +166.8                   |
| H                             | —               | H               | H               | NTet              | 410                                                | 137                                                 | 456                         | 183                          | 1.53                        | +436.3                 | +104.3                   |
| CH <sub>3</sub>               | —               | H               | H               | NTet              | 335                                                | 62                                                  | 436                         | 163                          | 1.52                        | +402.7                 | +96.2                    |
| H                             | —               | N <sub>3</sub>  | H               | NTet              | (238)                                              | (−35)                                               | 434                         | 161                          | 1.53                        | +800.9                 | +191.4                   |
| CH <sub>3</sub>               | —               | N <sub>3</sub>  | H               | NTet              | (235)                                              | (−38)                                               | 414                         | 141                          | 1.45                        | +768.5                 | +183.7                   |
| C <sub>3</sub> H <sub>7</sub> | —               | N <sub>3</sub>  | H               | NTet              | (228)                                              | (−45)                                               | 426                         | 153                          | 1.4                         | +719.4                 | +171.9                   |
| H                             | —               | H               | NH <sub>2</sub> | NTet              | 375                                                | 102                                                 | 375                         | 102                          | 1.58                        | +545.2                 | +130.3                   |

<sup>a</sup> Nlmi = 4,5-dinitroimidazolate.<sup>b</sup> NTr = 3-Nitro-1,2,4-triazolate.<sup>c</sup> NTet = 5-nitrotetrazolate.

Data source: [202]

produce a new class of ionic liquids [202, 412, 413]. Phase transition temperatures (mid-points of glass transition and/or melting points) were determined by DSC and compared to data for the corresponding, well-known nitrate salts (Table 27). That table also contains measured and calculated density and enthalpies of formation. The nitrodiacyanomethanide anion has a positive calculated HOF (32.2 kJ/mol), which is higher than that of dinitrocyanomethanide (−127.7 kJ/mol) and much higher than that of nitrate (−307.9 kJ/mol). With a constant anion, the effect of cation on density is in the order of 1,5-diamino-4-methyltetrazolium > 1,4-dimethyl-5-aminotetrazolium > 1,4,5-trimethyltetrazolium > 1,4-dimethyltriazolium > 1,3-dimethylimidazolium. The melting points of dinitrocyanomethanide salts were higher than those of nitrodiacyanomethanide analogues (see also [414]).

AMTN is an EIL, fitting the practical demands with a glass transition point of 218 K (−55 °C) and with good thermal stability of above 473 K (200 °C). Because of the asymmetrical triazolium cation and the symmetrical nitrate anion, efficient crystal packing is inhibited. The physical properties of four substituted triazolium salts are summarized in Table 28.

The combustion behavior of these EILs was investigated in a windowed bomb under pressures up to 15 MPa. This resulted in a linear burning characteristic with low-pressure dependence. Samples were transferred into glass test tubes (Ø 8 mm) and burnt by a method similar to the one used for solid propellant strands in a windowed

**Table 27:** Properties of nitrodicyanomethanide and dinitrocyanoamethanide salts.

| Compound                                                 | $T_{\text{melt}}$ |                 | $T_{\text{dec}}$ |     | $\rho_{\text{meas}}$ | $\rho_{\text{calc}}$ | $\Delta H_{\text{f lattice}}^{\text{f}}$ | $\Delta H_{\text{f}}$ |       |
|----------------------------------------------------------|-------------------|-----------------|------------------|-----|----------------------|----------------------|------------------------------------------|-----------------------|-------|
|                                                          | K                 | °C              | K                | °C  | g/cm <sup>3</sup>    | g/cm <sup>3</sup>    | kJ/mol                                   | kJ/mol                | kJ/g  |
| 1,5-Diamino-4-methyl-tetrazolium nitrodicyanomethanide   | 345               | 72              | 449              | 176 | 1.48                 | 1.52                 | +479.9                                   | +550.3                | +2.44 |
| 1,4-Dimethyl-5-amino-tetrazolium nitrodicyanomethanide   | 367               | 94              | 533              | 260 | 1.41                 | 1.45                 | +474.5                                   | +443.2                | +1.98 |
| 1,4,5-Trimethyltetrazolium nitrodicyanomethanide         | 323               | 50              | 513              | 240 | 1.38                 | 1.39                 | +472.4                                   | +404.6                | +1.81 |
| 1-Methyl-4-amino-1,2,4-triazolium nitrodicyanomethanide  | 332 <sup>b</sup>  | 59 <sup>b</sup> | 511              | 238 | —                    | 1.46                 | +487.4                                   | +440.4                | +2.11 |
| 1,4-Dimethyl-1,2,4-triazolium nitrodicyanomethanide      | 334               | 61              | 510              | 237 | 1.39                 | 1.39                 | +481.8                                   | +307.3                | +1.48 |
| 1,3-Dimethylimidazolium nitrodicyanomethanide            | 336               | 63              | 600              | 327 | 1.31                 | 1.36                 | +475.1                                   | +209.2                | +1.01 |
| 1,5-Diamino-4-methyl-tetrazolium dinitrocyanoamethanide  | 389               | 116             | 455              | 182 | 1.64                 | 1.62                 | +482.1                                   | +388.2                | +1.58 |
| 1,4-Dimethyl-5-amino-tetrazolium dinitrocyanoamethanide  | <sup>a</sup>      | <sup>a</sup>    | 418              | 145 | 1.56                 | 1.55                 | +476.4                                   | +281.4                | +1.15 |
| 1,4,5-Trimethyltetrazolium dinitrocyanoamethanide        | 362               | 89              | 488              | 215 | 1.49                 | 1.48                 | +471.3                                   | +245.8                | +1.01 |
| 1-Methyl-4-amino-1,2,4-triazolium dinitrocyanoamethanide | 219               | −54             | 494              | 221 | —                    | 1.56                 | +484.2                                   | +283.7                | +1.36 |
| 1,4-Dimethyl-1,2,4-triazolium dinitrocyanoamethanide     | 362               | 89              | 479              | 206 | 1.49                 | 1.49                 | +479.1                                   | +150.1                | +0.66 |
| 1,3-Dimethylimidazolium dinitrocyanoamethanide           | 352               | 79              | 540              | 267 | 1.47                 | 1.45                 | +477.9                                   | +46.5                 | +0.2  |
| 1,4-Dimethyl-5-amino-tetrazolium nitrate                 | 451               | 178             | 479              | 206 | 1.51                 | 1.53                 | +514.2                                   | +63.4                 | +0.36 |
| 1,4,5-Trimethyltetrazolium nitrate                       | <sup>a</sup>      | <sup>a</sup>    | 472              | 199 | 1.38                 | 1.45                 | +503                                     | +33.9                 | +0.19 |
| 1,4-Dimethyl-1,2,4-triazolium nitrate                    | 336               | 63              | 470              | 197 | 1.38                 | 1.45                 | +515                                     | −66                   | −0.41 |
| 1,3-Dimethylimidazolium nitrate                          | 344               | 71              | 556              | 283 | 1.36                 | 1.4                  | +513.8                                   | −169.6                | −1.07 |

<sup>a</sup> Decomposes before melting<sup>b</sup> Glass transition temperature

Data source: [202].

bomb under nitrogen at pressures up to 15 MPa at room temperature. Soon after ignition, using a melting wire, stable combustion developed with a distinct and intensively emitting reaction inside the condensed phase. Pure AMTN burned only at pressures above 13 MPa. The pressure dependence of AMTN and some of its mixtures with fuels was linear but very flat (low-pressure coefficient).

In addition to this, 4-amino-1-methyl-1,2,4-triazolium perchlorate (AMTP) was synthesized and characterized. With its melting point close to that of TNT, AMTP has potential as a melt cast explosive. For comparison, the 4-amino-1-*H*-1,2,4-triazolium

**Table 28:** Properties of triazolium derivative nitrates and perchlorates.

|                                          | Units             | AHTP              | AMTP              | AHTN              | AMTN     |
|------------------------------------------|-------------------|-------------------|-------------------|-------------------|----------|
| $T_g$                                    | °C                | —                 | —                 | —                 | −55      |
| $T_m$                                    | °C                | 83                | 84                | 67                | —        |
| $T_{dec}$ DSC                            | °C                | 291               | 290               | 229               | 259      |
| TGA                                      | °C                | 294               | 274               | 207               | 246      |
| Density at 298 K                         | g/cm <sup>3</sup> | 1.85 <sup>b</sup> | 1.64 <sup>b</sup> | 1.63 <sup>b</sup> | 1.44     |
| Nitrogen content                         | mass-%            | 30.36             | 28.22             | 47.61             | 43.47    |
| Impact sensitivity                       | Nm                | 5                 | 7.5               | >60               | 15       |
| Friction sensitivity                     | N                 | 18                | 64                | >360              | 144      |
| Oxygen balance                           | %                 | −21.7             | −44.3             | −38.1             | −64.5    |
| Decomposition enthalpy, DSC <sup>a</sup> | J/g               | 6056              | 5602              | 2635              | 2628     |
| Standard enthalpy of formation           | kJ/mol            |                   | +72 ± 18          | +2 ± 7            | −23 ± 10 |

<sup>a</sup> Measured in gold-plated and pressure-sealed pans<sup>b</sup> Density of powdered material

Data source: [266,267]

salts were also synthesized (AHTP = 4-amino-1-*H*-1,2,4-triazolium perchlorate, AHTN = 4-amino-1-*H*-1,2,4-triazolium nitrate). AHTP is very sensitive to friction and impact and must be handled with extreme caution.

The thermal decomposition of the EILs 1-methyl-4-amino-1,2,4-triazolium iodide, 1-methyl-4-amino-1,2,4-triazolium nitrate, 1-amino-3-methyl-1,2,3-triazolium iodide, and 1-amino-3-methyl-1,2,3-triazolium nitrate was studied by CRT at rates of approximately 2000 K/s [415]. The products formed by decomposition were analyzed by rapid-scan FTIR spectroscopy and TOF mass spectrometry. Decomposition studies involving the nitrate salts were conducted at 593–613 K (320–340 °C). The amino group was found to be involved in the initiation reaction, forming copious quantities of ammonia from the iodide compounds and N<sub>2</sub>O and H<sub>2</sub>O from the nitrate compounds. The extent of decomposition of the triazole ring was minimal at the considered temperatures. The melting points of 3-alkyl-1-amino-1,2,3-triazolium perchlorates with different length alkyl chains are summarized in Table 29.

The initial quaternization of 4-amino-1,2,4-triazole is often performed with an alkyl bromide, leading to the 1-alkyl-4-amino-1,2,4-triazolium bromide. Crystalline 1-ethyl-4-amino-1,2,4-triazolium bromide has extensive hydrogen bonding [376]. The bromides are only intermediates awaiting substitution of the bromide with more energetic oxidizing anions. The metathetical reaction, which exchanges the anions, is often done with the silver salts of the oxidizing anion, e.g., silver nitrate or silver perchlorate. This causes less soluble silver bromide to precipitate. The properties of 1-alkyl-4-amino-1,2,4-triazolium nitrates with different length alkyl chains are summarized in Table 30. Data is available for long alkyl chains up to C<sub>10</sub> but are not included here [377]. The melting point goes through a minimum at C<sub>4</sub>.

**Table 29:** Properties of 3-alkyl substituted 1-amino-1,2,3-triazolium perchlorates.

| Compound name,<br>alkyl = | Melting point |    |
|---------------------------|---------------|----|
|                           | K             | °C |
| Methyl                    | 359           | 86 |
| Ethyl                     | 303           | 30 |
| <i>n</i> -Propyl          | 306           | 33 |
| Allyl                     | 281           | 8  |
| <i>n</i> -Butyl           | 321           | 48 |

Data source: [362].

**Table 30:** Properties of 1-alkyl substituted 4-amino-1,2,4-triazolium nitrates.

| Compound name,<br>alkyl = | Melting point |     | Decomposition onset |                   | Density           |
|---------------------------|---------------|-----|---------------------|-------------------|-------------------|
|                           | K             | °C  | K                   | °C                | g/cm <sup>3</sup> |
| Methyl                    | 327           | 54  | 458                 | 185               | 1.57              |
| Ethyl                     | 278           | 5   | 458                 | 185               | 1.39              |
| <i>n</i> -Propyl          | 307           | 34  | 463                 | 190 (peak at 248) | 1.35              |
| <i>n</i> -Butyl           | 263           | −10 | 463                 | 190               | 1.31              |
| 1-(2-Ethanol)             | 283           | 10  | 453                 | 180               | 1.48              |
| Methylcyclopropyl         | 329           | 56  | 463                 | 190               | 1.36              |
| 1-(2-Propenyl)            | 283           | 10  | 438                 | 165               | 1.23              |

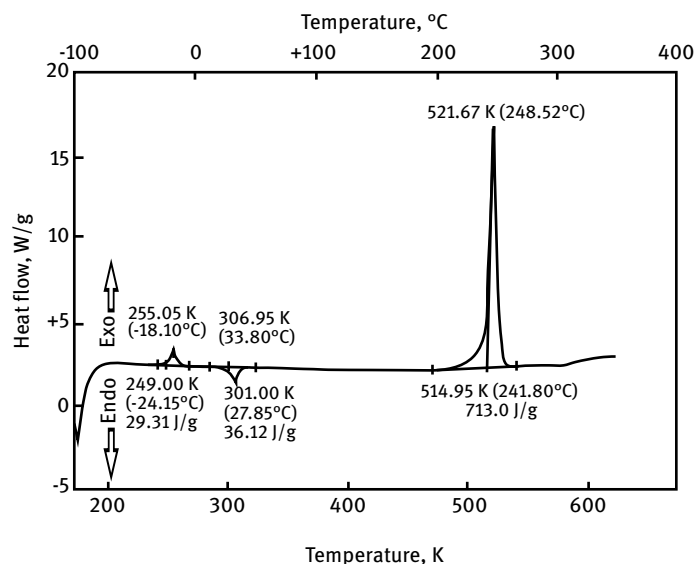
Data source: [359, 376, 377, 416].

A DSC thermogram of a typical ionic liquid (1-*n*-propyl-4-amino-1,2,4-triazolium nitrate) is shown in Figure 8 as an example. The event at 255 K (−18 °C) is a phase transition point.

The corresponding perchlorates are thermally more stable than the nitrates (see Table 31). Similar data are available for the triazolium nitrocyanamidate salts. The dinitramide salt is very friction sensitive and does not tend to crystallize but remains in the form of a yellow oil [359].

Ionic liquids based upon the halide and nitrate salts of 1-alkyl substituted-4-amino-1,2,4-triazolium cations (*n*-alkyl = methyl, decyl, isopropyl, allyl, and methylcyclopropyl) have been synthesized and characterized by vibrational spectra, multi-nuclear NMR, elemental analysis, and DSC [417]. Single-crystal XRD identified the crystal structures of 1-isopropyl-4-amino-1,2,4-triazolium nitrate, 1-methylcyclopropyl-4-amino-1,2,4-triazolium nitrate, and several halides. It also pointed out similarities, differences, and the effects of strong hydrogen bonding in all of the structures.

4-Amino-1-(cyanomethyl)-1,2,4-triazolium dinitramide was synthesized by quaternization of 4-amino-1,2,4-triazole with chloroacetonitrile and subsequent anion metathesis [418]. The product was characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FTIR,



**Figure 8:** DSC thermogram of 1-*n*-propyl-4-amino-1,2,4-triazolium nitrate. (Reproduced and modified from [377].)

**Table 31:** Properties of 1-alkyl substituted 4-amino-1,2,4-triazolium perchlorates.

| Compound name,<br>alkyl = | Melting point |     | Decomposition onset |     | Density (calc.)<br>g/cm <sup>3</sup> |
|---------------------------|---------------|-----|---------------------|-----|--------------------------------------|
|                           | K             | °C  | K                   | °C  |                                      |
| Methyl                    | 356           | 83  | 523                 | 250 | 1.62 (1.59 meas.)                    |
| Ethyl                     | 278           | 5   | 468                 | 195 | 1.54                                 |
| <i>n</i> -Propyl          | 273           | 0   | 463                 | 190 | 1.49                                 |
| <i>n</i> -Butyl           | 312           | 39  | 513                 | 240 | 1.44                                 |
| 1-(2-Ethanol)             | 283           | 10  | 448                 | 175 | 1.63                                 |
| Methylcyclopropyl         | 278           | 5   | 423                 | 150 | 1.49                                 |
| 1-(2-Propenyl)            | 262           | -11 | 458                 | 185 | 1.31                                 |

Data source: [359,376].

Raman spectra, DSC, TGA, density, and impact and friction sensitivity tests. The enthalpy of formation was calculated from the heat of combustion. With a m.p. of 343 K (+70 °C) and a glass transition point of 236 K (-37 °C), this dinitramide salt can be classified as an energetic ionic liquid.

4-Amino-1-methyl-1,2,4-triazolium dicyanamidate was used as an ionic liquid to suspend ball-milled nano-boron particles, creating fuel with a very high heat of combustion that is suitable for air-breathing engines [419]. The ionic liquid not only suspends the particles during ball-milling but also protects the freshly formed



surface from oxidation which would otherwise detract from the heat of combustion of the slurry. A typical slurry would contain 10 mass-% boron. It can also be used as a bipropellant fuel with NTO or RFNA as the oxidizer.

The structure of two different EILs and the nature of their binding to elemental boron surfaces were investigated by a combination of X-ray photoelectron spectroscopy (XPS), IR spectroscopy, zeta potential measurements, TGA, and calculations based on first-principles theory [420]. It was found that both 1-methyl-4-amino-1,2,4-triazolium dicyanamidate and 1-butyl-3-methylimidazolium dicyanamidate ionic liquids bind to boron well enough to resist removal by ultrasonic washing and to protect the boron surface from oxidation during air exposure of the washed powder. The data suggested that both the cation and the anion of the ionic liquids interact with the boron surface.

The structure of hydrazinium 3,5-dinitroamino-1,2,4-triazolate (HDNAT) was investigated with IR, MS,  $^{13}\text{C}$ -NMR, SEM, and XRD [421]. The X-ray crystal density of HDNAT was  $1.91\text{ g/cm}^3$ . The crystal belongs to a monoclinic system with the space group  $P2_1$ . The thermal decomposition of HDNAT was investigated by TG-DTA at a heating rate of  $10\text{ K/min}$  and by using DSC under non-isothermal conditions. The decomposition kinetic and thermodynamic parameters were obtained by the Kissinger and Ozawa method. HDNAT can be analyzed via HPLC with water/ acetonitrile/trifluoroacetic acid (97/3/0.1 by volume) as the mobile phase.

#### **Nitro-1,2,4-triazolate Salts and Azido-nitro-1,2,4-triazolate Salts**

5-Azido-3-nitro-1*H*-1,2,4-triazole can be prepared using commercially available raw chemicals in a three-step synthesis. From the free acid, several metal and nitrogen-rich salts with sodium, potassium, cesium, silver, lead, ammonium, guanidinium, and aminoguanidinium were prepared via simple acid-base reactions [422]. All compounds were characterized by IR, Raman, NMR, MS, and DSC. The sensitivities towards external stimuli (impact, friction, electrostatic discharge) were determined according to BAM standards. The metal salts are very sensitive and were tested as potential primary explosives.

#### **8.12.9 Di-Substituted 1,2,3-Triazole Salts**

The synthesis and structural characterization of ammonium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium 4,5-dicyano-1,2,3-triazolate salts provided information on a new group of high-nitrogen compounds [423]. The neutral parent compound 4,5-dicyano-2*H*-triazole was also prepared and spectroscopically characterized using  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR, IR, and Raman spectroscopy, as well as DSC and mass spectrometry. The impact and friction sensitivities of the salts were investigated using drop-hammer and friction apparatus methods. All compounds were found to be neither impact ( $>30\text{ J}$ ) nor friction sensitive ( $>360\text{ N}$ ). The crystal structures are summarized in Table 32.

Table 32: Crystal structures of 4,5-dicyano-2*H*-triazole and 4,5-dicyano-2*H*-triazolate salts.

| Compound name                                         | Crystal structure | Space Group                        | <i>a</i><br>Å | <i>b</i><br>Å | <i>c</i><br>Å | $\beta$<br>° | <i>V</i><br>Å <sup>3</sup> | <i>Z</i> |
|-------------------------------------------------------|-------------------|------------------------------------|---------------|---------------|---------------|--------------|----------------------------|----------|
| 4,5-Dicyano-2 <i>H</i> -triazole                      | monoclinic        | <i>P</i> 2 <sub>1</sub> / <i>c</i> | 6.0162(6)     | 11.2171(10)   | 7.5625(7)     | 94.214(8)    | 508.97(8)                  | 4        |
| Ammonium 4,5-dicyano-2 <i>H</i> -triazolate           | orthorhombic      | <i>Pnma</i>                        | 6.5646(13)    | 7.5707(16)    | 13.303(3)     |              | 661.1(2)                   | 4        |
| Guanidinium 4,5-dicyano-2 <i>H</i> -triazolate        | monoclinic        | <i>Cc</i>                          | 12.6000(11)   | 17.1138(15)   | 12.0952(9)    | 106.098(7)   | 2505.9(4)                  | 12       |
| Aminoguanidinium 4,5-dicyano-2 <i>H</i> -triazolate   | monoclinic        | <i>Pa</i>                          | 7.0921(9)     | 7.2893(9)     | 8.8671(11)    | 105.141(11)  | 442.48(10)                 | 2        |
| Diaminoguanidinium 4,5-dicyano-2 <i>H</i> -triazolate | monoclinic        | <i>P</i> 2 <sub>1</sub>            | 3.7727(4)     | 15.6832(17)   | 8.3416(10)    | 101.797(10)  | 483.13(9)                  | 2        |
| Triaminoguanidinium 4,5-dicyano-1,2,3-triazolate      | monoclinic        | <i>C</i> 2/ <i>c</i>               | 14.0789(14)   | 11.5790(11)   | 13.5840(14)   | 115.239(10)  | 2003.1(3)                  | 8        |

Data source: [423].

4,5-Dicyano-2*H*-1,2,3-triazole forms a 4,5-dicyano-2*H*-1,2,3-triazolate anion  $[\text{C}_4\text{N}_5]^-$  that can form salts with organic nitrogen-containing bases such as the ones listed in Table 31 or with metals [424].

### 8.12.10 Tri-Substituted 1,2,4-Triazolium and 1,2,4-Triazolate Salts

#### 3,4,5-Triamino-1,2,4-triazolium Salts

The parent amine of this group of salts, 3,4,5-triamino-1,2,4-triazole (“guanazine”) is relatively easily obtained by synthesis starting with hydrazine and dimethylcyanamide. It has a relatively high melting point of 527 K (254 °C) and has poor solubility in polar solvents. The enthalpy of formation of the parent amine was estimated to be +234.3 kJ/mol (+56 kcal/mol). The salts are well crystallized. The melting points of the nitrate, perchlorate, and dinitramide salts have already been detailed in Table 18.

Reactions of 3,4,5-triamino-1,2,4-triazole (guanazine) with strong acids ( $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{HN}(\text{NO}_2)_2$ ) resulted in a family of highly stable salts [425, 426]. All of the salts were characterized using spectroscopic as well as single-crystal XRD techniques. The X-ray structures were compared to those obtained from theoretical calculations. Initial safety testing (impact, friction) was also carried out on all of the new materials. Properties of 3,4,5-triamino-1,2,4-triazolium salts are listed in Table 33.

3,4,5-Triamino-1,2,4-triazolium 5-nitrotetrazolate can be synthesized in high yield from 3,4,5-triamino-1,2,4-triazole (guanazine) and ammonium 5-nitrotetrazolate [427]. The compound was characterized by vibrational (IR and Raman) and multi-nuclear NMR spectroscopy, elemental analysis, and single-crystal XRD. The crystal structure was triclinic, space group  $P\bar{1}$ ,  $a = 0.7194(5)$  nm,  $b = 0.8215(5)$  nm,  $c = 0.8668(5)$  nm,  $\alpha = 75.307(5)^\circ$ ,  $\beta = 70.054(5)^\circ$ ,  $\gamma = 68.104(5)^\circ$ ,  $V = 0.4421(5)$  nm<sup>3</sup>,  $Z = 2$ ,  $\rho = 1.722$  g/cm<sup>3</sup>. The <sup>15</sup>N NMR spectrum and X-ray crystal structure of 3,4,5-triamino-1,2,4-triazole (guanazine) was triclinic, space group  $P\bar{1}$ ,  $a = 0.5578(5)$  nm,  $b = 0.6166(5)$  nm,  $c = 0.7395(5)$  nm,  $\alpha = 114.485(5)^\circ$ ,  $\beta = 90.810(5)^\circ$ ,  $\gamma = 97.846(5)^\circ$ ,  $V = 0.2286(3)$  nm<sup>3</sup>,  $Z = 2$ , and  $\rho = 1.658$  g/cm<sup>3</sup>.

A series of new energetic salts based on the polyamino-1-guanyl-1,2,4-triazolium cation with three to five amino groups and the dinitramide anion were synthesized [428]. These new nitrogen-rich salts tended to have extensive hydrogen bonding and exhibited high densities and good thermal stabilities. Their properties were modified by varying the guanyl substituents and/or the amino substituents on the triazole ring. Based on theoretical calculations, 3,5-diamino-1-guanyl-1,2,4-triazole dinitramide, (density 1.78 g/mL, onset of exotherm 470 K = 197 °C, det. vel. 8775 m/s) had a higher detonation pressure and higher velocity values than other dinitramide energetic materials such as ADN or *N*-guanylurea-dinitramide (FOX-12). The structures of 3-amino-1-guanyl-1,2,4-triazole dinitramide, 3,5-diamino-1-guanyl-1,2,4-triazole dinitramide, 5-amino-*N*-amidino-1-guanyl-1,2,4-triazole dinitramide, and

Table 33: Properties of 3,4,5-triamino-1,2,4-triazolium salts.

| Compound name                               | Gross formula                                                                      | Molecular mass<br>g/mol | Melting point <sup>a</sup> |     | Decomposition temperature, onset | Crystal structure | Space group          | Unit cell parameters |                  |
|---------------------------------------------|------------------------------------------------------------------------------------|-------------------------|----------------------------|-----|----------------------------------|-------------------|----------------------|----------------------|------------------|
|                                             |                                                                                    |                         | K                          | °C  |                                  |                   |                      | a, b, c, nm          | α, β, γ, °       |
| 3,4,5-Triamino-1,2,4-triazolium nitrate     | [C <sub>3</sub> H <sub>7</sub> N <sub>6</sub> ][NO <sub>3</sub> ]                  | 177.15                  | 479                        | 206 | 245                              | Triclinic         | P1                   | 0.5523(2),           | 111.108(6),      |
|                                             |                                                                                    |                         |                            |     |                                  |                   |                      | 0.8260(3),           | 103.291(6),      |
| 3,4,5-Triamino-1,2,4-triazolium perchlorate | [C <sub>2</sub> H <sub>7</sub> N <sub>6</sub> ][ClO <sub>4</sub> ]                 | 214.59                  | 467                        | 194 | 275                              | Tetragonal        | I4 <sub>1</sub> /acd | 0.8508(3)            | 103.454(6)       |
|                                             |                                                                                    |                         |                            |     |                                  |                   |                      | 1.22899(18),         | 90, 90, 90       |
| 3,4,5-Triamino-1,2,4-triazolium dinitramide | [C <sub>2</sub> H <sub>7</sub> N <sub>6</sub> ][N(NO <sub>2</sub> ) <sub>2</sub> ] | 221.17                  | 418                        | 145 | 147                              | Monoclinic        | P2 <sub>1</sub> /c   | 1.22899(18),         | 90, 90, 90       |
|                                             |                                                                                    |                         |                            |     |                                  |                   |                      | 4.0875(6)            | 90, 90.6060(10), |
|                                             |                                                                                    |                         |                            |     |                                  |                   |                      | 0.36438(3),          | 90               |
|                                             |                                                                                    |                         |                            |     |                                  |                   |                      | 1.81307(17),         | 90.6060(10),     |
|                                             |                                                                                    |                         |                            |     |                                  |                   |                      | 1.22872(11)          | 90               |

<sup>a</sup> Melting point by DSC  
Data source: [426].

3,5-diamino-*N*-amidino-1-guanyl-1,2,4-triazole dinitramide were investigated using single-crystal XRD.

Thermally stable energetic salts were synthesized from 3,4,5-triamino-1,2,4-triazole, including the picrate and azotetrazolate salts [429]. 3,4,5-Triamino-1,2,4-triazolium picrate and bis(3,4,5-triamino-1,2,4-triazolium) 5,5'-azotetrazolate were characterized analytically, spectroscopically, and by XRD. The standard enthalpy of formation from calculations was predicted to be  $\Delta H_f^\circ = -498.3 \text{ kJ/mol}$  for the picrate and  $\Delta H_f^\circ = +524.2 \text{ kJ/mol}$  for the azotetrazolate. Predicted detonation velocities were 7015 and 7683 m/s, respectively.

The dinitramide salt of 3,4,5-triamino-1,2,4-triazole can be prepared via the addition of concentrated HCl to 3,4,5-triamino-1,2,4-triazole in deionized water followed by the addition of hydrogen dinitramide and purification [430]. It can be dissolved in and recrystallized from *N*-methyl pyrrolidone. The heat of solution was determined in a calorimeter [431].

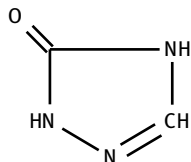
Highly dense nitrogen-rich ionic compounds are potential high-performance energetic materials for use in military and industrial venues. 3,4,5-triamino-1,2,4-triazolium (guanazinium) salts with promising energetic anions and a family of energetic salts based on nitrogen-rich cations and the 6-nitroamino-2,4-diazido-[1,3,5]triazinate anion (NADAT) were prepared and fully characterized by elemental analysis, IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR, and DSC [432]. The crystal structures of neutral NADAT and its biguanidinium salt were determined by single-crystal XRD. All the new salts exhibited desirable physical properties such as relatively high densities ( $1.63\text{--}1.78 \text{ g/cm}^3$ ) and moderate thermal stabilities ( $T_{\text{dec}} = 403\text{--}469 \text{ K} = 130\text{--}196^\circ\text{C}$ ) for 3,4,5-triamino-1,2,4-triazolium salts and ( $T_{\text{dec}} = 482\text{--}530 \text{ K} = 209\text{--}257^\circ\text{C}$ ) for 6-nitroamino-2,4-diazido[1,3,5]triazinate salts. Theoretical performance calculations gave detonation pressures and velocities in the range of 21.0–30.3 GPa and 7675–9048 m/s, respectively, which makes them competitive energetic materials.

#### 8.12.11 Tetra-Substituted 1,2,4-Triazolium Salts

Tetra-substitution, as in 1-alkyl-3-perfluoroalkyl-4,5-dimethyl-1,2,4-triazolium salts, was difficult to obtain [433]. Of the 19 triazolium salts synthesized and characterized, seven were liquids at 298 K (25°C). These were all nitrates and all had negative  $\Delta H_f^\circ$ 's [202]. Only four of the perchlorates had melting points of  $<373 \text{ K}$  ( $<100^\circ\text{C}$ ).

### 8.13 1,2,4-Triazol-5-one and Triazolone Derivatives

Triazolone, 1,4-dihydro-1,2,4-triazol-5-one,  $C_2H_3N_3O$ , CAS RN [930-33-6], differs from triazole in that the  $>CH_2$  group has been replaced by a keto  $>C=O$  group.



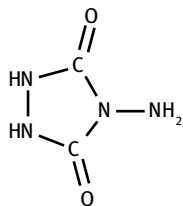
Triazolone-5

The parent molecule of several high-energy materials and unsubstituted triazolone-5 can be made from semicarbazide and formic acid or formic acid ester [434]. 1,2,4-triazol-5-one (TO) can be made by heating a mixture of hydrazodicarbonamide and formic acid to a reflux temperature, thus refluxing and removing unreacted formic acid [435]. TO serves as the starting product for NTO.

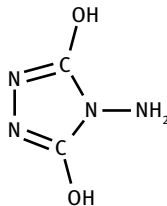
Triazolone-5 was investigated to better understand the thermal stability of some of its even more energetic derivatives. The structures of two isomers of 1,2,4-triazol-5-one (1,2,4-trihydro-1,2,4-triazol-5-one and 2,3,4-trihydro-1,2,4-triazol-5-one) were fully optimized by DFT computational methods [436]. The geometry, electron structure, net charges of atoms, and vibration spectroscopic properties were calculated. The stabilities of the two compounds were analyzed and 1,2,4-trihydro-1,2,4-triazol-5-one was found to be more stable than 2,3,4-trihydro-1,2,4-triazol-5-one, which was consistent with experimental results.

Hydroxylammonium 3-dinitromethanide-1,2,4-triazolone exhibits exceptional properties compared to its parent acid, 3-dinitromethyl-1,2,4-triazolone; namely higher density  $\rho = 1.91 \text{ g/cm}^3$  at 298 K, superior detonation performance ( $v_D = 8946 \text{ m/s}$ ), and improved thermal, impact, and friction stabilities [437]. The solid-state structure features of the new energetic salt were investigated by XRD. This revealed  $\pi$ -stacking and hydrogen-bonding interactions that contribute to closer packing and higher density.

1,2,4-Triazolidine-3,5-diones, urazoles, are five-membered heterocycles with three nitrogen atoms and two carbonyl groups. Urazine, 4-aminourazole, 4-amino-1,2,4-triazolidine-3,5-dione,  $C_2H_4N_4O_2$ , is an easily accessible heterocycle from low-cost starting materials. Aliphatic or aromatic substituents at position four and condensation with trinitromethane or trinitroethanol lead to new energetic materials [438]. Urazine exists in two tautomeric forms.



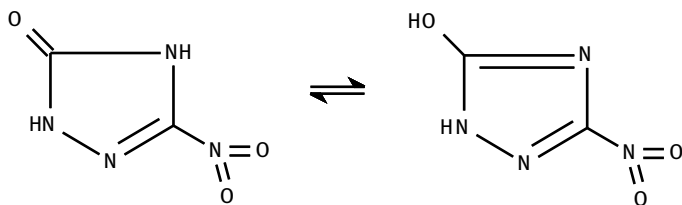
4-Amino-1,2,4-triazolidine-3,5-dione



4-Amino-1,2,4-triazole-3,5-diol

### 8.14 3-Nitro-1,2,4-triazole-5-one

A thoroughly investigated high-density energetic material derived from triazolone is 3-nitro-1,2,4-triazol-5-one, also known as 3-nitro-1,4-dihydro-1,2,4-triazol-5-one,  $C_2H_2N_4O_3$ , NTO, CAS RN [932-64-9], 5-oxo-3-nitro-1,2,4-triazole, 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one, 5-nitro-1,2,4-triazol-3-one; 3*H*-1,2,4-triazol-3-one, 1,2-dihydro-5-nitro-; or nitrotriazolone,  $M = 130.06$  g/mol. 3-Nitro-1,2,4-triazol-5-one exists in tautomeric structures and is a weak acid.



3-Nitro-1,2,4-triazol-5-one is a thermally stable, relatively insensitive explosive that has also been considered as an ingredient in solid propellants and gas generants. It forms salts with alkali metal hydroxides and strong organic bases. The current section summarizes only preparation and physical, chemical, and safety properties. Most of the work done on NTO during the past three decades has been for its application as an explosive. However, the information that is now available is also useful for its potential use as a solid propellant ingredient. This is one reason why this chapter on NTO is so detailed and contains a lot of new information gathered from the literature. NTO has high-energy release capability, high velocity of detonation, and good thermal stability and it is relatively insensitive to impact and spark discharge compared to RDX.

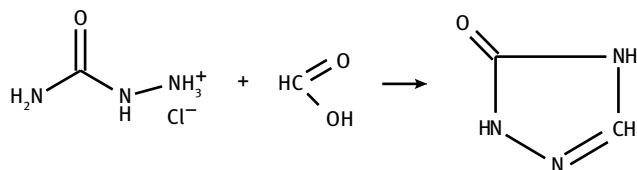
There are only a few chemicals like NTO that have lain dormant before being rediscovered for practical uses. NTO was discovered in 1905, at which time it was prepared by nitration of 1,2,4-triazol-5-one [439]. There was some renewed interest in NTO in the mid to late 1960s but none of these nor any of the subsequent chemical studies appear

to be directed to explosives. It was not until 1985 that Lee and Coburn published the first study on NTO as an explosive [440–442]. However, it was known that the French were secretly working on a new IHE as early as 1980, which was subsequently revealed in 1987 to be NTO [443–445]. In Europe, NTO is covered by the STANAG-4543 ED.1 specification.

#### 8.14.1 Preparation of NTO

NTO was first prepared by reaction of 1,2,4-triazol-5-one (TO) with fuming nitric acid [446]. Various types of nitrating agents have been used during the century which has passed since. All attempted to improve the yield, which may have eventually reached 83% if all had been done correctly. It is unusual that it would take this long to recognize the useful properties of a chemical.

The methods for the production of NTO differ mostly during the step used for the production of the precursor, TO. TO can be prepared by reaction of acetone semicarbazone with formic acid via diformylsemicarbazide (which undergoes a ring closure on heating), via semicarbazide hydrochloride with 85% formic acid



or triethylorthoformate, which gives TO in 64% yield [447]. Thermal decarboxylation of 1,2,4-triazole-5-one carboxylic acid gives TO in good yield.

3-Nitro-1,2,4-triazole-5-one (NTO) can be synthesized in a two-step process by reacting semicarbazide hydrochloride with formic acid to obtain 1,2,4-triazole-5-one and followed by nitration to NTO [448]. 3-Nitro-1,2,4-triazole-5-one (NTO) can be obtained by nitrating 1,2,4-triazole-3-one under different conditions [449]. The optimum conditions for nitration of TO were determined by varying the temperature (283–323 K = 10–50 °C), nitrating agent [HNO<sub>3</sub> with AcOH, Ac<sub>2</sub>O, (F<sub>3</sub>CCO)<sub>2</sub>O, NH<sub>4</sub>NO<sub>3</sub>; N<sub>2</sub>O<sub>4</sub> with CCl<sub>4</sub>, or ClCH<sub>2</sub>CH<sub>2</sub>Cl, N<sub>2</sub>O<sub>5</sub> with CCl<sub>4</sub> or ClCH<sub>2</sub>Cl]. The traditional method for making NTO is by nitrating 1,2,4-triazol-5-one in 70% nitric acid at a temperature of between 333 to 348 K (60 to 75 °C) [450]. The best NTO yield (81%) was achieved when diluting N<sub>2</sub>O<sub>4</sub> with CCl<sub>4</sub> [451]. The preparation of NTO can be simplified if it is done as a one-pot synthesis [452] (see also [453]).

The synthesis of 3-nitro-1,2,4-triazole-5-one was later scaled up to the 100-g batch size [454]. The operating conditions of NTO preparation were optimized by raising the reaction temperature in two stages and reducing the amount of nitrating agent. The dependence of reaction time and reaction temperature on NTO yield was determined.



The improvement of preparation technology has led to a high yield (81.8%) and excellent quality of NTO.

The synthesis of 5-nitro-1,2,4-triazol-3-one (NTO) from urea via chlorination followed by amination, formylation, and nitration was theoretically modeled, assuming the use of metal chlorides and metal oxides as catalysts to promote the reaction [455]. Reaction routes closely patterned after experimental processes were successfully reconstructed and the corresponding energy barriers were estimated for each elementary reaction. Reaction conditions different from those reported in the literature were used in fictitious reaction systems. The modeling results suggested that iron(III) chloride is a good catalyst for the chlorination reaction, iron(II) oxide is suitable for catalyzing amination, formylation, and nitration, and nitric acid is the better agent for nitration. Estimates of the comparable energy barriers for each reaction stage were considered to imply more feasible pathways for NTO synthesis that are yet to be explored.

Scaling up the production of NTO requires knowledge of the heat of reaction so that runaway reactions in the nitrator can be avoided and a proper amount of cooling is available. The heat of nitration and the heat of dissolution of 1,2,4-triazol-5-one (TO) in acidic environments were measured by differential reaction calorimetry [456]. The kinetics of nitration of TO in a 200-mL reactor were investigated by UV/Vis spectroscopy. Temperature changes were measured in a 10-L batch reactor during the TO nitration. A model of kinetics for the synthesis of NTO was proposed and it was used to simulate the phenomena occurring in the calorimeter and the reactors. The experimental data were compared with modeling results and with parameters of the Arrhenius equation for the synthesis of NTO with selected nitrating acid mixtures.

The heat release during nitration of 1,2,4-triazol-5-one (TO) in a nitric acid solution was determined using reaction calorimeters and the influence of the heats of reaction of individual steps on the total exothermic effect during the NTO manufacture process was examined [457]. Five types of thermal effects were differentiated and measured: the heat of dosing TO, the heat of dissolution of TO, the heat of reaction ( $\Delta H_r$ ), the heat of crystallization of NTO, and the heat caused by changes in concentration of nitric acid. The results showed that the  $\Delta H_r$  was the main contributor to the total exothermic heat release during synthesis processes in 66–96%  $\text{HNO}_3$ .

#### 8.14.1.1 Recrystallization of NTO

NTO was usually recrystallized from water or alcohols but this produced an undesirable crystal shape. Freshly prepared NTO is usually obtained in the form of jagged rod-like shape crystals. These readily agglomerate and become more sensitive to shock. As-prepared NTO has a crystal habit with length : diameter ratios in excess of 3 : 1. These irregular crystals had a low bulk density. Plastic-bonded explosives (PBX) blends incorporating the crystals were very viscous and difficult to pour. Several crystal modification methods were tested, including surfactants and stirring while crystallizing from aqueous solutions [458].

3-Nitro-1,2,4-triazol-5-one (NTO) is typically recrystallized in water but, unfortunately, NTO recrystallizes in jagged rod-like particles that have a tendency to agglomerate when using this method. The irregular and jagged crystal shapes produce highly variable results when mixing explosive formulations with NTO. It was discovered that NTO crystallizes from lower molecular weight alcohols (e.g., methanol, ethanol) in the form of spheroidal crystals rather than as jagged needles [459].

A study of the nucleation kinetics of spherulitic crystallization of NTO in *N*-methylpyrrolidone (NMP) and water and the influence of the solvent composition upon the metastable zone width and morphologic characteristics of the crystalline NTO showed that the metastable zone width of NTO solutions increased with the NMP content in the solvent [460]. The metastable zone width increased with increasing the cooling rate and with decreasing saturation temperature. Primary nucleation aided in the spherulitic crystallization of NTO. The induction period for nucleation was measured at different levels of supersaturation in various solvent compositions and was used to calculate interfacial energy. The interfacial energy obtained from nucleation experiments depended on the solvent composition and temperature.

Although the solubility of NTO in water at room temperature is less than 2%, solubility increases to ~10% in boiling water at 373 K. Notably, attempts have been made to recrystallize NTO from hot water. 3-Nitro-1,2,4-triazol-5-one has been recrystallized from water in an effort to prepare crystals with smaller size and narrower size distribution ranges in a batch cooling crystallizer [461–464]. Two mixing devices, i.e., a mechanically stirred system with and without ultrasound in aqueous media, were employed to compare mixing effects on the crystallization. Under ultrasound irradiation, the metastable zone width was significantly reduced by more than twofold, and the crystal size was shifted from 140–160  $\mu\text{m}$  to 50–70  $\mu\text{m}$ , with a narrower size distribution compared to the mechanically stirred system. However, in the mechanical stirrer, the mixing effect on NTO crystallization was negligible if the impeller speed was sufficient to suspend all crystals in the crystallizer. It was found that the crystal growth was not influenced by mixing. It was suggested that the NTO crystals were formed by primary heterogeneous nucleation that is common in a batch cooling system (see also [465, 466]).

NTO crystals were obtained from an NTO/H<sub>2</sub>O solution by a cooling method with ultrasound irradiation [467]. The morphology and the size distribution of NTO crystals were found to be very dependent on ultrasound frequency and sonication time. The shape of NTO crystals with a 47 kHz sonicator was cubic or tetragonal. On the other hand, the shape of NTO crystals with a 28 kHz sonicator appeared to be orthorhombic. The metastable zone width of the NTO/H<sub>2</sub>O system will decrease under ultrasound irradiation. The ultrasound effect on the metastable zone width became dominant dramatically when the cooling rate was smaller than 0.5 °C/min. In particular, at cooling rates smaller than 0.1 °C/min, the limit of the metastable zone widths with ultrasound was about 2 °C and was independent of the saturation temperature.

One of the methods to reduce the shock sensitivity of NTO is to recrystallize it and change the crystal morphology to assume a more spherical shape. More spherical (spherulitic) shapes could be obtained by cooling crystallization using a co-solvent. A very useful chapter on the crystallization of chemicals with special reference to NTO is contained in [468]. It includes nicely illustrated information on the best crystallization methods for NTO using different solvents and cooling rates.

Recrystallization of NTO in a co-solvent of water and *N*-methyl-2-pyrrolidone was performed to obtain 180  $\mu\text{m}$  spheroidal particles under conditions of rapid cooling and active stirring [469–471]. Scanning electron microscope (SEM) images showed that the spheroidal particles were rounded, dense, compact, and had no cavities. SEM images of the cross-section of particles showed that the particles were composed of needles with a diameter of several  $\mu\text{m}$  that were arranged radially outward from the center.

Very fine crystals of NTO can be obtained by recrystallizing from acetone [472]. Nano-NTO particles were prepared by a method of spray-freezing into liquid and SEM. Atomic force microscopy (AFM), XRD, TGA, and DSC analysis methods were used to characterize the particles [473]. The results showed that the NTO particles had an elongated shape with a size of 70–90 nm. With NTO particle size reduced to the nano-meter range, the XRD diffraction peaks broadened and the peak intensity weakened. Nano-NTO decomposed at a lower temperature and was less sensitive to impact stimuli compared with micro-NTO.

When using acetone as the solvent and by changing the distillation temperature, the initial concentration of the solution, and the vacuum system parameters, one can control the particle size distribution of NTO, which is separated out of the acetone solution by vacuum distillation of the solvent [474]. The experimental results showed that when the distillation temperature was at 333 K (60 °C), the vacuum in the system was 0.05–0.06 MPa. By employing vacuum distillation, one can get irregular and comparatively cubic crystal shapes, the particle size of which is around one  $\mu\text{m}$  and the size distribution range is narrow. The impact sensitivity of NTO decreased, seemingly through the process of being crystallized into ultra-fine size, while the detonation velocity increased. Another method is to operate with a solvent in the supercritical state and then precipitate the NTO crystals by suddenly injecting a non-solvent [475].

The volatile solvent re-crystallization of NTO on a glass substrate was studied to obtain the desired crystal shapes [476]. The observed phenomena confirmed that the crystal morphologies change from fractal to a cube-shaped structure due to the initial concentration increasing. This can be explained with diffusion-limited aggregation (DLA) theory. The fractal and cube-shaped structure NTO crystals were characterized by FTIR and XRD. The results showed that crystal morphology change cannot result in crystal structure transformation. It only affects its growth-oriented change. It would be difficult to predict the crystal morphology of NTO from theoretical information alone [477]. As this experience has shown, there are just too many variables.

Particles with spherical shape and specific size distribution are required for reproducible solids loading and mix fluidity during the processing of energetic mate-

rials for high explosive and rocket propellant applications. Spherical NTO of specific particle size distribution was prepared and the powders were characterized by XRD, thermal, and spectral methods [478]. The effects of spherical NTO of specific particle sizes of 150, 100, 25, 15, 10, and  $<5\mu\text{m}$  and their bi/trimodal mixtures on their micromeritic properties was measured. Based on the packability and flowability properties, bimodal mixtures with a coarse ( $150\mu\text{m}$ ) to fine ( $25\mu\text{m}$ ) ratio of 70 : 30 was found to be optimum for processing in explosive formulations. The study inferred that the spherical particle shape of NTO brings down the viscosity by about 75% for the same explosive content to binder ratio in comparison with non-spherical NTO.

### 8.14.2 Physical Properties of NTO

A very useful summary of the methods of preparation, recrystallization, and the physical properties of NTO is provided in an Australian military report [458]. It contains tables of properties and microscopic images of various crystal structures (see also [479]).

An excellent summary of all properties of NTO and many of its salts, supplemented by 85 references, was written by Singh and Felix [480]. The physical properties of NTO are summarized in Table 34.

One will note that the enthalpy of formation data is quite different. It is difficult to decide which is the most reliable data. One of the major disadvantages of NTO is its high vapor pressure and volatility. The equations for the vapor pressure of solid and liquid NTO are listed in Table 35.

NTO data on vapor pressure are shown together with thermocouple data in the high-temperature region. The Bourdon gauge data in the low-temperature region in

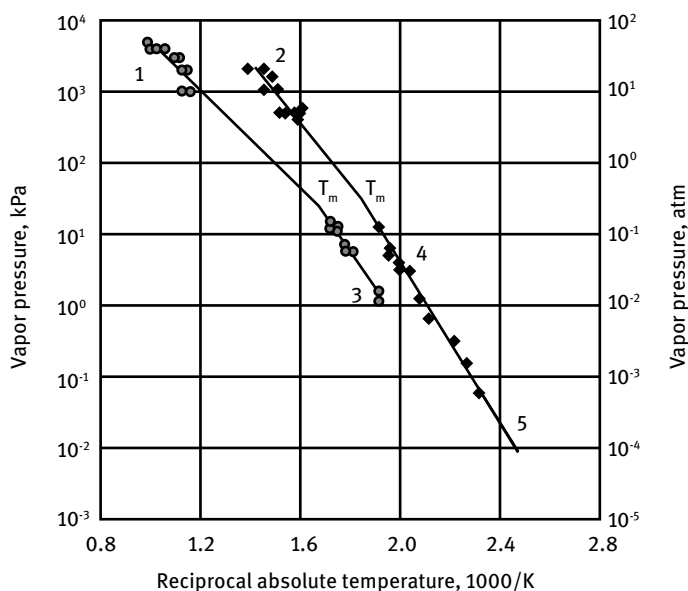
**Table 34:** Physical properties of NTO.

|                       | SI units               |              | Other units            |              | References |
|-----------------------|------------------------|--------------|------------------------|--------------|------------|
| Molecular mass        | 130.0623 g/mol         | —            | 7.6886 mol/kg          | —            | [14]       |
| Density at room temp. | 1930 kg/m <sup>3</sup> | —            | 1.93 g/cm <sup>3</sup> | —            | [440]      |
| Melting point         | 543 K (dec.)           | —            | 270 °C (dec.)          | —            |            |
| Enthalpy of formation | −79.29 kJ/mol          | −774.6 kJ/kg | −24.07 kcal/mol        | −185.1 cal/g | [62]       |
|                       | −100.7 kJ/mol          | —            | −14.300 kcal/mol       | —            | [440]      |
|                       | −129.4                 | —            | −30.93                 | —            | [481]      |
|                       | ± 1.1 kJ/mol           | —            | ± 0.26 kcal/mol        | —            |            |
|                       | −101 ± 13 kJ/mol       | —            | −24.14                 | —            | [482]      |
| Detonation velocity   | −121.3 kJ/mol          | −933 kJ/kg   | ± 3.1 kcal/mol         | —            |            |
|                       | 7400 m/s               | —            | −29.0 kcal/mol         | −223 cal/g   | [61]       |
|                       |                        | —            | —                      | —            |            |

**Table 35:** Vapor pressure and thermodynamic data on the evaporation and sublimation of NTO.

| Method                                     | State of matter | Temperature interval<br>K | Temperature dependence of pressure above condensed phase (pressure in atm)<br>atm | Heat of evaporation (or sublimation)<br>kJ/mol |
|--------------------------------------------|-----------------|---------------------------|-----------------------------------------------------------------------------------|------------------------------------------------|
| Static, Bourdon gauge                      | Solid           | 523–599                   | $\ln P = 23.326 - 13286.4/T$                                                      | (110.5)                                        |
|                                            | Liquid          | 599–640                   | $\ln P = 17.123 - 9914.4/T$                                                       | 82.4                                           |
| Thermocouples, burning surface temperature | Solid           | 500–600                   | $\ln p = 20.48 - 12984.4/T$                                                       | —                                              |
|                                            | Liquid          | 599–1015                  | $\ln p = 14.82 - 9914.4/T$                                                        | —                                              |

Data source: [483,484].

**Figure 9:** Vapor pressure of NTO and DAAzF as a function of reciprocal temperature. (Reprinted and modified from [484], with permission from ©2009 Elsevier; permission conveyed through RightsLink.)

Legend: Surface temperatures of burning DAAzF (1) and NTO (2) at different pressures, initial pressures in glass Bourdon gauges at decomposition of solid DAAzF (3) and NTO (4), and vapor pressure above solid NTO (line 5).

Figure 9 shows a good correlation between experimental surface temperatures in the interval of 0.4–2.1 MPa and the theoretical dependence of NTO boiling temperature on pressure. This was calculated using the heat of vaporization and at an experimental boiling temperature of 0.5 MPa. NTO is more volatile than DAAzF, which happened to

be part of the same investigation. The crossing of two straight lines in Figure 9 at the melting point is a good confirmation of these calculations.

The vapor pressure of NTO can also be expressed as

$$\log p = 12.5137 + 6296.553/T,$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The heat of sublimation is  $120.01 \pm 0.29$  kJ/mol ( $28.71 \pm 0.07$  kcal/mol) [485].

#### 8.14.2.1 Solubility and Solutions of NTO

NTO is nearly insoluble in water and is more soluble in methanol than in ethanol or propanol. The solubility of NTO in  $n$ -alkanols decreases with an increasing chain length of the hydrocarbon chain. A richly illustrated account of detailed solubility investigations for NTO in solvent mixtures and multi-phase systems is provided in [468]. The nucleation behavior, interfacial energy, seed crystals, effects of supersaturation, and the effects of cooling rates on crystal growth kinetics were studied in several solvent systems. Best results were obtained with water/ $N$ -methylpyrrolidone mixtures.

The solubility of NTO in water or acetone at room temperature is less than 2%. Solubility increases to ~10% in boiling water at 373 K. The solubility in water at 278 K (4.85 °C) is 0.72%, at 292.1 K (18.95 °C) it is 1.28%, and at 316.45 K (43.3 °C) it is 2.6%.

#### 8.14.2.2 Thermodynamic Properties of NTO

##### Heat Capacity of NTO

The heat capacity of NTO was determined using a continuous  $C_p$  mode of a microcalorimeter (Micro-DSC III) [486]. In the temperature range of 283 to 353 K, the heat capacity of NTO follows a linear relation with temperature, as expressed by the equation

$$C_p = 0.2806 + 2.7103 \times 10^{-3} T,$$

where  $C_p$  is the molar heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. The standard molar specific heat capacity of NTO was  $141.53 \text{ J mol}^{-1} \text{K}^{-1}$  at 298.15 K. Using the determined relationship of  $C_p$  with temperature  $T$ , thermodynamic functions (enthalpy, entropy, and Gibbs free-energy) of NTO between 283 and 353 K (relative to the standard temperature 298.15 K) were derived through thermodynamic relationships. The time of the thermal decomposition from initialization to thermal explosion (adiabatic time-to-explosion) was between 1.95 and 1.99 s depending on the heating rate. Another source [481] gives the heat capacity in the range from 320 to 420 K as

$$C_p = 0.00386T - 0.278,$$

where  $C_p$  is the molar heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin.

### Enthalpy of Formation of NTO

The standard molar enthalpies of formation of 1,2,4-triazol-5-one and 3-nitro-1,2,4-triazol-5-one have been determined from measurements of their energies of combustion in oxygen as  $-142.4 \pm 0.7$  kJ/mol and  $-129.4 \pm 1.1$  kJ/mol, respectively [481]. From measurements of the enthalpies of neutralization of 3-nitro-1,2,4-triazol-5-one with NaOH(aq) and KOH(aq), the enthalpies of formation of the crystalline sodium and potassium salts have been determined as  $-362.6 \pm 1.2$  kJ/mol and  $-385.1 \pm 1.1$  kJ/mol, respectively.

The Gibbs free-energy and entropy change of the NTO anion in aqueous solutions and the enthalpy change of the system  $[\text{Me}^{n+}(\text{G}) + n\text{NTO}^{-}(\text{G}) + m\text{H}_2\text{O}(\text{G})]$  were obtained for several rare-earth metal salts of NTO [487].

Gas-phase enthalpies of formation for NTO, 1,1-diamino-2,2-dinitroethene (=DADNE), LLM-105, TNT, RDX, TATB, HMX, and PETN were calculated using quantum composite methods [488]. Calculations for HMX and PETN hitherto represent the largest molecules attempted with these methods. Some calculations were close to one another, with a larger difference found between other methods. The mean absolute deviations between average experimental values and calculations were 12 to 50 kJ/mol (3 to 12 kcal/mol).

Two values were reported for the enthalpies of formation of NTO in both gas and solid phases. The values for the enthalpies of formation of NTO in gas phase were  $\Delta H_f(\text{G}) = -13.39$  kJ/mol =  $-3.2$  kcal/mol and  $-23.85$  kJ/mol =  $-5.7$  kcal/mol. In the solid phase, they were  $\Delta H_f(\text{S}) = -129.4$  kJ/mol =  $-30.927$  kcal/mol. From both the values, the enthalpy of sublimation of NTO can be calculated. Additionally, according to these data, the lattice energy of NTO becomes  $-110.46$  or  $-121.02$  kJ/mol [481]. A heat of NTO vaporization ( $82.4$  kJ/mol =  $19.7$  kcal/mol) was obtained as a difference between a heat of sublimation of  $110.5$  kJ/mol =  $26.4$  kcal/mol and a heat of melting of  $28.0$  kJ/mol =  $6.7$  kcal/mol. Heat of sublimation was calculated from the enthalpies of formation of solid ( $129.4$  kJ/mol =  $30.93$  kcal/mol) and gaseous NTO ( $13.4$  and  $23.8$  kJ/mol =  $3.2$  and  $5.7$  kcal/mol).

The temperature dependence of vapor pressure above solid NTO was obtained using initial vapor pressures of NTO measured in glass Bourdon gauge experiments on NTO decomposition. The heat of sublimation was  $110.5$  kJ/mol ( $26.4$  kcal/mol), calculated earlier from thermodynamic data, or  $107.9$  kJ/mol ( $25.8$  kcal/mol), calculated from experimental data [489].

Comparisons of the activation energies and frequency coefficients for the sublimation of NTO determined in a TGA apparatus with the activation energy for decomposition of NTO determined by T-jump/FTIR are summarized in Table 36 [490]. This illustrates that the low activation energies reported by some investigators were actually due to sublimation and not decomposition. A heat of melting of  $28.0$  kJ/mol ( $6.7$  kcal/mol =  $51.5$  cal/g) was calculated from NTO solubility in nitric acid solutions [491].

**Table 36:** Kinetics of NTO sublimation and decomposition.

| Activation energy |          | Pre-exponential factor | Temperature range | Method             |
|-------------------|----------|------------------------|-------------------|--------------------|
| kJ/mol            | kcal/mol | ln A, s <sup>-1</sup>  | K                 |                    |
| Sublimation       |          |                        |                   |                    |
| 107.9             | 25.8     | 29.2                   | 407–436           | Isothermal TGA     |
| 119.7             | 28.6     | 31.1                   | 407–448           | Non-isothermal TGA |
| 130.1             | 31.1     | 30.1                   | 453–503           | Non-isothermal TGA |
| Decomposition     |          |                        |                   |                    |
| 364               | 87.1     | 74.8                   | 562–572           | T-jump/FTIR        |

Data source: [490].

### 8.14.2.3 Molecular Structure of NTO

Manchot and Noll incorrectly attributed the molecular structure of NTO to be the hydroxy tautomer 5-hydroxy-3-nitro-1,2,4-triazole [439]. However, the stable room temperature configuration is not the C–OH hydroxy tautomer. The *aci* forms with a C–OH group and may form as intermediates during decomposition of NTO.

MO calculations were performed for several possible tautomers of 1,2,4-triazol-5-one and 3-nitro-1,2,4-triazol-5-one [492]. Calculations were also performed for some conjugate bases of these compounds. The results showed the *1H,4H* tautomer to be most stable. 5-hydroxy-*1H*-1,2,4-triazole and 3-nitro-5-hydroxy-*1H*-1,2,4-triazole were found to lie between 39.3 and 31.4 kJ/mol (9.4 and 7.5 kcal/mol), respectively, thus higher in energy than the corresponding *1H,4H* isomer. It was believed that the calculations may overestimate this relative energy by perhaps 4–12 kJ/mol (1–3 kcal/mol). The calculations also predicted that deprotonation is most likely at N4 of the lowest energy triazolone, but is almost equally likely at N1 and N4 for the corresponding nitrotriazolone (although the N4 position seems slightly favored). In the conjugate bases, a significant contribution from resonance participation of the nitro group was found. It was difficult to predict the site of electrophilic substitution in the triazolone when using the electrostatic potential (see also [493]).

The crystal structure of the  $\beta$  form of NTO has been determined by single-crystal XRD [494]. The unit cell is monoclinic, space group  $P2_1/c$ , with  $a = 9.326 \text{ \AA}$ ,  $b = 5.515 \text{ \AA}$ ,  $c = 9.107 \text{ \AA}$ ,  $\beta = 100.77^\circ$ ,  $\rho_c = 1.878 \text{ g/cm}^3$ . There are four molecules in the cell. An infinite extension of H-bonding in two-dimensional sheets occurs in the monoclinic form. Bond lengths and angles all have normal values. Efforts have been made to determine the crystal structure of  $\alpha$ -NTO. However, the structure was refined only to a low degree of accuracy. This was probably due to interference from twinning about the crystal needle axis. The unit cell is triclinic, space group  $P\bar{1}$ , with unit cell parameters of  $a = 5.12 \text{ \AA}$ ,  $b = 10.30 \text{ \AA}$ ,  $c = 17.9 \text{ \AA}$ ,  $\alpha = 106.7^\circ$ ,  $\beta = 97.70^\circ$ ,  $\gamma = 90.2^\circ$ ,  $\rho_c = 1.92 \text{ g/cm}^3$ . There are eight molecules in the cell. Ribbons of molecules formed by a relatively strong network of hydrogen bonds were observed.  $\alpha$ -NTO is the stable, dominating form.



A study of the tautomerization and ionization of NTO using MO self-consistent field (SCF) and Møller-Plesset (MP2) theories in parallel with DFT examined structures of the NTO anion, which compared well with the reported structure of NTO in its diaminoguanidinium salt [495]. The calculated IR frequencies compared well with those observed for crystalline NTO. The NTO anion was found to be more aromatic than the NTO molecule. Comparisons of bond lengths, calculated proton chemical shifts, and magnetic susceptibility anisotropies showed that the enol tautomers are more aromatic than NTO, which accounts for their enhanced stabilities.

The electron density and related properties of the quasi-stable  $\beta$  form of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO; space group  $P2_1/c$ ) have been determined from a low-temperature (100 K) XRD experiment, allowing calculation of the electron density, Laplacian, and electrostatic potential distributions [496]. The bonding critical weak points and the molecular dipole moment of 3.2 D were also obtained. NTO in the vapor phase may exist as dimer or as clusters of several molecules from which the decomposition originates [497].

The crystal structure of the metastable  $\beta$  form of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one ( $\beta$ -NTO, monoclinic,  $P2_1/c$ ) was investigated at five temperatures in the range of 100–298 K using single-crystal XRD [498]. A second-rank thermal expansion tensor has been determined to describe the thermal behavior of the crystal during warming and cooling. The most significant thermal expansion is in a plane that is almost perpendicular to the planes of all NTO molecules. Perpendicular to the plane of maximal thermal expansion, a modest thermal contraction takes place. Both thermal expansion and contraction of the crystal lattice indicated anharmonicity of the atomic thermal motion. The experimental thermal variation of the unit-cell parameters was in qualitative agreement with that previously obtained from MDs calculations. Rigid-body analysis of the molecular thermal motion was performed using the libration and translation second-rank tensors. Although the translation part of the thermal motion was not strongly anisotropic, the largest displacements of the NTO molecules were oriented in the plane of maximal thermal expansion of the crystal and had significant anharmonic components. The libration motion was more anisotropic, and the largest libration, as well as the largest translation principal axes, were directed along the C5–N5 bond in each NTO molecule.

The kinetic, potential, and electronic energy distributions in NTO were calculated from the experimental electron density using DFT functionals [499]. The spatial distribution of the electronic energy density was shown to be a useful descriptor of the chemical bonding and intermolecular interactions in this energetic molecule.

A DFT with different basis sets was applied to the study of 3-nitro-1,2,4-triazole-5-one (NTO) in both gaseous dimer and its bulk state [500]. The binding energies have been corrected for the basis set superposition errors. Six stable dimers (II–VII) were located. The corrected binding energy of the most stable dimer VII was predicted to be  $-53.66$  kJ/mol. It was found that the structures of the more stable dimers (V–VII) were associated through the hydrogen bonding interaction between the carbonyl

oxygen and the azole hydrogen of 3-nitro-1,2,4-triazole-5-one. The changes of Gibbs free-energies ( $\Delta G$ ) in the processes from the monomer to the dimers at 298.15 K were 8.51, 0.90, 0.35, -8.74, -10.67, and -11.06 kJ/mol for dimers from II to VII, respectively. Dimers V-VII possessing cyclic structures can be spontaneously produced from the isolated monomer at room temperature. Judged from the value of the band gap of 4.0 eV, it can be predicted that NTO is an insulator. Most atoms in NTO, with the exception of the C5 atom and nitro atoms, make up the upper valence bands. In contrast, the lower conduction bands mainly consist of the nitro N and O atoms. The population of the C-NO<sub>2</sub> bond is much less than those of the other bonds and the detonation may be initiated by the breakdown of this bond.

The fully optimized molecular geometries, electronic structures, and energies of 3-nitro-1,2,4-triazol-5-one and three isomers have been obtained by using DFT computational methods [501]. Three transition states (TS1, TS2, TS3) of hydrogen migration reactions have been located and confirmed by the IRC method, and the tautomerization process of NTO tautomers has been investigated. The results showed that one reaction is a primary path of NTO tautomerization, which has a reaction barrier of 122 kJ/mol.

In the vapor phase, NTO molecules can associate to form dimers. Six optimized stable NTO dimers found on the potential energy surface and their electronic structures have been obtained by using a DFT computational method [502]. The intermolecular interaction energy was calculated with basis set superposition error correction (BSSE) and zero-point energy correction. The greatest corrected intermolecular interaction energy of the dimer was -53.66 kJ/mol. It was found that the strong hydrogen bonds contribute to the dimers dominantly, while the binding energies are not only determined by hydrogen bonding. The dimerization process can occur spontaneously at lower temperatures or room temperature.

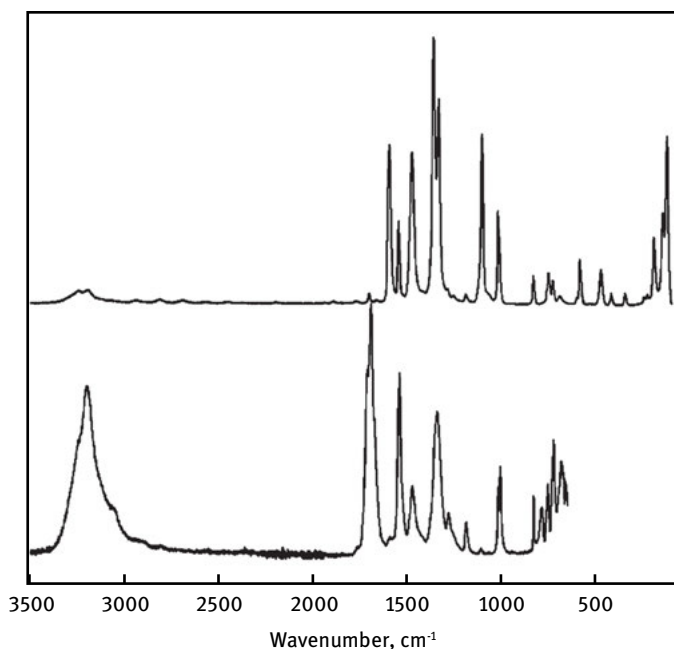
Certain isomeric compounds of NTO and their tautomers have been investigated by performing DFT calculations and also *ab initio* calculations. The optimized geometries, vibrational frequencies, electronic structures, and some thermodynamic values for the presently considered NTO isomers have been obtained in their ground states [503, 504]. Predicted detonation performances were evaluated by the K-J equations, based on the calculated densities and HOF values. The homolytic BDE of N-NO<sub>2</sub> and C-NO<sub>2</sub> scission for the molecules were calculated. The aromatic character of NTO and its isomers and tautomers were investigated by performing calculations using the gauge-invariant atomic orbital approach.

In trying to elucidate the stable forms of NTO, including its tautomers and anions, the geometries and properties of all compounds were calculated using DFT and quantum chemical methods [505]. Calculations were carried out for both the gas phase and for aqueous solutions. The chemical stability of these species was evaluated in terms of the Gibbs free-energy change. Two different solvation models were applied. Calculations showed that the overall differences in the results obtained using these two solvation models were negligible for all species considered. All possible NTO tautomers

were examined, and the results were in good agreement with previous studies performed in the gas phase. To estimate the acidic properties of NTO, anions of several NTO tautomers were analyzed. In addition to this,  $pK_a$  values were calculated using different approaches. When compared with available experimental data, it was found that the conductor-like screening model for real solvents leads to a more accurate estimation of the  $pK_a$  value than other methods, but it was proven that the pattern of deprotonation energy was correctly estimated (see also [506]).

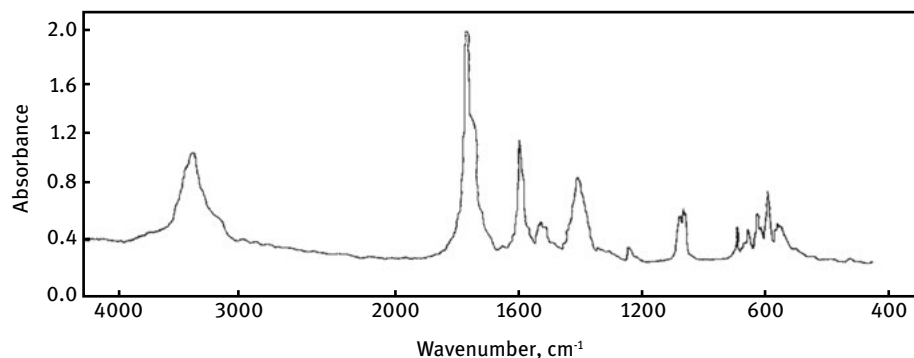
#### 8.14.2.4 Optical Properties of NTO

NTO exists in two polymorphic forms:  $\alpha$ -NTO and  $\beta$ -NTO. The IR and Raman spectra of NTO are demonstrated in Figures 10 and 11.



**Figure 10:** IR (top) and Raman (bottom) spectrum of NTO. (Reproduced and modified from [507] with permission from ©2004 American Chemical Society; permission conveyed through RightsLink.)

The IR band assignments to molecular vibrations demonstrated in Figure 11 are listed in Table 37. NTO has the  $-\text{NH}-\text{C}=\text{O}-\text{NH}-$  amide grouping in the ring, which gives rise to the characteristic absorption of the  $\text{C}=\text{O}$  bond at  $1720\text{ cm}^{-1}$ . The bands at  $1550$ ,  $1360$ , and  $790\text{ cm}^{-1}$  can be assigned to the asymmetric, symmetric, and stretching deformation of the  $-\text{NO}_2$  group.



**Figure 11:** Infrared spectrum of NTO. (Reprinted and modified from [508], with permission from ©1994 Elsevier; permission conveyed through RightsLink.)

**Table 37:** IR spectral assignments of NTO.

| Wavenumber, cm <sup>-1</sup> | Assignment                                             |
|------------------------------|--------------------------------------------------------|
| 3200s                        | $\nu(\text{N-H})$                                      |
| 1720s                        | $\nu(\text{C=O})$ (unsaturated ring exo $\text{C=O}$ ) |
| 1700sh                       | $\nu(\text{C=N})$                                      |
| 1550s                        | $\nu(\text{NO}_2)$ , asym.                             |
| 1470m                        | $\nu$ amide 2 (cis)                                    |
| 1360s                        | $\nu(\text{NO}_2)$ , sym.                              |
| 1280w                        | Amide 3                                                |
| 1190m                        | $\nu(\text{N-N})$ , ring                               |
| 1020m                        | $\nu(\text{C-N})$                                      |
| 1010m                        |                                                        |
| 830m                         | $\text{NO}_2$ deformation                              |
| 790m                         |                                                        |
| 760m                         |                                                        |
| 740m                         | Amide 4 and 5                                          |
| 690m                         |                                                        |
| 610m                         |                                                        |

Key: m, medium; s, sharp; sh, shoulder; w, weak.

Data source: [508].

The extraordinary thermal stability of NTO is due to the arrangement of its atoms. The vibrations of atoms against each other can lead to decomposition. However, before that point of breakup, infrared spectra can help to identify which atoms in the molecule cause which IR absorption band and which constitute the weakest link. Isotope labeling in NTO facilitates the assignment of absorption bands to certain locations in the molecule. The IR and Raman spectra of NTO and its compounds labeled

with the stable isotopes  $^{15}\text{N}$ ,  $^{13}\text{C}$ , and deuterium (D) [such as NTO- $^{15}\text{NO}_2$ , NTO- $^{13}\text{C}(3)$  or NTO-D] were measured in the region of  $100\text{--}3500\text{ cm}^{-1}$  [507]. Vibrational motions were experimentally assigned by using isotopic vibrational shifts. In addition, theoretical calculations were performed to assign those vibrational bands with good agreement of experimental and theoretical data. Furthermore, the experimental and calculated results indicate that the C—O bond length of NTO in the crystal state is longer than that of an isolated molecule in the gas phase because of intermolecular hydrogen bonding.

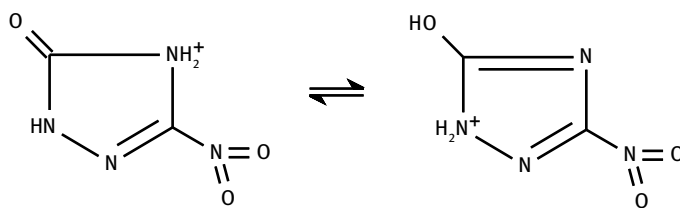
The Raman spectra of the  $\alpha$  form of NTO were measured in a high-pressure vessel diamond anvil cell at pressures up to 27.6 GPa [509]. In general, Raman bands showed a blue shift because of the nature of the molecule packing (which has a high-pressure effect) but some particular bands exhibited a red shift, disappearance, split, or slight shifting. Those red-shifting bands are the result of hydrogen bonds, i.e., carbonyl and amino groups that are likely to work as a stabilizer against stimuli to the molecule or crystal. This stabilizing nature might characterize the insensitivity of NTO. Computations predicted that the peak frequency in the power spectrum of the CO-stretching vibration should exhibit a red shift with an increase in pressure up to 10.0 GPa, while the peak intensity should considerably decrease under the same pressure process because this bond length increases with an increase in pressure up to the aforementioned GPa. At a pressure of  $>20.0$  GPa, a blue shift appeared. These results of the molecular dynamics calculations were in good agreement with experimental data.

### 8.14.3 Chemical Properties of NTO

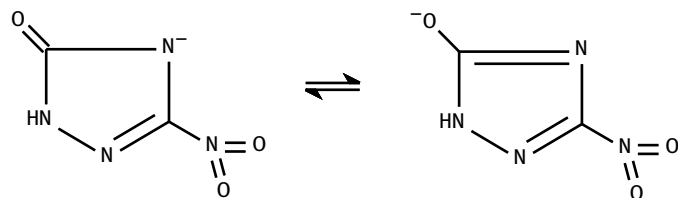
The oxygen balance of NTO is  $-24.6\%$ . An energetic compound does not have to be stoichiometric with an oxygen balance of  $0\%$  to be a very useful explosive and propellant ingredient.

#### 8.14.3.1 Reactions of NTO with Other Compounds

NTO is amphoteric and can form salts with both strong bases and strong acids.



NTO Cation



NTO Anion

The acid constants are  $pK_{a1} = 3.76$  and  $pK_{a2} = 11.25$ . Owing to the acidic nature of NTO, it forms salts with a large number of metals as well as aromatic and aliphatic amines, which are also useful in propellants. The ease of formation of a large number of salts offers a chance of making a wide variety of compounds that can be tailored to specific applications. Other sources reported the  $pK_a$  of NTO as 3.67 [510].

The reaction of NTO with ammonia would form an ammonium salt and the association with water would form a hydrate. Intermolecular interactions between NTO and ammonia or water were examined by computational chemistry methods [511]. The energy levels of two fully optimized geometries of  $\text{NTO} \cdots \text{NH}_3$  complexes have been calculated using a DFT method [512]. The intermolecular interaction energy was calculated with a zero-point energy correction and a BSSE. The greatest corrected intermolecular interactions of the  $\text{NTO} \cdots \text{NH}_3$  complexes were  $-3758 \text{ kJ/mol}$ . Electrons in complex systems transfer from  $\text{NH}_3$  to NTO. The strong hydrogen bonds contribute to the interaction energies dominantly. Natural bond orbital (NBO) analysis was performed to reveal the origin of the interaction. Based on vibrational analysis, the changes of thermodynamic properties from the monomer to complexes with temperatures ranging from 200 to 800 K have been obtained using a statistical thermodynamic method. It was found that two  $\text{NTO} \cdots \text{NH}_3$  complexes can be produced spontaneously from NTO and  $\text{NH}_3$  at normal temperatures.

#### 8.14.3.2 Salts of NTO

The most complete summary of properties of salts of NTO, including metal salts and salts of organic nitrogen-containing bases, was compiled by Singh and Felix in 2002 [513]. It includes properties of 50 salts and the information is backed up by 68 references.

#### Metal Salts of NTO

The metal salts of NTO are arranged here in the sequence of their column group numbers in the International Union of Pure and Applied Chemistry (IUPAC) periodic table of elements. Multi-element studies that do not fit into an individual group are discussed first.

Twenty-six metal salts of 3-nitro-1,2,4-triazol-5-one were prepared and characterized by using elemental analysis, DSC, TGA,  $^{13}\text{C}$ -NMR, XPS, electric conductivity, IR,

and powder XRD [514]. The results confirmed that these salts have a general formula as  $M(\text{NTO})_m \cdot n\text{H}_2\text{O}$ . Additional publications on NTO salts were in [515, 516]. Lead, copper, and ammonium salts of NTO can be used as burning rate catalysts in solid propellants [517].

It was attempted to establish a relationship between the standard enthalpy of formation and the standard enthalpy of formation divided by the exothermic denitration decomposition peak absolute temperature [518]. 3-Nitro-1,2,4-triazol-5-one and its salts are insensitive energetic materials with wide application prospects. The preparation, characterization, and application of NTO and its salts were reviewed [519].

The synthesis and properties of 3-nitro-1,2,4-triazol-5-one (NTO), including synthesis methods, crystal structure, quantum chemistry, thermal behaviors, and toxicity were reviewed in detail [520]. The molecular structure and thermodynamic properties of 21 types of NTO salts with alkali, alkaline earth, transition metals, and rare-earth metals were measured. The thermal decomposition products of NTO alkali metal salts were identified as carbonates with Li, Na, and K, and those of Rb and Cs salts of NTO were carbonate, metal oxide, and polymers. A relationship between the enthalpy of activation ( $\Delta H_{\text{act}}$ ) and the value of the peak temperature during decomposition of several NTO alkali metal salts was derived with 73 data points.

The molar enthalpies of dissolution in water of a variety of NTO salts of the general formula  $\text{Me}(\text{NTO})_n \cdot m\text{H}_2\text{O}$  (Me = Ba, Li, Ca, Na, Co, Mg, Ce, Pr, Gd, Tb, Dy, Y, Yb) were measured in a microcalorimeter. Five empirical formulae describing the differential enthalpy of dissolution, standard molar enthalpy of dissolution, relative apparent molar enthalpy, relative partial molar enthalpy, and enthalpies of dilution in water of these metal salts of NTO were obtained [521, 522]. Metal salts of NTO have been evaluated as burning rate modifiers for AN/hydroxy-terminated polybutadiene (HTPB) propellants [523]. The following sections describing the metal salts of NTO are arranged by the group number of the metal in the periodic table of elements.

### Group 1 Metals: Li, Na, K, Rb, Cs

The thermal stability of K, Cu, Pb, and  $\text{NH}_4$  salts of NTO has been described by [524, 525]. 1,2,4-Triazol-5-one (TO) and 3-nitro-1,2,4-triazol-5-one (NTO) and the mono- and dilithium salts of NTO were prepared and characterized by TGA and  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectra [526]. XRD crystal data of lithium salts of NTO revealed solid-state crystal structures that had not been reported previously.  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR verified solution state anion forms other than those that do exist in the solid state for  $\text{Li}(\text{NTO}) \cdot 2\text{H}_2\text{O}$  and  $\text{Li}_2(\text{NTO}) \cdot 5\text{H}_2\text{O}$ .

From measurements of the enthalpy of solution of metal salts of 3-nitro-1,2,4-triazol-5-one (NTO) in water, the standard enthalpies of formation of  $\text{KNT} \cdot \text{H}_2\text{O}$ ,  $\text{Ba}(\text{NTO})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{LiNTO} \cdot 2\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NTO})_2 \cdot \text{H}_2\text{O}$ , and  $\text{Gd}(\text{NTO})_3 \cdot 7\text{H}_2\text{O}$  were determined as  $-(676.9 \pm 2.6)$  kJ/mol,  $-(1627.0 \pm 2.5)$  kJ/mol,  $-(966.63 \pm 2.2)$  kJ/mol,  $-(1905.5 \pm 4.4)$  kJ/mol, and  $-(3020.1 \pm 6.4)$  kJ/mol, respectively [527]. From measurements of the enthalpy of precipitation of  $\text{KNT} \cdot \text{H}_2\text{O}$  crystal with  $\text{Pb}(\text{NO}_3)_2(\text{aq})$ ,

$\text{CuSO}_4(\text{aq})$  and  $\text{Zn}(\text{NO}_3)_2(\text{aq})$ , the standard enthalpies of formation of  $\text{Pb}(\text{NTO})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Cu}(\text{NTO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Zn}(\text{NTO})_2 \cdot \text{H}_2\text{O}$  were determined as  $-(247.4 \pm 5.9) \text{ kJ/mol}$ ,  $-(712.1 \pm 5.4) \text{ kJ/mol}$  and  $-(628.8 \pm 5.7) \text{ kJ/mol}$ , respectively.

$\text{Li}(\text{NTO})(\text{H}_2\text{O})_2$  was prepared by mixing 3-nitro-1,2,4-triazol-5-one (NTO) aqueous solution and lithium hydroxide aqueous solution and its thermal decomposition was studied by DSC, TG/DTG, and IR methods [528]. The kinetic parameters were obtained from the analysis of the DSC and TG/DTG curves using the Kissinger method, the Ozawa method, the differential method, and the integral method. The most probable mechanism function for the thermal decomposition of the first stage was suggested by comparing the kinetic parameters. The critical temperature of thermal explosion ( $T_b$ ) was 562 K (289 °C).

The lithium and potassium salts of NTO were prepared and characterized by elemental analysis, metal content determination, and FTIR [529]. The DSC thermogram indicated that the Li and K salts of NTO undergo exothermic decomposition in the temperature range of 530–633 K (257–360 °C). The TGA weight loss pattern revealed loss of water for Li/K salts of NTO in the temperature range of 388–428 K (115–155 °C). The compounds were insensitive to impact and friction (impact sensitivity, height of 50% explosion >170 cm, and friction insensitivity was negative at up to 36 kg<sub>f</sub>) stimuli despite the fact that even the parent molecule of NTO salts is in the hazard category of 1.1. The FTIR spectra of the gaseous products evolved during TGA of NTO salts indicated the release of  $\text{NO}_2$ . The formation of products such as  $\text{LiNCO}$  and  $\text{KNCO}$  was also observed. To assess the performance as energetic ballistic modifiers, NTO salts were incorporated in AP-HTPB composite propellants. The potassium salts enhanced the burning rates of the propellants.

The potassium salts of NTO,  $\text{KNTO} \cdot \text{H}_2\text{O}$ , was prepared by mixing an aqueous solution of NTO and potassium hydroxide and characterized by TGA, elemental analysis, and IR [530]. The crystal structure of  $[\text{KNTO} \cdot \text{H}_2\text{O}]$  was determined by single-crystal XRD. The crystal is monoclinic, space group  $P2_1/n$ , with crystal unit cell parameters of  $a = 0.6408(1) \text{ nm}$ ,  $b = 0.8218(1) \text{ nm}$ ,  $c = 1.2626(1) \text{ nm}$ ,  $\beta = 100.63^\circ(1)$ ,  $V = 0.6535(1) \text{ nm}^3$ ,  $Z = 4$ ,  $D_c = 1.892 \text{ g/cm}^3$ .

### Group 2 Metals: Be, Mg, Ca, Sr, Ba

The thermal stability of the barium salt of NTO,  $\text{Ba}(\text{NTO})_2 \cdot 3\text{H}_2\text{O}$ , was measured by TGA and DSC [531]. This salt was evaluated as a combustion catalyst and ballistic modifier for solid propellants.

The salt  $[\text{Sr}(\text{NTO})_2(\text{H}_2\text{O})_4]_2 \cdot 4\text{H}_2\text{O}$  was prepared by mixing an aqueous solution of NTO with an excess of strontium carbonate and crystallizing the salt from the filtrate [532]. The single-crystal structure was determined by XRD. The crystal is monoclinic, space group  $P2_1/c$ , with crystal unit cell parameters of  $a = 1.1034(1) \text{ nm}$ ;  $b = 2.2742(2) \text{ nm}$ ,  $c = 0.63398(9) \text{ nm}$ ,  $\beta = 101.798(13)^\circ$ ,  $V = 1.5573(4) \text{ nm}^3$ ,  $D_c = 1.936 \text{ g/cm}^3$ ,  $Z = 2$ . From measurements of the enthalpy of solution in water of  $[\text{Sr}(\text{NTO})_2(\text{H}_2\text{O})_4]_2 \cdot 4\text{H}_2\text{O}$  at 298.15 K, the standard enthalpy of formation, lattice



energy, lattice enthalpy, and standard enthalpy of dehydration have been determined as  $-(2545.2 \pm 4.7)$ ,  $-2114$ ,  $-2136$  and  $67.2$  kJ/mol, respectively.

Four alkaline earth metal salts of NTO,  $\text{Mg}(\text{NTO})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NTO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NTO})_2 \cdot 5\text{H}_2\text{O}$ , and  $\text{Ba}(\text{NTO})_2 \cdot 3\text{H}_2\text{O}$ , have been prepared from metal carbonates and NTO in aqueous suspensions at 333 K (60 °C) and characterized by TGA, DTA, and explosion delay measurements [533]. In the TGA, mass losses occurred in three steps. Decomposition reaction pathways involving slow thermolysis (decomposition) and rapid thermolysis (explosion) have been suggested. If heated in air, the oxidation-reduction reactions near the surface of the thermolyzing material  $[\text{M}(\text{NTO})_2 \cdot n\text{H}_2\text{O}]$  seem to be responsible for the decomposition and explosion. The activation energies for the explosion were in the range of 28–34 kJ/mol.

The magnesium salt of NTO,  $[\text{Mg}(\text{H}_2\text{O})_6](\text{NTO})_2 \cdot 2\text{H}_2\text{O}$ , can be prepared by adding magnesium carbonate hydroxide to the aqueous solution of NTO [534]. The crystal structure is monoclinic with space group  $C2/c$  and unit-cell parameters  $a = 2.3101(3)$  nm,  $b = 0.6472(1)$  nm,  $c = 1.4118(3)$  nm, and  $\beta = 124.05(1)^\circ$ . The standard molar enthalpy of formation is  $-(3015.4 \pm 4.2)$  kJ/mol.

In a similar study, the salt  $[\text{Mg}(\text{H}_2\text{O})_6](\text{NTO})_2 \cdot 2\text{H}_2\text{O}$  was prepared by adding magnesium carbonate hydroxide to the aqueous solution of NTO and its thermal decomposition mechanism was studied by DSC, TGA/DTG, and IR [535]. The results of a quantum chemical calculation showed that the bonds between the co-ordinate waters and the Mg atom have a covalent character to a certain extent. The net charges on nitrogen atoms of the NTO ring appeared to be negative while the nitrogen atom on the nitro group ( $-\text{NO}_2$ ) appeared to be positive, which indicated that  $-\text{NO}_2$  will lose first when the complex is heated. This result was in agreement with that of a thermal decomposition experiment. A calcium carbonylhydrazide complex ion,  $[\text{Ca}(\text{NH}_2\text{NHCONHNH}_2)_2(\text{H}_2\text{O})]$ , can form a stable salt with two mols of NTO using an aqueous solution of calcium 3-nitro-1,2,4-triazol-5-onate and carbonylhydrazide [536].

### Group 3: Sc, Y, La, Lanthanides

Several rare-earth metal (Pr, Nd, Sm) NTO salt hydrates were prepared, and the thermal stability was characterized by Xie et al. [537].

### Group 7–10: Mn, Fe, Co, Ni

The preparation and thermal decomposition mechanism of the Mn(II), Co(II), and Ni(II) salts of 3-nitro-1,2,4-triazol-5-one was studied [514, 538]. Six energetic transition metal salts of NTO  $[\text{M}(\text{NTO})_2]$ , with  $\text{M} = \text{Mn, Fe, Co, Ni, Cu, and Zn}$ , were prepared and characterized by TGA, DSC, and explosion delay measurements [539]. The melting points of the salts varied over a range of between 411 and 633 K (138–360 °C). Most salts decomposed before melting. The Fe(II) salt of NTO was the thermally most stable salt in this group. Several salts exploded in the TGA quickly after losing only 20–30% of the initial mass. In the DTA, the activation energies of the transition metal salts were lower than that of NTO, indicating that the metal cations catalyze the NTO de-

composition. It seems that the explosive behavior of NTO is quite enhanced due to the transition metal ions as these are known to be good oxidation catalysts. Thus, these salts may be explored as burning rate modifiers for solid propellants.

Single crystals of the cobalt salt of 3-nitro-1,2,4-triazol-5-one,  $[\text{Co}(\text{H}_2\text{O})_6](\text{NTO})_2 \cdot 2\text{H}_2\text{O}$ , were prepared and the crystal structure was determined by XRD [540]. The crystals were monoclinic with space group *Cc* and unit cell parameters of  $a = 2.3163(2)$  nm,  $b = 0.6451(1)$  nm,  $c = 1.4123(1)$  nm,  $\beta = 123.96(1)^\circ$ ,  $V = 1.7504(3)$  nm<sup>3</sup>, and  $Z = 4$ . From measurements of the enthalpy of solution in water at 298.15 K, the standard enthalpy of formation was calculated as  $-(2594.7 \pm 4.5)$  kJ/mol.

Several Co/Cu/Ni/Fe salts of NTO were prepared and characterized [541]. All of the salts exhibited exothermic decomposition in the DSC. The FTIR spectra of the gaseous products evolved during TGA of NTO salts and indicated the release of  $\text{NO}_2$  and cleavage of the NTO ring during the course of decomposition. The transition metal salts enhanced the burning rates of AP/HTPB composite propellants. The best catalytic effect was obtained with the Fe-NTO salt, which increased the burning rate by ~80% and reduced the pressure index ( $n$ ) to 0.18 (at 2 to 9 MPa).

#### Group 11: Cu, Ag, Au

The Pb, Cu(II), K,  $\text{NH}_4^+$ , and ethylenediamine salts of 3-nitro-1,2,4-triazol-5-one were prepared, and their densities, impact sensitivities, friction sensitivities, DSC, and critical temperatures of thermal explosion were determined [542].

Under linear temperature increase conditions, the mechanisms and kinetic parameters of thermal decomposition of NTO and NTO salts of the type  $\text{M}(\text{NTO})_m \cdot n\text{H}_2\text{O}$  for  $\text{M} = \text{Cu}$ ,  $m = 2$ ,  $n = 4$ ;  $\text{M} = \text{Pb}$ ,  $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3$ ,  $m = 2$ ,  $n = 0$ ;  $\text{M} = \text{K}$ ,  $\text{NH}_4$ ,  $m = 1$ ,  $n = 1$ , were obtained by TGA, DSC, IR, and XRD [525]. The thermal decomposition processes of  $\text{Cu} \cdot (\text{NTO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{K} \cdot \text{NTO} \cdot \text{H}_2\text{O}$  can be divided into three stages: dehydration, ring breaking, and forming metal oxide. However, the thermal decomposition process of  $\text{Pb} \cdot (\text{NTO})_2$  occurred in only two stages because there was no crystal water.

The 3-nitro-1,2,4-triazol-5-one silver salt was synthesized by the reaction of NTO sodium salt with silver nitrate aqueous solution [543]. Its thermal stability was characterized by DSC and TGA. The decomposition process of  $\text{AgNTO} \cdot 2\text{H}_2\text{O}$  was found to be divided into four stages: dehydration process, fracture and decomposition of the nitro group, breaking of the triazole ring, and the primary formation of inorganic materials. The ultimate generation of  $\text{Ag}_2\text{CO}_3$  and the maximum decomposition temperature was about 503 K (230 °C). The ultimate decomposition product was  $\text{Ag}_2\text{CO}_3$ .

#### Group 14: Pb

The lead salt of NTO  $[\text{Pb}(\text{NTO})_2(\text{H}_2\text{O})]$  was prepared by mixing aqueous solutions of sodium 3-nitro-1,2,4-triazol-5-onate and lead nitrate [544]. It was characterized by thermal analysis, elemental analysis, <sup>13</sup>C NMR, and IR measurements. The crystal structure of  $[\text{Pb}(\text{NTO})_2(\text{H}_2\text{O})]$  was determined by single-crystal XRD analysis. The crystal belongs to space group  $P2_1/n$  with crystal parameters of  $a = 0.7284(2)$ ,

$b = 1.2166(3)$ ,  $c = 1.2310(3)$  nm,  $\angle \beta = 90.36(2)^\circ$ ,  $V = 1.0908(4)$  nm<sup>3</sup>,  $Z = 4$ , and  $D_c = 2.96$  g/cm<sup>3</sup>.

Five transition metal salts of NTO,  $[M(\text{NTO})_n] \cdot m\text{H}_2\text{O}$  (where M is Ag, Hg, Cd, Cr, and Fe and where  $n = 1, 2, 2, 3, 3$  and  $m = 1, 2, 2, 8, 2$ , respectively) were prepared and characterized [545]. The thermal decomposition of these salts was investigated by TGA, DTA, and the explosive behavior was studied in terms of explosion delay and impact and friction sensitivities. Kinetic parameters have been derived using non-isothermal TGA data and a mechanism of thermolysis has also been proposed. It seems that dehydration takes place before the evolution of NO<sub>2</sub> and the subsequent ring rupture yields metal oxide. AgNTO on the other hand yields metallic silver. Dehydration in the case of HgNTO occurred in two steps; at each step, one NTO molecule was lost. All the salts were insensitive to impact and to friction up to a pistil load of 360 N. The order of activation energy for thermal decomposition of NTO and that of the corresponding dehydrated salts obtained was: NTO > FeNTO > AgNTO > CdNTO > HgNTO > CrNTO. The synthesis of 3-nitro-1,2,4-triazole-5-one and its lead salt was scaled up to the 100-g batch size [454] (see also [546]).

#### 8.14.3.3 Salts of NTO with Nitrogen Containing Bases

Overall, we have arranged salts by the cation first and by the anion last throughout this publication. For the nitrogen base salts of NTO discussed here, we have made an exception; salts and valuable propellant ingredients are discussed together as a group with their parent anion (NTO) instead of scattering the information over several nitrogen-based cation chapters [547–549]. In addition to the seven 1-hydro-3-nitro-1,2,4-triazol-5-one (NTO) salts, Table 38 contains data for three salts of 5-nitrotetrazole (NT) and three salts of 3,5-dinitro-1,2,4-triazole (DNTr). In this publication, we have not stated whether the DSC temperature shown was the onset of an exotherm or the maximum temperature of an exotherm and whether the samples were heated under inert gas or in air. Comparing the numbers for RDX and triaminoguanidinium nitrate (TAGN) in Table 38 to other literature data for RDX and TAGN, we assume the temperature shown is the start of the exotherms because the RDX exotherm maximum occurs typically at 513 K (240 °C) and the difference between air and nitrogen is only 5°. The source of this table did not state if the drop weight impact height shown is the 50% point determined by the Bruceton up-and-down method or if it is the minimum height at which the first initiation reaction was observed in one out of ten trials. Other studies also using the Type 12 tool reported drop weight sensitivities for RDX in the range of 31 cm for the 10% firing point and 45 cm for the 50% firing point [550]. Notably, both numbers are higher than the 22 cm listed for RDX in Table 38.

Table 38: Properties of NTO salts with nitrogen-containing bases.

| Compound name                                           | Acronym | Gross formula | Molecular mass | Nitrogen content | Oxygen balance | DTA exotherm | Drop-weight impact height <sup>a</sup> | Enthalpy of formation |                              |
|---------------------------------------------------------|---------|---------------|----------------|------------------|----------------|--------------|----------------------------------------|-----------------------|------------------------------|
|                                                         |         |               |                |                  |                |              |                                        | kJ/mol                | kcal/mol                     |
|                                                         |         |               | g/mol          | Mass-%           | %              | K            | °C                                     | cm                    |                              |
| Ethylenediammonium(1+)<br>3-nitro-1,2,4-triazol-5-onate | ENTO    | C6H12N10O6    | 320.223        | 43.74            | -60.0          | 523          | 250                                    | nogo                  | -468.6 ± 5.9<br>-112 ± 1.4   |
| Ammonium 3-nitro-1,2,4-triazol-5-onate                  | ANTO    | C2H5N5O3      | 147.093        | 47.61            | -38.1          | 463          | 190                                    | nogo                  | -276.6 ± 15.1<br>-66.1 ± 3.6 |
| Hydrazinium 3-nitro-1,2,4-triazol-5-onate               | HNTO    | C2H6N6O3      | 162.107        | 51.84            | -39.5          | 443          | 170                                    | 92                    | -159.0 ± 20.9<br>-38 ± 5     |
| Guanidinium 3-nitro-1,2,4-triazol-5-onate               | GuNTO   | C3H7N7O3      | 189.133        | 51.84            | -55.0          | 533          | 260                                    | nogo                  | -297.1 ± 12.6<br>-71 ± 3     |
| Aminoguanidinium 3-nitro-1,2,4-triazol-5-onate          | AGNTO   | C3H8N8O3      | 204.147        | 54.89            | -54.9          | 473          | 200                                    | nogo                  | -177.8 ± 9.6<br>-42.5 ± 2.3  |
| Diaminoguanidinium 3-nitro-1,2,4-triazol-5-onate        | DAGNTO  | C3H9N9O3      | 219.162        | 57.52            | -54.8          | 463          | 190                                    | 252                   | -87.9 ± 8.4<br>-21 ± 2       |
| Triaminoguanidinium 3-nitro-1,2,4-triazol-5-onate       | TAGNTO  | C3H10N10O3    | 234.177        | 59.81            | -54.7          | 443          | 170                                    | 103                   | +58.6 ± 16.7<br>+14 ± 4      |
| Ethylenediammonium(1+)<br>5-nitrotetrazolate            | ENT     | C4H10N12O4    | 290.200        | 57.92            | -49.6          | 489          | 216                                    | 42                    | +233.0 ± 12.6<br>+55.7 ± 3.0 |
| Guanidinium 5-nitrotetrazolate                          | GuNT    | C2H6N8O2      | 174.121        | 64.35            | -45.9          | 485          | 212                                    | 36                    | +71.1 ± 7.1<br>+17.0 ± 1.7   |

Table 38: (continued).

| Compound name                                       | Acronym | Gross formula | Molecu-<br>lar mass | Nitrogen<br>content | Oxygen<br>balance | DTA exotherm<br>K | °C  | Drop-<br>weight<br>impact<br>height <sup>a</sup><br>cm | Enthalpy of formation |             |
|-----------------------------------------------------|---------|---------------|---------------------|---------------------|-------------------|-------------------|-----|--------------------------------------------------------|-----------------------|-------------|
|                                                     |         |               |                     |                     |                   |                   |     |                                                        | kJ/mol                | kcal/mol    |
| Triaminoguanidinium<br>5-nitrotetrazolate           | TAGNT   | C2H9N11O2     | 219.165             | 70.3                | -47.5             | 429               | 156 | <15                                                    | +393 (calc.)          | +94 (calc.) |
| Ammonium 3,5-dinitro-1,2,4-<br>triazolate           | ADNTr   | C2H4N6O4      | 176.091             | 47.73               | -18.2             | 473               | 200 | 58                                                     | +2.5 ± 8.4            | +0.6 ± 2.0  |
| Diaminoguanidinium<br>3,5-dinitro-1,2,4-triazolate  | DAGDNTr | C3H8N10O4     | 248.160             | 56.44               | -38.7             | 513               | 240 | 34                                                     | +144.3 ± 19.7         | +34.5 ± 4.7 |
| Triaminoguanidinium<br>3,5-dinitro-1,2,4-triazolate | TAGDNTr | C3H9N11O4     | 263.175             | 58.54               | -39.5             | 509               | 236 | 31                                                     | +250.2 ± 0.8          | +59.8 ± 0.2 |
| For comparison:                                     |         |               |                     |                     |                   |                   |     |                                                        |                       |             |
| Diaminoguanidinium nitrate                          | DAGN    | CH8N6O3       | 152.113             | 55.25               | -31.6             | 513               | 240 | 35                                                     | -195.8                | -46.8       |
| Triaminoguanidinium nitrate                         | TAGN    | CH9N7O3       | 167.127             | 58.67               | -33.5             | 508               | 235 | 23                                                     | -48.1                 | -11.5       |
| 1,3,5-Trinitro-1,3,5-<br>hexahydrotriazine          | RDX     | C3H6N6O6      | 222.116             | 37.84               | -21.6             | 478               | 205 | 22                                                     | +66.9                 | +16.0       |

<sup>a</sup> ERL (NOL) Type 12 tool  
Data source: [547, 548, 551]

### Ammonium Salts of NTO

Ammonium 3-nitro-1,2,4-triazol-5-onate, also known as 3-nitro-1,2,4-triazol-5-one,  $\text{NH}_4^+$  salt; 3*H*-1,2,4-triazol-3-one, 1,2-dihydro-5-nitro-, monoammonium salt; ANTO;  $[\text{C}_2\text{H}_1\text{N}_4\text{O}_3^-]\text{NH}_4^+$ ,  $\text{C}_2\text{H}_5\text{N}_5\text{O}_3$ ,  $M = 147.093 \text{ g/mol}$ , CAS RN [127173-68-6],  $\Delta H_f = -197 \text{ kJ/mol} = -47.1 \text{ kcal/mol} = -320 \text{ cal/g}$ , is a solid which crystallized as orthorhombic crystals, space group *P*222, with unit cell parameters of  $a = 6.281(2) \text{ \AA}$ ,  $b = 8.423(2) \text{ \AA}$ ,  $c = 12.693(5) \text{ \AA}$ , and  $\rho = 1.65 \text{ g/cm}^3$ ,  $Z = 4$  [552]. The N4 proton is more acidic than the one at N1, and deprotonation is easier from N4 than from N1.

Under linear temperature increase conditions, the mechanism and kinetic parameters of thermal decomposition of NTO and  $\text{NH}_4\text{NTO}$  were obtained by TGA, DSC, IR, and XRD [525]. The decomposition process of  $\text{NH}_4\text{NTO} \cdot \text{H}_2\text{O}$  (ANTO) occurred in three stages, which were dehydration, deamination, and the decomposition reaction of NTO which formed in the second stage. However, if the sample was sealed in a closed stainless-steel cell or if the ammonia produced in the second stage did not escape as fast as it was produced, the gaseous ammonia catalyzed the decomposition of NTO. If the DSC was conducted under static air instead of flowing air, the result would be different. Under static air conditions and heating rates of 1 and  $2^\circ\text{C/min}$ , there was a sharp exothermic peak after the two endothermic peaks in the DSC curves. The temperatures at which the exothermic peaks appeared were 535.9 and  $535.6 \text{ K}$  ( $262.8$  and  $262.5^\circ\text{C}$ ), respectively. These are close to the temperature of the decomposition peak of NTO. Under the condition of static air, and heating rates of 5, 10, and  $20^\circ\text{C/min}$ , the exothermic peaks were shifted downwards substantially and appeared at 484.6, 494.4, and  $509.6 \text{ K}$  ( $211.5$ ,  $221.3$ , and  $236.5^\circ\text{C}$ ), respectively, which represents downwards shifts of  $23$ – $58^\circ\text{C}$ . Therefore, it became clear that the mechanism of thermal decomposition in the third stage of ANTO was different from that of pure NTO explosive under high heating rate conditions. The standard HOFs at  $298.15 \text{ K}$  of the crystalline silver and ammonium salts of 3-nitro-1,2,4-triazol-5-one are  $-269.9 \pm 1.1$  and  $-47.1 \pm 1.4 \text{ kJ/mol}$ , respectively [553].

Calculations of the geometrical structure of ammonium 3-nitro-1,2,4-triazol-5-onate by semi-empirical MO showed that there are four distinguished types of intermolecular hydrogen bonding in the crystal molecular/ionic system [554]. The binding energies of  $\text{NH}_4^+\text{NTO}^-$ ,  $\text{NTO}^-/\text{H}_2\text{O}$ , and  $\text{NH}_4^+/\text{H}_2\text{O}$  are  $-964$ ,  $-572$ , and  $-61.35 \text{ kJ/mol}$  ( $-230.516$ ,  $-136.671$ , and  $-14.664 \text{ kcal/mol}$ ), respectively. The charge densities show the deprotonation ability of various nitrogens of  $\text{NTO}^-$  ion, a result that corresponded to some earlier studies.

The ammonium 3-nitro-1,2,4-triazol-5-onate molecular system, which comprises the energetic compound 3-nitro-1,2,4-triazole-5-one with its two lowest-energy conformers L1 and L2, ammonia, and water molecules, was examined by a theoretical calculation of corresponding geometrical structures and localized bonding characters [555]. With the medium (or solvent) of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , three intermolecular hydrogen bonds formed in the  $\text{NTO} + \text{NH}_3 + \text{H}_2\text{O}$  system. This lowers the overall molecular energy and stabilizes the system.

The thermal decomposition of ammonium 3-nitro-1,2,4-triazol-5-onate monohydrate  $[\text{NH}_4(\text{NTO}) \cdot \text{H}_2\text{O}]$  was studied using a combination of thermal analysis-MS and *in-situ* thermolysis cell with rapid-scan FTIR [556]. The results showed that there are two endothermic steps and one exothermic step in the decomposition process of  $[\text{NH}_4(\text{NTO}) \cdot \text{H}_2\text{O}]$ . The detected off-gas products consisted of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{NO}_2$ .

### Hydroxylammonium Salts of NTO

The hydroxylammonium salt of NTO was prepared by reaction of the sodium salt of NTO with HAN. The salt melted at 461–463 K (188–190 °C) and in the DSC thermogram it showed two exotherms, one at 463 K (190 °C) and another at 543 K (270 °C), [557, 558]. The diethylhydroxylammonium salt of NTO melted at 381–383 K (108–110 °C) without apparent decomposition. The *N*-methylhydroxylammonium salt of NTO melted at 430–431 K (157–158 °C) and started to decompose even before it melted. The drop weight impact sensitivity of the hydroxylammonium and diethylhydroxylammonium salts of NTO was above 200 kg cm (insensitive). Another method for preparing the hydroxylammonium salt of NTO would be the neutralization of the hydroxylamine-free base in an aqueous solution with NTO [559].

The hydroxylammonium salt of 3-nitro-1,2,4-triazol-5-one (HANTO) was synthesized by the reaction of 3-nitro-1,2,4-triazol-5-one with NaOH and then with hydroxylammonium chloride [560]. The structure was confirmed by  $^{13}\text{C}$  NMR, IR, MS, elemental analysis, and XRD. HANTO crystals are triclinic, space group  $P\bar{1}$  with crystal unit cell parameters  $a = 0.662.5(2)$  nm,  $b = 0.712.4(4)$  nm,  $c = 0.722.1(3)$  nm,  $\alpha = 68.46(4)^\circ$ ,  $\beta = 71.36(3)^\circ$ ,  $\gamma = 67.50(3)^\circ$ ,  $V = 0.286.4(2)$  nm<sup>3</sup>,  $\rho_c = 1.891$  g/cm<sup>3</sup>, and  $Z = 2$ . There are intramolecular and intermolecular hydrogen bonds in the HANTO crystal.

### Hydrazinium Salts of NTO

The hydrazinium salt of NTO,  $\text{N}_2\text{H}_5^+[\text{C}_2\text{H}_1\text{N}_4\text{O}_3^-]$ ,  $\text{C}_2\text{H}_6\text{N}_6\text{O}_3$ , HNTO,  $M = 162.108$  g/mol, is very soluble in water. Twelve salts of 3-nitro-1,2,4-triazol-5-one (ammonium, hydrazinium, guanidinium, aminoguanidinium, diaminoguanidinium, triaminoguanidinium, *N*-carbamoylguanidinium, semicarbazidium, 1,5-diamino-1,2,4-tetrazolium, 3,4,5-triamino-1,2,4-triazolium, 3,6,7-triamino-7*H*-[1,2,4]triazolo-[1,5-*c*][1,2,4]triazol-2-ium, and 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium) were synthesized and fully characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, and elemental analysis [561]. The crystal structures of two salts were determined by single-crystal XRD. All energetic salts except one exhibited excellent thermal stability, with decomposition temperatures ranging from 476 to 543 K (203 to 270 °C). The densities of salts ranged from 1.65 to 1.88 g/cm<sup>3</sup>, as measured by a gas pycnometer. Theoretical performance calculations yielded predicted detonation pressures and detonation velocities for the energetic salts, which ranged from 24.4 to 38.1 GPa and 8136 to 9575 m/s, respectively. Hydrazinium(1+) 3-nitro-1,2,4-triazol-5-onate in particular had an outstanding detonation performance ( $P_{\text{CJ}} = 38.1$  GPa,  $v_{\text{Det}} = 9575$  m/s) with a satisfactory acidity

compared to that of NTO ( $pK_a = 5.63$  versus  $pK_a = 2.37$ ). Table 39 gives a summary of the properties of ammonium and hydrazinium 3-nitro-1,2,4-triazole-5-onate and several other NTO salts of nitrogen-containing bases.

Hydrazinium(1+) 3-nitro-1,2,4-triazol-5-onate can be prepared by the reaction of 3-nitro-1,2,4-triazol-5-one in ethanol with hydrazine hydrate in ethanol. Its structure can be characterized by employing elemental analysis, FTIR, XRD,  $^{13}\text{C}$  NMR, and  $^{15}\text{N}$  NMR [562]. The formation of HNTO is due to proton transfer from the N(4) atom, and it makes a higher nitrogen content and lower acidity than NTO. The non-isothermal reaction kinetics of the main exothermic decomposition reaction of HNTO were investigated by DSC. The decomposition reaction mechanism of HNTO with  $E_a = 195.29 \text{ kJ/mol}$  and  $\log A = 19.37 \text{ s}^{-1}$  can be expressed by the equation

$$\frac{d\alpha}{dt} = 10^{18.97} (1 - \alpha) [-\ln(1 - \alpha)]^{\frac{3}{5}} e^{(-2.35 \times 10^4/T)}.$$

The critical temperature of the thermal explosion was 464–474 K, the adiabatic time-to-explosion was 262 s, the impact sensitivity was  $H_{50} = 45.7 \text{ cm}$ , and the electrostatic spark discharge sensitivity was  $E_{50} > 5.4 \text{ J}$  (no ignition). The heat capacity of HNTO for the temperature range  $283 \text{ K} < T < 353 \text{ K}$  can be expressed by the equation

$$C_p = 0.1839 + 1.9966 \times 10^{-3} T$$

where  $C_p$  is the heat capacity in  $\text{J g}^{-1} \text{ K}^{-1}$  and  $T$  is the temperature in kelvin. The standard molar heat capacity  $C_p$  at 298.15 K was determined as  $79.44 \text{ J mol}^{-1} \text{ K}^{-1}$ .

The thermal decomposition mechanism of hydrazinium 3-nitro-1,2,4-triazol-5-onate (HNTO) was studied by DSC, TGA-DTG, and *in-situ* thermolysis/reflectance spectroscopy-FTIR (RSFTIR) [563]. The decomposition of HNTO was later simulated by MO quantum mechanical calculations. The results predicted that HNTO has two exothermic decomposition reaction stages. First, the nitro group breaks away from the HNTO molecule. Following this, the hydrazine group breaks away almost simultaneously with the carbonyl group, accompanying the azole ring which breaks in the first stage, which is then followed by second stage disintegration. The order of C–N bond strength is  $\text{C3–N4} > \text{N2–C3} > \text{N4–C5} > \text{N1–C5}$ . The weakest bond in NTO<sup>−</sup> is the N7–C3 bond.

A co-crystallized oxidizer composed of hydrazinium 3-nitro-1,2,4-triazol-5-onate (HNTO) and AN was synthesized by a solvent evaporation method [564]. The formation of co-crystals was confirmed by SEM, powder XRD, IR, and Raman spectroscopies. Compared to pure HNTO and AN, the co-crystals crystallized into a new polymorphic form and exhibited a reduced sensitivity to friction and impact. The DSC analysis showed the complete absence of all temperature-dependent phases of AN in the new co-crystal. This material can be used as a potential oxidizer for composite solid propellant formulations.



Table 39: Properties of NTO salts of nitrogen-containing inorganic and organic bases.

| Compound        | Compound name                                                               | Gross formula                                                 | T <sub>dec</sub><br>°C | ρ<br>g/cm <sup>3</sup> | ΔH <sub>f</sub><br>kJ/mol | OB<br>% | IS<br>J | P <sub>Cl</sub><br>GPa | v <sub>bet</sub><br>m/s | FS<br>N |
|-----------------|-----------------------------------------------------------------------------|---------------------------------------------------------------|------------------------|------------------------|---------------------------|---------|---------|------------------------|-------------------------|---------|
| 1               | Ammonium 3-nitro-1,2,4-triazol-5-onate                                      | C <sub>2</sub> H <sub>5</sub> N <sub>5</sub> O <sub>3</sub>   | 270                    | 1.68                   | 134.4                     | -38.0   | >40     | 28.7                   | 8518                    | 360     |
| 2               | Hydrazinium(1+) 3-nitro-1,2,4-triazol-5-onate                               | C <sub>2</sub> H <sub>6</sub> N <sub>6</sub> O <sub>3</sub>   | 203                    | 1.84                   | 279.1                     | -39.4   | 7       | 38.1                   | 9575                    | 360     |
| 3               | Guanidinium 3-nitro-1,2,4-triazol-5-onate                                   | C <sub>3</sub> H <sub>7</sub> N <sub>7</sub> O <sub>3</sub>   | 260                    | 1.66                   | 122.1                     | -54.9   | >40     | 24.4                   | 8145                    | 240     |
| 4               | Aminoguanidinium 3-nitro-1,2,4-triazol-5-onate                              | C <sub>3</sub> H <sub>8</sub> N <sub>8</sub> O <sub>3</sub>   | 226                    | 1.72                   | 211.6                     | -54.8   | >40     | 28.1                   | 8653                    | 360     |
| 5               | Diaminoguanidinium 3-nitro-1,2,4-triazol-5-onate                            | C <sub>3</sub> H <sub>9</sub> N <sub>9</sub> O <sub>3</sub>   | 212                    | 1.72                   | 329.9                     | -54.7   | 10      | 29.7                   | 8867                    | 80      |
| 6               | Triaminoguanidinium 3-nitro-1,2,4-triazol-5-onate                           | C <sub>3</sub> H <sub>10</sub> N <sub>10</sub> O <sub>3</sub> | 198                    | 1.65                   | 450.4                     | -54.7   | 7       | 27.9                   | 8677                    | 360     |
| 7               | N-carbamoylguanidinium 3-nitro-1,2,4-triazol-5-onate                        | C <sub>4</sub> H <sub>8</sub> N <sub>8</sub> O <sub>4</sub>   | 235                    | 1.88                   | -92.3                     | -55.1   | >40     | 29.5                   | 8725                    | 160     |
| 8               | Semicarbazidium 3-nitro-1,2,4-triazol-5-onate                               | C <sub>3</sub> H <sub>7</sub> N <sub>7</sub> O <sub>4</sub>   | 202                    | 1.66                   | 85.7                      | -42.9   | 10      | 25.6                   | 8181                    | 360     |
| 9               | 3,5-Diamino-1,2,4-triazolium 3-nitro-1,2,4-triazol-5-onate                  | C <sub>4</sub> H <sub>7</sub> N <sub>9</sub> O <sub>3</sub>   | 252                    | 1.74                   | 329.3                     | -59.3   | >40     | 26.8                   | 8439                    | 360     |
| 10              | 3,4,5-Triamino-1,2,4-triazolium 3-nitro-1,2,4-triazol-5-onate               | C <sub>4</sub> H <sub>8</sub> N <sub>10</sub> O <sub>3</sub>  | 260                    | 1.72                   | 451.8                     | -58.9   | >40     | 27.8                   | 8574                    | 324     |
| 11              | 3,6,7-Triamino-7H-[1,2,4]triazolo[5,1-c][1,2,4]triazol-2-ium                | C <sub>5</sub> H <sub>8</sub> N <sub>12</sub> O <sub>3</sub>  | 263                    | 1.69                   | 686.8                     | -62.0   | >40     | 24.6                   | 8136                    | 360     |
| 12              | 3-nitro-1,2,4-triazol-5-onate                                               |                                                               |                        |                        |                           |         |         |                        |                         |         |
|                 | 4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazolium 3-nitro-1,2,4-triazol-5-onate | C <sub>8</sub> H <sub>12</sub> N <sub>18</sub> O <sub>6</sub> | 230                    | 1.74                   | 797.7                     | -56.1   | >40     | 24.6                   | 8389                    | 360     |
| For comparison: |                                                                             |                                                               |                        |                        |                           |         |         |                        |                         |         |
| NTO             | 3-Nitro-1,2,4-triazol-5-one                                                 | C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>   | 275                    | 1.92                   | -237.8                    | -24.6   | >40     | 31.1                   | 8558                    | 360     |
| CL-20           | 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane                  | C <sub>6</sub> H <sub>2</sub> N <sub>12</sub> O <sub>12</sub> | 210                    | 2.04                   | 438.2                     | -10.9   | 4       | 43                     | 9650                    | 94      |
| TATB            | 1,3,5-Triamino-2,4,6-trinitrobenzene                                        | C <sub>6</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>   | 330                    | 1.93                   | -154.2                    | -55.8   | 50      | 31.2                   | 8114                    | >360    |
| RDX             | 1,3,5-Trinitro-1,3,5-triazacyclohexane                                      | C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>   | 230                    | 1.82                   | 92.6                      | -21.6   | 7       | 34.9                   | 8748                    | 120     |

Data source: [561].

### Alkylamine Salts of NTO

The crystal structure of the ethylenediammonium salt (ENTO) of 3-nitro-1,2,4-triazol-5-one,  $(\text{CH}_2\text{NH}_3)_2 \bullet 2\text{C}_2\text{N}_4\text{O}_3\text{H}$ ,  $M = 320.22 \text{ g/mol}$ , was determined by XRD [565]. The crystals are triclinic, space group  $P\bar{1}$ , with unit cell parameters of  $a = 6.528 \text{ \AA}$ ,  $b = 10.780 \text{ \AA}$ ,  $c = 14.236(3) \text{ \AA}$ ,  $\alpha = 81.11^\circ$ ,  $\beta = 87.13^\circ$ ,  $\gamma = 74.05^\circ$ ,  $V = 951.73 \text{ \AA}^3$ ,  $Z = 3$ , and  $\rho = 1.676 \text{ g/cm}^3$ . There are 1.5 formula units in the asymmetric unit.

The thermal stability of 15 ring-substituted arylammonium salts of NTO was studied by dynamic and isothermal TGA, DTA, and explosion delay measurements [566]. Some of the salts were found to dissociate and liberate amine by N–H bond heterolysis prior to explosion, whereas in other cases, the amine part was not liberated. However, the evolution of  $\text{NO}_2$  seemed to accelerate explosions. When heated in air, the oxidation-reduction reactions near the surface of thermolyzing materials may be responsible for the decomposition of these salts prior to explosion.

The dimethylammonium salt of NTO  $[(\text{CH}_3)_2\text{NH}_2^+][\text{C}_2\text{N}_4\text{O}_3\text{H}^-]$  was prepared by mixing 3-nitro-1,2,4 triazol-5-one (NTO) ethanol solution and dimethylamine aqueous solution [567]. Single crystals suitable for XRD measurement were obtained by recrystallization from the mixed solvents of dimethyl formamide and methanol at room temperature. The crystal is monoclinic, space group  $P2_1/c$ , with crystal parameters of  $a = 0.7116(1) \text{ nm}$ ,  $b = 0.8735(2) \text{ nm}$ ,  $c = 1.3160(3) \text{ nm}$ ,  $\beta = 101.12(2)^\circ$ ,  $V = 0.8026(3) \text{ nm}^3$ ,  $\rho_c = 1.450 \text{ g/cm}^3$ , and  $Z = 4$ . A theoretical investigation of  $[(\text{CH}_3)_2\text{NH}_2^+][\text{C}_2\text{N}_4\text{O}_3\text{H}^-]$  as a structure unit was carried out by quantum mechanical methods. The atomic net charge distribution and electron population analysis were calculated.

The dimethylamine salt of 3-nitro-1,2,4-triazol-5-one,  $[(\text{CH}_3)_2\text{NH}_2^+][\text{C}_2\text{N}_4\text{O}_3\text{H}^-]$ , can be prepared by simply mixing NTO ethanol solutions and dimethylamine aqueous solutions [568]. Single crystals suitable for XRD measurement were obtained by recrystallization with the mixed solvent of methanol and dimethyl formamide ( $v/v = 5:1$ ) at room temperature. The crystals were monoclinic, space group  $P2_1/c$ , with crystal unit cell parameters of  $a = 0.7116(1) \text{ nm}$ ,  $b = 0.8735(2) \text{ nm}$ ,  $c = 1.3160(3) \text{ nm}$ ,  $\beta = 101.12(2)^\circ$ ,  $V = 0.8026(3) \text{ nm}^3$ ,  $\rho_{\text{calc}} = 1.450 \text{ g/cm}^3$ , and  $Z = 4$ . The melting enthalpy ( $\Delta H_m$ ) and melting entropy ( $\Delta S_m$ ) of dimethylamine salt of 3-nitro-1,2,4-triazol-5-one were  $14.94 \pm 0.51 \text{ kJ/mol}$  and  $32.37 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. The apparent activation energy and the pre-exponential constants of the exothermic decomposition reactions were  $109.84 \text{ kJ/mol}$  and  $10^{9.41} \text{ s}^{-1}$ , respectively.

The heat capacity of the dimethylamine salt of 3-nitro-1,2,4-triazole-5-one (DMANTO) was determined by a continuous  $C_p$  mode with a microcalorimeter [569]. The heat capacity of DMANTO as a function of temperature is

$$C_p = 2.8884 \times 10^2 + 3.2774T$$

where  $C_p$  is the molar heat capacity in  $\text{J kg}^{-1} \text{ K}^{-1}$  and  $T$  is the temperature in kelvin. The relationships between specific heat capacity and thermodynamic functions, enthalpy, entropy, and Gibbs free-energy of DMANTO in the range from 283 to 353 K (which is relative to the standard temperature of 298.15 K) were calculated. Using the relationship

between  $C_p$  and  $T$  and the thermal decomposition parameters, the adiabatic time-to-explosion of DMANTO was predicted to be between 13.45 and 13.67 s.

Four amine salts of 3-nitro-1,2,4-triazol-5-one (NTO) were prepared from inexpensive raw materials [570]. The ethylenediamine, hydrazinium, and ammonium salts of NTO were synthesized by mixing a solution of NTO with ethylenediamine, hydrazine hydrate, or ammonium carbonate, respectively. The hydroxylammonium salt of NTO was prepared in two steps by first reacting an aqueous solution of NTO with NaOH, then with hydroxylammonium chloride. The crystals were recrystallized from water/ethanol solutions. The structures of compounds were confirmed by IR,  $^{13}\text{C}$  NMR, and elemental analyses. The thermal stabilities of the four amine salts of NTO were studied by DSC-TG, VST, and a thermal explosion test. The thermal stability of the ethylenediamine salt was superior to hydroxylammonium salt and hydrazine salt, while the stability of the ammonium was the most inferior.

### Guanidine and Guanidine Derivative Salts of NTO

The properties of many salts of NTO with guanidine and aminoguanidines have already been listed in Table 33. The diaminoguanidinium salt of 3-nitro-1,2,4-triazol-5-one,  $M = 219.16$  g/mol, was prepared via an ion exchange method and crystallized from the aqueous solution [571]. The crystals were triclinic, space group  $P\bar{1}$ , with unit cell parameters of  $a = 6.735(2)$  Å,  $b = 6.753(2)$  Å,  $c = 9.844(2)$  Å,  $\alpha = 88.29(2)^\circ$ ,  $\beta = 77.17(2)^\circ$ ,  $\gamma = 86.50(2)^\circ$ ,  $V = 435.7$  Å<sup>3</sup>,  $Z = 2$ , and  $\rho_{\text{XRD}} = 1.671$  g/cm<sup>3</sup>.

The aminoguanidinium salt of NTO (AGNTO) was prepared by mixing aminocarbamide bicarbonate and 3-nitro-1,2,4-triazol-5-one [572]. The product was characterized by elemental analysis and IR spectra. The crystal structure of AGNTO was determined by single-crystal XRD. The crystal shape is monoclinic and belongs to space group  $P2_1/n$ . Crystallographic data are  $a = 0.67870(10)$  nm,  $b = 2.7915(4)$  nm,  $c = 1.2739(2)$  nm;  $\beta = 96.930(10)^\circ$ ,  $V = 2.3959(6)$  nm<sup>3</sup>,  $Z = 12$ , and  $\rho_c = 1.698$  g/cm<sup>3</sup>. This salt would be a very promising energetic material and it could be used as a constituent in gas-generating formulations.

The monohydrate of the salt formed by carbonylhydrazide with 3-nitro-1,2,4-triazol-5-one (NTO) was prepared by mixing aqueous solutions of carbonylhydrazide and NTO and crystallizing slowly from the concentrated solution [573]. The crystalline product was characterized by elemental analysis and IR spectroscopy. The crystal structure was determined by single-crystal XRD. The crystal shape is triclinic and belongs to space group  $P$ , with  $a = 6.639(1)$  Å,  $b = 11.481(1)$  Å,  $c = 13.692(2)$  Å,  $\alpha = 70.56(1)^\circ$ ,  $\beta = 88.19(1)^\circ$ ,  $\gamma = 77.03(1)^\circ$ ,  $V = 958(2)$  Å<sup>3</sup>,  $Z = 4$ , and  $\rho_c = 1.651$  g/cm<sup>3</sup>. This salt is an ionic compound composed of one carbonylhydrazide (CHZ) cation and one NTO anion.

The diaminoguanidinium salt of NTO (DAGNTO) was prepared by mixing NaNTO aqueous solutions and diaminoguanidinium chloride aqueous solutions [574]. Single crystals suitable for X-ray measurement were obtained by recrystallization from water at room temperature. The crystal shape is triclinic and belongs to space

group  $P\bar{I}$ , with crystal unit cell parameters of  $a = 0.6732(3)$  nm,  $b = 0.6745(3)$  nm,  $c = 0.9840(4)$  nm,  $\alpha = 88.309(7)^\circ$ ,  $\beta = 77.255(6)^\circ$ ,  $\gamma = 86.520(7)^\circ$ ,  $V = 4.349(3)$  nm<sup>3</sup>,  $Z = 2$ , and  $\rho_c = 1.674$  g/cm<sup>3</sup>. Theoretical investigations of DAGNTO as a structural unit were performed by MO quantum chemistry methods. The apparent activation energy and pre-exponential constant of the exothermic decomposition reaction of DAGNTO were predicted to be 112.15 kJ/mol and  $10^{9.603}$  s<sup>-1</sup>, respectively. The critical temperature of thermal explosion was predicted as 481.7 K (208.6 °C).

The guanidinium salt of 3-nitro-1,2,4-triazol-5-one (GNTO) was synthesized by the reaction of NaNTO and guanidinium chloride solutions in water at 333 K (60 °C) [575]. The thermal stability and non-isothermal decomposition kinetics of GNTO were examined by DSC and TGA/DTG. The kinetic equation governing the decomposition of GNTO is

$$\frac{da}{dT} = 10^{23.71} (1-a)^{\frac{2}{3}} \left[ 1 - (1-a)^{\frac{1}{3}} \right]^{\frac{1}{2}} \exp(-2.602 \times 10^5 / RT).$$

The critical temperature of thermal explosion was predicted as 529.44 K (256.29 °C). The specific heat of GNTO was determined using a micro-DSC method and the standard molar specific heat capacity was 236.88 J mol<sup>-1</sup> K<sup>-1</sup> at 298.15 K. The calculations predicted an adiabatic time-to-explosion of GNTO as 102 s.

The guanilylurea salt of 3-nitro-1,2,4-triazol-5-one (GUNTO) was synthesized from guanilylurea hydrochloride and NTO as starting materials with total yields of over 85% [576]. Its structure was characterized by IR, NMR, MS, elemental analysis, and XRD. Calculation results showed that with a real density of 1.72 g/cm<sup>3</sup> and a calculated enthalpy of formation of -347.35 kJ/mol, the theoretical detonation velocity and detonation pressure predicted by the Kamlet formulas were 6683 m/s and 19.27 GPa, respectively. The material was insensitive to impact and friction and the drop height of impact sensitivity H50 was more than 125.8 cm. The exotherm peak temperature of the DSC thermogram at a heating rate of 10 °/min was 509.9 K (236.8 °C). In comparison with other amine salts of NTO, GUNTO has higher nitrogen content, better thermal stability, and lower sensitivity.

### Heterocyclic Amine Salts of NTO

3-Nitro-1,2,4-triazole-5-one forms energetic salts with several organic, nitrogen-rich bases. Many energetic salts composed strictly of azolium cations and azolate anions (e.g., 3-nitro-1,2,4-triazolate-5-one [NTO], 5-nitroimino-tetrazolate, 3-nitro-5-trifluoromethyl-1,2,4-triazolate, 3,5-dinitro-1,2,4-triazolate, 4,5-dinitro-imidazolate, 3,5-dinitro-pyrazolate, and 5-nitro-tetrazolate) were synthesized and characterized [577]. Most of the salts exhibited good physical properties, which include relatively high densities (1.38–1.75 g/cm<sup>3</sup>), high positive HOFs, and moderate detonation properties. Properties of the salts derived from heterocyclic amines with NTO and several other nitrotriazoles and nitrotetrazole are summarized in Table 40.

Table 40: Properties of salts derived from heterocyclic amines and nitroheterocyclic compounds.

| Compound name                                               | T <sub>m</sub> |     | T <sub>dec</sub> |     | D                 | OB   | N    | $\Delta H_f$ | P     | D    | I <sub>sp</sub> |
|-------------------------------------------------------------|----------------|-----|------------------|-----|-------------------|------|------|--------------|-------|------|-----------------|
|                                                             | K              | °C  | K                | °C  | g/cm <sup>3</sup> | %    | %    | kJ/mol       | gPa   | m/s  | s               |
| 3-Amino-1,2,4-triazolium 3-nitro-1,2,4-triazolate-5-one     | 515            | 242 | 515              | 242 | 1.71              | -60  | 52.3 | +363.6       | +1.7  | 24.8 | 8021 223        |
| 1-Amino-1,2,4-triazolium 3-nitro-1,2,4-triazolate-5-one     | 344            | 71  | 461              | 188 | 1.67              | -60  | 52.3 | +498.8       | +2.33 | 24.8 | 7973 238.3      |
| 4-Amino-1,2,4-triazolium 3-nitro-1,2,4-triazolate-5-one     | 404            | 131 | 448              | 175 | 1.68              | -60  | 52.3 | +497.8       | +2.32 | 25.1 | 8016 238.2      |
| 1-Methyl-5-amino-tetrazolium 3-nitro-1,2,4-triazolate-5-one | 460            | 187 | 475              | 202 | 1.65              | -59  | 55   | +502.5       | +2.19 | 24.4 | 8010 233.9      |
| 3-Amino-1,2,4-triazolium 3,5-dinitro-1,2,4-triazolate       | 422            | 149 | 453              | 180 | 1.72              | -43  | 51.9 | +274.1       | +1.13 | 25.2 | 7945 219        |
| 1-Amino-1,2,4-triazolium 3,5-dinitro-1,2,4-triazolate       | 440            | 167 | 474              | 201 | 1.72              | -43  | 51.9 | +406.2       | +1.67 | 26.5 | 8054 233.7      |
| 4-Amino-1,2,4-triazolium 3,5-dinitro-1,2,4-triazolate       | 399            | 126 | 449              | 176 | 1.69              | -43  | 51.9 | +408.2       | +1.68 | 25.4 | 7930 234        |
| 1-Methyl-5-amino-tetrazolium 3,5-dinitro-1,2,4-triazolate   | 412            | 139 | 468              | 195 | 1.63              | -43  | 54.3 | +413.7       | +1.6  | 23.5 | 7763 229.8      |
| 3-Amino-1,2,4-triazolium 5-nitro-tetrazolate                | 424            | 151 | 470              | 197 | 1.63              | -52  | 63.3 | +409.2       | +2.06 | 22.6 | 7865 219.2      |
| 5-Amino-tetrazolium 5-nitro-tetrazolate                     | 432            | 159 | 436              | 163 | 1.75              | -32  | 70   | +571.4       | +2.86 | 31.4 | 8843 246        |
| 1,5-Diamino-tetrazolium 5-nitro-tetrazolate                 | 401            | 128 | 434              | 161 | 1.71              | -33  | 71.6 | +650.8       | +3.03 | 30.7 | 8844 249.2      |
| 4-Amino-1,2,4-triazolium 5-nitroimino-tetrazolate           | 416            | 143 | 457              | 184 | 1.72              | -52  | 65.4 | +440.6       | +2.06 | 27   | 8506 218.9      |
| 5-Amino-tetrazolium 5-nitroimino-tetrazolate                | 438            | 165 | 438              | 165 | 1.63              | -33  | 71.6 | +487.5       | +2.27 | 25.5 | 8276 229        |
| 1,2,4-Triazolium 5-nitroimino-tetrazolate                   | 450            | 177 | 450              | 177 | 1.74              | -52  | 63.3 | +328         | +1.65 | 26   | 8334 208.7      |
| 1-Propyl-1,2,4-triazolium 5-nitroimino-tetrazolate          | 342            | 69  | 395              | 122 | 1.48              | -103 | 52.3 |              |       |      |                 |
| 3-Azido-1,2,4-triazolium 5-nitroimino-tetrazolate           | 362            | 89  | 408              | 135 | 1.68              | -40  | 70   | +694.2       | +2.89 | 25.9 | 8230 233.5      |
| 4-Amino-1,2,4-triazolium 4,5-dinitro-imidazole              | 410            | 137 | 422              | 149 | 1.65              | -59  | 46.3 | +354.4       | +1.48 | 23.6 | 7383 221.1      |
| 4-Amino-1,2,4-triazolium 5-nitro-tetrazolate                | 375            | 102 | 463              | 190 | 1.58              | -52  | 63.3 | +545.2       | +2.77 | 23.1 | 7792 233.7      |
| Ammonium 5-nitroimino-tetrazolate                           |                |     |                  |     | 1.65              | -27  |      | +83.9        | +0.57 | 27.1 | 8536 219.2      |
| 3-Nitro-1,2,4-triazole-5-one                                | 543            | 270 |                  |     | 1.93              | -25  |      | -101         | -0.78 | 33.4 | 8655 210.5      |
| 5-Nitro-amino-tetrazole                                     |                |     |                  |     | 2.06              | -12  |      | +252.3       | +1.94 | 48.5 | 10358 257.6     |

Data source: [577].

The crystals of the 3-amino-1,2,4-triazolium salt of 3-nitro-1,2,4-triazol-5-one, with  $M = 214.2 \text{ g/mol}$ , are monoclinic and belong to space group  $P2_1/c$ , with unit cell parameters of  $a = 6.539(2) \text{ \AA}$ ,  $b = 19.063(8) \text{ \AA}$ ,  $c = 6.749(4) \text{ \AA}$ ,  $\beta = 94.31^\circ$ ,  $V = 838.9(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{pyc}} = 1.716 \text{ g/cm}^3$ , and  $\rho_{\text{XRD}} = 1.700 \text{ g/cm}^3$  [578]. The amine groups are planar with the five-membered ring of 1,2,4-triazole, the dihedral angles between cations and anions are  $172.9^\circ$ , and the nitro groups are rotated  $4.2^\circ$  out of the plane of the triazolone. The proton is linked, not at the amine group, but the 4-position of 3-ATA. The charge of the anions is mainly concentrated at the N4 atom of NTO. All H atoms except those on the C atom are involved in hydrogen bonds.

A salt from 3,3-dinitroazetidine (DNAZ) and 3-nitro-1,2,4-triazol-5-one (NTO) was prepared by mixing DNAZ and NTO in ethanol solutions [579]. Single crystals suitable for XRD measurement were obtained, which belong to monoclinic, space group  $P2_1/n$ , with unit cell parameters of  $a = 1.4970(4) \text{ nm}$ ,  $b = 0.6325(2) \text{ nm}$ ,  $c = 2.2347(7) \text{ nm}$ ,  $\beta = 96.55(1)^\circ$ ,  $V = 2.1022(11) \text{ nm}^3$ ,  $\rho_c = 1.752 \text{ g/cm}^3$ , and  $Z = 8$ . Based on the analysis of the molecule structure, a theoretical investigation of the title compound was carried out and a natural atomic charge and NBO analysis were performed. The thermal stability of DNAZ • NTO was measured by DSC and TGA/DTG, yielding the apparent activation energy ( $E_a$ ) and pre-exponential constant ( $A$ ) of the main exothermic decomposition reaction.

The thermal behavior of NTO-DNAZ was studied under a non-isothermal condition by DSC and TGA/DTG methods [580]. The kinetic parameters were obtained from the analysis of the DSC and TG/DTG curves using the Kissinger method, the Ozawa method, the differential method, and the integral method. The main exothermic decomposition reaction mechanism of NTO • DNAZ was classified as a chemical reaction. The kinetic parameters of the reaction were  $E_a = 149.68 \text{ kJ/mol}$  and  $A = 10^{15.81} \text{ s}^{-1}$ . The standard specific heat capacity of NTO • DNAZ was  $352.56 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $298 \text{ K}$ .

The salts formed from *N,N*-dialkyl imidazole ( $\text{Cx-im}$ ,  $x = 3, 4, 5, 6$ ) for the cation and 3-nitro-1,2,4-triazole-5-one (NTO) for the anion have very low melting points and qualify as ionic liquids [581]. Their structures were identified by IR,  $^1\text{H}$  NMR, and elemental analysis. Their density, solubility, viscosity, and thermal properties were measured. The results showed that NTO-alkyl imidazolium ionic liquids dissolve in acetonitrile, dimethylformamide (DMF), dimethylsulfoxide (DMSO), and other organic solvents with a larger dielectric constant. Their density was greater than  $1.897 \text{ g/cm}^3$  and thermal transition temperatures of solid phase to liquid phase was less than  $238.7 \text{ K}$  ( $-34.4^\circ\text{C}$ ). The temperatures of 5% mass loss were about  $493 \text{ K}$  ( $220^\circ\text{C}$ ), having better thermal stability than some of the other EILs. A new ionic compound  $(3\text{-ATz})^+(\text{NTO})^-$  was synthesized by the reaction of 3-amino-1,2,4-triazole (3-ATz) with NTO in ethanol.

#### 8.14.3.4 Analysis Methods and Specifications of NTO

The assay of NTO can be determined by non-aqueous volumetric titration with a standardized solution of sodium methanolate in methanol [582]. The standard deviation was 0.16% after more than 20 repeated titrations on the same sample.

A silver nano-film was used as the surface-enhanced Raman spectroscopy (SERS) substrate for the analysis of NTO in aqueous solutions [583]. The detection limits of NTO in deionized (DI) water and aged tap water were 35 µg/L (0.35 ng) and 0.35 mg/L (3.5 ng), respectively. pH variation in the range of 4.7 to 9.1 did not affect the position of SERS NTO bands but affected the band intensity. The effect of eight common ions in natural waters on the SERS of 3.5 mg/L NTO was evaluated.  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  at 100 mg/L did not have a significant negative effect on the SERS of 3.5 mg/L NTO because NTO has a stronger affinity for the silver nano-film than the cations do. High chloride ion concentrations did interfere.

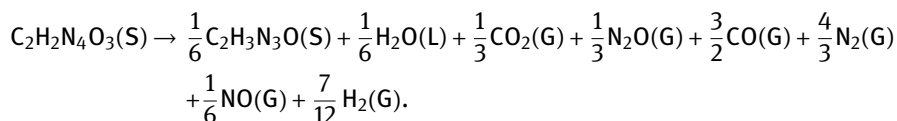
#### 8.14.3.5 Thermal Stability and Decomposition of NTO

##### Slow Thermal Decomposition of NTO

While information about the decomposition products of energetic materials is valuable for specifying the reaction pathways, kinetic constants are essential to describe burning or explosion processes. However, it is very difficult to acquire these data under such rapid phenomenon conditions. The rate of decomposition of NTO has been determined in the temperature range of slow, gradual thermal decomposition by IR spectroscopy, TGA, DTA [584], DSC [525], nitric oxide chemiluminescence [585], the analysis of the concentrations following partial decomposition in a sealed tube [586], and also with a study of isotope effects [587–590]. The rates obtained by these methods yielded activation energies ranging from  $E_a = 170$  to 502 kJ/mol ( $E_a = 40.7$  to 120 kcal/mol). However, when the value of  $E_a$  is plotted against its pre-exponential ( $\ln A$ ) counterpart, most of these pairs produce points that lie on or are close to a single line as shown for NTO and other explosives [591]. This coincidence is frequently referred to as the “kinetic compensation effect.” That is, an increase in  $E_a$  does not reduce the rate correspondingly because of an offsetting increase in the  $A$  factor. Consequently, widely scattered values of Arrhenius parameters for a heterogeneous global decomposition process may produce the same rate at a given temperature (i.e., they are isokinetic) but will predict very different rates. It is evident that considerable care must be exercised when determining and interpreting the kinetic constants for the decomposition of a volatile energetic compound such as NTO. In the unconfined state, the kinetic constants may be a mixture of the rates of sublimation and decomposition, the balance of which shifts with changes in the experimental conditions. With appropriate precautions, these two dominating processes may be separated and independently investigated. If a mathematical expression for the thermal decomposition rate of NTO is desired, then the kinetics which yield activation energies in the vicinity of 326–351 kJ/mol (78–87 kcal/mol)

rather than 188–217 kJ/mol (45–52 kcal/mol) should be used. However, there has been no consensus on the mechanism of thermolysis of NTO for a long period.

The thermal decomposition of NTO was studied using DSC, TGA-MS, and accelerating rate calorimetry (ARC) [592]. In the DSC, no endothermic phase transitions were observed on heating NTO through the temperature program. The DSC spectrum of NTO showed only one peak; a very strong exothermic peak at 508 K (235 °C). In the DTA, an exotherm was observed having an extrapolated onset temperature of 543 K (270 °C) and a broad shoulder beginning at 505 K (232 °C). The decomposition of NTO by TGA proceeded as a two-step reaction. In the TGA thermogram, the onset temperature for rapid decomposition occurred at 543 K (270 °C), 22 minutes into the run. The rate of mass loss was a maximum at 549 K (276 °C), at 23 minutes into the run. The residual solid (at 623 K = 350 °C) amounted to roughly 12% of the original NTO mass. An IR spectrophotometric examination of the residue showed that it was not 1,2,4-triazol-3-one. The gases that evolved during the TGA run (H<sub>2</sub>O, NO, CO<sub>2</sub>) were identified by mass spectroscopy as they were generated. In the ARC, the first exotherm had an onset temperature of 459 K (186 °C) and an adiabatic temperature rise (AT) of 1.6 °C. The associated pressure increase was 0.69 atm and the maximum self-heat rate occurred at 459 K (186 °C). The onset temperature for the second exotherm occurred at 481 K (208 °C). The rapid temperature increase occurred at 485 K (212 °C). As a result of this exotherm, AT was 18 °C and the pressure increase was 10 atm. The maximum self-heat rate was 282 °C/min and occurred at 496 K (223 °C). The chemical equation suggested for the overall net reaction was



It was found that the stability of NTO is sensitive to the thermal age of the sample when the sample was isothermally aged in the ARC bomblet at 458 K (185 °C) for 24 h. Kinetic analysis suggested an auto-catalytic decomposition mechanism.

Electron paramagnetic spectroscopy (EPR) and HPLC were used to examine the decomposition of plain NTO and deuterated NTO during the photochemical and thermochemical decomposition of NTO [590, 593]. Solutions monitored by EPR showed that the NTO nitro group abstracts hydrogen atoms from other species and/or acetone solvent, as evidenced by the observation of EPR spectra with NTO hydroxy nitroxide radicals. The HPLC global kinetic studies conducted between 498 and 518 K showed that the decomposition of NTO may occur by a solid-state autocatalytic reaction scheme for which initiation and propagation contribute to the observed kinetic behavior. The decompositions were found to have an average global activation energy of 368 kJ/mol (88.0 kcal/mol). A primary kinetic deuterium isotope effect of 1.67 (2.44 at 298 K) indicated that nitrogen-hydrogen bond cleavage plays a significant role in the loss of NTO or deuterated NTO.



Under linear temperature increase conditions, the mechanisms and the kinetic parameters of thermal decomposition of NTO and NTO salts of the type  $M(\text{NTO})_m \cdot n\text{H}_2\text{O}$  for  $M = \text{Cu}$ ,  $m = 2$ ,  $n = 4$ ;  $M = \text{Pb}$ ,  $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3$ ,  $m = 2$ ,  $n = 0$ ;  $M = \text{K}$ ,  $\text{NH}_4$ ,  $m = 1$ ,  $n = 1$ , were obtained by TGA, DSC, IR, and XRD [525]. The thermal decomposition processes of the salts were already discussed in other sections of this book.

The critical temperatures of thermal explosion for NTO and its ENTO, KNT0, copper salt (CuNTO), and lead salt (PbNTO) were obtained using the stationary theory of thermal explosion, the calculation formula of estimating the critical temperature of thermal explosion under non-isothermal DSC conditions, and the determination method for the critical temperature of the thermal explosion of small-scale solid explosives and its data treatment method [594, 595]. The results of the four methods were in general agreement with each other and the differences were within 5%. The results indicated that the heat-resistance of NTO and its salts and that of the common explosives (HMX, RDX, PETN, and tetryl) decreases in the order  $\text{HMX} > \text{NTO} > \text{ENTO} > \text{KNT0} > \text{RDX} > \text{PETN} > \text{tetryl} > \text{PbNTO} > \text{CuNTO}$ .

To analyze the thermal sensitivity of a high explosive, it is necessary to understand that the thermal sensitivity can be divided into at least three different regimes: **(1)** molecular sensitivity, **(2)** decomposition sensitivity, and **(3)** the sensitivity to starting a self-sustained reaction. All three regimes were examined as follows: the molecular sensitivity by mass spectroscopy, the thermal stability by DSC and chemiluminescence (CL), the thermal decomposition path by laser-induced mass spectrometry (LI-MS), and the sensitivity to a self-sustained reaction by a laser ignition method. The decomposition of NTO based on the mass spectra of NTO decomposition under the influence of electron impact (EI) 20 and 70 eV electrons and chemical ionization spectra was investigated [585, 596]. The large abundance of the molecular ion in these spectra showed that NTO is a more stable molecule than TNT or RDX. The data acquired for NTO was summarized as a proposed mass spectral fragmentation path. Laser ignition measurements showed a strong pressure dependence, which indicated a multiple-phase (condensed and gas phase) ignition mechanism. The laser ignition measurements also showed that the sensitivity to ignition of NTO is slightly higher than that of TNT. The results of the LI-MS method applied to NTO implied that the probable decomposition path is elimination of  $-\text{NO}_2$  followed by a breaking of the azole ring. The CL method was used for the determination of the activation energy and the frequency factor ( $E_a = 140 \text{ kJ/mol}$ ) and  $A_0 = 5 \times 10^6 \text{ s}^{-1}$  in the temperature interval 373–413 K (100–140 °C). CL data for RDX and TNT were acquired for comparison. The DSC spectrum of NTO showed only one peak; a very strong exothermic peak at 526 K (253 °C). The experimental work was complemented by some quantum mechanical calculations. These were conducted in an attempt to verify the initial steps in the decomposition path and to explain the high stability of NTO.

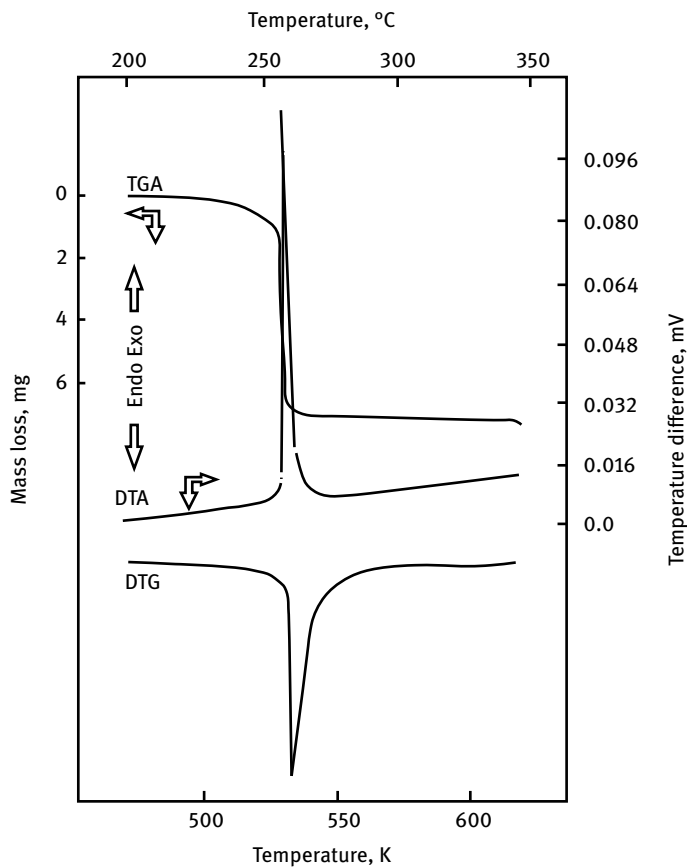
The early reaction chemistry of NTO induced by drop weight impact, shock, heat, and radiation has been investigated by XPS and chemical ionization mass spectrometry.

try (CIMS) to observe and identify the partial decomposition products in the damaged samples [597, 598]. Several reaction intermediates have been identified, the focus of the reaction being the single nitro group present on this molecule. XPS spectra indicated the loss of  $\text{NO}_2$  concentration in response to damage in all cases. Additional chemical states were suggested in the XPS nitrogen N(1s) spectrum by the appearance of a new peak at a binding energy below that of the triazole ring nitrogens. Mass spectrometry provided the molecularly specific information needed to identify molecular fragment species resulting from the decomposition reactions. Relative to the parent NTO molecule, mass peaks were observed that corresponded to the loss of one O atom, an NO fragment, and HONO formation.

To evaluate the hazards posed by NTO, its explosive properties were studied by differential thermal analyses and sensitivity tests [584]. NTO does not have very large exothermicity compared to ordinary explosives but it is classified as a self-reactive material that has shock initiation properties. Its impact sensitivity is not very high but the explosive strength is the same as that of TNT. The thermal decomposition of NTO proceeds according to the model of nucleus formation and growth, which states that germ nuclei grow linearly or two-dimensionally. The apparent activation energy is 219 kJ/mol.

The kinetics and mechanism of the thermal decomposition of NTO have been studied together with its morphology and evolved gaseous products using TGA, DTA, IR, DSC, XRD, and hot-stage microscopy [508]. The crystal belongs to the tetragonal system and has a  $c/a$  ratio of 0.329. The crystal structure unit cell parameters obtained from the XRD pattern were  $a = 20.000 \pm 0.005 \text{ \AA}$ ,  $b = 20.000 \pm 0.005 \text{ \AA}$ , and  $c = 6.573 \pm 0.005 \text{ \AA}$ . The kinetics of the thermolysis has been followed by both isothermal TGA and IR. The best linearity, with a correlation coefficient of 0.9937, was obtained for the Avrami-Erofeev equation,  $n = 3$ , in the range 0–83%  $\alpha$ , using isothermal TGA. A composite of three curves, the DTA, TGA, and DTG thermograms are shown in Figure 12. The TGA data indicated that NTO underwent decomposition in two steps; in the temperature range 524–535 K (251–262 °C) and then from 535 K (262 °C) onwards. The weight loss at the first stage was about 67%. The second stage is slower and results in about 23% mass loss. The DTA does not show any endotherms before the onset of the first exotherm, thus indicating that the compound decomposed without first melting. In DTA, the first exotherm was very sharp and occurred in the range 524–544 K (251–271 °C). The activation energy was found to be 186 kJ/mol, with  $\log(A)$  being  $16.64 \text{ s}^{-1}$ . The effect of a series of additives and metal oxides incorporated to an extent of 5% on the initial thermolysis of NTO has also been studied. Iron(III) oxide, copper(II) oxide, or magnesium oxide accelerated NTO decomposition. Evolved gas analysis (EGA) by IR showed that  $\text{CO}_2$ ,  $\text{NO}_2$ , NO, and  $\text{N}_2\text{O}$  were produced in larger amounts than CO and HCN. The cleavage of the C– $\text{NO}_2$  bond appears to be the primary step in the thermolysis of NTO.

Widely varied Arrhenius parameters have been published for the thermal decomposition of HMX, RDX, and NTO. Evaluation of these data revealed that an approxi-



**Figure 12:** TGA/DTA/DTG Thermograms of NTO decomposition. (Reprinted and modified from [508], with permission from ©1994 Elsevier; permission conveyed through RightsLink.)

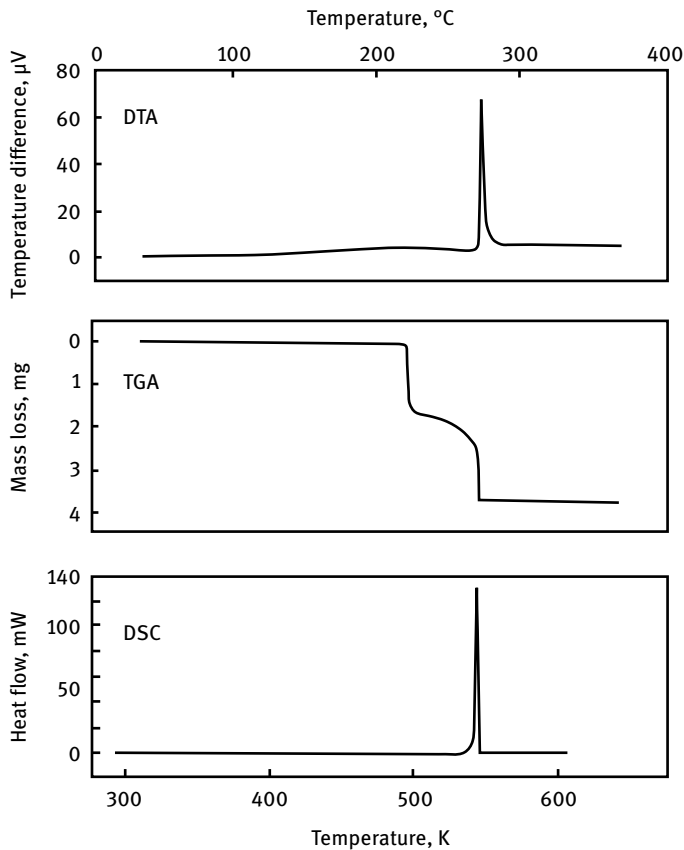
mately linear relationship exists between  $\ln A$  and  $E_a$  for each compound, which is irrespective of the phase [591]. This kinetic compensation effect accounts for and unifies most of the differences in the reported rates. The range of data is qualitatively attributable to differences in the sample characteristics and experimental conditions. All  $E_a \dots \ln A$  sets lying on, or close to, the compensation regression line consistently account for the rate of thermal decomposition under the conditions reported.  $E_a \dots \ln A$  sets not lying on or near the compensation regression line represent a different process, or are incorrect. The kinetic compensation effect provides a rational method to select Arrhenius parameters and eliminate bad data to describe the global thermal decomposition rate of an energetic material.

The thermal decomposition of NTO and other energetic materials was examined by DSC and DTA/TGA [599]. The results are summarized in Table 41 and are illustrated in Figure 13.

**Table 41:** DSC and DTA/TGA of 3-nitro-1,2,4-triazol-5-one (NTO).

| DSC                  | Temper-<br>ature,<br>°C | DTA/TG                   | Temper-<br>ature,<br>°C | Effect                           |
|----------------------|-------------------------|--------------------------|-------------------------|----------------------------------|
| $T_{\max}$           | 272/273                 | $T_{\max}$               | 274/272                 | Decomposition exotherm peak max. |
| $T_{\text{onset}}$   | 252/254                 | $T_{\text{onset}}$       | 255/258                 | Decomposition exotherm onset     |
| $T_{\text{e onset}}$ | 268/269                 | $T_{\text{e onset}}$     | 264/267                 | Extrapolated onset               |
|                      |                         | $T_{\text{mass loss 1}}$ | 216/216                 | Start decomposition              |
|                      |                         | Mass loss 1, %           | 40/18                   | Mass loss 1                      |
|                      |                         | $T_{\text{mass loss 2}}$ | 228/228                 | Start decomposition              |
|                      |                         | Mass loss 2, %           | 51/71                   | Mass loss 2                      |
|                      |                         | Total mass loss, %       | 91/89                   |                                  |
| Exoth. enthalpy      | 635/716                 | Exoth. enthalpy          | 328/345                 | Sublimation enthalpy by DTA      |

Data source: [599].



**Figure 13:** DSC and DTA/TGA results with NTO. (Reproduced and modified from [599].)

An exothermic extrapolated temperature of 542 K (268 °C) and a broad shoulder beginning at 505 K (232 °C) were observed (Figure 13). The residual solid (at 523 K = 350 °C) contained roughly 10% of the original NTO mass. This was in good agreement with [592]. The two stages in the TGA curve were caused by an impurity in the investigated NTO sample. Other analyses had shown that this particular sample was polluted with nitric acid and resulted in a low pH-value. Impurities can result in a different thermogram than would be obtained with a pure chemical substance.

NTO and many other triazole, tetrazole, triazine, tetrazine, furazan, and acyclic backbone compounds were shown by IR spectroscopy to convert to polymeric, melon-like, cyclic azine residues upon heating to  $T \geq 773$  K ( $\geq 500$  °C) [489, 490]. These compounds include NTO, 3-amino-5-nitro-1,2,4-triazole (ANTA), and nitroguanidine. The melon-like residue could suppress the burn rate of solid propellants because they have a high thermal resistance. In clarifying the pyrolysis mechanisms, the IR-active gaseous products from thermolysis were determined as a function of pressure and were related to the atom connectivity in the parent molecules from which they originated.

The thermal decomposition of NTO was examined over the temperature range 493–553 K (220–280 °C) using both neat NTO and NTO in aqueous and methanol solutions [586, 600]. The decomposition of NTO in the presence of TNT was also examined. Activation parameters were calculated for all thermolyses. The Arrhenius plot for NTO in the range 433–553 K (160–280 °C) gave an activation energy of 329 kJ/mol (78.6 kcal/mol) with a pre-exponential coefficient of  $2.53 \times 10^{29}$ . When mixtures of NTO and TNT were decomposed, the decomposition rate of both components was enhanced. Additives such as NO<sub>2</sub>, ammonia, nitric acid, and AN also accelerated the decomposition of NTO and TNT. Decomposition of deuterated NTO (neat and in solution) was noticeably slower than that of proteo-NTO, which is indicative of an intramolecular deuterium kinetic isotope effect. An intermolecular deuterium kinetic isotope effect (DKIE) was also observed when NTO was decomposed in deuterated solvent or a mixture with TNT-d(3). It was concluded that the rate-determining step in at least one NTO thermolysis pathway involved hydrogen transfer to the nitro group, followed by the subsequent loss of HONO. This mechanism is believed to be dominant at low temperatures, while at high temperatures C–NO<sub>2</sub> homolysis is probably a competitive decomposition pathway. It was concluded that TO, while formed in the decomposition of NTO, was not an intermediate in the principal NTO decomposition pathway. Furthermore, while it appeared that NTO and TO promoted TNT decomposition by the same mechanism, hydrogen transfer to a nitro group (the mode by which TNT enhanced the decomposition of the two triazolone rings) differed. The kinetics and products of the decomposition of eight other triazole-like rings were examined for comparison. Thermal stability was related to ring substitution; rings with NO<sub>2</sub> and NH<sub>2</sub> substituents decomposed more rapidly at 543 K (270 °C) than those with O or H

on carbon. Hydrogen transfer to the nitro group of NTO was supported by the observation that only rings substituted with either  $\text{NO}_2$  or  $\text{NH}_2$  exhibited an intermolecular deuterium kinetic isotope effect. For NTO, the DKIE at 543 K (270 °C) was  $r_{\text{H2O}}/r_{\text{D2O}} = 2.1$ .

Isotope labeling not only with deuterium on the two hydrogen atoms of NTO but also with  $^{15}\text{N}$  at the 1- and 2-positions. This was used to identify the weak links in the NTO molecule. The  $^{15}\text{N}$ —H coupling would provide unequivocal assignments for  $^1\text{H}$  and  $^{15}\text{N}$  NMR spectra and the acidic proton. The gas products HCN,  $^{15}\text{N}^{14}\text{N}$ ,  $^{15}\text{N}_2$ , and CO were detected by mass spectrometry [601, 602]. The products of thermal decomposition at 543 K (270 °C) were identified spectroscopically. NMR spectra revealed that thermal decomposition results in the formation of 2,4-dihydro-3H-1,2,4-triazol-3-one and ammonia (the latter was observed as ammonium ion). Solid and gaseous thermal decomposition products of NTO-1,2- $^{15}\text{N}$  were detected by NMR spectroscopy and mass spectrometry, respectively. For the first time, ammonia has been reported as a product. The production of ammonia as a thermal decomposition product from NTO was surprising and it was believed that the major counter anion is the conjugate base of NTO. The yield of ammonia varied from 5 to 10%. The yield of ammonium ion is probably limited by the availability of water for hydrolysis of the C—N group. A stepwise mechanism involving the homolysis of C—N bond followed by ring closure to form  $^{14}\text{N}$ — $^{15}\text{N}$  bond is the most probable mechanism.

The physical and chemical properties of the high explosive NTO have been investigated by IR spectroscopy and thin-film infrared laser pyrolysis to determine the initial chemical steps in the decomposition mechanism [141, 603]. It was found that the initial steps form carbon dioxide by a bimolecular reaction mechanism involving the reaction of two NTO molecules in the crystal. The relative insensitivity of NTO to accidental ignition is attributed to a unique crystal structure that holds reactive groups of the molecules apart from each other and forces disruption of the crystal structure (melting) before a reaction can take place. A similar mechanism has been found to explain the insensitivity of 2,4-dinitroimidazole compared with its structural isomer, 1,4-dinitroimidazole. It was found that NTO has a mechanism of thermal decomposition that is unique among high explosives. Whereas most explosives tend to react by loss of NO (or  $\text{HNO}_2$ ) in a unimolecular reaction, NTO has a bimolecular mechanism in which the nitro group of one molecule reacts with the carbonyl group of another NTO molecule, thereby forming  $\text{CO}_2$  as one of the initial products while still in the condensed phase. This mechanism may explain the low sensitivity of NTO to ignition by impact because the crystal structure is what keeps the groups separated and prevents ignition at temperatures lower than the melting point of NTO (535 K = 262 °C). The melting point is high because the NTO molecules form a hydrogen-bonded network which resists reorganization. It was suggested that the following characteristics may contribute to reducing the sensitivity of high explosives:

- a. bimolecular reaction mechanism (the rate depends on the local structure of the crystal)
- b. crystal structure that effectively separates reactive functional groups
- c. high melting point (preferably involving the formation of a hydrogen-bonded network)

Real-time surface analysis photoionization mass spectra of the shear-induced molecular-fragment emission from NTO were obtained by a surface analysis by laser ionization (SALI) apparatus [604]. Using vacuum UV single-photon ionization, the shear-induced NTO spectra were obtained with a spring-driven shearing device installed in a SALI chamber directly beneath the mass spectrometer sampling region. The shear-induced spectra were dominated by a peak at  $m/e$  99, which is not seen in the thermal or laser desorption spectra. This peak was assigned to the closed-shell triazole-diketone produced by a nitro-nitrite rearrangement and was followed by NO loss, then by rapid bimolecular H-atom removal. The stability of the cyclic diketone intermediate thus generated could help to explain the shock insensitivity of NTO. For comparison, spectra were obtained under either slow-heating or rapid pulsed-laser heating conditions. Laser-desorption spectra were also obtained, both on fresh NTO samples and samples that had been recovered from marginally sub-critical drop weight impact tests. Under the thermal or laser-desorption conditions, subsequent bimolecular H-atom removal to produce the closed-shell diketone was slower than unimolecular ring-opening adjacent to the carbonyl group. This sequence satisfactorily explains the following: **(1)** the initial formation of  $\text{CO}_2$  that has been previously reported, **(2)** the result of nitrogen double-labeling experiments, and **(3)** the fact that neither  $\text{NO}_2$  nor  $\text{HONO}$  have been seen as substantial initial products of NTO decomposition (at least not by this investigator).

Simultaneous STMBMS and TOF spectra have been developed to study reactions that occur during the thermal decomposition of energetic materials. The data obtained with these techniques are the identity of the reaction products and their rates of gas formation as a function of time. In the case of NTO, the pyrolysis of NTO resulted in the formation of gaseous products and a solid residue [485]. The identity of the major gaseous products and their origin from within the NTO molecules were determined based on the results from pyrolysis of isotope-labeled NTO,  $\text{NTO-3-}^{13}\text{C}$ ,  $\text{NTO-1,2-}^{15}\text{N}$ , and  $\text{NTO-}^2\text{H}$ . The identification of the products showed the major gaseous products to be  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{HNCO}$ ,  $\text{H}_2\text{O}$ , and some  $\text{N}_2\text{O}$ ,  $\text{CO}$ ,  $\text{HCN}$ , and  $\text{NH}_3$ . The  $\text{N}_2$  was mostly derived from the N-1 and N-2 positions with some being from the N-4 and N-1 or N-2 positions. The  $\text{CO}_2$  was derived from both carbons in the NTO molecule in comparable amounts. The overall thermal decomposition of NTO in the temperature range evaluated between 463 and 523 K (190 and 250 °C) involved four major processes: **(1)** NTO sublimation; **(2)** an apparent solid-solid phase transition between 463 and 468 K (190 and 195 °C); **(3)** a decomposition regime induced by the presence of exogenous  $\text{H}_2\text{O}$  at

the onset of decomposition; and (4) a decomposition regime that occurs at the onset of decomposition and continues until the depletion of NTO.

The thermal decomposition of NTO was studied by many groups of investigators. Such interest was a result of the unusual decomposition behavior of NTO (the isomerization of the nitro group into the *aci*-form at high temperatures, which was followed by its decomposition). This circumstance resulted in two kinetic equations with vastly different activation energies that can be used to describe the decomposition of NTO in the solid state: in the low-temperature region,  $E_a = 172.0 \text{ kJ/mol}$  (41.1 kcal/mol), which is characteristic for the rupture of C–NO<sub>2</sub> bonds, and in the high-temperature region,  $E_a = 322\text{--}368 \text{ kJ/mol}$  (77–88 kcal/mol), a formal value connected with *aci*-isomer decomposition, the concentration of which increased with temperature. According to thermocouple-aided measurements and burning-rate studies, low values of heat flux from the gas phase at pressures up to at least 2 MPa allowed consideration of the condensed-phase chemistry as determining the combustion of NTO [484]. Rate constants of the dominant combustion reaction in the pressure range of 0.4–10 MPa have been obtained from the Zeldovich expression. The average specific heat was calculated to be  $1.46 \text{ kJ kg}^{-1} \text{ K}^{-1}$  ( $0.35 \text{ cal g}^{-1} \text{ K}^{-1}$ ) from experimental data on thermal diffusivity ( $1.7 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ). Strand density was  $1.74 \text{ g/cm}^3$  and thermal conductivity of the condensed phase was assumed to be  $5.1 \times 10^{-2} \text{ kJ s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$  ( $0.00123 \text{ cal s}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1}$ ). The heat of reaction,  $Q$ , was taken as  $1297 \text{ kJ/kg}$  (310 cal/g), and the heat of melting as  $215.5 \text{ kJ/kg}$  (51.5 cal/g). During combustion, NTO is in the molten state at the surface, having been isomerized into the *aci*-form. Therefore, the kinetics of NTO decomposition derived from the combustion model, for the temperature range 630–790 K,

$$k = 10^{13.91} \times \exp(-19420/T) \text{ s}^{-1},$$

differ from the kinetics of decomposition in solid. In other studies, decomposition of NTO has been studied in solutions at reduced temperatures. However, it is not obvious if isomerization proceeded to completion at those conditions. At the same time, it is well-known that many salts of nitro compounds contain the nitro group in the *aci*-form. Decomposition rate constants of a water solution of NTO were close to rate constants of the leading combustion reaction.

This very detailed and all-encompassing review deals with the chemistry and thermolysis of NTO and plausible decomposition pathways followed during the decomposition of NTO induced by X-rays, UV, laser, or photochemical irradiation. It is a good introduction to the decomposition of NTO [605]. For a long time, controversy existed among investigators regarding the decomposition mechanism of NTO. One school of thought suggested that the first step in the thermal decomposition of NTO is the scission of the C–NO<sub>2</sub> bond, either by direct thermal activation or catalyzed by H atom transfer and loss of HONO. The other school of thought maintained that the first decomposition products are CO<sub>2</sub> and N<sub>2</sub>O. Other workers have also reported CO<sub>2</sub> and N<sub>2</sub> as gaseous products while others detected NO<sub>2</sub> and HONO in small amounts or not at all. High-speed photographic studies of the impact responses of NTO may help to



explain processes during shock initiation of the material. The thermal decomposition kinetics of NTO can be explained by using isotope-labeled NTO. Before NTO can advance to widespread use as an explosive, analytical methods of detection, as well as methods for the safe disposal of NTO, need to be developed.

An examination of NTO decomposition by TGA and DSC showed that the heating of NTO leads to competitive sublimation and condensed-phase exothermic decomposition events [606]. Model-free isoconversional analysis provided activation energies ( $E_a$ ) for these processes as a function of the extent of conversion,  $\alpha$ . Sublimation occurs most readily in an open pan. More than simple sublimation was observed, with a global activation energy of  $E_a = 130\text{--}140\text{ kJ/mol}$  for sublimation. Non-isothermal TGA and DSC traces run on pierced pan samples provided convincing evidence for competitive sublimation and condensed-phase decomposition of NTO. Confining NTO samples in a closed pan resulted in condensed-phase decomposition that leads to the formation of gaseous reaction products and showed autocatalytic behavior during the latter stages. Isoconversional analysis of DSC traces of closed-pan samples yield activation energies for exothermic decomposition that increase from  $E_a = 273\text{ kJ/mol}$  for  $\alpha = 0.01$  to a plateau of  $333\text{ kJ/mol}$  for  $0.17 \leq \alpha \leq 0.35$  prior to decreasing to  $184\text{ kJ/mol}$  for  $\alpha = 0.99$ . The decrease in  $E_a$  with  $\alpha$  during the latter stages of decomposition agrees with previous reports of autocatalytic behavior.

The literature dealing with crystal structure, thermolysis, solubility, crystallization, and the applications of NTO, including the experimental and theoretical aspects of the crystal structure of various NTO salts, was thoroughly reviewed again in 2003 [480]. This is an update of a similar paper published by the same author(s) in 2001. At that time, the mechanisms of NTO decomposition and the reasons for its good thermal stability were still not quite understood. The theoretical considerations on the decomposition of NTO have been critically reviewed and new insights that were obtained from these works have been highlighted. The reported parameter sensitivity and performance of NTO available in the literature have been summarized.

The kinetics of the thermal decomposition of NTO in the temperature interval from 473 to 533 K (200 to 260 °C) were investigated using gas evolution pressure measured with a glass Bourdon gauge [607]. The overall decomposition reaction included two distinct stages: a fast first-order decomposition and a subsequent autocatalytic reaction. The contribution of the first stage increased with increasing decomposition temperature and decreasing loading density of the Bourdon gauge ( $m/V$ ). A period of preliminary heating at a lower temperature strongly influenced the autocatalytic stage when the decomposition was carried out at a higher temperature. In the temperature domain 473–479 K (200–220 °C), the Arrhenius constants of the decomposition reaction were found to be close to the values usually observed for nitro compounds:  $E_a = 173\text{ kJ/mol}$  and  $\log_{10} k \approx 12.5\text{ (s}^{-1}\text{)}$ . It was shown that a simple model of NTO decomposition based on an autocatalytic reaction of the  $n^{\text{th}}$  order can describe the course of the decomposition at high temperature but the  $n$  number appears to be excessively high, up to  $n = 4$ . A new model of the decomposition was developed, including an

initial monomolecular reaction, decomposition of the crystalline substance, and an autocatalytic reaction of NTO dissolved in liquid decomposition products. This model gave the common order of an autocatalytic reaction with  $n = 1$ .

The strand burning rates of NTO were investigated at a pressure interval of 0.1–40 MPa and the temperature distribution profile in the combustion wave of NTO was measured at pressures of 0.4–2.1 MPa [483, 608]. Based on burn rate and thermocouple measurement data, the rate constants of NTO decomposition in the molten layer at 643–698 K (370–425 °C) were derived from a condensed-phase combustion model

$$k = 1.14 \times 10^{14} \times \exp(-39000/RT) \text{ s}^{-1}$$

and NTO vapor pressure above the liquid phase

$$\ln P = -9914.4/T + 17.12$$

and solid phase

$$\ln P = -12984.4/T + 22.78$$

were calculated. Taking into account the vapor pressure data obtained, the decomposition of NTO in the gas phase at 513–523 K (240–250 °C) was studied. The decomposition rate constants in the gaseous phase were found to be comparable with rate constants in the solid state. Therefore, a partial decomposition in the gas cannot substantially increase the total rate. High values of the activation energy for the solid-state decomposition of NTO are not likely to be connected with the sub-melting effect. This is because decomposition already occurs at temperatures well below the melting point. It has been suggested that abnormally high activation energy at the interval of 503–543 K (230–270 °C) must be attributed to the peculiarities of the NTO transitional process rather than strong bonds in the molecule. During decomposition, the NTO molecule may undergo isomerization into the *aci*-form, followed by C3–N2 heterocyclic bond rupture, resulting in the abnormally high value of the observed activation energy.

NTO is an insensitive molecule in comparison to general explosives and the NTO-based PBXs have a low vulnerability. The thermal decomposition characteristics of NTO and CL-20 were studied using TGA and DSC. The compatibility of the two explosives with silicone rubber used in PBX formulations, the decomposition kinetic parameters such as activation energies of decomposition, and the frequency factor of the decomposition reaction were evaluated by using non-isothermal DSC techniques [609]. Some of the results are shown in Table 42. The NTO/silicone combination was slightly less stable than NTO by itself.

In the NTO curves, no endothermic peak was demonstrated at the lower temperature region before decomposition but it accomplished a sharp exothermic peak from 547 to 561 K (274 to 288 °C) with a 5 to 30 °C/min. heating rate. The onset temperatures were 538, 543, 548, and 551 K (265, 270, 275, and 278 °C) for heating rates of 5, 10, 20, and 30 °C/min., respectively.

**Table 42:** Kinetic parameters of thermal decomposition of thermally resistant explosives.

| Explosive      | $E_a$                    | $\gamma_b^a$ | A                     | Temperature |         |
|----------------|--------------------------|--------------|-----------------------|-------------|---------|
|                | kJ/mol                   |              | s <sup>-1</sup>       | K           | °C      |
| CL-20          | 191.7 ± 3.5              | 0.9975       | $2.08 \times 10^{21}$ | 509–536     | 236–263 |
| CL-20          | (under 44 µm)<br>160.88  | 0.9884       | $2.5410^{13}$         | 514–538     | 241–265 |
| CL-20          | (under 246 µm)<br>226.83 | 0.9995       | $2.2810^{24}$         | 511–526     | 238–253 |
| NTO            | 352.7 ± 4.0              | 0.9983       | $9.85 \times 10^{35}$ | 547–561     | 274–288 |
| CL-20/silicone | 177.7 ± 5.6              | 0.9965       | $6.29 \times 10^{19}$ | 510–537     | 237–264 |
| NTO/silicone   | 258.7 ± 3.4              | 0.9980       | $1.71 \times 10^{27}$ | 540–556     | 267–283 |

<sup>a</sup>  $\gamma_b$ : correlation coefficient for linear regression

Data source: [609].

Thermal stability and decomposition kinetics for NTO were investigated by DSC and thermogravimetric-DTA (TGA-DTA) to obtain information on safety for handling, storage, and use [610]. The results of TGA analysis revealed that NTO decomposes completely in the temperature range of 523–573 K (250–300 °C). NTO is thermally stable until its decomposition. The decomposition kinetics of NTO were then studied by non-isothermal DSC under various heating rates. Kinetic parameters such as activation energy and the frequency factor for the thermal decomposition of energetic compounds were obtained via the methods proposed by ASTM E696 and Starink [611]. Other thermodynamic parameters which correspond to the activation of thermal decomposition and critical ignition temperatures of the compounds were also obtained.

DSC was used to study the catalytic effect of TAG-transition metal complexes (with or without the addition of graphene oxide) on the thermal decomposition of NTO [612]. The apparent activation energy of NTO decomposition was reduced by more than 180 kJ/g.

### Rapid Thermal Decomposition of NTO

Subsequent to studies of the slow decomposition of NTO, the objective of additional work was to determine the decomposition characteristics of NTO under combustion-like conditions by rapidly heated T-jump/FTIR spectroscopy [490, 613]. Discrepancies in the published global kinetic data for the thermal decomposition of NTO were shown to result partly from the inadequate consideration of the competing processes of sublimation and thermal decomposition. These processes were isolated and their kinetics determined separately. For sublimation,  $E_a = 107.9$  kJ/mol (25.8 kcal/mol),  $\ln(A, s^{-1}) = 29.2$  (isothermal at 0.002 atm);  $E_a = 119.7$  kJ/mol = 28.6 kcal/mol,  $\ln(A, s^{-1}) = 31.3$  (non-isothermal at 0.002 atm). The decomposition kinetics on semi-confined NTO (20 atm Ar pressure) determined by T-jump/FTIR spectroscopy yielded  $E_a = 364$  kJ/mol = 87.1 kcal/mol and  $\ln(A, s^{-1}) =$

74.8. From these and reported data, the kinetic constants for decomposition alone are  $E_a = 326\text{--}364\text{ kJ/mol}$  ( $78\text{--}87\text{ kcal/mol}$ ) and  $\ln(A, \text{s}^{-1}) = 67\text{--}78$ . Lower values of the Arrhenius parameters result predominately or partly from sublimation. An evaluation was made of whether T-jump/FTIR spectroscopy could determine the decomposition kinetics  $E_a$  and  $\ln A$  and thermochemical  $\Delta H_{\text{rm}}$  constants of an energetic material at high temperature and high heating rate.

A primary DKIE has been detected, suggesting that the N—H (or N—D) bond cleaves in the rate-determining step of NTO thermal decomposition. In another study, a DKIE and 1,2,4-triazol-3-one (TO) as a decomposition product were observed. TO itself does not exhibit a DKIE, suggesting that  $\text{—NO}_2$  of NTO accepts the transferred hydrogen followed by  $\text{C—NO}_2\text{H}$  cleavage. Similarly,  $\text{C—NO}_2$  bond homolysis leading to  $\text{NO}_2$  (or HONO) has been proposed to be the initial degradation reaction by laser-induced MS and Secondary Ion Mass Spectrometry (SI-MS), although very little  $\text{NO}_2$  was detected.

The pressure dependence of the relative concentrations of the initially detected IR-active gaseous products from NTO heated at  $300\text{ K/s}$  to  $723\text{ K}$  in Ar was determined in another study [489]. Below  $1\text{ atm}$ , NO dominated. However, between  $5$  and  $68\text{ atm}$ ,  $\text{CO}_2$  was the major decomposition product. The rationalization of this is that, at higher pressures, gaseous products are forced to remain in contact longer with the residue and the hot zone, which enhances secondary reactions and produces more stable products. Absorbances indicative of NO appeared after several minutes. No HONO was detected. Another study remarkably revealed ammonia (detected as ammonium ion) in addition to TO as decomposition products by NMR. In summary, three studies proposed that  $\text{C—NO}_2$  homolysis is a major reaction, but a large amount of  $\text{NO}_2$  was reported in only one of these studies. A fourth study theorized that  $\text{NO}_2$  formed as a secondary product from the oxidation of NO. The oxidant was not identified. Cleavage of the N—H bond was proposed by many to be the rate-determining step.  $\text{CO}_2$  was detected as the initial product by rapid laser heating and as the major product by rapid thermolysis at pressures greater than  $5\text{ atm}$  (see also [524, 525]).

Films of NTO transiently heated by a pulsed laser showed only CO as the initial reaction product; there was no evidence of NO or HONO. Thin films of NTO were subjected to rapid pyrolysis using a pulsed IR laser to determine the initial steps of thermal decomposition under conditions of rapid heating [614]. After heating, the film was quenched to  $77\text{ K}$  in about  $2\text{ ms}$ , thereby trapping reaction products, which were subsequently detected by transmission FTIR. The first observed product of the decomposition was  $\text{CO}_2$ . No evidence was found for the formation of  $\text{NO}_2$  or HONO in the early stages of thermal decomposition. The experimental results showed that the  $\text{CO}_2$  reaction product was formed by bimolecular oxygenation of the carbonyl group by the nitro group of an adjacent NTO molecule. This conclusion differed from mechanisms proposed by other investigators based on their slow heating experiments.

### 8.14.3.6 Computational Chemistry of NTO Decomposition Reactions

An *ab initio* quantum mechanical study of the energetics associated with several proposed initiation routes of NTO looked at geometries for all stationary points that were computed using restricted Hartree-Fock self-consistent field (HF SCF) analytical gradient methods [615]. The theoretical harmonic vibrational frequencies for NTO were scaled by a factor of 0.91 to account for the effects of anharmonicity and electron correlation. Their theoretical gas phase values for the bond lengths compared well with those of experimental values, except one for the C5–N1 bond. Harmonic vibrational frequencies were computed to characterize the species at the stationary points. The previously reported mechanisms examined included decomposition initiated by C–NO<sub>2</sub> homolysis, migration of ring substituents and ring-opening processes. Based on the energetics of the various schemes, the results of the computations suggested that C–NO<sub>2</sub> bond homolysis is the most probable initial step for the unimolecular decomposition of NTO.

In modeling the thermal decomposition kinetics of NTO, including 39 decomposition paths among 18 intermediates and 14 transition states, three types of intra-molecular proton migration and the direct scission of the C–NO<sub>2</sub> bond were regarded as the initial steps of the unimolecular decomposition of NTO [616]. The activation energies of the radicalization C–NO<sub>2</sub> homolysis step were calculated as 331.2, 333.8, and 337.4 kJ/mol (79.158, 79.781, and 80.652 kcal/mol) for the three types of proton migration. The activation energies of the ionization C–NO<sub>2</sub> scission step were 1098, 1101, and 1139 kJ/mol (262.488, 263.138, and 272.278 kcal/mol) for the three types of proton migration. The bottle-neck activation energies of the C–NO<sub>2</sub>H cleavage were 229.8, 264.7, and 298.1 kJ/mol (54.936, 63.257, and 71.247 kcal/mol). Two of the paths have the smallest bottle-neck activation energy. Both have two proton migration steps and one internal rotation step before C–NO<sub>2</sub>H cleavage. At lower temperatures, vibrational energy accumulated slowly. When the energy is high enough and the reaction time is long enough for structure transformation, these two mechanisms should be the most probable decomposition paths. At high temperatures, the shortest (four steps) mechanism which goes through radicalization C–NO<sub>2</sub> scission, should be the dominant path. There were five tautomers found in this study. Four of them are intra-molecular proton migration tautomers. The other one is an internal rotational tautomer. Their energy barriers for structure transfer are lower than any of the activation energies of the decomposition reactions, which makes them more likely as intermediates. This may be regarded as one explanation of the insensitive properties of NTO.

The 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one dimer reaction path leading to CO<sub>2</sub> in the gas phase was calculated by a DFT method [497]. *Ab initio* DFT calculations were used to study the structures and energies of the reactants, products, intermediate products, and transition states for the dimer reaction mechanism. It was found that there is a reaction path for the production of CO<sub>2</sub> through the dimer reaction with a potential energy barrier of 367 kJ/mol (87.8 kcal/mol). This study has revealed a series of NTO dimer reaction paths through four intermediates and five transition states with

the evolution of nitroso-TO, CO<sub>2</sub>, N<sub>2</sub>, HONO, and HCN, in that order. This seems to suggest that CO<sub>2</sub> is produced through a cluster of NTO molecules in the gas phase.

DFT calculations with dispersion-correction (DFT-DC) were used to study the effects of crystal lattice vacancies and pressure on the structure and initial decomposition of crystalline β-NTO [617]. A comparative analysis of the chemical behaviors of NTO in the ideal bulk crystal and vacancy-containing crystals under applied hydrostatic compression was considered. Calculations of formation energy, vacancy interaction energy, electron density difference, and frontier orbitals revealed that the stability of NTO can be effectively manipulated by changing the molecular environment. Bimolecular hydrogen transfer was suggested to be a potential initial chemical reaction in the vacancy-containing NTO solid at 50 GPa. This would take place before the C–NO<sub>2</sub> bond dissociation as a step that initiates its decomposition in the gas phase. The vacancy defects introduced into the ideal bulk NTO crystal can produce a localized site, where the initiation decomposition is preferentially accelerated and then promotes further decompositions.

#### 8.14.3.7 Photolysis of NTO

During UV photolysis, NTO abstracts hydrogen from the solvent or from other NTO molecules and forms a free radical: hydroxy-4-oxo-2,3,4-triazolyl nitroxide [590, 593]. The free radicals can be identified by electron spin resonance. If NTO is photolyzed in an alkaline solution with nitromethane, the nitromethane *aci* anion acts as a spin trapping agent, forming an NTO ring-intact anion free radical rather than a simple radical adduct [618]. The free radical is the product of electron transfer between *aci*-nitromethane and NTO. Its EPR signal consisted of a triplet of quartets. The photolysis of NTO in alkaline solutions is a candidate method for the disposal of NTO and the clean-up of NTO production waste waters.

The initial decomposition products of NTO were characterized using laser-induced decomposition of a solid sample [619]. The heating of solid NTO samples was achieved by irradiation with 7 ns pulses of 266 nm laser light while the gas-phase products were detected using 118 nm single-photon ionization in a TOF mass spectrometer. Product translational temperatures and relative product yields were obtained by analysis of time-of-arrival scans. The translational temperature depended linearly on the decomposition laser fluence and agreed with the results of a calculation of the temperature rise in the irradiated volume using a heat conduction equation. The relative product yields were used to determine the percentage decomposition of NTO as a function of temperature. The temperature dependence of the experimental fractional decomposition was consistent with that obtained from calculations of the temperature dependence of NTO unimolecular decomposition. The temperature dependence of the relative product yields was used to identify the initial channels. The initial reaction appeared to be bimolecular with a net loss of an O atom to yield nitroso-TO. Early unimolecular reactions included the loss of NO<sub>2</sub> and the nitro-nitrite rearrangement followed by a loss of NO.

Waste water from NTO production facilities may contain residual NTO that cannot be released to surface waters. A remediation method based on photochemical decomposition and Fenton oxidation of NTO has been evaluated by monitoring the mineralization of  $^{14}\text{C}$ -labeled NTO [620]. The  $\text{TiO}_2$ -catalyzed photodegradation ( $\lambda > 290\text{ nm}$ ,  $\text{TiO}_2$  0.4 g/L, NTO 150 mg/L) leads to the complete mineralization of NTO in 3 h. This degradation involves a simultaneous denitrification and ring scission of NTO, leading to nitrites, nitrates, and carbon dioxide. No significant photo-degradation of NTO was detected in the absence of the catalyst. Long-term irradiation over one week leads to complete degradation of concentrated NTO (5 g/L), suggesting that this method could be useful to clean up NTO wastes. Fenton oxidation offers an efficient cost-effective method for NTO remediation. This reaction is faster than the  $\text{TiO}_2$ -catalyzed photolysis and may find application in the mineralization of high concentrations of NTO (15 g/L). Fenton oxidation provokes ring cleavage and the subsequent elimination of the two carbon atoms of NTO as  $\text{CO}_2$ . During this reaction, the nitro group is completely transformed into nitrates.

#### 8.14.3.8 Radiolysis of NTO

NTO, RDX, HMX, and TATB were subjected to X-ray and UV radiation, and XPS was used to detect radiation-induced chemical changes [621]. In the group of four explosives, RDX was the most sensitive molecule to both the X-ray and UV radiation while HMX was only slightly less sensitive. NTO was found to be 1.5–3.0 times more sensitive to X-ray and UV damages than TATB. Radiation sensitivity decreased in the sequence  $\text{RDX} > \text{HMX} \gg \text{NTO} > \text{TATB}$ . The identification of decomposition products by chemical methods was consistent with the observed XPS data. XPS analysis of the X-ray-damaged residue suggested three decomposition products resulting from the loss of nitro, the reduction of nitro to nitroso, and the loss of NO. The direct loss of  $\text{NO}_2$  to produce 1,2,4-triazol-5-one is one possible mode of decomposition of NTO. Another product could be urazole resulting from the elimination of NO via a cyclic intermediate reduction of nitro to nitroso; this is also a possible decomposition mechanism as observed in RDX. It appears unlikely that the presence of decomposition products in damaged NTO will increase the sensitivity. Thus, it seems that NTO is unique among commonly used energetic materials in that it may not be sensitized by molecular degradation.

#### 8.14.4 Strand Burning of NTO

During strand burning of pressed pellets of NTO, burning does not transition into an explosion, as already discussed in this publication [622] (see also [483, 608]). NTO in the form of samples pressed into polymethylmethacrylate (PMMA) tubes of 7 mm diameter starts burning at 0.4 MPa at a rate of 0.3 mm/s. At atmospheric pressure, NTO can sustain combustion only when external heating is continuously provided by an electrically heated Nichrome wire. In doing so, a decomposition reaction with

the formation of gaseous products occurs but no gas-phase flame is observed. The gas flame appears at pressures when NTO is capable of sustained combustion. However, again, the burning is accompanied by the formation of copious yellow smoke and solid residue inside the tubes. The NTO burning rate-pressure dependence can be expressed as

$$r_b = 0.727p^{0.976}$$

for the pressure interval of 0.4–11.9 MPa, and

$$r_b = 1.56p^{0.667}$$

for the interval of 11.9–40 MPa, where  $r_b$  is the burning rate in mm/s and  $p$  is the pressure in MPa. The burning rates of NTO are close to the burning rates of TNT. As compared with HMX, NTO burns three times slower within the whole pressure interval.

#### 8.14.5 Explosive Performance of NTO

NTO has a calculated detonation velocity and pressure equivalent to that of RDX. Results from initial small-scale sensitivity tests indicated that NTO is less sensitive than RDX and HMX in all respects. A 4.13-cm-diameter unconfined plate-dent test at 92% of crystal density produced the detonation pressure predicted for NTO using Becker-Kistiakowsky-Wilson (equation of state, BKW) calculations [440, 441].

Measurements of detonation velocity of confined 12.7 mm charges pressed to 89.61 and 89.76% theoretical density, and a 15.9 mm charge pressed to 88.65% theoretical density gave scattered results. The detonation velocity for the 12.7 mm charges was relatively low at about 6000 m/s. The 15.9 mm charge gave a detonation velocity of 7440 m/s with a standard deviation of  $\pm 125$  m/s, thus indicating that stable detonation had been achieved [458]. Standard literature reference sources [62] list the detonation velocity, unconfined, as 7860 m/s at  $\rho = 1.80$  g/cm<sup>3</sup> and confined 7940 m/s at  $\rho = 1.77$  g/cm<sup>3</sup>, respectively.

#### 8.14.6 Critical Diameter of NTO Detonation

Tests on 12.7 mm diameter NTO samples showed that detonation can be achieved at this diameter at 91.0% theoretical density [458]. However, Lee and Coburn [440] also observed failure at 94.5% theoretical density for 12.7 mm diameter samples. NTO is not cap-sensitive. It will not detonate directly from an exploding bridgewire detonator (EBW) but requires a booster, which is typically RDX or PETN. The critical diameter of NTO may be close to 12.7 mm at 90% theoretical density, especially since detonations observed on confined charges at 12.7 mm diameter indicated potential instability. A provisional estimate for the unconfined critical diameter is  $11 \pm 2$  mm at 90% theoretical density.



### 8.14.7 Explosive and Safety Hazards of NTO

One of the many applications of NTO is as a replacement for RDX. Table 43 is a comparison of physical and sensitivity properties of NTO and RDX:

**Table 43:** Physical and explosive properties of NTO and RDX.

| Property                             | NTO                    |                        | RDX                    |                         |
|--------------------------------------|------------------------|------------------------|------------------------|-------------------------|
|                                      | SI units               | Other units            | SI units               | Other units             |
| Crystal density                      | 1930 kg/m <sup>3</sup> | 1.93 g/cm <sup>3</sup> | 1806 kg/m <sup>3</sup> | 1.806 g/cm <sup>3</sup> |
| DTA onset of exotherm                | >509 K                 | >236 °C                | 483 K                  | 210 °C                  |
| Enthalpy of formation                | −100.7 kJ/mol          | −14.30 kcal/mol        | +61.5 kJ/mol           | +14.71 kcal/mol         |
| Henkin critical temp. (0.64 mm size) | 510 K                  | 237 °C                 | 492.7 K                | 219.6 °C                |
| Impact sensitivity Type 12 tool      | 291 cm                 | —                      | 22 cm                  | —                       |
| Impact sensitivity Type 12B tool     | 293 cm                 | —                      | 41 cm                  | —                       |
| Spark sensitivity, 3 mil gap         | 0.91 J                 | —                      | 0.22 J                 | —                       |
| Spark sensitivity, 10 mil gap        | 3.40 J                 | —                      | 0.55 J                 | —                       |
| Vacuum stability, 48 h at 100 °C     | 0.2 mL/g               | —                      | —                      | —                       |
| Vacuum stability, 48 h at 120 °C     | 0.3 mL/g               | —                      | 0.12–0.9 mL/g          | —                       |

Data source: [440].

#### 8.14.7.1 Impact Sensitivity of NTO

In many instances, the properties of NTO were compared to those of RDX (the explosive it was often intended to replace) and to those of TNAZ and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, HNIW) (explosives evolving at about the same time). A high-speed photographic study has been performed on the initiation mechanisms of CL-20 and NTO by drop-weight impact [623]. CL-20 was found to be slightly more sensitive and NTO less sensitive than  $\beta$ -HMX in a drop-weight test apparatus. NTO was found to be sensitized by both hard high-melting-point grits (60  $\mu$ m borosilicate or Pyrex glass) and brittle polymers. The heat-sensitive film was used to confirm that the events seen using high-speed photography were indeed deflagrations. In the BAM Drop Weight Impact Sensitivity Test Apparatus, the impact sensitivity of NTO was  $\geq 120$  Nm [62].

#### 8.14.7.2 Friction Sensitivity of NTO

In the BAM friction sensitivity test apparatus, the friction sensitivity of NTO was found to have the status of “no reaction” at the maximum pistil load of 353 N [62].

### 8.14.7.3 Auto-Detonation Sensitivity of NTO

The critical temperatures of thermal explosion for NTO were obtained using the stationary theory of thermal explosion, the calculation formula of estimating the critical temperature of thermal explosion under non-isothermal DSC conditions, and the determination method for the critical temperature of thermal explosion of small-scale solid explosives and its data treatment method [594, 595]. The results of the four methods were in general agreement with each other and the differences were within 5%. The results indicated that the heat-resistance of NTO and that of the common explosives (HMX, RDX, PETN, and tetryl) decreased in the order  $\text{HMX} > \text{NTO} > \text{RDX} > \text{PETN} > \text{tetryl}$ .

Traditionally, the critical temperature  $T_b$  of thermal explosion for energetic materials was estimated using Semenov's thermal explosion theory and the non-isothermal kinetic equation based on Berthelot's expression using reasonable hypotheses. A simpler method can obtain the critical temperature from the onset temperature in non-isothermal DSC curves and rate constants [624]. The results obtained with this method coincided completely with the value of  $T_b$  obtained by Zhang's method [595].

### 8.14.8 Toxicity of NTO

NTO, which is 99.6% pure, was tested for mutagenic potentials with four different *S. typhimurium* strains and one *E. coli* strain by plate incorporation method according to Organisation for Economic Co-operation and Development (OECD) TG 471 at concentrations of 5, 10, 50, 100, and 250  $\mu\text{g}/\text{plate}$  for *Salmonella* strains and 100, 250, 500, 750, and 1000  $\mu\text{g}/\text{plate}$  for *E. coli* without activation [625]. The dose levels were 100, 500, 1000, 2500, and 5000  $\mu\text{g}/\text{plate}$  for both *Salmonella* and *E. coli* with activation. The results showed that NTO was not mutagenic in *S. typhimurium* and *E. coli*, both with and without activation. The negative result was also verified by a confirmatory mutation assay, again both with and without activation.

Testing NTO in a freshwater organism with seven-day survival and reproduction assay concluded that NTO was ranked as practically non-toxic when viewing these results in line with the Chemical Scoring System for Hazard and Exposure Identification [626].

The teratogenicity of NTO in rats was determined by teratogenesis tests. The results showed that the body weight gain in pregnant rats exposed to 2500  $\text{mg}/\text{kg}$  NTO decreased significantly. Corpus luteum formation and embryo implantation numbers also decreased significantly in rats exposed to 156–2500  $\text{mg}/\text{kg}$  NTO compared with the controls [627]. Deformities of fetal development were observed in rats exposed to 2500  $\text{mg}/\text{kg}$  NTO, while bone and viscera deformities were observed in rats exposed to 156–2500  $\text{mg}/\text{kg}$  NTO. It was concluded that NTO showed some teratogenicity in rats in the dose range of 156–2500  $\text{mg}/\text{kg}$ .

The genotoxicity of NTO was investigated using a battery of genotoxicity tests, which included the Ames test, CHO cell chromosome aberration test, mouse lymphoma mutagenesis test, and the rat micro-nucleus test [628]. NTO was not mutagenic in the Ames test or in *E. coli*. NTO did not induce chromosomal aberrations in CHO cells, with or without metabolic activation. In the mouse lymphoma mutagenesis test, all of the NTO-treated cultures had mutant frequencies that were similar to the average frequencies of solvent control-treated cultures, indicating a negative result. The potential *in vivo* clastogenicity and aneugenicity of NTO was evaluated using the rat peripheral blood micro-nucleus test. NTO was administered by oral gavage to male and female Sprague-Dawley rats for 14 d at doses up to  $2 \text{ g kg}^{-1} \text{ d}^{-1}$ . Flow cytometric analysis of peripheral blood demonstrated no significant induction of micro-nucleated reticulocytes relative to the vehicle control (polyethylene glycol, PEG-200). These studies showed that NTO was not genotoxic in either *in vitro* or *in vivo* tests and suggested a low risk of genetic hazards associated with NTO exposure.

The 4-h inhalation median lethal concentration (LC50) of NTO in male and female rats with nose-only exposure to the highest-achievable aerosol atmosphere concentration of NTO (0.18 mg/L) did not induce any compound-related mortality, adverse toxic signs, body weight changes, or gross necropsy findings [629]. A secondary objective was to determine the effect that two different routes of administration (inhalation and oral) had on the absorption of NTO into the bloodstream. Blood samples were collected and analyzed from exposed rats at seven different time points for those exposed via inhalation and six different time points for those given a calculated equivalent oral dose. The results of the blood absorption study indicated that, under these conditions, acute exposure to NTO via inhalation appears to induce higher whole blood NTO concentrations in laboratory rats compared to those exposed via oral gavage.

NTO was administered to male (0, 250, and  $500 \text{ mg kg}^{-1} \text{ d}^{-1}$ ) and female (0, 500, and  $1000 \text{ mg kg}^{-1} \text{ d}^{-1}$ ) Sprague-Dawley rats (15/sex/group) via oral gavage from weaning through puberty to study the effects on pubertal development [630]. Animals were examined daily for the onset of puberty. There were no differences in hormone levels or thyroid follicle and colloid scores between the NTO treatment groups and the control groups. These findings suggested that NTO is not acting as an estrogen or thyroid active compound but may affect steroidogenesis and cause direct testicular toxicity.

Gross external examinations of the offspring of parent rats that had been fed 0, 31, 125, and  $500 \text{ mg NTO kg}^{-1} \text{ d}^{-1}$  via oral gavage for four weeks did not indicate that NTO presents a developmental hazard [631].

## 8.14.9 Applications of NTO

### 8.14.9.1 NTO Applications as an Explosive

NTO is envisioned mostly as an explosive for castable formulations in low-vulnerability warheads [440, 441, 632, 633] and as an ingredient for PBX with proper binders and plasticizers. In Europe, the goal was to obtain a special “CF”

grade (which stands for “Coulé Fondu” in French, which means “Cast Melted ” in English) to be used in melt-cast formulations, where casting viscosity of the molten explosive can induce difficulties to control the filling process and with ensuring the casting of defect-free explosive grains [634]. This special grade can be obtained from a controlled crystallization process whose parameters have been tuned at lab scale and validated at pilot scale. NTO CF is now produced in Europe at an industrial scale, with a highly reproducible bulk density. Other NTO grades are also produced to be used in cast PBX or standard NTO/TNT formulations. Additional information on the applications of NTO as explosives and energetic materials will be included in future solid propellant volumes of the *Encyclopedia of Rocket Propellants*. An insensitive munition explosive formulation (IMX-101) consisted of 3-nitro-1,2,4-triazol-5-one (NTO), 2,4-dinitroanisole (DNAN), and nitroguanidine (NQ). Certain NTO salts are stab-sensitive and may serve as replacements for lead azide or mercury styphnate in percussion caps [635].

#### 8.14.9.2 NTO Derivative Applications as Ballistic Modifiers

The combustion of AP/HTPB composite solid propellants has been studied using the transition metal (Mn, Fe, Co, Ni, Cu, and Zn) salts of NTO as energetic burning rate modifiers [636–638]. The steady burning rate ( $r_b$ ) was considerably enhanced with  $\text{Cu}(\text{NTO})_2$  and  $\text{Fe}(\text{NTO})_2$  but was only moderately enhanced with  $\text{Zn}(\text{NTO})_2$  and  $\text{Co}(\text{NTO})_2$  at low concentration (2mass-%). The activity of these salts has been observed during the isothermal decomposition of AP at 533 K (260 °C). The values of ignition delay, ignition temperature, and the activation energy for ignition of AP were lowered when these salts were added to AP at 2mass-% concentration. The  $r_b$  of the propellants (both highly aluminized and less aluminized), with  $\text{Cu}(\text{NTO})_2$  as an additive at various concentrations, has been determined at high pressures and its activity during combustion was confirmed. The condensed phase activity of  $\text{Cu}(\text{NTO})_2$  during propellant decomposition has also been studied using TGA-DTG techniques.

#### 8.14.9.3 NTO as a Gas Generant

There are many patent applications including NTO as a gas generant, but only one is listed here as an example. Automotive airbag gas generant formulations with NTO provide an alternative to commercially used formulations containing sodium azide. One proposed composition contained 25–75 mass-% NTO [639]. The other principal ingredient of the composition would be 25–75 mass-% of an anhydrous oxidizing salt having a cation selected from metals of Group I-A of the Periodic Table (except sodium), calcium, strontium, or barium, and an anion like nitrate which is essentially free of carbon, hydrogen or halogens.

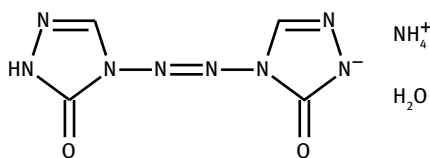
### 8.15 4-Amino-1,2,4-triazol-5-one

Another triazolone derivative of interest as an energetic material is 4-amino-1,2,4-triazol-5-one (ATO). It can be prepared by reacting phosgene with an acylhydrazide and then reacting the oxadiazolinone with hydrazine hydrate [640]. 4-amino-1,2,4-triazol-5-one can also be prepared by heating carbohydrazide and ethyl orthoformate on a water bath. The slow thermal decomposition of amino 1,2,4 triazol-5-one was measured by DSC and the flash pyrolysis of ATO was investigated by T-jump/FTIR spectroscopy [641].

The molecular structure of 4-amino-1,2,4-triazol-5-one was investigated and a density-functional theoretical computational investigation of its dimers and crystal band structure was done after single crystals suitable for XRD measurement had been obtained by recrystallization from distilled water at room temperature [642, 643]. The H-bond connections make the molecules of ATO form a three-dimensional structure from the solution. The hydrogen bond interactions in the gaseous dimers of ATO were studied by using a DFT computational method. The electron density in the N—NH<sub>2</sub> bond is less than those of other bonds, indicating that it is the weakest one.

The thermal stability of 4-amino-1,2,4-triazol-5-one (ATO) was studied under non-isothermal conditions by DSC in a sealed stainless-steel cell [644]. The melting enthalpy and melting entropy of ATO were  $21.34 \pm 0.49$  kJ/mol and  $46.54 \pm 0.30$  J mol<sup>-1</sup> K<sup>-1</sup>, respectively. The kinetic parameters were obtained from the analysis of DSC curves using several methods. The main exothermic decomposition reaction mechanism of ATO was classified as nucleation and growth, and the kinetic parameters of the reaction were  $E_a = 119.50$  kJ/mol and  $A = 10^{9.03}$  s<sup>-1</sup>. The HOF for ATO was computed by G3 theory. The detonation velocity and detonation pressure were estimated by using the K-J equation, based on the theoretical HOF and the determined crystal density.

The ammonium salt monohydrate of 4,4'-azo-1*H*-1,2,4-triazol-5-one, 4-[(5-oxo-1*H*-1,2,4-triazol-4-yl)azo]-1*H*-1,2,4-triazol-5-one, C<sub>4</sub>H<sub>4</sub>N<sub>8</sub>O<sub>2</sub> (AZTO•H<sub>2</sub>O) was synthesized via potassium permanganate oxidation using 4-amino-1,2,4-triazol-5-one (ATO) as the starting material [645].



4,4'-Azo-1*H*-1,2,4-triazol-5-one ammonium salt

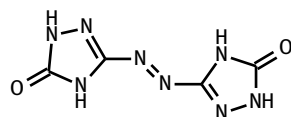
The thermal stability of AZTO•H<sub>2</sub>O was studied by DSC and the kinetic parameters of the non-isothermal exothermic decomposition reaction were calculated by the

Kissinger and Ozawa methods. The results showed that the heat of decomposition, apparent activation energy, and pre-exponential factor of  $\text{AZTO} \cdot \text{H}_2\text{O}$  were 247, 178 kJ/mol, and  $10^{15.74} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion and molar heat capacity at 298.15 K for  $\text{AZTO} \cdot \text{H}_2\text{O}$  was 506 K (233 °C) and  $271 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The kinetic rate equation describing the exothermic decomposition reaction of  $\text{AZTO} \cdot \text{H}_2\text{O}$  was

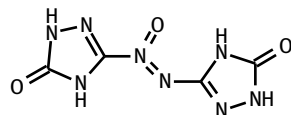
$$\frac{da}{dt} = 10^{15.74} / \beta \times 4(1-a)[- \ln(1-a)]^{\left(\frac{3}{4}\right)} \exp(-1.774 \times 10^5 / RT).$$

### 8.16 Azoxytriazolone

Azoxytriazolone (AZTO) and azotriazolone (azoTO) have been synthesized and characterized by a range of techniques and compared to existing IHE [646]. AZTO is unique in that it does not contain nitro groups like so many other energetic materials. AZTO can be made via electrolysis of aqueous NTO solutions. AZTO showed similar sensitivity to NTO in most tests but had better thermal stability. AzoTO displayed higher thermal and impact stability than AZTO but was more sensitive to ESD.



Azotriazolone



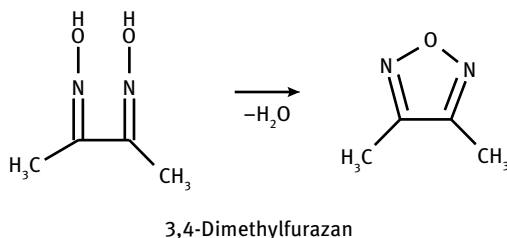
Azoxytriazolone

Attaching two nitro groups, one to each ring, to AZTO gives *N,N'*-dinitro-4,4'-azo-bis-(1,2,4-triazolone) (DNZTO), which is an even more energetic compound, similar to NTO. TGA-DTA and ARC measurements were performed to determine the thermal characteristics and kinetics of the DNZTO decomposition [647]. A single sharp and narrow exothermic decomposition occurred at 416, 423, 429, 430, 433, and 433.4 K (143, 150, 156, 157, 160, and 160.3 °C) at different heating rates (0.5, 1, 2, 3, 4, and 5 °C/min.). This suggests that the DNZTO composition was vulnerable to thermal runaway hazards. The FTIR-TGA-MS results showed that the decomposition products were  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ , NO,  $\text{CO}_2$ , CO, HCN, and  $\text{N}_2\text{O}$ . ARC detected a very low onset temperature at 389.7 K (116.6 °C) and a sharp rise in exothermic reaction at 401 K (128 °C), which was accompanied by a steep adiabatic pressure rise.

## 9 Furazan and Furazan Derivatives

Furazan, also known as 1,2,5-oxadiazole, 2-oxa-1,5-diazole,  $C_2H_2N_2O$ , CAS RN [288-37-9] is a liquid at room temperature that boils at 371 K (98 °C = 208 °F).

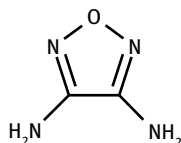
In addition to five-membered rings that carry only nitrogen as the heteroatom, there is the family of furazans which carry nitrogen and oxygen atoms in the ring and also form energetic compounds when one or more of the hydrogens are replaced by energetic groups like  $-NO_2$ ,  $-NF_2$ ,  $-N_3$ , or  $-NHNO_2$ . The most readily accessible furazan is 3,4-dimethylfurazan, 3,4-dimethyl-1,2,5-oxadiazole,  $C_4H_6N_2O$ , CAS RN [4975-21-7], which can be prepared by dehydrating dimethylglyoxime. It is a liquid that boils at 427–432 K (154–159 °C).



The main methods for constructing furazan rings are by dioxime dehydration and furoxan reduction. Once the furazan ring is formed, there are reactions of amino-substituted furazan derivatives, nitro-substituted furazan derivatives, and cyano-substituted furazan derivatives (all candidate energetic materials). An overview of the synthesis methods and performance of several typical furazan-based energetic compounds such as dinitro furazan (DNF), diaminoazofurazan (DAAF), 3,4-bis(4'-nitrofurazano-3'-yl)furoxan (DNTF), furazan ethers, and fused-ring furazan energetic compounds (MNOTO, 4,5,9,10-tetranitro-1,4,5,8-tetrazanaphthano (2,3-, 6,7)bisfurazan) provides a good introduction into this field of heterocyclic compound chemistry [648].

### 9.1 3,4-Diaminofurazan

3,4-Diaminofurazan, also known as 3,4-diamino-1,2,5-oxadiazole, 3,4-diamino-1-oxa-2,5-diazole, 1,2,5-oxadiazole-3,4-diamine, DAF,  $C_2H_4N_4O_1$ , CAS RN [17220-38-1],  $M = 100.08$  g/mol, is a precursor used most often for the synthesis of energetic furazan derivatives.



3,4-Diaminofurazan

3,4-Diaminofurazan (DAF) can be prepared by heating diaminoglyoxime (DAG) with potassium hydroxide followed by cooling to give white crystals. DAG as the precursor for diaminofurazan was prepared by adding glyoxal and hydroxylamine hydrochloride into a cooled solution of sodium hydroxide in water. A single crystal of DAG was then cultured by dehydration at high pressure for XRD [649]. The crystals were characterized by XRD, elemental analysis, and FTIR. The crystal habit is monoclinic, space group  $P2_1$  with unit cell parameters of  $a = 0.6763(8)$  nm,  $b = 0.3578(4)$  nm,  $c = 0.9658(12)$  nm,  $\beta = 90.78(2)^\circ$ ,  $V = 0.2338(5)$  nm<sup>3</sup>,  $Z = 2$ , and  $\rho_c = 1.678$  g/cm<sup>3</sup>. DAG melted at 476.6 K (203.5 °C). It has two steps of intense thermolysis between 482–485 and 485–513 K (209–212 and 212–240 °C) and decomposes completely at up to 513 K (240 °C). It is the decomposition of DAG that limits the yield of DAF. Normally DAF is produced by heating DAG and aqueous potassium hydroxide in a pressure bomb at 448 K (175 °C) for 2 h at 2.8 MPa pressure. The conversion of glyoxime into 3,4-diaminofurazan can also be achieved in a one-pot synthesis sequence in good overall yield using microwave irradiation [650].

3,4-Diaminofurazan is an important precursor for the synthesis of furazan-based energetic materials. 3,4-Diaminofurazan was prepared from glyoxal under atmospheric pressure in a yield of 56.4% with a purity of 98.4% [651]. Three convenient methods for the preparation of DAF were compared [652]. The results indicated that DAF can be obtained not only at atmospheric pressure but also at high pressure from the DAG, starting with the amination of glyoxal by a one- or two-step process. The yield (43%) of DAF prepared from glyoxal with other raw materials by only one step is larger than those (11 and 39%) of the other two methods. However, the reaction conditions must be controlled exactly and the reaction time is slightly longer. The process can be scaled up to a 500-g batch size [653].

DAF may be synthesized by the condensation of hydroxylamine with a variety of reagents, including dithiooxamide, cyanogen, glyoxal, or glyoxime to yield DAG. This is followed by cyclization to DAF by treatment with an aqueous base at 453 K (180 °C) in a pressure vessel [654, 655].

DSC and DTA showed that DAF undergoes a two-stage decomposition. The kinetics of the initial stage of thermal decomposition of DAF evaluated from TGA data gave an activation energy of 67 kJ/mol [656].

The thermal stability of DAF was determined by DSC and TGA-DTA [657]. The thermal degradation of DAF occurred in the temperature range of 503–548 K (230–275 °C). The TGA-DTA analysis of DAF indicated that DAF melted at about 455 K (182 °C) before



it decomposed. The influence of the heating rate (5, 10, 15, and 20 °C/min) on the DSC behavior showed that, as the heating rate was increased, decomposition temperatures of the compound also increased.

The hydrogen bonds in 3,4-diaminofurazan connect the molecules into a 3-D network, while hydrogen bonds in 3-amino-4-nitrofurazan connect the molecules into dimer chains [658].

Diaminofurazan contains three nitrogen atoms. With increasing acid strength, not only do the two amino groups that dangle from the ring become protonized, but one of the nitrogens in the ring can become protonized also [659].

Diaminofurazan was evaluated as an additive to nitramine propellants that would desirably reduce the pressure exponent. DSC and DTA revealed that DAF decomposed in two stages. The kinetics of the initial stage of thermal decomposition of DAF evaluated from TG data gave an activation energy ( $E_a$ ) of 67 kJ/mol [656]. The gases that evolved during decomposition contained  $-\text{CN}$ ,  $-\text{NH}$ ,  $-\text{OH}$ , and oxides of nitrogen. The mechanism of pressure coefficient reduction in nitramine propellants by DAG and DAF may involve the intermediate formation of a layer of thermally resistant melon-type multi-ringed polymers in the burning surface of propellants. Such thermally stable products of decomposition are thought to retard heat transfer from the gas phase to the condensed phase.

Two energetic *N*-trinitroethyl-substituted aminofurazans, as well as a nitramine (the *N*-nitration product of one of the amines), were synthesized and characterized by NMR, IR, elemental analysis, XRD, DSC, and TGA [660]. The densities were 1.82–1.87 g/cm<sup>3</sup>. They exhibited good thermal stability ( $T_{\text{dec}} = 432\text{--}503\text{ K} = 159\text{--}230\text{ °C}$ ), acceptable oxygen balance (–15.3%) and high positive HOFs (268–1259.5 kJ/mol). Predicted detonation pressures and velocities for the furazan derivatives were in the range of 35.4–40.8 GPa and 8900–9486 m/s, respectively. The oxidation of DAF by peroxide reagents leads to 3,4-dinitrofurazan [661].

## 9.2 Nitrofurazan and 3,4-Dinitrofurazan

First, 3,4-diaminofurazan (DAF) was prepared from glyoxal under atmospheric pressure in a yield of 56.4% with purity of 98.4% [651]. Next, 3,4-dinitrofurazan (DNF) in a yield of 62.5% with purity of 99.8% was synthesized from DAF by a one-step oxidation process using 50%  $\text{H}_2\text{O}_2$  as an oxidant in the presence of  $\text{H}_2\text{SO}_4$  with an initial concentration of 56.9% at 308 K (35 °C) for 3.5 h. The structure of DNF obtained by this method was then characterized by <sup>13</sup>C NMR, IR, MS, and elemental analysis.

3,4-Dinitrofurazan was synthesized from DAF in concentrated  $\text{H}_2\text{SO}_4$  with 50%  $\text{H}_2\text{O}_2$  as the oxidant in the presence of a tungsten oxide catalyst [662]. At a temperature of 308 K (35 °C), this process significantly increased the DNF yield from 39 to 58%. When compared to the yield with the conventional  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  catalyst under the same conditions, this was a significant improvement.

1,2,4-Oxadiazole is an isomer of furazan with a different arrangement of the heteroatoms in a five-membered ring, where only one nitrogen is adjacent to the oxygen atom and the two nitrogens are still separated by a  $-\text{CH}=\text{N}-$  link. 3-Nitro-5-guanidino-1,2,4-oxadiazole (NOG) was synthesized from diaminoglycoluril with *in-situ* generated dimethyldioxirane (DMDO) [663]. The impact sensitivity of NOG was more than 40 J; this coupled with the decomposition temperature of 563 K (290 °C) makes it a truly insensitive explosive. The density of NOG was  $1.766 \text{ g/cm}^3$ , and the enthalpy of formation was  $235.1 \text{ kJ/mol}$ .

The impact sensitivity of polynitrofurazans and similar nitroheterocyclic compounds can be predicted by interpolating between known data and applying structural adjustment factors [148, 149].

The HOFs in the gas phase and detonation properties (including heats of detonation, relative specific impulses, detonation velocities, and crystal densities) of nitrofurazans and nitrofuroxans have been calculated by quantum chemistry, molecular mechanics, and Monte Carlo methods [664]. The crystal densities, detonation properties, and sensitivities of most nitrofurazans and furoxans are high. Therefore, smaller molecules are recommended. The types, orders, and quantities of the linking groups in poly-furazans and poly-furoxans can affect the detonation properties.

### 9.3 3-Amino-4-nitrofurazan

3-Amino-4-nitrofurazan is an oxidation product of 3,4-diaminofurazan. 3-Amino-4-nitrofurazan, also known as  $\text{C}_2\text{H}_2\text{N}_4\text{O}_3$ ; 1,2,5-oxadiazol-3-amine, 4-nitro-; furazanamine, 4-nitro-; ANF, CAS RN [66328-69-6],  $M = 130.06 \text{ g/mol}$ , melts at  $397\text{--}398 \text{ K}$  ( $124\text{--}125 \text{ }^\circ\text{C}$ ).

3-Amino-4-nitrofurazan (ANF) was synthesized from 3,4-diamino-furazan (DAF) by an improved method using oxalic acid with sodium tungstate as a co-catalyst (instead of sulfuric acid) and 30%  $\text{H}_2\text{O}_2$  was used as oxidant (instead of 50%  $\text{H}_2\text{O}_2$ ) [665]. The effects of the reaction temperature, reaction duration, and quantity of the catalyst on the conversion of DAF to ANF were optimized by orthogonal design. The optimal reaction conditions were obtained as follows: the reaction temperature was  $333 \text{ K}$  ( $30 \text{ }^\circ\text{C}$ ), the reaction time was 6 h, and the mol ratio of the co-catalyst to DAF was 1:1. The conversion of DAF was about 33.7% under the optimized reaction conditions.

3-Amino-4-nitrofurazan, 3-amino-3'-nitro-4,4'-azoxyfurazan (ANAF), and 3-amino-3'-nitro-4,4'-azofurazan (ANAzF) can be prepared by oxidizing 3,4-diaminofurazan (DAF), 3,3'-diamino-4,4'-azoxyfurazan (DAAF), and 3,3'-diamino-4,4'-azofurazan (DAAzF), respectively, with an oxidizing mixture of hydrogen peroxide, sodium tungstate or ammonium persulfate, and methanesulfonic acid [ $\text{H}_2\text{O}_2/\text{CH}_3\text{SO}_3\text{H}/\text{Na}_2\text{WO}_4$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ] to produce above 65% yield of ANF and ANAF and 15% yield of ANAzF [666–668]. The experiments showed that the mixture of  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{WO}_4$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  in  $\text{CH}_3\text{SO}_3\text{H}$  media is a new type of efficient

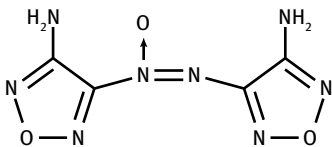
oxidant for the synthesis of compounds with one or more furazan rings with amino and nitro groups as substituents.

3,4-Dinitraminofurazan can be obtained by the nitration of DAF with 100%  $\text{HNO}_3$  [669]. 3-Amino-4-azidofurazan can be prepared by diazotization and substitution of DAF with  $\text{NaNO}_2$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{NaN}_3$ . 3-Azido-4-nitrofurazan and 3,3'-diazido-4,4'-azoxyfurazan can be obtained by the oxidation of 3-amino-4-azidofurazan with 30%  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{WO}_4$  in  $\text{CH}_3\text{SO}_3\text{H}$ . The thermal stability of these compounds was studied by TGA-DSC, and their theoretical density, standard enthalpy of formation, detonation velocity, and detonation pressure were predicted by a quantum mechanical computational method. The results showed that the introduction of the  $-\text{N}=\text{N}(\text{O})-$  group enhances the thermal stability of furazan compounds. The introduction of the  $-\text{N}_3$  group improved the standard enthalpy of formation of these compounds. The enthalpy of formation of 3-amino-4-nitro furazan increased from 183.26 to 571.40 kJ/mol after the amino group was transformed to an azido group. The introduction of the nitramino group  $-\text{NHNO}_2$  significantly increased the density, detonation velocity, and detonation pressure of these energetic materials.

DFT and MP2 calculations were made to examine proton transfer in 3-amino-4-nitrofurazan [670]. The results suggested that the A form is the most stable form of 3-amino-4-nitrofurazan in the gas phase and it is the predominant tautomer in solution. In addition, the variation of dipole moments in the gas phase, the specific solvent effects with the addition of one mol of water near the electrophilic centers of tautomers, the transition state of proton transfer assisted by a water molecule, and the potential energy surface were investigated.

#### 9.4 3,3'-Diaminoazofurazan and 3,3'-Diaminoazoxyfurazan

3,3'-Diamino-4,4'-azoxyfurazan, also known as DAAF, DAAOF,  $\text{C}_4\text{H}_4\text{N}_8\text{O}_3$ , CAS RN [78644-89-0],  $M = 212.13$  g/mol, has a density of  $1.747$  g/cm<sup>3</sup> and melts at 522 K (249 °C), which is an unusually high melting point for an energetic material.



3,3'-Diamino-4,4'-azoxyfurazan (DAAF)

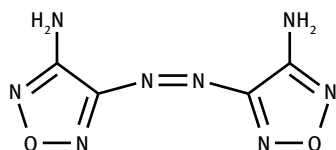
DAAF is an energetic compound that has received a lot of attention both as an explosive and as a propellant ingredient also. A series of furazan-based energetic materials derived from 3,4-diaminofurazan (DAF) were synthesized and characterized. These

compounds included diaminoazoxyfurazan (DAAF), diaminoazofurazan (DAAzF), dinitroazoxyfurazan (DNAF), aminonitrofurazan (ANF), dinitrobisfurazanopyrazine (PIPER), and tetrazoxytetrafurazan (TATFO) [671]. Characterization testing included small-scale safety testing (impact, friction, ESD, thermal stability), DSC analysis, VTS, and ingredient compatibility (by DSC). Results from these tests indicated that most of the materials have excellent thermal stability, as determined by DSC analysis. However, the small-scale safety properties and ingredient compatibilities of most of these materials with standard propellant ingredients were found to be unsuitable for an acceptable propellant ingredient. The most promising furazan-based material investigated was DAAF, which was assessed based upon this criteria. The enthalpy of formation of DAAF was +422 kJ/mol (+100.8 kcal/mol) and the density was 1.7426 g/cm<sup>3</sup>. The enthalpy of formation of DAAzF was +500 kJ/mol (+119.4 kcal/mol) and the density was 1.728 g/cm<sup>3</sup>. The enthalpy of formation of DNAF was +775 kJ/mol (+185.3 kcal/mol).

The oxidation of 3,4-diaminofurazan with a variety of peroxide oxidation reagents leads to mixtures of 3,3'-diamino-4,4'-azoxyfurazan (DAAF), 3,3'-diamino-4,4'-azofurazan (DAAzF), and 3-amino-4-nitrofurazan, which can be separated by differing solubilities [672, 673].

Pure DAAF is an orange-yellow crystalline powder with a DSC onset of exotherm at 521 K (248 °C) and an XRD crystal density of 1.747 g/cm<sup>3</sup>. In the drop weight impact sensitivity tester, DAAF was found to have a drop height of greater than 320 cm (2.5 kg, Type 12 tool) and elicited no response to spark (>0.36 J) or friction (>36 kg<sub>f</sub>, BAM). DAAF had a measured  $\Delta H_f = +443$  kJ/mol = +106 kcal/mol. In the Henkin test, the critical temperature was determined to be 514 K (241 °C). The measured detonation velocity was 8.020 mm/ $\mu$ s.

3,3'-Diamino-4,4'-azofurazan, also known as 4-[(Z)-(4-amino-1,2,5-oxadiazol-3-yl)azo]-1,2,5-oxadiazol-3-amine, DAAzF, C<sub>4</sub>H<sub>4</sub>N<sub>8</sub>O<sub>2</sub>, CAS RN [78644-90-3], *M* = 196.13 g/mol, has a density of 1.736 g/cm<sup>3</sup> and melts at 598 K (325 °C) with decomposition, which is an unusually high melting point for an energetic material.



3,3'-Diamino-4,4'-azofurazan (DAAzF)

Although the azo-compound, 3,3'-diamino-4,4'-azofurazan (DAAzF), has less available oxygen than the azoxy compound DAAF, it has a higher measured enthalpy of formation,  $\Delta H_f$  (+535 kJ/mol = +128 kcal/mol). Other sources give the enthalpy of formation as +522 kJ/mol (+124.9 kcal/mol = +637 cal/g).

The detonation velocity of DAAzF was determined to be 7.6 km/s at a packing density of 1.65 g/cm<sup>3</sup>. The thermal stability of DAAzF was also attractive, with it having a DSC onset of 588 K (315 °C), which is much higher than that of DAAF. The DAAzF, a dark-orange crystalline solid, was found to be insensitive to impact (H50 >320 cm, Type 12 tool), spark (>0.36 J), and friction (>36 kg<sub>f</sub>, BAM). DAAzF cannot be initiated by laboratory impact drop tests. However, it has, in some aspects, better explosive performances than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), which is generally considered to be the standard of IHE. The explosive performance of DAAzF was lower in both velocity and pressure as the increase in HOF was not sufficient to offset the drop in oxygen balance compared to DAAF [674, 675].

The decomposition mechanism of DAAzF was examined by DSC with different heating rates (see also [676]). It was found that the values of the activation energy  $E_a$  for DAAzF decomposition were 336.8 and 329.7 kJ/mol, as calculated by Kissenger's method and Ozawa's method, respectively, and the value of  $\ln A$  was 67.535 [677].

3,3'-Diamino-4,4'-azoxyfurazan process optimization studies were performed to improve the original synthesis method and to address issues with purity and manufacturability. Previously, only recrystallization would result in the desired particle size. Ultimately, a complete solution to all observed issues was found with a new synthesis process. This allowed DAAF to be prepared without any impurities, with good particle size distribution, and without the need for recrystallization. All that was made possible along with the production of a minimum of hazardous waste [678–680].

The compatibility of DAAzF with other energetic materials was studied by using a pressure DSC method [681]. The energetic materials included HMX, RDX, NC, NG, DINA, aluminum powder, and 3,4-dinitrofurazanfuroxan (DNTF). The results showed that there were deleterious interactions between DAAzF and DNTF, DINA, HMX, or RDX, while only weak interactions between DAAzF and NC, NG, NC+NG, or Al were seen. According to the evaluated standard of compatibility, the binary systems of DAAzF with NC, NG, NC+NG, and Al are compatible, but the binary system of DAAzF with DNTF is outright hazardous.

3,3'-Diamino-4,4'-azoxyfurazan (DAAF) along with 1,4-dihydrazino tetrazine (DHTz) and 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) were synthesized and characterized by IR, NMR, MS, TGA-DTA, DSC, TGA-FTIR, and impact and friction sensitivity tests [682]. DAAF is insensitive to mechanical stimuli whereas DAAT and DHTz are vulnerable to impact stimuli. The theoretical explosive power of DAAF, DAAT, and DHTz alone and their combinations with well-known IHE as well as that of propellants based on them were calculated.

The thermal decomposition of DAAzF has been investigated under isothermal conditions at 473–593 K (200–320 °C) using thin-walled glass manometers of the compensation type (spoon gauge, Bourdon gauge) [683]. The kinetic equation of DAAzF decomposition in the solid state was

$$k = 5.0 \times 10^{11} \exp(-21320/T) \text{ s}^{-1}$$

and in the gas phase it was

$$k = 3.3 \times 10^{12} \exp(-21020/T) \text{ s}^{-1}.$$

Based on the burning rate and thermocouple measurement data, rate constants of DAAzF decomposition in the molten layer at 873–1073 K (600–800 °C) have been derived from a condensed-phase combustion model

$$k = 4.6 \times 10^8 \exp(-16680/T) \text{ s}^{-1}$$

which was in good agreement with kinetic data obtained in solution at 235–260 °C. The mechanism of DAAzF thermolysis and combustion includes initial rupture of the C–N bond between the azo-group and furazan ring, with subsequent nitrogen evolution and decomposition of the heterocyclic ring. In the combustion wave, the heat release from the decomposition of the stable furazan ring follows the heat release from the azo-group decomposition, thus resulting in a distinct two-stage flame structure. Previously, the only kinetic data of DAAzF thermal decomposition ( $E = 336.8 \text{ kJ/mol}$ ,  $A = 10^{26.4} \text{ s}^{-1}$ ) had been obtained in non-isothermal conditions using DSC. Based on all indications, these were characteristic of a total process of DAAzF decomposition in both solid and gas phases accompanied by evaporation, rather than characteristic of the DAAzF breaking bonds strength. The rate constants  $k$  of DAAzF decomposition were calculated as a ratio of the initial gas evolution rate to the final volume of gases. In the  $\ln k$  vs. reciprocal temperature co-ordinates in an Arrhenius-type graph, the experimental points fell on a straight line, as described by the following equation:

$$k = 7.8 \times 10^{20} \exp(-32680/T) \text{ s}^{-1}.$$

Vapor-pressure data of DAAzF derived from thermocouple measurements of burning surfaces are shown in Figure 9 in comparison to those of NTO.

Many more energetic compounds carry aminofurazan building blocks. Some contain three or more furazan rings lined up like pearls on a necklace while others have multiple fused rings like a spider web or caged structures like a diamond [684].

The *trans*- and *cis*-isomers of azofurazan and azoxyfurazan may differ in their thermal stability. One or the other may be the first one to decompose when heated. DFT calculations were performed to understand the thermal *trans-cis* isomerization and initial thermal decomposition of DAAzF, DAAF, 3,3'-dinitro-4,4'-azofurazan (DNAzF), and 3,3'-dinitro-4,4'-azoxyfurazan (DNAF or DNOAF) [685]. The relative energy between the *trans*- and *cis*-isomer was calculated. It was found that a negative correlation existed between the relative energy and the sensitivity for these energetic azofurazan and azoxyfurazan compounds, where the higher relative energy means the lower the sensitivity. It was also found that the oxidation of the azo-group to an azoxy group could cause the decrease in the relative energy between the *trans*- and *cis*-isomer, as well as the alteration of the isomerization mechanism. An inversion mechanism operates for azofurazan compounds (DAAzF and DNAF) while a rotation mechanism works for azoxyfurazan compounds (DAAF and DNOAF). The energy of an external stimu-

lus should firstly trigger the *trans-cis* isomerization, rather than the breakage of C—N bond.

DFT calculations indicated that DAAzF is more stable than DAAF [686]. In addition to this, the oxidation of the azo group has a significant influence on the energy difference between *trans*- and *cis*-isomer of azofurazan. The energy difference between the isomers of DAAF is only about half of that of DAAzF. A self-desensitization effect could be responsible for the low sensitivity of azofurazan. This desensitization mechanism may be useful in the design of other high energetic density materials.

Instead of sulfuric acid/hydrogen peroxide oxidation of aminofurazans to azofurazans, electrochemical anodic oxidation has been shown to be an effective tool for the oxidation of aminofurazans to azofurazans in ca. 1% aqueous alkali solution at room temperature [687]. The electrochemical reaction is simple and convenient, eliminating the use of expensive and toxic organic or inorganic oxidants. The green economic preparation of desired azo compounds is very clean, producing only H<sub>2</sub> as a result of cathodic reduction.

A good survey paper reviewed the synthesis, properties, performance, and safety characteristics of DAAF and 18 formulations based on it [688]. Though DAAF has only a moderate crystal density, it offers a highly positive HOF and, hence, superior performance when compared to TATB. It is friction and impact insensitive but is more sensitive to shock than TATB and has an exceptionally small critical diameter (3 mm). It performs very well at low temperatures unlike other insensitive explosives (see also [689]).

The conversion of DAF to DAAF would best be performed in a solvent in which DAF is very soluble and DAAF is not. The solubilities of DAF and DAAF were investigated by high-pressure liquid chromatography with ultraviolet detection in water, dichloromethane, acetonitrile, ethyl acetate, methanol, and acetone between 293 and 313 K [690]. This helps to select the best solvent for the preparation and recrystallization of DAAF.

The heat capacity of 3,3'-diamino-4,4'-azofurazan (DAAzF) was determined by DSC. In the temperature range of 253–373 K, the heat capacity ( $c_p$ ) versus  $T$  relationship can be fitted into a linear equation, as follows:

$$c_p = 0.0028T + 0.26456$$

where  $c_p$  is the heat capacity in J g<sup>-1</sup> K<sup>-1</sup> and  $T$  is the temperature in kelvin [691]. The standard molar heat capacity is 215.53 J mol<sup>-1</sup> K<sup>-1</sup> at 298.15 K. Thermodynamic functions of DAAF, including enthalpy, entropy, Gibbs free-energy increments, and differential functions [ $H_T - H_{298.15}$ ], [ $S_T - S_{298.15}$ ], and [ $G_T - G_{298.15}$ ] were calculated. The combustion energy of DAAF was measured in an oxygen-bomb calorimeter and was found to be  $\Delta U_c = -(13188.43 \pm 32.77)$  J/g. The standard molar enthalpy of combustion at 298.15 K was determined to be  $\Delta H_c = -(2575.68 \pm 6.42)$  kJ/mol. The standard molar enthalpy of formation was calculated to be  $\Delta H_f = +429.98 \pm 6.44$  kJ/mol. The detona-

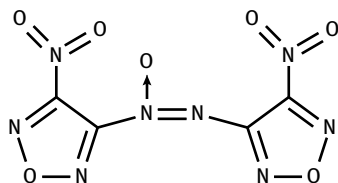
tion velocity and detonation pressure were calculated as 7.31 km/s and 23.61 GPa using the Kamlet-Jacobs equations and the experimental enthalpy of formation.

Connecting two furazan rings without an intermediate azo or azoxy bridge gives bifurazan compounds, which have also been tested as propellant ingredients. One intermediate for the synthesis of other bifurazans is 4,4'-diamino-3,3'-bifurazan. This can be made in a one-pot synthesis from 3,4-di(hydroximinomethyl)furoxan and hydroxylamine, with pH increasing over the course of the reaction from 1 to 10 [692]. Oxidation of 4,4'-diamino-3,3'-bifurazan with trifluoroacetic acid/H<sub>2</sub>O<sub>2</sub> gives 4,4'-dinitro-3,3'-bifurazan. This has a density of 1.85 g/cm<sup>3</sup>, melts at 358 K (85 °C), and has a drop weight sensitivity H<sub>50</sub> similar to that of PETN.

### 9.5 Nitroazofurazan and Nitroazoxyfurazan

Nitroazofurazan and nitroazoxyfurazan are of interest as nitrogen-rich compounds without any hydrogen. Their combustion products would not contain any water, which sometimes interferes with the operation of chemical lasers. These compounds would therefore be useful as gas generants for chemical lasers. 3,3'-Azoxybis(4-nitrofurazan), 3,3'-azobis(4-nitrofurazan), and 3,3'-bis(4-nitrofurazan) were patented as propellant ingredients [693]. The synthesis of the dinitrated bifurazans is described in the literature. In the case of 3,3'-azoxybis(4-nitrofurazan), C<sub>4</sub>N<sub>8</sub>O<sub>7</sub>, see [694].

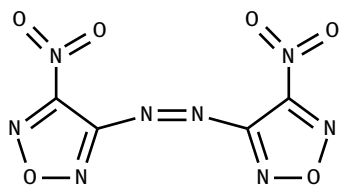
Both diaminofurazan (DAF) and diaminoazofurazan (DAAzF) were converted to dinitroazoxyfurazan, 3,3'-azoxybis(4-nitrofurazan) (DNAF) in oxidations with a mixture of ammonium persulfate and hydrogen peroxide in concentrated sulfuric acid.



3,3'-Azoxybis(4-nitrofurazan)

3,3'-azobis(4-nitrofurazan), (Z)-bis(4-nitro-1,2,5-oxadiazol-3-yl)diazene, C<sub>4</sub>N<sub>8</sub>O<sub>6</sub>, *M* = 256.093 g/mol, can be made by reaction of a dinitrofurazan with a base of acetonitrile [695].





3,3'-Azobis(4-nitrofuran)

3,3'-Bis(4-nitrofuran),  $C_4N_6O_6$ , can be synthesized by oxidation of 4,4'-diamino-3,3'-bifurazan [654]. Diaminofurazan (DAF) generated from glyoxal can be oxidized by a mixture of hydrogen peroxide and concentrated sulfuric acid to produce diamino-azoxyfurazan (DAAF), which was subsequently oxidized to form dinitroazoxyfurazan (DNAF) [696]. The total yield of DNAF was 11%.

The synthesis of 3,3'-diamino-4,4'-azofurazan (DAAzF), 3,3'-diamino-4,4'-azoxyfurazan (DAAF), and 3,3'-dinitro-4,4'-azoxyfurazan (DNAF) was improved. The yield of the prepared DAAzF by using a different oxidant can reach 65.6% [697]. The compounds were characterized by DSC-TG elemental analysis, IR,  $^1H$  NMR, and MS methods. The results showed that the sensitivity of DNAF explosives is high but DAAzF and DAAF explosives have low sensitivity.

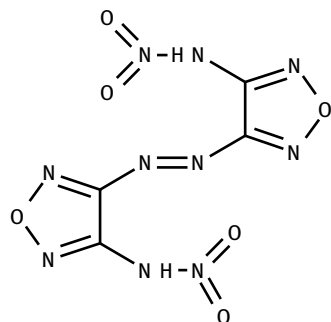
MO quantum chemical computations of the molecular structure and thermal decomposition of 3,3'-dinitro-4,4'-azoxyfurazan (DNAF) and a geometry optimization showed that *trans*-DNAF has a twisting configuration due to the substituted  $NO_2$  on the furazan rings and the oxidation of the azo-group [698]. The BDE of the two C—N bonds which connect the furazan rings and azoxy-group were found to be 276 and 385 kJ/mol (65.9 and 92 kcal/mol), respectively. This suggests that the C—N bond on the side of O-atom of the azoxy-group is relatively weak.

Other sources reported that DNAF has a density of 1.91 g/cm<sup>3</sup>, a standard molar enthalpy of formation of 640 kJ/mol, a detonation velocity of 9390 m/s, and a detonation pressure of 40.5 GPa (see also [699]).

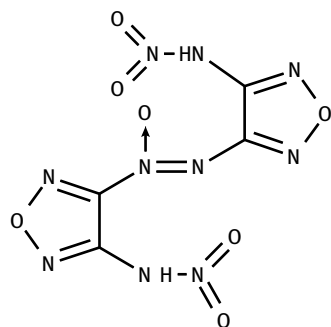
## 9.6 Nitroaminofurazans

The structural, electronic, and physicochemical properties of 4,4'-bis(nitramino)-azofurazan with a density of 1.89 g/cm<sup>3</sup> and 4,4'-bis(nitramino)azoxyfurazan with a density of 1.96 g/cm<sup>3</sup> as HEDMs were compared and a new family of nitrogen-rich energetic salts based on these two nitroaminofurazans were synthesized and fully characterized [700]. Based on experimental evidence and theoretical calculations, 4,4'-bis(nitramino)azoxyfurazan and its ionic derivatives were found to exhibit higher detonation velocities and pressures and higher densities than their azofu-

razan analogues. This supports the added value of introducing the *N*-oxide moiety into energetic materials.

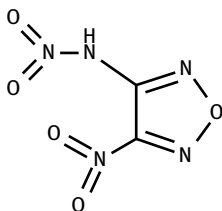


4,4-Dinitramino-3,3-azofurazan



4,4-Dinitramino-3,3-azoxyfurazan

3-Nitramino-4-nitrofurazan, *N*-(4-nitro-1,2,5-oxadiazol-3-yl)nitramide, has a density of 1.93 g/cm<sup>3</sup> and forms salts with many bases such as ammonia, hydroxylamine, hydrazine, and TNAZ [701]. 3-Nitramino-4-nitrofurazan melts at 333 K (60 °C) and starts decomposing at 374 K (101 °C). The heat of combustion is 6556 J/g (1567 cal/g), which corresponds to a HOF of +251 kJ/mol (+60 kcal/mol). There is only one hydrogen in the entire molecule and that is the one that makes it an acid that forms salts with many different bases. For instance, the hydroxylammonium salt has a density of 1.875 g/cm<sup>3</sup> and starts decomposing at 436 K (163 °C) [702]. This salt has a heat of combustion of 1648 cal/g, which corresponds to a HOF of +75.3 kJ/mol (+18 kcal/mol). 3-Nitramino-4-nitrofurazan and its salts are suitable as propellant ingredients.



3-Nitramino-4-nitrofurazan

3,3'-Diamino-4,4'-bifurazane, 3,3'-diaminoazo-4,4'-furazane, and 3,3'-diaminoazoxy-4,4'-furazane were nitrated in 100%  $\text{HNO}_3$  to produce the corresponding 3,3'-dinitramino-4,4'-bifurazane, 3,3'-dinitramino-4,4'-azofurazane, and 3,3'-dinitramino-4,4'-azoxyfurazane, respectively [703]. The neutral compounds showed very imposing explosive performance but possess lower thermal stability and higher sensitivity than RDX. More than 40 nitrogen-rich compounds and metal salts derived from these nitramines were prepared and characterized by low-temperature XRD, IR and Raman spectroscopy, multi-nuclear NMR, DSC, and elemental analysis. Calculated energetic performances using the EXPLO5 code, based on calculated HOFs and X-ray densities, showed promising high energetic performances of the nitraminofurazanes as energetic materials. The sensitivities towards impact, friction, and ESD were also tested.

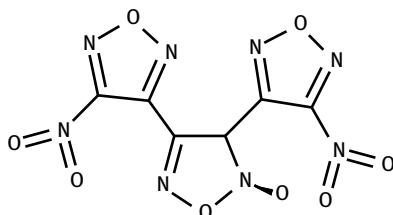
The spontaneous Raman scattering by the products of hydrazinium 3-nitro-4-nitraminofurazanate decomposition on a rapidly heated platinum filament was used to identify intermediate products of the decomposition reaction. This is a new method that is similar to the frequently used T-jump/FTIR method [704].

## 9.7 Multi-Ringed Furazans

Now that single-ringed furazans have enabled the synthesis of a series of energetic compounds, investigations have extended the search to multi-ringed, catenated, or annulated furazan derivatives. Part of that effort was already rewarded in the synthesis of compounds that contain two furazan rings bridged by an azo or azoxy group. Other compounds are linked by C—C or C—N bonds. DFT computational methods were used to study the HOFs, electronic structure, energetic properties, and thermal stability for a series of bridged difurazan derivatives with different linkages and substituent groups [705]. The results showed that the  $-\text{N}_3$  group and azo bridge ( $-\text{N}=\text{N}-$ ) play a very important role in increasing the HOF values of the difurazan derivatives. The calculated energetic properties indicated that the  $-\text{ONO}_2$ ,  $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{N}=\text{N}-$ , or  $-\text{N}(\text{O})=\text{N}-$  groups are effective structural units for enhancing the detonation performance for most of the furazan derivatives. An analysis of the BDE for several relatively

weak bonds suggested that the N–O bond in the ring is the weakest bond and that ring cleavage is likely to happen early on in thermal decomposition. Overall, the –NH–NH–, –N=N–, or –N(O)=N– group were confirmed as known effective bridges for enhancing the thermal stability of furazan derivatives.

3,4-Bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole-*N*-oxide (BNFF) can be prepared from the amine by slow oxidation with hydrogen peroxide.



3,4-Bis(4-nitro-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole-*N*-oxide (BNFF)

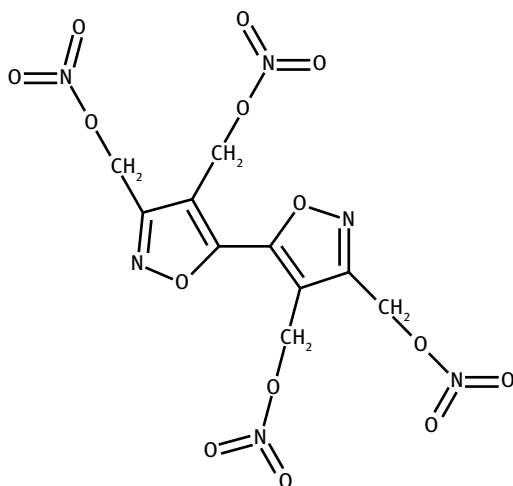
High-energy materials based on isomeric dinitrobi-1,2,5-oxadiazole structures comprising nitrofurazan and nitrofuroxan sub-units were synthesized [706]. Due to planarity and strong non-covalent interactions, these materials display high-density values, as determined by single-crystal XRD. The thermal, impact, and friction sensitivities of both isomers were similar to that of nitroesters. Their high detonation performance along with high density, high HOF, and good oxygen balance make these compounds promising as explosives and high-energy oxidizers.

DFT computations were made to predict the enthalpies of formation, energetic properties, and thermal stability for a series of furazano[3,4-*b*]pyrazine derivatives with different substituents or nitrogen-containing heterocycles [707]. It was found that –N<sub>3</sub> or nitrogen-containing heterocycles improve the energy content of these derivatives. The calculated detonation velocities and detonation pressures indicated that the insertion of –NO<sub>2</sub>, –NF<sub>2</sub>, or –NO<sub>2</sub>-substituted heterocycles will enhance the detonation performance. An analysis of the BDE for relatively weak bonds suggested that most of the derivatives were expected to have good thermal stability. The N–O bond in the furazano[3,4-*b*]pyrazine ring is the weakest bond. Ring cleavage may happen as the first step in thermal decomposition.

## 10 Oxazole and Oxadiazole Derivatives

### 10.1 Oxazole Derivatives

Oxazoles contain one oxygen atom and one nitrogen atom in a five-membered ring. The heteroatoms are usually in the 1,2-positions. Tetrakisnitroxymethylbiisoxazole, bis-isoxazole tetramethylene tetranitrate, 3,3'-biisoxazole-4,4',5,5'-tetrakis(methyl nitrate),  $C_{10}H_8N_6O_{14}$ , BITN, and bisnitroxymethylbiisoxazole, 3,3-bis-isoxazole-5,5'-bis-methylene dinitrate,  $C_8H_6N_4O_8$ , BIDN, are new energetic materials with promising properties and easy synthesis routes [708–710].



Tetrakisnitroxymethylbiisoxazole

### 10.2 Oxadiazole Derivatives

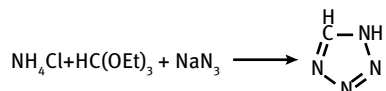
Quantum chemical calculations for 3,3'-bi-1,2,4-oxadiazole derivatives with difluoronitromethyl, fluorodinitromethyl, and trinitromethyl groups have been carried out and they predict promising energetic performances for both explosive and propulsive applications [711, 712].

(5-Nitroimino-4-hydro-1,3,4-oxadiazol-2-yl)methyl nitrate has a high density of  $1.898 \text{ g/cm}^3$  at 149 K [713]. (5-nitroimino-4-hydro-1,3,4-oxadiazol-2-yl)methyl nitrate and 4-amino-1,2,4-triazolium(5-nitroimino-4-hydro-1,3,4-oxadiazol-2-yl) methyl nitrate have low melting points (359.82 and 358.8 K = 86.67 and 85.65 °C), which make them suitable for use as melt-cast explosives.

## 11 Tetrazoles

### 11.1 Tetrazole

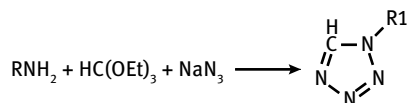
Tetrazole, also known as *1H*-tetrazole, *2H*-tetrazole,  $\text{CH}_2\text{N}_4$ , CAS RN [288-94-8],  $M = 70.053 \text{ g/mol}$ , is the parent molecule of a wide range of high-nitrogen chemicals that are very useful as gas generants and propellant ingredients. Tetrazole itself is not used as such; it is mostly utilized in the form of substituted tetrazoles and their salts. Triazole compounds are often not energetic enough and pentazole remains largely a wishful thought due to its predicted instability. Neither of the two five-membered ring compounds are used in gas generants. Tetrazoles are positioned in the family of five-membered ring heterocyclic amines and they have sufficient energy, high nitrogen content, and are yet stable enough to be handled safely. The most straightforward method for the synthesis of *1H*-tetrazole is the reaction of sodium azide with ammonium chloride and orthoethyl formate in glacial acetic acid.



Tetrazole is the core ring structure for numerous tetrazole derivatives which are valuable as sources of nitrogen in gas generants and as building blocks for HEDMs. The properties of tetrazole compounds have been summarized in several books and review publications, including: [2, 714–718]. The Fedoroff *Encyclopedia of Explosives and Related Items* contains sections on numerous tetrazoles [719]. Open-chained compounds with a composition similar to tetrazole  $(\text{CH}_2)_n\text{N}_4$  were once called “tetrazotic acid,” but this compound is known only in the form of some of its derivatives. These should not be confused with the ring-closed tetrazole derivatives.

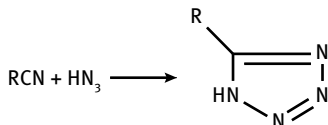
#### 11.1.1 Preparation of Tetrazole and Tetrazole Derivatives

A versatile method of preparing 1-alkyl tetrazoles is by reaction of primary amines with ethylorthoformate and sodium azide, resulting in the formation of 1-monosubstituted tetrazoles.



Bifunctional alkylenediamines react easily and involve both amino groups, thus resulting in the formation of the corresponding bistetrazolyl derivatives with an alkylene group in the middle.

Syntheses requiring hydrogen azide as a reactant are dangerous due to the explosive nature of hydrogen azide. Position-5-substituted alkyltetrazoles can be safely prepared in a continuous method in a micro-flow reactor with dwell times of two to three minutes at 533 K (260 °C) [720].



Various tetrazole derivatives can be obtained by reaction of diaminoguanidine with nitrous acid [721, 722].

### 11.1.2 Physical Properties of Tetrazole

1*H*-Tetrazole forms colorless crystals that melt at 430–431 K (157–158 °C), have a density of 1.477 g/cm<sup>3</sup>, and sublime (boil) at 493 ± 23 K (220 ± 23 °C). Other sources listed the melting point as 429.6 K (156.5 °C). The vapor pressure of tetrazole in the range 333–404 K can be expressed by the equation

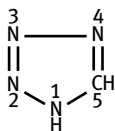
$$\ln P = 31.215 - 10586/T$$

where *P* is the vapor pressure in Pascal and *T* is the temperature in kelvin.

Tetrazole and substituted tetrazoles are amphoteric (amphiprotic) compounds that can form salts with strong acids as well as strong bases. Tetrazolium and tetrazolate salts will be discussed in a later section. We have to first summarize the physical and chemical properties of the neutral non-ionized compounds; although these are only of academic interest, they are often cited in comparison to the substituted compounds which are of interest as rocket propellants and explosives.

#### 11.1.2.1 Molecular Structure of Tetrazole

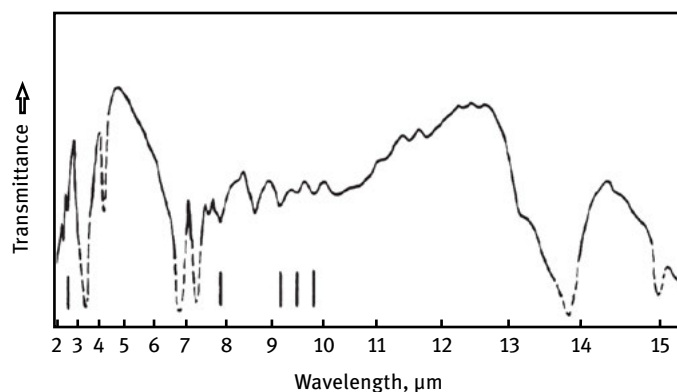
The tetrazole ring structure is stabilized through resonance as a pseudo-aromatic ring. The stability varies with the type of substituents and depends on the loss or addition of protons, forming tetrazolium cations or tetrazolate anions. The numbering of positions in the tetrazole molecule starts at one of the terminal nitrogens and continues in the direction of the adjacent nitrogens, leaving the sole carbon atom in position five.



5*H*-Tetrazole

1*H*-Tetrazole and 2*H*-tetrazole are a tautomeric pair and are aromatic while 5*H*-tetrazole is not. The stability of tetrazole is indicated by the relatively high melting point, 428 K = 155 °C, without decomposition, and the relative stability of the ring compound in chemical reactions involving side groups, e.g., the diazotization of 5-aminotetrazole. The apparent stability of the tetrazole ring indicates that a considerable resonance or stabilizing energy must be present in the system.

The names, formulas, and XRD powder patterns of 29 tetrazole derivatives from known materials were summarized in a publication to identify the crystal structures [723]. A summary of the IR spectra of nitrogen-rich organic compounds contains IR spectra of tetrazole and several tetrazole derivatives [722]. The IR spectrum of tetrazole is shown in Figure 14. The IR spectrum does not contain many characteristic features because the molecule is so symmetrical.



**Figure 14:** Infrared spectrum of tetrazole. (Reproduced and modified from [722], with permission from the Levering Estate.)

XRD analyses and MO calculations of 1*H*-tetrazole were carried out to explain its high stability [724]. Based on XRD results, the five bonds in the ring have been found to have intermediate lengths (between single and double bond lengths). The 1*H*-tetrazole molecule is quite stable because of its aromaticity. The N1—C5 distance of 1.315 Å is significantly shortened compared to the N—C bond in pyrrolidine. The molecular structure, which was calculated by the *ab initio* MO calculation of one 1*H*-tetrazole molecule at MP2/6-31G\* level, showed a good agreement with experimental results except for the abnormally short N1—C5 distance. Calculations of dimers and trimers showed that 1*H*-tetrazole can be stabilized by a strong intermolecular electrostatic interaction between the protons and the delocalized electrons over the ring.

Over the years, the tetrazole moiety has become a strategic group in many industrial applications like gas generants, propellants, and pharmaceuticals. Tetrazoles are



well established as high-nitrogen compounds in gas-generant and propulsion applications.

In addition to forming tetrazolium and tetrazolate salts where protons are exchanged, the neutral tetrazole molecule as a ligand can surround a central metal atom in tetrazolo metal salt complexes. 1*H*-tetrazolo (1HT)-metal complexes were investigated as gas generants for airbag inflators [725]. Thermal stability DSC measurements, sensitivity tests, and deflagration tests were conducted to investigate the influences of the metals on the decomposition characteristics of the complexes. The DSC measurements revealed that the 1HT-metal interaction stabilized the complexes. The deflagration tests indicated that the metals in the substance had a substantial impact on the burning rate.

#### 11.1.2.2 Molecular Structure of Tetrazole Derivatives

DFT computations were performed to study the HOFs, electronic structure, energetic properties, and pyrolysis mechanism of a series of heterocyclic amines, including triazole, tetrazole, furazan, tetrazine, and fused heterocycles [726]. It was found that tetrazole and tetrazine are effective structural units for increasing the  $\Delta H_f^\circ$ 's of the derivatives. Seventy-one compounds had better predicted detonation properties than RDX and 25 compounds had better predicted detonation properties than HMX.

Several observations in the literature indicate that the reactivity of side-chain substituents on tetrazoles (and other azoles as well) depends strikingly on whether the trivalent (pyrrole-type) nitrogen atom is located at the 1- or the 2-position of the tetrazole ring. This dependence has been observed in decarboxylation, hydrogen exchange, diazotization, nucleophilic substitution, and other reactions. Physical measurements have been carried out on several tetrazole derivatives using  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR, and dissociation constants were measured on a group of isomeric pairs of tetrazole derivatives [727].

#### 11.1.2.3 Thermodynamic Properties of Tetrazoles

The HOFs and densities of thirteen different tetrazole derivatives were measured and evolved gas volume, adiabatic flame temperature, and predicted product gas composition for burning mixtures with copper(II) oxide were calculated through chemical equilibrium calculations using these values [728]. Closed bomb tests were conducted for each mixture to measure the pressure-time history and the temperature-time history of burning pellets. There was a good correlation between the theoretical amounts of generated gases and the maximum pressure. It was found that the rate of gas release of six of the tetrazole derivatives can be better than that of the currently used 5-aminotetrazole (5-AT). In some instances, HCN,  $\text{NO}_2$ , and  $\text{NH}_3$  were found in the exhaust gas even though these toxins were not predicted theoretically. There are two literature values for the  $\Delta H_f^\circ$  of 1*H*-tetrazole of 334.3 kJ/mol (79.9 kcal/mol) and 320.5 kJ/mol (76.6 kcal/mol). The lower value may be in error due to the existence of tautomers in the gas phase.

**Table 44:** Heats of combustion and enthalpies of formation of tetrazole and tetrazole derivatives.

| Compound name              | Gross formula                                               | Heat of combustion |               | Enthalpy of formation |          |
|----------------------------|-------------------------------------------------------------|--------------------|---------------|-----------------------|----------|
|                            |                                                             | kJ/mol             | kcal/mol      | kJ/mol                | kcal/mol |
| 1 <i>H</i> -Tetrazole      | CH <sub>2</sub> N <sub>4</sub>                              | 916 ± 0.9          | 219.03 ± 0.21 | +237                  | +56.66   |
| 5-Aminotetrazole           | CH <sub>3</sub> N <sub>5</sub>                              | 1030 ± 2.3         | 246.20 ± 0.56 | +208                  | +49.67   |
| 5-Aminotetrazolium nitrate | CH <sub>4</sub> N <sub>6</sub> O <sub>3</sub>               | 938 ± 1.9          | 224.1 ± 0.45  | −28                   | −6.58    |
| 5-Nitroaminotetrazole      | CH <sub>2</sub> N <sub>6</sub> O <sub>2</sub>               | 931                | 222.6         | +252                  | +60.30   |
| 5-Guanyltetrazole          | C <sub>2</sub> H <sub>5</sub> N <sub>7</sub>                | 1671 ± 1.5         | 399.46 ± 0.37 | +169.7                | +40.57   |
| Guanidinium                | C <sub>2</sub> H <sub>7</sub> N <sub>9</sub> O <sub>2</sub> | 1899 ± 1.6         | 453.8 ± 0.38  | +111                  | +26.59   |
| 5-nitroaminotetrazolate    |                                                             |                    |               |                       |          |
| 5,5'-Hydrazotetrazole      | C <sub>2</sub> H <sub>4</sub> N <sub>10</sub>               | 1924 ± 4.4         | 459.9 ± 1.06  | +565                  | +135.14  |
| For comparison:            |                                                             |                    |               |                       |          |
| Diaminoguanidinium nitrate | CH <sub>8</sub> N <sub>6</sub> O <sub>3</sub>               | 1380 ± 0.4         | 329.8 ± 0.10  | −157                  | −37.56   |
| Nitroaminoguanidine        | CH <sub>5</sub> N <sub>5</sub> O <sub>2</sub>               | 1130 ± 0.7         | 270.1 ± 0.18  | +22                   | +5.30    |
| Nitroguanidine             | CH <sub>3</sub> N <sub>3</sub> O <sub>3</sub>               | 873                | 208.6         | —                     | —        |

Data Source: [249].

The heats of combustion of a wide range of triazole and tetrazole derivatives were determined in a combustion bomb calorimeter. The enthalpies of formation can be derived from these numbers [249, 250] (Table 44). A continuation of this effort provided data for 36 additional high nitrogen compounds [250].

A computational approach to the prediction of the HOFs of energetic salts from electronic structure and VBT calculations used as its starting point reliable  $\Delta H_f^\circ$  data for energetic precursor molecules [167]. The  $\Delta H_f^\circ$  of more complex energetics species such as substituted imidazole, 1,2,4-triazole, and tetrazole molecules containing methyl substituents were calculated in this way and compared to experimental data (Table 45).

Tetrazole and tetrazole derivatives are the basis of many energetic materials due to their 80% nitrogen content, thermal stability, and high enthalpy of formation. A structure-property relationship study focused on the optimized geometries of tetrazole derivatives obtained from DFT calculations [729, 730]. The HOFs of tetrazole derivatives were calculated by designing appropriate isodesmic reactions. The increase in **nitro groups** on azole rings demonstrated a remarkable increase in the enthalpy of formation. Density can be predicted by using a consistent valence force field (CVFF) method. An increase in the number of nitro groups increased the density. Detonation properties of the designed compounds were evaluated by using the K-J equation based on predicted densities and the enthalpy of formation. Designed tetrazole derivatives showed predicted detonation velocities of over 8 km/s and detonation pressures of about 32 GPa. Thermal stability was evaluated via BDE of the weakest C—NO<sub>2</sub> bond.

**Table 45:** Comparison of calculated and experimental gas-phase enthalpy of formation of some neutral tetrazole derivatives.

| Compound                  | Enthalpy of formation, calculated |          | Enthalpy of formation, measured |             |
|---------------------------|-----------------------------------|----------|---------------------------------|-------------|
|                           | kJ/mol                            | kcal/mol | kJ/mol                          | kcal/mol    |
| 1-Methyltetrazole         | +316.3                            | +75.6    | +323.0 ± 2.1                    | +77.2 ± 0.5 |
| 2-Methyltetrazole         | +296.2                            | +70.8    | +328.4 ± 0.8                    | +78.5 ± 0.2 |
| 5-Methyltetrazole         | +286.2                            | +68.4    | +280.7 ± 2.5                    | +67.1 ± 0.6 |
| 1,5-Dimethyltetrazole     | +267.4                            | +63.9    | +273.2 ± 2.9                    | +65.3 ± 0.7 |
| 1-Methyl-5-aminotetrazole | +316.7                            | +75.7    | +302.5 ± 2.9                    | +72.3 ± 0.7 |
| 2-Methyl-5-aminotetrazole | +290.4                            | +69.4    | +298.7 ± 2.9                    | +71.4 ± 0.7 |
| 5-Aminotetrazole          | +335.6                            | +80.2    | +323.8 ± 2.5                    | +77.4 ± 0.6 |

Data source: [167].

### 11.1.3 Chemical Properties of Tetrazole

Tetrazole can be easily deprotonated using common bases such as ammonia, hydrazine, or alkali and alkaline earth metal hydroxides or carbonates forming the corresponding tetrazolate salts of these bases.

In ionic compounds, the tetrazolate ion can often take the place of the azide moiety where it releases a comparable amount of energy upon combustion. However, in covalent bonds in organic compounds, the tetrazole group is more stable and versatile than the azido group. It can also be modified by substitution on the ring to produce a wide range of materials with different  $pK$  values.

Special interest has been devoted to the tetrazolium tetrazolate salts in which one of the tetrazole rings carries a positive charge and the other a negative charge (see also [10]). EILs based on the tetrazolium cation have also been reported (see *Encyclopedia of Liquid Fuels*, chapter “Cyano Compounds and Nitriles”). Although these appear attractive, they can be prepared only via multi-step syntheses. Tetrazoles have been used to develop a wide range of highly energetic ionic liquids. Tetrazole compounds are important energetic materials for applications in gas-generating agents and tetrazole polymers in solid propellants [731].

#### 11.1.3.1 Thermal Stability and Thermal Decomposition of Tetrazole

Tetrazole melts at 429.6 K (156.5°C) and starts decomposing soon thereafter. The kinetic parameters of the thermal decomposition of tetrazole (5,5'-bitetrazole, and 5-alkyl-, and 5-aryl-substituted tetrazoles) in melts of neat substances and nitrobenzene solutions have been determined using a manometric method [732]. The proposed mechanism involves limiting stages of the monomolecular decomposition, which determine the observed rate of nitrogen formation, proceeding to the fast reversible transformation of the 1*H*- and 2*H*-forms and the reversible opening of the

2*H*-form followed by the formation and subsequent cleavage of the corresponding intermediate diazo compound.

The thermal decomposition of 1*H*-tetrazole has been examined at various heating rates and different endpoint temperatures [733]. A pyroprobe was used as a heating device and the gaseous decomposition products were analyzed by FTIR. As a result, two different mechanisms for the thermal decomposition of 1*H*-tetrazole were proposed, which are dependent on the decomposition temperature. At the lower decomposition temperature, the most likely start of 1*H*-tetrazole decomposition is the cleavage of C5—N1 and N3—N4 bonds. This is because HCN and HN<sub>3</sub> will be detected as decomposition products at lower temperatures. At the higher decomposition temperature, various decomposition reactions may occur simultaneously to form such products as HCN, NH<sub>3</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub>.

A very good summary of the various reaction paths taken by tetrazole and tetrazole derivatives during their thermal decomposition is given in Reference [718]. One of the potential reaction products is the thermally more stable melamine. There are several publications about the decomposition of tetrazole itself [734–736].

The thermal stability, product composition, and decomposition mechanism of some polymeric and low-molecular tetrazoles as well as sigma-complexes [PdCl<sub>2</sub>L<sub>2</sub>] (L = low-molecular or polymeric tetrazole ligand) were investigated by TGA, evolved gas volumetry, MS, IR, and UV spectrometry [737]. The kinetic and activation parameters of the decomposition were determined over a wide temperature range in a vacuum, air, and inert atmosphere. The volatile products and condensed residues were analyzed. The thermolysis of di(tetrazol-5-yl)amine under controlled conditions was accompanied by the evolution of 2.5 mols of nitrogen. The decomposition of some polymeric and low-molecular tetrazoles under specific conditions led to the sample ignition and formation of nitrogen as the main gaseous product and condensed residues of unusual structure.

#### 11.1.3.2 Thermal Stability and Thermal Decomposition of Tetrazole Derivatives

The mutual interconversion and decomposition reactions of four tetrazole isomers (1*H*-TZ, 2*H*-TZ, 5*H*-TZ, and an *N*-heterocyclic carbene (14*H*)) have been studied theoretically using *ab initio* computational chemistry [738]. Computations allowed resolution of the existing discrepancies in the mechanism and key intermediates of tetrazole thermolysis. The tautomeric equilibria between 1*H*-TZ, 2*H*-TZ, and 14*H* turned out to play a very important role in the mechanism of thermal decomposition. Although the barriers of monomolecular tautomeric transformations were found to be high (209–293 kJ/mol = 50–70 kcal/mol), the concerted double H atom transfer reactions in the H-bonded complexes of tetrazole tautomers have profoundly lower barriers (75.3–117 kJ/mol = 18–28 kcal/mol). For all species considered, the unimolecular reactions of N<sub>2</sub> elimination were predicted to dominate over the elimination of hydrazoic acid. In agreement with existing experimental data, the effective activation energy of thermolysis was calculated to be 151 kJ/mol (36.2 kcal/mol).

#### 11.1.4 Strand Burning of Tetrazoles

The current section deals only with the strand burning of the unsubstituted tetrazole by itself. There are several other sections later in this chapter that discuss strand burning of 5-aminotetrazole and other tetrazole derivatives.

When investigating the burning of pressed mixtures of tetrazole and sodium tetrazolate, an unusual type of self-organization in combustion accompanied by a formation of a peculiar dynamic dissipative structure was observed. When a pressed mixture of tetrazole and sodium tetrazolate burned, both in an inert atmosphere and in air, an incandescent liquid spheroidal reaction zone of definite size was observed. This feature has been described as a liquid flame [739–742]. The flame formed during the combustion of this structure has the appearance of a luminous mobile fluid sphere, as observed by high-speed photography. This flame leads the process and is accompanied by a considerable gas evolution and an intensive dispersion of condensed products [743]. The conductivity in the combustion wave was measured to investigate the morphology of condensed products formed by liquid-flame combustion. The chemical compositions of the gaseous and condensed products of the thermal decomposition and combustion of pure tetrazole, sodium tetrazolate, and a mixture of both of them were studied by  $^1\text{H}$  NMR, IR, mass spectrometry, gas chromatography, elemental analysis, and XRD [744–746]. The porous residue left behind after the tetrazole/sodium tetrazolate combustion is like a “klinker,” which is a desirable residue structure for gas generants in airbag inflators because less dust clogs the filters (which can make people cough when airbags are deployed).

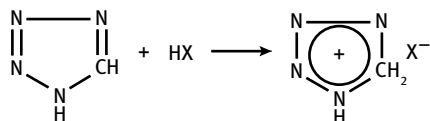
The combustion behavior of tetrazole and 5-chlorotetrazole was studied in the form of pressed strands in a window constant-pressure bomb in the pressure range of 0.1–36 MPa [747]. Temperature profiles in the combustion wave were measured using thin tungsten-rhenium thermocouples embedded in the strands. Analysis of condensed combustion products was carried out using IR spectrophotometry. The principal feature of tetrazole combustion has been shown to consist in the formation of stable energetic nitrile derivatives in the combustion products rather than equilibrium adiabatic composition, resulting in incomplete heat release. Periodic variations in the surface temperature involved a gradual accumulation of a product of high decomposition/boiling temperature at the burning surface, followed by ejecting thereof in the gas and clearing the surface.

The combustion products and temperature distribution in the flame zone of a self-sustained decomposition combustion wave of tetrazole and 5-chlorotetrazole were measured in the absence of air [748, 749]. During the combustion of tetrazole in the absence of an oxidizing agent, non-equilibrium adiabatic combustion products and stable high-energy nitrile derivatives are formed. This prevents the release of all the energy stored in the energetic material. The thermal decomposition takes place at 423–523 K (150–250 °C). The combustion of tetrazole takes place in an unconventional regime that is characterized by a cyclic variation of the surface temperature. This is due to the repeated accumulation of the thermal decomposition products on the sur-

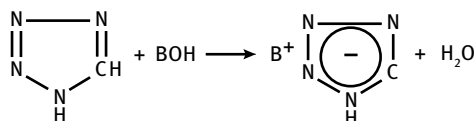
face layer (boiling temperature of the decomposition products is significantly higher than the boiling temperature of the tetrazole), which leads to the subsequent removal of the formed layer and cleaning of the surface.

## 11.2 Tetrazolium and Tetrazolate Salts

Tetrazole is amphoteric and can become protonated when reacted with strong acids.



Tetrazole is a weak acid and has an acidity constant of  $\text{p}K_{\text{a}} = 4.90$  and can act as an acid when reacted with strong bases like BOH, where B is the cation of a strong base [246]:



An excellent summary review of azole (imidazole, triazole, tetrazole) salts with 387 references is given in [109]. Depending on the type of substituent(s) on the two tetrazole rings, energetic salts can be formed in which both the cation and the anion contain a tetrazole ring [750].

### 11.2.1 Tetrazolium Salts

Relatively little work was done on the nitrate or perchlorate salts of the unsubstituted tetrazole. Substantially more work was done on substituted tetrazoles. Substituents on the tetrazole ring can improve the thermal stability and the energy content of these compounds. The most common substituted tetrazole is the 5-aminotetrazole and a substantial amount of work was done on salts derived from 5-aminotetrazole (abbreviated as 5-AT). The physical properties of tetrazolium and substituted tetrazolium salts are summarized in Table 46. The perchlorates are the most stable and the dinitramides are the least stable tetrazolium salts. All are potentially explosive and some are very friction sensitive.

The most facile route for the formation of 1*H*-tetrazole is the reaction of sodium azide with ammonium chloride and orthoethyl formate in glacial acetic acid. 1*H*-Tetrazole was deprotonated using alkali hydroxides or carbonates yielding the corresponding metal salts [753]. The nitrogen-rich salts  $\text{NH}_4\text{TZ} \cdot \text{H}_2\text{O}$  and  $\text{N}_2\text{H}_5\text{TZ}$  were synthesized by the reaction of 1*H*-tetrazole with aqueous  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  solutions,

**Table 46:** Physical properties of tetrazolium and tetrazolate salts.

| Parent amine          | Anion/Cation                                  | Melting point |         | Decomposition temperature |     | Density<br>g/cm <sup>3</sup> | Standard enthalpy of formation (calculated) |          | Impact sensitivity, kg-cm (2-kg weight) | References |
|-----------------------|-----------------------------------------------|---------------|---------|---------------------------|-----|------------------------------|---------------------------------------------|----------|-----------------------------------------|------------|
|                       |                                               | K             | °C      | K                         | °C  |                              | kJ/mol                                      | kcal/mol |                                         |            |
| 1 <i>H</i> -Tetrazole | None                                          | 430           | 156     | 461                       | 188 | 1.53                         | +237                                        | +56.6    | —                                       | [2]        |
| Tetrazolium           | ClO <sub>4</sub> <sup>−</sup>                 | —             | —       | —                         | —   | 2.02                         | —                                           | —        | —                                       | [751]      |
| Tetrazolium           | N(NO <sub>2</sub> ) <sub>2</sub> <sup>−</sup> | —             | —       | —                         | 130 | 1.82                         | +367                                        | +87.7    | 2J                                      | [751]      |
| Tetrazolate           | NH <sub>4</sub> <sup>+</sup>                  | —             | —       | —                         | 216 | 1.34                         | +154                                        | +36.8    | >100J                                   | [752]      |
| Tetrazolate           | N <sub>2</sub> H <sub>5</sub> <sup>+</sup>    | —             | —       | —                         | 232 | 1.39                         | +145                                        | +34.6    | >100J                                   | [752]      |
| 5-Amino-tetrazole     | None                                          | 474–479       | 201–205 | 480                       | 206 | 1.65                         | +208                                        | +49.7    | >120J                                   | [2]        |
|                       | NO <sub>3</sub> <sup>−</sup>                  | 447–448       | 174–175 | 450                       | 177 | 1.847                        | +80.5                                       | +19.25   | —                                       | [2]        |
|                       |                                               | dec.          |         |                           |     |                              |                                             |          |                                         |            |
|                       | ClO <sub>4</sub> <sup>−</sup>                 | —             | —       | —                         | —   | 1.874                        | +158.3                                      | +37.8    | —                                       | [2]        |

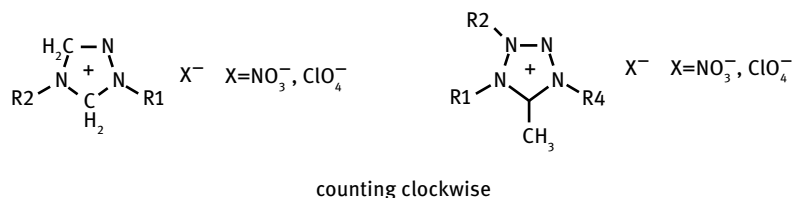
respectively [752]. All compounds were characterized using vibrational (IR and Raman) spectroscopy, multi-nuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>14</sup>N, <sup>15</sup>N) NMR spectroscopy, and elemental analysis. The structures in the crystalline state were determined using low-temperature XRD. The physico-chemical properties of all compounds were investigated using DSC and the HOFs were calculated using heats of combustion obtained by bomb calorimetry. The sensitivities were tested using the BAM drophammer and friction tester. Ammonium tetrazolate crystallizes in monoclinic crystal shapes, space group *P2<sub>1</sub>/n*, with unit cell parameters of *a* = 7.211(1) Å, *b* = 4.0108(8) Å, *c* = 17.991(4) Å, *β* = 91.97(3)°, *V* = 520.0(2) Å<sup>3</sup>, *Z* = 4, *ρ* = 1.343 g/cm<sup>3</sup>. Hydrazinium tetrazolate crystallizes in orthorhombic crystal shapes, space group *Ccca*, with unit cell parameters of *a* = 6.763(1) Å, *b* = 17.7510(4) Å, *c* = 16.3160(8) Å, *V* = 1958.7(3) Å<sup>3</sup>, *Z* = 16, *ρ* = 1.385 g/cm<sup>3</sup>. Tetrazolium dinitromethanide salts can be very insensitive to impact [754].

Properties of methyl-substituted tetrazoles, aminotetrazoles, and quaternary salts were omitted from Table 46 but are available in the literature. Properties of some of the tetrazolium compounds are also found in a separate chapter on ionic liquids in this book.

5-Alkyl-1,2,4-tetrazoles can be quaternized at N4 by reaction with equivalent amounts of alkyl iodides under neat conditions to produce quaternary salts in >98% isolated yields. In this case, 2-amino-1,2,4-tetrazole was readily quaternized at N4 with a concentrated solution of strong acid (nitric or perchloric acid) using methanol as a solvent to form salts in nearly quantitative yields and high purity [404].

The *N*-amino group behaves as an electron-withdrawing group in high-nitrogen heterocycles. Exchanging the position of the amino group from one to four on the

tetrazole ring does affect the physical properties of the resulting salts; e.g., the melting point of the nitrate salt is lowered by 52 °C while having a minimal change in the melting point for the analogous perchlorate (8 °C lower). Concomitantly the thermal stability of the nitrate is improved by 32 °C while that of the perchlorate is lowered by 27 °C. Properties of these triazolium and tetrazolium salts are summarized in Table 47.



The rapid thermal decomposition of substituted tetrazolium salts was analyzed by T-jump/time-of-flight mass spectrometer (TOFMS) capable of high heating rates (up to 10<sup>6</sup> K/s) and rapid sampling. This included 5-amino-1-methyl-1*H*-tetrazolium dinitramide, 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide, 1,5-diamino-1*H*-tetrazolium nitrate, 1,5-diamino-4-methyl-1*H*-tetrazolium azide, and 5-aminotetrazolium dinitramide [755]. In the area of high-oxygen carriers, complex nitrate anions were successfully combined with tetrazolium cations to yield CO/H<sub>2</sub>O balanced ionic liquids of interest for liquid monopropellants [756].

#### 11.2.1.1 Computational Chemistry for Tetrazolium Salts

Numerous theoretical computational studies have been done for tetrazole and other heterocyclic compounds. In most cases the objective was to obtain more accurate data on the enthalpy of formation of the parent molecule, tetrazole, itself and also of the derivatives obtained by substituting one or more hydrogens with other groups (preferably explosophoric groups). Similar calculations were performed for the tetrazolium and tetrazolate salts. Doing the predictive calculations on a computer was much safer than trying to prepare these sensitive compounds in the laboratory and risking explosions before the compound could be burned in a calorimeter. Other calculations attempted to establish a correlation between the impact sensitivity and the bond energy of the weakest bond in the molecule.

A computational approach to the prediction of the HOFs of solid-state energetic salts from an electronic structure and VBT calculations used as its starting point reliable HOF's for energetic precursor molecules and ions [167]. The  $\Delta H_f^\circ$ 's of more complex energetics species, such as substituted imidazole, 1,2,4-triazole, and tetrazole molecules and ions containing amino, azido, and nitro (including methyl) substituents were calculated using an isodesmic approach at the MP2/complete basis set level. Based on comparisons to experimental data for neutral analogues, this isodesmic approach was accurate to <12 kJ/mol (<3 kcal/mol) for the predicted cation



Table 47: Densities and thermochemical results for synthesized triazolium and tetrazolium salts at 298 K.

| Compound name | R1              | R2              | R4              | R5              | X <sup>-</sup>   | T <sub>m</sub> /T <sub>g</sub> |           | T <sub>dec</sub> | $\rho_{\text{calc}}$ | $\rho_{\text{meas.}}^b$ | Const. vol. comb. energy | Molar enthalpy |        | Molar enthalpy formation |
|---------------|-----------------|-----------------|-----------------|-----------------|------------------|--------------------------------|-----------|------------------|----------------------|-------------------------|--------------------------|----------------|--------|--------------------------|
|               |                 |                 |                 |                 |                  | °C                             | °C        |                  |                      |                         |                          | kJ/mol         | kJ/mol |                          |
| Triazole 2    | NH <sub>2</sub> | H               | —               | —               | NO <sub>3</sub>  | 121                            | 149       | 175              | 1.75                 | 1.69                    | 368.80                   | 1536.24        |        | +34.65                   |
| Triazole 3    | NH <sub>2</sub> | H               | —               | —               | ClO <sub>4</sub> | 91                             | 235       | 1.92             | 1.80                 |                         | 434.49                   | 1807.99        |        | +357.01                  |
| Triazole 5    | NH <sub>2</sub> | CH <sub>3</sub> | —               | —               | NO <sub>3</sub>  | -62 (Tg)                       | 217       | 1.60             | 1.51                 |                         | 480.84                   | 2006.26        |        | -174.68                  |
| Triazole 6    | NH <sub>2</sub> | CH <sub>3</sub> | —               | —               | ClO <sub>4</sub> | 108                            | 253       | 1.77             | 1.66                 |                         | 614.43                   | 2562.10        |        | +431.78                  |
| Triazole 7    | H               | NH <sub>2</sub> | —               | —               | NO <sub>3</sub>  | 69 (69)                        | 181 (180) | 1.75             | 1.64                 |                         | 334.28                   | 1391.81        |        | -109.79                  |
| Triazole 8    | H               | NH <sub>2</sub> | —               | —               | ClO <sub>4</sub> | 83 (84)                        | 208 (210) | 1.92             | —                    |                         | 420.49                   | 1749.42        |        | +298.43                  |
| Triazole 10   | CH <sub>3</sub> | NH <sub>2</sub> | —               | —               | NO <sub>3</sub>  | -60 (Tg)                       | 221 (185) | 1.60             | 1.55                 |                         | 477.81                   | 1993.58        |        | -187.36                  |
| Triazole 11   | CH <sub>3</sub> | NH <sub>2</sub> | —               | —               | ClO <sub>4</sub> | 86 (83)                        | 259 (250) | 1.77             | 1.66                 |                         | 562.66                   | 2345.49        |        | +215.17                  |
| Triazole 13   | NH <sub>2</sub> | —               | —               | NH <sub>2</sub> | NO <sub>3</sub>  | —                              | —         | 1.76             | 1.65                 |                         | 373.44                   | 1555.02        |        | -89.49                   |
| Triazole 14   | NH <sub>2</sub> | —               | —               | NH <sub>2</sub> | ClO <sub>4</sub> | —                              | —         | 1.93             | 1.83                 |                         | 499.30                   | 2078.54        |        | +484.64                  |
| Tetrazole 17  | NH <sub>2</sub> | —               | CH <sub>3</sub> | CH <sub>3</sub> | NO <sub>3</sub>  | -59 (Tg)                       | 170       | 1.55             | 1.50                 |                         | 587.85                   | 2453.37        |        | +129.52                  |
| Tetrazole 18  | NH <sub>2</sub> | —               | CH <sub>3</sub> | CH <sub>3</sub> | ClO <sub>4</sub> | 51                             | 182       | 1.71             | —                    |                         | 672.96                   | 2811.76        |        | +538.53                  |
| Tetrazole 21  | —               | NH <sub>2</sub> | CH <sub>3</sub> | CH <sub>3</sub> | NO <sub>3</sub>  | 94                             | 173       | 1.55             | —                    |                         | 595.95                   | 2487.26        |        | +163.41                  |
| Tetrazole 22  | —               | NH <sub>2</sub> | CH <sub>3</sub> | CH <sub>3</sub> | ClO <sub>4</sub> | 140                            | 238       | 1.71             | 1.65                 |                         | 763.32                   | 3184.44        |        | +911.21                  |

Data Source: [404].

and anion  $\Delta H_f$ 's. The  $\Delta H_f$ 's of the energetic salts in the solid state were derived from lattice energy (UL) calculations using a VBT approach. Some of the tetrazolium salts are also low-melting ionic liquids.

Energetic heterocyclic compounds derive most of their energy either from oxidation of the carbon backbone as with traditional energetic materials (such as TNT and HMX) or from their high positive HOFs, such as nitrogen-rich compounds, including 3,3'-azobis(6-amino-1,2,4,5-tetrazine) and tetrazole azide.

In trying to synthesize tetrazolium azotetrazolate salts, disodium 5,5'-azotetrazolate pentahydrate was reacted with 1,4-dimethyl-5-aminotetrazolium iodide or 1,5-diamino-4-methyltetrazolium iodide. However, the metathetical reaction of sodium azotetrazolate with tetrazolium iodide at reflux in water yielded only dihydrated species (1,4-dimethyl-5-aminotetrazolium azotetrazolate dihydrate (**1**) or 1,5-diamino-4-methyl-tetrazolium azotetrazolate dihydrate (**3**)) in both instances [740]. The numbers in parentheses refer to the salts listed in Table 48. However, when silver azotetrazolate was used instead of the sodium salt in dry methanol, the anhydrous compounds 1,4-dimethyl-5-aminotetrazolium azotetrazolate (**2**) and 1,5-diamino-4-methyl-tetrazolium azotetrazolate (**4**) formed. All materials were fully characterized using elemental analysis, MS, vibrational (IR, Raman) and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ) spectroscopy, DSC, and XRD. Decomposition started at the melting points. The detonation pressures and velocities were calculated from the energies of formation using the EXPLO5 code and are summarized in Table 48. Because these compounds are slightly under-oxidized, their performance can be boosted by adding some oxidizer like AN or ADN. Performance calculations were made for tetrazolium azotetrazolates with ADN, increasing the detonation pressure from 20 to 31 GPa and increasing the detonation velocity from 7800 to 8800 m/s. The impact sensitivity was >30 J and the friction sensitivity was above 360 N. There was no reaction in the ESD test.

DFT and volume-based thermodynamics (VBT) calculations were performed to screen 34 protonated and 34 methylated tetrazolium energetic salts with high energy and good stability [758]. Combinations of tetrazolium cations containing different substituents ( $-\text{CH}_3$ ,  $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{CN}$ ,  $-\text{N}_3$ ,  $-\text{NH}_2$ ) with energetic anions ( $\text{NO}_3^-$ ,  $\text{N}(\text{NO}_2)_2^-$ ,  $\text{N}_3^-$ ,  $\text{ClO}_4^-$ ) were made to predict their densities, thermodynamic properties, and explosive performances. The focus was primarily on investigating the role of different substituents and energetic anions in the design of high-energy salts. The volumes of the cations and anions were estimated to obtain the crystal densities of the salts from electronic structure calculations. The HOFs of cations, anions, and lattice energies of the salts were calculated separately to obtain the  $\Delta H_f$ 's of the salts based on Born-Haber energy cycles. Using these densities and HOFs, the detonation velocities and detonation pressures of the salts were predicted by K-J equations. When the H atom of the tetrazolium cation is replaced by  $-\text{CH}_3$ ,  $-\text{CN}$ , or  $-\text{NH}_2$ , the density of its nitrate salt is smaller than that of unsubstituted tetrazolium nitrate. The  $\Delta H_f$ 's of the nitrate salts containing the protonated tetrazolium cations are larger

Table 48: Properties of tetrazolium azotetrazolate salts.

| Number | Compound name                                             | Formula                                                       | Nitrogen content |  | Density<br>g/cm <sup>3</sup> | Onset of decomposition |     | Enthalpy of formation<br>kJ/kg | Detonation pressure<br>GPa | Detonation velocity<br>m/s |
|--------|-----------------------------------------------------------|---------------------------------------------------------------|------------------|--|------------------------------|------------------------|-----|--------------------------------|----------------------------|----------------------------|
|        |                                                           |                                                               | Mass %           |  |                              | K                      | °C  |                                |                            |                            |
| 1      | 1,4-Dimethyl-5-aminotetrazolium azotetrazolate dihydrate  | C <sub>8</sub> H <sub>20</sub> N <sub>20</sub> O <sub>2</sub> | 65.4             |  | 1.441                        | 470                    | 197 | +2700                          | 20.2                       | 7820                       |
| 2      | 1,4-Dimethyl-5-aminotetrazolium azotetrazolate            | C <sub>8</sub> H <sub>16</sub> N <sub>20</sub>                | 71.4             |  | 1.431                        | 466                    | 193 | +3800                          | 20.0                       | 7803                       |
| 3      | 1,5-Diamino-4-methyl-tetrazolium azotetrazolate dihydrate | C <sub>6</sub> H <sub>18</sub> N <sub>22</sub> O <sub>2</sub> | 71.6             |  | 1.546                        | 456                    | 183 | +2200                          | 22.4                       | 8090                       |
| 4      | 1,5-Diamino-4-methyl-tetrazolium azotetrazolate           | C <sub>6</sub> H <sub>14</sub> N <sub>22</sub>                | 78.1             |  | 1.427                        | 443                    | 170 | +4100                          | 21.1                       | 7977                       |

Data source: [757].

than those of the nitrate salts containing the methylated tetrazolium cations with the same substituent and substitution position.

#### 11.2.1.2 Tetrazolium Azide

The enthalpy of formation of tetrazolium azide,  $\text{CHN}_7$ , is +458 kJ/mol (+109.5 kcal/mol). It is closely related to 5-azidotetrazole, which is stable at room temperature but is extremely shock and friction sensitive and detonates readily. Tetrazolium azide, a very nitrogen-rich material (88.3% N) with high shock and friction sensitivity, can be prepared in good yield by the diazotation reaction of 5-aminotetrazole, followed by treatment of the formed diazonium salt with sodium azide [759]. Synthesis in diethyl ether/methanol and recrystallization from diethyl ether afforded colorless cubes which formed monoclinic crystals, space group  $P1_21/n1$ , with unit cell parameters of  $a = 1346.6(5)$  pm,  $b = 499.6(2)$  pm,  $c = 1360.9(5)$  pm,  $\beta = 105.14(1)^\circ$ ,  $V = 0.884(2)$  nm<sup>3</sup>,  $Z = 8$ , and  $\rho = 1.670$  g/cm<sup>3</sup>. The observed structural parameters were in good accordance with the results from MO calculations (1 picometer = 1 pm =  $10^{-12}$  m = 0.01 Å; 1 nano-meter = 1 nm = 10 Å). A variety of heterocyclic groups (tetrazolo-pyridines, tetrazolo-pyridazines, tetrazolo-pyrimidines, tetrazolo-azines, tetrazolo-purines, etc.) have been reported to exhibit tetrazole-azide isomerization.

#### 11.2.2 Tetrazolate Salts

Tetrazole and 5-methyltetrazole form salts with quaternary alkylammonium ions. These salts behave as ionic liquids. Several of these ionic liquids were prepared, starting with 5-methyltetrazole and followed by *N,N*-dimethylbutylamine, isopropylamine, diisopropylamine, butylamine, or *n*-pentylamine. These were tested as solvents for AP or potassium perchlorate with a view of using them as monopropellants [184].

When 1-butylamine, 1-pentyl amine, or 1-hexylamine reacted with 5-methyl-1*H*-tetrazole, molten salts were formed. Indeed, the melting point ranges for the [1-butylammonium][5-methyl-1-tetrazolate], [1-pentylammonium][5-methyl-1-tetrazolate], and [1-hexylammonium][5-methyl-1-tetrazolate] were remarkably low at between 235 to 239 K (−38 to −34 °C), 238 to 243 K (−35 to −30 °C), and 235 to 241 K (−38 to −32 °C), respectively. When plotting the melting point versus the alkyl chain length of the primary amines, the shape of the plot is noticeably similar to that demonstrated for imidazolium-based ILs with a minimum of melting point at chain lengths with four to six carbon atoms. The wide range of temperatures at which the alkylammonium 5-methyl-1*H*-tetrazolates are liquids is particularly attractive for rocket propulsion under varied environmental conditions as well as for storage considerations.

Energetic ILs (EILs) can be formed from tetrazolium cations with oxidizing anions (perchlorate, nitrate, dinitramide) or energetic cations with tetrazolide anions [760].

Claimed in this patent are EILs comprising a tetrazolide anion and/or a tetrazolium cation.

Various tetrazolate salts of nitrogen-rich amines have been considered as ionic liquid fuels in combination with HAN as either monopropellants or electrospray colloid working fluids [761–765]. Table 49 is a summary of the properties of tetrazolate salts.

**Table 49:** Properties of tetrazolate salts.

| Fuel #          | Fuel name                                                   | Formula                                        | $\Delta H_f(G)$<br>kJ/mol | Density<br>g/cm <sup>3</sup> | Melting point<br>K |
|-----------------|-------------------------------------------------------------|------------------------------------------------|---------------------------|------------------------------|--------------------|
| 1               | 1-Butyl-3-methylimidazolium dicyanamide                     | C <sub>10</sub> H <sub>15</sub> N <sub>5</sub> | +363.40                   | 1.06                         | 267                |
| 2               | 1-Butyl-3-methylpyrrolidinium dicyanamide                   | C <sub>11</sub> H <sub>20</sub> N <sub>4</sub> | +218.90                   | 1.02                         | 223                |
| 3               | Hydrazinium 5-aminotetrazolate                              | CH <sub>7</sub> N <sub>7</sub>                 | +383.60                   | 1.48                         | 398                |
| 4               | Guanidinium 5-aminotetrazolate                              | C <sub>2</sub> H <sub>8</sub> N <sub>8</sub>   | +205.40                   | 1.54                         | 399                |
| 5               | Aminoguanidinium 5-aminotetrazolate                         | C <sub>2</sub> H <sub>9</sub> N <sub>9</sub>   | +302.30                   | 1.51                         | 366                |
| 6               | Guanylguanidinium 5-aminotetrazolate                        | C <sub>3</sub> H <sub>10</sub> N <sub>10</sub> | +306.90                   | 1.41                         | 414                |
| 7               | 4-Amino-1 <i>H</i> -1,2,4-triazolium 5-aminotetrazolate     | C <sub>3</sub> H <sub>7</sub> N <sub>9</sub>   | +565.00                   | 1.62                         | 387                |
| 8               | 4-Amino-1-methyl-1,2,4-triazolium 5-aminotetrazolate        | C <sub>4</sub> H <sub>9</sub> N <sub>9</sub>   | +546.00                   | 1.46                         | 249                |
| 9               | 4-Amino-1-ethyl-1,2,4-triazolium 5-aminotetrazolate         | C <sub>5</sub> H <sub>11</sub> N <sub>9</sub>  | +523.40                   | 1.39                         | 235                |
| 10              | 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium 5-aminotetrazolate | C <sub>3</sub> H <sub>9</sub> N <sub>11</sub>  | +655.10                   | 1.57                         | 444                |
| For comparison: |                                                             |                                                |                           |                              |                    |
|                 | Hydroxylammonium nitrate                                    | NH <sub>3</sub> OHNO <sub>3</sub>              | −79.68                    | 1.83                         | 316.05             |

Data Source: [761].

Propellants **1**, **2**, **8**, and **9** in Table 48 demonstrated storability that is equal to or better than that of hydrazine. The remaining six propellants were not storable propellants and, therefore, they were dropped from further consideration.

A series of nitrogen-rich nitroguanidyl-functionalized tetrazolate salts paired with guanidinium-derivatized and heterocycle-based cations were synthesized. Most exhibited better thermal stability, higher density, and a more positive HOF than their tetrazolate analogues [766].

DFT and VBT calculations have been performed to study the crystal densities, HOFs ( $\Delta H_f$ 's), and energetic properties for a series of ionic salts composed of triamino-

guanidinium or ammonium cations and substituted tetrazolate anions [767]. Substitution with  $-\text{NF}_2$ ,  $-\text{CH}_2\text{NF}_2$ ,  $-\text{CF}_2\text{NF}_2$ , or  $-\text{C}(\text{NO}_2)_2\text{NF}_2$  groups increased the densities of the salts. The densities of the tetrazolate salts were affected not only by different substituents but also by different cations. The  $-\text{CN}$  or  $-\text{N}_3$  groups were effective substituents for increasing the  $\Delta H_f$ 's of the salts. The triaminoguanidinium cation was more effective than the ammonium cation for increasing the  $\Delta H_f$ 's of the tetrazole-based salts. Substitution with  $-\text{NO}_2$ ,  $-\text{NF}_2$ , or  $-\text{C}(\text{NO}_2)_2\text{NF}_2$  groups enhanced the explosive performance of the salts.

While it is relatively easy to prepare alkali metal salts of tetrazole, the reactions forming heavier metal salts are more complex. Many metal salts (in particular their perchlorates) are shock-sensitive.

1*H*-Tetrazole was deprotonated using alkali hydroxides or carbonates. This yielded the corresponding metal salts (Li, Na, K, Rb, and Cs), the crystal structures of which were determined using single-crystal XRD. In addition to this, the compounds were characterized using IR, Raman and NMR spectroscopy, elemental analysis, and DSC [753].

There are many publications on complex transition metal salts with tetrazole ligands in the literature, but most of those investigations were aimed at stab-sensitive primary explosives as replacements for lead azide and lead styphnate. We are not attempting to cover this area in this book and, therefore, have not listed these literature references.

## 12 Neutral Mono-Substituted Tetrazole Derivatives

### 12.1 5-Aminotetrazole

5-Aminotetrazole, also known as  $\text{CH}_3\text{N}_5$ , 2*H*-tetrazol-5-amine, tetrazolyl-5-amine, 1*H*-tetrazol-5-ylamine, 5-amino-1,2,3,4-tetrazole, 5-AT, CAS RN [4418-61-5],  $M = 85.07$  g/mol, is a versatile high-nitrogen compound that is widely used in automobile airbag inflator gas generants. It has a very high nitrogen content (82% N). It is readily available and produced in large quantities. Commercial products are usually sold as the monohydrate, CAS RN [15454-54-3]. 5-Aminotetrazole is amphoteric and can form salts with strong bases as well as strong acids. The  $pK$  of 5-aminotetrazole in  $\text{H}_2\text{O}$  is 1.82.

#### 12.1.1 Preparation of 5-Aminotetrazole

5-Aminotetrazole can be prepared by (1) diazotization of aminoguanidine or (2) by reaction of cyanoguanidine or dicyandiamide with hydrazoic acid. Both methods give good results and yield 5-AT in a sufficiently pure state for any potential use. Method (1) is rapid and safe but the yield is low (about 75%), while method (2) is slow

and the reactant, hydrazoic acid, is highly toxic, dangerous, and explosive but gives a higher overall yield and better product quality. Instead of using free hydrazoic acid, cyanamide or dicyandiamide and an azide salt are reacted to produce 5-AT [768].

5-Aminotetrazole can be produced from dicyandiamide and sodium azide in water with zinc bromide as a catalyst [769]. The effects of the reactant molar ratio, catalyst consumption, temperature, and reaction time were measured. The results revealed that, when the molar ratio of sodium azide to dicyandiamide is 1:1.6 and the catalyst consumption of sodium azide to zinc bromide is 1:0.3, the reaction temperature is 348–358 K (75–85 °C), the reaction time is 5.5 h, and the yield of 5-aminotetrazole can reach 83.6%.

5-Aminotetrazole was synthesized by diazotization of aminoguanidinium nitrate and intra-molecular cyclization under basic conditions [770]. The resulting 5-amino-tetrazole was characterized by IR,  $^{13}\text{C}$  NMR, and MS. A mechanism of the reaction was proposed. The key variables affecting the yield, such as acidity or the basicity of the reaction system, reaction temperature, and time were optimized. The optimized procedures were as follows: pH = 2–3,  $T = 293\text{--}303\text{ K} = 20\text{--}30\text{ }^{\circ}\text{C}$ , and  $t = 0.5\text{ h}$  for diazo-reaction; pH = 8–9,  $T = 358\text{--}363\text{ K} = 85\text{--}90\text{ }^{\circ}\text{C}$ , and  $t = 3.5\text{ h}$  for intra-molecular cycliza-tion. The yield of 5-aminotetrazole could be up to 77%.

1-Aminotetrazole carries the amino group on a nitrogen atom instead of the carbon atom, just as in 5-AT. 1-Aminotetrazole has a chain of five catenated nitrogen atoms and is thermally less stable than 5-AT. A three-step synthesis method of 1-aminotetra-zole by condensation, cyclization, and hydrolysis reactions was studied using ben-zaldehyde, triethyl ortho-formate, and hydrazine hydrate as raw materials [771]. The structures of intermediates and products were characterized using IR, NMR, and ele-mental analysis. The influence of the condensation-reaction temperature and molar ratio of triethyl ortho-formate to benzaldehyde hydrazone in cyclization reaction on reaction yield was investigated. The optimum reaction conditions were defined as fol-lows: a condensation-reaction temperature of 273–278 K (0–5 °C) and the molar ratio (triethyl ortho-formate):(benzaldehyde hydrazone) was 1.8:1. The total yield of the three-step reaction was 49.5% (see also [772, 773]).

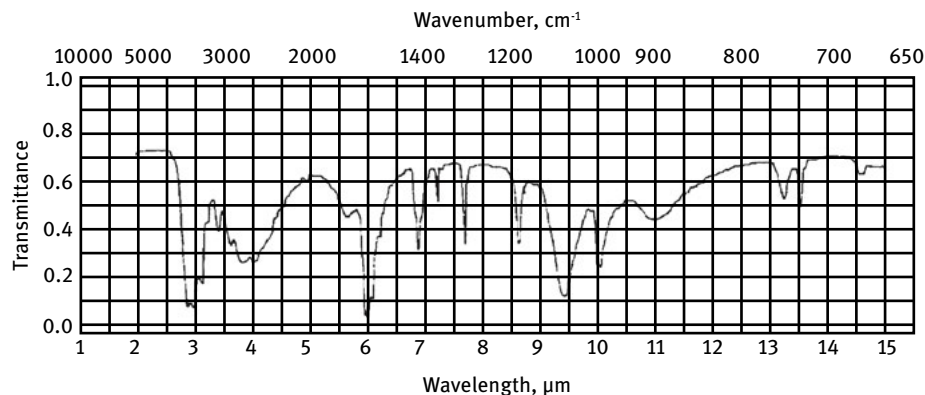
### 12.1.2 Physical Properties of 5-Aminotetrazole

5-Aminotetrazole forms colorless crystals that melt at 474–479 K (201–205 °C). The monohydrate, which is the common form of commerce, CAS RN [15454-54-3], melts at 471–474 K (198–204 °C) and the melting results in a loss of water. The vapor pressure of 5-aminotetrazole in the range 383–443 K can be expressed by the equation

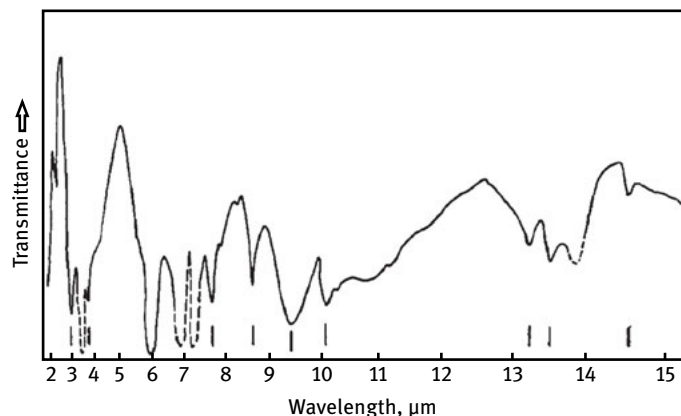
$$\ln P = 32.929 - 13540/T$$

where  $P$  is the vapor pressure in Pascal and  $T$  is the temperature in kelvin.

The IR spectra of aminotetrazole are shown in Figures 15 and 16 [774, 775]. The Pristera and Fredericks [774] spectra were taken with a sample of the material sus-



**Figure 15:** Infrared spectrum of 5-aminotetrazole. (Reproduced and modified from [774].)



**Figure 16:** IR Spectrum of 5-aminotetrazole. (Reproduced and modified from [722], with permission from the Levering Estate.)

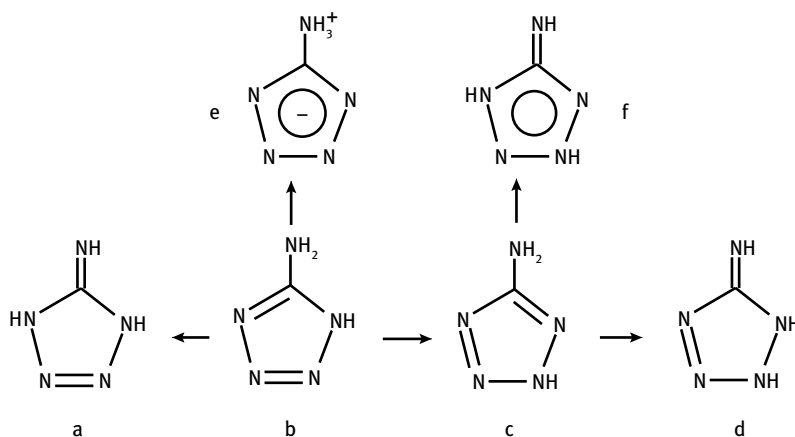
pended in white mineral oil. The mineral oil absorption was always superimposed on the spectrum of the other compound. The main oil absorption bands have been marked by dotted lines in the figures, while the bands considered to be due to the compound under study have been marked with a small vertical line.

#### 12.1.2.1 Molecular Structure of 5-Aminotetrazole

Powder XRD, Rietveld analysis, and DFT calculations were used to investigate the crystal structure of 5-aminotetrazole [776]. It crystallized in an orthorhombic crystal, space group  $P2_12_12_1$  with a 1*H*-form molecule. The orthorhombic phase was stable up to at least 11.6 GPa.



The tautomerism and intra-molecular hydrogen shifts of 5-amino-tetrazole in the gas phase were studied by MO quantum chemical calculations and the six possible tautomers of 1*H*, 4*H*-5-imino-tetrazole (**1**), 1*H*-5-amino-tetrazole (**2**), 2*H*-5-amino-tetrazole (**3**), 1*H*,2*H*-5-imino-tetrazole (**4**), the meso-ionic form (**5**) and 2*H*,4*H*-5-imino-tetrazole (**6**) were investigated [777]. Among these tautomers, there were 2 amino- forms, 3 imino- forms, and 1 meso-ionic structure form. In all the tautomers, 2-*H* form (**3**) was the energetically preferred one in the gas phase. The energy barriers of amino- → imino-tautomerism reactions required were 59 to 73 kcal/mol in the gas phase.



**a:** 1*H*,4*H*-5-imino-tetrazole

**b:** 1-*H*-5-amino-tetrazole

**c:** 2-*H*-5-amino-tetrazole

**d:** 1*H*,2*H*-5-imino-tetrazole

**e:** the mesoionic form

**f:** 2*H*,4*H*-5-imino-tetrazole

#### 12.1.2.2 Thermodynamic Properties of 5-Aminotetrazole

The enthalpies of formation for 49 tetrazole derivatives were calculated with a DFT method and designed isodesmic and isogyric reactions [778]. The average absolute deviation for five compounds for which experimental  $\Delta H_f$ 's were available was less than 2 kcal/mol. The calculated  $\Delta H_f$ 's indicated that most neutral 2*H*-isomers are predicted to be more stable than the corresponding 1*H*-isomers, whereas the one-substituted tetrazolate anions are more stable than the corresponding two-substituted ones. Results consistently showed that C-substituted tetrazoles are more stable than the corresponding N-substituted isomers. The enthalpy of formation of 5-aminotetrazole is +585 cal/g = +49.7 kcal/mol = +208 kJ/mol. The density is 0.0596 lb/in.<sup>3</sup> = 1.65 g/cm<sup>3</sup>.

The enthalpy of formation of the homologue 2-methyl-5-aminotetrazole  $C_2H_5N_5$ , is  $+500 \text{ cal/g} = +49.5 \text{ kcal/mol} = +207 \text{ kJ/mol}$ .

### 12.1.3 Chemical Properties of 5-Aminotetrazole

5-Aminotetrazole is amphoteric, a property that enables it to form salts with strong acids such as nitric acid, as well as with strong bases such as potassium hydroxide. Its tautomeric form is a 5-iminotetrazole. 5-Aminotetrazole is a weak acid ( $pK_a \approx 6$ ) [779]. It has often been employed as a cation precursor in the synthesis of energetic salts because it behaves as a weak base with strong inorganic acids ( $pK_a \leq 0$ ) under normal conditions. It can be protonated by perchloric, nitric, sulfuric, picric, and hydrohalic acids (HX, X = Cl, Br, I). Both nitrates and potassium salts are used in airbag inflator gas generant formulations along with the parent compound.

5-Aminotetrazole can be easily deprotonated in an aqueous solution using strong bases (hydrazine, biguanidine, LiOH, and NaOH). Hydrazinium 5-aminotetrazolate, biguanidinium 5-aminotetrazolate, and 1-amino-1,2,4-triazolium 5-aminotetrazolate were synthesized by using this methodology. The reaction of guanidinium,  $K^+$ ,  $Rb^+$ , or  $Cs^+$  carbonates and aminoguanidine bicarbonate with 5-aminotetrazole resulted in the formation of salts with concomitant release of carbon dioxide [753, 780]. Similar reactions of 5-AT with alkaline earth metal carbonates lead to hydrated alkaline earth metal salts of 5-amino-1*H*-tetrazole [781].

### 12.1.4 Thermal Decomposition of 5-Aminotetrazole

As in the case of the unsubstituted tetrazole, the thermolysis of 5-AT may start with the tautomeric imino form, which is more labile. The thermal decomposition of the imino form starts just after the melting stage and results in the evolution of hydrogen azide. An increase in the temperature leads to another pathway of thermal decomposition involving corresponding amino forms, which decompose with the elimination of nitrogen. The apparent activation energies of the thermal decomposition of imino forms are in the range of 180–200 kJ/mol. The thermal decomposition of the unsubstituted tetrazole was already discussed in an earlier section of this book. The thermal decomposition of bi- and multiple-substituted tetrazoles will be described in a section further down in this chapter.

The rapid thermolysis of mono- and di-aminotetrazoles was studied by flash pyrolysis with IR analysis of the decomposition products [782]. The thermal decomposition of 5-AT was studied by TGA, DSC, DTA, and via EGA [783]. Solid products of thermal decomposition were identified by IR. Gaseous products were identified by IR and MS. Theoretical considerations of thermodynamic characteristics and bond energies in the 5-AT tautomeric forms and intermediates have been carried out by a MO-SCF computational method. Based on IR and available literature data, it was shown that dehydrated 5-AT exists mainly in the imino form in the solid state. Thermal treatment leads to increased content of the amino form. The thermal decomposition of

the imino form of 5-AT started just after melting and resulted in hydrogen azide and carbodiimide formation. Linear polymers of carbodiimide and melamine derivatives have been identified in the solid residue. At higher temperatures, decomposition of the amino form of 5-AT leads to the evolution of nitrogen. Apparent activation energies of these routes determined from non-isothermal TGA data were 165 and 135 kJ/mol, respectively.

The thermal decomposition of 1-methyl-5-aminotetrazole and 1,5-diaminotetrazole was investigated using TGA, DSC, and thermal volumetric analysis (TVA) [784]. The solid residues and the high boiling point and gaseous products of the decomposition were collected and identified using IR and MS. Both aminotetrazoles started to decompose just after melting; 1-methyl-5-aminotetrazole at 495 K and 1,5-diaminotetrazole at 460 K. Both 1-methyl-5-aminotetrazole and 1,5-diaminotetrazole, in the solid state (and probably in the melt), co-existed in both amino and imino tautomeric forms. Two competing mechanisms of tetrazole ring-breaking with the elimination of either nitrogen or hydrogen azide were proposed.

The hydrohalide (HCl, HBr, HI) salts of 5-amino-1*H*-tetrazole were flash-pyrolyzed under 0.5 MPa of Ar by T-jump/FTIR spectroscopy, and the gaseous products were determined at 623, 673, and 723 K (350, 400, and 450 °C) [785, 786]. Comparison of the products indicated that two global decomposition pathways exist, two reaction channels which give somewhat different products. The first is the dissociation of the salt to form HX and 5-AT followed by decomposition of neutral 5-AT. The second involves the decomposition of the  $[5\text{-AT}]^+$  ion directly. The ratio of these two channels depends on the compound. The first channel is favored over the second channel in the order  $\text{HCl} > \text{HBr} > \text{HI}$ , which is the trend of the  $\text{p}K_{\text{a}}$  values of these acids. This information enables both the relative ordering of the burning rates as a function of pressure. It also allows the determination of the trend of the pressure dependence of the individual burning rates of these compounds. This provides a better understanding of the global decomposition pathways.

The thermal decomposition of 5-AT, 1-methyl-5-aminotetrazole (MAT), 1,5-diaminotetrazole (DAT), poly-1-vinyl-5-aminotetrazole (PVAT), and the sodium salt of 5-aminotetrazole (SAT) have been studied by TGA, TVA, DSC, DTA, and EGA [787]. The kinetic parameters of the thermal decomposition of aminotetrazoles were calculated either by using the Ozawa method or by the method of invariant kinetic parameters. The gaseous products, volatile condensed products, and solid residues were identified by FTIR and GC/MS. Based on the content of the products of thermal decomposition and the kinetic consideration, a mechanism of thermal decomposition of aminotetrazoles has been proposed. Two routes for splitting the tetrazole ring, which leads either to the elimination of nitrogen or hydrogen azide, were suggested. The contribution of each route is changing upon the advancement of the process. It was assumed that hydrogen azide splits out from the prothotropic forms of the tetrazole ring, which have hydrogen atoms by nitrogens in the ring.

Secondary reactions significantly extend and change the variety of the products of the thermal decomposition of aminotetrazoles.

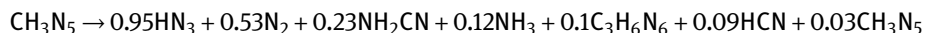
The pathway and *ab initio* direct kinetics of the decomposition of 5-AT to  $\text{HN}_3$  and  $\text{NH}_2\text{CN}$  was investigated by computational methods [788]. Rate constants were evaluated by conventional transition-state theory and canonical variational transition-state theory with tunneling effect over 300 to 2500 K. The results indicated that the tunneling effect and the variational effect are small for the calculated rate constants. The fitted three-parameter expressions calculated using the two different methods were

$$k(T) = 4.07 \times 10^{11} \times T^{0.84} \times e^{(-24200/T)} \text{ s}^{-1}$$

and

$$k(T) = 2.09 \times 10^{11} \times T^{0.89} \times e^{(-23600/T)} \text{ s}^{-1}.$$

The kinetics of the 5-AT thermal decomposition in the condensed phase at high heating rates ( $>100 \text{ K/s}$ ) was studied by a dynamic mass spectrometric thermal analysis using a molecular beam sampling system and the product composition as a function of time was determined [789]. Two routes of 5-aminotetrazole decomposition can be distinguished, one yielding  $\text{HN}_3$  and  $\text{NH}_2\text{CN}$  (route 1), and the other  $\text{N}_2$  and  $\text{CH}_3\text{N}_3$  (route 2). The activation energy and rate constant of 5-AT decomposition were determined for each route. In all experiments at different heating rates, the  $m/e = 43$  peak ( $\text{HN}_3$ ) had a single maximum coinciding with the first maximum of the  $m/e = 28$  peak intensity. Thus, the experimentally observed stepwise character of the thermal decomposition of 5-AT is due to the decomposition of 5-AT itself at the first stage and reactions involving only secondary products at the second stage. Taking melamine ( $\text{C}_3\text{H}_6\text{N}_6$ ) into account, the overall 5-AT thermal decomposition reaction ( $T = \sim 628 \text{ K} = \sim 355^\circ\text{C}$ , heating rate of  $\sim 135 \text{ K/s}$ ) can be expressed by:



The thermal decomposition of 5-aminotetrazole was studied theoretically using computational techniques [790]. The unimolecular primary decomposition reactions of the three most stable isomers of 5-AT were studied in the gas phase and the melt using a simplified model of the latter. In contrast to all previous publications, a consideration of the bimolecular reactions of 5-AT demonstrated that bimolecular reactions are very important, especially in the condensed phase. It was found that the imino form undergoes fast isomerization to the amino form in the H-bonded dimers and does not participate in the 5-AT thermolysis. On the contrary, amino (and probably the 2H isomer) are the main isomers of 5-AT in the melt and gas phase. The  $\text{N}_2$  elimination reaction was found to be the dominant unimolecular channel of the amino and 2H isomer decomposition in both the gas phase and melt. In agreement with the existing experimental data,  $\text{HN}_3$  elimination dominates for some of the considered complexes. It was concluded that the initial stages of thermolysis of 5-AT

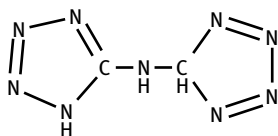
cannot be satisfactorily described by the simple unimolecular reactions proposed in the literature. The solid-state decomposition was found experimentally to be negligible for 5-AT. Thermolysis proceeds in the melt and gas phases.

A specular reflection isopotential method was used to investigate the unimolecular decomposition mechanisms of 5-iminotetrazole, 1*H*-5-aminotetrazole, and 2*H*-5-aminotetrazole [791]. Based upon the predicted relative reaction barriers, the initial gaseous products of 5-iminotetrazole unimolecular decomposition are  $\text{HN}_3$  and  $\text{NH}_2\text{CN}$ . On the other hand, the initial gaseous products of 1*H*-5-aminotetrazole and 2*H*-5-aminotetrazole unimolecular decomposition were predicted to be  $\text{N}_2$  and metastable  $\text{CH}_3\text{N}_3$ . These predicted unimolecular decomposition products and activation barriers were in excellent agreement with thermal decomposition experiments reported by others.

A study of the tautomerization and decomposition channels of aminotetrazoles, mainly 5-aminotetrazole and 1,5-diaminotetrazole, showed that one-substituted-aminotetrazoles, two-substituted-aminotetrazole, and one-substituted-iminotetrazoles are the most common isomers of aminotetrazoles [792]. There are two mechanisms for the decomposition of aminotetrazoles: In the first mechanism, the two bonds of the tetrazole ring break off, resulting in  $\text{RN}_3$  and  $\text{NH}_2\text{CN}$ . The second decomposition channel comprises of two steps: Firstly the N—N bond is cleaved, leading to  $\text{RN}_3$ . Then the produced  $\text{RN}_3$  loses one molecule  $\text{N}_2$ . The tautomerization mechanisms of aminotetrazoles represented by 5-aminotetrazole and 1,5-diaminotetrazole were investigated by using high-level quantum chemistry calculations. The results showed that the active energy of the first decomposition pathway is lower than that of other paths. Therefore, it is the most probable reaction path.

Adding one or two methyl groups on the ring to 5-AT results in tetrazoles with slightly different properties. 1-Methyl-5-amino-1*H*-tetrazole,  $\text{C}_2\text{H}_5\text{N}_5$ ; 1*H*-Tetrazol-5-amine, 1-methyl-; CAS RN [5422-44-6] can form salts similar to 5-AT.

5-Aminotetrazole, which is a primary amine with an  $-\text{NH}_2$  group, is one of the most widely used heterocyclic gas generant constituents. Similar properties can be achieved from salts of a secondary amine,  $\text{R}_2\text{NH}$ , which was bis(1*H*-tetrazolyl)amine, *N*-(5*H*-tetrazol-5-yl)-1*H*-tetrazol-5-amine, (also abbreviated as BTA) in this case. It is also amphoteric like 5-AT itself, forming salts with strong bases.



Bis(1*H*-tetrazolyl)amine

The burning rate of the ammonium salt of bis(1*H*-tetrazolyl)amine has been tested as a gas generant ingredient. The burning rate of bis(1*H*-tetrazolyl) amine ammonium

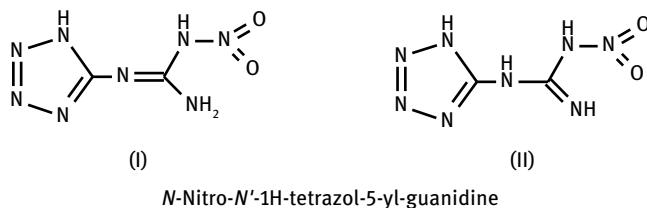
salt and potassium nitrate phase-stabilized AN mixtures; this was examined and an equation for the burning rate as a function of pressure and temperature was obtained [793]. The burning rates predicted by the regression equations were in good agreement with the observed values. The temperature sensitivities were also predicted using the regression equation and compared with the observed values. Good agreement was found between the predicted and observed values.

## 12.2 *N*-Substituted 5-Aminotetrazoles

*N*-Substituted aminotetrazoles can be obtained by reaction of cyanogen azide with primary amines [794] or with secondary amines [795]. During the reaction, traces of moisture resulted in the formation of a byproduct sodium 5-azidotetrazolate, which was subsequently isolated and removed as a highly explosive and shock-sensitive solid. Tetrazoles synthesized from secondary amines included 5-dimethylaminotetrazole, 5-diethylaminotetrazole, 5-(pyrrolidin-1-yl)-1*H*-tetrazole, 5-(piperidin-1-yl)-1*H*-tetrazole, 1,4-bis(1*H*-tetrazol-5-yl)piperazine, 5-(morpholin-4-yl)-1*H*-tetrazole, and several similar tetrazole derivatives [796].

## 12.3 Other Mono-Substituted Tetrazole Compounds

Tetrazole can be linked to a nitroguanidine group, giving *N*-nitro-*N'*-1*H*-tetrazol-5-yl-guanidine, also known as tetrazol-5-yl-*N*-nitroguanidine, *N*-(5-tetrazolyl)-nitroguanidine; Guanidine, *N*-nitro-*N'*-1*H*-tetrazol-5-yl;  $C_2H_4N_8O_2$ , AT-NQ,  $M = 172.11$  g/mol, CAS RN [92260-29-2]. It decomposes at 513–518 K (240–245 °C). There are two tautomeric forms possible for this molecule but structure (I) is more likely than structure (II) because the conjugated N=C double bond is in resonance with the aromatic system in the ring. Another possibility would be a zwitterionic structure.



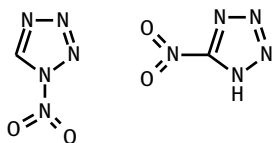
This is a weak acid and forms a guanidinium salt and a potassium salt. The guanidinium salt of *N*-nitro-*N'*-1*H*-tetrazol-5-yl-guanidine,  $C_3H_5N_8O_2$ ,  $M = 189.16$  g/mol, has been prepared and patented as an additive to double-base propellants [797]. It melts at 509–513 K (236–240 °C).

1-(Tetrazol-5-yl)-2-nitroguanidine and 1-nitroguanyl-1,2,4-triazole were synthesized by reaction of 1-nitro-2-methylisothiurea with amino heterocycles (5-aminotetrazole, 3,5-diamino-1,2,4-triazole, and 5-amino-1,2,4-triazole) [798]. 1,2,4-Triazolyl and tetrazolyl derivatives of nitroguanidine were investigated by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$ -NMR spectroscopy. NMR data showed that a product of the reaction between 1-nitro-2-methylisothiurea and 5-amino-1,2,4-triazole is not 1-nitroguanyl-3(5)-amino-1,2,4-triazole, as was assumed previously. It was 1-(1,2,4-triazol-3(5)-yl)-2-nitroguanidine instead. Based on NMR data, the most prevalent structures are the 1,2,4-triazole- and tetrazole-type structures; other possible structures imply an imine form [799].

## 12.4 Nitro- and Nitramino-Tetrazole Derivatives

### 12.4.1 1-Nitrotetrazole and 5-Nitrotetrazole

The enthalpy of formation ( $\Delta H_f^\circ$ ) in the gas phase of 1-nitrotetrazole was theoretically investigated by employing DFT and isodesmic reactions [156]. A correlation was developed between impact sensitivity h50% and the defined sensitivity index. Based on this empirical relationship and its extrapolation, the impact sensitivities of compounds, for which experiments were not available, were extrapolated. 1-Nitrotetrazole is a nitramine while 5-nitrotetrazole, CAS RN [55011-46-6], is a C—NO<sub>2</sub> nitro compound.



1-Nitrotetrazole    5-Nitrotetrazole

Both 4,5-dinitroimidazole and 5-nitrotetrazole, with electron-withdrawing nitro-substituents on the ring, are strong NH acids ( $\text{pK}_a = 0.8$  for 5-nitro-tetrazole). 5-Nitro-2*H*-tetrazole (**1**), 1-methyl-5-nitrotetrazole (**2**), and 2-methyl-5-nitrotetrazole (**3**) were synthesized, starting from the corresponding 5-amino-substituted tetrazoles [800]. The compounds were characterized by analytical and spectroscopic methods and their solid-state structures were determined by low-temperature XRD. Computational methods were used to estimate the energies of formation ( $\Delta U_f^\circ$ ) of the molecules, which are highly endothermic and were calculated as follows: (**1**) 2527 kJ/kg, (**2**) 2253 kJ/kg, and (**3**) 2006 kJ/kg. Calculated detonation velocities ( $V_{\text{det}}$ ) and detonation pressures ( $P_{\text{det}}$ ) were (**1**)  $V_{\text{det}} = 9457 \text{ m/s}$  and  $P_{\text{det}} = 390 \text{ kbar}$ , (**2**)  $V_{\text{det}} = 8085 \text{ m/s}$  and  $P_{\text{det}} = 257 \text{ kbar}$ , and (**3**)  $V_{\text{det}} = 8109 \text{ m/s}$  and  $P_{\text{det}} = 262 \text{ kbar}$ . These performances are comparable to commonly used secondary explosives (e.g., RDX). All three neutral compounds could be easily initiated by impact (<2J) and with

high detonation velocities. Excellent combined oxygen and nitrogen contents offer a more powerful and environmentally friendly alternative to commonly used primary explosives in initiating devices.

DFT computations were used to study the HOFs, electronic structure, energetic properties, and the pyrolysis mechanism of a series of trinitromethyl-substituted heterocycles, including triazole, tetrazole, furazan, tetrazine, and fused heterocycles [726]. It was found that tetrazine and tetrazole are effective structural units for increasing the  $\Delta H_f$ 's of the derivatives. The substitution of hydrogen by a combination of nitro and trinitromethyl groups is very useful for improving their  $\Delta H_f$ 's. The calculated energetic properties indicated that the combination of the nitro and trinitromethyl groups is very helpful for improving detonation properties and oxygen balances (OB).

The DFT method was used to study the HOFs, energetic properties, and thermal stability for a series of trinitromethyl-substituted tetrazole derivatives with different substituents [801]. It was found that the  $-\text{NO}_2$ ,  $-\text{NHNO}_2$ , or  $-\text{NF}_2$  groups play a very important role in increasing the HOFs of the derivatives. The calculated detonation velocities and pressures indicated that the group  $-\text{CF}_2\text{NF}_2$ ,  $-\text{NHNO}_2$ ,  $-1H$ -tetrazolyl,  $-2H$ -tetrazolyl, or  $-1,2,4,5$ -tetrazinyl are effective structural units for enhancing the detonation performance of the rings they are attached to. An analysis of the BDE for several relatively weak bonds indicated that incorporating the  $-\text{NHNO}_2$  and  $-\text{NH}_2$  group into the parent ring decreased their thermal stability. Considering the detonation performance and thermal stability, 37 compounds in this study could be viewed as potential high-energy compounds. Their OB were close to zero.

Sodium 5-nitrotetrazolate is a useful intermediate in the synthesis of primary explosives. To minimize the accumulation of hazardous materials in one location, sodium 5-nitrotetrazolate can be prepared by a flow method in a micro-reactor [802]. The sodium salt of 5-nitrotetrazolate can be prepared by reacting aqueous solutions of 5-aminotetrazole (an acid) and sodium nitrite in a continuous flow system at ambient temperature [803], or in a batch process at or above 338 K (65 °C) [804].

Free nitrotetrazole is extremely sensitive but the salts are more stable. 5-Nitrotetrazole is an acid that can form salts with ammonia and alkali metal hydroxides. These salts are suitable as energetic materials in rocket propellants, gas generants, and explosives. Ammonium 5-nitrotetrazolate is usually prepared as the hemihydrate or kept in solution. It can be used as the starting material for the synthesis of other 5-nitrotetrazolate salts of hydrazinium, guanidinium, aminoguanidinium, or even triaminoguanidinium cations. High-nitrogen content energetic salts of ammonium, hydrazinium, guanidinium, aminoguanidinium, diamino-guanidinium, and triaminoguanidinium with 5-nitro- $2H$ -tetrazolate anions were synthesized and characterized (also in form of their hydrates), as detailed in Table 50 from Reference [805].

Metal salts of the 5-nitrotetrazolate anion with alkali metal cations,  $\text{Li}^+$  (**1**),  $\text{Na}^+$  (**2**),  $\text{K}^+$  (**3**),  $\text{Rb}^+$  (**4**), and  $\text{Cs}^+$  (**5**), were synthesized either by the digestion of



**Table 50:** Properties of 5-nitro-2*H*-tetrazolate salts.

| Cation<br>Space group                         | NH <sub>4</sub> <sup>+</sup><br><i>P</i> 2 <sub>1</sub> / <i>c</i> | N <sub>2</sub> H <sub>5</sub> <sup>+</sup><br><i>P</i> 2 <sub>1</sub> / <i>c</i> | C(NH <sub>3</sub> ) <sub>3</sub> <sup>+</sup> | H <sub>2</sub> NNHC(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup><br><i>P</i> 2 <sub>1</sub> / <i>n</i> | (H <sub>2</sub> NNH) <sub>2</sub> C(NH <sub>3</sub> ) <sup>+</sup><br><i>P</i> 2 <sub>1</sub> | (H <sub>2</sub> NNH) <sub>2</sub> C(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup><br><i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> |
|-----------------------------------------------|--------------------------------------------------------------------|----------------------------------------------------------------------------------|-----------------------------------------------|-------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| Constant<br>volume<br>energy of<br>combustion | −1860                                                              | −2110                                                                            | −2250                                         | −2470                                                                                                 | −2630                                                                                         | −2690                                                                                                                                    |
| Predicted<br>detonation<br>velocity, m/s      | 7950                                                               | 8750                                                                             | 7500                                          | 8190                                                                                                  | 8230                                                                                          | 8480                                                                                                                                     |
| Predicted<br>detonation<br>pressure,<br>GPa   | 23.9                                                               | 30.1                                                                             | 20.1                                          | 24.7                                                                                                  | 24.4                                                                                          | 26.0                                                                                                                                     |

Data source: [805].

an acid copper salt of 5-nitrotetrazole with a metal hydroxide or by reaction of ammonium 5-nitrotetrazolate with a suitable metal base (MOH, MHCO<sub>3</sub>, or M<sub>2</sub>CO<sub>3</sub>) in aqueous or alcoholic solution [806]. The compounds were characterized by analytical methods (elemental analysis and mass spectrometry) and spectroscopic methods (NMR and vibrational spectroscopy). The lighter metal salts (**1**) and (**2**), incorporated three and two crystal water molecules in the hydrate sphere, respectively, whereas the heavier alkali metal derivatives formed anhydrous species, and thus showed enhanced sensitivity to friction and shock. The crystal structure of each of the new materials was determined by XRD: (**1**) and (**3**) were monoclinic, *P*2<sub>1</sub>/*c*; (**2**) was triclinic, *P* $\bar{1}$ ; (**4**) was monoclinic, *Cc*; (**5**) was monoclinic, *C*2/*c*. The thermal stability of compounds 1–5 was assessed by DSC measurements and showed significant thermal stability. The energies of combustion of (**1**) and (**2**) were measured in an oxygen bomb calorimeter and found to be 1340(15) cal/g (**1**) and 1200(20) cal/g (**2**). This was used to calculate their standard molar HOFs, which were found to be −610 kJ/mol (**1**) and −360 kJ/mol (**2**).

An improved procedure for the synthesis of ammonium 5-nitrotetrazolate allowed the preparation of the material on a larger scale [807]. Ammonium 5-nitrotetrazolate was selectively alkylated with bromoacetonitrile, yielding 5-nitrotetrazol-2-ylacetoneitrile. A 1,3-dipolar cycloaddition of azide ion to 5-nitrotetrazol-2-ylacetoneitrile resulted in 5-(5-nitrotetrazol-2-ylmethyl) tetrazole, which was used to synthesize energetic salts with ammonium, guanidinium, and aminoguanidinium cations. All compounds were characterized by analytical (elemental analysis and mass spectrometry) and spectroscopic methods (IR, Raman, and NMR spectroscopy), and the crystal structures were determined by low-temperature XRD. The sensitivities and energetic properties of all compounds were determined.

Properties of three nitrogen base salts of 5-nitrotetrazole, ethylenediammonium(1+) 5-nitrotetrazolate, guanidinium 5-nitrotetrazolate, and triaminoguanidinium 5-nitrotetrazolate have been assembled in Table 38 along with properties of seven salts of 1-hydro-3-nitro-1,2,4-triazol-5-one (NTO) [547, 548, 551].

In 2013, a safety property classification and military ordnance qualification was completed for a new primary explosive consisting of copper(I) 5-nitrotetrazolate (also referred to as DBX-1) [808]. This primary stab-sensitive explosive is an environmentally friendly replacement material for lead azide. This is the first primary explosive that has been qualified by the US Navy in over 90 years. The introduction of DBX-1 will eliminate lead from various applications while ensuring all platform requirements are achieved, thus utilizing a green energetic material.

A DFT computational method was used to calculate the optimized geometries, IR spectra, and thermodynamic properties of seven nitrotetrazoles [809]. Their HOFs were computed accurately using designed isodesmic and isogyric reactions. The calculated total energies and HOFs consistently showed that C-nitrotetrazoles were more stable than the N-isomers.

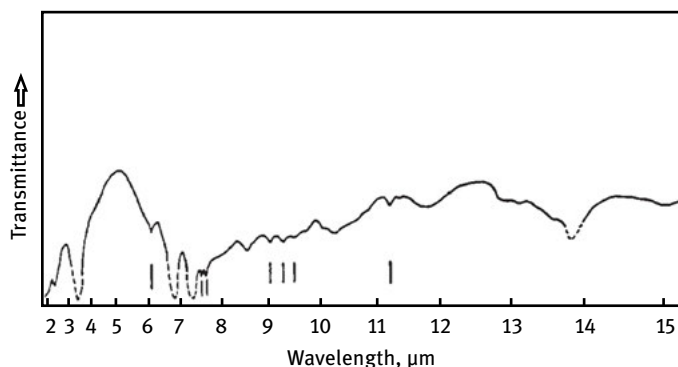
2-Methyl-5-nitrotetrazole was tested as an additive to AN for an AN linear burning rate study and compared to GAP and TNT (Sinditskii et al. 2005). 2-Methyl-5-nitrotetrazole in the form of white plate-like crystals, with a density of 1.64 g/cm<sup>3</sup> and a melting point of 359 K = 86 °C, can be prepared by methylation of 5-nitrotetrazole [810]. Alkylation of 5-AT does not alkylate the amino group but methyl groups go into both the 1- and the 2-position. With diethyl sulfate, only one alkyl group is used, whereas with dimethyl sulfate, both alkyl groups are used.

5-Nitrotetrazole is very hygroscopic. In the TGA the loss of mass at 388–393 K (115–120 °C) was 75%. The detonation velocity was 8.5 km/s (at a packing density of 1.7 kg/m<sup>3</sup>) [811, 812].

#### 12.4.2 5-Nitramino-1*H*-tetrazole

5-Nitramino-1*H*-tetrazole, also known as 5-nitroamino-1*H*-tetrazole; 2*H*-tetrazol-5-amine, *N*-nitro-; is a 5-AT derivative with more acidic properties than 5-AT due to the electron-sucking property of the nitro group on the –NH<sub>2</sub> group. It forms salts with many bases such as the ammonium salt CH<sub>2</sub>N<sub>6</sub>O<sub>2</sub>•H<sub>3</sub>N, CAS RN [57877-65-3].

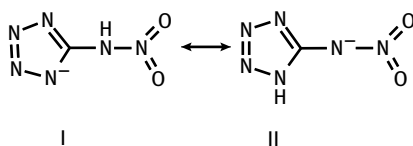
Three 5-nitraminotetrazole (NATZ) high-nitrogen energetic salts, (ethylene diamine)<sup>+</sup>(NATZ)<sup>–</sup>, (NH<sub>2</sub>NH<sub>2</sub>)<sup>+</sup>(NATZ)<sup>–</sup>•0.5H<sub>2</sub>O, and (carbohydrazide)<sup>+</sup>(NATZ)<sup>–</sup>, were synthesized and characterized by elemental analysis, IR spectra, DSC, TGA-DTG, and single-crystal XRD [813]. The results showed that the crystal belongs to a monoclinic system with space group *Pn*, and unit cell parameters of *a* = 0.37389(1) nm, *b* = 1.2396(5) nm, *c* = 0.8699(4) nm, *β* = 92.212(7)°, *V* = 0.4029 nm<sup>3</sup>; *ρ* = 1.815 g/cm<sup>3</sup>, and *Z* = 2. At a heating rate of 10 K/min., the thermal decomposition process of (NH<sub>2</sub>NH<sub>2</sub>)<sup>+</sup>(NATZ)<sup>–</sup>•0.5H<sub>2</sub>O consisted of one endothermic peak without residues, while the others consisted of one endothermic peak and one exothermic peak.



**Figure 17:** IR Spectrum of 5-nitroaminotetrazole. (Reproduced and modified from [722], with permission from the Levering Estate.)

The salts of 5-nitroaminotetrazole absorb in the region of 6.4 to 6.47 microns. The free acid, 5-nitroaminotetrazole, absorbs at 6.18 microns (Figure 17).

5-Nitroaminotetrazole is a dibasic acid; the anion may have structure I or II in its monobasic salts.



5-Nitroaminotetrazole

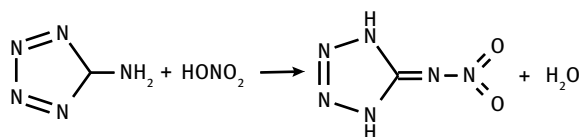
Only structure II, which represents an increased conjugation in the salt form over the free acid, can explain the shift away from the visible region. Based on this IR absorption data the “aci-nitro form,” represented by structure II is more likely for the monobasic salt structure of 5-nitroaminotetrazole. The publication [775] contains IR spectra of the potassium, di(ethylammonium), and anilinium salts of 5-nitroaminotetrazole.

Diammonium 5-nitraminotetrazolate melts at 493–494 K (220–221°C) and diguanidinium 5-nitraminotetrazolate melts at 498–499 K (225–226°C). The HOF of ammonium 5-nitraminotetrazolate,  $C_1N_7H_5O_2$ ,  $M = 147.1$ , is  $+222 \text{ cal/g} = +32.66 \text{ kcal/mol} = +136.6 \text{ kJ/mol}$  and the density is  $0.0538 \text{ lb/in.}^3 = 1.49 \text{ g/cm}^3$  [61].

Rapid thermal decomposition of nitraminotetrazole and nitraminotriazole was followed by instant IR analysis of the decomposition products to identify the weak link (“trigger linkage”) where the decomposition starts [814–816]. 5-Nitroaminotetrazole forms energetic salts with several bases [577].

## 12.5 5-Nitrimino-1*H*-tetrazole

Nitrimino compounds contain substituted =NH groups instead of —NH<sub>2</sub> groups (just as in amino compounds). Rather than introducing a nitro group to the ring, treating 5-AT with fuming nitric acid results in the formation of 5-nitriminotetrazole. The nitration of 5-amino-1*H*-tetrazole, 5-amino-1-methyl-1*H*-tetrazole, or 5-amino-2-methyl-2*H*-tetrazole with HNO<sub>3</sub> (100%) gave 5-(nitrimino)-1*H*-tetrazole, CAS RN [18588-16-4], 1-methyl-5-(nitrimino)-1*H*-tetrazole, or 2-methyl-5-(nitramino)-2*H*-tetrazole [817]. These energetic compounds were characterized using IR, Raman, multi-nuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>14</sup>N, and <sup>15</sup>N) NMR, MS, XRD, DSC, bomb calorimetry, and elemental analysis. The thermal decompositions were investigated by gas-phase IR as well as DSC. The heats of explosion, detonation pressures, and detonation velocities were calculated, revealing that the calculated performance values were similar to those of common explosives such as TNT and RDX. Sensitivity testing by BAM methods (drophammer and friction) revealed that the materials were too sensitive for a LOVA propellant.



Similarly, nitration of 1-methyl-5-aminotetrazole results in the formation of 1-methyl-5-nitriminotetrazole. Both compounds, 5-nitriminotetrazole and 1-methyl-5-nitriminotetrazole, are acidic and can form salts with many nitrogen-rich cations including carbohydrazide [818]. Diaminouronium 5-nitriminotetrazolate crystallizes in the monoclinic chiral space group *Pn*. Its density of 1.806 g/cm<sup>3</sup> (calculated using XRD) is quite high in comparison with other tetrazolate salts, whereas its 1-methyl homolog has a density of only 1.585 g/cm<sup>3</sup>. The physical properties of diaminouronium 5-nitriminotetrazolate are listed in Table 51. Sensitivity tests with diaminouronium 5-nitriminotetrazolate produced the results listed in Table 52.

Nitriminotetrazole can also be obtained by the diazotization of nitroaminoguanidine to nitroguanylazide and subsequent ring formation under alkaline conditions. Nitriminotetrazole, CH<sub>2</sub>N<sub>6</sub>O<sub>2</sub>, CAS RN [18588-16-4], has a molecular mass of 130.066 g/mol, an oxygen balance of −12.3%, forms monoclinic crystals with space group *P2<sub>1</sub>/c* (No. 14) with *a* = 9.4010(3) Å, *b* = 5.4918(1) Å, *c* = 9.3150(3) Å, *α* = 90°, *β* = 105.762(3)°, *γ* = 90°, *V* = 462.84(2) Å<sup>3</sup>, *Z* = 4, and has a density of 1.87 g/cm<sup>3</sup>. It also has a predicted detonation pressure of 363 kbar, and a predicted detonation velocity of 9173 m/s, which is higher than that of TNT (*P* = 202 kbar, *v*<sub>Det</sub> = 7150 m/s). The enthalpy of formation was calculated from the heat of combustion determined in a calorimeter bomb and found to be +264 kJ/mol. In the DSC, nitriminotetrazole showed a very low

**Table 51:** Solid-state properties of diaminouronium 5-nitriminotetrazolate.

|                                                | Density           | Enthalpy of formation $\Delta H_f^\circ$ |        | Detonation velocity <sup>a</sup> | CJ pressure <sup>a</sup> |
|------------------------------------------------|-------------------|------------------------------------------|--------|----------------------------------|--------------------------|
|                                                | g/cm <sup>3</sup> | kcal/mol                                 | kJ/mol | m/s                              | kbar                     |
| Diaminouronium 5-nitriminotetrazolate          | 1.806             | +70.4                                    | +294.6 | 8979                             | 337                      |
| Diaminouronium 1-methyl-5-nitriminotetrazolate | 1.585             | +80.1                                    | +335.4 | 8172                             | 252                      |

<sup>a</sup> computed using EXPLO5 computer code.

Data source: [818].

**Table 52:** Sensitivity properties of diaminouronium 5-nitriminotetrazolate.

| Compound                                       | BAM<br>drophammer | BAM friction<br>tester | ESD    | Particle size          |
|------------------------------------------------|-------------------|------------------------|--------|------------------------|
| Diaminouronium 5-nitriminotetrazolate          | 5 J               | 108 N                  | 0.20 J | 500–1000 $\mu\text{m}$ |
| Diaminouronium 1-methyl-5-nitriminotetrazolate | 3 J               | 160 N                  | 0.15 J | 100–500 $\mu\text{m}$  |

Data source: [818].

decomposition point at 395 K (122°C). The heat of decomposition  $\Delta H_{\text{dec}}$  was 2638 J/g. Nitriminotetrazole is very sensitive towards impact (<1.5 J) and friction (<8 N). Since the value is comparable with lead azide, it should be considered to be a primary explosive and, therefore, should only be handled with appropriate precautions [819]. The rapid thermal decomposition of 5-nitriminotetrazole on a heated platinum filament has been observed with a Raman spectrometer and intermediate species formed during its decomposition could be identified [704].

1-Methyl-5-nitriminotetrazole and 2-methyl-5-nitraminotetrazole, which were obtained by the nitration of 1-methyl-5-aminotetrazole or 2-methyl-5-aminotetrazole, were deprotonated using an aqueous ammonia solution yielding the energetic compounds ammonium 1-methyl-5-nitriminotetrazolate and ammonium 2-methyl-5-nitriminotetrazolate [819–821]. The TAG salt of this tetrazole is described in a section dedicated to TAG salts in *Encyclopedia of Liquid Fuels* (chapter “Amides and Imides,” Section 14.6.3).

The properties of the parent nitrimines 1-methyl-5-nitriminotetrazole (**1**) and 2-methyl-5-nitraminotetrazole (**2**) were: (**1**)  $\text{C}_2\text{H}_4\text{N}_6\text{O}_2$ , molecular mass 144.11 g/mol, orthorhombic crystals, space group  $P2_12_12_1$  (No. 19),  $a = 6.6140(1) \text{ \AA}$ ,  $b = 8.5672(2) \text{ \AA}$ ,  $c = 19.2473(4) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 1090.62(4) \text{ \AA}^3$ ,  $Z = 8$ , and  $\rho = 1.755 \text{ g/cm}^3$ ; and (**2**)  $\text{C}_2\text{H}_4\text{N}_6\text{O}_2$ , molecular mass 144.11 g/mol, monoclinic crystals, space group  $P2_1/c$  (No. 14),  $a = 9.5278(9) \text{ \AA}$ ,  $b = 7.7308(7) \text{ \AA}$ ,  $c = 8.4598(9) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 112.875(9)^\circ$ ,  $\gamma =$

90°,  $V = 574.1(1) \text{ \AA}^3$ ,  $Z = 4$ , and  $\rho = 1.667 \text{ g/cm}^3$ . The nitrogen-rich salts were tested and characterized using IR, Raman, multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ , and  $^{15}\text{N}$ ) NMR spectroscopy, and elemental analysis. The molecular structures in the crystalline state were determined using low-temperature single-crystal XRD. The thermal behavior and the decomposition products were investigated using DSC and IR spectroscopy for the analysis of the off-gassing. The HOFs were calculated using bomb calorimetric measurements of the heat of combustion. The relevant detonation parameters outperformed the values of TNT. The sensitivities were determined using BAM methods, which showed moderate values against impact and friction (drop-hammer and friction tester). Long-term stabilities were also tested. XRD crystallography of the aminoguanidinium salts gave: monoclinic  $P2_1/c$ ,  $a = 370.06(2) \text{ pm}$ ,  $b = 2079.06(9) \text{ pm}$ ,  $c = 859.69(5) \text{ pm}$ ,  $\beta = 99.120(5)^\circ$ ,  $V = 65306(6) \text{ pm}^3$ ,  $Z = 4$ , and  $\rho_{\text{calc}} = 1.639 \text{ g/cm}^3$ . The diaminoguanidinium salt gave: monoclinic  $P2_1$ ,  $a = 365.39(2) \text{ pm}$ ,  $b = 788.82(5) \text{ pm}$ ,  $c = 1124.95(7) \text{ pm}$ ,  $\beta = 91.818(6)$ ,  $V = 32408(3) \text{ pm}^3$ ,  $Z = 2$ , and  $\rho_{\text{calc}} = 1.651 \text{ g/cm}^3$ .

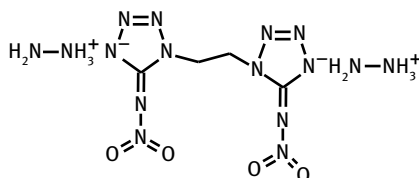
Syntheses of salts with 3-nitroiminotriazolate and 5-nitroiminotetrazolate as anions yielded nitro-containing energetic salts that were thermally stable to  $>473 \text{ K}$  ( $>200^\circ\text{C}$ ) (measured by TGA) [822]. Di(aminoguanidinium) 5-nitroiminotetrazolate crystallized in the monoclinic space group  $P2_1/c$  with an essentially planar 5-nitroiminotetrazolate dianion. Based on experimental and calculated densities and theoretical calculations, all of the salts had calculated detonation pressures and velocities that exceeded those of TNT and a few had values that approached those of TATB.

Alkylation of 5-AT with 2-chloroethanol leads to a mixture of the N-1 and N-2 isomers of (2-hydroxyethyl)-5-aminotetrazole [823]. Treatment of 1-(2-hydroxyethyl)-5-aminotetrazole (**2**) with  $\text{SOCl}_2$  yielded 1-(2-chloroethyl)-5-aminotetrazole (**3**). 1-(2-Azidoethyl)-5-aminotetrazole (**4**) was generated by the reaction of (**3**) with sodium azide. Nitration of (**2**), (**3**), and (**4**) with  $\text{HNO}_3$  (100%) yielded in the case of **2** and **3** 1-(2-hydroxyethyl)-5-nitriminotetrazole (**5**) and 1-(2-chloroethyl)-5-nitriminotetrazole (**6**). Other compounds described were 1-(2-nitratoethyl)-5-nitriminotetrazole monohydrate, 1-(2-Azidoethyl)-5-nitriminotetrazole, potassium 1-(2-azidoethyl)-5-nitriminotetrazolate, sodium 1-(2-chloroethyl)-5-nitriminotetrazolate, ammonium 1-(2-chloroethyl)-5-nitriminotetrazolate, 1-(2-hydroxyethyl)-5-aminotetrazolium nitrate, 1-(2-azidoethyl)-5-aminotetrazolium nitrate, 1-(2-azidoethyl)-5-aminotetrazolium perchlorate monohydrate, and various copper complexes with these compounds. All compounds were characterized by low-temperature single-crystal XRD, IR, Raman and NMR spectroscopy, elemental analysis, MS, and DSC. The HOFs of selected compounds were computed by using heats of combustion obtained by bomb calorimetry or calculated by the atomization method. With these values and the densities determined from XRD, several detonation parameters were calculated using the EXPLO5 program. Also, the sensitivities towards impact and friction were determined using a BAM drop-hammer and a friction tester.

The reactions of 5-nitriminotetrazole with 1-methyl-5-aminotetrazole as well as 2-methyl-5-aminotetrazole were investigated [824]. In the first reaction, 1-methyl-5-aminotetrazole was protonated, yielding 1-methyl-5-aminotetrazolium 5-nitrimino-1*H*-tetrazolate monohydrate. In the latter case, no protonation could be observed and only a co-crystallization of unreacted 5-nitraminotetrazole and 2-methyl-5-aminotetrazole was obtained. Products were characterized by low-temperature single-crystal XRD, IR, Raman and NMR spectroscopy, elemental analysis, as well as DSC. The HOFs were calculated from experimentally obtained heats of combustion. Using these and the X-ray densities, several detonation parameters were computed using EXPLO5 software. The sensitivities towards impact, friction, and electrostatic discharge were determined.

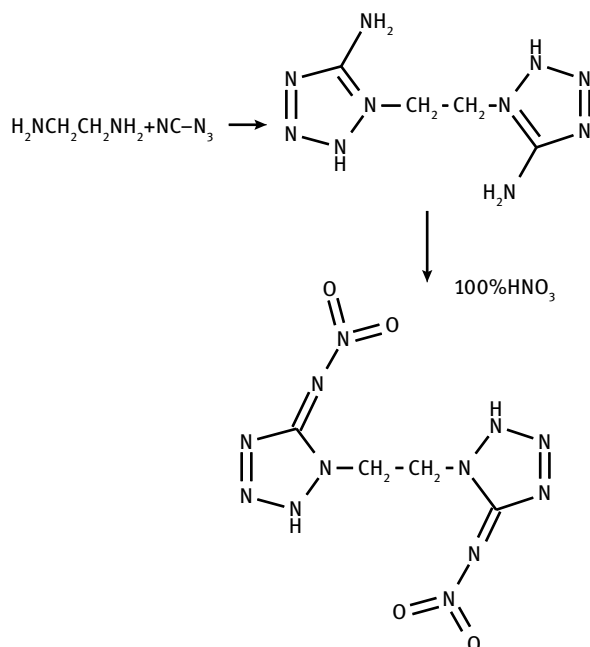
Starting with the alkylation of 5-aminotetrazole and going through several intermediate steps, 1-(2-nitratoethyl)-5-nitriminotetrazole monohydrate and 1-(2-azidoethyl)-5-nitriminotetrazole was synthesized and characterized [823]. Several 5-nitriminotetrazoles and 5-nitraminotetrazoles with 2-nitro-2-azapropyl substitution in the 1-position were synthesized and characterized as energetic materials [825]. HEDMs with ethylene- and propylene-bis(5-nitroiminotetrazolate) as the anions were synthesized and characterized by IR, NMR, elemental analyses, and density [826].

The HOFs and the predicted detonation pressures and velocities were calculated. By using the experimental values for the densities of the nitroiminotetrazolate salts, the detonation pressures and velocities were calculated using Cheetah 5.0. The dihydrazinium salt of 1,2-di(5-nitriminotetrazolo)ethane has a density of 1.733 g/cm<sup>3</sup>, an enthalpy of formation of +1067 kJ/mol, a predicted detonation pressure of 35.27 GPa, and a predicted detonation velocity of 9478 m/s. The oxygen balance is -50.2%.



Bishydrazinium salt of 1,2-di(5-nitriminotetrazolo)ethane

Mono-, di-, and tri-substituted nitroiminotetrazoles can be synthesized from aminotetrazoles (obtained from the reaction of cyanogen azide with primary amines) by treatment with 100% nitric acid and were characterized by spectroscopic methods, elemental analysis, and (in some cases) XRD [827, 828]. The HOFs of these energetic materials were calculated as were their detonation pressures and velocities.



Hydrazinium 5-nitrimino-1H-tetrazolate and dihydrazinium nitriminotetrazolate monohydrate were synthesized by the reaction of hydrazine with 5-nitriminotetrazole [829]. The salts were characterized by single-crystal XRD, NMR, IR and Raman spectroscopy, and DSC. The sensitivities towards impact, friction, and electrical discharge were determined. Several detonation parameters (e.g., the heat of explosion, detonation velocity) were computed by using the EXPL05 computer code based on calculated HOFs and X-ray densities.

The hydroxylammonium salts of monodeprotonated 5-nitriminotetrazole, double deprotonated 5-nitriminotetrazole, 1-methyl-5-nitriminotetrazole, and 2-methyl-5-nitraminotetrazole were prepared from the corresponding 5-nitriminotetrazoles as free acids and an aqueous solution of hydroxylamine or the metathesis reactions of hydroxylammonium hydrochloride with the silver salt of the corresponding nitriminotetrazole, respectively [830]. The energetic salts were characterized by single-crystal XRD, NMR, IR and Raman spectroscopy, as well as DSC. The sensitivities towards impact, friction, and electrical discharge were determined. Several detonation parameters (e.g., the heat of explosion, detonation velocity) were computed by using the EXPL05.04 computer code based on calculated HOFs and X-ray densities.

The structural and chemical properties of triaminoguanidinium 1-methyl-5-nitriminotetrazolate  $\text{C}_3\text{H}_{12}\text{N}_{12}\text{O}_2$  have been investigated at room pressure and under high-



pressure isothermal compression using XRD, and Raman and IR spectroscopy [831]. The shock sensitivity of energetic materials depends on the behavior of these materials upon sudden compression. Some undergo phase changes at high pressures. There was a reversible martensitic structural transformation to a new crystalline phase. Beyond 15 GPa, pressurization induced irreversible chemical reactions.

## 13 Mono-Substituted Tetrazolium and Tetrazolate Salts

### 13.1 5-Aminotetrazolium Nitrate

5-Aminotetrazolium nitrate, also known as  $C_1H_4N_6O_3$ ,  $CH_3N_5 \bullet HNO_3$ ,  $[CH_4N_5]^+ [NO_3]^-$ , 5-aminotetrazole nitrate, 2*H*-tetrazol-5-amine, nitrate (1:1), 5-ATN, CAS RN [43146-62-9],  $M = 148.081$  g/mol, is a very useful propellant ingredient with high nitrogen content (56.75% N) and good oxygen balance (−10.8%). 5-ATN and oxidizing potassium salts are sometimes used in gas generant formulations along with the parent compound 5-AT.

The oxygen balance of 5-aminotetrazolium nitrate is −10.8%%. As such, it does not require much additional oxidizer for self-deflagration. 5-Aminotetrazolium nitrate melts and decomposes explosively once it reaches 447–448 K (174–175 °C). The enthalpy of formation of 5-aminotetrazolium nitrate is +130 cal/g = +19.25 kcal/mol = +80.5 kJ/mol.

The combustion behavior of salts of 5-aminotetrazole with inorganic acids (HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>) and picric acid was investigated at 0.1–40 MPa in a windowed constant-pressure bomb [832]. Preliminary IR-spectrometry analyses of the salts pointed to the protonation of a nitrogen atom on the tetrazole ring. The temperature distribution in the combustion wave was measured with thin tungsten-rhenium micro-thermocouples. The salts of 5-AT with inorganic non-oxidizing acids all had higher burning rates than 5-AT itself despite the decrease in their energetic properties, which occurred due to salt formation. The stronger the acid, the higher the burning rate became.

For the preparation of 5-ATN, 20 g (0.235 mols) of anhydrous 5-AT is placed in an ice bath then neutralized with 22 mL (0.350 mols) of concentrated nitric acid. It is then stirred for about one hour [833]. Following that, about 70 mL of water is added directly to the slurry and the entire mixture is then heated quickly to boiling. The hot solution is vacuum filtered and allowed to cool at ambient conditions while stirring. The white crystals formed during cooling are vacuum filtered and washed with cold water, then forced through a No. 14 mesh screen to form granules. The wet material is dried in air at ambient conditions and forms well-flowing granules. Using TGA, the 5-ATN dried at ambient conditions was found to contain about 1.0 mass-% water. As tested on a Bureau of Explosives (BOE) impact apparatus, the air-dried material showed no pos-

itive fires at drop heights up to 25 in. (equivalent to about 231 kg cm). However, when 5-ATN granules were dried at 105 °C for 4 h to remove any remaining moisture, this material showed positive fires at about 4 in. (equivalent to about 37 kg cm). This demonstrates how 5-ATN becomes more sensitive to impact stimuli when completely dry. The dried 5-ATN was tested using a DSC at a heating rate of 10 °C/min. The 5-ATN melted at 429.9 K (156.8 °C) and then decomposed exothermically with an onset of exotherm at 450.3 K (177.2 °C) and a peak at 455.6 K (182.5 °C). The 5-ATN was also tested using a TGA at a heating rate of 10 °C/min and found to have an 89.3 mass-% gas conversion up to 723 K (450 °C), with a 67.5 mass-% gas conversion up to about 467 K (194 °C). The DSC and TGA data show that the 5-ATN auto-ignites at about 453 K (180 °C) with a large release of energy. Gas generant compositions were patented with a combination of 5-ATN and an oxidizer. The oxidizer may be selected from a group, including non-metal and metal nitrates, nitrites, chlorates, chlorites, perchlorates, or oxides.

5-Aminotetrazolium nitrate is obtained in good yield through direct neutralization of a 5-AT base with dilute nitric acid in an aqueous solution and can be crystallized and recrystallized from water and/or methanol [834]. The crystalline salt was characterized using Raman and multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) NMR spectroscopy. The molecular structure of 5-aminotetrazolium nitrate in the crystalline state was determined by XRD and found to be monoclinic, space group  $P2_1/c$ ,  $a = 1.05493(8)$  nm,  $b = 0.34556(4)$  nm,  $c = 1.4606(1)$  nm,  $\beta = 90.548(9)^\circ$ ,  $V = 0.53244(8)$  nm<sup>3</sup>,  $Z = 4$ , and  $\rho_{\text{X-ray}} = 1.847$  g/cm<sup>3</sup>. The thermal stability of 5-aminotetrazolium nitrate was determined using DSC; the compound decomposed at 440 K (167 °C). The heat of combustion of 5-aminotetrazolium nitrate was determined experimentally using oxygen bomb calorimetry and found to be  $6020 \pm 200$  kJ/kg. The standard enthalpy of formation ( $\Delta H_{298}^\text{f}$ ) of 5-aminotetrazolium nitrate was calculated using quantum mechanical considerations at the electron-correlated *ab initio* MP2 (second-order MP2 perturbation theory) level of theory and found to be +87 kJ/mol = +586 kJ/kg. The theoretical detonation velocity and the detonation pressure of 5-aminotetrazolium nitrate were calculated using the empirical equations by Kamlet and Jacobs and predicted to be 8.90 mm/s and 35.7 GPa.

A series of nitrogen-rich molecules including 5-aminotetrazolium nitrate and hydrazinebistetrazole were studied using laser-induced breakdown spectroscopy [835]. The atomic emission intensities and intensity ratios of the constituent elements were shown to correlate with the mol fractions and stoichiometries of the molecules. In addition, the amount of oxygen present in the molecule influenced the emission intensities of molecular fragments such as  $\text{C}_2$ .

5-Aminotetrazolium nitrate (5-ATN) can be synthesized from 5-aminotetrazole monohydrate ( $5\text{-AT} \cdot \text{H}_2\text{O}$ ) and concentrated nitric acid. The effect of nitric acid dosage, reaction time, and reaction temperature on the yield of 5-ATN was measured to optimize the yield [836]. The best synthesis conditions determined by orthogonal experiments were as follows: 5 g 5-AT, 15 mL nitric acid, reaction temperature 293 K

(20 °C), and reaction time 15 min. (with a yield of 92.6%). Compared with previous studies, the reaction temperature and time were decreased while the yield improved. SEM picture showed that the surface of 5-ATN was smooth, and humidity storage tests showed that the unwanted water absorption of the product was reduced.

5-Aminotetrazolium nitrate (5-aminotetrazole nitrate) and oxidizing potassium salts are used in gas generant formulations along with the parent compound 5-AT. One example for a gas generant formulation incorporates a combination of 5-aminotetrazole nitrate and an oxidizer [837]. The oxidizer may be selected from a group, which can include non-metal and metal nitrates, nitrites, chlorates, chlorites, perchlorates, and oxides. 5-Aminotetrazole nitrate is characterized as an oxygen-rich fuel and is therefore considered to be a self-deflagrating fuel. To tailor the oxygen balance in certain applications, however, the use of an oxidizer is preferred. These compositions are used for inflating airbags and actuating seatbelt pretensioners in passenger-restraint devices. 5-Aminotetrazolium nitrate can be used in the synthesis of glycidyl nitrate [838].

### 13.2 5-Aminotetrazolium Perchlorate

Protonation of 5-amino-1*H*-tetrazole with perchloric acid in water gave 5-amino-1*H*-tetrazolium perchlorate (**1**) in good yield and purity, or an adduct (**2**) of (**1**) with excess 5-AT depending on the experimental conditions used [839]. 5-Amino-1*H*-tetrazolium perchlorate can also be prepared by metathesis of 5-amino-1*H*-tetrazolium bromide with anhydrous silver perchlorate in an alcoholic solution. Both perchlorate salts were characterized by NMR, Raman and IR spectroscopy, DSC, MS, and elemental analysis. The crystal structures of compounds (**1**) and (**2**) were determined by XRD. Both salts crystallized in monoclinic cells in the space group  $P2_1/n$  (**1**)  $a = 5.3691(6) \text{ \AA}$ ,  $b = 7.8470(6) \text{ \AA}$ ,  $c = 15.2770(13) \text{ \AA}$ ,  $\beta = 91.381(8)^\circ$ ,  $V = 643.45(10) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 1.915 \text{ g/cm}^3$ , and (**2**)  $a = 5.2615(1) \text{ \AA}$ ,  $b = 8.5311(2) \text{ \AA}$ ,  $c = 21.4870(4) \text{ \AA}$ ,  $\beta = 96.127(1)^\circ$ ,  $V = 958.96(3) \text{ \AA}^3$ ,  $Z = 4$ , and  $\rho = 1.874 \text{ g/cm}^3$ . With an impact and friction sensitivity of  $I = 1.5 \text{ J}$  and  $F = 8 \text{ N}$ , respectively, and an ESD sensitivity of  $0.1 \text{ J}$ , perchlorate (**1**) is a powerful primary explosive, whereas the presence of a second tetrazole ring in (**2**) makes it a very stable compound ( $I = 22 \text{ J}$ ,  $F = 260 \text{ N}$ ,  $\text{ESD} = 0.4 \text{ J}$ ).

The enthalpy of formation of 5-aminotetrazolium perchlorate  $\text{C}_4\text{H}_4\text{N}_5\text{O}_4\text{Cl}$  ( $M = 185.53 \text{ g/mol}$ ) is  $+204 \text{ cal/g} = +37.8 \text{ kcal/mol} = +158.3 \text{ kJ/mol}$ . The enthalpies of formation of 12 salts formed by the reaction of the bases 4-amino-1,2,4-triazole (**A**), 1-amino-1,2,4-triazole (**B**), and 5-aminotetrazole (**C**) upon reaction with the acids  $\text{HNO}_3$ ,  $\text{HN}(\text{NO}_2)_2$ ,  $\text{HClO}_4$ , and  $\text{HC}(\text{NO}_2)_3$  were studied using DFT calculations [270]. For the production of energetic salts, 5-aminotetrazole and  $\text{HClO}_4$  were identified as the preferred base and acid, respectively.

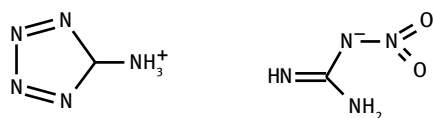
### 13.3 5-Aminotetrazolium Dinitramide

5-Aminotetrazolium dinitramide (5-aminotetrazolium dinitramide) is one of the most promising candidates for energetic high-nitrogen compounds [840, 841]. The highly energetic isomers azidoformamidinium dinitramide and 5-aminotetrazolium dinitramide were synthesized by the reaction of potassium dinitramide and azidoformamidinium perchlorate or 5-aminotetrazolium perchlorate, respectively [751]. Both compounds have an oxygen balance of  $O = 0.0$ , which means they are perfectly balanced to burn to nothing else but  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (besides  $\text{N}_2$ ). 1*H*-tetrazolium dinitramide and 2-methyl-5-aminotetrazolium dinitramide were synthesized using 1*H*-tetrazolium perchlorate and 2-methyl-5-aminotetrazolium perchlorate. A full characterization of the chemical properties (single-crystal XRD, IR and Raman spectroscopy, multi-nuclear NMR spectroscopy, DSC, and MS) and energetic characteristics were measured and the HOFs were calculated (CBS-4M) by MO computational methods. 1*H*-tetrazolium perchlorate is very hygroscopic and it was difficult to obtain XRD spectra of the dry salt.

### 13.4 Other 5-Aminotetrazolium Salts

5-Amino-1*H*-tetrazolium halogenide salts (Cl, Br, I) are useful starting materials to synthesize energetic materials by metathesis reactions. Hydrate halide salts of 5-amino-1*H*-tetrazole (5-ATHX, X = Cl, Br, I) were synthesized and characterized [842]. The compounds were characterized by using elemental analysis, mass spectrometry, IR and Raman spectroscopy, multi-nuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) spectroscopy, and DSC.

The nitroguanidine salt of aminotetrazole, 5-aminotetrazolium nitroguanidinate,  $\text{C}_2\text{H}_6\text{N}_9\text{O}_2$ , has a molecular mass of  $M = 188.13$  g/mol and is registered as CAS RN [92260-29-2].



5-Aminotetrazolium nitroguanidinate

### 13.5 5-Aminotetrazolate Salts

5-Aminotetrazole (5-AT) behaves as a weak acid and can be used to obtain nitrogen-rich energetic salts and ionic liquids. Nine energetic nitrogen-rich salts based on 5-AT in anionic form were prepared, thus demonstrating that 5-AT is indeed amphoteric

[779]. Some of these salts had very low melting points and were stable nitrogen-rich ionic liquids that contain the 5-AT anion. This discovery was reported in [779] for the first time. In addition, three other energetic 5-aminotetrazolium salts were prepared for comparison. The properties of these aminotetrazolate and aminotetrazolium salts are summarized in Table 53. These 5-AT salts have been characterized by IR, NMR, elemental analysis, thermal stability, phase behavior, and density by gas pycnometer. 4-Amino-2-methyl-1,2,4-triazolium 5-aminotetrazolate has the highest nitrogen content (68%) of any known room-temperature ionic liquid.

The numbers in parentheses that follow refer to the compounds listed in Table 53. 1,4-Dimethyl-5-aminotetrazolium 5-aminotetrazolate (**4**) and 1,3-dimethyl-5-aminotetrazolium 5-aminotetrazolate (**5**) have been synthesized by metathesis reactions between silver 5-aminotetrazolate and a suitable tetrazolium iodide salt [843]. In addition to this, the free acid 1,4-dimethyl-5-iminotetrazole (**7**) was synthesized by deprotonation of 1,4-dimethyl-5-aminotetrazolium iodide using potassium hydroxide. Further to this, 1,4-dimethyl-5-iminotetrazole (**7**) was alternatively used to synthesize (**4**). All three compounds (**4**, **5**, and **7**) were characterized using analytical and spectroscopic methods and the crystal structures of (**4**) and (**7**) were determined by low-temperature XRD, with findings as follows:

1,4-Dimethyl-5-aminotetrazolium 5-aminotetrazolate (**4**) crystallized in monoclinic crystals, space group  $P2_1/n$ , with unit cell parameters of  $a = 6.7422(4) \text{ \AA}$ ,  $b = 9.8362(5) \text{ \AA}$ ,  $c = 13.0637(8) \text{ \AA}$ ,  $\beta = 97.985(5)^\circ$ ,  $V = 857.95(9) \text{ \AA}^3$ . 1,4-Dimethyl-5-iminotetrazole (**7**) crystallized in triclinic shape crystals, space group  $P\bar{1}$ , with unit cell parameters of  $a = 6.256(1) \text{ \AA}$ ,  $b = 6.773(1) \text{ \AA}$ ,  $c = 6.773(1) \text{ \AA}$ ,  $\alpha = 102.24(3)^\circ$ ,  $\beta = 97.96(3)^\circ$ ,  $\gamma = 100.39(3)^\circ$ ,  $V = 271(3) \text{ \AA}^3$ . The HOFs of (**4**) and (**5**) were experimentally determined using bomb calorimetry and their validity was checked against the results of quantum chemical calculations.

Whenever silver 5-aminotetrazolate is used in the synthesis of other compounds, one has to remember that it is very shock sensitive and should not be stored in the dry state [844]. Energetic 5-aminotetrazolium and 1, 5-diaminotetrazolium salts were readily synthesized by the reaction of 5-aminotetrazolium nitrate or 1,5-diaminotetrazolium nitrate with ammonium 5-nitroiminotetrazolate, ammonium 1-methyl-5-nitroiminotetrazolate, bis(ammonium) ethylene bis(5-nitroiminotetrazolate), or diammonium iminobis(5-tetrazolate) in water under mild conditions [845]. All products were recovered as highly crystalline materials in excellent yields and purities and were fully characterized by IR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectroscopy, DSC, and elemental analyses.

A T-jump/TOF mass spectrometer was used to probe the decomposition of several aminotetrazole-containing energetic materials (5-amino-1-methyl-1*H*-tetrazolium dinitramide, 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramide, 1,5-diamino-1*H*-tetrazolium nitrate, 1,5-diamino-4-methyl-1*H*-tetrazolium azide, and 5-aminotetrazolium dinitramide) under very high heating rates of  $10^5$ – $10^6$  K/s [846, 847]. Subtle differ-

Table 53: Properties of energetic nitrogen-rich 5-aminotetrazolate salts.

| Compound | Compound name                                           | Nitrogen content |  | $T_m(T_g)$ |       | $T_{dec}$ |     | $\rho_{meas}$     |      | $\rho_{calc}$     |  | $\Delta H_f$ | Det. press. | Det. vel. |
|----------|---------------------------------------------------------|------------------|--|------------|-------|-----------|-----|-------------------|------|-------------------|--|--------------|-------------|-----------|
|          |                                                         | Mass %           |  | K          | °C    | K         | °C  | g/cm <sup>3</sup> |      | g/cm <sup>3</sup> |  | kJ/mol       | GPa         | m/s       |
| 2        | Hydrazinium(1+)<br>5-aminotetrazolate                   | 83.72            |  | 398        | 125   | 437       | 164 | 1.48              | 1.55 | 1.55              |  | +383.6       | 24.8        | 8786      |
| 3        | Guanidinium<br>5-aminotetrazolate                       | 77.74            |  | 399        | 126   | 493       | 220 | 1.54              | 1.46 | 1.46              |  | +205.4       | 19.4        | 8055      |
| 4        | Aminoguanidinium<br>5-aminotetrazolate                  | 79.21            |  | 369        | 96    | 484       | 211 | 1.51              | 1.49 | 1.49              |  | +302.3       | 20.1        | 8149      |
| 5        | Guanylguanidinium<br>5-aminotetrazolate                 | 75.23            |  | 414        | 141   | 480       | 207 | 1.41              | 1.44 | 1.44              |  | +306.9       | 16.3        | 7529      |
| 6        | 4-Amino-1,2,4-triazolium<br>5-aminotetrazolate          | 74.53            |  | 387        | 114   | 490       | 217 | 1.62              | 1.55 | 1.55              |  | +565.0       | 23.3        | 8360      |
| 7        | 4-Amino-1-methyl-1,2,4-triazolium<br>5-aminotetrazolate | 68.82            |  | 249        | (−24) | 447       | 174 | 1.46              | 1.49 | 1.49              |  | +546.0       | 18.9        | 7334      |
| 8        | 4-Amino-1-ethyl-1,2,4-triazolium<br>5-aminotetrazolate  | 63.92            |  | 235        | (−38) | 444       | 171 | 1.39              | 1.44 | 1.44              |  | +523.4       | 16.4        | 7397      |
| 9        | 1,5-Diamino-4-methyl-tetrazolium<br>5-aminotetrazolate  | 77.36            |  | 444        | 171   | 463       | 190 | 1.57              | 1.56 | 1.56              |  | +655.1       | 23.2        | 8385      |
| A        | 5-Aminotetrazolium<br>5-nitrotetrazolate                | 200.12           |  | 432        | 159   | 436       | 163 | 1.75              | —    | —                 |  | +571.4       | 31.4        | 8843      |
| B        | 5-Aminotetrazolium<br>5-nitroiminotetrazolate           | 214.13           |  | 438        | 165   | 438       | 165 | 1.63              | —    | —                 |  | +487.5       | 25.5        | 8276      |
| C        | 5-Aminotetrazolium picrate                              | 314.18           |  | 420        | 147   | 487       | 214 | 1.85              | —    | —                 |  | +400.6       | 29.5        | 8182      |

Data source: [762].

ences between materials in functional group placement and anion composition allowed for further interpretation of the decomposition pathway of the tetrazole structure and various anions. Two decomposition pathways for the tetrazole ring were observed, which resulted in the primary formation of  $\text{HN}_3$  or  $\text{N}_2$ . The  $\text{N}_2$  formation pathway occurred when functional groups were placed symmetrically around the tetrazole ring, whereas asymmetric placement resulted in  $\text{HN}_3$  production. The azide salt had a lower decomposition temperature than the similar dinitramidate salt.

5-Aminotetrazole is amphoteric and can form 5-aminotetrazolium salts with acids as well as 5-aminotetrazolates with strong bases. Some of the 5-aminotetrazolates of heterocyclic amines and other nitrogen bases behave as ionic liquids and are difficult to crystallize. The melting points and enthalpies of formation of several of these that are of interest as high-nitrogen constituents for rocket propellants have been determined and are summarized in Tables 54 and 55 [779].

**Table 54:** Melting points and enthalpies of formation of 5-aminotetrazolate salts.

| Compound name                                               | Gross formula                          | Enthalpy of formation | Density<br>g/cm <sup>3</sup> | Melting point |     |
|-------------------------------------------------------------|----------------------------------------|-----------------------|------------------------------|---------------|-----|
|                                                             |                                        | kJ/mol                |                              | °C            | K   |
| 1-Butyl-3-methylimidazolium dicyanamide                     | $\text{C}_{10}\text{H}_{15}\text{N}_5$ | +363.4                | 1.06                         | −9            | 267 |
| 1-Butyl-3-methylpyrrolidinium dicyanamide                   | $\text{C}_{11}\text{H}_{20}\text{N}_4$ | +218.9                | 1.02                         | −50           | 223 |
| Hydrazinium 5-aminotetrazolate                              | $\text{CH}_7\text{N}_7$                | +383.6                | 1.48                         | 125           | 398 |
| Guanidinium 5-aminotetrazolate                              | $\text{C}_2\text{H}_8\text{N}_8$       | +205.4                | 1.54                         | 126           | 399 |
| Aminoguanidinium 5-aminotetrazolate                         | $\text{C}_2\text{H}_9\text{N}_9$       | +302.3                | 1.51                         | 93            | 366 |
| Guanylguanidinium 5-aminotetrazolate                        | $\text{C}_3\text{H}_{10}\text{N}_{10}$ | +306.9                | 1.41                         | 141           | 414 |
| 4-Amino-1 <i>H</i> -1,2,4-triazolium 5-aminotetrazolate     | $\text{C}_3\text{H}_7\text{N}_9$       | +565.0                | 1.62                         | 114           | 387 |
| 4-Amino-1-methyl-1,2,4-triazolium 5-aminotetrazolate        | $\text{C}_4\text{H}_9\text{N}_9$       | +546.0                | 1.46                         | −24           | 249 |
| 4-Amino-1-ethyl-1,2,4-triazolium 5-aminotetrazolate         | $\text{C}_5\text{H}_{11}\text{N}_9$    | +523.4                | 1.39                         | −38           | 235 |
| 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium 5-aminotetrazolate | $\text{C}_3\text{H}_9\text{N}_{11}$    | +655.1                | 1.57                         | 171           | 444 |

Data source: [761].

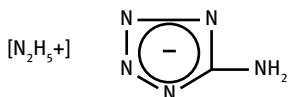
**Table 55:** Properties of energetic nitrogen-rich aminotetrazolate salts.

| Compound name                                               | Gross formula                                                | $T_m$ ( $T_g$ ) |       | $T_{dec.}$ |     | Density (meas.)   | Density (calc.)   | $\Delta H_f$ (cation) | $\Delta H_f$ (lattice energy) | $\Delta H_f(L)$ | $\Delta H_f(L)$ | Det. Press. | Det. Vel. |
|-------------------------------------------------------------|--------------------------------------------------------------|-----------------|-------|------------|-----|-------------------|-------------------|-----------------------|-------------------------------|-----------------|-----------------|-------------|-----------|
|                                                             |                                                              | K               | °C    | K          | °C  | g/cm <sup>3</sup> | g/cm <sup>3</sup> | kJ/mol                | kJ/mol                        | kJ/mol          | kJ/g            | GPa         | m/s       |
| Hydrazinium 5-aminotetrazolate                              | CH <sub>7</sub> N <sub>7</sub>                               | 398             | 125   | 437        | 164 | 1.48              | 1.55              | 770.0                 | 570.2                         | +383.6          | +3.28           | 24.8        | 8786      |
| Guanidinium 5-aminotetrazolate                              | C <sub>2</sub> H <sub>8</sub> N <sub>8</sub>                 | 399             | 126   | 493        | 220 | 1.54              | 1.46              | 566.7                 | 545.1                         | +205.4          | +1.43           | 19.4        | 8055      |
| Aminoguanidinium 5-aminotetrazolate                         | C <sub>2</sub> H <sub>9</sub> N <sub>9</sub>                 | 369             | 96    | 484        | 211 | 1.51              | 1.49              | 646.7                 | 528.2                         | +302.3          | +1.90           | 20.1        | 8149      |
| Guanylguanidinium 5-aminotetrazolate                        | C <sub>3</sub> H <sub>10</sub> N <sub>10</sub>               | 414             | 141   | 480        | 207 | 1.41              | 1.44              | 620.9                 | 497.8                         | +306.9          | +1.65           | 16.3        | 7529      |
| 4-Amino-1 <i>H</i> -1,2,4-triazolium 5-aminotetrazolate     | C <sub>3</sub> H <sub>7</sub> N <sub>9</sub>                 | 387             | 114   | 490        | 217 | 1.62              | 1.55              | 910.7                 | 529.5                         | +565.0          | +3.34           | 23.3        | 8360      |
| 4-Amino-1-methyl-1,2,4-triazolium 5-aminotetrazolate        | C <sub>4</sub> H <sub>9</sub> N <sub>9</sub>                 | 249             | (−24) | 447        | 174 | 1.46              | 1.49              | 866.7                 | 504.5                         | +546.0          | +2.98           | 18.9        | 7334      |
| 4-Amino-1-ethyl-1,2,4-triazolium 5-aminotetrazolate         | C <sub>5</sub> H <sub>11</sub> N <sub>9</sub>                | 235             | (−38) | 444        | 171 | 1.39              | 1.44              | 828.2                 | 488.6                         | +523.4          | +2.65           | 16.4        | 7397      |
| 1,5-Diamino-4-methyl-1,2,3,4-tetrazolium 5-aminotetrazolate | C <sub>3</sub> H <sub>9</sub> N <sub>11</sub>                | 444             | 171   | 463        | 190 | 1.57              | 1.56              | 974.3                 | 503.0                         | +655.1          | +3.29           | 23.2        | 8385      |
| 5-Aminotetrazolium 5-nitrotetrazolate                       | C <sub>2</sub> H <sub>4</sub> N <sub>10</sub> O <sub>2</sub> | 432             | 159   | 436        | 163 | 1.75              | —                 | —                     | 516.9                         | +571.4          | +2.86           | 31.4        | 8843      |
| 5-Aminotetrazolium 5-nitroiminotetrazolate                  | C <sub>2</sub> H <sub>4</sub> N <sub>11</sub> O <sub>2</sub> | 438             | 165   | 438        | 165 | 1.63              | —                 | —                     | 497.9                         | +487.5          | +2.27           | 25.5        | 8276      |
| 5-Aminotetrazolium picrate                                  | C <sub>7</sub> H <sub>6</sub> N <sub>8</sub> O <sub>7</sub>  | 420             | 147   | 487        | 214 | 1.85              | —                 | —                     | 466.5                         | +400.6          | +1.28           | 29.5        | 8182      |

Data source: [762].



Hydrazinium 5-aminotetrazolate,  $\text{CH}_7\text{N}_7$ , has a density of  $1.48 \text{ g/cm}^3$  and an enthalpy of formation of  $383.60 \text{ kJ/mol}$  and melts at  $398 \text{ K}$ . It has a nitrogen content of  $83.73 \text{ mass-\%}$ .



Hydrazinium(1+) 5-aminotetrazolate

Hydrazinium 5-aminotetrazolate was synthesized via two facile routes. Both the reaction of 5-amino-1*H*-tetrazole with hydrazine hydrate in aqueous solution and the reaction of 5-amino-1*H*-tetrazole with diluted hydrazine solution in THF yielded hydrazinium 5-aminotetrazolate in excellent purities and good yields [848]. Hydrazinium 5-aminotetrazolate can be recrystallized from hot ethanol yielding colorless needle-shaped crystals which can be washed with diethyl ether. Hydrazinium 5-aminotetrazolate crystallizes in the chiral orthorhombic space group  $P2_12_12_1$  with four molecules in the unit cell. Hydrazinium 5-aminotetrazolate was characterized by XRD, IR, Raman, NMR spectroscopy, MS, elemental analysis, and DSC. The HOF was calculated to be  $+373 \text{ kJ/mol}$ . With this value and the X-ray density, several detonation parameters (heats of explosion, detonation pressure, detonation velocity, explosion temperature) were calculated. An astoundingly high value ( $9516 \text{ m/s}$ ) was obtained for the detonation velocity. Therefore, experimental tests to determine the velocity of detonation will have to be performed. However, despite a detonator with  $0.2 \text{ g}$  silver acetylide nitrate, a  $1 \text{ g}$  PETN, and a booster charge of  $2 \text{ g}$  PETN, the powder sample could not be detonated. The sensitivities towards impact, friction, and electrostatic discharge were determined with the BAM drop-hammer, friction tester, and an ESD test machine. It was found to be very insensitive (BAM drop-hammer:  $>100 \text{ J}$ ; friction tester:  $>360 \text{ N}$ , ESD:  $>3.0 \text{ J}$ ). The properties of hydrazinium 5-aminotetrazolate are summarized in Table 56. In addition to its use as an explosive, the use of hydrazinium 5-aminotetrazolate in solid propellant compositions was calculated and tested in combination with oxidizers, e.g., ADN.

The tautomerism of all possible forms of 5-aminotetrazole in the gas phase and solution was studied theoretically [849]. Computational chemistry calculations were performed and it was found that 5-aminotetrazole in the 2*H* form should be the most stable isomer in both the gas phase and in solution. In addition, the aggregation and proton exchange of various isomers of 5-aminotetrazole with hydrazine was investigated in the gas phase and in solution. This also gave the standard enthalpy of formations of the different structures of hydrazinium 5-aminotetrazolate in the gas phase, eventually narrowing it down to a single value for the standard enthalpy of formation of hydrazinium 5-aminotetrazolate. The calculated values were in excellent agreement with the experimentally reported HOF for the hydrazinium 5-aminotetrazolate.

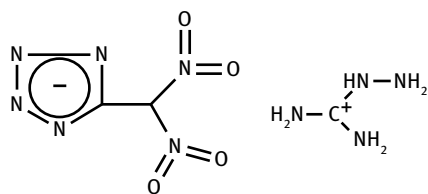
**Table 56:** Properties of hydrazinium 5-aminotetrazolate.

| Formula        | CH <sub>7</sub> N <sub>7</sub> |
|----------------|--------------------------------|
| Molecular mass | 117.14 g/mol                   |
| $T_m$          | 391–395 K = 118–122 °C         |
| $T_{dec}$      | 459 K = 186 °C                 |
| Crystal system | Orthorhombic                   |
| Space group    | $P2_1 2_1 2$ (No. 18)          |
| Color/Habit    | Colorless needles              |
| $a$            | 9.7179(6) Å                    |
| $b$            | 13.5958(8) Å                   |
| $c$            | 3.8056(3) Å                    |
| $V$            | 502.81(6) Å <sup>3</sup>       |
| $Z$            | 4                              |
| $\rho_{calc.}$ | 1.547 g/cm <sup>3</sup>        |
| $P_{det}$      | 296 kbar                       |
| $V_{det}$      | 9516 m/s                       |

Data source: [848].

Bis(1,2,3-triaminoguanidinium) bis(5-aminotetrazolate) monohydrate,  $2[\text{CH}_3\text{N}_6^+] \cdot 2[\text{CH}_2\text{N}_5^-] \cdot \text{H}_2\text{O}$ ,  $M = 396.4$ , is a high-nitrogen compound [850]. It crystallized in monoclinic, space group  $C2/c$  crystals with  $a = 10.448(2)$  Å,  $b = 10.387(1)$  Å,  $c = 15.544(3)$  Å,  $\beta = 93.11(1)^\circ$ ,  $V = 1684.4(5)$  Å<sup>3</sup>,  $Z = 4$ , and  $\rho_{X\text{-ray}} = 1.56$  g/cm<sup>3</sup>.

Energetic mono and dianionic 5-dinitromethyltetrazolate salts, prepared by combining stoichiometric amounts (1:1 or 1:2 mol ratio) of 5-dinitromethyltetrazole and various azoles and amines, exhibit thermodynamic properties as well as detonation velocities and pressures that make them competitive with some common energetic materials [851]. Aminoguanidinium 5-dinitromethyltetrazolate exhibited different particle shapes when crystallized from solutions of varying concentrations. Di(aminoguanidinium) 5-dinitromethyltetrazolate, when treated with a solvent-diffusion process, produced nano-particles with a branched net structure.



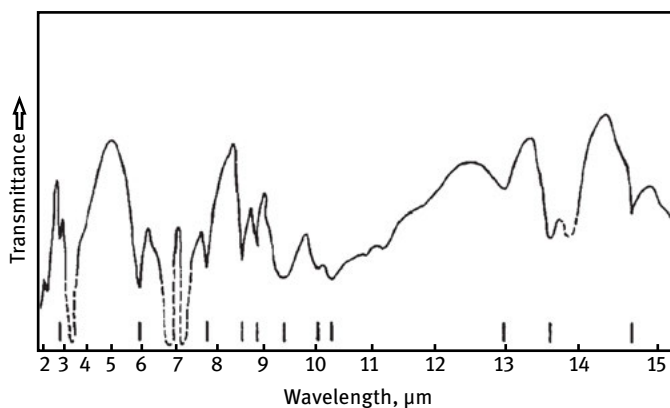
Aminoguanidinium 5-dinitromethyltetrazolate

5-Aminotetrazolate (5-AT) salts based on eight different di- and tri-substituted imidazolium cations were synthesized and characterized by IR and NMR spectroscopy and elemental analysis [198] (see the imidazolium salt section) (see also [852]).

## 14 Other Tetrazole Compounds

### 14.1 5-Hydrazino-1*H*-tetrazole

5-Hydrazino-1*H*-tetrazole, 5-tetrazolylhydrazine,  $\text{CH}_4\text{N}_6$ ,  $M = 100.083 \text{ g/mol}$ , is a nitrogen-rich compound that contains 83.97 mass-% nitrogen and has an oxygen balance of -63.9%. It melts at 472 K (199 °C) and decomposes at 480 K. 5-Hydrazinotetrazole can be obtained via the decomposition of 5,5'-azotetrazole [253]. The IR spectrum of 5-tetrazolylhydrazine is shown in Figure 18.



**Figure 18:** IR Spectrum of 5-hydrazino-1*H*-tetrazole. (Reproduced and modified from [722], with permission from the Levering Estate.)

5-Hydrazinotetrazole and 5-aminotetrazole have spectra that are markedly similar. The strong band at 6.0  $\mu\text{m}$  is believed due to the amino grouping present. Absorption bands were present in the four regions characteristic of aromatic amines, which were medium bands at 2.8 to 3.3  $\mu\text{m}$  and 12.5 to 15  $\mu\text{m}$ , and strong bands at 6.08 to 6.23 and 7.5 to 8.0  $\mu\text{m}$ . Three bands were found in the spectrum of 5-hydrazinotetrazole which were not in the spectrum of 5-aminotetrazole; these were at 8.97, 10.35, and 12.93  $\mu\text{m}$ . These were found to correspond to bands in hydrazine itself.

The acid hydrolysis of azotetrazole (5,5'-azoditetrazole) anion with dilute acids gives 5-hydrazinotetrazole. However, other high nitrogen products have also been isolated, one of which is explosive [853]. 5-Hydrazinotetrazole was synthesized with 5,5'-azotetrazolate as the starting material by acidifying with hydrochloric acid and

Table 57: Properties of 5-hydrazinotetrazolium salts.

| Salt No. | Compound name<br>HT = 5-Hydrazino-tetrazolium | T <sub>melt</sub> |       | T <sub>dec</sub> |       | d <sub>calc</sub> |                   | d <sub>meas</sub> |                   | OxBal | N Content | ΔH <sub>f</sub> |        | P <sub>det</sub> | V <sub>det</sub> | Im-pact sens | Isp   |
|----------|-----------------------------------------------|-------------------|-------|------------------|-------|-------------------|-------------------|-------------------|-------------------|-------|-----------|-----------------|--------|------------------|------------------|--------------|-------|
|          |                                               | K                 | °C    | K                | °C    | g/cm <sup>3</sup> | g/cm <sup>3</sup> | g/cm <sup>3</sup> | g/cm <sup>3</sup> |       |           | Mass %          | kJ/mol |                  |                  |              |       |
| 4        | HT nitrate                                    | 434.3             | 161.2 | 446.8            | 173.7 | 1.71              | 1.834             | 1.834             | 1.834             | -14.7 | 61.1      | +310.5          | +1.90  | 39.5             | 9450             | 10.8         | 277.5 |
| 5        | HT perchlorate                                | —                 | —     | 463.9            | 190.8 | 1.959             | 2.068             | 2.068             | 2.068             | -4.0  | 41.9      | +195.2          | +0.97  | 41.7             | 9196             | 11.3         | 256   |
| 6        | HT dicyanamide                                | 365.4             | 92.3  | 423.7            | 150.6 | 1.52              | 1.531             | 1.531             | 1.531             | -81.4 | 75.4      | +430.7          | +2.58  | 17.4             | 7052             | >40          | 196.1 |
| 7        | HT dinitramide                                | —                 | —     | 461.8            | 188.7 | 1.78              | 1.846             | 1.846             | 1.846             | -3.9  | 60.9      | +516.3          | +2.49  | 46.8             | 9626             | 6.8          | 288.7 |
| 8        | HT 5-nitrotetrazolate                         | —                 | —     | 457.5            | 184.4 | 1.70              | 1.711             | 1.711             | 1.711             | -33.5 | 71.6      | +768.7          | +3.58  | 32.5             | 8885             | 4.3          | 263.1 |
| 9        | HT nitroformate                               | —                 | —     | 452.7            | 179.6 | 1.82              | —                 | —                 | —                 | -3.2  | 50.2      | +419.4          | +1.67  | 39.2             | 9206             | —            | 280.4 |
| 10       | HT 4,5-dinitroimidazolate                     | —                 | —     | 455.6            | 182.5 | 1.73              | 1.747             | 1.747             | 1.747             | -43.4 | 54.3      | +572.5          | +2.28  | 31.3             | 8602             | >40          | 246.3 |
| 12       | HT 5-nitrimidazolate                          | 437.6             | 164.5 | 471.7            | 198.6 | 1.67              | 1.724             | 1.724             | 1.724             | -43.6 | 76.4      | +1424.3         | +4.32  | 35.1             | 9227             | 28.4         | 269.3 |
| AT-DT    | 5-Aminotetrazolium dinitramide                | 358.1             | 85    | 390.1            | 117   | 1.856             | —                 | —                 | —                 | 0     | 58.3      | +78.6           | —      | 38.4             | 9429             | —            | —     |
| AT-NT    | 5-Aminotetrazolium 5-nitrotetrazolate         | 432.1             | 159   | 436.1            | 163   | —                 | —                 | —                 | —                 | -32   | 70.0      | +571.4          | —      | 31.4             | 8843             | —            | —     |
| RDX      |                                               | 477.2             | 204.1 | 503.1            | 230   | 1.82              | —                 | —                 | —                 | -21.6 | 37.8      | +83.8           | +0.38  | 35.2             | 8977             | 7.4          | 265.1 |
| HMX      |                                               | 549.1             | 276   | 560.1            | 287   | 1.91              | —                 | —                 | —                 | -21.6 | 37.8      | +105            | +0.361 | 39.6             | 9320             | 7.4          | 272.1 |

Data source: [8 56].

recrystallizing [854, 855]. Its structure was characterized by FTIR, melting point, and elemental analyses. The yield of 5-hydrazinotetrazole was 55–60% and the melting point was 469–472 K (196–198.9 °C).

Eight high-density energetic salts that contained the 5-hydrazino-1*H*-tetrazolium cation and oxidizing or nitrogen-rich anions were synthesized and characterized by IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, elemental analysis, DSC, and impact sensitivity [856]. Four compounds were characterized by single-crystal XRD. The results showed that the extensive hydrogen-bonding interactions between the cations and anions form a complex 3-D network, which contributes greatly to the high density of the 5-hydrazinotetrazolium salts. It was also found that the incorporation of hydrazino groups into a heterocyclic ring increased the HOF and the overall nitrogen content of the entire molecule. In addition, calculated detonation properties of the energetic salts identified them as competitively energetic compounds. In some cases, they were viewed as even superior to those of HMX. The properties of hydrazinotetrazolium salts are summarized in Table 57.

## 14.2 5-Cyanotetrazole

5-Cyanotetrazole, 5*H*-tetrazole-5-carbonitrile,  $\text{C}_2\text{H}_1\text{N}_5$ , CAS RN [1004771-58-7],  $M = 95.07\text{ g/mol}$ , is a stable high-nitrogen compound with 73.7% N. It melts at 372 K (99 °C). It is slightly acidic and forms salts with many nitrogen-containing bases. The enthalpy of formation of 5-cyanotetrazole is  $+1010\text{ cal/g} = 96.02\text{ kcal/mol} = 402\text{ kJ/mol}$ .

The reaction of cyanogen ( $\text{NC-CN}$ ) with  $\text{MN}_3$  ( $M = \text{Na, K}$ ) in liquid  $\text{SO}_2$  leads to the formation of the 5-cyanotetrazolate anion as the monohemihydrate sodium or potassium salts, respectively [857]. Both can be used as starting materials for the synthesis of salts containing the 5-cyanotetrazolate anion and nitrogen-rich cations, namely ammonium, hydrazinium, semicarbazidium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium. Several salts were characterized by low-temperature single-crystal XRD, as detailed in Table 58. DSC and sensitivity tests were used to assess the thermal stability and sensitivity against impact and friction. Constant volume energies of combustion, detonation velocity, and the pressure of the salts were calculated.

Looking at the energetic salts of cyanotetrazolate-1- and -2-oxides offers a unique opportunity to compare the effects of tetrazole 1- versus 2-oxidation. 5-Cyanotetrazole-2-oxide can be synthesized by oxidation of the 5-cyanotetrazolate anion with Oxone, while the corresponding 1-oxide can be synthesized by the rearrangement of azidoaminofurazan [858]. Both chemical (multi-nuclear NMR, IR and Raman spectroscopies, mass spectrometry, etc.) as well as explosive (impact, friction, and ESD sensitivities) properties were measured for these energetic salts, and predicted explosive performances were calculated using the EXPLO5 computer code.

**Table 58:** Crystal structures of 5-cyanotetrazolate salts.

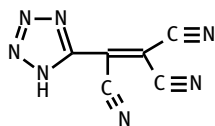
| Cation name<br>Units                 | Formula                                          | MW     | Crystal<br>system | Space<br>group                     | <i>a</i><br>Å | <i>b</i><br>Å | <i>c</i><br>Å |
|--------------------------------------|--------------------------------------------------|--------|-------------------|------------------------------------|---------------|---------------|---------------|
| Ammonium                             | C <sub>2</sub> H <sub>4</sub> N <sub>6</sub>     | 112.11 | monoclinic        | <i>P</i> 2 <sub>1</sub> / <i>c</i> | 3.7801(1)     | 14.0833(4)    | 9.4141(3)     |
| Semicarbazidium                      | C <sub>3</sub> H <sub>6</sub> N <sub>8</sub> O   | 170.16 | monoclinic        | <i>C</i> 2/ <i>c</i>               | 11.1655(7)    | 10.0335(4)    | 14.1418(8)    |
| Guanidinium                          | C <sub>3</sub> H <sub>6</sub> N <sub>8</sub>     | 154.16 | monoclinic        | <i>P</i> 2 <sub>1</sub> / <i>c</i> | 3.6733(1)     | 11.5516(3)    | 16.6453(5)    |
| Triaminoguanidinium•H <sub>2</sub> O | C <sub>3</sub> H <sub>11</sub> N <sub>11</sub> O | 217.23 | triclinic         | <i>P</i> 1                         | 6.6838(5)     | 7.9159(5)     | 10.2312(7)    |

**Table 58:** (continued).

| Cation name<br>Units                 | Formula                                          | $\alpha$<br>° | $\beta$<br>° | $\gamma$<br>° | <i>V</i><br>Å <sup>3</sup> | <i>Z</i> | Density, XRD<br>g/cm <sup>3</sup> |
|--------------------------------------|--------------------------------------------------|---------------|--------------|---------------|----------------------------|----------|-----------------------------------|
| Ammonium                             | C <sub>2</sub> H <sub>4</sub> N <sub>6</sub>     | 90            | 97.507(3)    | 90            | 496.88(2)                  | 4        | 1.499                             |
| Semicarbazidium                      | C <sub>3</sub> H <sub>6</sub> N <sub>8</sub> O   | 90            | 110.230(6)   | 90            | 1486.6(1)                  | 8        | 1.521                             |
| Guanidinium                          | C <sub>3</sub> H <sub>6</sub> N <sub>8</sub>     | 90            | 92.778(3)    | 90            | 705.47(3)                  | 4        | 1.451                             |
| Triaminoguanidinium•H <sub>2</sub> O | C <sub>3</sub> H <sub>11</sub> N <sub>11</sub> O | 73.09         | 88.94(1)     | 68.96         | 481.1(2)                   | 2        | 1.499                             |

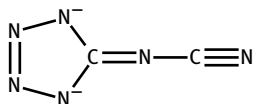
Data source: [857].

The reaction of tetracyanoethylene and sodium azide in DMF leads to the production of the sodium salt of 5-tricyanovinyltetrazole, 2-(1*H*-tetrazol-5-yl)ethene-1,1,2-tricarbonitrile, C<sub>6</sub>HN<sub>7</sub>, which is a high-energy compound [859].



5-Tricyanovinyltetrazole

The dianion of 5-cyanoiminotetrazoline (C<sub>2</sub>N<sub>6</sub><sup>2-</sup>) represents a nitrogen-rich binary CN anion, forming salts with surprisingly high thermal stability [860].

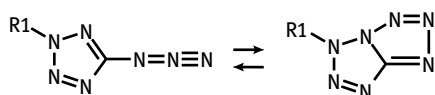


Dianion of 5-cyanoiminotetrazoline

A variety of salts of 5-cyanoiminotetrazoline was prepared and the cesium salt was found to have a surprisingly high melting point of 607 K (334 °C). Metal complexes with 5-cyanotetrazole, 5-nitrotetrazolium, and 5-aminotetrazole as ligands were prepared and tested [861].

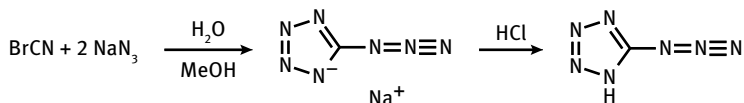
### 14.3 5-Azido-1*H*-tetrazole

5-Azidotetrazole, tetrazolylazide  $\text{CHN}_7$ , is closely related to tetrazolium azide but the properties are quite different [862]. 5-Azidotetrazole can easily isomerize to a bicyclic tetrazole.

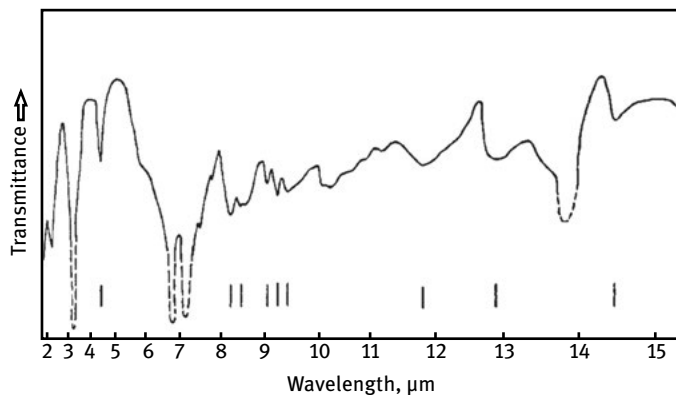


5-Azido-1*H*-tetrazole (tetrazyl azide, tetrazolyl azide,  $\text{CHN}_7$ ,  $M = 111.07$ ) contains 88.29 mass-% nitrogen and is one of the most nitrogen-rich organic compounds. It is very sensitive and will explode at the slightest touch. It melts at 347–348 K (74–75 °C) and begins to decompose at 438 K = 165 °C. Tetrazolyl azide can be prepared in three ways: by reacting 5-hydrazinotetrazole with sodium nitrite and hydrochloric acid at 273 K (0 °C); by reaction of cyanogen bromide and sodium azide in water; and from the Cu salt of 1-guanyl-4-nitrosaminoguanyltetrazene following treatment with acid. A quite uncommon reaction is the alkaline degradation of the primary explosive tetracene using  $\text{Ba}(\text{OH})_2$ . 5-Azidotetrazolate salts, especially that of silver, are hypersensitive to mechanical stimuli. The azido group has a relatively strong absorption band in the region of 4.67 and 7.8–8  $\mu\text{m}$  (Figures 19 and 20).

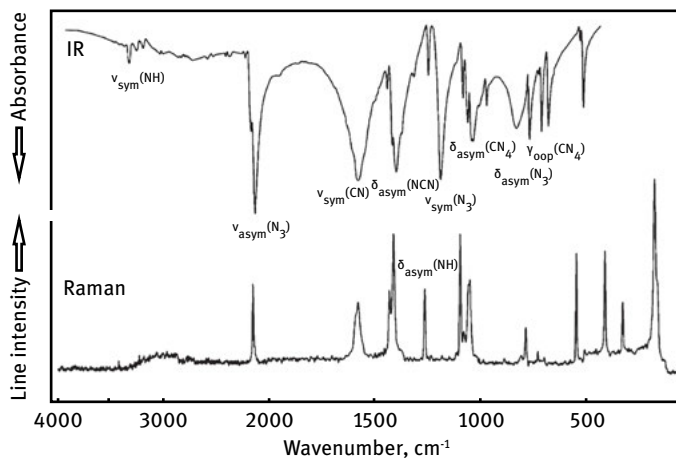
Due to the highly explosive nature of 5-azido-1*H*-tetrazole, its characterization has not been fully achieved and described in the literature yet. The previously published crystal structure was of low quality and, therefore, the position of the hydrogen atom was not certain. To resolve these problems, 5-azido-1*H*-tetrazole was prepared in an improved synthesis, then reinvestigated and recharacterized [863]. The reaction of cyanogen bromide with two equivalents of sodium azide at low temperatures yielded sodium 5-azidotetrazolate, which was protonated using dilute hydrochloric acid.



5-Azido-1*H*-tetrazole synthesis



**Figure 19:** IR Spectrum of 5-azidotetrazole in hydrocarbon oil. (Reproduced and modified from [722], with permission from the Levering Estate.)



**Figure 20:** IR (top) and Raman (bottom) spectra of 5-azidotetrazole. (Republished and modified from [863], with the permission of ©2008 John Wiley & Sons; permission conveyed through RightsLink.)

The product 5-azido-1*H*-tetrazole was isolated and characterized using multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) NMR, IR, Raman, MS, and XRD. The HOF of 5-azido-1*H*-tetrazole was calculated using quantum mechanical methods, giving an enthalpy of formation of solid 5-azido-1*H*-tetrazole as  $\Delta H_f^{o298}(\text{S}) = +611 \text{ kJ/mol}$ . Further to this, several detonation parameters were estimated using the EXPLO5 software, giving a calculated detonation pressure of 327 kbar and a detonation velocity of 8986 m/s, which is higher than those of TNT or RDX. The X-ray structure showed monoclinic crystals, space group  $P2_1/c$ ,  $a = 13.265(2) \text{ \AA}$ ,  $b = 4.9693(6) \text{ \AA}$ ,  $c = 16.304(3) \text{ \AA}$ ,  $\beta = 127.04(1)^\circ$ ,  $V = 857.9(3) \text{ \AA}^3$ ,



$Z = 8$ , and  $\rho = 1.720 \text{ g/cm}^3$ . The position of the hydrogen atom at the nitrogen atom N1 was confirmed by a strong hydrogen bond. The HOF of 5-azido-1*H*-tetrazole was calculated and several detonation parameters were estimated. The thermal behavior was investigated using DSC and the sensitivity was tested using the BAM drop-hammer, ESD, and friction tester.

Several salts containing the 5-azido-1*H*-tetrazolate  $\text{CN}_7^-$  anion were prepared by the deprotonation of 5-azido-1*H*-tetrazole [864]. The highly explosive compounds hydrazinium, ammonium, aminoguanidinium, guanidinium, lithium, sodium, potassium, cesium, and calcium azidotetrazolate were prepared and characterized by low-temperature single-crystal XRD, IR, Raman, multi-nuclear NMR spectroscopy, mass spectrometry, and DSC. Not all salts could be characterized since some of the metal salts exploded spontaneously. Hydrazinium 5-azido-1*H*-tetrazolate contains the highest nitrogen content (87.48%) of all known tetrazole salts. The impact, friction, and ESD sensitivity of several salts were measured and the theoretical detonation pressure, velocity, and specific impulse were calculated. Ammonium 5-azidotetrazolate has been patented as a foaming agent for foamed plastics [865].

DFT computational methods were used to predict the properties of azidoazole compounds, and the structures, energetic properties, and decomposition mechanisms of compounds, such as 2-azido-1,3-imidazole (I), 3-azido-1*H*-1,2,4-triazole (II), 5-azido-1*H*-tetrazole (III), and azido-pentazole (IV) [866]. The energy performance was examined by calculating the specific impulse. The order of increasing specific impulses was  $\text{I} < \text{II} < \text{III} < \text{IV}$ . The predicted specific impulse of III and IV was higher than that of HMX. Decomposition mechanisms were investigated by considering various possible weak trigger bonds as well as the azide  $\leftrightarrow$  azole isomerization. It was predicted that the azide  $\leftrightarrow$  azole isomerization participates in the pyrolysis of I and II but not III and IV. The pyrolysis of III starts from the breakage of N1–N2 and that of IV from the synergistic rupture of N2–N3 and N4–N5. The low activation energies in the pyrolysis suggest III and IV will be quite unstable.

#### 14.4 5-Methyl-1*H*-Tetrazole

5-Methyl-1*H*-tetrazole,  $\text{C}_2\text{H}_4\text{N}_4$ , CAS RN [4076-36-2], melts at 415–419 K (142–146 °C) and is thermally stable, however, there are no known uses as a rocket propellant or gas generant. Methyltetrazoles are of relatively little interest as rocket propellants or gas generants. Nevertheless, we do have data on their melting points, enthalpies of formation, and heat of fusion, as summarized in Table 59 [867], which also provides a comparison to the unsubstituted tetrazole and the more popular 5-aminotetrazole. Some of these compounds are liquids at room temperature. Vapor pressures, heat of

**Table 59:** Properties of tetrazole, 5-aminotetrazole, and several methyltetrazoles.

| No. | Compound name             | Gross formula                                | Melting point |             | Heat of fusion<br>kJ/mol | Enthalpy of formation<br>$\Delta H_f^{298}$<br>kJ/mol |
|-----|---------------------------|----------------------------------------------|---------------|-------------|--------------------------|-------------------------------------------------------|
|     |                           |                                              | K             | °C          |                          |                                                       |
| 1   | Tetrazole                 | CHN <sub>4</sub>                             | 429           | 156         | 17.7 ± 0.6               | +237.1 ± 0.9                                          |
| 2   | 1-Methyltetrazole         | C <sub>2</sub> H <sub>3</sub> N <sub>4</sub> | 315           | 42          | 15.7 ± 0.4               | +234.7 ± 0.5                                          |
| 3   | 2-Methyltetrazole         | C <sub>2</sub> H <sub>3</sub> N <sub>4</sub> | 286           | 13          | 12.4 ± 0.4               | +281.6 ± 0.6                                          |
| 4   | 5-Methyltetrazole         | C <sub>2</sub> H <sub>3</sub> N <sub>4</sub> | 418           | 145         | 16.0 ± 0.5               | +184.4 ± 2.6                                          |
| 5   | 1,5-Dimethyltetrazole     | C <sub>3</sub> H <sub>5</sub> N <sub>4</sub> | 349           | 76          | 14.7 ± 0.4               | +186.1 ± 2.7                                          |
| 6   | 2,5-Dimethyltetrazole     | C <sub>3</sub> H <sub>5</sub> N <sub>4</sub> | 257           | −16         | 13.5 ± 0.4               | +202.5 ± 2.9                                          |
| 7   | 5-Aminotetrazole          | CH <sub>3</sub> N <sub>5</sub>               | 475           | 202         | —                        | +207.8 ± 2.3                                          |
| 8   | 1-Methyl-5-aminotetrazole | C <sub>2</sub> H <sub>5</sub> N <sub>5</sub> | 501           | 228         | —                        | +182.2 ± 4.5                                          |
| 9   | 2-Methyl-5-aminotetrazole | C <sub>2</sub> H <sub>5</sub> N <sub>5</sub> | 377.6–378.6   | 104.5–105.5 | —                        | +206.8 ± 2.6                                          |

Data source: [867].

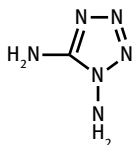
vaporization or sublimation, and entropies of fusion and evaporation were also listed in the original publication but are not included in Table 59.

## 14.5 Di-substituted Neutral Tetrazole Derivatives

1,5-Dimethyl-1*H*-tetrazole, C<sub>3</sub>H<sub>6</sub>N<sub>4</sub>, CAS RN [5144-11-6], can be used as the starting ingredient in other tri-substituted tetrazole derivatives. Substituted tetrazoles can be made from nitriles instead of cyanamide and hydrazoic acid [868].

### 14.5.1 1,5-Diamino-1*H*-tetrazole

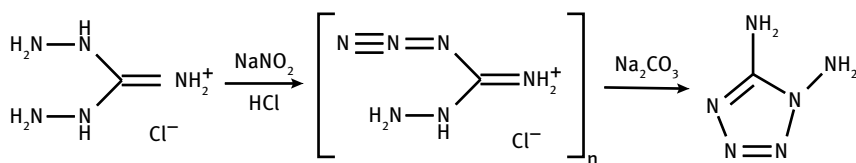
1,5-Diaminotetrazole, tetrazole-1,5-diamine, C<sub>1</sub>H<sub>4</sub>N<sub>6</sub>, DAT, CAS RN [2165-21-1], *M* = 100.09 g/mol, is a useful intermediate in the synthesis of other more energetic tetrazole derivatives. 1,5-Diaminotetrazole melts at 460–461 K (187–188 °C) (dec.). 2,5-Diaminotetrazole melts at 398–400 K (125–127 °C) (dec.).



1,5-Diamino-tetrazole (DAT)

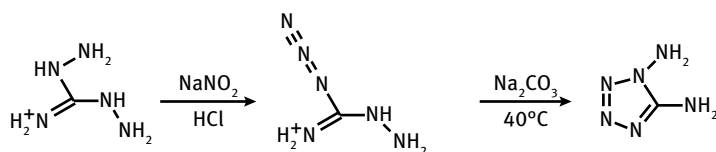
1,5-Diaminotetrazole can be synthesized from thiosemicarbazide and sodium azide in the presence of lead(II) oxide and ammonium chloride in DMF as the solvent [869]. Unfortunately, this method results in the formation of lots of lead azide, which is difficult to dispose of due to its shock sensitivity. A summary of synthesis methods for DAT is provided in [870].

A milestone in the synthesis of DAT was achieved when chemists reacted the sodium salt of 5-aminotetrazole with hydroxylamine-*O*-sulfonic acid and obtained a mixture of 1,5-diaminotetrazole (1,5-DAT) and 2,5-diaminotetrazole (2,5-DAT), where the first constituted ~8.5% of the reaction yield [871].



A method developed at the Klapoetke group in Munich avoids the formation of lead azide and instead uses the diazotation of diaminoguanodinium chloride. This reaction mixture is brought to pH 8 to deprotonate the intermediate formed, which cyclizes, thus yielding 1,5-DAT in 58% yield. That method is similar to the scheme developed by Galvez-Ruiz. The synthesis conditions must be perfectly controlled because the reaction of nitrous acid with aminoguanidinium is strongly dependent on the pH value as well as on the amounts of reactants. Otherwise, it might lead to the azide derivative, which is a very explosive byproduct.

Another synthesis method for 1,5-diamino-1*H*-tetrazole was introduced that avoided azide as a hazardous byproduct. 1,5-diamino-tetrazole can be prepared by the diazotization of a solution of diaminoguanidinium chloride in water with sodium nitrite, followed by extraction with hot EtOH. Once the extracting solvent leaves via evaporation, pure 1,5-diamino-1*H*-tetrazole remains. This can be recrystallized from water and has a melting point of 458–460 K (185–187 °C) [872].

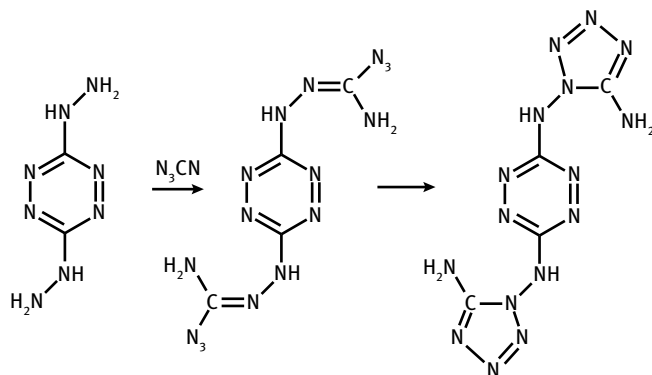


1,5-Diaminotetrazole Synthesis

An improved synthesis method for 1,5-diamino-1*H*-tetrazole also uses the diazotization of diaminoguanidinium chloride [819]. Another synthesis method oxidizes

thiosemicarbazide with lead oxide and reacts the intermediate *N*-aminocarbodiimide with hydrazoic acid.

1,5-Diamino-1*H*-tetrazole derivatives can be obtained by reaction of mono-substituted hydrazines such as 2,5-dihydrazinotetrazine with cyanogen azide [873]. Azido-hydrazones were postulated as intermediates in this reaction (see scheme).



1,5-Diamino-1*H*-tetrazole is best prepared starting with diaminoguanidinium(1+) chloride as a precursor raw material [874]. 1,5-Diamino-tetrazole isomerization reaction kinetics were studied based on DFT methods. The geometry structure, vibration frequencies, natural bonding orbital, and zero-point energy (ZPE) of stationary points involved in the reaction were calculated [754]. The isomerization reaction displays azide-cyclization mechanisms. In the gaseous case, the reaction is exothermic and spontaneous, with a low reaction activation energy.

A DFT method was applied to compute bond energies and electronic structures of 1,5-diamino tetrazole in both gaseous and crystalline states [875]. The crystal structure compared well with experimental data. The overlap populations of N(1)–N(2) bonds were much less than those of other bonds. Therefore the N(1)–N(2) bond was predicted to first rupture by external stimuli.

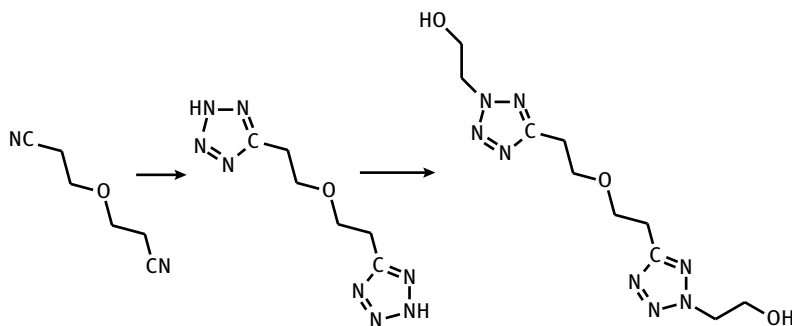
#### 14.5.2 Nitroalkyl Di-Substituted Tetrazole Derivatives

Combining trinitroethyl functionality with mono-, di- or triaminotriazoles via a Mannich reaction with trinitromethane and formaldehyde results in very energetic materials such as 1-trinitroethylamino-5-amino-tetrazole (TTD) or 1,5-bis-(trinitroethylamino)tetrazole (BTDD) [876]. TTD has an enthalpy of formation of +356 kJ/mol, a density of 1.831 g/mL, a detonation velocity of 9194 m/s, and an impact sensitivity of 30 J. However, it has poor thermal stability with an onset of exotherm at 399 K (126 °C).

A series of dense energetic *N*-trinitroethyl-substituted mono-, bis-, and tri-aminotetrazoles were obtained by reacting primary amines with *in-situ* generated cyanogen azide. This was followed by the trinitroethyl functionalization, which involved a condensation of a hydroxymethyl intermediate prepared by a reaction of formaldehyde with trinitromethane [877]. These compounds were characterized by NMR, IR, elemental analysis, DSC, and XRD. The HOFs for all compounds were calculated and then combined with experimental densities to determine the detonation pressures and velocities of the energetic materials. For tetrazole- and tetrazine-based high-density energy compounds with oxygen balance equal to zero see Reference [726].

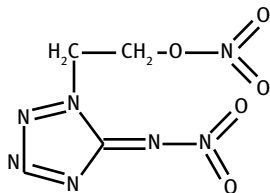
Convenient access to 5-(trinitromethyl)-2*H*-tetrazole (HTNTz) has been developed by the exhaustive nitration of 1*H*-tetrazole-5-acetic acid [878]. HTNTz was converted into ammonium, guanidinium, rubidium, cesium, copper, and silver 5-(trinitromethyl)-2*H*-tetrazolates. The reaction of HTNTz with hydrazine or hydroxylamine resulted in the loss of one nitro group from the alkyl rest and the formation of hydrazinium 5-(**d**initromethyl)tetrazolate and hydroxylammonium 5-(**d**initromethyl)-1*H*-tetrazolate, respectively. Acid treatment of both 5-(**d**initromethyl)tetrazolates resulted in the isolation of 5-(dinitromethylene)-4,5-dihydro-1*H*-tetrazole, which was then converted into potassium 5-(dinitromethyl)-1*H*-tetrazolate by reaction with  $K_2CO_3$ . The 5-(trinitromethyl) and 5-(dinitromethyl)tetrazoles are highly energetic materials that explode upon impact or heating.

A series of di-, tri-, and tetrakis-tetrazoloalkanes were synthesized from the corresponding nitriles and sodium azide [879]. These were then alkylated to give hydroxy-terminated chains for possible use as high-energy oligomers in energetic binders for solid propellants.



Diols with tetrazole rings and alkyl groups between the two oxygen atoms can be used as building blocks for high-nitrogen polymers. These are suitable for solid propellants, gas generants [880–888], and low-temperature clean-burning pyrotechnic gas generators [889].

1-(2-Nitratoethyl)-5-nitriminotetrazole was formed by the reaction of 1-(2-hydroxyethyl)-5-aminotetrazole and 100%  $\text{HNO}_3$  [890].



1-(2-Nitratoethyl)-5-nitriminotetrazole

This compound has acidic properties and forms salts with bases. Nitrogen-rich salts such as the ammonium, hydroxylammonium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium 1-(2-nitratoethyl)-5-nitriminotetrazolate were prepared and characterized by single-crystal XRD, IR and Raman spectroscopy, multi-nuclear NMR, elemental analysis, and DSC. The enthalpies of formation were calculated and several detonation parameters such as the detonation pressure, velocity, energy, and temperature were computed. The sensitivities towards impact, friction, and electrical discharge were tested using the BAM drop-hammer impact sensitivity test apparatus, a friction sensitivity tester, as well as a small-scale electrical discharge device.

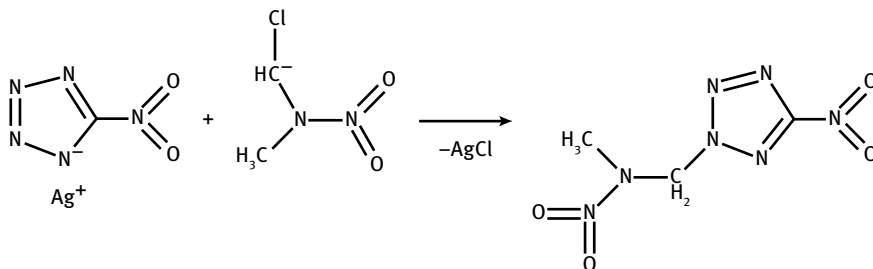
Hydroxylammonium 2-dinitromethyl-5-nitrotetrazolate (HADNMNT) crystal structure was determined by  $^{15}\text{N}$  NMR and gauge independent atomic orbital (GIAO) calculations [891]. The thermal decomposition temperature, the explosion probabilities of impact sensitivity, and the friction sensitivity were 141.9 °C, 96%, and 100%, respectively. The detonation parameters of HADNMNT were predicted to be equal to those of HMX.

### 14.5.3 Other Neutral Di-Substituted Tetrazole Derivatives

1-Methyl-5-nitrotetrazole and 2-methyl-5-nitrotetrazole have been evaluated as initiating explosives [892]. Although isomers, they exhibited markedly different thermal and explosive properties. 2-Methyl-5-nitrotetrazole is an energetic material with properties both of primary and secondary explosives. It is sensitive to mechanical and electrostatic shock comparable with primary explosives but does not ignite to explosion when unconfined.

The reaction of 1-chloro-2-nitro-2-azapropane with silver nitrotetrazolate yielded 1-nitrotetrazolato-2-nitro-2-azapropane (NTNAP), also known as *N*-methyl-*N*-[(5-nitrotetrazol-2-yl)methyl]nitramide, as a white solid substance [819, 893]. The highly energetic compound was characterized using vibrational (IR and Raman) and multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ) NMR spectroscopy, elemental analysis,

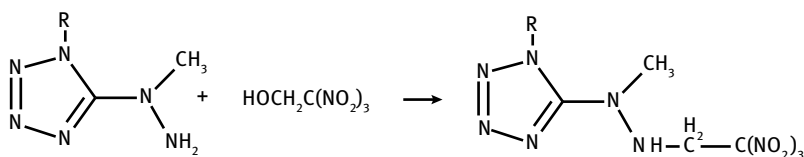
and low-temperature single-crystal XRD. 1-Nitrotetrazolato-2-nitro-2-azapropane is a covalently bound room-temperature stable solid that contains a nitramine group and a nitrotetrazolate ring unit in the molecule. It was hydrolytically stable at ambient conditions.



1-Nitrotetrazolato-2-nitro-2-azapropane

This compound has an oxygen balance of  $-35.5\%$ , impact sensitivity of 6 J, and friction sensitivity of 60 N. The covalent compound is thermally reasonably stable, melts without decomposition at 373 K ( $100^\circ\text{C}$ ), and shows decomposition with an onset of exotherm at about 453 K ( $180^\circ\text{C}$ ).

The synthesis of 1-methyl-5-(1-methyl-2-(2,2,2-trinitroethyl)hydrazinyl)-1*H*-tetrazole (MMTHT) and 2-(5-(1-methyl-2-(2,2,2-trinitroethyl)hydrazinyl)-1*H*-tetrazol-1-yl)ethanol (MTHTE) utilizes a condensation of the starting amino derivative with 2,2,2-trinitroethanol [819].



R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>

1-Methyl-5-(1-methyl-2-(2,2,2-trinitroethyl)hydrazinyl)-1*H*-tetrazole, MMTHT, C<sub>5</sub>H<sub>9</sub>N<sub>9</sub>O<sub>6</sub>, has a molecular mass of 291.21 g/mol, an oxygen balance of  $-46.7\%$ , and a density of 1.63 g/cm<sup>3</sup>. The onset of decomposition by DSC (2 K/min) was relatively low at 355.6 K ( $82.5^\circ\text{C}$ ), impact sensitivity was  $>30$  J, friction sensitivity was 108 N (visible flame), the predicted detonation pressure was 277 kbar, and the detonation velocity was 8307 m/s.

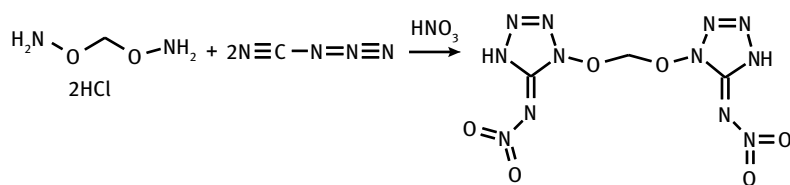
The trinitromethyl and fluorodinitromethyl functionalities have proven to be useful functional groups in the synthesis of high-performing explosives as well as oxidizers for rocket propellants, such as 5-(polynitromethyl)-tetrazole and 2-(2-nitro-2-azapropyl)-5-(trinitromethyl)-2*H*-tetrazole [712, 894].

#### 14.5.4 Di-Substituted Tetrazoles: Nitro-Amino-Tetrazole and Nitro-Imino-Tetrazole

Nitriminotetrazoles and the corresponding metal nitramino-tetrazolates salts have been known for a long time; they are, after all, relatively cheap and easy to manufacture via various routes. There are two main methods employed to do this, the first of which uses the protonation of 5-aminotetrazole using warm concentrated  $\text{HNO}_3$  to form 5-aminotetrazole nitrate, followed by dehydration with concentrated  $\text{H}_2\text{SO}_4$  to form 5-nitriminotetrazole. Another synthetic route is based on the cyclization of nitroguanylazide (also known as nitroazidoformamidine). A third less frequently used method is the *N*-nitration of aminotetrazoles using tetranitromethane.

2-Amino-5-nitrotetrazole can be prepared by the amination of the parent anion with *O*-tosylhydroxylamine [318]. The 5-*H*-tetrazolate anion has also been aminated using the addition of hydroxylamine *O*-sulfonic acid to either 1-aminotetrazole or 2-aminotetrazole. The prepared materials have been characterized by XRD, NMR, IR, and Raman spectroscopy, and by mechanical impact and electrostatic discharge sensitivity testing. Their predicted explosive performances were calculated using the EXPLO5 computer code. The prepared *N*-amino energetic materials, which can also be used as new ligands for high-energy capacity transition metal complexes, exhibited high explosive performances (in the range of RDX and HMX) and a range of sensitivities from low to extremely high.

Oxy-5-aminotetrazoles can be obtained from the reaction of cyanogen azide and alkyl oxyamine in 100% nitric acid, giving a series of highly energetic oxy-5-nitroiminotetrazolates in good yield [895]. These compounds exhibited good physical and detonation properties, such as moderate thermal stabilities, high densities, high enthalpies of formation, high detonation pressures, and fast detonation velocities. For example, methylenebis(1-oxy-5-nitroiminotetrazole) had an enthalpy of formation of +3.47 kJ/mol, a density of 1.90 g/cm<sup>3</sup>, a detonation pressure of 46.7 GPa, and a detonation velocity of 9867 m/s.

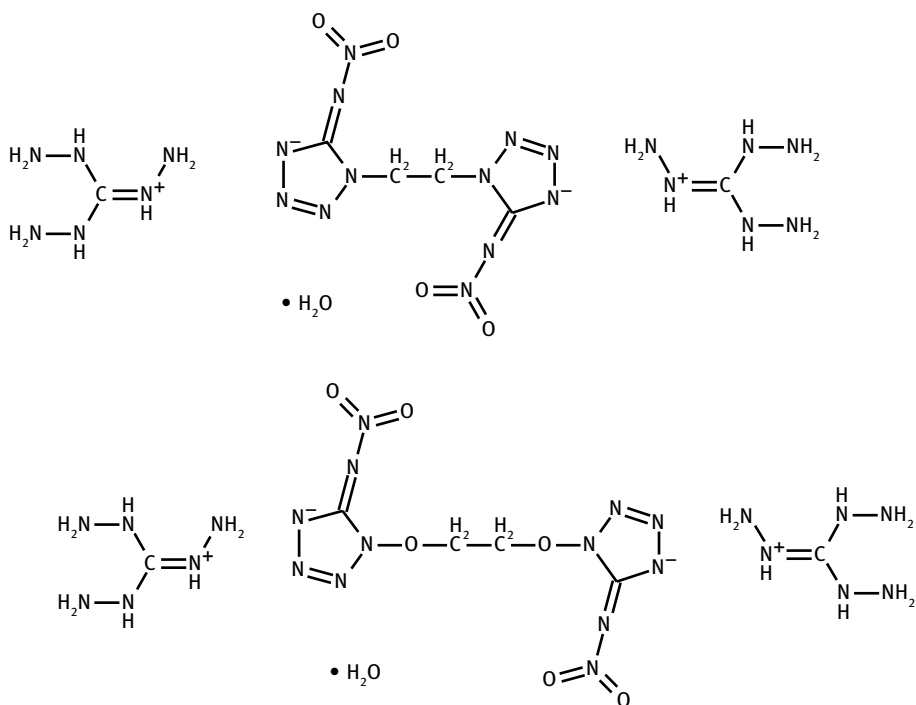


Methylenebis(1-oxy-5-nitroiminotetrazole)

Highly energetic 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) salts can be obtained by reacting equimolar quantities of the acidic 1,1'-ethylenebis(oxy)bis-(5-nitroimino-tetrazole) and energetic bases in aqueous solution [230, 896]. Metathesis of silver 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) with diamino-guanidinium chloride or triaminoguanidinium chloride gave the corresponding oxy-nitroimino-tetrazolate salts. These salts were characterized by IR, NMR, ele-



mental analysis, DSC, and (in some cases) by single-crystal XRD. The HOFs for all compounds were calculated with Gaussian 03 and then combined with measured densities to calculate predicted detonation pressures and velocities. The impact sensitivities of all salts were found to be less than those of the parent compounds. The physical and detonation properties of these oxy-nitroimino-tetrazolate salts were comparable to the analogous diaminoguanidinium and triaminoguanidinium 1,1'-ethylenebis(5-nitroimino-tetrazolate) salts.



## 14.6 Di-Substituted Tetrazolium and Tetrazolate Salts

### 14.6.1 1,5-Diamino-1*H*-tetrazolium Salts

1,5-Diamino-1*H*-tetrazole (**2**, DAT) can easily be protonated by reaction with strong mineral acids like nitric acid or perchloric acid, yielding 1,5-diaminotetrazolium nitrate (**2a**) and perchlorate (**2b**). The numbers in parentheses refer to the compounds listed in Table 60. The reaction of 1,5-diamino-1*H*-tetrazole with iodomethane followed by the metathesis of the iodide with silver nitrate, silver dinitramide, or silver azide led to a new family of 1,5-diamino-4-methyl-1*H*-tetrazolium salts. The added methyl group goes into the 4-position. In all cases, stable salts were obtained and fully characterized by IR, Raman, MS, multi-nuclear NMR spectroscopy,

Table 60: Properties of 1,5-diaminotetrazolium salts.

| Comp. No. | Name                                                     | Formula                                                     | Melting point      |                    | Density (calc.) | Const. vol. heat of combustion |       | Enthalpy of formation |          | Det. pressure | Det. velocity |
|-----------|----------------------------------------------------------|-------------------------------------------------------------|--------------------|--------------------|-----------------|--------------------------------|-------|-----------------------|----------|---------------|---------------|
|           |                                                          |                                                             | K                  | °C                 |                 | l/g                            | cal/g | kJ/mol                | kcal/mol |               |               |
| 2a        | 1,5-Diamino-1 <i>H</i> -tetrazolium nitrate              | CH <sub>5</sub> N <sub>7</sub> O <sub>3</sub>               | 411–412            | 138–139            | 1.727           | 7899                           | 1888  | +254                  | +60.7    | 33.3          | 8774          |
| 2b        | 1,5-Diamino-1 <i>H</i> -tetrazolium perchlorate          | CH <sub>5</sub> N <sub>6</sub> ClO <sub>4</sub>             | 370–371            | 97–98              | 1.902           | 4067                           | 972   | +192                  | +45.9    | 32.2          | 8383          |
| 7b        | 1,5-Diamino-4-methyl-1 <i>H</i> -tetrazolium nitrate     | C <sub>2</sub> H <sub>7</sub> N <sub>7</sub> O <sub>3</sub> | 394–395            | 121–122            | 1.506           | 10276                          | 2456  | +174                  | +41.7    | 23.4          | 7682          |
| 7c        | 1,5-Diamino-4-methyl-1 <i>H</i> -tetrazolium dinitramide | C <sub>2</sub> H <sub>7</sub> N <sub>9</sub> O <sub>4</sub> | 358–359            | 85–86              | 1.719           | 8933                           | 2135  | +385                  | +92.1    | 33.6          | 8827          |
| 7d        | 1,5-Diamino-4-methyl-1 <i>H</i> -tetrazolium azide       | C <sub>2</sub> H <sub>7</sub> N <sub>9</sub>                | 408–410<br>decomp. | 135–137<br>decomp. | 1.417           | 15037                          | 3594  | +676                  | +161.6   | 20.8          | 7405          |

Data source: [872].

elemental analysis, XRD, and safety testing (impact and friction sensitivity). Most of the salts exhibited good thermal stability. Both the perchlorate and the dinitramidate have melting points well below 373 K (100 °C), yet high decomposition onsets with maximum exotherm peaks at 441–465 K (168–192 °C) (except for the azide). Preliminary sensitivity testing of the crystalline compounds indicated rather low impact sensitivities for all compounds, the worst being that of the perchlorate and the dinitramide with a value of 7 J. The friction sensitivities of the 1,5-diamino-1*H*-tetrazole perchlorate and the 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramidate were 60 and 24 N, respectively. The enthalpies of combustion ( $\Delta H_c^\circ$ ) of the salts were determined experimentally using oxygen bomb calorimetry. The HOFs calculated from these heats of combustion are summarized in Table 60 along with predicted detonation velocities and detonation pressures. The highly friction-sensitive 1,5-diamino-4-methyl-tetrazolium dinitramidate was also synthesized by a metathetical reaction of the corresponding iodide and silver dinitramidate [897].

1,5-Diamino-1*H*-tetrazole can easily form salts by reacting with strong acids. It also forms energetic complexes resulting from co-ordinating with six DAT molecules as ligands with metal perchlorates. All of these DAT complex compounds are sensitive to mechanical stimuli. They also possess good explosive properties.

A study of the combustion behavior of 1,5-diaminotetrazole (DAT), its salt with perchloric acid, and its coordination compounds with Ni(II), Co(II), Cu(II), Cd, and Zn perchlorates in the pressure range from 0.1 to 36 MPa showed that, despite the high energy content, 1,5-diaminotetrazole starts to burn only at extremely high pressures (above 24 MPa) [898, 899]. Diaminotetrazole perchlorate had the maximum burning rate among all known organic perchlorates. The burning rates of the coordination compounds were also very high, with the burning rate of  $[\text{Cu}(\text{DAT})_6](\text{ClO}_4)_2$  reaching the record value (for laminar combustion) of 1670 mm/s at a pressure of 34 MPa.

Energetic coordination compounds using 1,5-diaminotetrazole as ligand, Co or Cu as the central cation, and picric acid as the outer ion were synthesized and characterized by elemental analysis, FTIR spectroscopy, DSC, and TGA-DTG [900]. The two complexes accelerated the combustion of a GAP/HNIW propellant and the thermal decomposition of AP, HMX, and HNIW.

#### 14.6.2 1,5-Diaminotetrazolium Nitrate

Diaminotetrazole can form (1+), (2+), or (3+) tetrazolium nitrates or perchlorates, but the most common salts are the tetrazolium(1+) salts. In addition to the 1,5-diaminotetrazolium nitrate, the 1,5-diaminotetrazolium dinitramidate and perchlorate have also been investigated as HEDMs.

The presence of two amino groups on the tetrazole ring results in high-melting nitrate and perchlorate salts. If one wants to make ionic liquids, one should switch to amino/methyl tetrazolium compounds to achieve lower melting materials.

The heat of combustion of 1,5-diaminotetrazolium nitrate was determined experimentally using an oxygen bomb ( $\Delta H_{\text{comb.}} = 7900 \pm 300 \text{ kJ/kg}$ ) [901, 902]. The standard HOF of 1,5-diaminotetrazolium nitrate was obtained via *ab initio* quantum chemical computations ( $\Delta H_f^\circ = +254 \text{ kJ/mol} = +1558 \text{ kJ/kg}$ ). The detonation velocity ( $D$ ) and detonation pressures ( $P$ ) of 1,5-diaminotetrazolium nitrate were calculated using empirical equations by Kamlet and Jacobs, resulting in  $D = 8.77 \text{ mm}/\mu\text{s}$  and  $P = 33.3 \text{ GPa}$ .

*In-situ* synchrotron XRD, optical Raman, and IR spectroscopy were used to examine the structural properties, equation of state, and vibrational dynamics of 1,5-diaminotetrazolium nitrate under high pressure at room temperature [903]. The X-ray measurements showed that the pressure-volume relations remained smooth to 12 GPa. XRD measurements at pressures above 12 GPa were not possible in this study because of sample decomposition resulting from several factors. XRD revealed no indication of a phase transition to at least 12 GPa, but slight variations in the  $c/b$  unit cell ratio suggested modifications within the hydrogen bonding sub-lattice. Vibrational spectra indicated that the ambient phase of 1,5-diaminotetrazolium nitrate remained the dominant phase up to 33 GPa.

In a similar study, the isothermal structural properties, equation of state, and vibrational dynamics of 2-methyl-5-nitramino-2*H*-tetrazole were studied under high pressure using synchrotron XRD and optical Raman, and IR micro-spectroscopy [904]. Up to 15 GPa, analysis of the XRD patterns revealed no indication of a phase transition, and the pressure-volume isotherm remained smooth.

Three 1,5-diaminotetrazole nitro-substituted azolate salts were synthesized and characterized by IR, NMR, elemental analysis, thermal stability, phase behavior, density, and impact sensitivities [905]. The 1,5-diamino-4*H*-tetrazolium 5-nitrotetrazolate salts crystallized in the orthorhombic system *Pbca*. The predicted detonation pressure was from 28.05 to 29.88 GPa and the detonation velocities were from 8343 to 8655 m/s, thus making them competitive energetic materials. Most of the compounds had a slightly negative oxygen balance approaching zero (−23.8 to −33.5%).

1,5-Diaminotetrazolium nitrate ( $\text{CH}_5\text{N}_7\text{O}_3$ , HDATN) was synthesized from 1,5-diaminotetrazole as the raw material with a yield of 95.3% [906]. HDATN contains seven nitrogen atoms. Its nitrogen content is 60.1%, which is more than that of 5-aminotetrazolium nitrate (5-ATN). The structure was characterized by elemental analysis, IR spectrum, NMR, and mass spectrum. A possible fragmentation mechanism on heating was discussed. The thermal stability of the nitrate salt was investigated by TGA-DSC and DTA. In the DTA at  $5^\circ/\text{min}$ , there was an endotherm (melting) at 393.46 K (120.46 °C) but the mass did not change. HDATN started to break down after melting, with the first mass loss plateau seen from 400 to 430 K (127 to 157 °C), with an exotherm peak at 422 K (149 °C), and the second from 472 to 503 K (199 to 230 °C). The melting point shifted at higher heating rates to 419.9 K (144.75 °C). The kinetic parameters, including activation energy and pre-exponential factors, were calculated by using the Kissinger equation. The activation energy of the first decomposition step was

106.07 kJ/mol and that of the second step was 110.42 kJ/mol. The enthalpy of formation of the nitrate salt was measured as  $-271.78 \text{ kJ/mol} = -1667.36 \text{ cal/g}$ . The density was predicted from molecular calculations as  $1.713 \text{ g/cm}^3$ . The predicted detonation velocity was 8738 m/s with a pressure of 32.86 GPa.

### 14.6.3 1,5-Diaminotetrazole-Derived Energetic Salts

1,5-Diaminotetrazole is not a particularly strong base and will only form salts with relatively strong mineral acids ( $\text{pK}_a = 0$ ) under normal conditions. The direct reaction of 1,5-diaminotetrazole with concentrated perchloric acid formed the 1,5-diaminotetrazolium perchlorate [907]. The monoclinic, space group  $P2_1/n$  (No. 14), crystals with an X-ray density of  $1.909 \text{ g/cm}^3$  were sensitive to impact or friction. The crystals were soluble in a wide array of polar solvents such as methanol, ethanol, acetonitrile, DMSO, DMF, or water. In DSC studies, the material melted cleanly at 398–403 K (125–130 °C), followed by accelerating decomposition as the temperature was increased beyond the melting point. Experimental evidence strongly supported the protonation of a nitrogen atom of the tetrazole ring, including the structure observed in a single-crystal XRD. Quantum chemical calculations were performed to determine the relative energies of all possible *N*-protonated structures of the 1,5-diaminotetrazole ring. The predicted geometry of the most stable isomer compared favorably with the experimentally observed structure.

### 14.6.4 Other Di-Substituted Tetrazolium and Tetrazolate Salts

5-Amino-1-methyltetrazole and 5-amino-2-methyltetrazole can be obtained by methylation of the sodium salt of 5-aminotetrazole with dimethyl sulfate or methyl iodide. Di-substituted amino- and/or methyltetrazolium perchlorate salts with nitrate or perchlorate anions had higher melting points and decomposed at higher temperatures than the nitrate derivatives. The densities of these salts range between 1.5 and  $1.7 \text{ g/cm}^3$ . All six tetrazolium salts had positive  $\Delta H_f$ 's ranging between 130 to 911 kJ/mol, with the perchlorates being five or six times as positive as the analogous nitrates [202]. 2-Amino-4, 5-dimethyl tetrazolium perchlorate had a much higher melting point,  $T_d$ , and  $\Delta H_f$  than 1-amino-4, 5-dimethyltetrazolium perchlorate (413 vs. 324 K = 140 vs. 51 °C; 511 vs. 455 K = 238 vs. 182 °C, and 911 vs. 539 kJ/mol). This may correlate somewhat with the extent of the hydrogen bonding. Perchlorates had higher values than nitrates for all properties studied ( $T_m$ ,  $T_d$ ,  $d$ ,  $\Delta H_f$ ). One of the tetrazolium nitrates melted at <298 K (<25 °C) and only three of the salts melted at <373 K (<100 °C).

Several nitrogen-rich salts of 2-methyl-5-nitraminotetrazole were synthesized and characterized, with a particular focus placed on their properties as new energetic materials [908]. The triaminoguanidinium and diaminouronium salts especially showed promise as RDX replacements. Both demonstrated good performances, appropriate stabilities, facile synthesis, and moderate sensitivities, which are the main demands for a new energetic filler. 2-Methyl-5-nitraminotetrazole was

formed by the nitration of 2-methyl-5-aminotetrazole. 2-Methyl-5-aminotetrazole was obtained via an improved synthesis starting from sodium 5-aminotetrazolate, which was methylated with dimethyl sulfate in dimethyl formamide, producing 2-methyl-5-aminotetrazole in 29% yield. Nitrogen-rich salts such as guanidinium, 1-aminoguanidinium, 1,3-diamino-guanidinium, 1,3,5-triamino-guanidinium, azido-formamidinium, hydrazinium, and diaminouronium 2-methyl-5-nitraminetetrazolate were prepared by facile deprotonation or metathesis reactions.

Eight energetic salts based on 1-methoxy-5-nitroiminotetrazole, that was obtained by nitration of 1-methoxy-5-aminotetrazole, were synthesized [909]. Guanidinium, aminoguanidinium, diaminoguanidinium, triaminoguanidinium, carbonydiazidinium, 3-amino-1,2,4-triazolium, 4-amino-1,2,4-triazolium, and 3,5-diamino-1,2,4-triazolium 1-methoxy-5-nitroiminotetrazolate salts were prepared, purified, and characterized by vibrational spectroscopy (IR, Raman), multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) NMR spectroscopy, elemental analysis, and single-crystal XRD. The HOFs and detonation properties (pressure and velocity) were calculated. Thermal stabilities were measured by DSC and the sensitivities toward impact and friction were determined by BAM test methods.

1-Methyl-5-aminotetrazole (**4**) (MAT) can easily be protonated by strong acids such as nitric acid or perchloric acid, yielding 1-methyl-5-aminotetrazolium nitrate (**4a**) or 1-methyl-5-aminotetrazolium perchlorate (**4b**) [910]. Methylation, rather than protonation, of **4** with iodomethane followed by the exchange of the iodide (**5a**) for nitrate (**5b**), perchlorate (**5c**), azide (**5d**), or dinitramide (**5e**) yielded a series of energetic dimethylated aminotetrazolium salts. In all cases, stable salts were obtained and characterized by vibrational (IR, Raman) spectroscopy, multi-nuclear NMR spectroscopy, mass spectrometry, and elemental analysis and structure determination was carried out by XRD. Compounds **4a**, **4b**, and **5c** crystallized in the monoclinic space group  $P2_1n$ , whereas compounds **5b** and **5e** crystallized in the orthorhombic space group  $P2_12_12_1$  and **5d** in the orthorhombic  $Fddd$ . Safety testing (impact, friction, and electrostatic sensitivity) and thermal stability measurements (DSC) showed that all exhibited good thermal stabilities (decomposition above 423 K = 150 °C). The constant volume energies of combustion ( $\Delta U_{\text{comb}}$ ) of **4a**, **5b**, **5d**, and **5e** were determined experimentally using oxygen bomb calorimetry and found to be -10.5 kJ/g = -2.51 kcal/g, -13.3 kJ/g = -3.19 kcal/g, -18.8 kJ/g = -4.5 kcal/g, and -10.7 kJ/g = -2.57 kcal/g, respectively. From the experimentally determined density, the chemical composition and energies of formation (back-calculated from the heats of combustion), detonation pressures and velocities of **4a** (8100 m/s, 25.6 GPa), **5b** (7500 m/s, 20.2 GPa), **5d** (8200 m/s, 21.7 GPa), and **5e** (7500 m/s, 21.2 GPa) were predicted using the EXPLO5 code. The enthalpies of formation of the coordination compounds of perchlorates of Cu, Co, Zn, and Cd with 1,5-diaminotetrazole were calculated from the heats of solution of these salts in water [911–914].

Several energetic salts were synthesized via the quaternization of azido or the nitro derivatives of substituted tetrazoles by reaction with nitric or perchloric acid (or

iodomethane followed by metathesis reaction with silver nitrate or silver perchlorate) [328]. Most of the salts exhibited good thermal stabilities and low melting points. The heat of combustion energies was measured in an oxygen bomb calorimeter, and the standard molar enthalpies of formation were derived from the heat of combustion data.

Hydroxylammonium 2-dinitromethyl-5-nitrotetrazolate was synthesized via neutralization reaction with hydroxylamine and 2-dinitromethyl-5-nitrotetrazole and its properties were characterized by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{15}\text{N}$  NMR, elemental analysis, and DSC [915]. The detonation velocity and detonation pressure of hydroxylammonium 2-dinitromethyl-5-nitrotetrazolate were calculated by DFT and K-J equation. The peak temperature of the DSC curve at a heating rate of  $10^\circ\text{C}/\text{min}$  was 418.4 K ( $145.3^\circ\text{C}$ ). Its predicted detonation velocity, detonation pressure, and specific impulse are 9.240 km/s, 39.54 GPa, and  $2639.8 \text{ N s kg}^{-1}$ , respectively.

Substitutions on 5-methyl-1-aminotetrazole by trinitroethyl moiety and furazan ring increased the oxygen balance and improved the detonation properties [916]. The structures of both compounds were determined by XRD, and their thermal stability and explosive performance were also investigated.

Properties of three nitrogen-base salts of 3,5-dinitrotetrazole, ammonium 3,5-dinitro-1,2,4-triazolate, diaminoguanidinium 3,5-dinitro-1,2,4-triazolate, and triaminoguanidinium 3,5-dinitro-1,2,4-triazolate have been assembled in Table 38, along with properties of seven salts of 1-hydro-3-nitro-1,2,4-triazol-5-one (NTO) [547, 548].

## 14.7 Tri-Substituted Tetrazolium and Tetrazolate Salts

The initiation of decomposition of several tri-substituted tetrazolium salts was studied by CRT at around 573 K ( $300^\circ\text{C}$ ) using rapid-scan FTIR spectroscopy and TOF mass spectrometry to identify the products evolved from samples subjected to heating rates of about 2000 K/s [917]. The compounds studied included 2-amino-4,5-dimethyl-tetrazolium nitrate (2AdMTZN) and 1-amino-4,5-dimethyl-tetrazolium nitrate (1AdMTZN). Methyl nitrate ( $m/e = 77$ ) was visible in some FTIR spectra. The resultant nitrogen-rich amino-methyl-tetrazole ( $m/e = 99$ ) was found to decompose to form primarily molecular nitrogen and methyl isocyanide. Unlike the 2AdMTZ salts, the 1AdMTZ salts were found to initiate decomposition at lower temperatures by at least  $50^\circ\text{C}$ . Decomposition was found to proceed through three major pathways: formation of the corresponding methylated anion and 1-amino-5-methyl-tetrazole, formation of ammonia by the amino group, and expulsion of nitrogen from the tetrazole cation itself. 1-Amino-5-methyl tetrazole was found to rapidly decompose to form mainly ammonia and nitrogen.

The thermal decomposition of 1,5-diamino-4-methyl-1*H*-tetrazolium nitrate (**2b**), 1,5-diamino-4-methyl-1*H*-tetrazolium dinitramidate (**2c**) and 1,5-diamino-4-methyl-

1*H*-tetrazolium azide (**2d**) were investigated by TGA and DSC [918]. Mass spectrometry and IR spectroscopy were used to identify gaseous decomposition products. Decomposition in the cases of **2c** and **2d** appeared to be initiated by a proton transfer to form the corresponding acids  $\text{HN}_3$  and  $\text{HN}_3\text{O}_4$ , whereas, in the case of **2b**, a methyl group transfer to  $\text{MeONO}_2$  was observed as an initial process. The gaseous products after the exothermic decomposition were comparable and were in agreement with the possible decomposition pathways predicted for the corresponding compounds by way of proposed possible decomposition schemes. The onset of decomposition temperatures of **2b** and **2c** were significantly higher than those of **2d** and were supported by an evaluation of the values of the activation energy, according to the Ozawa and Kissinger method.

1,4-Dimethyl-5-aminotetrazolium 5-nitrotetrazolate was synthesized from 1,4-dimethyl-5-aminotetrazolium iodide and silver 5-nitrotetrazolate [919]. Both compounds were characterized using vibrational (IR and Raman) and multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ) NMR spectroscopy, elemental analysis, and single-crystal XRD. 1,4-Dimethyl-5-aminotetrazolium 5-nitrotetrazolate represents an example of an energetic material that contains both a tetrazole-based cation and anion. 1,4-Dimethyl-5-aminotetrazolium 5-nitrotetrazolate was hydrolytically stable with a melting point of 463 K (190 °C) (decomposition). The impact sensitivity was very low (30 J), and it was not sensitive towards friction (>360 N).

1,3-Dimethyl-5-amino-1*H*-tetrazolium 5-nitrotetrazolate (**5b**) was synthesized from 1,4-dimethyl-5-amino-1*H*-tetrazolium iodide (**5a**) and silver 5-nitrotetrazolate. Both compounds (**5a** and **5b**) were characterized using IR, Raman, and multi-nuclear  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR spectroscopy, elemental analysis, and single-crystal XRD [920]. Salt **5a** crystallized in orthorhombic crystal shapes with space group *Pbca*, and unit cell parameters of  $a = 11.5016(4) \text{ \AA}$ ,  $b = 13.7744(5) \text{ \AA}$ ,  $c = 13.7744(5) \text{ \AA}$ ,  $V = 1638.2(1) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho = 1.955 \text{ g/cm}^3$ , whereas salt **5b** crystallized in monoclinic crystal shapes, space group *C1c*, with unit cell parameters of  $a = 14.5228(8) \text{ \AA}$ ,  $b = 5.0347(2) \text{ \AA}$ ,  $c = 13.7217(7) \text{ \AA}$ ,  $\beta = 112.11(1)^\circ$ ,  $V = 929.6(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 1.630 \text{ g/cm}^3$ . The sensitivity of **5b** to classical stimuli was determined by using standard BAM tests and its thermal stability was assessed by DSC measurements. In addition, its heat of combustion was determined by bomb calorimetry measurements. The EXPLO5 was used to calculate the detonation pressure ( $P$ ) and velocity ( $D$ ) of salt **5b** ( $P = 13.3 \text{ GPa}$  and  $D = 6379 \text{ m/s}$ ), as well as those of its mixtures with AN ( $P = 23.2 \text{ GPa}$  and  $D = 7862 \text{ m/s}$ ) and ADN ( $P = 29.6 \text{ GPa}$  and  $D = 8594 \text{ m/s}$ ). Compound **5b** is a hydrolytically stable solid with a high melting point (433 K = 160 °C). It is thermally stable up to 463 K (190 °C) with a very low sensitivity to friction (>360 N) and impact (>30 J) and has good performance in combination with an oxidizer.

*In-situ* high-pressure room temperature synchrotron XRD and IR micro-spectroscopy were used to examine the structural and vibrational properties and the equation of state of 1,4-dimethyl-5-aminotetrazolium 5-nitrotetrazolate crystals [921]. The X-ray measurements showed a smoothly varying pressure-volume relationship



to 20 GPa. However, the anisotropic ratios of the unit cell parameters revealed a discontinuity near 3.3 GPa, which can be attributed to an irreversible isostructural phase transition.

## 14.8 Other Neutral and Ionic Tetrazole Derivatives

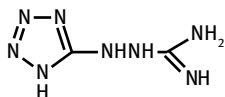
### 14.8.1 Tetrazolylcarbamides

As part of a PhD thesis, the following compounds were prepared and characterized by IR spectra and elemental analysis [922]:

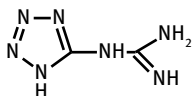
- 5-hydrazinotetrazolium hydrochloride
- 1-(5-tetrazolyl)-semicarbazide
- 4-(5-tetrazolyl)-semicarbazide
- *N*-(5-tetrazolyl)urea
- *N*-(5-tetrazolyl)urethane
- 5-tetrazolylammonium cyanate
- *N*-(5-tetrazolyl)carbamyl azide

5-Guanyl“amino”tetrazole,  $C_2H_5N_7$ , *N*-1*H*-tetrazol-5-yl-guanidine, 1-(1*H*-tetrazol-5-yl)-guanidine, 5-guanyltetrazole, CAS RN [66591-60-4] or [68134-09-8],  $M = 127.11$ , is a high nitrogen compound with 77.1% N. 5-Guanyl“amino”tetrazole is a reaction product of cyanamide and 5-aminotetrazole and it can be used in gas generators for the inflation of airbags [923, 924].

The nomenclature used by some authors for this compound seems to be illogical. While commonly called “5-guanylaminotetrazole,” the correct name would be 5-guanyltetrazole because the amino group in 5-AT has been replaced by a guanyl group. As the amino group is no longer there, “amino” should not be part of the name of this compound. Below we have used a strikethrough type font to indicate that the word amino should not be there. The molecular structures of these two compounds are shown here for comparison.



5-Guanylaminotetrazole  $C_2H_6N_8$



5-Guanyltetrazole  $C_2H_5N_7$

The enthalpy of formation of 5-guanylamino-tetrazole is  $+255 \text{ cal/g} = 32.4 \text{ kcal/mol} = +135.6 \text{ kJ/mol}$  and the density is  $0.0509 \text{ lb/in.}^3 = 1.409 \text{ g/cm}^3$ .

The thermal stability of 5-guanylamino-tetrazole was evaluated by DTA-TGA. In a high-temperature deterioration test, the weight loss of the material was only 0.2% when heated for 400 h at 383 K, and neither discoloration nor deterioration in appearance was observed. In addition, 5-guanylamino-tetrazole was found to be insensitive to impact and friction. The combustion of a stoichiometric  $\text{Sr}(\text{NO}_3)_2$ /5-guanylamino-tetrazole mixture indicated that the mixture had excellent combustion properties and generated sufficient gas to inflate airbags.

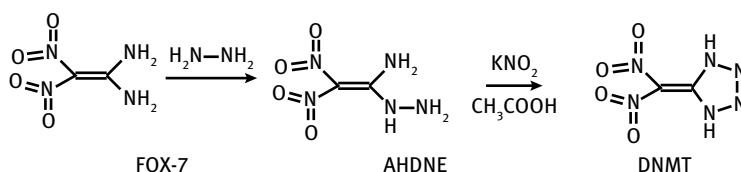
5-guanylamino-tetrazole also forms a nitrate salt with nitric acid,  $\text{C}_2\text{H}_5\text{N}_7 \cdot \text{HNO}_3$ ,  $\text{C}_2\text{H}_6\text{N}_8\text{O}_3$ ,  $M = 190.12$ . Chemical Abstracts called this guanidine, 1*H*-tetrazol-5-yl-, mononitrate; CAS RN [66591-61-5]. This compound has been patented as a nitrogen source for fire extinguishers [925, 926]. The enthalpy of formation of 5-guanylamino-tetrazolium nitrate is  $+95 \text{ cal/g} = +18.06 \text{ kcal/mol} = +75.6 \text{ kJ/mol}$  and the density is  $0.0591 \text{ lb/in.}^3 = 1.636 \text{ g/cm}^3$  [61].

The crystal structure and an improved synthetic procedure for the synthesis of 1-(2*H*-tetrazol-5-yl)guanidine and 1-(2*H*-tetrazol-5-yl)guanidinium nitrate have been described in [927]. The compounds were structurally characterized by spectroscopic (FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR) and elemental analysis. The molecular structure of tetrazolylguanidinium nitrate crystals was obtained from low-temperature single-crystal XRD. This salt crystallized as its hemihydrate in the orthorhombic space group *Fdd2*, with a crystal density of  $1.69 \text{ g/cm}^3$ . The molar enthalpy of formation of  $-281.7 \text{ kJ/mol}$  of the hemihydrate  $\text{C}_2\text{H}_7\text{N}_8\text{O}_{3.50}$  was calculated from the heat of combustion, however, this number is different from the number for the anhydrous salt listed in [61]. Another high-nitrogen compound is bis-triaminoguanidinium 5,5'-azotetrazolate.

#### 14.8.2 Other Tetrazole Compounds with C—C Linkages

1,1,3,3-Tetra(1*H*-tetrazol-5-yl)propane (TPP) is a propane chain with two tetrazole rings attached at each end. TTP can be synthesized by the reaction of propane-1,1,3,3-tetracarbonitrile with sodium azide in the presence of zinc bromide. The onset of the decomposition of TPP is at  $549 \text{ K} = 276^\circ\text{C}$ . Its predicted enthalpy of formation is  $1045 \text{ kJ/mol}$ . The reactions of TTP with four molar equivalents of imidazole, 4-nitroimidazole, 4-amino-4*H*-1,2,4-triazole, 1,2,4-triazole, 3-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, 3-nitro-1,2,4-triazole, 3,4-diaminofurazan, 5-aminotetrazole, melamine, 2,4,6-trinitroaniline, or guanidine in MeOH resulted in the formation of 1,1,3,3-tetra(1*H*-tetrazol-5-yl)propane-based tetraanionic energetic salts. The structures of these 12 salts were determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, MS, and elemental analysis [928]. All of these compounds showed good thermal stabilities above  $453 \text{ K} = 180^\circ\text{C}$ , as confirmed by TGA-DTA. Densities, HOFs, and detonation properties were calculated.

1,4-Dihydro-5*H*-(dinitromethylene)-tetrazole, 5-(dinitromethylene)-1,4-dihydro-tetrazole,  $C_2H_2N_6O_4$ ,  $M = 174.075$  g/mol, can be synthesized from 1,1-diamino-2,2-dinitroethene (DADNE, FOX-7) by reaction with hydrazine. This forms aminohydrazino-dinitroethene as an intermediate, which can then be diazotized to form a tetrazole ring. The 1,4-dihydro-5*H*-(dinitromethylene)-tetrazole diammonium salt,  $C_2H_8N_8O_4$ ; MW 208.14; 53.8% N, was synthesized and structurally characterized by single-crystal XRD [929].



The calculated X-ray density is  $1.615 \text{ g/cm}^3$ . The onset of exotherm in the DSC heated at  $10 \text{ K/min}$  was  $437 \text{ K} = 164^\circ\text{C}$  with a peak at  $482 \text{ K} = 209^\circ\text{C}$ . The critical temperature of thermal explosion was  $455.8 \text{ K} = 182.7^\circ\text{C}$ . The molar heat capacity was  $301 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $298 \text{ K}$ . The predicted detonation velocity was  $9100 \text{ m/s}$  and the detonation pressure was  $35.3 \text{ GPa}$ .

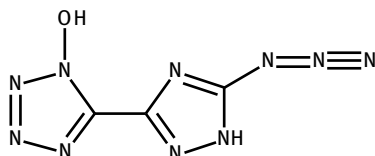
5-(1,2,4-Triazol-3-yl)tetrazoles with selected energetic moieties like nitro, nitrimino, and azido groups on the triazole ring make good energetic compounds and have been studied. To achieve the objective of a comparative study on the influence of those variable energetic moieties on structural and energetic properties, a complete characterization (including IR, Raman, NMR, and XRD) was conducted [263, 930]. The standard enthalpies of formation were calculated for all compounds and revealed high positive HOF for each one. The calculated detonation parameters were in the range of  $8000 \text{ m/s}$ . As expected, the measured impact and friction sensitivities, as well as the decomposition temperatures, strongly depended on the energetic moiety on the triazole ring.

Similar compounds can be made where the 1-position of the tetrazole ring carries a hydroxyl group. For example, three 5-(1,2,4-triazol-C-yl)tetrazol-1-ol compounds with selected energetic moieties including nitrimino, nitro, and azido groups on the triazole ring were synthesized and characterized by IR, NMR, MS, XRD, and DSC [263, 931]. The detonation parameters were calculated and compared to RDX. The sensitivities towards impact, friction, and electrostatic discharge were determined by experiments.

N—C bonded (non-bridged) 5-(1,2,3-triazol-1-yl)tetrazoles can be synthesized by the Cu(I)-catalyzed 1,3-dipolar azide-alkyne cycloaddition click reaction using 5-azido-*N*-(propan-2-ylidene)-1*H*-tetrazole [932]. For example, the click reaction in the presence of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and Na ascorbate at  $338\text{--}343 \text{ K}$  ( $65\text{--}70^\circ\text{C}$ ) for 48 h in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  co-solvent was found to be limited to only terminal alkynes that have

EWG,  $\text{CF}_3\text{C}\equiv\text{CH}$ , and  $\text{SF}_5\text{C}\equiv\text{CH}$ , giving rise to isopropylidene-[5-(4-trifluoromethyl-1,2,3-triazol-1-yl)tetrazol-1-yl]amine and isopropylidene-[5-(4-pentafluorosulfanyl-1,2,3-triazol-1-yl)tetrazol-1-yl]amine. When carried out under conditions using CuI and 2,6-lutidine as catalysts at 273 K (0 °C) for 13 h in  $\text{CHCl}_3$ , the reaction was versatile toward all alkynes, even those with electron-donating groups. HOFs, detonation pressures, detonation velocities, and impact sensitivities were reported for these 5-(1,2,3-triazol-1-yl)tetrazoles.

Several metal and nitrogen-rich salts of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol, 5-(5-azido-1*H*-1,2,4-triazol-3-yl)-1-hydroxy-tetrazole,  $\text{C}_3\text{H}_2\text{N}_{10}\text{O}$ , AzTTO, including Ag, Cu(I), Cu(II), K, Cs, ammonium, hydrazinium, guanidinium, and aminoguanidinium were prepared and characterized by IR, NMR, MS, DSC, and XRD [274]. The sensitivities towards impact, friction, and ESD were determined according to BAM standards, thereby revealing most of the metal salts to be highly sensitive and the nitrogen-rich salts to be mostly insensitive. The metal salts were tested as candidates for primary explosives.

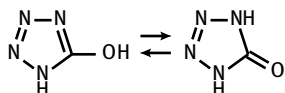


5-(5-Azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol

*N*-trinitroethyl-substituted mono-, bis-, and tri-5-aminotetrazoles were obtained by reacting primary amines with *in-situ* generated cyanogen azide, followed by the trinitroethyl functionalization that involved the condensation of a hydroxymethyl intermediate (prepared by a reaction with formaldehyde) with trinitromethane [933]. These compounds were then characterized by NMR, IR, elemental analysis, DSC, and XRD. The HOFs were calculated with Gaussian 03 and then combined with experimental densities to calculate the predicted detonation pressures and velocities.

### 14.8.3 Tetrazolone

5-Hydroxytetrazole is a tautomeric form of tetrazolone-5, 1,4-dihydropyridine-5-one,  $\text{CH}_2\text{N}_4\text{O}$ , CAS RN [16421-52-6],  $M = 86.05$  g/mol.



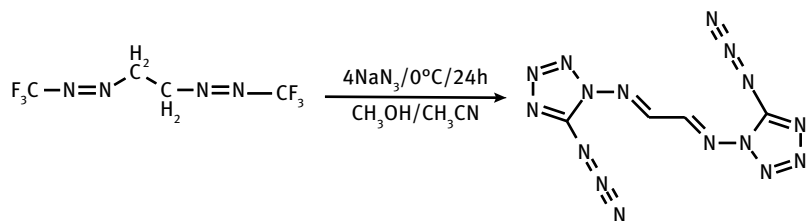
Tautomeric structures of tetrazolone-5

Tetrazolone-5 (5-oxotetrazole) can be prepared by diazotization of 5-aminotetrazole in the presence of  $\text{CuSO}_4$ . Tetrazolone-5 can be isolated after removing the copper in the form of  $\text{CuS}$  and the sulfate as  $\text{BaSO}_4$ . Because of the explosive nature of the tetrazole diazonium cation, the diazotization should be carried out in dilute sulfuric acid at  $0^\circ\text{C}$  with a ratio of water/diazonium salt of approximately 1000/1. The enthalpy of formation of 5-hydroxytetrazole = tetrazolone-5 is  $-17\text{ cal/g} = -1.463\text{ kcal/mol} = -6.12\text{ kJ/mol}$ . The density is  $1.699\text{ g/cm}^3$ . Tetrazolone-5 has two acidic protons and can therefore be doubly deprotonated. Only strong or medium-strong bases like guanidine or triaminoguanidine can deprotonate tetrazolone. Only the single deprotonated salts were synthesized in this study. The following numbers refer to the compound numbers in that study. Seven nitrogen-rich salts, guanidinium (**2**), aminoguanidinium (**3**), diaminoguanidinium (**4**), triaminoguanidinium (**5**), ammonium (**6**), hydrazinium (**7**), and hydroxylammonium (**8**) were prepared by facile deprotonation or metathesis reactions [934]. All compounds were characterized by low-temperature single-crystal XRD. They crystallized in common space groups with densities ranging from  $1.554$  to  $1.625\text{ g/cm}^3$ . Salts were characterized by IR, Raman, NMR, elemental analysis, and DSC. The HOFs were calculated by quantum mechanical methods. With these values and the X-ray densities, several detonation parameters were calculated. The salts of tetrazolone have calculated detonation velocities between  $7257\text{ m/s}$  (**2**) and  $9034\text{ m/s}$  (**8**). The sensitivities (impact, friction, and electrical discharge) were tested by standard BAM methods. Tetrazolone and its salts are quite insensitive explosives with decomposition points between  $447\text{ K} = 174^\circ\text{C}$  (**5**) and  $512\text{ K} = 239^\circ\text{C}$  (**1**). The thermal decomposition of 5-hydroxytetrazole was investigated [935].

#### 14.8.4 Azidotetrazole Derivatives

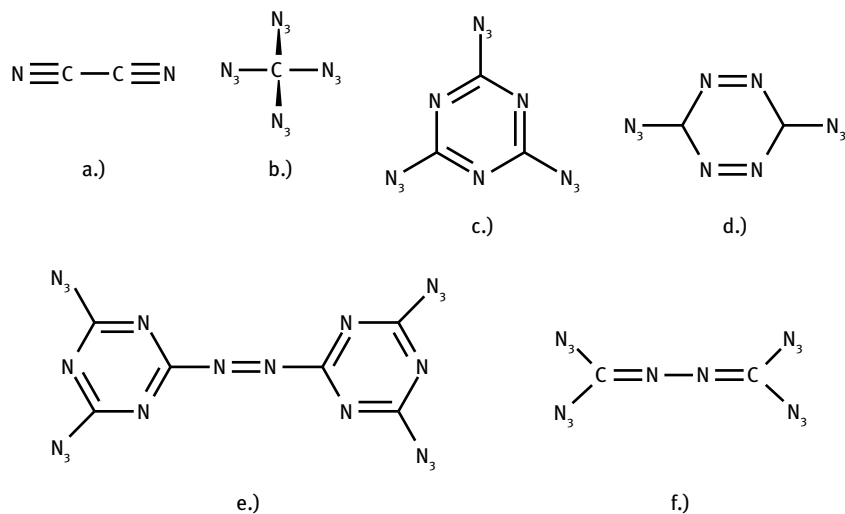
The treatment of triaminoguanidinium chloride with two equivalents of sodium nitrite under acidic conditions, followed by the cyclization with stoichiometric amounts of either sodium hydroxide solution or solid sodium carbonate, yielded 1-amino-5-azidotetrazole, 5-azido-1-diazidocarbamoyltetrazole, and 1-(aminoazido-carbamoyl)-5-azidotetrazole [936]. These three compounds have been characterized using Raman, IR, NMR spectroscopy, mass spectrometry, XRD, and DSC. The sensitivity values obtained from measurements showed an extremely high sensitivity toward mechanical and thermal stimuli.

Base-catalyzed activation of the C–F bond in trifluoromethylazo-substituted cyclic and acyclic alkanes provides a route to di-substituted azidotetrazoles. For example, the reaction of 1,2-bis(trifluoromethylazo)ethane with four equivalents of  $\text{NaN}_3$  gave the alkyl-bridged bis(5-azido-1*H*-tetrazol-1-yl)-1,2-dimine, also called *N,N'*-bis(5-azido-1*H*-tetrazol-1-yl)-1,2-diiminoethane, with 75% yield [937].



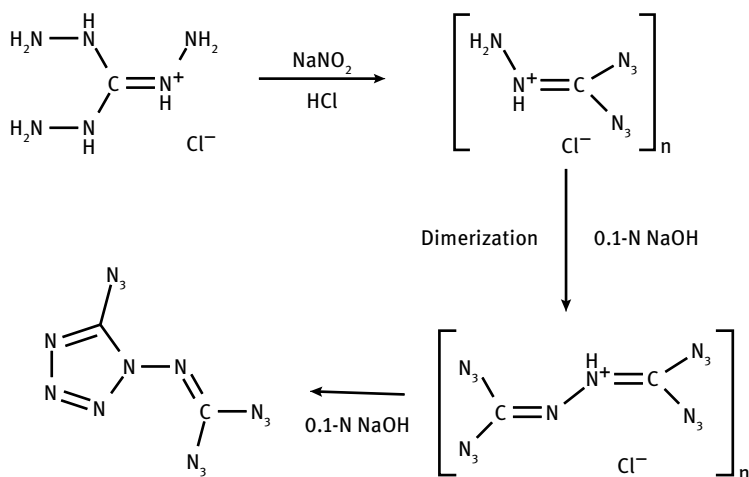
*N,N'*-bis(5-azido-1*H*-tetrazol-1-yl)-1,2-diiminoethane

There are many carbon-nitrogen compounds with high nitrogen content that are of interest as gas generant ingredients. One of them was theorized to be an open-chain compound called tetraazido-2,3-diazabuta-1,3-diene [which is also called isocyanogen tetraazide or *N*-(diazidomethylene)-carbonohydrazonic diazide], CAS RN [67880-23-3] with the gross formula  $C_2N_{14}$ . For a while, it was not certain if  $C_2N_{14}$  existed in an open-chain (f) or a ring-closed form.



The binary CN compounds demonstrated here are: a.) dicyanogen, b.) tetraazido-methane, c.) triazidotriazine, d.) diazidotetrazine, e.) tetraazidoazotriazine (TAAT) and f.)  $C_2N_{14}$  (open chain form).

The synthesis of the closed form of 1-diazidocarbamoyl-5-azidotetrazole, 2-(5-azidotetrazol-1-yl)-1,3-diaza-guanidine,  $C_2N_{14}$ , CAS RN [1306278-47-6],  $M = 220.115$  g/mol, was discovered in 2011 while it was being synthesized by the diazotization of triaminoguanidinium chloride in water with two equivalents of sodium nitrite [938]. A suggested mechanism of this reaction is:



1-Diaزيدocarbamoyl-5-azidotetrazole, *N*-(5-azido-1*H*-tetrazol-1-yl)-carbonimidic diazide, CAS RN [1306278-47-6],  $\text{C}_2\text{N}_{14}$ , can be obtained as a colorless crystalline solid after recrystallization from diethyl ether. It has a melting point of 351 K = 78 °C and decomposition starts at 383 K = 110 °C. Single crystals of 1-diaزيدocarbamoyl-5-azidotetrazole suitable for XRD were obtained via recrystallization from diethyl ether. 1-Diaزيدocarbamoyl-5-azidotetrazole has a density of 1.723 g/cm<sup>3</sup> and an enthalpy of formation of +1495 kJ/mol. It crystallizes in the orthorhombic space group *Pbcn* with a cell volume of 1697.6(2) Å<sup>3</sup>. The sensitivity of  $\text{C}_2\text{N}_{14}$  is beyond our capabilities of measurement because, at the smallest possible loading in shock and friction tests, it still leads to explosive decomposition. The shock and friction sensitivity of 1-diaزيدocarbamoyl-5-azidotetrazole no doubt lies well under the limits of 0.25 J in impact. The 1 N in friction sensitivity can be experimentally determined.

Later investigations proved that the open-chain form tetraazido-2,3-diazabuta-1,3-diene exists only as a short-lived intermediate and cyclicizes early at 253 K (−20 °C) to the more stable 1-diaزيدocarbamoyl-5-azidotetrazole [939].  $\text{C}_2\text{N}_{14}$  would make a good propellant, source of nitrogen, or explosive had it not had high sensitivity.

A theoretical study that included the performance prediction of the high-nitrogen compound  $\text{C}_2\text{N}_{14}$  performed a computational optimization of four theoretically possible isomers using a DFT method. The vibration frequencies of four isomers were analyzed at the same ground level [940]. The frontier orbital energy difference, theoretical density, enthalpy of formation, theoretical detonation velocity, and detonation pressure of the four isomers were evaluated. The results showed that the MO energy difference of the four isomers is 359, 434, 553, and 553 kJ/mol, respectively. The theoretical densities are 1.682, 1.809, 1.742, and 1.743 g/cm<sup>3</sup>, respectively. The enthalpies of formation are 1521, 1435, 1404, and 1404 kJ/mol, respectively. The theoretical detonation

velocities (detonation pressures in parentheses) are 8405 m/s (30.63 GPa), 8725 m/s (34.52 GPa), 8454 m/s (31.68 GPa), and 8456 m/s (31.70 GPa), respectively.

#### 14.8.5 Thermal Decomposition of Bi- and Multi-Substituted Tetrazoles

Crystalline 1*H*-tetrazole is very sensitive to impact (<4 J) but not to friction. In contrast, the (substituted) guanidinium salts have sensitivities much lower than those of RDX and HMX. The gas products from rapid thermolysis of aminotetrazoles can affect the burn rate of a composite propellant containing these chemicals [941]. 1,5- and 2,5-diaminotetrazole decomposes by two competitive reactions. One reaction gives HCN, NH<sub>3</sub>, and N<sub>2</sub> and the other gives NH<sub>2</sub>CN, NH<sub>3</sub>, and N<sub>2</sub>. The observed product ratios reflect the competition of these two reactions. No melamine-like cyclic azines form from the self-reaction of NH<sub>2</sub>CN because NH<sub>2</sub>CN is rapidly evolved from the sample and diluted into the cool Ar atmosphere of the cell. Non-competitive decomposition reactions occurred with 1- and 5-aminotetrazole. 1-AT produced HCN, NH<sub>3</sub>, and N<sub>2</sub>, while 5-AT produced HN<sub>3</sub> and NH<sub>2</sub>CN. However, at 5.86 MPa (850 psia) of Ar, 5-AT produced melamine-like cyclic azine and NH<sub>4</sub>N<sub>3</sub> aerosols. 5-AT was the only aminotetrazole that produced melamine-like products upon heating of the unconfined material.

In a review of the literature on the thermal decomposition of tetrazole derivatives, it was shown that there are two radically different pathways of the tetrazole cycle fragmentation that leads to the formation of dinitrogen or azides [942]. The elimination of dinitrogen from 2,5-di-substituted tetrazoles resulted in a nitrilimine. The elimination of dinitrogen from 1,5-di-substituted tetrazoles led to the formation of nitrene. The stabilization of active intermediate products depends on the chemical properties of the substituents and the conditions under which the process is carried out. This leads to a wide spectrum of final products for the thermal decomposition of multi-substituted tetrazoles. Kinetic studies of the thermolysis of tetrazoles showed that the mechanism of heterocycle fragmentation can vary with varying temperatures. The elimination of dinitrogen from tetrazoles is usually preceded by a high-polarity transition state.

DFT computations and a semi-empirical quantum chemical computation were performed on a series of tetrazole derivatives and their metal salts to investigate the relationship between the relative order of impact sensitivity and activation energy of thermal decomposition [943]. The results showed that the relative order of sensitivity for the tetrazole derivatives compounds can be predicted by examining the activation energy for breaking down the weakest link of the tetrazole ring.

The combustion behavior and thermal decomposition kinetics of 2-methyl-5-nitrotetrazole were studied by measuring temperature profiles in the combustion wave of a compressed pellet with thin tungsten-rhenium thermocouples embedded in the strands [944]. Analyses of gaseous and condensed combustion products and the thermolysis products by GC, IR-, UV-, and mass-spectrometry showed that the combustion of the endothermic molecule containing the oxidizing nitro group proceeded in

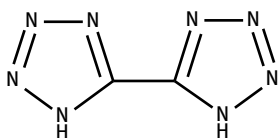


the gas phase. The 2-methyl-5-nitrotetrazole monomolecular decomposition reaction was rate-controlling and determined the burning rate.

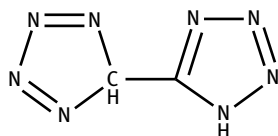
Ionic salts containing 5-amino-2-methyl- and 5-amino-1,3-dimethyltetrazolium cations with energetic anions (perchlorate, nitrate, azide, and dinitramide) have been synthesized and characterized using vibrational and  $^{15}\text{N}$  NMR spectroscopy and XRD [945]. Unexpectedly, salts based on the asymmetric 5-amino-1,3-dimethyltetrazolium cation had higher densities than analogue compounds containing the isomeric 5-amino-1,4-dimethyltetrazolium cation. This was regardless of the lower symmetry of the former. This can be attributed to secondary interactions between the cation and anion and is reflected in the higher detonation parameters of these compounds. This represents a new class of nitrogen-rich, high-performing materials with low sensitivity and good potential for energetic applications.

## 14.9 Bitetrazole and Bitetrazole Derivatives

Linking two tetrazole rings can be done in multiple ways. The most common method is via a C—C bond at the 5-position, which gives 5,5'-bitetrazole, also known as 5,5'-bistetrazole, 5-tetrazolyl-tetrazole(5), ditetrazole, 5-(1*H*-tetrazol-5-yl)-1*H*-tetrazole, CAS RN [2783-98-4],  $\text{C}_2\text{H}_2\text{N}_8$ ,  $M = 138.09$ ; a high-nitrogen compound with 81.1% N. These compounds are commonly called bistetrazole although the more correct name would be bitetrazole. For instance, the compound formed by connecting two benzene rings is correctly called *biphenyl* and not *bisphenyl*. Therefore, the correct name, as per Chemical Abstract IUPAC conventions, is 5,5'-bi-2*H*-tetrazole, CAS RN [2783-98-4].



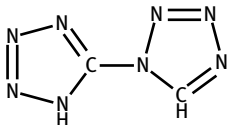
5,5'-Bi-2*H*-tetrazole CAS RN [2783-98-4]



5-(1*H*-tetrazol-5-yl)-5*H*-tetrazole CAS RN [634151-41-0]

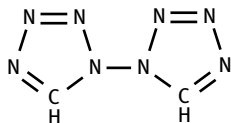
Alternate names are 5,5'-bi-1*H*-tetrazole and 5,5'-bis-1*H*-tetrazole. The location of the hydrogen atom(s) may vary depending on the conditions during synthesis. In addition to linking two tetrazole rings directly with a C—C linkage at the 5-position, there are less common isomers with a C—N linkage or an N—N linkage between the two rings.

The isomer is 5-(tetrazol-1-yl)-2*H*-tetrazole, also called 1-(1*H*-tetrazol-5-yl)tetrazole or 2'*H*-1,5'-bitetrazole, CAS RN [103518-52-1]; the linkage is from atom five on the first ring to atom one on the second ring.



1-(2*H*-Tetrazol-5-yl)-1*H*-tetrazole, CAS RN [103518-52-1]

If the connection is from the N1 nitrogen atom to another N1 nitrogen atom on the other ring, the resulting 1,1'-bitetrazole, also called 1-(tetrazol-1-yl)tetrazole, CAS RN [1316336-11-4], is an isomer to the more common 5,5'-bitetrazole.



1,1'-Bitetrazole, CAS RN [1316336-11-4]

In addition to linking two tetrazole rings directly with a C—C, C—N, or N—N linkage, there are also azotetrazole compounds with an —N=N— bridge and hydrazotetrazole compounds with an —NH—NH— bridge between the two rings. There are also secondary amines with two tetrazolyl rings linked by an imino —NH— group. These will be discussed in a later section in this chapter. Bitetrazole derivatives are nitrogen-rich, high-performing, insensitive energetic compounds that are suitable as sources of nitrogen in gas generants for inflators [946].

#### 14.9.1 Preparation of Bitetrazole and Bitetrazole Derivatives

Bitetrazole is rarely used but is most often applied in its salt form, especially as bitetrazolate salts with nitrogen-rich cations. A common bitetrazolate salt is the diammonium salt that can be made using hydrazine hydrate and cyanogen as starting materials [947–951]. Diammonium 5,5'-bi-1*H*-tetrazolate can be prepared by reacting cyanogen (dicyan), sodium azide, and ammonium chloride in water as a reaction medium. The first step is using oxaldiimidic acid dihydrazide that is obtained by the reaction of hydrazine hydrate with cyanogen. Oxalimidic acid dihydrazide is synthesized by reaction of dicyanogen and hydrazine hydrate in a polar solvent at 263 to 323 K (–10 to 50 °C) for 2–30 h using a molar ratio of hydrazine hydrate to cyanogen of 2.5–3.5. This yields a crystalline product that is then dissolved in an aqueous solution of a weak acid such as acetic acid. The next step is the dropwise adding of an aqueous solution of sodium nitrite to form an azide and to effect the cyclization reaction by

heating. 5-Cyano-1*H*-tetrazole is an intermediate in this reaction. The bitetrazole is first deprotonated by sodium hydroxide and then the sodium salt is converted to the less soluble ammonium salt by the addition of ammonium chloride. This process is advantageous as the 5,5'-bi-1*H*-tetrazole diammonium salt is synthesized and the precipitated crystals that are produced as a result are simply isolated by filtration to obtain the 5,5'-bi-1*H*-tetrazole diammonium salt, thus maintaining a yield better than 90%. The 5,5'-bi-1*H*-tetrazole diammonium salt, which has low toxicity and is easy to handle, is used as a gas-generating agent for airbags. Depending on the method chosen, cyanogen can either be prepared and isolated in an additional pre-step and treated with either sodium azide or hydrazoic acid or it can be generated *in-situ* from sodium cyanide and manganese dioxide as the oxidizing agent under acidic conditions and be further treated with sodium azide.

Barium 5,5'-bitetrazolate and several similar barium salts were obtained by metathesis reaction between bitetrazolium and similar sulfates and soluble barium salts [952].

Both the sodium salt and the potassium salts are useful intermediates in the synthesis of other bitetrazolate salts. The synthesis of bitetrazole, potassium bitetrazolate, guanidinium bitetrazolate, and aminoguanidinium bitetrazolate by way of the intermediate product manganese bitetrazolate was improved by adding acetic acid and cupric sulfate [953]. Potassium bitetrazole was formed by high-temperature substitution reactions between manganese bitetrazolate, and potassium carbonate. Bitetrazole carbonate, guanidinium carbonate, or aminoguanidinium bicarbonate react directly to produce guanidinium bitetrazolate and aminoguanidinium bitetrazolate. The products were characterized by DSC-TGA, elemental analysis, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and MS methods. The shock sensitivity test results showed that the sensitivity of bitetrazole itself is higher than that of bitetrazolate salts.

5,5'-Bitetrazole and its salts can be prepared by reaction of azides with cyanogen in the presence of Lewis acids, organic carboxylic acids, or alkylsulfonic acids. Thus, the reaction of sodium azide with cyanogen in acetonitrile in the presence of  $\text{AlCl}_3$  gives 5,5'-bitetrazole with a yield of 75.6% [954].

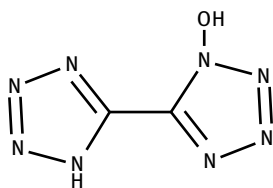
The diammonium salt  $\text{C}_2\text{H}_2\text{N}_8 \cdot 2\text{NH}_3$ ; 5,5'-bi-2*H*-tetrazole, ammonium salt (1:2); CAS RN [944393-83-3], is a useful high-nitrogen compound. Most patents deal with the diammonium salt of bitetrazole, but if the pH of a solution of the diammonium salt is acidified with sulfuric acid to pH <4.5, one can isolate the monoammonium salt as well [955].

5-(Tetrazol-1-yl)-2*H*-tetrazole or 1,5-bitetrazole can be synthesized by the cyclization of 5-amino-1*H*-tetrazole, sodium azide, and triethyl orthoformate in glacial acetic acid [956]. A methyl-substituted derivative of 1,2-methyl-5-(tetrazol-1-yl)tetrazole (**2**) can be obtained by this method by starting from 5-amino-2-methyl-tetrazole instead of 5-AT. Selected salts of 1,5'-bitetrazole with nitrogen-rich and metal (alkali and transition metal) cations, including hydroxylammonium, triaminoguanidinium, copper(I), and silver, as well as copper(II) complexes were prepared and characterized by IR, Ra-

man, NMR spectroscopy, MS, DSC, and single-crystal XRD. Their sensitivities towards physical stimuli (impact, friction, ESD) were determined according to BAM standard test methods. Energetic performance parameters (detonation velocity, pressure, etc.) were calculated with the EXPLO5 program, based on predicted HOFs derived from computed enthalpies. Other methods for the preparation of bitetrazole are described in [957, 958]. There are many energetic bicyclic azolium salts [109, 180].

Both 1,1'-diamino-5,5'-bitetrazole and 1,2'-diamino-5,5'-bitetrazole have been prepared by the amination of the parent anion with *O*-tosylhydroxylamine and characterized by XRD, NMR, IR, Raman, mechanical impact, and electrostatic discharge sensitivity measurement. Their explosive performances were calculated using the EXPLO5 computer code [318]. Instead of amino groups, hydrazino groups can be attached to one or both rings in bitetrazole, resulting in 5,5'-hydrazinobitetrazole, which can form salts with alkali metals [959].

The nitrogen-rich energetic compound 5-(1*H*-tetrazolyl)-1-hydroxytetrazole, also known as 1-hydroxy-5-(1*H*-tetrazol-5-yl)tetrazole, was obtained in good yield via sodium 5-cyanotetrazolate sesquihydrate, 5-aminohydroximoyl tetrazole, 5-chlorohydroximoyl-tetrazole, and 5-azidohydroximoyl-tetrazole monohydrate [960].



5-(1*H*-Tetrazolyl)-1-hydroxytetrazole

It can be deprotonated twice by various bases. Several ionic derivatives such as bis(hydroxylammonium), bis(hydrazinium), bis(guanidinium), bis(aminoguanidinium), bis(ammonium), and diaminouronium 5-(1-oxidotetrazolyl)-tetrazolates were synthesized and characterized. All compounds were characterized by NMR, IR, Raman, mass spectroscopy, elemental analysis, DSC, and tested for impact, friction, and ESD sensitivity.

1,1'-Dinitramino-5,5'-bitetrazole and 1,1'-dinitramino-5,5'-azobitetrazole are extremely sensitive and powerful explosives [961]. Selected nitrogen-rich salts were prepared to adjust sensitivity and performance values. The compounds were characterized by XRD, IR and Raman spectroscopy, NMR, elemental analysis, and DTA/DSC. Calculated energetic performances based on calculated HOFs and X-ray densities supported the predicted high performances of the 1,1'-dinitramino-5,5'-bitetrazoles as energetic materials. Most of the compounds showed sensitivities in the range of primary explosives and, therefore, should only be handled with great care.

### 14.9.2 Physical Properties of Bitetrazole and Bitetrazole Derivatives

The predicted density of 5,5'-bitetrazole is  $1.593 \pm 0.06 \text{ g/cm}^3$  based on theoretical computations, but measured XRD density is  $\rho_{\text{X-ray}} = 1.738 \text{ g/cm}^3$ .

There are two different data sets offered for the enthalpy of formation in the PEPCODED.DAT database [61]:  $+1093 \text{ cal/g} = +150.9 \text{ kcal/mol} = +631 \text{ kJ/mol}$  and  $+797 \text{ cal/g} = 110.0 \text{ kcal/mol} = +460 \text{ kJ/mol}$ . However, it is not known which is correct. Neither one matches the experimentally determined HOF of  $+127.08 \pm 0.23 \text{ kcal/mol} = +531.7 \pm 0.96 \text{ kJ/mol}$ , which is somewhere between these two extreme values [962].

The enthalpy of formation of guanidinium 5,5'-bitetrazolate,  $\text{C}_3\text{H}_7\text{N}_{11}$ , MW 197.17, with 78.1% N, is  $+369 \text{ cal/g} = +72.7 \text{ kcal/mol} = +304 \text{ kJ/mol}$ . The density is  $0.0566 \text{ lb/in.}^3 = 1.567 \text{ g/cm}^3$ . The enthalpy of formation of tetramethylammonium bitetrazolate,  $\text{C}_6\text{H}_{13}\text{N}_9$ ,  $M = 211.23 \text{ g/mol}$ , is  $+118 \text{ cal/g} = +24.9 \text{ kcal/mol} = +104.3 \text{ kJ/mol}$ . The density is  $0.0488 \text{ lb./in.}^3 = 1.351 \text{ g/cm}^3$ . The X-ray crystal structure of 5,5'-bitetrazole at 130 K showed that 5,5'-bitetrazole exists as the 1*H*,1'*H*-tautomer and packs in chains held together by pairs of intermolecular hydrogen bonds [963]. It crystallized in the monoclinic space group  $P2_1/n$  with  $a = 4.945(1) \text{ \AA}$ ,  $b = 6.367(1) \text{ \AA}$ ,  $c = 8.491(1) \text{ \AA}$ ,  $\beta = 99.233(7)^\circ$ ,  $\rho_{\text{X-ray}} = 1.738 \text{ g/cm}^3$ , and  $Z = 2$ .

1,1'-Dihydroxy-5,5'-bistetrazole (1,1'-BTO) was synthesized using dichloro-glyoxime, sodium azide, and dimethyl formamide as primary materials and reacted with hydroxylammonium chloride to form dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (which is also known under its code name of TKX-50) with a yield of 73.2% [964]. There are strong inter- and intra-molecular hydrogen bonds in the solid crystal. These hydrogen bonds effectively improved the density of TKX-50 to  $1.918 \text{ g/cm}^3$ . Based on this density, detonation parameters were calculated as close to 9698 m/s, the detonation pressure was 42.4 GPa, the friction sensitivity was 120 N, and the impact sensitivity was 20 J. A method for the purity analysis of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) using HPLC was established by optimizing the chromatographic conditions [965].

Following the synthesis, theoretical performance (sea-level  $I_{\text{sp}}$ ) of a composite modified double-base (CMDB) propellant, hydroxy-terminated polybutadiene (HTPB) propellant, nitrate ester plasticized polyether (NEPE) propellant, and GAP propellant containing dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) was calculated. It was found that the theoretical specific impulse of the TKX-50 propellant was  $2623.7 \text{ N s kg}^{-1}$ , which is  $6.5 \text{ N s kg}^{-1}$  higher than that of the RDX propellant [966]. TKX-50 would be a good replacement for RDX in CMDB propellants. When substituting TKX-50 for AP in HTPB propellants and AP and HMX in GAP propellants, similar improvements of theoretical specific impulses were predicted, also in comparison to HMX or CL-20 as replacements for AP [967].

Crystals of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (HATO) were synthesized and characterized [891]. HATO exhibited excellent thermal stability. The decomposition temperature was 503.4 K (230.3°C), and the volume of released gas during a thermal stability test was 0.30 mL/g at 373 K (100°C) for 48 h. It had low mechanical

sensitivities; the explosion probabilities of impact sensitivity and friction sensitivity were 16 and 24%, respectively.

### 14.9.3 Chemical Properties of Bitetrazole and Bitetrazole Derivatives

There are many patents on the use of 5,5'-bitetrazolates of nitrogen-containing cations as gas generants in airbag inflators. 5,5'-Bitetrazole can give off one or two protons and form dibasic bitetrazolate salts with strong bases. It can also be protonated to form tetrazolium salts. The constants of proton detachment and the addition of protons for 5,5'-ditetrazole and of protonation of 1,1'-diphenyl-5,5'-bitetrazole in aqueous solutions were determined by spectrophotometric and potentiometric methods [968]. The aqueous  $pK_a$  values for the first and second ionizations (anion formation) of 5,5'-bitetrazole ( $R=H$ ) were 1.41 and 4.25; the first and second  $pK_{BH^+}$  values for protonation were -5.47 and -10.91.

5,5'-Bitetrazole starts decomposing soon after melting at  $563\text{ K} = 290^\circ\text{C}$ . The kinetic parameters of the thermal decomposition of tetrazole and 5,5'-bitetrazole in melts of neat substances and nitrobenzene solutions have been determined using a manometric method [732]. The proposed mechanism involved limiting stages of the monomolecular decomposition. This determines the observed rate of nitrogen formation, proceeding to the fast reversible transformation of the 1*H*- and 2*H*-forms and the reversible opening of the 2*H*-form. It is followed by the formation and subsequent cleavage of the corresponding intermediate diazo compound.

The alkaline earth metal (Be, Mg, Ca, Sr, Ba) salts of 5,5'-bitetrazole were prepared and characterized by low-temperature XRD, IR, Raman and NMR spectroscopy, elemental analysis, and DSC [969]. The Sr and Ba salts can be used in coloring pyrotechnical compositions and thus avoid the use of perchlorates, making the formulation more environmentally friendly.

Eight different salts formed from twice-deprotonated 5,5'-bitetrazole: ammonium (**1**), hydrazinium(1+) (**2**), hydroxylammonium (**3**), guanidinium (**4**), aminoguanidinium (**5**), diaminoguanidinium (**6**), triaminoguanidinium (**7**), and diaminouronium (**8**). The numbers refer to the compounds listed in Table 61. 5,5'-Bitetrazolate salts have been synthesized and characterized by single-crystal XRD, NMR, IR and Raman spectroscopy, and DSC [970]. The sensitivity towards impact, friction, and ESD was determined. Several propulsions and detonation parameters (e.g., heat of explosion, detonation velocity) were computed based on calculated HOFs and X-ray densities. Some select properties of these eight high-nitrogen compounds are summarized in Table 61.

Although the alkali metal bitetrazolates are of little interest as rocket propellants, they deserve to be studied as intermediates in the preparation of other bitetrazolate salts. For example, the monoammonium and the bisammonium bitetrazolates are useful gas generant ingredients. The alkali metal 5,5'-bitetrazolates of Li, Na, K, Rb, and Cs, the mono and bis-ammonium, and the mono- and bis(1-ethyl-3-methylimi-

Table 61: Calculated and measured properties of bitetrazolate salts of nitrogen-rich cations.

| Compound name                                          | Formula              | $\Delta H_f(S)$<br>kJ/mol | $I_{sp}$<br>s | N<br>Mass % | OB<br>%c | $\rho_{RD}$<br>g/cm <sup>3</sup> | $T_{Expt}$<br>K | $P_{C-J}$<br>kbar | $V_{Det.}$<br>m/s | Drop weight impact<br>J | Friction<br>N | ESD<br>J |
|--------------------------------------------------------|----------------------|---------------------------|---------------|-------------|----------|----------------------------------|-----------------|-------------------|-------------------|-------------------------|---------------|----------|
| 1 Diammonium 5,5'-bitetrazolate                        | $C_2H_8N_{10}$       | +1589.3                   | 172.3         | 81.36       | -74.34   | 1.590                            | 1976            | 189               | 7417              | 35                      | >360          | 0.6      |
| 2 Dihydrazinium(1+) 5,5'-bitetrazolate                 | $C_2H_{10}N_{12}$    | +1476.9                   | 225.2         | 83.13       | -71.21   | 1.531                            | 2744            | 236               | 8265              | 40                      | 360           | 0.23     |
| 3 Dihydroxylammonium 5,5'-bitetrazolate                | $C_2H_8N_{10}O_2$    | +1543.6                   | 227.9         | 68.61       | -47.02   | 1.742                            | 3243            | 317               | 8854              | 10                      | >240          | 0.1      |
| 4 Di(guanidinium) 5,5'-bitetrazolate                   | $C_4H_{12}N_{14}$    | +1369.7                   | 165.8         | 76.53       | -87.41   | 1.586                            | 1869            | 176               | 7199              | 40                      | >360          | 1.0      |
| 5 Di(aminoguanidinium) 5,5'-bitetrazolate dihydrate    | $C_4H_{18}N_{16}O_2$ | +1328.1                   | 174.6         | 69.54       | -74.46   | 1.568                            | 2049            | 193               | 7504              | 40                      | 324           | 1.0      |
| 6 Bis(diaminoguanidinium) 5,5'-bitetrazolate dihydrate | $C_4H_{20}N_{18}O_2$ | +1260.2                   | 190.1         | 71.56       | -72.65   | 1.520                            | 2320            | 205               | 7711              | 30                      | 360           | 0.7      |
| 7 Di(triaminoguanidinium) 5,5'-bitetrazolate           | $C_4H_{18}N_{20}$    | +1207.8                   | 224.1         | 80.89       | -78.53   | 1.535                            | 2698            | 238               | 8181              | 15                      | 285           | 0.7      |
| 8 Bis(diaminouronium) 5,5'-bitetrazolate dihydrate     | $C_4H_{14}N_{16}O_2$ | +1313.7                   | 204.8         | 70.42       | -65.35   | 1.742                            | 2676            | 288               | 8562              | 35                      | 360           | 0.5      |

Data source: [970].

dazolium) salts of 5,5'-bitetrazole were synthesized and characterized by NMR and IR spectroscopy, elemental analysis, and combined TGA/DSC [971]. It is interesting to note that, in the IR spectra, all bands slowly shifted to lower wavenumbers when proceeding from lithium to cesium as counter ions with increasing ion radii. A distinct effect of the atomic weight of the counter ion on the lattice vibrations of the bitetrazolate ion could be observed. Bis(1-ethyl-3-methylimidazolium) 5,5'-bitetrazolate,  $C_{14}H_{22}N_{12}$ , is the first known ionic liquid derived from bitetrazole. It melts at just  $368\text{ K} = 95^\circ\text{C}$  and can, therefore, be classified as an ionic liquid. The decomposition of the substance follows at  $523\text{ K} = 250^\circ\text{C}$ . The monoammonium salt started to decompose at an onset temperature of  $555\text{ K} = 282^\circ\text{C}$  and the diammonium salt measured for direct comparison showed decomposition at  $563\text{ K} = 290^\circ\text{C}$ . Other 5,5'-bitetrazolate salts have been reported in [972].

#### 14.9.4 Bitetrazole Derivatives with Substituents on the Rings

The oxygen balance of bitetrazole derivatives can be improved by adding hydroxyl or nitro groups to the rings.

##### 14.9.4.1 1,1'-Hydroxyl-5,5'-Bitetrazole

1,1'-Hydroxyl-5,5'-bitetrazole, 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diol, is an energetic compound that is more acidic than bitetrazole itself and can form a wide range of salts. The dihydroxylammonium salt of 1,1'-hydroxyl-5,5'-bitetrazole, which is also called dihydroxylammonium 5,5'-bi(s)tetrazole-1,1'-diolate, has been tested as a new insensitive but powerful explosive. It has been given the code name TKX-50.

Dihydroxylammonium 5,5'-bitetrazole-1,1'-diolate (TKX-50) and the intermediates 5,5'-bitetrazole-1,1'-diol dihydrate, 5,5'-bitetrazole-1,1'-diol dimethanolate, and dimethylammonium 5,5'-bitetrazole-1,1'-diolate were prepared and characterized by XRD, NMR, vibrational spectroscopy, DSC, mass spectrometry, and sensitivity tests [973]. TKX-50 outperforms all other recently developed explosive materials such as ONC and CL-20. It differs in that it is simple and cheap to prepare from commonly available chemicals. It is easily prepared, is exceedingly powerful, and possesses the required thermal insensitivity, low toxicity, and safety of handling to replace the most commonly used military explosive also, which is RDX.

The isomeric 5,5'-bi(2-hydroxytetrazole) can be prepared by oxidation of 5,5'-bitetrazole using commercially available Oxone (potassium peroxydisulfate) [974]. Once 5,5'-bi(2-hydroxytetrazole) became available with the necessary purity, the nitrogen-rich salts including ammonium, hydroxylammonium, guanidinium, aminoguanidinium, triaminoguanidinium, 5-aminotetrazolium, and aminonitroguanidinium could be prepared and characterized by XRD, NMR, vibrational spectroscopy, DSC, and MS, and compared to their 5,5'-bi(tetrazole-1-oxide) analogues. The impact, friction, and electrical spark sensitivities of all these compounds were measured and several detonation parameters, such as the detonation velocities



and detonation pressures, were also calculated based on calculated HOFs and the X-ray densities.

1*H*,1'*H*-5,5'-Bitetrazole-1,1'-diol was synthesized starting from glyoxal, which is converted to glyoxime after treatment with hydroxylamine [975]. The chlorination of glyoxime with Cl<sub>2</sub> gas in ethanol (and the subsequent chloro/azido exchange) yielded diazidoglyoxime. This was cyclized under acidic conditions (HCl gas in diethyl ether) to give 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diol dihydrate. A large variety of nitrogen-rich salts of 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diol such as diammonium, dihydrazinium, bis-guanidinium, bis(aminoguanidinium), diaminoguanidinium salt monohydrate, triaminoguanidinium salt monohydrate, 1-amino-3-nitroguanidinium salt dihydrate, diaminouronium salt monohydrate, bis(oxalyldihydrazidinium), oxalyldihydrazidinium salt dihydrate, 3,6-dihydrazino-1,2,4,5-tetrazinium, 5-aminotetrazolium, bis(5-amino-1-methyl-1*H*-tetrazolium) salt, bis(5-amino-2-methyl-2*H*-tetrazole) adduct, and 1,5-diaminotetrazolium salt were synthesized using Brønsted acid-base or metathesis reactions. All compounds were fully characterized by IR and Raman spectroscopy, NMR, elemental analysis, DSC, and XRD. The HOFs were calculated and several detonation parameters such as the detonation pressure, detonation velocity, explosion energy, and explosion temperature were computed. The sensitivities towards impact, friction, and ESD were tested using the BAM drop-hammer, a Peters friction sensitivity tester, as well as a small-scale ESD tester.

Hydroxylammonium 1,1'-dihydroxyl-5,5'-bistetrazolate has been developed as a solid propellant ingredient in China under the designation TKX-50 [976]. The performance of TKX in comparison to HMX or CL-20 as monopropellant under different pressures was calculated using a minimum free energy method. The performance of propellant formulations CL-20-CMDB and TKX-50-CMDB obtained by replacing HMX with CL-20 or TKX-50 was calculated under the standard condition ( $p_c:p_a = 70:1$ ). TKX-50 was predicted to have improved performance and, at pressures in the range 1–10 MPa, it has lower combustion temperature, higher characteristic velocity, and specific impulse than HMX. Its combustion products have lower average relative molecular mass than those of HMX. Using TKX-50 in CMDB propellant formulations increases specific impulses and it also effectively decreases smoke in the rocket motor exhaust plume.

1,1'-Dihydroxy-5,5'-bitetrazole (H2DHBT) was synthesized via substitution and cyclization using dichloroglyoxime as starting material [977]. Its DSC exothermic decomposition peak temperature was 504 K = 231 °C. The theoretical density of an optimized geometry of H2DHBT obtained by quantum chemical calculations was 1.789 g/cm<sup>3</sup>. The HOF of solid-state H2DHBT was +558.9 kJ/mol. The predicted detonation velocity and detonation pressure of H2DHBT using the K-J equation were 8475 m/s and 32.4 GPa, respectively. H2DHBT can be used as an energetic anion through the deprotonation of one or two of the hydroxyl groups.

In addition to the hydroxylammonium salt, the guanidinium salt of 1,1'-dihydroxy-5,5'-bitetrazole was also prepared and characterized [978]. Using

1,1'-dihydroxy-5,5'-bitetrazole and guanidinium carbonate as raw materials, guanidinium 1,1'-dihydroxy-5,5'-bitetrazolate (G2DHBT) was synthesized and characterized by NMR, IR, elementary analysis, and XRD. G2DHBT crystallized in monoclinic, space group  $P2_1/c$  crystals with  $a = 3.6477(14) \text{ \AA}$ ,  $b = 16.966(7) \text{ \AA}$ ,  $c = 9.546(4) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 97.465(6)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 585.8(4) \text{ \AA}^3$ ,  $Z = 2$ , and  $\rho_{\text{X-ray}} = 1.634 \text{ g/cm}^3$ . The thermal stability and the mechanical sensitivity of G2DHBT were tested by DSC and standard method GJB 772A-97, respectively. The solid-state HOF of G2DHBT was calculated using the CBS-4M method and found to be  $+387.69 \text{ kJ/mol}$ . The detonation parameters and performance as a monopropellant were predicted by using the K-J equation and the minimum free energy method, respectively. The DSC thermal decomposition peak was at  $562.9 \text{ K} = 289.8^\circ\text{C}$ . The 50% drop height was  $112.2 \text{ cm}$ , the detonation velocity was  $7202 \text{ m/s}$ , the detonation pressure was  $22.1 \text{ GPa}$ , and the specific impulse was  $1977 \text{ Ns/kg}$ .

Using dichloroglyoxime as raw material, dihydroxylammonium 5,5'-bitetrazole-1,1'-diolate was synthesized via substitution, cyclization, and metathesis reaction with a total yield of 81.7% [979]. Wet diazidoglyoxime was found to increase the operational safety and dilithium 5,5'-bistetrazole-1,1'-diolate (which has a high solubility in water) was used to increase the yield of the metathesis reaction. The properties of dihydroxylammonium 5,5'-bitetrazole-1,1'-diolate, such as thermal stability, mechanical sensitivity, morphology, particle size, and particle size distribution, were investigated. In the DSC, when heated at a rate of  $10 \text{ K/min}$ , the maximum of the exothermic peak was at  $249^\circ\text{C}$ . The standard volume of gas evolved during 48 h at  $373 \text{ K}$  was  $0.3 \text{ mL/g}$ . The drop weight impact sensitivity was 16% with a 10 kg drophammer, at 25 cm drop height, and 50% with a 5 kg drophammer at 100 cm drop height.

5-Aminotetrazolium 1'-hydroxy-1*H*,1'*H*-5,5'-bitetrazol-1-olate (5-ATHTO) was synthesized from glyoxal, hydroxylamine, and aminoguanidine carbonate at  $373 \text{ K}$  ( $100^\circ\text{C}$ ). With a reaction time of 5 h, the yield of 5-ATHTO was up to 86% [980]. The structure of 5-ATHTO was identified by NMR, IR, and MS. The thermal stability was analyzed by DSC and the compound decomposed at about  $513 \text{ K}$  ( $240^\circ\text{C}$ ), thus indicating good thermal stability. The theoretical density of 5-ATHTO was predicted to be  $1.85 \text{ g/cm}^3$ . The HOF of the compound was predicted as  $808.5 \text{ kJ/mol}$ . The heat of detonation, detonation pressure, and detonation velocity of 5-ATHTO, as predicted by the K-J equation, were  $1504 \text{ J/g}$ ,  $32.6 \text{ GPa}$ , and  $8.25 \text{ km/s}$ , respectively. The 50% drop height during impact sensitivity testing was  $52 \text{ cm}$ , indicating that this is an insensitive energetic compound with good detonation performance.

Sodium 5,5'-bistetrazole-1,1'-diolate tetrahydrate (SBTD•4H<sub>2</sub>O), a key intermediate for the synthesis of energetic salts based on 1,1'-dihydroxyl-5,5'-bistetrazole (BTD), was synthesized by a one-pot synthesis using dichloroglyoxime as starting material. It was characterized by IR, XRD, DSC, TGA, elemental analysis, SEM, and impact and friction sensitivity [981]. SBTD•4H<sub>2</sub>O crystallized in triclinic space group  $P1$  and the cell parameters were  $a = 5.6440(11) \text{ \AA}$ ,  $b = 6.4476(17) \text{ \AA}$ ,  $c = 8.303(11) \text{ \AA}$ ,

$\angle\alpha = 100.131(5)^\circ$ ,  $\angle\beta = 96.789(3)^\circ$ ,  $\angle\gamma = 112.157(3)^\circ$ ,  $V = 1$ , and  $D_c = 1.761 \text{ g/cm}^3$ . At the heating rate of  $10 \text{ K min}^{-1}$ ,  $\text{SBTD} \cdot 4\text{H}_2\text{O}$  started to lose crystal water at  $84.4^\circ\text{C}$ . It began to decompose at  $641.9 \text{ K}$  ( $368.8^\circ\text{C}$ ), with a peak decomposition temperature of  $671.7 \text{ K}$  ( $398.6^\circ\text{C}$ ). This indicated that  $\text{SBTD} \cdot 4\text{H}_2\text{O}$  had good thermal stability. Impact sensitivity  $H_{50}$  of  $\text{SBTD} \cdot 4\text{H}_2\text{O}$  was greater than  $100 \text{ cm}$ .

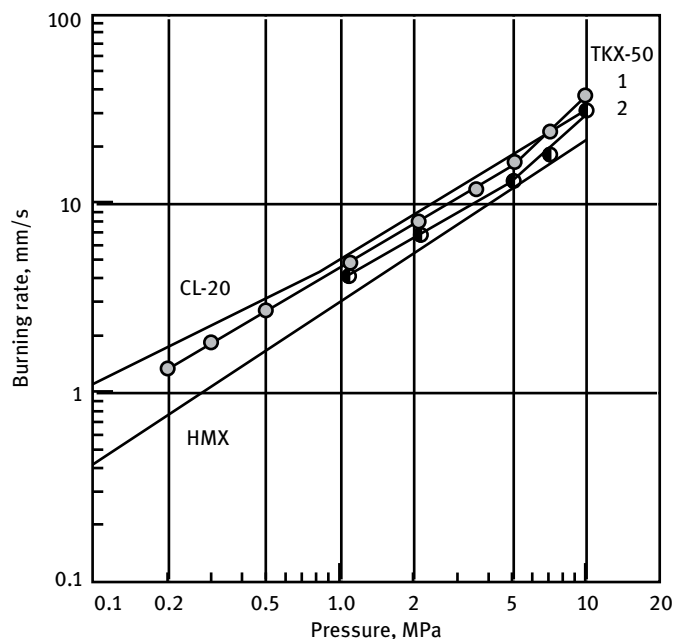
Dilithium 5,5'-bistetrazole-1,1'-diolate, disodium 5,5'-bistetrazole-1,1'-diolate, and dipotassium 5,5'-bistetrazole-1,1'-diolate were synthesized from 5,5'-bistetrazole-1,1'-diole with high yields of over 90%. Dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate was synthesized by an ion exchange reaction with lithium ions with a high yield of 94% [982]. The enthalpies of dissolution and the entropies of dissolution of these salts were measured.

Studies of the thermal decomposition under non-isothermal and isothermal conditions, enthalpy of formation, burning behavior, and flame structure of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate ( $\text{C}_2\text{H}_8\text{N}_{10}\text{O}_4$ , TKX-50) have shown that TKX-50 burns slightly faster than HMX and approaches the burning rate of CL-20 [983]. The combustion of TKX-50 has been shown to obey a mechanism, with the leading reaction taking place in the condensed phase. The rates of TKX-50 decomposition in both solid and liquid phases proved to be slightly higher than the corresponding rates of decomposition of RDX. Decomposition of TKX-50 is initiated by the decomposition of free hydroxylamine formed in the reaction of dissociation of the salt. An intermediate decomposition product is the ammonium salt of 5,5'-bis(2-hydroxytetrazole), which then further decomposes in the second stage at elevated temperatures. The energy of combustion in a calorimeter bomb under oxygen pressure was  $\Delta U_{\text{comb}}(\text{TKX-50}) = 8704 \pm 53 \text{ J/g}$  or  $2054 \pm 16 \text{ kJ/mol}$  with a molecular mass of  $\text{TKX-50} = 236.15 \text{ g/mol}$ . From this, one calculates the enthalpy of formation  $\Delta H_f^{298}$  as  $+111 \pm 16 \text{ kJ/mol}$ . This was quite different from the enthalpy of formation reported by other sources ( $+446.6 \text{ kJ/mol}$ ). In the DSC thermograms, a narrow and sharp exothermic peak corresponding to thermal decomposition was visible at  $493\text{--}518 \text{ K}$  ( $220\text{--}245^\circ\text{C}$ ) depending on the heating rate. A second more extended exothermic peak was observed at  $278\text{--}290^\circ\text{C}$ .

The decomposition of TKX-50 in TGA experiments occurred in two stages. The first stage ended after 44% mass had been lost ( $463\text{--}519 \text{ K} = 190\text{--}236^\circ\text{C}$ ). The second, slightly slower stage resulted in about 25% solid residue ( $638 \text{ K} = 365^\circ\text{C}$ ). The kinetic rate equation for the TKX-50 decomposition was

$$k = 5.0 \times 10^{13} \exp(18840/T) \text{ s}^{-1}$$

and the activation energy was  $E_a = 156.6 \text{ kJ/mol}$ . When measuring the strand burning rate of TKX-50 pellets in a windowed combustion bomb, it was found that TKX-50 burned slightly faster than HMX and approached the burning rate of CL-20. The dependence of the burning rate on pressure displayed a break at a pressure of  $5 \text{ MPa}$ . Figure 21 shows a comparison of the burn rate of TKX-50 with that of CL-20 and HMX.



**Figure 21:** Strand burning rate of TKX-50 in comparison to that of CL-20 and HMX. (Reprinted and modified from Sinditskii et al. 2015, with permission from ©2015 Elsevier; permission conveyed through RightsLink.)

The calculated detonation velocity of TKX-50 (9190 m/s at the maximum density of 1.877 g/cm<sup>3</sup>) was slightly less than the detonation velocity of HMX (9230 m/s at the maximum density of 1.904 g/cm<sup>3</sup>) but higher than the velocity of RDX detonation (8990 m/s at the maximum density of 1.806 g/cm<sup>3</sup>).

Dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate is an energetic material with low sensitivity and excellent calculated detonation performance. The compatibility of TKX-50 with nitrocellulose (NC), an NC/NG mixture (mass ratio 1.25:1), TNT, RDX, AP, hexanitroethane, HMX, HNIW (CL-20), GAP, HTPB, aluminum powder, boron powder, and centralite was studied by DSC [984]. The results showed that TKX-50/hexanitroethane possessed good compatibility, TKX-50 and HMX had moderate compatibility, but the compatibility of TKX-50 with TNT, CL-20, centralite, NC, AP, Al, GAP, TKX-50/RDX, TKX-50/NC + NG, TKX-50/B, and TKX-50/HTPB was poor.

Thermal decomposition of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) was studied using TGA, DSC, and ARC [985]. Non-isothermal and isothermal kinetic parameters were obtained at both atmospheric and low (up to 0.3 Torr) pressures. The gas products of thermolysis were detected *in-situ* using IR spec-

troscopy and the structure of solid-state decomposition products was determined by XRD and SEM. Diammonium 5,5'-bitetrazole-1,1'-diolate was directly identified to be the most important intermediate of the decomposition process. None of the Arrhenius parameters reported before could properly describe the complex two-stage decomposition process of TKX-50. Nonetheless, isoconversional methods combined with isothermal measurements yielded the most reliable kinetic parameters of TKX-50 thermolysis. In contrast to the literature reports, the thermal stability of TKX-50 was determined in the ARC experiments to be lower than that of RDX but close to that of CL-20.

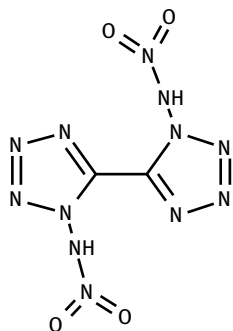
Hydrazinium 5,5'-bitetrazole-1,1'-diolate (HA • BTO) was prepared by the reaction of 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diolate (BTO) with hydrazinium(1+) chloride and was fully characterized [986]. XRD results showed that the salt belongs to the triclinic space group  $P\bar{1}$  with a relatively high density of 1.912 g/cm<sup>3</sup> at 298 K. The salt had good thermal stability with an onset of decomposition temperature above 473 K (200 °C). The enthalpy of formation based on the heat of combustion measured by oxygen bomb calorimetry was +425.6 kJ/mol, which is the same level as TKX-50 and four times higher than that of RDX. The predicted detonation pressure and detonation velocity of the salt was calculated as 36.1 GPa and 8931 m/s, which are higher than those of RDX. The impact and friction sensitivities were 28 J and 120 N, which are better than those of TKX-50.

Two salts based on 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diolate (BTO) anion with pyrazole (**1**) and imidazole (**2**) cations were synthesized via metathetical reactions [987]. Structural characterization was done by elemental analysis, FTIR, NMR, XRD, and MS. Thermal analysis by DSC and TGA-DTG provided data for the calculation of non-isothermal kinetic parameters. Both salts showed acceptable thermal stabilities as the decomposition temperatures were above 473 K (200 °C). The enthalpies of formation for these salts calculated using the measured heat of combustion were +70.6 kJ/mol for (**1**) and -47.8 kJ/mol for (**2**), respectively.

*Ab initio* calculations for a series of energetic ionic salts based on 5,5'-bitetrazole-1,1'-diolate predicted the physicochemical and detonation characteristics of these energetic ionic salts, including structural, electronic, vibrational, and performance parameters (enthalpies of formation, detonation pressures, and detonation velocities) [988]. Strong intermolecular hydrogen bonds are observed in hydrazinium and hydroxylammonium cations compared to other cations. Hydroxylammonium and hydrazinium cations produce the highest density that is relative to other cations when combined with the 5,5'-bitetrazole-1,1'-diolate anion.

#### 14.9.4.2 1,1'-Dinitramino-5,5'-bitetrazole

1,1'-Dinitramino-5,5'-bitetrazole, *N*-[5-(1-nitramidotetrazol-5-yl)tetrazol-1-yl]nitramide, C<sub>2</sub>H<sub>2</sub>N<sub>12</sub>O<sub>4</sub>, is an energetic material with an acidic character. It forms energetic salts with many bases.



1,1'-Dinitramino-5,5'-bitetrazole

Potassium 1,1'-dinitramino-5,5'-bitetrazolate is one of the most energetic primary explosives. This is due to its high initiation power and the exclusion of heavy metals like lead. The alkali metal salts such as the lithium, sodium, rubidium, and cesium salts were synthesized by reaction of the highly soluble ammonium salt with the corresponding metal hydroxide solutions [989]. In addition, the highly explosive silver salt and several other transition metal(II) amine complexes with nickel, copper, and zinc were prepared in a similar manner. The structure of all compounds was determined by XRD. The sensitivities toward impact, friction, heat, and ESD and their behavior on laser irradiation of the transition metal complexes were explored.

#### 14.9.4.3 Ditetrazolylamine

Instead of linking two tetrazole rings over the C—C bond at the 5-position, they can be linked via a C—NH—C bridge, forming a secondary amine, ditetrazolylamine, also known as imino-bis-tetrazole, bistetrazolylamine, bis-(1(2)*H*-tetrazol-5-yl)-amine, 5,5'-bis(1*H*-tetrazolyl)-amine, H2BTA, BTA, often obtained as *N*-1*H*-tetrazol-5-yl-1*H*-tetrazol-5-amine monohydrate; 2*H*-tetrazol-5-amine, *N*-2*H*-tetrazol-5-yl-, hydrate (1:1); C<sub>2</sub>H<sub>3</sub>N<sub>9</sub>•H<sub>2</sub>O, CAS RN [251110-84-6], *M* = 171.12 (hydrate). This compound has a melting point of 536 K (263 °C) (decomp.) This compound may also confusingly be called imino-5,5'-bistetrazole or *N,N*-bis(1*H*-tetrazol-5-yl)amine or 5-(tetrazol-5-ylamino)tetrazole. A more correct name would be di-5,5'-tetrazolylamine or ditetrazol-5-yl-amine [841, 990]. It usually is obtained in the form of a monohydrate which is also called BTA $\mathbf{w}$  (the  $\mathbf{w}$  stands for *water*).

Linking two tetrazole rings at the 5-position via an —NH— group gives ditetrazol-5-ylamine (imino-5,5'-bistetrazole). It can give off two protons and form dibasic salts with strong bases. A bis(4-aminotriazolium) imino-5,5'-bistetrazolate would be a compound with a record high nitrogen content (C<sub>6</sub>H<sub>4</sub>N<sub>17</sub> = 75.8 mass-% nitrogen).

Di(tetrazol-5-yl)amine has been synthesized in a four-step process starting with cyanuric chloride. It is characterized by IR spectroscopy and <sup>1</sup>H and <sup>13</sup>C NMR [991].

The kinetic and activation parameters of the decomposition in air and argon have been determined over the temperature range of 473–515 K (200–242 °C). The kinetic curves had an evident S-shape and fitted an equation of autocatalysis of the first order

$$\frac{d\alpha}{dt} = k_1(1 - \alpha) + k_2\alpha(1 - \alpha),$$

where the rate constant of non-catalytic decomposition  $k_1$  and the rate constant of catalytic reaction  $k_2$  satisfy the Arrhenius equations

$$k_1 = 10^{15.6 \pm 0.5} \exp[-(197 \pm 5)/RT] \text{ s}^{-1}$$

and

$$k_2 = 10^{17.5 \pm 0.7} \exp[-(201 \pm 7)/RT] \text{ s}^{-1}$$

( $R$  is measured in  $\text{kJ mol}^{-1} \text{ K}^{-1}$ ). Every 5,5'-bis(tetrazolyl)amine molecule splits out 2.5 molecules of  $\text{N}_2$ . The purity of nitrogen formed is better than 97.5 vol.-%. The evolution of  $\text{N}_2$  is accompanied by the formation of the condensed product of an unusual structure. The calorimetric data have confirmed the autocatalytic manner of the decomposition. The total reaction heat is about 440 cal/g.

The acid-catalyzed cyclization reaction of sodium dicyanamide and sodium azide in the ratio of 1:2 produced 5,5'-bis(1*H*-tetrazolyl)amine (also called di-1*H*-tetrazol-5-yl amine) in high yield (88%) as the monohydrate [992]. Dehydration of the monohydrate at an elevated temperature and reduced pressure gave anhydrous 5,5'-bis(1*H*-tetrazolyl)amine, which exhibited greater impact sensitivity than the hydrated form, BTaw. A BTaw sample with no excess water was obtained by drying at 323 K (50 °C), whereas anhydrous BTA was generated by removing water of hydration at 393 K (120 °C). The HOF of BTaw is +203 kJ/mol, while the HOF of anhydrous BTA is +633 kJ/mol, derived from measured heats of combustion of 1714 and 1858 kJ/mol, respectively. Predicted detonation velocities were 7792 m/s for BTaw and 9120 m/s for BTA. Predicted detonation pressures were 220 kbar for BTaw and 343 kbar for BTA, as calculated using the program EXPLO5. Di-1*H*-tetrazol-5-yl amine forms complexes with copper salts [993].

Thermoanalytical experiments were performed on bis-(1(2)*H*-tetrazol-5-yl)-amine monohydrate and anhydrous bis-(1(2)*H*-tetrazol-5-yl)-amine in an effort to better characterize the thermal stability and decomposition of these compounds by doing ARC, DSC, and TGA heating rate studies in a helium atmosphere [994, 995]. A two-step mass loss was observed in all experiments. The first step represents dehydration and the second step is a result of decomposition. An initial 9–10% mass loss was observed in the 403–433 K (130–160 °C) range. This corresponded to the loss of 1 mol of  $\text{H}_2\text{O}$  from 1 mol of BTaw. The average enthalpy of dehydration was  $268 \pm 15 \text{ J/g}$  or  $43 \pm 2 \text{ kJ/mol}$  BTaw. Kinetic parameters were determined for both of these steps using several different methods. The activation energy of BTaw (BTA) decomposition was  $193 \pm 5 \text{ kJ/mol}$ .

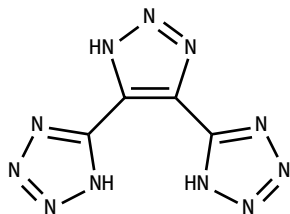
EGA was used to determine the composition of gaseous decomposition products. Hydrogen azide, ammonia, and hydrogen cyanide appeared as the major products in the FTIR trace, beginning at approximately 513 K (240 °C).

High-energy density salts that contained nitrogen-rich cations and the 5-(tetrazol-5-ylamino)tetrazolate anion were synthesized by metathesis reactions of sulfate salts with barium compounds such as bis[5-(tetrazol-5-ylamino)tetrazolate] or barium iminobis(5-tetrazolate) in an aqueous solution. They were characterized by IR, NMR spectroscopy, elemental analysis, DSC, and impact sensitivity [952].

5,5'-Bis(1*H*-tetrazolyl)amine. 5,5'-bis(1*H*-tetrazolyl)amine (BTA) was investigated under compression at room temperature [996]. Powder XRD using synchrotron radiation and micro-Raman spectroscopy were carried out to pressures up to 12.9 GPa. BTA conserved the crystalline structure of its room condition phase up to the highest pressure, i.e., an orthorhombic unit cell (*Pbca*).

#### 14.9.4.4 4,5-Di(tetrazol-5-yl)-1,2,3-triazole

Instead of linking two tetrazole rings directly over the C—C bond at the 5-position, they can also be linked via a triazole ring as a go-between. The resulting molecule has three azole rings linked by C—C bonds. 5,5'-(1*H*-1,2,3-Triazole-4,5-diyl)bis-1*H*-tetrazole, also known as 4,5-di(tetrazol-5-yl)-1,2,3-triazole; 2*H*-tetrazole, 5-[4-(2*H*-tetrazol-5-yl)-1*H*-1,2,3-triazol-5-yl]-; 5-[4-(1*H*-tetrazol-5-yl)-1*H*-triazol-5-yl]-1*H*-tetrazole, ditetrazolyltriazole, LLM-137, CAS RN [869060-66-2], C<sub>4</sub>H<sub>3</sub>N<sub>11</sub>, *M* = 205.15 g/mol, has a predicted density of 2.035 g/cm<sup>3</sup>.



4,5-Di(tetrazol-5-yl)-1,2,3-triazole

4,5-Bis(tetrazol-5-yl)-1,2,3-triazole can be made by dissolving ZnCl<sub>2</sub>, NaN<sub>3</sub>, and 4,5-dicyano-1,2,3-triazole in an organic solvent, refluxing for 0.5–2 h, filtering, collecting the precipitated solid, adding it to a basic solution, stirring, filtering, collecting the filtrate, regulating pH to 1, vacuum filtration, washing, and drying [256].

#### 14.9.4.5 Other Ditetrazole Derivatives

DFT computations were performed to study the effects of different substituents and bridge groups on the enthalpies of formation, thermal stability, and predicted detonation properties for a series of diiminotetrazole derivatives [997]. The isodesmic reac-



tion method was used to calculate the enthalpies of formation of the derivatives using total energies obtained from electronic structure calculations. The BDE and bond orders for the weakest bonds were analyzed to see what limits the thermal stability of the diiminotetrazole derivatives. The detonation velocities and pressures were predicted by the semi-empirical K-J equations and were based on the theoretical densities and enthalpies of formation.

#### 14.10 Azotetrazole, Azoxytetrazole, Hydrazotetrazole, and Azotetrazolates

Azotetrazoles are sometimes called azobistetrazoles or azoditetrazoles, however, the “bis” or “di” specifier is unnecessary. The correct name, as per the Chemical Abstracts and IUPAC guidelines, is 5,5'-(1,2-diazenediyl)bis[2*H*-tetrazole], or bis(1*H*-tetrazol-5-yl)diazene, C<sub>2</sub>H<sub>2</sub>N<sub>10</sub>, CAS RN [28623-02-1].

Symmetrical azotetrazoles can connect the —N=N— bridge to the tetrazole rings either at the carbon atoms at the 5-positions or at the nitrogen atoms such as the nitrogen atoms in the 1-positions of the tetrazole ring. If the connection is to the nitrogen atoms in the 1-positions, a continuous chain of ten nitrogen atoms is formed and the compound is called 1,1'-azotetrazole or 1,1'-(1,2-diazenediyl)bis1*H*-tetrazole, CAS RN [1282522-34-2] or “N10.” The 5,5'-azotetrazole is the more common form because 5-AT as a starting reactant is more readily available than 1-AT.

Azotetrazole can be made by oxidizing aminotetrazole in an alcoholic solution with permanganates or peroxydisulfates [998]. Azotetrazole in free form at room temperature is unstable. In water, it quickly converts into hydrazinotetrazole, which is accompanied by the release of nitrogen.

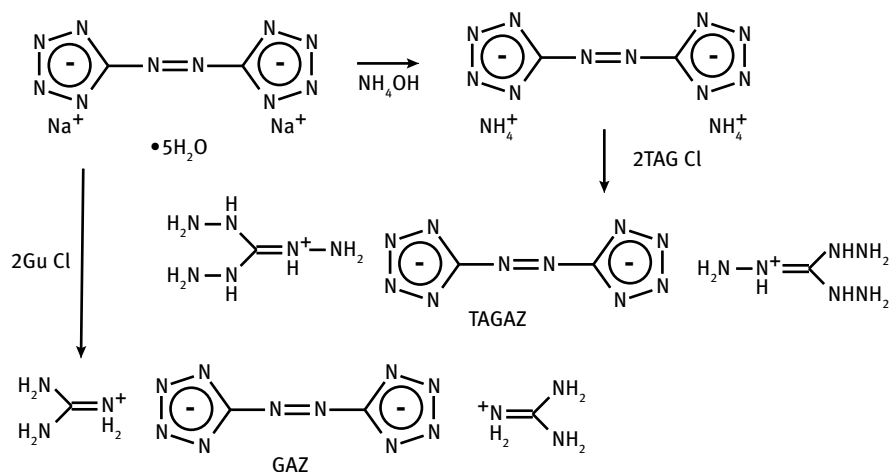
The reaction of 1-aminotetrazole with acidic sodium dichloroisocyanurate produced 1,1'-azo(tetrazole) [999]. The unusual chain of ten nitrogen atoms in this compound was confirmed by XRD. The physical and explosive properties of the azo compound were characterized.

The detailed potential energy surface of N10 was investigated using quantum mechanical calculations. Probable decomposition pathways were outlined by canonical transition state theory modeling [1000]. Among all the channels of reactions studied, ring-opening of the N<sub>10</sub> compound, followed by N<sub>2</sub> elimination to form a linear molecule was predicted to be the primary decomposition channel. Based on the thermal decomposition mechanism of N10, the probability of being successful in attempting to synthesize N12 and N14 was explored. These longer nitrogen chain compounds having higher nitrogen content than N10 would make good HEDMs. By comparing their energetic barriers with the corresponding primary N<sub>2</sub>-elimination reaction of N10, it was concluded that the predicted structures could theoretically exist at room temperature.

As a first step in this direction, a stable catenated N11 salt was synthesized by an azo coupling reaction from 1,5-diaminotetrazole [1001]. This was the first example of an azo reaction between an N—NH<sub>2</sub> diazonium salt and an amine derivative. The product structure was confirmed by XRD and its physical and explosive properties were characterized.

Unfortunately, 5,5'-azotetrazolates are not stable under mineral-acidic conditions because neutral 5,5'-azotetrazole decomposes into 5-hydrazinotetrazole, dinitrogen, and formic acid. With dilute nitric acid, the degradation produced 5-azidotetrazole as well as gaseous products [1002]. An effort has been started to replace 5,5'-azotetrazolates with bitetrazolates. The corresponding salts of 5,5'-bitetrazole are stable in acidic media and show performance similar to 5,5'-azotetrazolates.

Ammonium, guanidinium, or triaminoguanidinium azotetrazolates were synthesized, characterized, and thermolyzed [1003, 1004].



Guanidinium azotetrazolate was thermally the most stable of the three salts and had the highest heat release (2804 J/g) during its exothermic decomposition (Table 62). FTIR of the decomposition products of azotetrazolate salts showed bands at 3264 and  $2358\text{ cm}^{-1}$  which may be attributed to gaseous species such as  $\text{NH}_3$  and  $\text{HCN}$  or  $\text{NH}_2\text{CN}$ . The sensitivity test results showed that ammonium azotetrazolate (AZT) and guanidinium azotetrazolate are insensitive to impact and friction stimuli ( $\text{H50\%} > 170\text{ cm}$  and  $> 36\text{ kg}$ ) while TAGAZ (sometimes also designated as TAGzT) exhibited a relatively sensitive nature (drop weight  $\text{H50\%}$  51 cm and friction load  $157\text{ N} = 16\text{ kg}_f$ ). Triaminoguanidinium azotetrazolate (abbreviated as TAGAZ or TAGzT) was incorporated into solid propellant formulations to establish the compatibility of this class of compounds. The burning rate data obtained indicated that triaminoguanidinium azotetrazolate acted as an efficient energetic additive in CMDDB propellant formulations in the high-pressure region.

**Table 62:** Thermal stability of azotetrazolate salts (DSC results).

|       | Onset temperature of decomposition, $T_i$ |     | Maximum of exotherm, $T_{max}$ |     | Final temperature of exotherm, $T_f$ |     | Heat release during decomposition |
|-------|-------------------------------------------|-----|--------------------------------|-----|--------------------------------------|-----|-----------------------------------|
|       | °C                                        | K   | °C                             | K   | °C                                   | K   | J/g                               |
| AAZ   | 181                                       | 454 | 212                            | 485 | 226                                  | 499 | 1380                              |
| GAZ   | 182                                       | 455 | 259                            | 532 | 261                                  | 534 | 2804                              |
| TAGAZ | 181                                       | 454 | 204                            | 477 | 221                                  | 494 | 1352                              |

Data source: [1004].

The synthesis, characterization, and thermolysis studies of hydrazinium azotetrazolate (HAZ) by TGA and DSC indicated that hydrazinium azotetrazolate decomposed in the range of 423–453 K (150–180 °C) [1005]. The pattern of decomposition of HAZ dihydrate was predicted with the help of the pyrolysis GC/MS technique and a probable decomposition mechanism was proposed.

DFT methods were used to study the enthalpies of formation ( $\Delta H_f$ 's), electronic structure, energetic properties, and thermal stability for bridged bitetrazole (ditetrazole) derivatives with different linkages between the rings and different substituent groups on the rings [1006]. The  $-N_3$  group and azo bridge ( $-N=N-$ ) are effective in increasing the  $\Delta H_f$ 's of the bitetrazole derivatives. The calculated detonation velocities and detonation pressures indicated that the  $-NO_2$ ,  $-NF_2$ ,  $-N=N-$ , or  $-N(O)=N-$  group are effective for enhancing the detonation performance for these compounds. An analysis of the BDE for several relatively weak bonds suggested that the N–N bond in the rings or outside the rings is the weakest one and N–N cleavage is likely to happen first in thermal decomposition. Overall, the  $-CH_2-CH_2-$  or  $-NH-NH-$  group is an effective bridge for enhancing the thermal stability of the bridged bitetrazoles. The enthalpy of formation of 5,5'-hydrazotetrazole,  $C_2H_4N_{10}$ ,  $M = 168.12$  g/mol, is  $+804$  cal/g =  $+135$  kcal/mol =  $+565$  kJ/mol. It contains 83.3% nitrogen. Other azotetrazolate salts are described in [972] and [1007].

A two-step synthesis method for some azotetrazolate non-metallic salts was introduced, including for guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium azotetrazolate [1008]. The physical and chemical properties and explosive performance of the ammonium salt and hydrazinium salt were also studied. It was shown that these materials have high HOF, large gas production, good thermal stability, and high heat of reaction, and they may have possible applications as gas generants, low-signature propellants, low-smoke, or non-smoke pyrotechnics, and high-performance explosives.

DFT methods with corrections for long-range dispersion interactions were evaluated for their capabilities to describe the crystallographic lattice properties of a set of

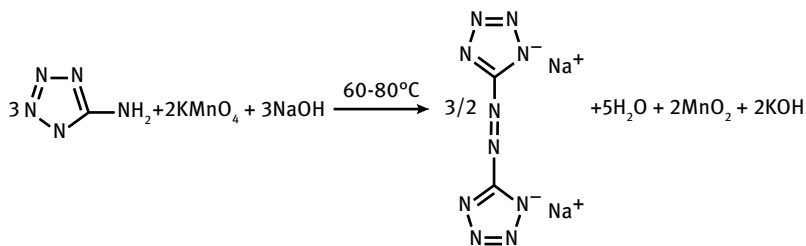
26 high nitrogen-content salts including eight azotetrazolates and five iminobistetrazolates [1009].

DFT calculations were used to study two compounds, 1,1'-azobis(tetrazole) and 1,1'-azobis(5-methyltetrazole), with a ten-catenated nitrogen atoms chain [1010]. In addition to this, the structures of substituted azobis(tetrazoles) with ten catenated nitrogen atoms and various energetic groups ( $-\text{CF}_3$ ,  $-\text{C}(\text{NO}_2)_3$ ,  $-\text{N}_3$ ,  $-\text{NH}_2$ ,  $-\text{NHNH}_2$ ,  $-\text{NHNO}_2$ ,  $-\text{NO}_2$ ,  $-\text{OCH}_3$ ,  $-\text{OH}$ , and  $-\text{ONO}_2$ ) were computed. The optimized geometry, frontier MOs, electrostatic potential, and IR and NMR spectra were calculated. The effects of different substituents on the density, enthalpy of formation, heat of explosion, detonation velocity, and pressure and sensitivity of the azobis(tetrazole) derivatives were then examined. The properties of several compounds were predicted to be superior to CL-20, RDX, or HMX.

A similar family of salts was derived from azotetrazole, which carries a hydroxyl group on each of the two tetrazole rings, 5,5'-azotetrazole-1,1'-diol. The following sections provide information on specific azotetrazolate salts.

#### 14.10.1 Alkali Metal 5,5'-Azotetrazolates

5,5'-Azotetrazolate salts have been known for more than 120 years and a lot of work was done on these compounds since they were first discovered. 5,5'-Azotetrazole is a dibasic acid and can form salts in which one or both rings carry a negative charge. Salts of azotetrazole were prepared in 1898 by Thiele by oxidation of 5-AT with potassium permanganate. The same process is still in use today. Azotetrazolates, of a heavy metal, were later patented as primary explosives in initiators and blasting caps because they are stab-sensitive. The lead salt may be even more drop-weight sensitive than mercury fulminate. The alkali metal and earth alkaline metal salts of 5,5'-azotetrazole are well characterized. Na, K, Ca, Ba, and  $\text{NH}_4$  salts of azotetrazole were the first ones to be discovered and have their properties described. They crystallize with two to eight molecules of water in the sphere of hydration. Loss of water increases their friction and shock sensitivity remarkably. Sodium 5,5'-azotetrazolate can be obtained by oxidation of 5-AT with sodium permanganate. It is often used as an intermediate in the preparation of other azotetrazolate salts that are even more rich in nitrogen. Five water molecules are complexed to the azotetrazolate ion. 5-aminotetrazole (5-AT) is added to a 2-M aqueous solution of sodium hydroxide, followed by the addition of potassium permanganate, which produces the NaZT. The insoluble  $\text{MnO}_2$  byproduct forms a sludge that is difficult to filter while the solution is still hot.



5,5'-Azotetrazole synthesis

Replacing the alkaline metal with nitrogen-rich cations such as ammonium, hydrazinium, guanidinium, or triaminoguanidinium leads to the synthesis of stable high-nitrogen compounds. These have received a lot of attention since the search began for safer automotive airbag inflator gas generants [1011–1013].

Alkaline earth metal salts of 5,5'-hydrazine-1,2-diylbis(1*H*-tetrazole) can be used as flame colorants in pyrotechnic flares and display fireworks, thus eliminating the need for environmentally unfriendly perchlorates or chlorates [1014].

#### 14.10.2 Ammonium 5,5'-Azotetrazolate

The enthalpy of formation of ammonium 5,5'-azotetrazolate is +443 kJ/mol (+105.9 kcal/mol).

#### 14.10.3 Hydrazinium(1+) 5,5'-Azotetrazolate

The enthalpy of formation of hydrazinium(1+) 5,5'-azotetrazolate is +858 kJ/mol [61]. The reaction of  $[\text{N}_2\text{H}_5^+]_2[\text{SO}_4]^{2-}$  with barium 5,5'-azotetrazolate gave new HEDMs based on the 5,5'-azotetrazolate dianion [901, 1015]. The dihydrazinium salt of  $[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-}$  (**1**), its dihydrate (**2**), and its dihydrazinate (**3**) were prepared and characterized. Synthesis in water produced yellow needles of the dihydrate  $[\text{N}_2\text{H}_5^+]_2[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-} \cdot 2\text{H}_2\text{O}$  (**2**): monoclinic,  $P2_1/c$ ,  $a = 8.958(2) \text{ \AA}$ ,  $b = 3.6596(7) \text{ \AA}$ ,  $c = 16.200(3) \text{ \AA}$ ,  $\beta = 96.834(3)^\circ$ ,  $V = 527.3(2) \text{ \AA}^3$ ,  $Z = 2$ , and  $\rho_{\text{X-ray}} = 1.564 \text{ g/cm}^3$ . Synthesis in anhydrous hydrazine instead of water gave yellow dihydrazinate crystals  $[\text{N}_2\text{H}_5^+]_2[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-} \cdot 2\text{N}_2\text{H}_4$  (**3**): triclinic,  $P\bar{1}$ ,  $a = 4.6208(6) \text{ \AA}$ ,  $b = 8.585(1) \text{ \AA}$ ,  $c = 9.271(1) \text{ \AA}$ ,  $\alpha = 108.486(2)^\circ$ ,  $\beta = 95.290(2)^\circ$ ,  $\gamma = 102.991(2)^\circ$ ,  $V = 334.51(8) \text{ \AA}^3$ ,  $Z = 1$ , and  $\rho_{\text{X-ray}} = 1.461 \text{ g/cm}^3$ . The compounds were characterized by elemental analysis and vibrational (IR, Raman) and multi-nuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ ). These compounds represent high nitrogen HEDMs with one of the highest nitrogen contents reported to date:

- (1)  $[\text{N}_2\text{H}_5^+]_2[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-} = \text{C}_2\text{H}_{10}\text{N}_{14} = 85.2\%$
- (2)  $[\text{N}_2\text{H}_5^+]_2[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-} \cdot 2\text{H}_2\text{O} = \text{C}_2\text{H}_{14}\text{N}_{14}\text{O}_2 = 73.3\%$
- (3)  $[\text{N}_2\text{H}_5^+]_2[\text{N}_4\text{C}-\text{N}=\text{N}-\text{CN}_4]^{2-} \cdot 2\text{N}_2\text{H}_4 = \text{C}_2\text{H}_{18}\text{N}_{18} = 85.7\%$ .

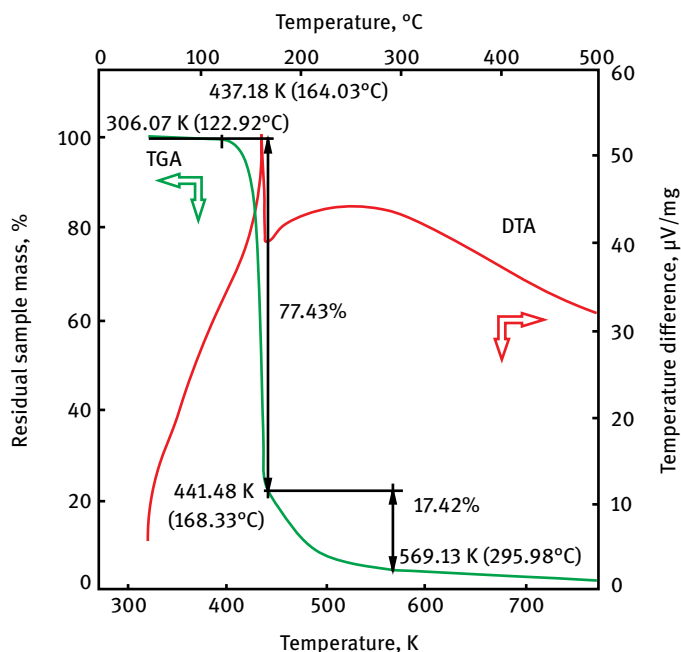
The standard HOF of the solvate-free compound (**1**) was computed to be  $\Delta H_f^\circ = 264 \text{ kcal/mol} = 1147 \text{ kcal/kg} = 1105 \text{ kJ/mol}$  and is one of the highest ever reported. The compounds are stable at room temperature and are almost insensitive to friction and impact, however, they detonate violently when the explosion is initiated, e.g., by rapid heating over the decomposition temperature or by using an initiator. No detonation was observed in the drophammer test (5 kg, 50 cm). In the DTA/TGA measurements at a heating rate of 5 K/min, and using samples of about 12 mg in open aluminum crucibles, the first mass loss after the evaporation of water in (**2**) and hydrazine in (**3**) was detected at about 393 K (120 °C) followed by explosion at 436 K = 163 °C and 447 K = 174 °C.

Similar salts were obtained from dimethylamine, trimethylhydrazine, and 5,5'-azotetrazole [1016]. Ammonium and hydrazinium salts of the 5,5'-azotetrazolate dianion with methylated ammonium and hydrazinium cations were prepared. The compounds were characterized by elemental analysis, vibrational (IR, Raman) spectroscopy, and multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ) NMR spectroscopy. The crystal structures of the di[ammonium], the bis[dimethylammonium], and the bis[trimethylhydrazinium] 5,5'-azotetrazolate salts were determined. Additional 5,5'-azotetrazolate salts of alkylhydrazines, guanidine, and triaminoguanidine were prepared and characterized by elemental analysis, vibrational (IR, Raman) spectroscopy, and multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ) NMR spectroscopy [1017]. The crystal structures of the di-tert-butylhydrazinium, the ethylenedihydrazinium, the diguanidinium, and the bis-triaminoguanidinium azotetrazolate were determined. The thermal, shock, and friction sensitivities of all compounds were investigated and their explosion products were analyzed.

The thermal decomposition of hydrazinium azotetrazolate was evaluated in comparison to GuN, TAGN, and TAGAT and five other nitrogen-rich additives [1018]. In contrast to similar guanidinium or triaminoguanidinium salts, hydrazinium azotetrazolate was found to decompose in a single stage (Figure 22).

The steep slope in the TGA thermogram corresponded to the exothermic decomposition observed in the simultaneous DTA between 396 and 441 K (123 and 168 °C), resulting in a substantial 77% weight loss followed by an endothermic decomposition resulting from the breakage of relatively strong C–N bonds in the residue. This suggests that the decomposition initiated with the homolytic cleavage of N–NH<sub>2</sub> bonds and was followed by the exothermic opening of the azotetrazolate ring.

The structure of dihydrazinium 5,5'-azotetrazolate dihydrate was determined by neutron diffraction at 25 K and revealed no significant deviations from the previously reported room-temperature structure determined by XRD [1019]. The vibrational spectrum of dihydrazinium 5,5'-azotetrazolate dihydrate was also measured at 25 K by inelastic neutron scattering (INS) spectroscopy. Solid-state quantum chemical calculations were used to simulate the INS spectrum. Based on the simulations and analysis of the experimental data, it was possible to assign the normal vibrational modes. This helped to explain the decomposition mechanism of this compound.



**Figure 22:** DTA-TGA thermogram of hydrazinium azotetrazolate. (Republished and modified from [1018], with permission of the ©2009 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

The isothermal structural properties, equation of state, and vibrational dynamics of dihydrazinium 5,5'-azotetrazolate dihydrate were studied under high pressure using synchrotron XRD and optical Raman and IR micro-spectroscopy [1020]. At pressures near 4.5 GPa, XRD characterization revealed an abrupt discontinuity in the compressibility. When correlated with the mode splitting and intensity changes observed in the spectroscopic measurements, this suggested the onset of a subtle isostructural phase transition.

The enthalpies of formation of a series of salts of 5,5'-azotetrazole with nitrogenous onium bases were determined by calorimetric measurements in a bomb calorimeter with a modified oxygen bomb [1021]. Samples were burnt without using a crucible. The enthalpies of formation were calculated from measured heats of combustion.

The thermal decomposition of guanidinium, ammonium, melaminium, and sodium 5,5'-azotetrazole salts, the kinetic parameters of the controlling chemical reaction, and the detailed decomposition mechanisms of 5,5'-azotetrazole salts have been investigated [1022].

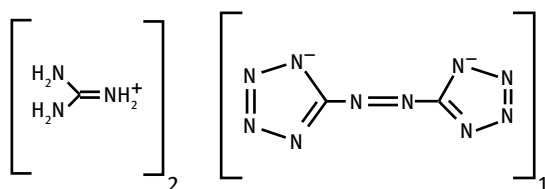
The thermal decomposition of dihydrazinium 5,5'-azotetrazolate under isothermal and non-isothermal conditions in solid and liquid phases was measured and

a relationship between the basicity and the thermal stability of 5,5'-azotetrazole salts was demonstrated [1023]. A boundary of the possible existence of 5,5'-azotetrazole salts in terms of the basicity index  $pK_a$  was determined. Gaseous and condensed products of decomposition were analyzed and a mechanism of thermal decomposition of 5,5'-azotetrazole was proposed. The enthalpies of formation of some 5,5'-azotetrazole salts were determined and the most reliable values were chosen based on the analysis of the data obtained and those available in publications. The enthalpy of formation of dihydrazinium 5,5'-azotetrazolate is  $+858 \text{ kJ/mol} = +205 \text{ kcal/mol}$ .

#### 14.10.4 Bis(guanidinium) 5,5'-Azotetrazolate

##### 14.10.4.1 Preparation of Bis(guanidinium) 5,5'-Azotetrazolate

Some of the guanidinium salts of nitrogen-rich heterocyclic acids have already been described in *Encyclopedia of Liquid Fuels* in the chapter titled "Amides and Imides." This section describes a few more guanidinium salts that are outstanding because of their good thermal stability and high nitrogen content. Guanidinium 5,5'-azotetrazolate, also known as  $\text{C}_4\text{H}_{12}\text{N}_{16}$ , bis(guanidinium) 5,5'-azotetrazolate, di(guanidinium) 5,5'-azotetrazolate, GZT, GAZ, GuZT, Gu2AzT, can be obtained by reacting 5-aminotetrazole monohydrate with potassium permanganate in an aqueous sodium hydroxide solution to form sodium 5,5'-azotetrazolate dihydrate as an intermediate, then reacting 5,5'-azotetrazolate dihydrate with guanidinium nitrate or guanidinium chloride to obtain guanidinium 5,5'-azotetrazolate [1024–1026]. Properties of this salt are also listed in *Encyclopedia of Liquid Fuels*, in the "Amides and Imides" chapter under guanidinium salts (there may be some duplication of information).



Guanidinium 5,5'-azotetrazolate GAZ GuZT

Guanidinium azotetrazolate (GuZT) was evaluated as an additive for a high regression rate fuel mixture with HTPB [1027]. GuZT was found to react with N100, a common curative for HTPB. A test grain made with N100, HTPB, and GAT formed a foam that was about one and a half times its original volume. An alternative isocyanate curative was found, polyisocyanate (PAPI), with which it did not react.

Guanidinium azotetrazolate can be synthesized from 5-aminotetrazole (5-AT) by oxidation-reduction reactions [1028]. A study of the effects of reaction temperature, reaction time, the molar ratio of reactants, and NaOH concentration on the yield showed that the optimum conditions were as follows: based on 0.1 mol of 5-AT, NaOH concen-



tration was 1.5 mol/L, mol ratio (5-AT):(KMnO<sub>4</sub>) = 3:3, the reaction temperature was 80 °C, and the reaction time was 60 min. Under the optimum conditions, the yield of a scaled-up test was better than 80%. The structure and thermal stability of the compound were characterized by elemental analysis, IR, <sup>1</sup>H-NMR, and TG-DTA.

In previous years, the Naval Surface Warfare Center's Indian Head Division (NSWC-IHD) had made approximately 12 kg of GuZT at the 50-gallon scale. To develop a more efficient process, the engineers more than doubled the quantity of GuZT obtained per batch by increasing the concentration of reactants in the reaction solution [1029]. This was done based on a design of experiments (DOE), screening guanidinium azotetrazolate synthesis parameters for effects on product yield, purity, and particle characteristics for the synthesis of GuZT at the 100-gallon scale. Based on this DOE, by using 20% excess and a more concentrated (1.3 g/mL) solution of guanidinium chloride (Gu-HCl) and cooling to 5 °C before filtering the product maximized the yield. The product had a density of 1.538 g/cm<sup>3</sup>. The product GuZT should be washed with water to remove sodium and chloride ion impurities. Washing with water will cause loss of some of the wanted products. The solubility of GuZT in water at different temperatures is listed in Table 63.

**Table 63:** Solubility of guanidinium azotetrazolate in water.

| Temperature |      | GuZT solubility |
|-------------|------|-----------------|
| K           | °C   | mg/mL           |
| 278         | 5    | 4.4             |
| 305.6       | 32.5 | 6.3             |
| 333         | 60   | 10.4            |

Data source: [1029].

Guanidinium azotetrazolate was synthesized by oxidation and cation replacement with 5-aminotetrazole (5-AT) as the starting material [1030]. Guanidinium azotetrazolate was characterized by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analysis, HPLC, MS, and SEM. Thermochemical properties of GuZT were analyzed by DSC and its friction sensitivity and impact sensitivity were tested. The optimal conditions for the synthesis of GuZT were as follows: KOH concentration 1.5 mol/L, *n*(5-AT) : *n*(KMnO<sub>4</sub>) : *n*(GuN) = 1.0:1.0:1.1, oxidation reaction temperature 333 K (60 °C), oxidation reaction time 60 min, cation replacement reaction temperature 353 K (80 °C). Under optimal conditions, the GuZT yield can reach 97% and the purity is higher than 99%. The product crystallized in uniform yellow acicular crystals. The thermal decomposition temperature of GuZT was 529.7 K (256.6 °C).

#### 14.10.4.2 Physical Properties of Bis(guanidinium) 5,5'-Azotetrazolate

The measured enthalpy of formation of bis(guanidinium) 5,5'-azotetrazolate is +410 kJ/mol (+98 kcal/mol) and the calculated enthalpy of formation is +486.5 kJ/mol (+116 kcal/mol). Its melting point is 535 K = 262 °C and its density is 1.54 g/cm<sup>3</sup>. The physical properties of bis(guanidinium) 5,5'-azotetrazolate and related high-nitrogen compounds are summarized in Table 64.

**Table 64:** Physical properties of guanidinium and triaminoguanidinium 5,5'-azotetrazolates.

| Compound name                                 | Gross formula                                  | Mol. mass | Nitro-gen content | Den-sity  | Melting point |            | Enthalpy of formation | Refer-ences  |
|-----------------------------------------------|------------------------------------------------|-----------|-------------------|-----------|---------------|------------|-----------------------|--------------|
|                                               |                                                | g/mol     | mass-%            |           | K             | °C         |                       |              |
| Bis(guanidinium) 5,5'-azotetrazolate          | C <sub>4</sub> H <sub>12</sub> N <sub>16</sub> | 284.25    | 78.84             | —         | 511–512       | 238–239    | measured +410         | [1026]       |
|                                               |                                                |           |                   |           |               |            | calculated +486.5     |              |
|                                               |                                                |           |                   | 1.538     | —             | —          | —                     | [1029]       |
|                                               |                                                |           |                   | 1.538     | —             | —          | 410                   | [1011]       |
| Bis(triamino-guanidinium) 5,5'-azotetrazolate | C <sub>4</sub> H <sub>18</sub> N <sub>22</sub> | 374.34    | 82.32             | 1.60      | 482 (dec.)    | 209 (dec.) | calculated +1171      | [1031]       |
|                                               |                                                |           |                   |           | 469–470       | 196–197    |                       | [1007, 1032] |
|                                               |                                                |           |                   | 78.84     | 1.54          | 513 (dec.) | +410 kJ/mol =         | [1033]       |
|                                               |                                                |           |                   | hydrate?? |               |            | +98 kcal/mol          |              |

#### 14.10.4.3 Thermal Stability of Bis(guanidinium) 5,5'-Azotetrazolate

GuZT is thermally quite stable and suffers a weight loss of only 1% after being stored for 50 d at 403 K (130 °C). It melts at a relatively high temperature of 511–512 K (238–239 °C). A comparative thermal stability evaluation of GuZT in comparison to several other azotetrazolate salts showed that GuZT was the thermally most stable compound of the group [1031].

Bis(guanidinium) 5,5'-azotetrazolate thermal decomposition studies were carried out using DSC with 2–3 mg samples pressed in aluminum caps and heated at different rates [1034, 1035]. When heated at a rate of 10 K/min, GuZT has only one exothermic peak at 535 K = 262 °C with an energy release of 837–1255 J/g (200–300 cal/g). Plotting the decomposition rate vs. 1/*T* gives a rather high activation energy of 194 kJ/mol (46.3 kcal/mol). Manometric experiments were carried out in thin-walled glass manometers of the compensation type (glass Bourdon gauge). A sample of GuZT (10–15 mg) was loaded into a vial of 12–15 cm<sup>3</sup> volume. The vial was evacuated,

sealed, and immersed in a thermostat bath containing molten Wood's metal. The temperature in the thermostat was maintained constant with an accuracy of  $\pm 0.5^\circ\text{C}$ . These studies showed that the GuZT is quite thermally stable. The initial rate of GuZT decomposition in the solid state was 10–16 times less than in the melt, while the activation energies were similar (177 and 174 kJ/mol = 42.3 and 41.6 kcal/mol, respectively). GuZT decomposition resulted in the liberation of 3 mols of nitrogen, 1.9 mols of ammonia, and 1 mol of readily condensable products along with the formation of a condensed residue.

The thermal decomposition of bis(guanidinium) 5,5'-azotetrazolate under isothermal and non-isothermal conditions in solid and liquid phases was measured and a relationship between the basicity and the thermal stability of 5,5'-azotetrazole salts was demonstrated [1023]. A boundary of possible existence of 5,5'-azotetrazole salts in terms of the basicity index  $\text{p}K_{\text{a}}$  was determined. Gaseous and condensed products of decomposition were analyzed and a mechanism of thermal decomposition of 5,5'-azotetrazole was proposed. The enthalpies of formation of some 5,5'-azotetrazole salts were determined. The most reliable values were chosen based on the analysis of the data obtained and those available in publications. The enthalpy of formation was +410 kJ/mol (+98 kcal/mol).

#### 14.10.4.4 Burning Rate Studies of Bis(guanidinium) 5,5'-Azotetrazolate

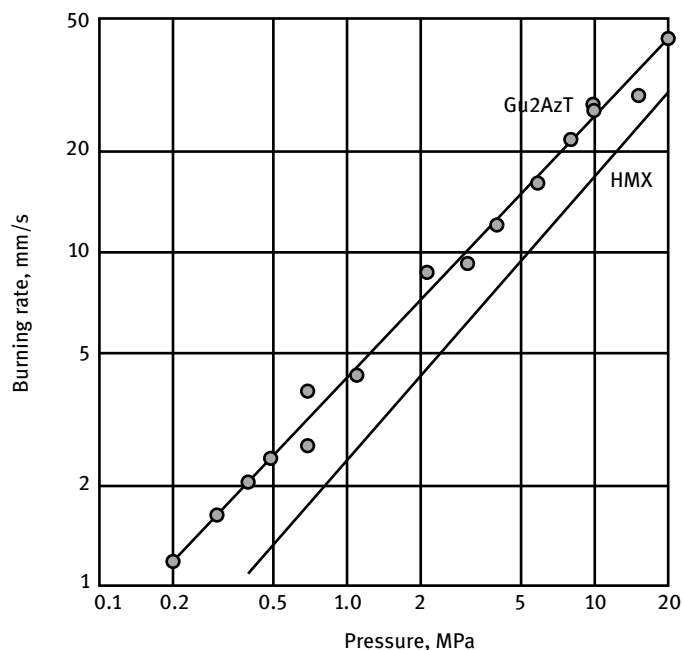
The burning rates of GuZT were measured in the pressure interval 0.1–20 MPa in a constant-pressure bomb of 1.5 L volume that was equipped with windows [1034, 1035]. Samples for testing were prepared as pressed cylinders at 0.82–0.84% of their theoretical maximum density ( $1.538\text{ g/cm}^3$ ) and were confined in transparent acrylic tubes of 4 mm i.d. A video camera was used to determine the character of the combustion process as well as the burning rates. GuZT in the form of samples pressed into 4-mm acrylic tubes can sustain burning at pressures down to 0.2 MPa and showed stable burning above 0.6 MPa. The burning was flameless at all pressures studied and accompanied by the formation of copious white smoke and a solid residue inside the tubes. The burning rate of GuZT at 10 MPa was 25.6 mm/s, which is 1.5 times faster than HMX (Figure 23). The GuZT burning rate-pressure dependence can be expressed as  $r_b = 0.69p^{0.78}$ , mm/s for the pressure interval 0.2–20 MPa.

#### 14.10.4.5 Sensitivity of Bis(guanidinium) 5,5'-Azotetrazolate

The shock and friction sensitivity of bis(guanidinium) 5,5'-azotetrazolate is much less than that of TAGZT or AGZT (Table 65).

#### 14.10.4.6 Applications of Bis(guanidinium) 5,5'-Azotetrazolate

TAGZT and GuZT are being investigated as additives for propellant formulations, not only for the purposes of burning rate modification but also as ingredients that may help existing and future formulations meet the demands of insensitive munitions (IM), safety, and long-term aging requirements. From a performance perspective, TAGZT



**Figure 23:** Strand burning rate of GuZT in comparison to HMX. (Reproduced and modified from [1034] in accordance with Creative Commons CC BY-NC-ND 3.0.)

**Table 65:** Shock and friction sensitivity of GuZT in comparison to TAGZT or AGZT.

| Compound abbreviation | Impact sensitivity |                   | Friction sensitivity |                 |
|-----------------------|--------------------|-------------------|----------------------|-----------------|
|                       | N m                | kg <sub>f</sub> m | N                    | kg <sub>f</sub> |
| TAGZT                 | 1.47–1.57          | 0.15–0.16         | 106                  | 10.8            |
| AGZT                  | 6.9                | 0.7               | 353                  | 36              |
| GuZT                  | 7.4                | 0.75              | 353                  | 36              |

Data source: [1025].

has proven significantly better at increasing the burning rate of RDX-based composite propellants than its similarly structured counterpart, GuZT. Previous thermal decomposition studies have shown that the hydrazine that is formed in the decomposition of TAGzT undergoes a very strong and rapid interaction with RDX. At temperatures near the melting point of RDX, the reaction rate of hydrazine with RDX is faster than the rate of decomposition of RDX by itself. To determine why GUzT is less effective as a burning rate modifier in RDX-based composite propellants, STMBMS and Fourier Transform ion cyclotron resonance (FTICR) mass spectrometry methods were used to

examine the thermal decomposition of GuZT [1036]. Previous thermal decomposition studies had shown that the decomposition of GuZT is a complex multi-step non-linear process that predominantly involves the formation of volatile gases such as ammonia and nitrogen and a non-volatile residue that subsequently decomposes to form higher molecular weight products. Bis(guanidinium) 5,5'-azotetrazolate can be used as a gas generant in airbag inflators in place of, or along with, other high-nitrogen compounds, potentially using copper diammine dinitrate as the oxidizer [1037–1040].

#### 14.10.5 Bis(aminoguanidinium) 5,5'-Azotetrazolate

Bis(aminoguanidinium) 5,5'-azotetrazolate (AGZT) and bis(diaminoguanidinium) 5,5'-azotetrazolate (DAGZT) are high-nitrogen compounds with very high nitrogen content (AGZT 80.22% N, oxygen balance –76.4%; DAGZT 81.36% N, oxygen balance –74.4%). However, due to their shock and friction sensitivity, they are not likely to find widespread uses as gas generant or propellant additives. GuZT is thermally more stable and TAGZT contains more nitrogen.

Some of the properties of AGZT and DAGZT are summarized in Table 66. Figure 24 provides a comparison of thermal stabilities of the various guanidinium and guanidinium derivative azotetrazolate salts.

Some of the properties of bis(triaminoguanidinium) 5,5'-azotetrazolate (TAGAT, TAGAZ, TAGzT) have already been described in *Encyclopedia of Liquid Fuels*, chapter “Amides and Imides.” Bis(triaminoguanidinium) 5,5'-azotetrazolate [which is also called di(triaminoguanidinium) 5,5'-azotetrazolate, TAGzT, TAGAT,  $C_4H_{18}N_{22}$ ,  $M = 374.34 \text{ g/mol} = 2.6714 \text{ mol/kg}$ ] is a unique energetic high-nitrogen compound that has received a lot of attention during the past two decades. TAGzT is also described as a carbonohydrazone dihydrazide (TAG), compound with 5,5'-(1,2-diazenediyl)bis[2H-tetrazole] (2:1) (azotetrazole),  $C_2H_2N_{10} \bullet 2CH_8N_6$ , CAS RN [2165-23-3].

##### 14.10.5.1 Preparation of TAGzT

The synthesis of bis-(triaminoguanidinium)-5,5'-azotetrazolate (TAGzT) by a two-step method with 5-aminotetrazole (5-AT) as the starting material has been improved [1032]. First sodium-5,5'-azotetrazolate pentahydrate was synthesized by oxidizing 5-AT with potassium permanganate in 15% aqueous sodium hydroxide solution with a yield of 75.6%. Then cation replacement between sodium-5,5'-azotetrazolate pentahydrate and TAGN gave TAGZT with a yield of 73.3%. The melting point of the material obtained was 469–470 K (196–197°C), which was in agreement with literature data. The structure of the TAGZT crystal was further characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR, and elemental analysis.

The manufacture of bis(triaminoguanidinium) azotetrazolate (TAGzT), along with its precursor which is sodium azotetrazolate pentahydrate (NaZT), has been scaled up at the NSWC-IHD. In 2003, the NSWC-IHD successfully validated both the NaZT and

TAGzT 100-gallon batch scale processes, and in 2006, the TAGzT process was optimized to improve operational safety and to maximize the product yield [1041].

TAGzT normally crystallizes in long needle-like crystals that present manufacturing challenges. TAGzT's crystal habit results in low packing densities and creates challenges in the process, starting from mixing through to extrusion. Recrystallizing the existing TAGzT needle-like structures to various particle sizes and shapes had to be conducted to improve the morphology of the crystals for propellant formulations.

#### 14.10.5.2 Physical Properties of TAGzT

The calculated enthalpy of formation of bis(triaminoguanidinium) 5,5'-azotetrazolate is +2908 kJ/kg = +1089 kJ/mol, its melting point is 482 K = 209 °C (with decomposition), and its density is 1.60 g/cm<sup>3</sup>. Another source gives the enthalpy of formation of TAGzT as +1075 kJ/mol = +257 kcal/mol [1023]. Table 66 is a summary of the properties of TAGzT with other high-nitrogen compounds and RDX for comparison.

**Table 66:** Properties of high-nitrogen explosives based on tetrazole derivatives.

| Compound abbreviation | Gross formula                                               | Molecular mass | Enthalpy of formation |       | Density           |
|-----------------------|-------------------------------------------------------------|----------------|-----------------------|-------|-------------------|
|                       |                                                             | g/mol          | kJ/mol                | kJ/kg | g/cm <sup>3</sup> |
| RDX                   | C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub> | 222.12         | +70.6                 | +318  | 1.80              |
| DAAF                  | C <sub>4</sub> H <sub>4</sub> N <sub>8</sub> O <sub>3</sub> | 212.13         | +478                  | +2255 | 1.7               |
| BTATz                 | C <sub>6</sub> H <sub>4</sub> N <sub>14</sub>               | 248.17         | +883                  | +3560 | 1.76              |
| TAGzT <sup>a</sup>    | C <sub>4</sub> H <sub>18</sub> N <sub>22</sub>              | 374.34         | 1089                  | +2908 | 1.60              |

<sup>a</sup> Corrected value

Data source: [1042].

The properties of guanidinium and mono-, di-, and tri-aminoguanidinium 5,5'-azotetrazolates and bis(azidoformamidinium) 5,5'-azotetrazolate (AFZT) are summarized in Table 67.

#### 14.10.5.3 Molecular Structure of TAGzT

Bis(triaminoguanidinium) bis(5-azotetrazolate) (TAGzT) crystallizes in the centrosymmetric monoclinic space group  $P2_1/n$  with unit-cell parameters  $a = 3.962(1)$  Å,  $b = 15.019(2)$  Å,  $c = 12.981(1)$  Å, and  $\beta = 95.30(2)^\circ$  [1043]. The crystal is held together by an extensive three-dimensional network of hydrogen bonds.

The room-temperature isothermal compression behavior of bis-triaminoguanidinium azotetrazolate (TAGzT) was investigated by *in-situ* Raman spectroscopy to pressures near 17 GPa [1044]. Two prominent peaks near 1370 and 1470 cm<sup>-1</sup> arise from the C—N and N=N symmetric stretches, respectively. These results, together with micro-Raman spectroscopic analyses of the recovered and decompressed samples, suggest that TAGzT does not undergo any phase transitions within this pressure range.

**Table 67:** Properties of guanidinium and mono-, di-, and tri-aminoguanidinium 5,5'-azotetrazolates, and bis(azidoformamidinium) 5,5'-azotetrazolate.

| Compound abbreviation                    | AFZT                                          | GZT                                            | AGZT hydrate                                     | AGZT                                           | DAGZT                                          | TAGZT                                          |
|------------------------------------------|-----------------------------------------------|------------------------------------------------|--------------------------------------------------|------------------------------------------------|------------------------------------------------|------------------------------------------------|
| Empirical formula                        | C <sub>4</sub> H <sub>8</sub> N <sub>20</sub> | C <sub>4</sub> H <sub>12</sub> N <sub>16</sub> | C <sub>4</sub> H <sub>16</sub> N <sub>18</sub> O | C <sub>4</sub> H <sub>14</sub> N <sub>18</sub> | C <sub>4</sub> H <sub>16</sub> N <sub>20</sub> | C <sub>4</sub> H <sub>18</sub> N <sub>22</sub> |
| Molar mass, g/mol                        | 336.24                                        | 284.14                                         | 332.18                                           | 314.16                                         | 344.19                                         | 374.33                                         |
| Nitrogen content, mass-%                 | 83.31                                         | 78.84                                          | 75.87                                            | 80.22                                          | 81.36                                          | 82.32                                          |
| Oxygen balance, %                        | -57.1                                         | -78.8                                          | -72.2                                            | -76.4                                          | -74.4                                          | -72.7                                          |
| <i>T</i> <sub>initial decomp.</sub> , K  | 400–418                                       | 523–538                                        | 488–503                                          | 215–230                                        | 464–481                                        | 466–485                                        |
| <i>T</i> <sub>initial decomp.</sub> , °C | 127–145                                       | 250–265                                        | 215–230                                          | 215–230                                        | 191–208                                        | 193–212                                        |
| <i>E</i> <sub>act</sub> , kcal/mol       | 38.18                                         | 49.64                                          | —                                                | 50.50                                          | 43.51                                          | 39.18                                          |
|                                          | ± 0.84                                        | ± 0.49                                         |                                                  | ± 1.56                                         | ± 0.25                                         | ± 0.20                                         |
| <i>E</i> <sub>act</sub> , kJ/mol         | 160 ± 3.5                                     | 208 ± 2.1                                      | —                                                | 211 ± 6.5                                      | 182 ± 1.0                                      | 164 ± 0.8                                      |
| Δ <i>U</i> <sub>comb.</sub> , cal/g      | -2672.1                                       | —                                              | -3058.4                                          | —                                              | -3178.9                                        | —                                              |
| Δ <i>U</i> <sub>comb.</sub> , J/g        | -11180                                        | —                                              | -12796                                           | —                                              | -13301                                         | —                                              |
| Δ <i>H</i> <sub>comb.</sub> , kcal/mol   | -897.3                                        | —                                              | -1013.6                                          | —                                              | -1094.5                                        | —                                              |
| Δ <i>H</i> <sub>comb.</sub> , kJ/mol     | -3754                                         |                                                | -4241                                            |                                                | -4579                                          |                                                |
| Δ <i>H</i> <sub>f</sub> , kcal/mol       | +247.8                                        | +98                                            | +90.9                                            | +104                                           | +169.4                                         | +257                                           |
| Δ <i>H</i> <sub>f</sub> , kJ/mol         | +1037                                         | +410                                           | +380                                             | +435                                           | +709                                           | +1075                                          |
| Density, g/cm <sup>3</sup>               | 1.624                                         | 1.538                                          | 1.559                                            | 1.540                                          | 1.599                                          | 1.602                                          |
| Impact sensitivity, J                    | 3                                             | 32                                             | >40                                              | 15                                             | 4                                              | 4                                              |
| Friction sensitivity, N                  | 12(+)                                         | >360(-)                                        | >360(-)                                          | >360(-)                                        | >360(-)                                        | 60(+)                                          |
| Detonation pressure, GPa                 | 215.6                                         | 154                                            | 181.4                                            | 165.6                                          | 204.5                                          | 241.7                                          |
| Detonation velocity, m/s                 | 7201                                          | 6192                                           | 6690                                             | 6418                                           | 7045                                           | 7654                                           |

Data source: [1031].

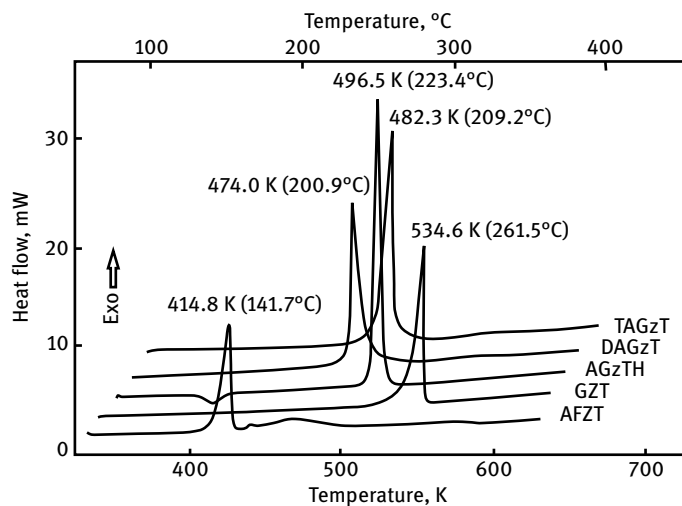
**14.10.5.4 Thermal Stability, Decomposition, and Compatibility of TAGzT**

STMBMS and FTICR methods were used to examine the thermal decomposition of the mixtures of TAGzT and RDX [1045]. Hydrazine that is formed in the decomposition of TAGzT undergoes a very strong and rapid reaction with RDX. At temperatures near the melting point of RDX, the reaction rate of hydrazine with RDX is faster than the rate of decomposition of RDX by itself. The main interaction between hydrazine and RDX involves the removal of the NO<sub>2</sub> groups from RDX and their reaction with hydrazine to form primarily H<sub>2</sub>O and N<sub>2</sub>O. Since the reaction of hydrazine with RDX is rapid compared to the decomposition of RDX alone, compounds that decompose to form hydrazine at a temperature near the decomposition temperature of the nitramine ingredient should be good burn rate modifiers for nitramine-based composite propellants.

The premature and slow reaction of TAGzT with other propellant ingredients such as RDX may limit the useful life of composite propellants. Using computational chemistry, attempts have been made to predict such reactions and to simulate the complex

reaction processes that control the behavior of heterogeneous energetic materials in munitions throughout their life cycle [1046].

The thermal decomposition of TAGzT in comparison to several other azotetrazolate salts was investigated by DSC [1031]. Figure 24 shows an overlay composite of several thermograms on a common temperature scale for samples heated at a heating rate of 10 K/min. The least stable salt was bis(azidoformamidinium) 5,5'-azotetrazolate (AFZT) and the most stable salt was diguanidinium azotetrazolate (GZT).



**Figure 24:** DSC thermograms of several different 5,5'-azotetrazolate salts. (Reprinted and adapted from [1031], with permission from the ©2005 American Chemical Society; permission conveyed through RightsLink.)

The burning rate, laser ignition, and flash pyrolysis (T-jump/FTIR spectroscopy) characteristics of TAGzT were determined [1047]. It was found that TAGzT exhibits one of the fastest low-pressure burning rates measured to date for an organic compound. Both the decomposition and ignition behavior of TAGzT are dominated by condensed phase reactions. T-jump/FTIR spectroscopy indicated that condensed phase reactions release about 65% of the energy, which helps to explain the high burning rate at low pressure.

Data collected with simultaneous TGA-modulated beam MS and FTICR MS methods were used to construct a general qualitative decomposition model of TAGzT that captures the major steps that control the thermal decomposition of TAGzT [1048]. The analysis showed that four primary reaction pathways control the decomposition of TAGzT. The first pathway describes the initial decomposition of TAGzT to form triaminoguanidine (TAG) in the gas phase and azotetrazolate (AT). The second pathway represents the decomposition of TAG in the gas phase to form ammonia, HCN, N<sub>2</sub>,



and hydrazine. The third pathway is the decomposition of the molecule formed from the AT anion. AT does not evolve as a gas phase product during the decomposition of TAGzT. However, AT eliminates  $N_2$  from each tetrazolate ring, thus leaving the central core ( $C_2H_2N_6$ ) to evolve as a gaseous product. The fourth pathway involves the decomposition of a non-volatile product that forms after the decomposition of TAGzT is complete. Results of the analysis showed that both chemical and physical processes are contributing to the decomposition behavior of TAGzT and that these reaction processes are coupled, non-linear, and complex.

The compatibilities of TAGzT with the main components of propellants were studied by DSC and VST [1049]. Results showed that TAGzT has good or fair compatibility with NC, GAP, polyethylene glycol (PEG), diethylphthalate (DEP), 2-nitrodiphenylamine (2-NDPA), HMX, RDX, and aluminum powder (Al), but poor compatibility with NC+NG, *m*-dihydroxybenzene (resorcinol), and *N*-nitrodihydroxyethylamine dinitrate (DINA). TAGzT had no interactions with DEP, GAP, 2-NDPA, or Al. It had only moderate interactions with NC, HMX, or PEG but intensive interactions with DINA, resorcinol, and RDX [1050].

The thermal decomposition of TAGzT under isothermal and non-isothermal conditions in solid and liquid phases was measured and a relationship between the basicity and the thermal stability of 5,5'-azotetrazole salts was demonstrated [1023]. A boundary of possible existence of 5,5'-azotetrazole salts in terms of the basicity index  $pK_a$  was determined. Gaseous and condensed products of decomposition were analyzed and a mechanism of thermal decomposition of 5,5'-azotetrazole was proposed. The enthalpies of formation of some 5,5'-azotetrazole salts were determined and the most reliable values were chosen based on the analysis of the data obtained and those available in publications. The enthalpy of formation is +1075 kJ/mol (+257 kcal/mol).

#### 14.10.5.5 Strand Burning Rate of TAGzT

It has been shown that the replacement of a portion of RDX with TAGzT in nitramine-based propellant systems leads to a dramatic increase in the overall burning rate of the propellant. Several studies aimed at elucidating the combustion characteristics of TAGzT and its mixtures with RDX have been conducted, and some insight into the burning rate modification mechanisms have been gained as a result. Interestingly, TAGzT has been shown to not detonate at diameters of up to 1 in. Three high-nitrogen compounds [triaminoguanidinium azotetrazolate (TAGzT); 3,6-bis-nitroguanyl-1,2,4,5-tetrazine ( $NQ$ )<sub>2</sub>Tz; bis(triaminoguanidinium) 3,6-bis-nitroguanyl-1,2,4,5-tetrazinate (TAG)<sub>2</sub> ( $NQ$ )<sub>2</sub>Tz] were prepared and characterized for thermal stability, burning rate, sensitivity, and energy content [1051]. TAGzT has one of the fastest burning rates ever measured for an organic compound. 3,6-Bis-nitroguanyl-1,2,4,5-tetrazine has one of the lowest pressure exponents ever measured for a pure organic compound. A low-pressure exponent is usually indicative of condensed phase reactions dominating the combustion process. Table 68 gives

**Table 68:** Comparison of the burning rates and pressure coefficients of TAGzT and other high-nitrogen compounds.

| Compound abbreviation                   | Burning rate at 68 atm = 6.87 MPa |       | Pressure coefficient <i>n</i> |
|-----------------------------------------|-----------------------------------|-------|-------------------------------|
|                                         | cm/s                              | in./s |                               |
| TAGzT                                   | 4.89                              | 1.92  | 0.67                          |
| (NQ) <sub>2</sub> Tz                    | 2.0                               | 0.79  | 0.163                         |
| (TAG) <sub>2</sub> (NQ) <sub>2</sub> Tz | 2.3                               | 0.91  | 0.366                         |
| BTATz                                   | 4.59                              | 1.81  | 0.49                          |
| DAATO3.5                                | 5.39                              | 2.12  | 0.275                         |
| HMX                                     | 2.11                              | 0.83  | 0.84                          |

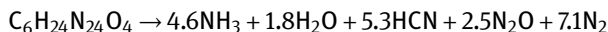
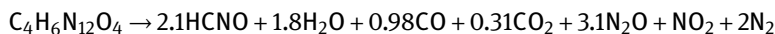
Data Source: [1051].

a comparison of the burning rates and pressure coefficients of TAGzT and other high-nitrogen compounds.

TAGzT has a relatively low theoretical adiabatic decomposition flame temperature of 841 K. T-jump FTIR analysis of TAGzT decomposition products indicates that the decomposition proceeds along the following pathway:



Likewise, the decompositions of (NQ)<sub>2</sub>Tz and (TAG)<sub>2</sub>(NQ)<sub>2</sub>Tz proceed along the following pathways:

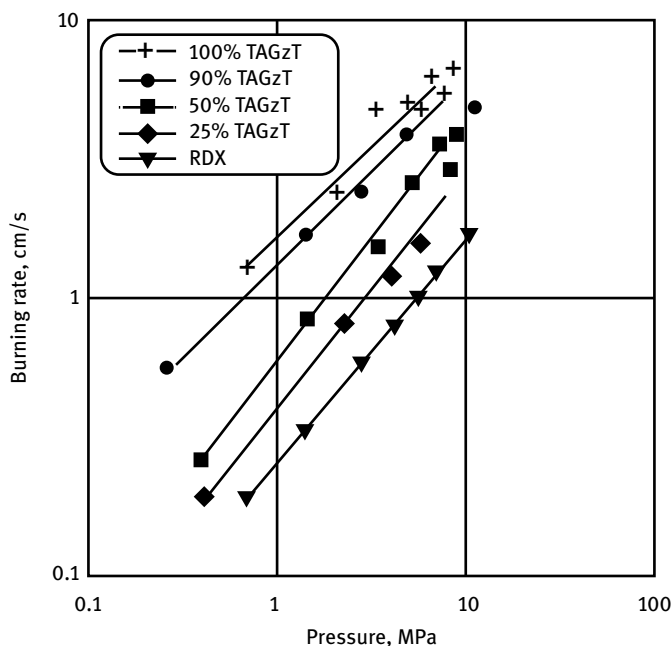


A two-phase combustion model with detailed chemistry for TAGzT with detailed output for burning rates and product distribution was developed and compared with experimental results [1052]. Semi-quantitative agreement was achieved. In particular, the experiments and model agreed that the gas phase flames plateau for long distances above the propellant surface, and equilibrium is not reached.

The common crystalline habit (needle-like structures) of TAGzT is not conducive to high bulk densities, thereby limiting the amount of propellant that can occupy a volume. In addition, the crystal habit of the material presents several challenges with manufacturing processes. Recrystallization of the existing TAGzT needle-like structures to various particle sizes and shapes had to be conducted to try to improve the morphology of the crystals for formulation.

Mixtures of 75, 50, 25, and 10% RDX with TAGzT were mixed with the non-solvent methanol, then stirred, dried, and pressed into 6.6-mm pellets [1053, 1054]. TAGzT can significantly increase the burning rate of RDX. TAGzT and RDX have a synergistic interaction during combustion. A mixture of 10 RDX/90 TAGzT burned five times faster than pure RDX and about 1.2 times faster than pure TAGzT, while having a lower pressure

sensitivity than that of both parent compounds (Figure 25). A mixture of 50 RDX/50 TAGzT had a burning rate of 3.37 cm/s at 6.7 MPa with a slope of 0.91 (which was much too high). The sea level theoretical specific impulse of such a mixture would be 232s at a chamber pressure of 6.7 MPa. This burning rate graph is very useful because it contains the data for the two pure compounds as well as data for their mixtures.



**Figure 25:** Strand burning rates of TAGzT/RDX mixtures. (Reprinted and modified from [1054], with permission from ©2007 Begell House, Inc.)

When tested for detonability, pure TAGzT exhibited no detonation propagation, even at 25.4 mm sample diameter. However, a 50:50 mix of TAGzT and RDX sustained detonation at 12.5 mm. The sensitivity properties of TAGzT and TAGzT/RDX mixtures are summarized in Table 69 in comparison to safety data for HMX.

#### 14.10.5.6 Sensitivity of TAGzT

Tables 69 and 70 provide a comparison of the sensitivity parameters of TAGzT with those of the other compounds tested and some literature data. Because TAGzT contains no oxygen, the chemistry that dominates the ignition and combustion is more centered on reactions in the condensed phase rather than on the C + O or H + O oxidation chemistry that takes place in the gas phase. The enthalpy of formation of TAGzT is +1075 kJ/mol = +257 kcal/mol. The burning rate of TAGzT was found to be one of the fastest burning compounds known to exist (Table 71), comparable to the high-nitrogen

**Table 69:** Sensitivity parameters of TAGzT in comparison with those of other energetic compounds.

| Compound abbreviation                   | Impact sensitivity, 50% point | DSC exotherm onset |       | Friction sensitivity |                 | Spark sensitivity |
|-----------------------------------------|-------------------------------|--------------------|-------|----------------------|-----------------|-------------------|
|                                         | cm                            | K                  | °C    | N                    | kg <sub>f</sub> | J                 |
| TAGzT                                   | 25                            | 468                | 195   | 981                  | 10.0            | 0.312             |
| (NQ) <sub>2</sub> Tz                    | 65                            | 501                | 228   | >353                 | >36             | >0.36             |
| (TAG) <sub>2</sub> (NQ) <sub>2</sub> Tz | 114                           | 439                | 166   | >353                 | >36             | >0.36             |
| BTATz                                   | 32                            | 537                | 264   | >353                 | >36             | <0.36             |
| DAATO3.5                                | 50                            | 450                | 177   | 19.6–137             | 2–14            | fails             |
| HMX                                     | 25                            | 523                | 249.9 | 133                  | 13.6            | >0.36             |

Data Source: [1051].

**Table 70:** Sensitivity properties of TAGzT and a TAGzT/RDX mixture.

| Compound abbreviation | Impact sensitivity <sup>a</sup> , 50% point | DSC, onset of exotherm |     | Friction sensitivity | Spark sensitivity |
|-----------------------|---------------------------------------------|------------------------|-----|----------------------|-------------------|
|                       | cm                                          | K                      | °C  | N                    | J                 |
| TAGzT                 | 25                                          | 468                    | 195 | 98                   | 0.312             |
| 50% TAGzT/50% RDX     | 18.9                                        | 440                    | 167 | 80                   | >0.36             |
| HMX                   | 22.4                                        | 523                    | 250 | 133                  | >0.36             |

<sup>a</sup> Drop weight mass was not listed

Data source: [1054].

compounds 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-3,5-*N*-oxide (DAATO<sub>3.5</sub>) and 3,6-bis-(1*H*-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz). However, despite its remarkable combustion behavior and the fact that it has a high calculated detonation performance, it has not been found to be sensitive to shock initiation and transition to detonation, even at diameters as large as 4.1 cm (1 5/8 in.). In a large-scale gap test, and with a 4.1 cm D × 10 cm H (1.625 in. D × 4 in.) donor charge of PBX9205, the TAGzT did not detonate. The witness plate showed no dent and traces of unreacted TAGzT were found. This insensitivity to shock initiation is all the more intriguing because of TAGzT's sensitivity to impact and friction (which is roughly similar to that of HMX). Speculation into the mechanism of this behavior is open to discussion [1055]. Table 71 provides a comparison of the sensitivities and detonation velocities of TAGzT and other energetic materials.

A summary of energetic materials published lists the properties and methods for the preparation of AZT, guanidinium azotetrazolate (GuZT), and triaminoguanidinium azotetrazolate (TAGzT) [1056]. TAGzT has the advantage of being able to reduce the combusting temperature, enhancing the burning rate of propellants, and producing a lot of gas. GuZT, with the advantages of reducing the combusting temperature and producing relatively cool gases, has been widely used in gas generators.

**Table 71:** Comparison of the sensitivities and burning rates of TAGzT and other energetic materials.

| Compound abbreviation | Impact sensitivity, | DSC exotherm |       | Friction sensitivity |                 | Spark sensitivity | Burning rate at | Burning rate |
|-----------------------|---------------------|--------------|-------|----------------------|-----------------|-------------------|-----------------|--------------|
|                       | 50% point           | onset        |       |                      |                 |                   | 1000 psi        | exponent     |
|                       | cm                  | K            | °C    | N                    | kg <sub>f</sub> | J                 | cm/s            |              |
| TAGzT                 | 25                  | 468          | 195   | 98.1                 | 10.0            | 0.312             | 4.89            | 0.67         |
| BTATz                 | 32                  | 537          | 264   | >353                 | >36             | <0.36             | 4.59            | 0.49         |
| DAATO3.5              | 50                  | 450          | 177   | 19.6–137             | 2–14            | <0.36             | 5.39            | 0.275        |
| HMX                   | 25                  | 523          | 249.9 | 133                  | 13.6            | >0.36             | 2.11            | 0.84         |

Data Source: [1055].

#### 14.10.5.7 Applications of TAGzT

Originally, TAGzT was proposed as a source of nitrogen in pyrotechnic fire extinguishers that snuff out fires by depriving them of oxygen from the air [925, 926, 1042]. Interest has since shifted to its ability to increase the burning rate of many propellant formulations, particularly those containing nitramines.

Burn-rate modeling is critical for developing new rocket missile and gun propellants and for providing a fundamental screening tool that can result in substantial cost savings compared to missile and gun firings. The detailed chemical kinetics and the burn rate prediction of TAGzT and NC were applied to several burner-stabilized flames relevant to the combustion of solid propellants to calculate the burning rates of TAGzT, with and without a nitrate ester-based propellant [1057, 1058]. The model employed a detailed, chemical reaction mechanism containing 59 species and 368 reactions. Calculations showed that TAGzT enhances the burning rate of the base propellant over a range of pressures used for rockets and guns by a factor of three at 10 MPa.

Triaminoguanidinium 5,5'-azotetrazolate has been included in the NILE (Navy insensitive low-erosion) gun propellant mixture to reduce barrel wear. This propellant was developed at the NSWC-IHD. The NILE mixture was successfully tested as a propellant in, for example, a 105-mm howitzer [1059].

#### 14.10.6 Bis(semicarbazidium) 5,5'-Azotetrazolate

The metathesis reactions between sodium 5,5'-azotetrazolate ( $[\text{Na} + ]_2\text{ZT}^{2-}$ ) pentahydrate and 1,3-dimethyl-5-aminotetrazolium iodide, or semicarbazidium chloride in water, lead to the formation of the corresponding  $\text{ZT}^{2-}$  salts as the hydrated species **(2)** and **(4)** [1060]. The anhydrous derivatives **(1)** and **(3)** were synthesized by reaction of silver 5,5'-azotetrazolate with a suitable halogenide salt in methanol. Alternatively, the crystal water in the hydrated salts **(2)** and **(4)** can be quantitatively but slowly removed under a vacuum. This leads to a safe synthesis for compounds **(1)** and **(3)**, which does not depend on the use of highly sensitive silver salts. The formation of the salts was confirmed by analytical and spectroscopic methods. In addition to this,

the crystal structures of **(2)** and **(4)** were determined using low-temperature XRD and found to be as follows **(2)**: monoclinic  $P_2(1/n)$ ,  $a = 9.3101(3) \text{ \AA}$ ,  $b = 6.5383(2) \text{ \AA}$ ,  $c = 19.5637(5) \text{ \AA}$ ;  $\beta = 90.48(1)^\circ$ ;  $V = 1190.84(6) \text{ \AA}^3$ , and **(4)**: triclinic  $P\bar{1}$ ,  $a = 4.563(5) \text{ \AA}$ ,  $b = 7.362(5) \text{ \AA}$ ,  $c = 11.334(5) \text{ \AA}$ ;  $\alpha = 105.125(5)^\circ$ ,  $\beta = 90.48(1)^\circ$ ,  $\gamma = 102.871(5)^\circ$ ;  $V = 357.2(5) \text{ \AA}^3$ . Unfortunately, the semicarbazidium salts **(3)** and **(4)** have relatively low thermal stabilities ( $<403 \text{ K} = <130^\circ\text{C}$ ) and the tetrazolium salts **(1)** and **(2)** decompose above  $463 \text{ K} = 190^\circ\text{C}$ . All four compounds can be classified as insensitive and have good explosive performances: **(1)**  $P = 19.0 \text{ GPa}$  and  $v_{\text{det.}} = 7667 \text{ m/s}$ ; **(2)**  $P = 25.1 \text{ GPa}$  and  $v_{\text{det.}} = 8585 \text{ m/s}$ ; **(3)**  $P = 23.4 \text{ GPa}$  and  $v_{\text{det.}} = 8125 \text{ m/s}$ ; and **(4)**  $P = 20.0 \text{ GPa}$  and  $v_{\text{det.}} = 7694 \text{ m/s}$ . All release (mainly) environmentally benign gases when they decompose.

#### 14.10.7 Bis(azidoformamidinium) 5,5'-Azotetrazolate

Bis(azidoformamidinium) 5,5'-azotetrazolate (AFZT),  $\text{C}_4\text{H}_8\text{N}_{20}$ ,  $[\text{H}_2\text{N}^+=\text{C}(\text{N}_3)\text{NH}_2]_2=[\text{AT}^{2-}]$ ,  $M = 336.24 \text{ g/mol}$ , 83.31% N, OB = -57.1%, can be prepared by the reaction of the respective azidoformamidinium nitrate with a hot aqueous solution of Na2AT followed by the fractional crystallization of the azotetrazolate [1031]. An alternate method is the diazotization of aminoguanidinium 5,5'-azotetrazolate (AGZTH), where ethyl nitrite is slowly added to a warm solution ( $313 \text{ K} = 40^\circ\text{C}$ ) of AGZTH in water. The solution was kept at  $313 \text{ K} = 40^\circ\text{C}$  for 1 h and then cooled to  $278 \text{ K} = 5^\circ\text{C}$ . Orange AFZT crystals were obtained, separated by filtration, and washed with EtOH and Et<sub>2</sub>O. During the crystallization process, the formation of nitrogen was observed. The physical and sensitivity properties of AFZT in comparison to several other azotetrazolate salts have already been summarized in Table 67. AFZT melts at  $407 \text{ K}$  ( $134^\circ\text{C}$ ) with decomposition. The thermal decomposition of AFZT in comparison to several other azotetrazolate salts was investigated by DSC. Figure 24 demonstrates an overlay composite of several thermograms on a common temperature scale for samples heated at a heating rate of  $10 \text{ K/min}$ . The least stable salt was AFZT, and the most stable salt was GZT.

#### 14.10.8 5,5'-Azotetrazolates of Heterocyclic Cations

The preparation of 1,3-dimethyl-5-aminotetrazolium 5,5'-azotetrazolate was already described in a previous section. Salts of 5,5'-azotetrazolate with 5-aminotetrazole and 2,4,6-triamino-s-triazine cations were synthesized and evaluated as potential ingredients for gun propellants [1061]. These salts were characterized by density measurement, NMR and IR spectroscopy, and DSC. In the DSC, 5-aminotetrazolium 5,5'-azotetrazolate began to decompose at  $407.4 \text{ K} = 134.3^\circ\text{C}$  with a peak exotherm at  $443 \text{ K} = 170^\circ\text{C}$ . 2,4,6-Triamino-s-triazinium 5,5'-azotetrazolate began to decompose at  $521.4 \text{ K} = 248.3^\circ\text{C}$  with a peak exotherm at  $543 \text{ K} = 270^\circ\text{C}$ . Their reactions to mechanical stimuli were also determined by small-scale sensitivity testing, small-scale shock reactivity testing, and small-scale internal blast testing.

#### 14.10.9 Other Azotetrazole Derivatives

Attempts have been made (at least on paper) to improve the stability of azotetrazole by adding stabilizing substituents to one or both of the tetrazole rings. It was hoped that such substitutions would result in a more stable resonance structure of the electron cloud-connected via the  $\text{—N=N—}$  bridge.

The potential curves of the decomposition of 1-methyl-5-azotetrazole (1-MAT) and 2-methyl-5-azotetrazole (2-MAT) were calculated by a quantum chemistry method [1062]. The activation energies of decomposition are 245.9 and 183.2 kJ/mol, respectively. Thermal stability and decomposition mechanisms have been studied based on ground state and dynamic conditions. The calculated results indicated that the thermal stability of 1-MAT is better than that of 2-MAT. Ring-opening is the first step in decomposition.

The properties of 1,1'-dimethyl-5,5'-azotetrazole (DMATA) and its influence on the theoretical specific impulse, burning rate, pressure exponent, and chemical stability of modified double-base propellants have been studied [1063]. It was discovered that DMATA may increase the specific gas volume and burning rate of propellants.

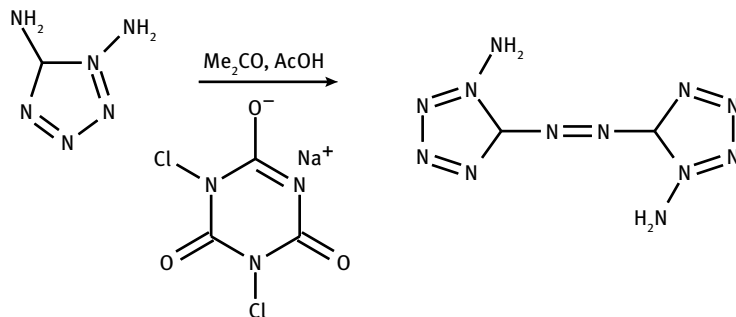
The potential curves of thermal decomposition for 1,1'-dimethyl-5, 5'-azotetrazole (1,1'-DM-5,5'-AT) and 2,2'-dimethyl-5,5'-azotetrazole (2,2'-DM-5,5'-AT) were calculated by use of *ab initio* calculation by a quantum chemistry method and the activation energies of two-step decomposition reactions were predicted [1064]. The ring-opening reaction controls the decomposition rate. The predicted thermal stability of 1,1'-DM-5,5'-AT is better than that of 2,2'-DM-5,5'-AT. The structures of 1,1'-DM-5,5'-AT and 2,2'-DM-5,5'-AT are planar, the bond lengths in the tetrazole rings have aromatic characteristics, and the tetrazole ring satisfies the  $4n+2$  rule [1064]. The calculated aromaticity index, net charge in the ring, and relation energy of electrons revealed that the predicted thermal stability of 1,1'-DM-5,5'-AT is better than that of 2,2'-DM-5,5'-AT, in accordance with experiment results [1065, 1066].

To prepare for the eventual future synthesis of an as yet unknown 2,2'-bis-(trinitromethyl)-5,5'-azotetrazole compound, a DFT method was used to calculate the molecular structure [1067]. Its properties, such as its electronic structure, IR spectrum, HOF, thermodynamic properties, and crystal structure were predicted by computer. This compound is most likely to crystallize in the  $P2_1$  space group, and the corresponding cell parameters would be  $a = 5.46 \text{ \AA}$ ,  $b = 9.72 \text{ \AA}$ ,  $c = 14.05 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ , and  $Z = 2$ . The detonation velocity and pressure were also estimated by using the empirical K-J equations and were predicted to be 8.28 km/s and 31.61 GPa respectively. The oxygen balance of this compound is +13.79%, which indicates that it could serve as an oxidizer. BDE calculations showed that the  $\text{C(13)—N(21)O}_2$  and  $\text{C(14)—N(30)O}_2$  bonds are the weak bond locations where thermal decomposition is likely to start.

The structures, IR spectra, and cation stability of guanidinium (GuZT), aminoguanidinium (AGZT), diaminoguanidinium (DAGZT), triaminoguanidinium

(TAGZT), azidoformamidineum (AFZT), ammonium (AZT), and hydrazinium (HZT) 5,5'-azotetrazolate were investigated by dynamic functional theory calculations [1068]. The calculated results indicated that the carbon and nitrogen atoms of the cations in seven non-metallic salts are  $sp^2$  hybrid atoms, and the ranges of characteristic absorption peaks in IR spectra of the seven non-metallic salts were approximative consistent. All their cations are stable, and their stabilities decreased with the increase in their nitrogen contents. To characterize their infrared spectra, the frequency analytical calculations were performed for the seven salts at the same level of theory. The cation decompositions of seven salts were calculated to predict the cation stability.

1,1'-Diamino-5,5'-azotetrazole, which was obtained from the reaction of 1,5-diaminotetrazole with acetone, sodium dichloroisocyanurate, and acetic acid, respectively, was well characterized [1069]. Its structure was confirmed by X-ray crystallography and the thermal stability and explosive performance were also investigated.

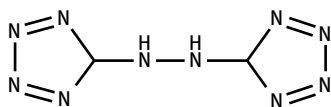


1,1'-Diamino-5,5'-azotetrazole, also known as 5-[(1-amino-1 $\lambda$ 5,2,3,4-tetrazacyclopenta-1,3-dien-5-yl)azo]-1 $\lambda$ -5,2,3,4-tetrazacyclopenta-1,3-dien-1-amine,  $C_2H_6N_{12}$ , DAZT, can be synthesized using acetic acid and 1,1'-diisopropylideneamino-5,5'-azotetrazole as the raw material [1070]. The maximum yield was 97.6% under optimum reaction conditions. The thermal decomposition behavior of DAZT was investigated by TG-DSC and DTA techniques. In the DTA at  $5^\circ/\text{min}$ , the melting endotherm was at 427–439 K (154–166  $^\circ\text{C}$ ), and the peak temperature was 432.94 K (159.79  $^\circ\text{C}$ ) with no obvious mass loss, and the melting enthalpy was 72.35 J/g. The exotherm was at 439–458 K (166–185  $^\circ\text{C}$ ) with a peak temperature of 451.91 K (178.76  $^\circ\text{C}$ ) and a decomposition enthalpy of 1024.83 J/g. The activation energy of decomposition was 138.57 kJ/mol.



### 14.11 Hydrazotetrazole Derivatives

Hydrazotetrazole, also known as 1,2-bis(5*H*-tetrazol-5-yl)hydrazine, is a hydrazine derivative with two tetrazolyl rings attached to two opposite nitrogen atoms. This compound has also been called 1,2-ditetrazolylhydrazine or 5,5'-hydrazinebistetrazole or bistetrazolohydrazine or *N,N'*-bistetrazolohydrazine but these are not the correct names.



5,5'-Hydrazotetrazole

The enthalpy of formation of 5,5'-hydrazotetrazole,  $C_2H_4N_{10}$ ,  $M = 168.12$  g/mol, is  $+804$  cal/g =  $+135$  kcal/mol =  $+565$  kJ/mol. It contains 83.3% nitrogen. The density of 5,5'-hydrazotetrazole is  $1.841$  g/cm<sup>3</sup> and the predicted detonation velocity is  $8523$  m/s with a detonation pressure of  $27.7$  GPa.

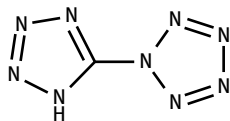
Solutions of *N,N'*-azobistetrazolate salts in anhydrous hydrazine were reduced to salts of *N,N'*-bistetrazolohydrazine [1071]. Several salts of this highly energetic, nitrogen-rich anion were prepared this way and characterized by elemental analysis, IR, and Raman and multi-nuclear NMR spectroscopy.

In the DSC, and with a heating rate of  $5^\circ/\text{min.}$ , 5,5'-hydrazotetrazole began to decompose at  $483$  K ( $210^\circ\text{C}$ ). It decomposed violently at  $506$  K ( $233^\circ\text{C}$ ) [1072], which was its peak temperature also. The enthalpy of reaction was  $632.1$  J/g. The activation energy of 5,5'-hydrazotetrazole decomposition was  $230.8$  kJ/mol and the pre-exponential factor was  $3.43 \times 10^{23} \text{ s}^{-1}$ . The decomposition enthalpy of HBT was  $576.45$  J/g when the heating rate was  $5^\circ/\text{min.}$  In the TGA, the maximum weight loss temperature was from  $493$  to  $506$  K ( $220$  to  $233^\circ\text{C}$ ) with heating rates from  $2$  to  $20^\circ\text{C}/\text{min.}$

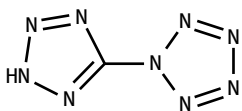
Most 5,5'-hydrazinobistetrazole derivatives reported in the literature are sensitive to oxidation and react with atmospheric oxygen to yield the corresponding 5,5'-azobistetrazolates as time goes by. A free acid 5,5'-hydrazinobistetrazole (HBT) was prepared which seemed to be stable on air for extended periods of time [1073]. The compound was fully characterized by analytical and spectroscopic methods and its structure was determined by XRD. The HOF is  $+414$  kJ/mol. The predicted detonation velocity is  $8523$  m/s and the detonation pressure is  $27.7$  GPa. It has a low impact sensitivity of  $>30$  J, friction sensitivity of  $\sim 108$  N, and was used as a starting material for the synthesis of other 5,5'-azobistetrazolates [551, 1074, 1075].

A series of nitrogen-rich molecules, such as hydrazinobistetrazole, 5-aminotetrazolium nitrate, bis(2,2,2-trinitroethyl)-hydrazodicarboxylate, RDX, TNT, melamine, sucrose, and L-glutamine were studied using laser-induced breakdown spectroscopy





1-(1H-tetrazol-5-yl)pentazole

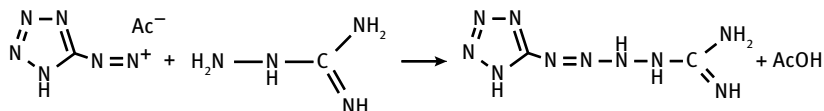


1-(2H-Tetrazol-5-yl)pentazole

Tetrazolylpentazole was identified as an intermediate in the reaction of tetrazolediazonium chloride with lithium azide by low-temperature  $^{15}\text{N}$  NMR spectroscopy. The decomposition of  $^{15}\text{N}$ -labeled tetrazolylpentazole to form  $^{15}\text{N}$ -labeled tetrazole azides and dinitrogen was followed by low-temperature  $^{15}\text{N}$  NMR spectroscopy. The structures of the species involved in this decomposition were optimized by computational methods at different levels of theory, and the structures of the transition states and the activation barriers for the decomposition were identified. The stability of tetrazolylpentazole and its corresponding anion pentazolyltetrazolate was calculated to be 63–67 kJ/mol (15–16 kcal/mol) and 88–92 kJ/mol (21–22 kcal/mol), respectively, and was later found by a different method to be more like 48 kJ/mol (11.4 kcal/mol) and 74 kJ/mol (17.7 kcal/mol), respectively [862, 1079]. The activation energy for the decomposition increased while the decomposition energy of the substituted pentazole decreased with greater electron-donating character of the substituent of the pentazole. Thus, anionic pentazoles were predicted to be more stable than neutral pentazoles. Methylpentazole was predicted to be among the most stable pentazoles even though it does not contain an aromatic system.

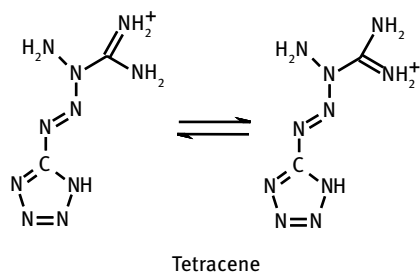
High-nitrogen compounds such as 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-s-tetrazine (BTATz) or mixed *N*-oxides of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAATO3.5) can be used as working fluids in electrical discharge micro-thrusters [1080].

Aminoguanidine is a useful intermediate for numerous high-nitrogen compounds. Aminoguanidinium sulfate or aminoguanidinium hydrogen carbonate and sodium nitrite react in a solution slightly acidified with acetic acid to form “tetracene” through aminotetrazole and its diazo salt [1081, 1082]:



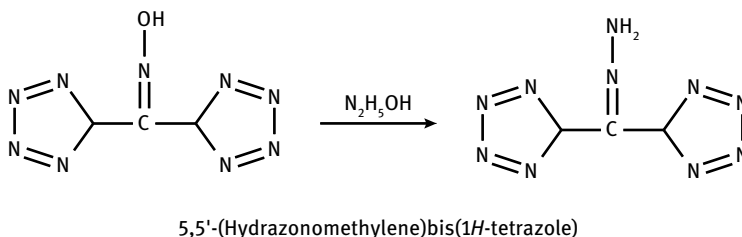
The more accurate designation for this compound is 1-(5-tetrazolyl)-4-guanyltetrazene. It forms shock-sensitive heavy-metal salts with silver or copper.

Tetracene (tetrazene), 1-[2-(1*H*-tetrazol-5-ylimino)hydrazino]guanidine, 4-(1*H*-tetrazol-5-yl)tetraaz-1-ene-1-carboximidamide,  $C_2H_6N_{10}$ , CAS RN [539-57-1],  $M = 170.136$  g/mol, is a hydrazine-derived primary explosive with a strongly positive enthalpy of formation ( $+1005$  kJ/kg =  $+189$  kJ/mol). Tetracene is slightly more impact-sensitive than mercury fulminate. The molecular structure of tetracene, a primary explosive with a tetrazole ring, had been the subject of many debates until a more detailed X-ray and molecular structure study was conducted [1083] and was supported by Complete Neglect of Differential Overlap (CNDO) quantum-mechanical calculations [1084] that showed that the primary explosive tetracene exists in the solid state as the zwitterion form of 1-amino-1[(1*H*-tetrazol-5-yl)azo]guanidine hydrate.

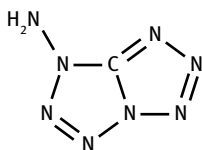


The positive charge can be on either of the two nitrogen atoms or even on the carbon atom of the guanidinium group. This resonance structure gives the compound unusual stability; thus both the Hofmann [1085] and Patinkin [1081] structures are wrong. The thermal decomposition of tetracene was modeled by computer calculations [1086].

A family of nitrogen-rich energetic tetrazoles, di(1*H*-tetrazol-5-yl)methanone oxime and 5,5'-(hydrazonomethylene)bis(1*H*-tetrazole), was synthesized from inexpensive starting materials [1087]. These tetrazoles had excellent thermal stabilities and very high nitrogen contents as well as acceptable impact and friction sensitivities and were employed as precursors to nitrogen-rich energetic salts. The hydrazinium and hydroxyl ammonium salts of 5,5'-(hydrazonomethylene)bis(1*H*-tetrazole) exhibited excellent detonation velocities (9050 and 8839 m/s, respectively) as well as very good detonation pressures and thermal stabilities.



A not yet synthesized 8-N conjoined energetic compound 1-amino-tetrazolo-[4,5-b]tetrazole, tetrazolo[1,5-e]tetrazol-4-amine has been designed using a DFT method on a computer [1088]. It looks promising when seen on the computer screen, however, the question arises of whether it can actually be synthesized? The optimized geometry, vibration analysis (including thermochemistry and IR spectrum), NMR data, NBOs and charges, and the electrostatic potential were calculated in order to inspect the electronic structure properties and interactions of chemical bonds. Properties such as density, enthalpy of formation considering the enthalpy of phase transition and detonation performance could be predicted. The detonation velocity and pressure of this compound were predicted to be 8.90 km/s and 33.83 GPa, respectively. The compound had a highly positive HOF (+792 kJ/mol = +189 kcal/mol) but the question arose of whether it will decompose before it can be synthesized?



1-Amino-tetrazolo-[4,5-b]tetrazole

#### 14.13.1 Polymeric Tetrazole Derivatives

5-Phenyl-1H-tetrazole can be obtained from phenylcyanide and sodium azide with trimethylammonium chloride [184]. Instead of azido groups in GAP (poly[(azidomethyl)ethylene oxide], GAP), similar energetic binders can be obtained by attaching tetrazolyl groups to the polymer chain by a Diels-Alder reaction. A new, safe, and sustainable process to produce tetrazoles was designed; it achieved high yields under mild conditions.

Nitrogen-rich polymers can be obtained either by radical polymerization (poly(methyl-1-(1-vinyl-1H-tetrazol-5-yl)hydrazine)) or polycondensation reactions [1089]. The nitrogen-rich polymers prepared by polycondensation reactions of the 1,1-methyl-1H-tetrazolylhydrazine possessed high thermal stability (> 513 K = > 240 °C) and were insensitive towards impact and friction. The advantage of these polymers is that the

functional groups are stabilized by the formed carbamates, reducing the chemical reactivity. Nevertheless, the NH-proton of the carbamate structure was able to form hydrogen bridges, leading to increased adhesion forces between the energetic filler and the polymer. The energetic polymers formed by radical polymerization bears hydrazine moieties that increase the solubility in acids, along with possible adhesion forces with energetic fillers. The 5-azido-1*H*-tetrazoles were prepared by diazotation of tetrazolyl hydrazines.

A polyvinyl(tetrazole) can be formed by a water-based method and used as gas generant for the inflation of airbags [1090]. Preferred vinyl tetrazoles include 5-amino-1-vinyltetrazole, poly(5-vinyltetrazole), poly(2-methyl-5-vinyltetrazole), and poly(1-vinyltetrazole).

Miscible polymer pairs can be formed with an energetic polymer, such as poly(2-methyl-5-vinyl tetrazole) (PMVT), and a non-energetic polymer PEG with the molecular mass (weight) of between 1000 to 4000. This polymer blend (PEG/PMVT) can be formed from an acetonitrile solution upon removal of the solvent in which both polymers were soluble [1091]. The blend can also be precipitated by adding non-solvent-like hexane to a solution of PEG/PMVT in acetonitrile at or below 0°C. With PEG E1000, blends have been formed with PEG:PMVT ratios of 1:1 to 1:1.8 by weight. This blend has been characterized with regard to its unique glass transition temperature,  $T_g$ , as well as its ability to form transparent films. Interaction between chains in the form of weak C—H...O hydrogen bonding has been identified from IR band broadening. A PMVT/GAP polymer blend can also be formed in a narrow range of temperatures. This polymer blend is useful as a desensitizing energetic binder for propellants and PBX. A PBX composition containing 91 mass-% RDX and 9% PEG-PMVT polymer blend had a drop-weight-impact sensitivity better than Comp B.

Poly(5-amino-1-vinyl) tetrazole and poly(2-methyl-5-vinyltetrazole) are nitrogen-rich polymers that have been patented as nitrogen-rich energetic binders for solid propellants and gas generants [1092]. Poly(methylvinyltetrazol), PMVT,  $(C_4N_4H_6)_n$ , is a high-enthalpy polymer with high nitrogen content (~46%N). It has an enthalpy of formation of  $\Delta H_f = +1255 \text{ kJ/kg}$  and a density of  $\rho = 1.28 \text{ g/cm}^3$ .

#### 14.13.2 Record-Length Catenated Nitrogen Chains in Heterocyclic Compounds

As an outgrowth of the development effort of high-nitrogen and high-energy compounds, a competitive effort has been started to synthesize molecules with very long chains of catenated nitrogen atoms. In most cases, these chains are stabilized by aromaticity in the participating rings. The rings are mostly five-membered rings and, at the time of writing this, the maximum number of nitrogens arranged in one “hand-holding” sequence is eleven.

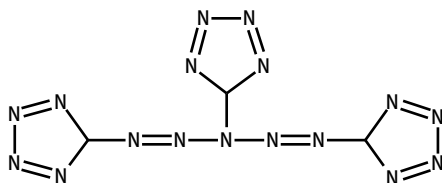
The construction of a catenated nitrogen chain of eight nitrogen atoms was achieved through the oxidative azo coupling of an N—NH<sub>2</sub> moiety. The amino group

attached to a triazole ring was first transformed into a diazonium ion under acidic conditions. A subsequent nucleophilic attack of the amino group of the 1-amino-1,2,3-triazole on this diazonium cation produced the desired structure containing eight catenated nitrogen atoms. The resulting N8 compound, 1,1'-azobis-1,2,3-triazole, had a nitrogen content of 68.27% [258].

The synthesis of N10 has already been described in preceding chapters [999, 1000]. Based on the thermal decomposition mechanism of N10, the probability of being successful in attempting to synthesize N12 and N14 was explored. These longer nitrogen chain compounds that have higher nitrogen contents than N10 would make good HEDMs. By comparing their energetic barriers with the corresponding primary N<sub>2</sub>-elimination reaction of N10, it was concluded that the predicted structures could theoretically exist at room temperature. As a first step in this direction, a stable catenated N11 salt has been synthesized by an azo coupling reaction from 1,5-diaminotetrazole [1001]. Researchers have synthesized heterocyclic compounds with highly catenated chains of nitrogen atoms through a strategy of oxidative azo coupling of N—NH<sub>2</sub> moieties [1093].

It is difficult to predict the exact number of nitrogen atoms that will finally be the limit to the catenated nitrogen atom chains, but indications are that the recent advances in the synthesis of such extended nitrogen chains will definitely open new methods for the synthesis of new high-nitrogen materials [1094]. Computational work by theoreticians is setting the stage to guide the hands of synthetic chemists.

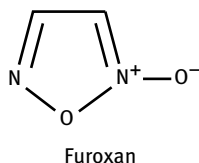
An N5-linear energetic moiety of pentazadiene has been constructed from a triazene precursor. Thus, a series of 1,3,5-tri(tetrazol-5-yl)pentaza-1,4-dienes have been synthesized in moderate to high yields by treatment of 1,3-bis(tetrazol-5-yl)-triazenes with 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride under mild conditions. All compounds were fully characterized using IR spectroscopy, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and DSC. Calculations predicted that the methyltetrazole homolog has a HOF of 1699 kJ/mol.



## 15 Furoxans and Oxazoles

### 15.1 Furoxan

Furoxan, 1,2,5-oxadiazole 2-oxide, furazan 2-oxide, CAS RN [497-27-8],  $M = 86.049$  g/mol, is a heterocycle of the isoxazole family and an amine *N*-oxide derivative of furazan.



Furoxan and its derivatives are actively researched as potential high-density explosives. Furoxans can be formed by the dimerization of nitrile oxides. Many energetic compounds have been examined that have other rings attached to the furoxan ring [1095].

Aminonitrobenzodifuroxan can be synthesized from 3,5-dinitrobenzoic acid [1096]. Another energetic furoxan is 3,4-dinitrofurazanofuroxan, which was crystallized from acetone and water, and was characterized by XRD, elemental analyses, and FTIR [1097]. The crystals were orthorhombic, space group *P*222, with crystal unit cell parameters of  $a = 1.0746(7)$  nm,  $b = 1.5099(10)$  nm,  $c = 0.6596(4)$  nm,  $V = 1.0702(1)$  nm<sup>3</sup>,  $Z = 4$ , and  $\rho_{\text{XRD}} = 1.937$  g/cm<sup>3</sup>.

### 15.2 Furazans

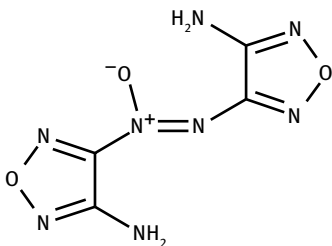
Furazans derive their name from furan by replacing one or two  $-\text{CH}=\text{}$  groups in the five-membered ring with  $-\text{N}=\text{}$  atoms. The oxygen atom remains in the ring. Various methods for the synthesis of high-energy-density compounds were published that included the use of aminofurazan as the precursor. Oxidation, nitration, diazotization, condensation, and nucleophilic displacement reactions were used to reinforce the energy content of the molecule.

Furazan, 1-oxa-2,5-diazole, CAS RN [288-37-9], is a heterocyclic aromatic organic compound consisting of a five-atom ring containing one oxygen and two nitrogen atoms. It boils at  $371\text{ K} = 98^\circ\text{C}$ . Furazan and its derivatives can be obtained from the oxime derivatives of 1,2-diketones.

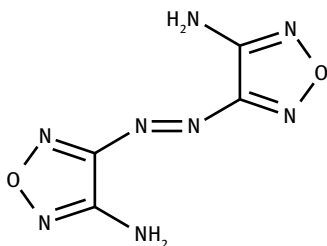
3,4-Diaminofurazan, 1,2,5-oxadiazole-3,4-diamine, DAF, has been an important precursor to a series of furazan-based HEDMs that are of interest as both propellant and explosive ingredients. This compound has already been described in an earlier section in this chapter.



The oxidation of DAF with  $\text{H}_2\text{O}_2$  yields 4,4-diamino-3,3-azoxyfurazan,  $\text{C}_4\text{H}_4\text{N}_8\text{O}_3$ , DAAF, CAS RN [78644-89-0],  $M = 212.126 \text{ g/mol}$ , or 4,4-diamino-3,3-azofurazan,  $\text{C}_4\text{H}_4\text{N}_8\text{O}_2$ , DAAzF, CAS RN [1248439-96-4],  $M = 196.127 \text{ g/mol}$  [661].



4,4-Diamino-3,3-azoxyfurazan (DAAF)



4,4-Diamino-3,3-azofurazan (DAAzF)

DAAF has a crystal density of  $1.747 \text{ g/cm}^3$ ,  $\Delta H_f = +443 \text{ kJ/mol} = +106 \text{ kcal/mol}$  and a drop weight sensitivity with a 50% point at  $H_{50} > 320 \text{ cm}$  (with a 2.5-kg weight in the Type 12 machine) [672].

DAAF and 4,4'-diamino-3,3'-azofurazan (DAAzF) are obtained from the furazan precursor 3,4-diaminofurazan (DAF), which readily oxidizes to form mixtures of DAAF, DAAzF, and 3-amino-4-nitrofurazan. The first two were examined for future roles in insensitive explosive applications. Despite its large internal energy (measured enthalpy of formation =  $+536 \text{ kJ/mol}$ ), DAAzF is insensitive to impact ( $H_{50} > 320 \text{ cm}$ , Type 12), spark ( $> 0.36 \text{ J}$ ), and friction ( $> 36 \text{ kg}$ , BAM). When compared to DAAF, DAAzF has a lower detonation velocity and CJ pressure, presumably because the increase in the HOF is not sufficient to offset the loss of the one azoxy oxygen in the molecule. DAAzF has a DSC onset comparable to that of HNS ( $588 \text{ K} = 315^\circ\text{C}$ ) and a higher calculated  $\Delta H_f$  ( $+611 \text{ kJ/mol}$ ) than DAAF.

Neither DAAF nor DAAzF can be initiated by laboratory impact drop tests. Nonetheless, both (in some respect) have better explosive performances than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), and therefore meet the current standards for insensitive high explosives. The thermal stability of DAAzF is equal to that of hexanitrostilbene (HNS), yet DAAzF is a better explosive. The tetrazole derivative 3,6-bis-(1*H*-1,2,3,4-tetrazol-5-ylamino)-*s*-tetrazine (BTATz) was measured to have

exceptional positive HOFs, yet it is insensitive to explosive initiation. Because of its high burn rate and low sensitivity to pressure, this material is of great interest as a rocket propellant and gas generant additive. The vapor pressure of DAAzF is listed in Table 72.

**Table 72:** Thermodynamic data on the evaporation and sublimation of DAAzF.

| State of matter | Temp. interval<br>K | Temperature dependence of pressure above condensed phase<br>(pressure in atm, temperature in kelvin) | Heat of evaporation (or sublimation)<br>kJ/mol |
|-----------------|---------------------|------------------------------------------------------------------------------------------------------|------------------------------------------------|
| Solid           | 523–599             | $\ln P = 18.610 - 11963.6/T$                                                                         | (99.6)                                         |
| Liquid          | 599–1015            | $\ln P = 11.623 - 7758.8/T$                                                                          | 64.4                                           |

Data source: [683].

The thermal decomposition of 3,3'-diamino-4,4'-azofurazan (DAAzF) was investigated under isothermal conditions at 473–593 K (200–320 °C) using a thin-walled glass manometer of the compensation type. The kinetic rate equation for the thermal decomposition of molten DAAzF in the temperature range 830–1180 K is [484, 683]:

$$k = 10^{8.66} \exp(-16680/T)$$

where  $k$  is the rate constant in  $\text{s}^{-1}$  and  $T$  is the temperature in kelvin. The kinetic rate equation of DAAzF decomposition predominantly in the solid state was

$$k = 5.0 \times 10^{11} \exp(-21320/T)$$

and in the gas phase

$$k = 3.3 \times 10^{12} \exp(-21020/T).$$

Based on the burning rate and thermocouple measurement data, rate constants of DAAzF decomposition in the molten layer at 873–1073 K (600–800 °C) have been derived from a condensed-phase combustion model and can be expressed by

$$k = 4.6 \times 10^8 \exp(-16680/T),$$

which is in good agreement with kinetic data obtained in solution at 508–533 K (235–260 °C). The mechanism of DAAzF thermolysis and combustion includes the initial rupture of the C–N bond between the azo-group and furazan ring with subsequent nitrogen evolution and decomposition of the heterocyclic ring. In the combustion wave, the heat released from the decomposition of the stable furazan ring follows the heat release from azo-group decomposition, resulting in a distinct two-stage flame structure. For these calculations, the average specific heat, thermal diffusivity, and sample density were taken as  $1.67 \text{ kJ kg}^{-1} \text{ K}^{-1}$  ( $0.4 \text{ cal g}^{-1} \text{ K}^{-1}$ ),  $1.4 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ , and  $1.67 \text{ g/cm}^3$ , respectively. The heat of reaction in the melt,  $Q$ , was taken as  $1840 \text{ kJ/kg}$  ( $440 \text{ cal/g}$ ) or

86 kcal/mol). The heat of melting,  $\Delta H_{\text{fus}}$  (35.1 kJ/mol or 8.4 kcal/mol or 43 cal/g) was obtained as the difference between heats of sublimation and evaporation.

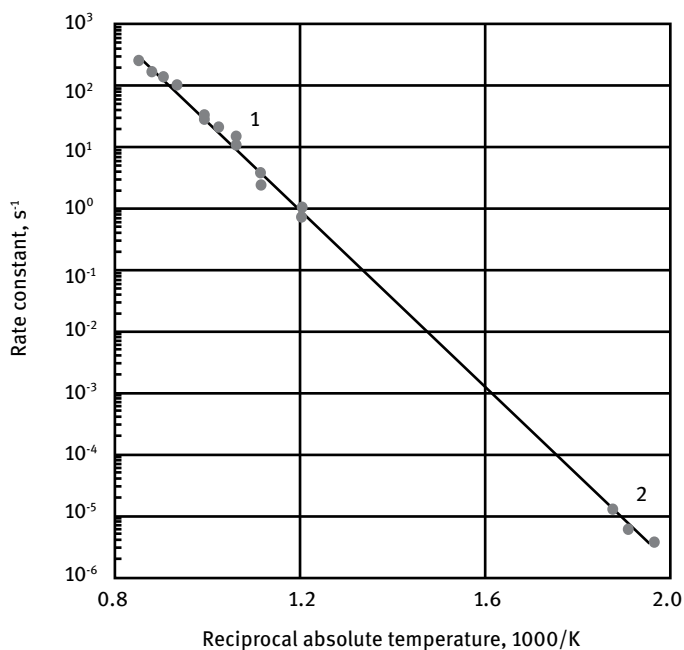
As can be seen in Figure 26, kinetic parameters of DAAzF decomposition derived from the combustion model

$$k = 10^{8.66} \exp(-16680/T)$$

are in good agreement with the experimental rate constants of DAAzF decomposition in the solution at lower temperatures. Using rate constants of DAAzF decomposition derived from the combustion model in the temperature interval of 873–1073 K (600–800 °C) and data on the DAAzF decomposition in solution at low temperatures, one can calculate the kinetics of DAAzF decomposition in the widened temperature interval 523–1073 K (250–800 °C):

$$k = 10^{7.61} \exp(-15570/T).$$

The activation energy of DAAzF decomposition in the liquid state in this temperature interval is 129.4 kJ/mol (32.9 kcal/mol).



**Figure 26:** Comparison of DAAzF rate constants in a wide temperature interval. (Reprinted and modified from [484], with permission from ©2009 Elsevier; permission conveyed through RightsLink.)

Legend: Rate constants of the leading reaction in DAAzF combustion (1, data points and line), and rate constants of DAAzF decomposition in solution (2, data points only).

Thirteen different furazan-functionalized tetrazolate-based energetic salts were prepared by direct treatment of neutral 4-amino-3-(5-tetrazole)furazan and a Lewis base or by simple metathesis reactions of its barium salt formed *in-situ* with the corresponding sulfate salts in an aqueous solution [1098]. Physical properties, such as melting point, thermal stability, density, hypergolicity, and sensitivity to shock were measured. The relationship between their structures and these properties was also determined. Most of the salts exhibited better thermal stability than their 5-nitrotetrazolate and 5-nitraminotetrazolate analogues as well as other furazan-based salts. The structures of representative aminoguanidinium, triaminoguanidinium, and 1,4-dimethyl-5-aminotetrazolium salts were further confirmed by single-crystal XRD and their densities, enthalpies of formation, detonation pressures and velocities, and specific impulses were calculated.

Macrocyclic derivatives with diazenfurazanyl fragments were synthesized by oxidative macrocyclocondensation of various diamines of the furazan series as follows: 3,4-diaminofurazan 4,4-diamino-3,3-diazenofurazan and diaminodifurazanyl under the action of different oxidizers [1099]. Some of the compounds had good thermal stability (about 473 K [200 °C]), high enthalpy of formation 2920–5021 kJ/kg (700–1200 kcal/kg), and high density (1.7–1.93 g/cm<sup>3</sup>).

DFT and VBT calculations have been performed to study the crystal densities, HOFs, energetic properties, thermodynamics of formation, and impact sensitivity for the salts composed of heterocycle-functionalized nitraminofurazanate anions and triaminoguanidinium cation [1100]. The results showed that the triaminoguanidinium nitraminofurazanate-based salts have high densities and positive enthalpies of formation. The substitution of the oxygen-containing substituent (–NO<sub>2</sub> or –C(NO<sub>2</sub>)<sub>3</sub>) helps enhance the densities and detonation properties of the nitraminofurazanate-based salts. The substitution of –C(NO<sub>2</sub>)<sub>3</sub> offers the best performance. Incorporating the conjugated bridge –N–N– or –N–N–N–N– into the heterocycle-functionalized nitraminofurazanate-based salts is favorable for further improving the density and detonation properties of its salt. The tetrazole-functionalized salts exhibit the best detonation properties among the three-salt series.

Energetic salts based on bis(*N*-dinitroethyl)aminofurazan were synthesized and characterized using NMR, IR, elemental analysis, density analysis, and DSC [1101]. These salts exhibited high densities (1.72 to 1.94 g/cm<sup>3</sup>) and low solubilities in water. Based on the experimental densities, the detonation pressures and velocities of the energetic salts were calculated, ranging from 26.1 to 39.4 GPa and 8055 to 9388 m/s, respectively. These values were higher than those of TNT and similar to those of RDX.

3,3'-Diamino-4,4'-azoxyfurazan (DAAF) along with 3,3'-azobis(6-amino-1,2,4,5-tetrazine) [DAAT] and 1,4-dihydrazino tetrazine (DHTz) were synthesized and characterized by IR, NMR, MS, TG-DTA, DSC, TG-FTIR, impact, and friction sensitivity tests [682]. DAAF is insensitive to mechanical stimuli whereas DAAT and DHTz are vulnerable to impact stimuli. The theoretical explosive power of DAAF, DAAT,

and DHTz alone and their combinations with well-known IHE as well as that of propellants based on them were calculated.

The thermal decomposition behaviors and thermal properties of diaminoazofurazan (DAAzF) and diaminoazoxyfurazan (DAAF) were studied by DSC with heating rates of 2.5, 5, 10, and 20 °C/min using TGA/DTG at a heating rate of 10 °C/min, VST, and thermal explosion tests [677]. The values of calculated activation energies of DAAzF and DAAF were 333.3 and 219.3 kJ/mol, with a natural logarithm of pre-exponential factors ( $\ln A$ ) of 67.535 and 49.230 s<sup>-1</sup>, respectively. Loss of weight during constant temperature at atmospheric pressure was 0.08% at 100 °C/48 h and 0.47% at 100 °C/48 h. The thermal explosion temperatures for five and 1000 s delay were 648 K (375 °C) and 552.6 K (279.5 °C) for DAAzF and 493 K (220 °C) and 495 K (222 °C) for DAAF, respectively. These results indicated that DAAzF and DAAF have good thermal stability and that the thermal stability of DAAzF is superior to that of DAAF. Sensitivity tests indicated that DAAzF and DAAF are insensitive to impact, friction, and electrostatic spark. Average particle size diameters of DAAzF and DAAF were less than 10 μm. Diaminofurazan, 3,4-diamino-1,2,5-oxadiazole, is a useful precursor for the preparation of new energetic materials, including 3,3'-dinitroamino-4,4'-azoxyfurazan. 3,3'-Dinitroamino-4,4'-azoxyfurazan has the highest calculated crystal density of 2.02 g/cm<sup>3</sup> at 173 K (the gas pycnometer measured density is

**Table 73:** Properties of 3,3'-dinitroamino-4,4'-azoxyfurazan and some of its salts in comparison to RDX.

| Compound name                       | $T_{\text{dec.}}^a$ |     | Oxygen balance | Density, pycn. | $\Delta H_f^{298}$ , calculated |       | Impact sensitivity | Friction sensitivity | Theor. $I_{sp}$ |
|-------------------------------------|---------------------|-----|----------------|----------------|---------------------------------|-------|--------------------|----------------------|-----------------|
|                                     | K                   | °C  |                |                | kJ/mol                          | kJ/g  |                    |                      |                 |
| 3,3'-Dinitroamino-4,4'-azoxyfurazan | 363                 | 90  | 10.6           | 1.96           | +730.0                          | +2.42 | 2                  | 10                   | 283             |
| ditto, ammonium salt                | 421                 | 148 | -4.8           | 1.83           | +523.8                          | +1.59 | 16                 | 360                  | 270             |
| ditto, hydroxylammonium salt        | 450                 | 177 | 4.3            | 1.90           | +651.8                          | +1.77 | 19                 | 120                  | 286             |
| ditto, hydrazinium(1+) salt         | 465                 | 192 | -8.7           | 1.84           | +863.1                          | +2.36 | 15                 | 60                   | 280             |
| ditto, guanidinium salt             | 519                 | 246 | -19.0          | 1.74           | +564.6                          | +1.34 | 35                 | 360                  | 240             |
| ditto, triamino-guanidinium salt    | 441                 | 168 | -25.1          | 1.76           | +1259.5                         | +2.47 | 17                 | 120                  | 256             |
| For comparison: RDX                 | 483                 | 210 | 0              | 1.82           | +80.0                           | +0.36 | 7.4                | 120                  | 258             |

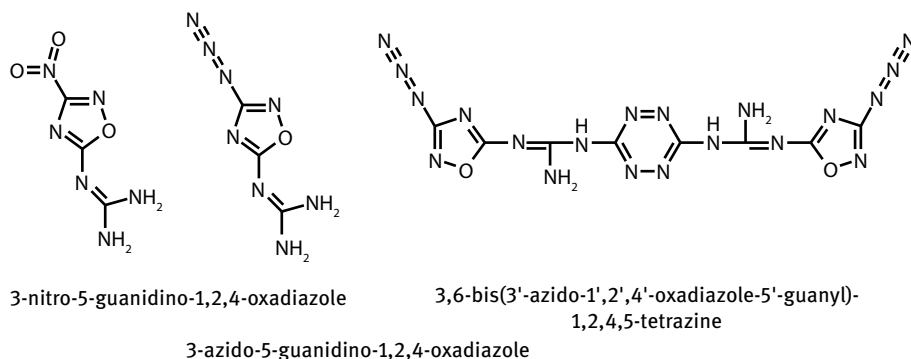
<sup>a</sup> Thermal decomposition temperature (onset) under nitrogen gas, DSC, 5 °C/min.

Data source: [1102].

1.96 g/cm<sup>3</sup> at 298 K) for any *N*-oxide energetic compounds yet reported [1102]. It forms salts with ammonium, hydrazinium, hydroxylammonium, or triaminoguanidinium cations, which by themselves are useful as energetic compounds, possibly even as replacements for AP in solid propellants. Table 73 is a summary of the properties of 3,3'-dinitroamino-4,4'-azoxyfurazan and some of its salts in comparison to RDX.

A theoretical study on the thermal decomposition mechanism of 3,3'-dinitro-4,4'-azoxyfurazan (DNAF) showed that *trans*-DNAF has a twisting configuration due to the substituted NO<sub>2</sub> on the furazan rings and the oxidation of azo-group [698]. The BDE of the two C—N bonds that connect the furazan rings and azo-group were found to be 275.7 and 385 kJ/mol (65.9 and 92 kcal/mol), respectively, suggesting that the C—N bond on the side of the O-atom of the azoxy-group is relatively weak.

Two high-nitrogen energetic compounds, 3-azido-5-guanidino-1,2,4-oxadiazole (AOG), containing 66.65% N, and 3,6-bis(3'-azido-1',2',4'-oxadiazole-5'-guanyl)-1,2,4,5-tetrazine (AOG2Tz), containing 67.62% N, were synthesized and characterized by DSC [1103]. AOG and AOG2Tz decomposed at 469 K = 196 °C and 483 K = 210 °C, respectively. They have a high density, favorable detonation properties, and a low sensitivity to impact.

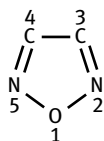


For additional information on furazans as energetic materials see also [1]. That publication places particular focus on DAAzF and also on compounds containing linked furazan and tetrazine rings. Azido- and/or nitro-substituted furazans are even more energetic than aminofurazans [694]. Hydroxylammonium salts of furazans would be interesting as energetic materials and sources of nitrogen for gas generators [702].

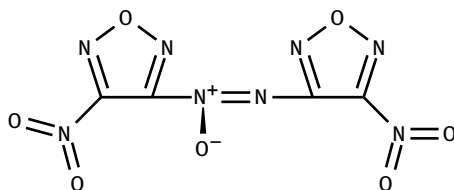
Nitrogen-bridged furazan-based polyheterocyclic compounds were prepared and characterized by enthalpies of formation, thermal stability, and detonation properties [1104]. This included 3,6-bis(furazan-5-ylamino)-1,2,4,5-tetrazine (FSF), 3,4-bis(1,2,4,5-tetrazine-3-ylamino)-furazan (SFS), 3,4-bis(1*H*-1,2,3,4-tetrazole-5-ylamino)-furazan (TFT), and 1,5-bis(furazan-3-ylamino)-1*H*-1,2,3,4-tetrazole (FTF).

### 15.3 Furoxans

1-Oxa-2,5-diazol-2-oxide (furoxan) is the parent compound of another family of energetic materials. There may be some confusion as to which heteroatom on the oxadiazole ring the counting of positions starts on. We assume that the counting starts on the oxygen atom and that it goes counterclockwise.

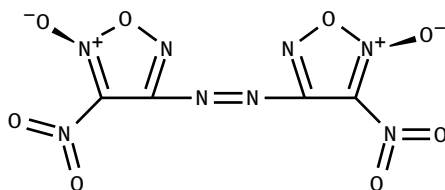


Dinitrodiazenefuroxan, azoxynitrofuroxan,  $C_4N_8O_7$ , (DNAF) has received much attention because of its energy potential due to it being superior to that of HMX. However, a more detailed characterization of this compound is needed before it can be used [699, 1105]. It has a density of  $1.82 \text{ g/cm}^3$ , an oxygen balance of  $-5.9\%$ , and an enthalpy of formation of  $+154.7 \text{ kJ/mol}$ .



Dinitrodiazenefuroxan

4,4'-Dinitro-3,3'-diazonofuroxan, DDF,  $C_4N_8O_8$ ,  $M = 288.092 \text{ g/mol}$ , is a primary explosive. The two rings are connected by a  $-N=N-$  bridge with one oxygen atom outside of each furoxan ring.



4,4'-Dinitro-3,3'-diazonofuroxan

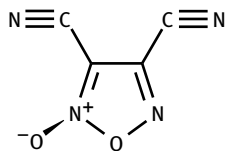
DDF has a positive enthalpy of formation of ( $\Delta H_f = +668 \text{ kJ/mol} = +159.6 \text{ kcal/mol}$ ). It has the highest detonation velocity of any known explosive at  $10 \text{ km/s}$  (measured experimentally) and a density that matches that of single crystals of  $2.02 \text{ g/cm}^3$ .

3-Nitro-5-guanidino-1,2,4-oxadiazole,  $C_3H_4N_6O_3$ , was synthesized from diaminoglycoluril with *in-situ* generated DMDO and used as an intermediate for the additional energetic materials with oxadiazole rings [663]. The impact sensitivity of 3-nitro-5-guanidino-1,2,4-oxadiazole was more than 40J (which is essentially insensitive). In the DSC, the decomposition temperature was 563 K (290 °C) whereas unsubstituted 1,2,4-oxadiazole became unstable at 361 K (88 °C). The density of 3-nitro-5-guanidino-1,2,4-oxadiazole is 1.766 g/cm<sup>3</sup>. It has an oxygen balance of -46.5% and an enthalpy of formation of +235.1 kJ/mol.

Attaching the furoxan ring to a benzene ring and loading the benzene ring up with nitro groups has led to a family of powerful benzofuroxan (phenylfuroxan) explosives, e.g., 3-nitro-4-(3,4,5-trinitrophenyl)furoxan [1106, 1107]. 4,6-Dinitrobenzofuroxan is an explosive that is less powerful than RDX [1108].

The thermal decomposition of 3,4-dinitrofurazanofuroxan (DNTF) under different pressure conditions and its reactions with catalysts were investigated by using DSC and TGA [1109]. The results showed that when the pressure increased, the endothermic fusion peak temperature of DNTF was almost constant, however, the major exothermic decomposition peak temperature at 2 MPa shifted to a higher temperature and the decomposition became more violent. Compared to the atmospheric reaction, the decomposition heat gain was obvious. The kinetic parameters of DNTF decomposition were obtained; the values of  $E_a$  and  $\ln A$  were 58.8 kJ/mol and 1.08 s<sup>-1</sup> for ambient pressure and 205.1 kJ/mol and 33.64 s<sup>-1</sup> for 2 MPa, respectively.

3,4-Dicyanofuroxan, 2-oxy-furazan-3,4-dicarbonitrile, (sometimes erroneously called 4,5-dicyanofuroxan), DCFO,  $C_4N_4O_2$ , CAS RN [17557-81-2],  $M = 136.068$  g/mol, has been evaluated as a gas generant for gas dynamic lasers but was eventually discarded due to safety reasons [1110].



3,4-Dicyanofuroxan

3,4-Dicyanofuroxan melts at 310–311 K (37–38 °C). A series of tests were made to determine the detonation propagation characteristics of 3,4-dicyanofuroxan. It was found that a detonation could be propagated through tubing as small as 2.5-mm (0.098-in.) internal diameter. Propagation was found to occur both in the solid state at ambient temperature and in the liquid state at 347 to 350 K (74 to 77 °C). A detonation sensitivity (a pseudo-card-gap) test was conducted and indicated that neat DCFO would be classified as a Class A explosive. More than 75 cards were required to prevent the detonation of neat DCFO; 70 cards or more designates a Class A explosive. A different



approach was to emphasize storable diluent compounds based on the substitution of carbon monoxide for a portion of the nitrogen in the GDL medium. This was aimed at alleviating problems associated with the fuel. Carbonyl diisocyanate, CDI,  $C_3O_3N_2$ , was characterized as a possible storable diluent and its combustion characteristics were determined in a small combustion facility.

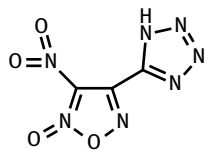
3,4-Dicyanofuroxan is the starting product in the synthesis of 3,4-bis(1*H*-5-tetrazolyl)furoxan by converting the  $-CN$  groups to tetrazole rings by reaction with sodium azide.



3,4-bis(1*H*-5-tetrazolyl)furoxan

3,4-Bis(1*H*-5-tetrazolyl)furoxan (H2BTF) has two acidic hydrogen atoms and can form monoanionic or dianionic salts. Nine different salts of H2BTF with hydrazinium or triazolium and tetrazolium cations with varying degrees and types of substituents on the heterocyclic cation ring were synthesized and thoroughly characterized by multinuclear NMR and IR spectroscopy, DSC, gas density pycnometer, and elemental analyses [1111]. The densities of the energetic salts ranged between 1.63 and 1.79 g/cm<sup>3</sup>, as measured by a gas pycnometer. The hydrazinium salt of H2BTF has a calculated density of 1.820 g/cm<sup>3</sup>. Detonation pressures and detonation velocities were calculated to be 23.1–32.5 GPa and 7740–8790 m/s, respectively, and compared to the performance of RDX. Similar compounds with stronger bases were synthesized; both hydrogens of H2BTF were active in protonating nitrogen-rich bases during this process of forming dianionic salts [1112].

A series of energetic salts based on 4-nitro-3-(5-tetrazole)furoxan,  $C_3HN_7O_5$ , HTNF, have been synthesized and characterized by NMR, IR, elemental analysis, and DSC [1113].



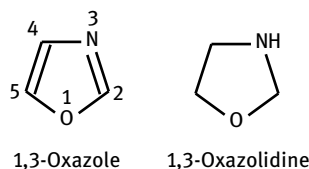
4-Nitro-3-(5-tetrazole)furoxan (HTNF)

The crystal structures of neutral HTNF and its ammonium and *N*-carbamoylguanidinium salts have been determined by single-crystal XRD. The densities of these salts

were found to range from 1.63 to 1.84 g/cm<sup>3</sup>. Impact sensitivities have been determined by hammer tests and the results ranged from 2J (very sensitive) to >40J (insensitive). Theoretical performance calculations predicted detonation pressures and velocities in the ranges 25.5–36.2 GPa and 7934–8919 m/s, respectively, which make them competitive energetic materials in comparison to RDX.

### 15.4 Oxazoles

Because oxazole contains one oxygen atom in the ring and one less CH group, it would have a better oxygen balance compared to pyrrole. Oxazoles have an oxygen and a nitrogen separated by one carbon atom. The counting starts at the oxygen atom and not at the nitrogen atom.



Oxazoles are aromatic compounds but less so than thiazoles. Oxazole, 1,3-oxazole, C<sub>3</sub>H<sub>3</sub>ON, CAS RN [288-42-6], is a weak base; its conjugate acid has a pK<sub>a</sub> of 0.8 compared to 7 for imidazole. It has a boiling point of 342–343 K (69–70 °C) and a density of 1.050 g/cm<sup>3</sup>. Oxazolidine has both double, unsaturated bonds reduced to saturated bonds. If one adds a –CH<sub>2</sub>– group to the ring to make a symmetric molecule, one obtains morpholine. An entire book has been devoted to the chemistry of oxazoles: [1114]. Oximes serve as intermediates in the synthesis of oxaza heterocyclic compounds [1115].

Substituted oxazoles and oxazolidinium salts have been evaluated as energetic ingredients. 4,5-Dicyanooxazole, a low hydrogen content fuel, has been synthesized, characterized, and evaluated as a gas generant for gas dynamic lasers [1116]. Water (steam) in the exhaust attenuates the output of chemical lasers. Because of a need for a low hydrogen content fuel for use in gas dynamic lasers, 4,5-dicyano oxazole was prepared as a possible candidate for evaluation. Its physical properties were found to be well within desired limits for fuel requirements. However, difficulties inherent in the synthetic process made the production of the test or operational quantities excessively tedious and costly.

Quaternary methyl-alkyl-oxazolidinium salts with nitrate and perchlorate as the anion have been characterized as energetic compounds [202]. They melt below 373 K and are thermally stable at up to 523 K.

## 16 Pentazoles

Future sets of this encyclopedia of rocket propellants will contain a section on all-nitrogen and high-nitrogen compounds because pentazole and pentazole ions were studied in the hope of potential applications of such compounds in solid propellants and gas generants [1117]. Other hydronitrogens were described in this volume in the chapter on “Hydronitrogen Compounds.”

### 16.1 Theoretical Considerations About Pentazoles

While the existence of pentazole or hydrogen pentazole was once questioned [1118], the successful synthesis of the chain-like V-shaped  $N_5^+$  cation in 1999 by Christe and co-workers [1119] sparked renewed interest in all-nitrogen compounds, be they open-chained or ring-closed. Extensive theoretical and experimental work on the cyclic pentazole anion  $N_5^-$  resulted in its detection in the gas phase by mass spectroscopy in 2002 [1120, 1121].

The decomposition barrier for the cyclic  $N_5^-$  anion has been estimated to be 108.8 kJ/mol (26 kcal/mol) by using high-level *ab initio* calculations [1122], but the detection of the pentazole anion in the condensed phase by NMR spectroscopy has proven difficult. There are other pentazole compounds where the  $N_5$  ring has been stabilized by fused aromatic rings. It was hoped that the attachment of an oxygen atom to the pentazole ring would stabilize the molecule but that has not yet been confirmed. Quantum mechanical *ab initio* calculations gave a predicted enthalpy of formation of the ammonium pentazolate of +12.1 kJ/mol (+2.9 kcal/mol) and a density of 1.6 g/cm<sup>3</sup>.

The synthesis of the pentazole anion has been suggested and attempted using substituted aryl pentazoles as precursors. Future computational studies should be able to show if selective oxidation of aryl pentazoles is possible without destroying the  $N_5$  ring. The pentazole anion is expected to form strong ferrocene-like sandwich complexes in the presence of metal cations (e.g.,  $Fe_2^+$ ), which should favor its formation and stabilization in solution.

The structures of protonated pentazole cations ( $RN_5H^+$ ), oxygen-containing anions such as  $N(NO_2)_2^-$ ,  $NO_3^-$ , and  $ClO_4^-$ , and the corresponding ion pairs were investigated by *ab initio* quantum chemistry calculations [1123]. The stability of the pentazole cation was explored by examining the decomposition pathways of several mono-substituted cations ( $RN_5H^+$ ) to yield  $N_2$  and the corresponding azidinium cation. The HOFs of these cations were calculated based on isodesmic (bond-type conserving) reactions. The decomposition may involve a proton-transfer reaction from the cation to the anion.

The kinetic stability of dinitramide, trinitrogen dioxide, pentazole, and oxopentazole anions was evaluated in the gas phase and in solution by using high-level *ab*

*initio* and DFT calculations [1122]. Theoretical UV spectra, solid-state HOFs, density, as well as propellant performance for the corresponding ammonium salts were predicted. All calculated properties for dinitramide (the only stable anion of the four candidates known so far) were in excellent agreement with experimental data. Oxopentazolate is expected to be approximately 1200 times more stable than pentazolate in solution, with a barrier exceeding 30 kcal/mol, which should enable handling at room temperature. Based on calculation results, further study and attempted synthesis of these materials was deemed worthwhile [1124].

The possibility of the existence of cyclopentazan, which is a polynitrogen compound with a formula of  $N_5H_5$ , has been examined, including in comparison to the pentazolate anion, which is an all-nitrogen aromatic compound with a formula of  $N_5^-$  [1125]. The synthesis of various arylpentazoles was followed by oxidative or reductive ways, which led to the pentazolate anion. Polynitrogen-based compounds, triazanes, and azimines were then used in attempted cycloadditions, in the hope that this would lead to cyclopentazan. Complexing the polynitrogen-compound with various metal cations may result in more stable compounds.

## 16.2 Experimental Preparations of Pentazoles

The first successful synthesis of  $N_5^+$  cation was achieved in 1999 by Christe and co-workers, although it was an open-chain  $N_5$  and not the ring-shaped pentazole [1119].  $N_5^+$  salts can be made by reacting  $N_2F^+$  with hydrazoic acid to yield  $N_5^+ + HF$ , then reacting the  $N_5^+$  solution with  $AsF_6^-$  or  $SbF_6^-$  forms a stable  $N_5^+$  salt [1126]. The heavy  $SbF_6^-$  anion required to stabilize the labile  $N_5^+$  is not a good choice for rocket propellant. It is, however, interesting and novel chemistry nevertheless, and could lead to new potential rocket propellants.

# 17 Six-Membered Rings with One Nitrogen Atom

## 17.1 Pyridine

Coal tar was once a major source of raw materials for the organic chemical industry. Pyridine,  $C_5H_5N$ , CAS RN [110-86-1],  $M = 79.0999$  g/mol, was a common contaminant in benzene that was derived from coal tar.



Pyridine

Pyridine has a melting point of 232 K ( $-41^{\circ}\text{C}$ ), a boiling point of 388.5 K ( $115.4^{\circ}\text{C}$ ), a density of  $0.9780\text{ g/cm}^3$  at 298 K ( $25^{\circ}\text{C}$ ), and an enthalpy of formation of  $+99.96 \pm 0.50\text{ kJ/mol}$  ( $+23.89\text{ kcal/mol}$ ). Complete reduction of pyridine leads to hexahydropyridine, which is called piperidine. These compounds have been considered as fuels in hypergolic bipropellants. Their salts with oxidizing acids (nitric acid, perchloric acid) have been considered as additives in solid propellants and explosives.

Pyridine mixed with energetic hypergolizing agents was used successfully in combination with hydrogen peroxide, leading to very fast hypergolic ignition, with ignition delay times as short as 3 ms [1127].

### 17.1.1 Pyridinium Salts

Pyridinium salts with oxidizing acids (nitric acid, perchloric acid) have been considered as additives in solid propellants and explosives. Pyridinium perchlorate is not very soluble in water. For this reason, pyridinium perchlorates have been used to purify pyridine by recrystallization of the salt or to identify substituted pyridine bases by doing melting-point measurements. Occasional explosions have occurred when the salts were overheated or scraped during drying. Pyridinium perchlorate melts at 561 K ( $288^{\circ}\text{C}$ ), decomposes at 613 K ( $340^{\circ}\text{C}$ ) forming white fumes, and auto-ignites soon thereafter, burning with a sooty flame. Mixtures of pyridinium perchlorate and AP burn cleanly and rapidly. Pyridinium perchlorate is almost as powerful an explosive as TNT, with a lead block expansion of 95% of that of TNT, but is much more sensitive to impact (40% of that of picric acid).

Melting temperatures, glass transition temperatures, decomposition temperatures, heat capacities, and viscosities for a large series of pyridinium-based ionic liquids were measured. For comparison, data for several imidazolium and quaternary ammonium salts were included [1128]. Many of these compounds did not crystallize but formed glasses at temperatures between 188 and 223 K. Viscosities generally increased with increasing number and length of alkyl substituents on the cation, with the pyridinium salts typically being slightly more viscous than the equivalent imidazolium compounds.

Pyridinium or piperidinium nitrate or perchlorate were patented as additives to WFNA and were supposed to improve ignition with hydrocarbon fuels [1129]. Pyridinium nitrate is an ionic liquid. The thermal stability and decomposition kinetics of the ionic liquid pyridinium nitrate was investigated by non-isothermal TGA in an inert atmosphere (under nitrogen) [1130]. For the kinetic experiments, the thermal behavior of the sample was studied in the temperature interval from 360 up to 600 K at four different heating rates (5, 10, 15, and 20 K/min.). The kinetic parameters (activation energy and pre-exponential factor) of pyridinium nitrate decomposition under nitrogen atmosphere were evaluated by two model-free methods; the Friedman method and the Kissinger-Akahira-Sunose method. Depending on the calculation model used, the obtained activation energy and pre-exponential factor values (with respect to the degree

of sample conversion during the kinetic experiment for the method) ranged in the intervals of 76.36–112.56 kJ/mol and  $1.72 \times 10^5$ – $1.42 \times 10^{10}$  min.<sup>-1</sup>, respectively. Based on the kinetic parameters it was established that decomposition of pyridinium nitrate occurred as a first-order reaction. Some alkylpyridinium salts have also been identified as ionic liquids.

Perchlorate salts of pyridine, 2-chloropyridine, and 2-hydroxypyridine have been prepared and characterized by gravimetric TGA, DTA, and elemental analyses [1131]. Both substituted pyridinium salts were thermally less stable than the unsubstituted pyridinium perchlorate. Pyridinium perchlorate melted at 374 K (101°C), the 2-chloropyridinium perchlorate melted at 395 K (122°C), and the 2-hydroxypyridinium perchlorate melted at 366 K (93°C). Isothermal TGA gave the kinetics of thermal decomposition in the temperature range of 563–683 K (290–410°C) using both model fitting and isoconversional methods. The isoconversional method has been found to be superior to the conventional model-fitting method, and it was able to describe the decomposition process of these salts more accurately. Explosion delay measurements have been carried out to investigate the response of the salts under conditions of rapid heating. The thermolysis of pyridinium perchlorates involves a proton transfer from the pyridinium ion to the perchlorate anion as the rate-determining step.

### 17.1.2 Other Energetic Pyridinium Salts

The crystal structure of pyridinium dinitramide was examined and the question of oxygen coordination versus nitrogen coordination was clarified, also for the lithium dinitramide dihydrate [1132]. Pyridinium dinitramide had already been characterized in a separate study.

The reaction yield during the synthesis of pyridinium dinitramide (Py-DN) is 10% higher than that achieved with other dinitramide salts such as ammonium dinitramide (ADN). This is because Py-DN was directly converted without the sequential precipitation of intermediates [1133, 1134]. A thermal analyzer, a UV-visible spectrophotometer, and an FTIR spectrophotometer were used to characterize the physical and chemical properties of the synthesized Py-DN. The results were compared with previously prepared salts such as ADN and guanidinium dinitramide (GuDN). The characteristic endothermic and exothermic decomposition temperatures of Py-DN were 350.5 K (77.4°C) and 417.8 K (144.7°C), respectively, and the material had a heat of combustion caloric value of 1739 J/g. A low onset of exotherm can reduce the preheating temperature required for thruster operations.

### 17.1.3 Aminopyridines

Aminopyridines have properties similar to aniline and have been evaluated as ingredients in rocket propellants. The 2- and 4-aminopyridines form a mono-perchlorate salt with perchloric acid, whereas the 3-aminopyridine can even form a diperchlorate salt with an excess of acid [1135].

### 17.1.4 Nitropyridines

Unlike benzene, pyridine is resistant to direct nitration and more aggressive nitration methods, or other circuitous synthesis routes must be sought for making nitropyridines [1136]. The nitro group can go into the 2-, 3-, or 4-position in relation to the nitrogen atom in the ring. There are more compounds described in the literature that carry one or more additional substituent on the pyridine ring in addition to the nitro group. Nitropyridine-*N*-oxides are potential propellant ingredients.

### 17.1.5 Dinitropyridine and Trinitropyridine

A different method was found for the synthesis of 2,4,6-trinitropyridine and 2,6-diazido-4-nitropyridine [1137]. The substances were characterized by IR and DSC. 2,4,6-Trinitropyridine is thermally stable and comparable to trinitrobenzene (TNB) and its shock sensitivity is comparable to that of RDX. The explosive performance of 2,4,6-trinitropyridine and 2,6-diazido-4-nitropyridine was superior to that of TNT or TNB. Dinitropyridine and dinitropyridine derivatives with additional hydroxyl-, amino-, or *N*-oxide groups have been patented as insensitive explosives [1138]. A study of the formation of trinitropyridine-*N*-oxide from dinitroethanol and nitric acid pointed toward the possibility of making trinitropyridine, which cannot be obtained by direct nitration [1139, 1140]. The predicted detonation velocities for trinitropyridine-*N*-oxide and trinitropyridine were 8450 and 7880 m/s, respectively. 2,4,6-Trinitropyridine-1-oxide can be obtained from 2,2-dinitroethanol potassium salt and phosphoric acid along with 2,4,6-trinitropyridine as a byproduct [1141]. Treating 2,4,6-trinitropyridine-1-oxide in 2-N H<sub>2</sub>SO<sub>4</sub> with aqueous NaNO<sub>2</sub> produced more 2,4,6-trinitropyridine. 2,4,6-Trinitropyridine-1-oxide decomposed without melting while 2,4,6-trinitropyridine melted without decomposition.

Properties of polynitro-bridged pyridine derivatives were predicted by quantum mechanical MO computations [1142]. Gas-phase HOFs for the designed compounds were calculated using isodesmic reactions and their solid-phase HOFs were estimated using the Politzer approach. All designed compounds had large solid-phase HOFs, larger than 700 kJ/mol. Based on the predicted crystal densities, solid-phase HOFs, and chemical energies, detonation properties were then evaluated using K-J empirical equations. The results revealed that predicted detonation velocities and the pressures of all of the designed compounds should be above 9.3 km/s and 40 GPa, respectively. In addition, the lowest BDE indicated the weak points limiting their thermal stability. The impact sensitivity of polynitropyridines and similar polynitroheteroarenes and nitroheterocyclic compounds can be predicted by interpolating between known data and applying structural factors [148, 149].

### 17.1.6 Polyazidopyridines

The nitrogen content and energy content of pyridine can be increased by attaching azide groups. The most interesting energy characteristics were found for 2,4,6-triazido-

3,5-dicyanopyridine, which considerably surpasses 2,4,6-triazido-1,3,5-triazine in the enthalpy of formation (+5740 kJ/kg) but is much less explosive [1143].

### 17.1.7 Pyridine-N-Oxides

Explosives with low sensitivity and high energy containing pyridine rings were sought. The nitramine group with N—NO<sub>2</sub> bonds was introduced into this effort as much as possible [1144]. Based on research into the regular relationship between molecular structures, crystal structures, and explosive properties as well as safety of performance, the molecular structures of several target compounds and their synthetic methods were designed. Then synthetic routes were outlined with different synthetic reactions such as condensation, *N*-nitration, *N*-oxidation, and *C*-nitration.

2,6-Diamino-3,5-dinitropyridine-1-oxide and aminonitropyrimidine-1,2-dioxides were prepared and showed stability and insensitivity comparable to that of TATB, which has a legendary good thermal stability [1145]. Although the stability of the new compounds was good, the explosive performance lagged behind the established goal. In trying to create chemical structures similar to TATB, 3,5-dinitro-2,4,6-triaminopyridine was prepared by oxidative amination of 2-chloro-3,5-dinitropyridine or 2,6-diamino-3,5-dinitropyridine or by treatment of this with hydroxylamine [1146]. 3,5-Dinitro-2,4,6-triaminopyridine-1-oxide was prepared by oxidation of the parent heterocycle with hydrogen peroxide, or by treatment of 2,6-diamino-3,5-dinitropyridine-1-oxide with hydroxylamine. The intra-molecular and intermolecular hydrogen bonding contributes to the thermal stability and low impact sensitivity of these molecules.

2,6-Dinitro-3,5-diaminopyridine-*N*-oxide, DADNPO, CAS RN [181766-17-6], C<sub>5</sub>H<sub>5</sub>N<sub>5</sub>O<sub>5</sub>, *M* = 215.13 g/mol, is a structural isomer to 2,6-diamino-3,5-dinitropyridine-1-oxide and is commercially available from EURENCO [1147]. DADNPO is a new explosive that can tolerate temperatures about 40 °C higher than HNS, and with the same degree of degradation. This explosive can therefore be used in hotter bore holes than HNS shaped charges for oil well completion, with equal performance. The detonation velocity is approximately 7000 m/s, the friction sensitivity is >350 N, and the impact sensitivity is >19 J.

## 17.2 Piperidine and Piperidine Derivatives

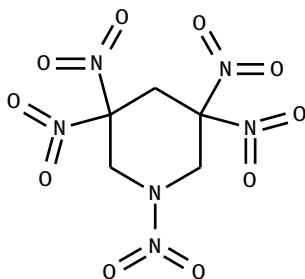
### 17.2.1 Piperidine

Piperidine, also known as hexahydropyridine, pentamethyleneimine, C<sub>5</sub>H<sub>11</sub>N, CAS RN [110-89-4], with a molecular mass of 85.1475 g/mol, is a cyclohexane in which one CH<sub>2</sub> group has been replaced by an NH group. It is a ring-closed secondary amine. It can be made via the reduction of pyridine. The application of piperidine and alkyl-substituted piperidines as hypergolic rocket fuels has been patented for compounds with the general formula (CH<sub>2</sub>)<sub>5</sub>NR, where R is an alkyl group [1148].



Piperidine, hexahydropyridine, pentamethyleneimine,  $C_5H_{11}N$ , is the parent compound of a series of energetic materials. Piperidine itself is a secondary amine with a freezing point of 264 K ( $-9^\circ\text{C}$ ), a boiling point of 379 K ( $106^\circ\text{C}$ ), and a density of  $0.8606\text{ g/cm}^3$ .

(3,3,5,5-Tetranitropiperidin-1-yl)acetic acid is a precursor for the synthesis of 1,3,3,5,5-pentanitropiperidine,  $C_5H_6N_6O_{10}$ , CAS RN [71706-07-5],  $M = 310.135\text{ g/mol}$ .



1,3,3,5,5-Pentanitropiperidine

Treatment of 2,2-dinitropropane-1,3-diol with glycine in water at 338–343 K ( $65\text{--}70^\circ\text{C}$ ) for 5 h gave (3,3,5,5-tetranitropiperidin-1-yl)acetic acid. Exhaustive nitration of the latter in a mixture of 100% nitric acid and trifluoroacetic anhydride for 12 h gave 1,3,3,5,5-pentanitropiperidine [1149]. (3,3,5,5-Tetranitropiperidin-1-yl)acetic acid and 1,3,3,5,5-pentanitropiperidine were characterized by IR, NMR, DSC, and elemental analysis. 1,3,3,5,5-Pentanitropiperidine has a melting point of 393–398 K ( $120\text{--}125^\circ\text{C}$ ) and a density of  $1.82\text{ g/cm}^3$ .

2,2,6,6-Tetramethyl-1-oxopiperidinium perchlorate has been synthesized and the IR, UV, and NMR spectra have been recorded [1150]. An XRD structural study of 2,2,6,6-tetramethyl-oxopiperidinium perchlorate  $[C_5H_6(CH_3)_4NO]^+ClO_4^-$  has been carried out, with results as follows: space group  $P2_12_12_1$ ,  $a = 14.01$ ,  $b = 11.045$ ,  $c = 8.139\text{ \AA}$ , and  $Z = 4$ . The structure was determined by the heavy-atom method and refined by the method of least squares. According to the IR spectra, the crystals have a twisted “bathtub” conformation with an angle twist of  $24^\circ 30'$ . The melting point of the crystals was 430–431 K ( $157\text{--}158^\circ\text{C}$ ).

Polynitropiperidines would make good rocket propellants and explosives. *N*-Nitroalkyl-3,3,5,5-tetranitropiperidines can be prepared by condensation of 2,2,4,4-tetranitropentane-1,5-diol with a dinitroalkylamine such as  $H_3CC(NO_2)_2(CH_2)_nNH_2$  [1151]. Examples are *N*-2,2,2-trinitroethyl-3,3,5,5-tetranitropiperidine,  $C_7H_8N_8O_{14}$ , with a melting point of 436–441 K ( $163\text{--}168^\circ\text{C}$ ), and *N*-3,3,3-trinitropropyl-3,3,5,5-tetranitropiperidine,  $C_8H_{10}N_8O_{14}$ , with a melting point of 415–417 K ( $142\text{--}144^\circ\text{C}$ ). 1,3,3,5,5-Pentanitropiperidine,  $C_5H_6N_6O_{10}$ ,  $M = 310.14\text{ g/mol}$ , can be prepared by nitration of 3,3,5,5-tetranitropiperidine with concentrated nitric acid [1152]. It melts at 393–398 K ( $120\text{--}125^\circ\text{C}$ ) and has a density of  $1.82\text{ g/cm}^3$  and a heat of combustion

of 2056 cal/g. Its Trauzl lead block indentation was 165% of that of TNT. Its impact sensitivity was 35–40 cm with a 2-kg mass. 3,3,5,5-tetranitropiperidine,  $C_5H_7N_5O_8$ , with a melting point of 396–400 K (123–127 °C) can be prepared by reaction of 2,2,4,4,-tetranitropentane-1,5-diol with ammonium acetate [1153].

### 17.2.2 Piperidinium Salts

Piperidine forms salts with strong acids. Piperidinium nitrate and piperidinium perchlorate, along with a long list of alkyl- and arylammonium nitrates, have been claimed as propellant ingredients, typically as monopropellants in nitric acid solution that are similar to CAVEA [1154, 1155], or as additives in JP-4, which helps the ignition of kerosene fuels in a ramjet [1156]. This latter patent claims piperidinium nitrate, pyridinium nitrate, or 2-methylpyridinium nitrate as fuel additives. The piperidinium or pyridinium nitrates or perchlorates can also be dissolved in  $HNO_3$ ,  $H_2O_2$ , or  $RNO_2$  solvents to make more energetic monopropellants [1157].

Piperidinium nitrate was studied by FTIR and FT-Raman spectroscopy in the range of 100–4000  $cm^{-1}$  at 300 K, and FTIR spectra were recorded down to 90 K [1158]. DSC measurements exhibited two phase transitions at 256 and 295 K.

Piperidine was chosen as a reference compound for DFT calculations to predict the HOFs for seven  $C-NF_2$  or  $C-NO_2$  substituted heterocyclic ring compounds via designed isodesmic reactions [1159]. Similar to the behavior of many other amines, piperidine forms solid Lewis adducts with diborane and other boranes that are hypergolic with nitric acid and can be used as fuel grains in hybrid rockets [1160].

## 17.3 Morpholine and Morpholine Derivatives

### 17.3.1 Morpholine

Morpholine, also known as 1,4-oxazinane, tetrahydro-1,4-oxazine, tetrahydrop-oxazine,  $O(CH_2CH_2)_2NH$ ,  $C_4H_9NO$ , CAS RN [110-91-8], is a heterocyclic amine and a base that can form salts with strong acids. Because it already contains some oxygen, it is not useful as a fuel. It is mostly used for pH adjustment in boiler feedwater treatments to reduce corrosion in steam plants. Morpholine mixed with energetic hypergolizing agents was used as rocket fuel in combination with hydrogen peroxide [1127].

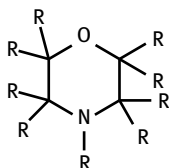
Morpholine forms salts with strong acids. Morpholinium dinitramide melts at 355–357 K (82–84 °C) [1161]. The enthalpy of formation of morpholinium dinitramide is –226 kJ/mol (–54 kcal/mol) [1161].

### 17.3.2 Morpholine Derivatives

The counting in heterocyclic rings containing O and N as heteroatoms starts at the O atom, not at the N atom. The energy content of morpholine can be improved by ni-

trating the N—H in the ring with a nitrating mixture consisting of fuming nitric acid and acetic anhydride, forming a nitramine. An example is *N*-nitromorpholine, 4-nitromorpholine,  $C_4H_8N_2O_3$ , with a molecular mass of 132.1179 g/mol [1162].

A patent [1163] claims the application of alkyl-substituted morpholines as hypergolic rocket fuels. The patent covers compounds with the general formula  $O(CR_2)_4NR$ , where R can be a hydrogen or a lower alkyl group



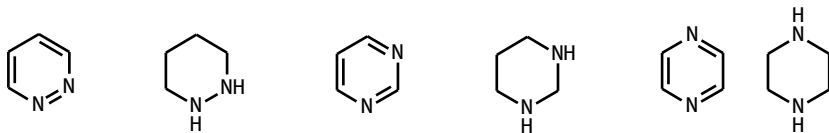
Alkylmorpholine

### 17.3.3 Other Oxazine Derivatives

Two geminal azido nitro compounds, 5-azido-3-*tert*-butyl-5-nitrotetrahydro-2*H*-1,3-oxazine and 5-azido-3,5-dinitrotetrahydro-2*H*-1,3-oxazine (AZDNOX), were synthesized and characterized [1164]. The first compound and its dinitro analog, 3-*tert*-butyl-5,5-dinitrotetrahydro-2*H*-1,3-oxazine, have been obtained in good yields by the reactions of 5-nitrotetrahydro-2*H*-1,3-oxazine salts with azide and nitrite ions in the presence of potassium ferricyanide. Combustion behaviors of AZDNOX and 3,5,5-trinitrotetrahydro-2*H*-1,3-oxazine (TNOX), have been studied. Burning rate measurements have been performed in a constant-pressure bomb in the pressure range of 0.1–15 MPa and temperature profiles in the combustion wave of AZDNOX and TNOX were measured using thin tungsten-rhenium thermocouples.

## 18 Six-Membered Rings with Two Nitrogen Atoms

If two nitrogen atoms are introduced into the benzene ring, they can occupy three different positions: the 1,2 vicinal position: pyridazine; the 1,3 unsymmetrical position: pyrimidine; and the 1,4 symmetric position: pyrazine. All three diazine isomers and their hydrogenated relatives are stable and form the nucleus of numerous compounds of interest as energetic materials and pharmaceuticals.



Pyridazine   Hexahydropyridazine   Pyrimidine   Hexahydropyrimidine   Pyrazine   Piperazine

## 18.1 Pyridazine

Pyridazine, also known as 1,2-diazine,  $C_4H_4N_2$ , CAS RN [289-80-5], is a colorless liquid with a freezing point of 265 K ( $-8^\circ\text{C}$ ) and a boiling point of 481 K ( $208^\circ\text{C}$ ). The density is  $1.107\text{ g/cm}^3$ . It is a strong base and forms salts with many acids. Several books have been devoted to the chemistry of pyridazines [1165, 1166]. The latter volume substantially updated the original pyridazines volume which was first published in 1973.

### 18.1.1 Pyridazinium Salts

Pyridazinium monoperchlorate,  $(C_4H_4N_2)HClO_4$ , undergoes structure and phase transitions with changing temperature. This has been characterized by XRD, dielectric, and optical measurements [1167–1169]. At room temperature the crystal is monoclinic, space group  $P2_1/n$ . Anomalous behavior is characteristic of first-order phase transitions at 343 and 339 K on heating and cooling, respectively.

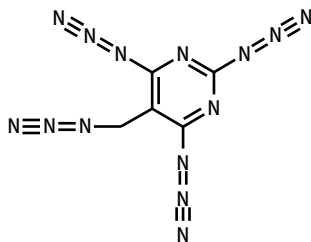
Quaternary pyridazinium salts with varying lengths alkyl group and terminal fluorine substitution in the alkyl group with nitrate or perchlorate as the anion had low melting points 289–331 K ( $16$ – $58^\circ\text{C}$ ), making them ionic liquids with good thermal stability [202].

### 18.1.2 Tetrahydropyridazine and Hexahydropyridazine

Hexahydropyridazine is a cyclic hydrazine but is rarely used in its pure state. Most work is done on hexahydropyridazine derivatives but they do not seem to be suitable as rocket propellants. Tetrahydropyridazine can be prepared by oxidation of 1-aminopyrrolidine. Hexahydropyridazine can be prepared by reduction of tetrahydropyridazine [1170, 1171]. Another process for making hexahydropyridazine runs via catalytic cyclization and alcoholysis using diformylhydrazine and 1,2-dichlorobutane or 1,2-dibromobutane as starting reagents [1172].

## 18.2 Pyrimidine

Pyrimidine, 1,3-diazine,  $C_4H_4N_2$ , CAS RN [289-95-2], forms low-melting colorless crystals that melt at room temperature from between 293–295 K ( $20$ – $22^\circ\text{C}$ ) and boil at 397 K ( $124^\circ\text{C}$ ). It is soluble in water and forms salts with strong acids such as nitric acid or perchloric acid. Alicyclic imines with two nitrogen atoms may be derived from imidazolidine or hexahydropyrimidine. These amines are potentially useful hypergolic fuels. The theoretical performance of 1,3-dimethylimidazolidine and its homologue 1,3-dimethylhexahydropyrimidine as hypergolic fuels was predicted from computational chemistry calculations [1173]. An entire book has been devoted to the chemistry of pyrimidines [1174].



2,4,6-Triazido-5-(azidomethyl)-pyrimidine (TAAMP)

In search of potential ionic liquids, it was found that one or more additional azidomethyl groups dramatically decreased the melting points of the corresponding azidopyrimidines [1175, 1176]. 2,4,6-triazido-5-(azidomethyl)-pyrimidine,  $C_5H_2N_{14}$ , has a nitrogen content of 75.96 mass-%, a HOF of 1452.7 kJ/mol, melts at 295.6 K (22.5 °C), decomposes at 466 K (193 °C), and has a density of 1.65 g/cm<sup>3</sup>. Theoretical calculations showed that these polyazido compounds are very energetic. In this family of compounds, 3,6-di(azido)-tetrazine has the highest reported HOF of ~1101 kJ/mol (6709 kJ/kg). It melts and decomposes at 403 K (130 °C) and has a density of 1.72 g/cm<sup>3</sup>. 2,4,6-Triazidotriazine has a HOF of 1050 kJ/mol, melts at 367 K (94 °C), decomposes at 453 K (180 °C), and has a density of 1.72 g/cm<sup>3</sup>. The compound 4,4',6,6'-tetra(azido)azo-1,3,5-triazine has a HOF of 2171 kJ/mol (6164 kJ/kg). 2,4,6-Triazidopyrimidine was found to be a precursor to carbon nano-tubes in the presence of  $Ni(ClO_4)_2$ . Thermal decomposition of some of these compounds gave nitrogen-rich nano-layered, nano-clustered, and nano-dendritic carbon nitrides, depending on the different heating processes.

5-Nitropyrimidine is often used as an intermediate for the synthesis of chemicals that may be used as pharmaceutical drugs or herbicides. The impact sensitivity of polynitropyrimidines and similar polynitroheteroarenes and nitroheterocyclic compounds can be predicted by interpolating between known data and applying structural adjustment factors [148, 149].

### 18.2.1 Pyrimidinium Salts

Protonation or alkylation of pyrimidine typically takes place at only one of the ring nitrogen atoms.

### 18.2.2 Hexahydropyrimidine

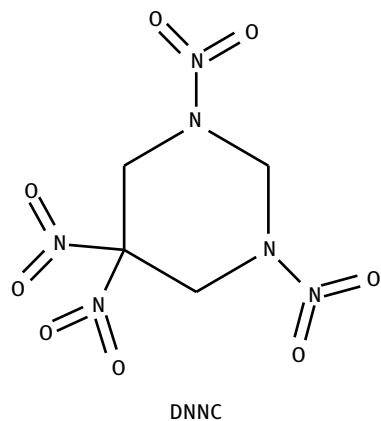
Hexahydropyrimidine is the fully reduced form of pyrimidine. It is a ring-closed secondary amine. Several books have been devoted to the chemistry of pyrimidines and several sections in the books on pyrimidines deal with the reduced pyrimidines: [1177, 1178]. 1,3,5,5-Tetranitrohexahydropyrimidine is a thermally stable, high-melting ener-

getic compound. It can be prepared by nitration of 1,3-diisopropyl-5,5-dinitrohexahdropyrimidine with 90%  $\text{HNO}_3$ .

Triple aminoalkylation of nitromethane with formaldehyde and *tert*-butylamine resulted in a cyclic Mannich base, the nitrolysis of which gave 1,3,5-trinitro-hexahdropyrimidine (TNP) [1179]. Two of the nitro groups are on a nitrogen atom, thus making this a nitramine, and one of the nitro groups is attached to a carbon atom. Hydroxymethylation and subsequent nitration converted it to 5-nitroxymethyl-1,3,5-trinitrohexahdropyrimidine. Both compounds exhibited explosive properties.

The kinetics and mechanism of the thermal decomposition of 1,3,5-trinitrohexahdropyrimidine (TNP), morphology, and the gaseous products evolved were analyzed using TGA, DTA, DSC, IR, XRD, and hot-stage microscopy [1180]. The elementary cell parameters obtained from the XRD pattern were:  $a = 18.818 \pm 0.005 \text{ \AA}$ ,  $b = 18.818 \pm 0.005 \text{ \AA}$ , and  $c = 4.867 \pm 0.005 \text{ \AA}$ . Kinetic rate parameters were evaluated from the induction period as well as from isothermal TGA. The activation energy of TNP decomposition was 202.05 kJ/mol, and the pre-exponential factor  $\log A$  (in units of  $\text{s}^{-1}$ ) was 22.78 based on results from TGA measurements. Slightly different data,  $E_{\text{act}} = 181.133 \text{ kJ/mol}$  and  $\log A = 20.97 \text{ s}^{-1}$  were obtained from IR measurements. The cleavage of the N—N bond appears to be the primary step in the thermolysis of TNP.

1,3,5,5-Tetranitrohexahdropyrimidine, also known as DNNC,  $\text{C}_4\text{H}_6\text{N}_6\text{O}_8$ , CAS RN [81360-42-1],  $M = 266.126 \text{ g/mol}$ , was synthesized from 2,2-dinitro-1,3-propanediol by a cyclization reaction with *tert*-butylamine and formaldehyde followed by nitration. This replaced the *tert*-butyl groups with nitro groups. DNNC has been evaluated as an oxidizer and as a replacement for AP [1181].



DNNC has a density of  $\rho = 1.82 \text{ g/cm}^3$ , an enthalpy of formation of +46 kJ/mol (+11 kcal/mol), and a melting point of 424–427 K (151–154 °C). The impact sensitivity in an Allegany Ballistics Laboratory (ABL) tester was 3.5 cm and the friction sensitivity in the ABL friction sensitivity tester was 660 lbf at 8 ft/s.

### 18.3 Pyrazines

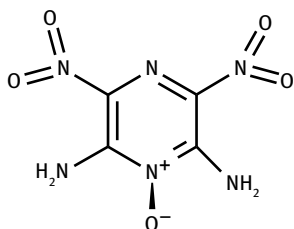
Pyrazine,  $C_4H_4N_2$ , 1,4-diazine, 1,4-diazabenzene, p-diazine, CAS RN [290-37-9], forms low-melting colorless crystals with a density of  $1.031 \text{ g/cm}^3$  that melt at 326 K ( $53^\circ\text{C}$ ) and boil at 388 K ( $115^\circ\text{C}$ ). It is soluble in water and forms salts with strong acids such as nitric acid or perchloric acid. A comprehensive review of the entire chemistry of pyrazines is published in [1182].

#### 18.3.1 Tetra-Substituted Pyrazine Derivatives

2,6-Diamino-3,5-dinitropyrazine is a precursor for making 2,6-diamino-3,5-dinitropyrazine-1-oxide, which has been investigated as an IHE. 2,6-Diamino-3,5-dinitropyrazine, 3,5-dinitro-2,6-pyrazinediamine; 2,6-pyrazinediamine, 3,5-dinitro-;  $C_4H_4N_6O_4$ , DADNPZ; CAS RN [52173-59-8],  $M = 200.11 \text{ g/mol}$ , melts at 573–623 K ( $300\text{--}350^\circ\text{C}$ ) (dec.), has a density of  $1.860 \text{ g/cm}^3$ , and a HOF of  $-22.6 \text{ kJ/mol}$  ( $-5.4 \text{ kcal/mol} = -27 \text{ cal/g}$ ).

#### 18.3.2 2,6-Diamino-3,5-dinitropyrazine-1-oxide

2,6-Diamino-3,5-dinitropyrazine-1-oxide, also known as LLM-105, ANPZ-O,  $C_4H_4N_6O_5$ , CAS RN [194486-77-6],  $M = 216.11 \text{ g/mol}$ , melts at 575 K ( $302^\circ\text{C}$ ) (dec.), has a density of  $1.913 \text{ g/cm}^3$ , and an enthalpy of formation of  $-13.0 \text{ kJ/mol}$  ( $-3.1 \text{ kcal/mol} = -14 \text{ cal/g}$ ). 2,6-Diamino-3,5-dinitropyrazine-1-oxide is an *N*-oxide and is an IHE.



2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105)

2,6-Diamino-3,5-dinitropyrazine-1-oxide, which was developed at the Lawrence Livermore National Laboratory, is also referred to as LLM-105 [227, 1183–1185]. Its structure is related to that of 2,6-dinitro-3,5-diaminopyridine-*N*-oxide. It is thermally stable, has a density of  $\rho = 1.913 \text{ g/cm}^3$ , a melting point of  $348^\circ\text{C}$  (dec.), and a detonation velocity of 8730 m/s. LLM-105 has performance and insensitivity properties between those of HMX and TATB. Its calculated energy content is about 81% that of HMX but 15% more than that of TATB and 30% more than that of TNT. DSC traces (exotherm onset 627 K =  $354^\circ\text{C}$ ) indicated that it is thermally more stable than most known high explosives and is nearly identical to TATB. It is insensitive to shock, spark, and friction and its impact insensitivity (drophammer results) ( $DH_{50} = 117 \text{ cm}$ ) approaches that of TATB ( $DH_{50} > 177 \text{ cm}$ ),

however, it is less sensitive than RDX. The impact sensitivity is dependent on particle morphologies. Coarse particles (80  $\mu\text{m}$ ) had a DH50 of 115–120 cm but smaller (rapidly precipitated or ball-milled) powder was more sensitive and had DH<sub>50</sub> values in the 55–80 cm range. In the crystal lattice, these IHE pack in either graphite-like sheets (TATB and DAAF) or a herringbone arrangement (FOX-7 and LLM-105). This maximizes the amount of  $\pi$  stacking between each molecule, which enhances stability.

There are various methods to prepare compound LLM-105, with most methods starting from commercially available 2,6-dichloropyrazine and oxidizing 2,6-diamino-3,5-dinitropyrazine in the final step to the 1-oxide [1186, 1187]. Other synthesis methods start with 2,6-diaminopyrazine-1-oxide (DAPO) [1188, 1189]. DAPO can be made by the nitrosation of iminodiacetonitrile to *N*-nitroso biscyanomethylamine and via the formation of DAPO via condensation of hydroxylamine with *N*-nitroso biscyanomethylamine.

The thermal and shock sensitivities of PBX formations based on 2,6-diamino-3,5-dinitropyrazine-1-oxide (commonly called LLM-105, which stands for Lawrence Livermore Molecule #105) were investigated using a one-dimensional time to explosion (ODTX) apparatus to generate times to thermal explosion at various initial temperatures [1190]. A four-reaction chemical decomposition model was developed to calculate the time to thermal explosion versus reciprocal absolute temperature curve. LLM-105 exhibited thermal and shock sensitivities intermediate between those of TATB and HMX.

LLM-105 has performance that is superior to TATB and TATB-like insensitivity. A recrystallization study on LLM-105 included the use of an ionic liquid solvent to aid in dissolution [1191]. The use of ionic liquids in recrystallizing highly insoluble energetic materials is a new technique. The recrystallization study evaluated alternative methods to achieve the desired particle size, purity, and morphology of LLM-105.

The enthalpies of formation for 2,6-diamino-3,5-dinitropyrazine (**I**), 2,6-diamino-3,5-dinitropyrazine-1-oxide (**II**) (LLM-105), and 2,6-diamino-3,5-dinitropyrazine-1,4-dioxide (**III**) were calculated using quantum mechanical computational methods to obtain accurate energies. These were compared with experimental values that were available for (**I**) and (**II**) [1192]. 2,6-Diamino-3,5-dinitropyrazine (**I**) was theoretically identified as the most stable compound, both thermodynamically (least endothermic) and with respect to its impact sensitivity. The gas phase enthalpy of formation was predicted as +126.8 kJ/mol (+30.3 kcal/mol). The enthalpy of sublimation was predicted as 108.4 kJ/mol (25.9 kcal/mol). This leads to an enthalpy of formation for the solid of +18.4 kJ/mol (+4.4 kcal/mol), which was in fair agreement with the experimental value of –13.0 kJ/mol (–3.1 kcal/mol). Based on their calculations, LLM-105 has a high density of 1.92 g/cm<sup>3</sup>, a detonation velocity of 8516 m/s (literature: 8730 m/s), and a detonation pressure of 320 kbar (literature 359 kbar), which are comparable to those of RDX. However, LLM-105 is much less impact sensitive than RDX and is not sensitive towards electrostatics and friction. 2,6-Diamino-3,5-dinitropyrazine 1,4-dioxide (**III**) was identified as a promising nitrogen-rich explosive that exceeded



the explosive power of **(II)**. Its performance is comparable, or slightly superior, to that of RDX.

LLM-105 can be prepared by methoxylation, nitration, amination, and oxidation using 2,6-dichloropyrazine as the starting material. The effects of the methoxylation reaction condition, different nitration systems, different amination systems, and the volume ratio of trifluoroacetic acid and hydrogen peroxide on the total yield of LLM-105 were investigated [1193, 1194]. Optimized synthesis conditions were: 25% sodium methoxide methanol solution; reflux for 3 h; 2,6-dimethoxypyrazine as intermediate for nitration; 20% oleum and potassium nitrate nitration system; the reaction at room temperature for 3 h; protonic solvent ethanol as amination solvent; the reaction at 333 K (60 °C) for 2 h; the volume ratio of trifluoroacetic acid and 30% hydrogen peroxide as 3:2; the reaction at 318 K (45 °C) for 6 h. The total yield of LLM-105 was 54%.

2,6-Diaminopyrazine, as the precursor of LLM-105, was synthesized via cyclization with *N*-nitrosobis(cyanomethyl) amine as the starting material. Following that, LLM-105 was synthesized via three different routes: nitration and *N*-oxidation for the first route, *N*-oxidation and nitration for the second route, and finally, acetylation, *N*-oxidation, and nitration for the third route [1195]. Through the comparisons of the reaction conditions of nitration and *N*-oxidation and the total yield and purity of the target product of the three different routes, it was found that the route with acetylation, *N*-oxidation, and nitration (with a yield of LLM-105 of 45.8% and purity over 99%) was the best choice. Detonation velocity, detonation pressure, DSC, and sensitivities of impact for LLM-105 were measured and the results showed that the capabilities of LLM-105 are greater than that of TATB. The structures of the intermediates and LLM-105 were characterized by <sup>1</sup>H-NMR, IR, and MS spectra. An improved synthesis method for 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) gave a total yield of 54% [1196].

2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105) was synthesized by methoxylation, nitration, amination, and oxidation using 2,6-dichloropyrazine as starting material, with an overall yield of 60.2% [1197]. LLM-105 and its intermediates were characterized by IR, <sup>1</sup>H NMR, MS, and elemental analysis. The structure of LLM-105 was computed using a B3LYP quantum mechanical method. A study of the relationship between the steady geometric configuration and the temperature of thermodynamic properties showed that all atoms of the pyrazine ring are mainly coplanar, and that the values of heat capacity and entropy increase with increasing temperature (over the temperature range of 273 to 1000 K).

The nitration reaction process for the synthesis of 2,6-diamino-3,5-dinitropyrazine was investigated using 2,6-dimethoxypyrazine as raw material under different nitration conditions, including mixed acid, oleum-nitric acid, and oleum-KNO<sub>3</sub> [1198]. The effect of the mixed acid ratio, reaction time, and reaction temperature on the yield of the nitration reaction product were explored. The optimal process conditions of the nitration were determined as follows: reaction temperature 298 K (25 °C), reaction time 3 h, 20% oleum-KNO<sub>3</sub> system (molar ratio 3.5:1) in which KNO<sub>3</sub> is in excess of 100%, and a 0.1 mol dosage of 2,6-dimethoxypyrazine. Under these conditions, the yield of 2,6-dimethoxy-3,5-dinitropyrazine was 67.8%.

As already discussed earlier, gas-phase enthalpies of formation for NTO, DADNE, LLM-105, TNT, RDX, TATB, HMX, and PETN were calculated using quantum composite methods [488]. Calculations for HMX and PETN dealt with the largest molecules attempted with these methods at any time before. Some calculations were close to one another, with a larger difference found between other methods used. The mean absolute deviations between average experimental values and calculations were 12 to 3 kcal/mol.

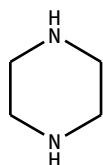
While the mono-*N*-oxide of 2,6-diamino-3,5-dinitropyrazine can be prepared by a variety of different methods and has been described in detail, the di-*N*-oxide, 2,6-diamino-3,5-dinitropyrazine-1,4-dioxide, is more difficult to obtain. Very little has been published about this more energetic (that is, more energetic than LLM-105) compound. One of the synthesis methods starts with pyrazine-2,3-dicarboxylic acid and goes through a series of nitration, amination, and oxidation steps [1199].

### 18.3.3 Pyrazinium Salts

Pyrazine is less basic than pyridine, pyridazine, or pyrimidine. The acidity constant ( $pK_a$ ) is 0.37. It forms salts with strong acids. Quaternary pyrazinium salts with varying lengths of alkyl group and terminal fluorine substitution in the alkyl group with perchlorate as the anion had low melting points of 345–375 K (72–102°C) and good thermal stability [202].

## 18.4 Piperazine

The completely reduced pyrazine is piperazine, a dual secondary amine, also known as  $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$ ,  $\text{C}_4\text{H}_{10}\text{N}_2$ , 1,4-diazane, 1,4-diazacyclohexane, hexahydropyrazine, piperazidine, diethylenediamine, CAS RN [110-85-0]. Piperazine is a symmetric molecule with the base properties of a double secondary amine.



Piperazine

One of its derivatives, 1,4-dimethylpiperazine, a tertiary diamine that is dissolved in gasoline, kerosene, JP-4, isooctane, or cyclohexane, has been patented as a hypergolic rocket fuel [1200]. Piperazine is a white crystalline solid with a melting point of 379 K (106°C), a boiling point of 419 K (146°C), and demonstrates complete miscibility with water. A form in which piperazine is commonly available industrially is as the hexahydrate,  $\text{C}_4\text{H}_{10}\text{N}_2 \cdot 6\text{H}_2\text{O}$ , which melts at 317 K (44°C) and boils at 398–403 K (125–130°C).

Its acidity ( $\text{pK}_a$ ) is 9.8 and it forms monoprotinated and diprotinated salts with strong acids. Many modern notable drugs contain a piperazine ring as part of their molecular structure.

#### 18.4.1 Piperazinium Salts

Piperazine can form mononitrate and dinitrate (PIPDN) salts. The thermal decomposition of piperazinium(2+) dinitrate was examined by DSC and rapid-scan FTIR [1201]. The decomposition of PIPDN initially yields  $\text{HNO}_3$  but then generates a significant amount of *N,N*-dinitrosopiperazine along with small molecule fragments. The presence of nitrosamines strongly increases the health hazard of the materials upon heating. No nitramines were detected as thermolysis products. The crystal structure of PIPDN was determined during the same effort.

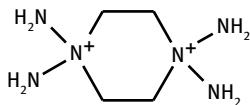
Piperazinium(2+) dinitrate and piperazinium(2+) diperchlorate have been examined as potential propellant ingredients. Piperazinium(2+) dinitrate, 1,4-diazacyclohexane dinitrate,  $[\text{H}_2\text{N}(\text{C}_2\text{H}_2)_2\text{NH}_2](\text{NO}_3)_2$ , melts at 468 K (195 °C) and, in the DTA, the two maxima of two exotherm peaks are at 540 and 577 K (267 and 304 °C) [1202].

Piperazinium(2+) diperchlorate crystallizes as  $[\text{H}_2\text{N}(\text{C}_2\text{H}_2)_2\text{NH}_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ , the dihydrate. The IR spectrum of the compound exhibited characteristic absorptions at  $1100\text{ cm}^{-1}(\text{s})$ ,  $970\text{ cm}^{-1}(\text{m})$ , and  $620\text{ cm}^{-1}(\text{s})$ . This is due to the Cl—O stretching vibrations of  $\text{ClO}_4$  with  $T_d$  symmetry. The broad absorption band at  $3480\text{ cm}^{-1}$  and a medium intensity band at  $1630\text{ cm}^{-1}$  are the characteristics of lattice water. The absorption frequencies at  $3180\text{ cm}^{-1}(\text{s})$  and  $1595\text{ cm}^{-1}(\text{s})$  are attributed to the  $-\text{NH}_2$  groups of the piperazinium cation.

The thermal stability of piperazinium(2+) diperchlorate dihydrate was measured by simultaneous TGA and DTA in an argon atmosphere at a heating rate of 2/min [1203]. From the TGA, one can see that the compound loses weight in two stages. The first stage registers a loss of 9.5%, which occurs in the temperature range of 328–443 K (55–170 °C). The weight loss observed was attributed to the dehydration process as it corresponded to the calculated weight loss of 11% for the removal of two molecules of water of hydration from the parent compound. There was an endothermic peak around 348 K (75 °C) in the DTA curve. The anhydrous material was found to be stable up to 513 K (240 °C). In the second stage, between 513 and 553 K (240 and 280 °C), the compound decomposed with a mild explosion, and the reaction was highly exothermic. No residue was left behind at 553 K (280 °C). The DTA displayed a sharp exothermic peak at 563 K (280 °C). The mass spectrum was extremely complex and showed masses that were attributed to two linked diazane rings.

Piperazinium(2+) bis-dinitramide melts at 485–487 K (212–214 °C) [1161]. The enthalpy of formation of piperazinium(2+) bis-dinitramide was not measured but was extrapolated from similar compounds with known properties and was concluded to be  $-236\text{ kJ/mol}$  (calc.) ( $-56.4\text{ kcal/mol}$ ) [1161].

*N,N,N',N'*-Tetraaminopiperazinium is a quaternary dianionic cation that can form salts with many energetic anions, including an 5,5'-azotetrazolate [1204, 1205].

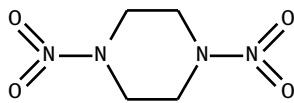


N,N,N',N'-Tetraaminopiperazinium Dication

#### 18.4.2 Piperazine Derivatives

Instead of having two loose alkyl groups dangling from the sides of the  $-\text{N}(\text{NO}_2)-$  group, the secondary amine from which a nitramine is derived could be a heterocyclic amine where the ring contains two or more  $-\text{CH}_2-$  or  $-\text{NH}-$  or  $-\text{O}-$  groups. Piperazine derivatives of particular interest are the nitramine and the dinitramine in which one or both hydrogens on the nitrogen(s) are replaced by nitro groups, thus forming cyclic nitramines.

1,4-Dinitropiperazine, 1,4-dinitro-1,4-diazacyclohexane,  $\text{C}_4\text{H}_8\text{N}_4\text{O}_4$ , CAS RN [4164-37-8], DNPP, 1,4-DNDC,  $M = 176.13 \text{ g/mol}$ , is a cyclic nitramine that is similar to RDX, except that it contains only two instead of three nitramino  $>\text{N}-\text{NO}_2$  links in the ring.



1,4-Dinitropiperazine, DNPP

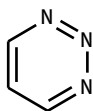
1,4-Dinitropiperazine melts at 490 K and the heat of fusion is  $33.29 \text{ kJ/mol}$  [1206]. The standard enthalpy of formation of solid DNPP is  $+53 \pm 2 \text{ kJ/mol}$  ( $+12.7 \pm 0.4 \text{ kcal/mol}$ ) and the enthalpy of sublimation of DNPP is  $111 \pm 0.8 \text{ kJ/mol}$  ( $26.6 \pm 0.2 \text{ kcal/mol}$ ). The heat of combustion of DNPP is  $2669 \pm 1.7 \text{ kJ/mol}$  ( $638 \pm 0.4 \text{ kcal/mol}$ ) [1207].

The synthesis of 1,4-dinitro-2,3-dinitraminopiperazine was achieved by a circuitous route, starting with a Mannich reaction of ethylenediamine, glyoxal, and urea to form 2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one, which was nitrosated to give 2,5-nitroso-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one, then nitrated to give 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one. This was then hydrolyzed to give 1,4-dinitro-2,3-dinitraminopiperazine, which is a highly energetic compound [1208].

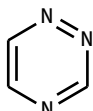
Attaching two azidoethyl groups to the nitrogens in the 1,4-positions of piperazine makes a more energetic molecule, 1,4-bis-(2-azidoethyl)-piperazine. The double chloride salt has a formula of  $\text{C}_8\text{H}_{18}\text{N}_8\text{Cl}_2$  which has been described in a publication [1209]. It crystallized in monoclinic shapes, space group  $P2_1/n$  (No. 14), with crystal lattice parameters of  $a = 6.5246(3) \text{ \AA}$ ,  $b = 7.7090(4) \text{ \AA}$ ,  $c = 13.9243(6) \text{ \AA}$ ,  $\beta = 101.240(3)^\circ$ ,  $V = 686.93(6) \text{ \AA}^3$ , and  $Z = 2$ .

## 19 Triazines

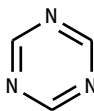
Triazines are six-membered aromatic heterocycles that contain three nitrogen atoms in a symmetrical arrangement (*s*-triazines = 1,3,5-triazines) or unsymmetrical (= 1,2,3- or 1,2,4 triazines) arrangement:



1,2,3-Triazine



1,2,4-Triazine



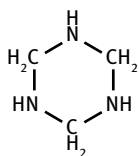
1,3,5-Triazine

Two comprehensive reviews of the entire chemistry of triazines have been published [1210, 1211]. Many energetic compounds are based on triazine [1212].

The thermal decomposition mechanism of *s*-tetrazine was studied by combining the *ab initio* molecular dynamics (AIMD) method and the DFT method [1213]. The dissociation channel was first simulated in several trajectories based on an AIMD method, then further examined using Gaussian 98 to locate the minimum points and the transition structure. High-accuracy single-point calculations were performed and the rate constants were calculated by a microcanonical variational transition state theory. The studies suggested that *s*-tetrazine undergoes concerted triple dissociation to form one N<sub>2</sub> and two HCN.

### 19.1 Hexahydrotriazine

Hexahydrotriazine, 1,3,5-triazacyclohexane, 1,3,5-triazinane, C<sub>3</sub>H<sub>9</sub>N<sub>3</sub>, CAS RN [110-90-7], is a cyclic trifunctional secondary amine.



Hexahydrotriazine, 1,3,5-triazacyclohexane

Hexahydrotriazine forms salts with many acids. The mononitrate salt melts at 445–448 K (172–175 °C). In the DTA, the maximum exothermic peak is at 486 K (213 °C) [1202].

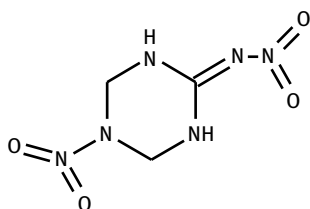
## 19.2 Mono-Substituted Triazines

Unlike other heterocyclic rings such as tetrazines and tetrazoles, the s-triazine ring is quite stable. It tends to undergo depolymerization before catastrophic decomposition. When the more energetic explosophoric groups are attached, the resulting materials have good thermal stability and high energy content.

## 19.3 Di-Substituted Triazines

### 19.3.1 Di-Substituted Hexahydrotriazines

1,3,5-Hexahydrotriazine is a ring-closed secondary amine. Substituents can be carried on either the carbon and/or the nitrogen atoms. 2-Nitroimino-5-nitro-hexahydro-1,3,5-triazine (NNHT) has been tested as a less sensitive explosive [1214].



2-Nitroimino-5-nitro-hexahydro-1,3,5-triazine (NNHT)

The thermal behavior and decomposition reaction kinetics of 2-nitroimino-5-nitro-hexahydro-1,3,5-triazine were investigated by TGA-DTA and DSC under atmospheric pressure and flowing nitrogen gas conditions [1215]. The results showed that the thermal decomposition process of NNHT has two mass loss stages. The kinetic parameters of the exothermic decomposition reaction mechanism were  $E_a = 132 \text{ kJ/mol}$  and  $\log(A) = 12.56 \text{ s}^{-1}$ , respectively. The kinetic equation can be expressed as:

$$\frac{d\alpha}{dt} = 10^{12.86} (1 - \alpha)^{\frac{3}{2}} \exp(-1.5849 \times 10^4 / T).$$

The critical temperature of thermal explosion of NNHT obtained from the peak temperature ( $T_p$ ) is  $T_{bp} = 467 \text{ K}$ . The drop weight sensitivity was compared to the thermal sensitivity of the material. A different kinetic rate equation describing the thermal decomposition reaction of NNHT was obtained by TGA-DTA and an integral isoconversional non-linear method [1216]. The standard molar heat capacity of NNHT was  $218 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $298 \text{ K}$ .

The thermal properties and the decomposition mechanism of NNHT were studied by DSC-TGA-IR-MS methods [1217]. The results showed that two steps, the hexahydric ring framework cracking and the nitroamino group  $[\text{N}-\text{NO}_2]$  breaking initiate the major exothermic decomposition process. The gaseous products were  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{HCHO}$ ,  $\text{NH}_3$ ,  $\text{CH}_2$ ,  $\text{NH}_2$ ,  $\text{CHO}$ ,  $\text{HCN}$ ,  $\text{HNCO}$ , and  $\text{NO}_2$ .

## 19.4 Tri-Substituted Triazines

The high symmetry of *s*-triazine derivatives imparts outstanding thermal stability to these molecules. A primary example is melamine dinnerware made from melamine-formaldehyde polymers. The same thermal stability is also imparted to explosives derived from triazines such as RDX. The behavior of triazines with substituents on the C-atoms (2,4,6-substituted) is quite different from molecules with substituents on the N-atoms (1,3,5-substituted).

### 19.4.1 1,3,5-Trinitro-1,3,5-hexahydrotriazine (RDX)

Concerning the energetic materials, the most famous *N*-substituted triazine is 1,3,5-trinitrotriazine, RDX, which is a cyclic nitramine. Trying to find the correct location to place the information on RDX in this book at hand depended on deciding whether to list it under nitramines (along with open-chain linear nitramines) in *Encyclopedia of Liquid Fuels*, chapter “Nitramines,” or to list it here under heterocyclic compounds with triazines. Once the decision was made about moving RDX to chapter “Nitramines,” HMX had to be moved as well to the section on eight-membered ring heterocyclic nitramine compounds.

#### 19.4.1.1 RDX Derivatives

Substituting some or all the hydrogens in the hexahydrotriazine ring with more energetic groups will result in energetic materials that have improved properties.

One of the more energetic derivatives, where three of the hydrogens in RDX have been replaced with trifluoromethyl groups, is 1,3,5-trinitro-2,4,6-tris(trifluoromethyl)-hexahydrotriazine (TTFMRDX).

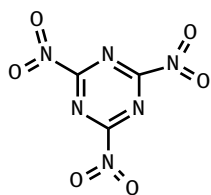
#### 2,4,6-Trinitro-1,3,5-triazine

Electrophilic nitration of 1,3,5-triazine should lead to nitrotriazines with nitro groups on the C-atom instead of the N-atom. However, in contrast to the nitration of aromatic compounds, that of heteroaromatic compounds containing several nitrogen atoms is significantly inhibited due to the acceptor effect of the nitrogen atoms present in the ring (the nitration rate decreases 10<sup>6</sup>-fold upon substitution of one C=N for a C=C fragment). Nitration in acidic media creates additional difficulties due to easier protonation of nitrogen-containing heterocycles in comparison to aromatic rings, which also reduces the nitration rate. In general, direct nitration of six-membered azines is possible only if the heterocycle contains some activating groups (e.g., amino or hydroxy groups) or if it has *N*-oxide groups to start with. However, no more than two nitro groups can be incorporated simultaneously, irrespective of the nature of the heterocycle. An excellent overview of the chemistry of nitro-1,3,5-triazines is provided in [1218].

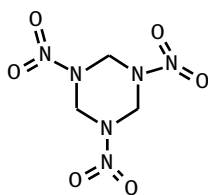
A few dimethylamino-substituted mononitro-1,3,5-triazines were prepared by photochemical oxidation of azido-1,3,5-triazines in the presence of oxygen or

by ozonization of the corresponding hydroxyaminotriazines or nitrosotriazines. A hypothetical route to 2,4,6-trinitro-1,3,5-triazine would be the trimerization of nitrocyanogen. While nitrotriazines were elusive, nitraminotriazines and nitromethyl-, and dinitromethyl- and trinitromethyltriazines were produced. Nitration of melamine gives dinitroammeline in 44–52% yield. 2,4,6-Tris-(trinitromethyl)-1,3,5-triazine was very difficult to synthesize [1219].

2,4,6-Trinitro-1,3,5-triazine, cyanuric trinitrate, is closely related to hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), except that the nitro groups are not on the nitrogens as in nitramines, but they are attached to the carbon atoms of the triazine ring.



2,4,6-Trinitro-1,3,5-triazine



RDX

2,4,6-Trinitro-1,3,5-triazine would be a desirable high-energy material to have but all efforts to synthesize it so far have been unsuccessful. Nucleophilic nitration of cyanuric chloride with silver nitrite was the first, albeit unsuccessful, attempt to synthesize 2,4,6-trinitro-1,3,5-triazine. Several theoretical studies exploring the molecular structure, predicted enthalpy of formation, and performance as an explosive have been conducted [1220]. The standard enthalpy of formation  $\Delta H_f$  was calculated and found to be equal to  $+192 \text{ kJ/mol} = +46 \text{ kcal/mol}$  and the predicted density was  $2.1 \text{ g/cm}^3$ . Both values are higher than those of RDX [1221, 1222].

The molecular structures of all possible mono-, di-, and tri-nitro-substituted triazine compounds have been considered as potential candidates for HEDMs by using a quantum chemical treatment [1223]. Geometric and electronic structures, thermodynamic properties, and detonation performances of these nitro-substituted triazines were systematically studied using a DFT method. Predicted thermal stabilities were evaluated from the homolytic BDE. The results of the calculations indicated that mono-, di-, and tri-nitro-substituted derivatives of symmetric 1,3,5-triazine were expected to be more stable than their 1,2,3 and 1,2,4 counterparts.

The condensed phase theoretical enthalpy of formation, density, and explosive performance of six triazine derivatives with varying amounts of nitro groups and dinitrotriazolyl groups on the triazine ring were computed [1224]. The compounds hypothesized included 2-[3,5-dinitro-1,2,4-triazolyl(1)]-1,3,5-triazine, 2-[3,5-dinitro-1,2,4-triazolyl(1)]-6-nitro-1,3,5-triazine, 2-[3,5-dinitro-1,2,4-triazolyl(1)]-4,6-dinitro-1,3,5-triazine, 2,4-bis[3,5-dinitro-1,2,4-triazolyl(1)]-1,3,5-triazine, 2,4,6-tris[3,5-dinitro-1,2,4-triazolyl(1)]-1,3,5-triazine, and 2,4,6-trinitro-1,3,5-triazine.

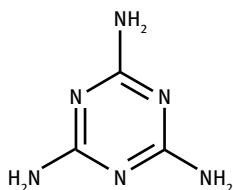


### 19.4.2 2,4,6-Triamino-s-triazine (Melamine)

Melamine, 1,3,5-triazine-2,4,6-triamine, 2,4,6-triamino-s-triazine,  $C_3H_6N_6$ , CAS RN [108-78-1],  $M = 126.12$  g/mol, is a thermally very stable heterocyclic amine. Formally, it can be considered as a trimer of cyanamide  $N\equiv C-NH_2$ . Melamine can be produced by the pyrolysis of urea or guanidinium carbonate and by many other methods.

The kinetics of the potassium hydroxide-catalyzed formation of melamine from dicyandiamide in diethylene glycol monoethyl ether at 383–423 K (110–150 °C) is consistent with the rate of depolymerization of dicyandiamide to cyanamide [1225]. The rate of formation of melamine from a mixture of dicyandiamide and cyanamide (1 : 1 in molar ratio) was almost identical to that from cyanamide alone. These results suggested a mechanism involving rate-determining depolymerization of dicyandiamide to cyanamide followed by the condensation of the cyanamide produced with dicyandiamide, leading to melamine by cyclization.

The reaction of melamine with formaldehyde produces melamine resins, which are thermally stable and very durable thermosetting polymers used for many household items.



1,3,5-Triazine-2,4,6-triamine

An excellent summary of the preparation and properties of melamine and melamine derivatives has been compiled. This publication is a good starting point for further study [1226].

#### 19.4.2.1 Properties of Melamine

Melamine is a white solid with a very high melting point (with decomposition) of 618 K (345 °C) and a density of 1.574 g/cm<sup>3</sup>. It is slightly soluble in water (3.240 g/L at 293 K [20 °C]).

Melamine crystallizes in monoclinic crystals, space group  $P2_1/a$ , with  $a = 10.537(2)$  Å,  $b = 7.477(1)$  Å,  $c = 7.275(1)$  Å,  $\beta = 112^\circ 9'$ , and  $Z = 4$  [1227–1229]. The enthalpy of formation of melamine is  $-87.07$  kJ/mol ( $-20.81$  kcal/mol =  $-165$  cal/g) and the density is 1.573 g/cm<sup>3</sup> [61].

The pyrolysis of melamine has been studied within the temperature range 473–773 K (200–500 °C) [1230, 1231]. The results indicated three stages of decomposition with the loss of one, two, and three molecules of ammonia per two molecules of melamine corresponding to the formation of melam, melem, and melon, respectively. High-pressure pyrolysis of melamine leads to carbon nanotubes.

Trihydrazinotriazine,  $C_3H_9N_9$ , is also called triaminomelamine,  $N,N',N''$ -triaminomelamine,  $M=171.17$  g/mol. It is a good source of nitrogen for solid gas generators (73.65% N) [1232]. The enthalpy of formation of trihydrazinotriazine is +393.9 kJ/mol (+94.14 kcal/mol = +550 cal/g) and its density is 1.63 g/cm<sup>3</sup> [61]. Trihydrazinotriazine crystals are monoclinic, space group *Cc*, with unit cell parameters of  $a = 3.625$  Å,  $b = 17.603$  Å,  $c = 11.026$  Å,  $\beta = 101.9^\circ$ , and  $Z = 4$  [1233].

### 19.4.3 Melaminium Salts

#### 19.4.3.1 Melaminium Nitrate

Melamine forms a dinitrate salt with nitric acid, but only with an excess of acid [1135]. The gross formula is  $C_3H_8N_8O_6$ , CAS RN [10308-79-9]. Melaminium(2+) dinitrate melts at 477 K (204 °C). In the DTA, the maximum exotherm peak is 610 K (337 °C), making it thermally the most stable salt from a group of 15 heterocyclic compounds investigated [1202]. Melaminium(2+) dinitrate has been patented as an explosive for use in oil and gas exploration where high-temperature stability is required [1234].

Two energetic salts of the melaminium(1+) cation were prepared and characterized by XRD [1235]. The first was melaminium dinitramide, which crystallized in triclinic crystals, space group  $P\bar{1}$ , with  $a = 6.6861(11)$  Å,  $b = 6.9638(16)$  Å,  $c = 10.447(2)$  Å,  $\alpha = 99.07(3)^\circ$ ,  $\beta = 98.30(3)^\circ$ ,  $\gamma = 108.50(3)^\circ$ ,  $V = 445.6(2)$  Å<sup>3</sup>,  $Z = 2$ , and  $\rho = 1.74$  g/cm<sup>3</sup>. Melaminium nitrate crystallized in monoclinic crystals, space group  $P2_1/c$ ,  $a = 3.5789(7)$  Å,  $b = 20.466(4)$  Å,  $c = 10.060(2)$  Å,  $\beta = 94.01(2)^\circ$ ,  $V = 735.0(3)$  Å<sup>3</sup>,  $Z = 4$ , and  $\rho = 1.71$  g/cm<sup>3</sup>. The crystal structures of both salts showed distinct monoprotonated melaminium cations and dinitramide- or nitrate anions, respectively. Efficient packing in the solid state is achieved by extensive hydrogen bonding between two-dimensional zigzag ribbons of the melaminium cations and the respective anions, resulting in high densities of the solid-state structures.

The Raman and FTIR spectra of melaminium(1+) nitrate and its deuterated analogue were recorded in the solid phase [1236]. Molecular geometry and vibrational frequency values of melaminium(1+) nitrate in the electronic ground state were calculated using a DFT method. The calculated results showed that the optimized geometry can well reproduce the crystal structure, and the theoretical vibrational frequency values showed good agreement with experimental values. Melaminium nitrate (in proper dilution to make it non-explosive) is also used as a slow-release fertilizer.

#### 19.4.3.2 Melaminium Perchlorate

Melamine forms mono- and di-protonated salts with strong acids such as perchloric acid. Both melaminium(1+) perchlorate and melaminium(2+) diperchlorate have been made and characterized. They usually crystallize as hydrates with one or several molecules of water in the hydrate sphere (layer). They are potentially explosive.

Melaminium(2+) diperchlorate hydrate, melamine perchlorate, 2,4,6-triamino-1,3,5-triazine-diiium diperchlorate hydrate,  $C_3H_8N_6^{2+} \cdot 2ClO_4^- \cdot H_2O$ , has a high density

( $\rho = 1.94 \text{ g/cm}^3$ ) and its crystal structure is extensively hydrogen bonded and contains water dimers [1237]. Melaminium(2+) diperchlorate hydrate was among a group of melaminium salts prepared and characterized as prospective materials for non-linear optical applications and polarizability. The first and second hyperpolarizability was calculated [1238].

The constituents in 2,4,6-triamino-1,3,5-triazinium(1+) perchlorate monohydrate,  $\text{C}_3\text{H}_7\text{N}_6^+ \cdot \text{ClO}_4^- \cdot \text{H}_2\text{O}$ , are linked via hydrogen bonds of the  $\text{O}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{O}$ ,  $\text{N}-\text{H}\cdots\text{N}$ , and  $\text{N}-\text{H}\cdots\text{Cl}$  types [1239]. All the H atoms of the melaminium cation are involved in the hydrogen bonds. The melaminium residues are interconnected by four  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds. The ribbons are interconnected by other hydrogen bonds as well as by  $[\pi]-[\pi]$  interactions [centroid-centroid distance =  $3.8097 \text{ \AA}$ ]. The crystals are triclinic, space group  $P\bar{1}$ ;  $a = 5.654(4) \text{ \AA}$ ;  $b = 7.553(7) \text{ \AA}$ ;  $c = 11.893(10) \text{ \AA}$ ;  $\alpha = 102.72(4)^\circ$ ;  $\beta = 94.58(3)^\circ$ ;  $\gamma = 110.78(2)^\circ$ ;  $V = 456.1(7) \text{ \AA}^3$ ;  $Z = 2$ ;  $D_{\text{X-ray}} = 1.781 \text{ g/cm}^3$ ; m.p.  $> 470 \text{ K}$ .

Powder XRD analysis confirmed that melaminium(1+) perchlorate monohydrate crystals belong to the triclinic system with space group  $P\bar{1}$  [1240]. FTIR and FT-Raman spectra and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature. Functional group assignment has been made for the melaminium cations and perchlorate anions. Vibrational spectra absorption bands were predicted using quantum chemical DFT calculations and were compared to experimental values.

Single crystals of melaminium perchlorate monohydrate were grown from aqueous solution by slow solvent evaporation at room temperature and used for structural and thermal analysis [1241]. X-ray powder diffraction analysis confirmed that melaminium perchlorate monohydrate crystallizes in the triclinic (space group  $P\bar{1}$ ) structure and the calculated lattice parameters were  $a = 5.6275 \pm 0.0780 \text{ \AA}$ ,  $b = 7.6926 \pm 0.1025 \text{ \AA}$ ,  $c = 12.0878 \pm 0.2756 \text{ \AA}$ ,  $\alpha = 103.89 \pm 1.01^\circ$ ,  $\beta = 94.61 \pm 0.92^\circ$ ,  $\gamma = 110.22 \pm 0.81^\circ$ , and  $V = 468.95 \text{ \AA}^3$ . The thermal decomposition behavior of melaminium perchlorate monohydrate was studied by TGA at three different heating rates of 5, 10, and  $20^\circ\text{C/min}$ . The decomposition of melaminium perchlorate monohydrate occurred in three stages, which included dehydration and decomposition. Dehydration took place between 373 and 393 K ( $100$  and  $120^\circ\text{C}$ ). A rapid mass loss of  $\sim 57\%$  occurred during the second stage between 573 and 623 K ( $300$ – $350^\circ\text{C}$ ). This was due to the elimination of melaminium cations. The thermal decomposition of melamine proceeded in stages and was accompanied by the detachment of ammonia. Melamine first decomposed into melam and then melon. The values of the effective activation energy ( $E_a$ ) and the pre-exponential factor ( $\ln A$ ) of each stage of thermal decomposition for all heating rates were calculated using three different methods. A significant variation of  $E_a$  with conversion ( $\alpha$ ) indicated that the process is kinetically complex.

Melaminium(1+) perchlorate has been patented as a propellant in mixtures with NC [1242]. Melaminium(1+) perchlorate has a melting point of 568 K ( $295^\circ\text{C}$ ) and is stable to 573 K ( $300^\circ\text{C}$ ).

### 19.4.3.3 Melaminium Nitroformate

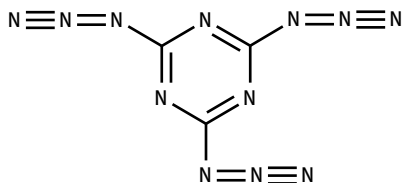
Melaminium nitroformate (MNF) is a very stable nitroformate salt with interesting properties and qualifies as a potential propellant ingredient. It was thermally more stable than some of the other nitroformate salts investigated in the same study. Although two and three-fold protonated melaminium salts are known, the reaction between melamine and nitroform only afforded a 1:1 adduct [1243]. While studying the formation of melaminium salts, however, several single-crystal X-ray structures can be obtained. Two different modifications of MNF have been determined: a high-density modification with a density of  $1.914\text{ g/cm}^3$  and a low-density modification with a density of  $1.771\text{ g/cm}^3$ . The high-density modification of MNF crystallized in the space group  $P2_1/n$  (No. 14) with four formula units per unit cell, whereas the low-density modification crystallized in the chiral space group  $P2_1$  (no. 4) with two independent formula units per unit cell. Depending on the solvent from which MNF was crystallized, two distinctly different structures of MNF could be obtained on recrystallizing MNF from either dimethylsulfoxide or methanol. MNF melts at 391 K (118 °C) and starts to decompose at 416 K (143 °C). IR, Raman, and NMR spectra of the various polymorphs have been determined. The calculated enthalpy of formation for the high-density form is  $-15.48\text{ kJ/mol}$  ( $-3.7\text{ kcal/mol}$ ) and the predicted velocity of detonation is  $8693\text{ m/s}$ .

### 19.4.3.4 Other Melaminium Salts

Thermal decomposition and the non-isothermal kinetics of the thermal decomposition of melaminium 3-nitro-1,2,4-triazol-5-one salt (MNTO) were studied under non-isothermal conditions using DSC and TGA [1244]. The kinetic parameters were obtained from the analysis of the DSC and TGA curves using Kissinger and Ozawa methods. The critical temperature of thermal explosion ( $T_b$ ) was 574 K. The results showed that MNTO is thermally more stable than NTO when compared in terms of the critical temperature of thermal explosion.

### 19.4.4 Cyanuric Triazide

Cyanuric triazide, also known as 2,4,6-triazido-1,3,5-triazine, TAT,  $\text{C}_3\text{N}_{12}$ , CAS RN [5637-83-2],  $M = 204.113\text{ g/mol}$ , is a unique compound in that it consists of only carbon and nitrogen. Cyanuric triazide can be prepared by slowly introducing powdered cyanogen chloride into an aqueous solution of sodium azide with efficient cooling. Cyanuric triazide is extremely sensitive to impact and friction (0.1 N pistil load) and is an effective initiating primary explosive [1245], however, it is not used in practice due to its high vapor pressure. It forms colorless crystals melting with incipient decomposition at 367 K (94 °C = 201 °F). It is a good high-nitrogen compound containing 82.36 mass-% N.



2,4,6-Triazido-1,3,5-triazine (TAT)

The enthalpy of formation is  $+916 \text{ kJ/mol} = +4489.2 \text{ kJ/kg} = +219 \text{ kcal/mol} = +1072.9 \text{ kcal/kg}$ . In the lead block test, the bulging of the cavity was  $415 \text{ cm}^3/10 \text{ g}$ . The drop weight impact sensitivity of TAT is not much different from that of lead azide but it has not been used as a percussion cap stab-sensitive initiator. The drop weight sensitivity of cyanuric triazide was compared to that of other organic azides [1246].

Pulsed laser photolysis of cyanuric triazide resulted in all-nitrogen cations, which were detectable by MS spectrometry [1247]. Fragment peaks may be composed only of nitrogen atoms (atomic mass is 14) but the peak at mass 70 was strong. The fragment of mass 70 ( $14 \times 5$ ) was identified as  $\text{N}_5^+$ , which is considered to have covalent bonds. XRD studies of cyanuric triazide indicated the hexagonal prism-shaped crystals to be of space group  $C6_3/m$  [1248].

The infrared and Raman spectra of cyanuric triazide were obtained using pure crystalline samples and  $\text{CH}_2\text{Cl}_2$  solutions [1249]. Twenty-three of the 26 vibrational fundamentals and several combination bands could be assigned.

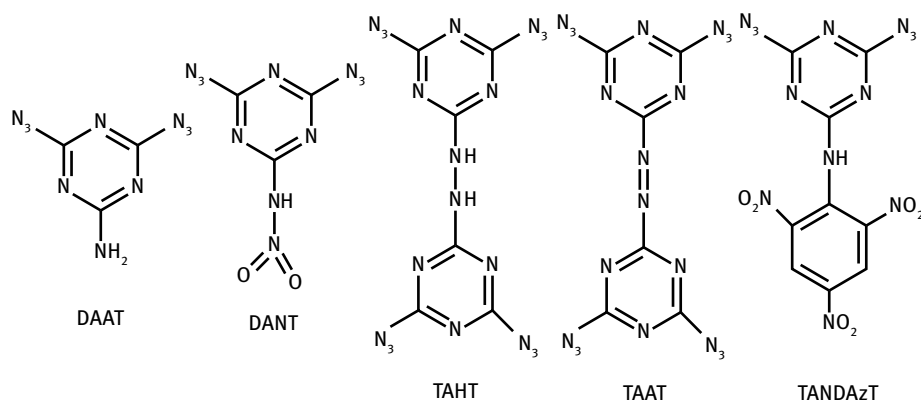
The azide-tetrazole isomerism in several polyazido-1,3,5-triazines, triazido-sym-heptazine, and some diazido-1,2,4,5-tetrazines was investigated by *ab initio* quantum chemical methods to determine whether the polyazides are suitable starting materials for the synthesis of the isomeric tetrazoles [1250]. In the gas phase, polyazidoheterocycles do not cyclize to form tetrazoles. An electron-donating amino group favors the ring closure to tetrazoles, whereas an electron-withdrawing nitro group favors the linear azides. Solvation in polar solvents favors the formation of a tetrazole ring system due to higher charge separation in the tetrazole ring system. However, for all polyazido-1,3,5-triazines, including triazido-s-heptazine, the effects of solvation are not strong enough to shift the equilibrium to the tetrazole side, which explains why several attempts to detect these compounds have failed. Diazidoazo- and hydrazotetrazines will readily cyclize to the tetrazoles in polar solvents.

A nitrogen-rich  $\text{C}_3\text{N}_{12}$  solid was predicted through a transformation from a molecular precursor, cyanuric triazide ( $\text{C}_3\text{N}_3)(\text{N}_3)_3$ , under extremely high pressure and temperature [1251]. The transformation mechanism is mainly governed by azide-tetrazole chain-ring tautomerism leading to the  $\text{sp}^2$  to  $\text{sp}^3$  orbital activation of all carbon atoms. The phase diagram and the equation of state were calculated together with the ambient metastability of the new  $\text{C}_3\text{N}_{12}$  solid, which had a material density of  $2.926 \text{ g/cm}^3$  and an energy density of  $15.56 \text{ kJ/g}$ .

Cyanuric triazide was compressed in a diamond anvil cell at pressures up to 63 GPa [1252]. Infrared spectra indicated the high-pressure formation of a lattice built of trietrazole molecular units.

#### 19.4.5 Other Tri-Substituted Triazines

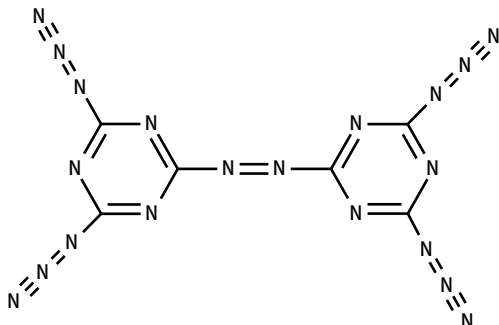
2,2'-Diamino-4,4'-diazidoazotriazine, AMAZT,  $C_6H_4N_{16}$ ,  $M = 300.21$  g/mol, has been evaluated as a burning rate modifier. DFT calculations of the proton transfer in the gas phase and solvent effects on the structural transformation for a series of nitrogen-rich energetic salts derived from nitroamino-1,3,5-triazine predicted that proton transfer from the cations to anions within the salts in the gas-phase may result in neutral hydrogen-bonding complexes [1253]. These salts may be stabilized as ionic structures in the liquid state with solvation energies in the range of  $-37.72$  to  $+69.37$  kJ/mol. These ionic salts exhibited relatively high densities in the range of  $1.63$ – $1.96$  g/cm<sup>3</sup>. A combination of adding  $NH_3OH^+$  to the cation and the addition of a  $-NO_2$  or  $-NF_2$  group to the nitraminotriazine ring anion can improve the detonation performance. Most of the ammonium, hydroxylammonium, and hydrazinium salts were promising energetic materials. Several triazidotriazine derivatives are of interest as propellant ingredients or explosives.



Triazidotriazine Derivatives

The crystal morphologies, thermal behavior, sensitivity, and performance of 2-amino-4,6-diazido-*s*-triazine and its derivatives have been investigated using SEM, DSC, and TGA [1254]. The crystal morphologies of 4,6-diazido-*N*-nitro-1,3,5-triazine-2-amine (DANT), DAAT, 4,4',6,6'-tetraazido-hydrazo-1,3,5-triazine (TAHT), 4,4',6,6'-tetraazido-azo-1,3,5-triazine bis(4,6-diazido-1,3,5-triazin-2-yl)diazene (TAAT), and 2,4,6-trinitrophenyl-4,6-diazido-1,3,5-triazinyl-2-amine (TANDAzT) crystals depend on the conditions of crystallization and determine their sensitivity. The TGA/DSC thermal analysis indicated that there was only one step for the decomposition of

DAAT, while at least three steps were observed for the other materials. DAAT started to decompose at around 421 K (148 °C) with a peak temperature of 470 K (197 °C), while TAHT started to decompose at 440 K (167 °C) with shoulder-peak near 466–480 K (193–207 °C). DANT decomposed with a heat release of ~2500 J/g, which is much higher than that of DAAT thus indicating that the heat of decomposition and its release rate is greatly enhanced by the transformation of an amino to a nitroamino group. The thermal stability of TANDazT was slightly worse than that of DAAT, and it decomposed in the liquid state with a melting point of about 444 K (171 °C).

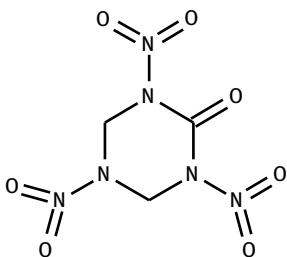


4,4',6,6'-Tetra(azido)azo-1,3,5-triazine,  $C_6N_{20}$ , 79.54% N (TAAT)

TAAT has the highest experimentally measured enthalpy of formation reported for any energetic organic compound measured up to this time (+2171 kJ/mol) [1255].

### 19.5 Multi-Substituted Triazines

2-Oxo-1,3,5-trinitro-1,3,5-triazine, K-6, 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane, 1,3,5-trinitro-1,3,5-triazinan-2-one,  $C_3H_4N_6O_7$ ,  $M = 236.100$  g/mol, is a close relative of RDX. It has a density of  $1.932$  g/cm<sup>3</sup>, a DSC exotherm at 478 K (205 °C), and a measured explosive performance that is 4% greater than that of HMX [1256].



2-Oxo-1,3,5-trinitro-1,3,5-triazine

K-6 can be synthesized by reacting urea, formaldehyde, and *tert*-butyl amine to yield 5-*tert*-butyl-2-oxo-1,3,5-hexahydrotriazine. Nitrolysis of the *tert*-butyl group and further nitration gave K-6 in 21–57% yield, depending on the choice of the nitrolysis reagent. K-6 has superior hydrolytic stability compared to other cyclic dinitroureas, including tetranitroglycoluril (TNGU), K-55, and HK 55 [446]. Its properties are: m.p. = 469 K = 196 °C, impact sensitivity drop height 50% point at  $H_{50}$  = 61 cm, and its explosive performance is equivalent to that of HMX.

The multi-component reaction of 2,4,6-trichloro-1,3,5-triazine with potassium trinitromethanide and trinitroethanol was used for the synthesis of a hetaryl trinitroethyl ether, 2,4-bis(2,2,2-trinitroethoxy)-6-trinitromethyl-1,3,5-triazine, which was used as a precursor for the synthesis of substituted trinitroethoxytriazine by sequential nucleophilic substitution processes. This resulted in several trinitroethoxytriazines bearing a range of functional groups, including 2,4,6-tris-(2,2,2-trinitroethoxy)-1,3,5-triazine [1257].

Computations for 2,4,6-trinitro-1,3,5-triazine-1,3,5-trioxide (TNTATO) using molecular mechanics and DFT predicted the crystal structure, IR spectrum, electronic structure, thermodynamic properties, pyrolysis mechanism, thermal stability, gas-phase and condensed-phase HOFs, detonation performance, and burning rate of TNTATO [1258]. TNTATO has a symmetric hyperconjugation structure that contributes to its stability. TNTATO has a positive oxygen balance and can be used as an oxidizer.

## 19.6 Multi-Ringed Triazines

Instead of having only one triazine ring in the energetic molecule, it has also been attempted to link two triazine rings via an azo —N=N— or a hydrazo —NH—NH— linkage. The other method of connecting is to fuse two rings so they share two atoms along a side of the hexagon.

The syntheses of 4,4',6,6'-tetra(amino)hydrazo-1,3,5-triazine (**1**), tetra(hydroxyl-amino)-hydrazo-1,3,5-triazine (**2**), tetra(hydrazino)-hydrazo-1,3,5-triazine (**3**), and tetra(azido)hydrazo-1,3,5-triazine (**4**) are described in [1259]. Compound (**4**) was oxidized to 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (**5**). The thermal and sensitivity properties of (**4**) and (**5**) were reported in addition to all physical properties of the new compounds. High-nitrogen compounds containing polyazides possess very high HOFs because their energy content rapidly increases with the number of energetic azido groups in the molecule. However, they are notorious for their extreme sensitivity to spark, friction, and impact as well as for their poor thermal stability. Therefore their applications are very limited. Examples include 3,6-diazido-1,2,4,5-tetrazine and cyanuric azide (2,4,6-triazido-1,3,5-triazine). 4,4',6,6'-tetra-(azido)hydrazo-1,3,5-triazine (TAHT) (**3**) and 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT) (**4**) were synthesized and characterized by elemental analysis, XRD, DSC, HOF, and IR and NMR spectroscopy [1255, 1260]. Remarkably, the HOFs of these



polyazido compounds are much higher than those of polynitro and high-nitrogen compounds. The hydrazo and azo linkages not only desensitized the compounds but also dramatically increased the melting point of the polyazido products. The properties are summarized in Table 74.

**Table 74:** Properties of polyazido high-nitrogen triazine compounds.

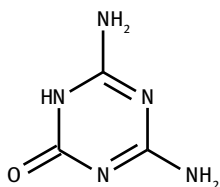
| Compound                                            | Density           | DSC fast decomp. |     | Impact H50 (Type 12) | Friction (BAM) |                 | ESD spark |
|-----------------------------------------------------|-------------------|------------------|-----|----------------------|----------------|-----------------|-----------|
|                                                     | g/cm <sup>3</sup> | K                | °C  | cm                   | N              | kg <sub>f</sub> | J         |
| Cyanuric triazide                                   | —                 | 460              | 187 | 6.2                  | <4.9           | <0.5            | <0.36     |
| 4,4',6,6'-Tetra(azido)hydrazo-1,3,5-triazine (TAHT) | 1.649             | 475              | 202 | 18.3                 | 28.4           | 2.9             | <0.36     |
| 4,4',6,6'-Tetra(azido)azo-1,3,5-triazine (TAAT)     | 1.724 (1.674)     | 473              | 200 | 6.2                  | 23.5           | 2.4             | <0.36     |
| For comparison:<br>PETN                             |                   | 451              | 178 | 14.5                 | 53.0           | 5.4             | >0.36     |

Data source: [1244].

Fourteen simple triazines and 16 different azo —N=N— or hydrazo —NH—NH— linked symmetrical and unsymmetrical triazine derivatives with two triazine were synthesized and characterized [1231, 1261]. The substituents on the rings included chloro, amino, methoxy, hydrazino, and azido groups. When studying the thermal decomposition of the 16 compounds, the linkage between two triazine rings did not appear to alter the decomposition of substituents or act as a trigger mechanism for the decomposition of the triazine ring. Except for the azido-substituted triazine rings, the compounds studied had high thermal stability.

### 19.7 Other Triazine Derivatives

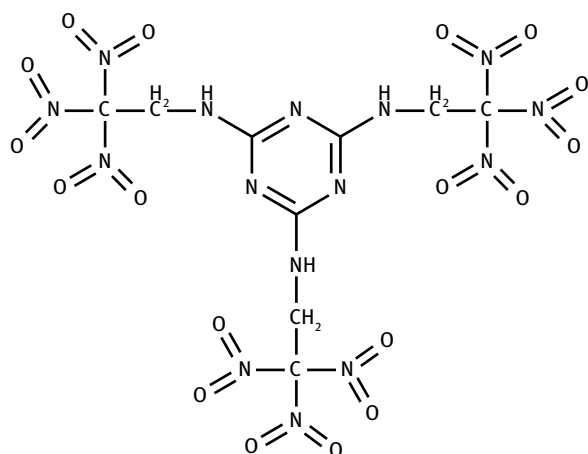
The oxygen balance of energetic triazine derivatives can be improved by not only attaching oxygen-containing groups like —NO<sub>2</sub> or forming salts with oxygen-containing anions, but also by incorporating oxygen in the ring or attaching it in a carbonyl group that is part of the ring; e.g., 2,4-diamino-1,3,5-triazine-6-one, 4,6-diamino-1*H*-1,3,5-triazin-2-one.



2,4-Diamino-1,3,5-triazine-6-one

Energetic salts (nitrate, perchlorate) prepared from 2,4-diamino-1,3,5-triazine-6-one, were synthesized and fully characterized by IR and NMR spectroscopy, elemental analysis, and DSC and had good thermal stability and low impact sensitivity [1262]. The density of the nitrate was  $1.691 \text{ g/cm}^3$  and the density of the perchlorate was  $1.854 \text{ g/cm}^3$ . Most of the salts decomposed at temperatures above 453 K (180 °C). The 2,4-diamino-1,3,5-triazine-6-one nitrate and 2,4-diamino-1,3,5-triazine-6-one perchlorate in particular decomposed at 576 K (303 °C) and 609 K (336) °C, respectively, and were fairly stable. Salts prepared from 2,4-diamino-1,3,5-triazine-6-one would have only a few advantages over salts prepared from melamine, with the latter being the more economical option.

Another way to increase the energy content of melamine-based triazines is to substitute one or two of the hydrogens on the amino groups with more energetic groups. An example is 2,4,6-tris(2,2,2-trinitroethylamino)-1,3,5-triazine. A simple route for the synthesis of 2,4,6-tris(2,2,2-trinitroethylamino)-1,3,5-triazine, N2,N4,N6-tris(2,2,2-trinitroethyl)-1,3,5-triazine-2,4,6-triamine, TTET,  $\text{C}_9\text{H}_9\text{N}_{15}\text{O}_{18}$ , CAS RN [384856-74-0],  $M = 615.258 \text{ g/mol}$ , has been developed [1263].



2,4,6-Tris(2,2,2-trinitroethylamino)-1,3,5-triazine (TTET)

The TTET compound was fully characterized by multi-nuclear ( $^1\text{H}$ ,  $^{13}\text{C}$ ) NMR and IR spectroscopy, elemental analysis, electron ionization mass spectrometry, and DSC. TTET was found to have good physical properties such as good thermal stability ( $T_{\text{dec}} = 459\text{ K} = 186^\circ\text{C}$ ), reasonable impact sensitivity (21.5 J), and high density ( $1.88\text{ g/cm}^3$ ). The detonation properties of TTET obtained with the empirical K-J equations identified it as a competitively energetic compound. Other compounds superior in predicted performance to RDX were 2-(3-nitro-1,2,4-oxadiazole)imino-5-nitro-hexahydro-1,3,5-triazine and 2-(3-nitro-1,2,4-oxadiazole)imino-5-nitroso-hexahydro-1,3,5-triazine [1264].

3,4,5-Triamino-1,2,4-triazolium (guanazinium) salts with promising energetic anions and the 6-nitroamino-2,4-diazido[1,3,5]triazinate anion (NADAT) were prepared and characterized by elemental analysis, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and DSC [432]. The crystal structures of neutral NADAT were determined by single-crystal XRD. All the new salts exhibited desirable physical properties such as relatively high densities ( $1.63\text{--}1.78\text{ g/cm}^3$ ) and moderate thermal stabilities ( $T_{\text{dec}} = 482\text{--}530\text{ K} = 209\text{--}257^\circ\text{C}$ ) for 6-nitroamino-2,4-diazido-1,3,5-triazinate salts.

A collection of 110 energetic salts including many triazine derivatives were designed on paper (or the computer screen) using DFT methods to predict the enthalpies of formation, electronic structure, and energetic properties of a series of triazine-based ionic and non-ionic compounds [1265]. It was observed that the  $\text{--N}_3$  group, triazole, tetrazole, triazine, and tetrazine are effective structural units for increasing the  $\Delta H_f^\circ$ 's. The presence of the  $\text{--NO}_2$  and  $\text{--NHNO}_2$  groups in the same structure was found to help improve densities through strong inter- and intra-molecular hydrogen bonding. One of the theoretical molecules was the 2,4,6-trinitroamino-1,3,5-triazinate anion in the form of its ammonium or guanidinium salt. The predicted explosive performance indicated that most of the compounds would outperform RDX and TATB.

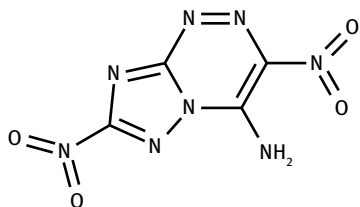
A new class of nitroguanidyl-functionalized nitrogen-rich materials derived from 1,3,5-triazine and 1,2,4,5-tetrazine was synthesized through reactions between *N*-nitroso-*N'*-alkylguanidines and the hydrazine derivatives of 1,3,5-triazine or 1,2,4,5-tetrazine [1266]. These compounds were characterized using NMR and IR spectroscopies, elemental analysis, and DSC. The HOFs for all compounds were calculated and then combined with experimental densities to determine the detonation pressures and detonation velocities. For some of the compounds, the predicted explosive performances were comparable to that of RDX. Another energetic nitroimine compound is dinitroammeline, 4,6-bis(nitroimino)-1,3,5-triazinan-2-one [1267].

### 19.7.1 Cyanuric Acid

Cyanuric acid, also known as 1,3,5-triazine-2,4,6-triol, 1,3,5-trihydroxytriazine,  $C_3H_3N_3O_3$ , CAS RN [108-80-5], can serve as the anion for several energetic salts. Ammonium, hydrazinium, aminoguanidinium, diaminoguanidinium, triaminoguanidinium, aminonitroguanidinium, aminocarbonylguanidinium, and dimethylbiguanidinium cyanurates were synthesized by metathetical reactions. The crystal structures of a few were determined by single-crystal XRD and further characterized by UV-vis, FTIR,  $^1H$  NMR, MS, and elemental analysis [1268]. DTA and TGA results showed that all compounds had high thermal stabilities. Impact sensitivities determined by the fall hammer test showed impact sensitivities of  $>60$  J, which are less sensitive than that of TATB (50 J).

## 19.8 Fused-Ring Triazines

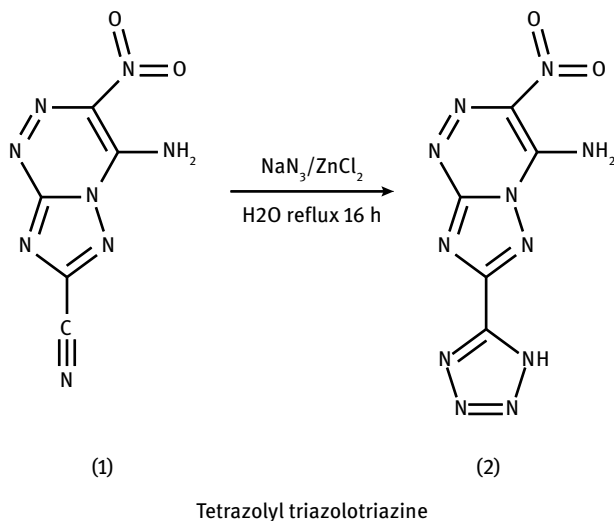
A fused-ring conjugated energetic molecule, 4-amino-3,7-dinitro-[1,2,4]triazolo[1,5-c][1,2,4]triazine, also known as 3,7-dinitro-[1,2,4]triazolo[1,5-c][1,2,4]triazin-4-amine,  $C_4H_2N_8O_4$ , TTX,  $M = 226.11$  g/mol, has been synthesized in a two-step process, starting from the known 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) [1269].



4-Amino-3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazine (TTX)

Characterization of TTX showed that it possesses energetic properties approaching those of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) but with a higher thermal stability and lower sensitivity towards impact and friction. TTX crystalized as monoclinic crystals, space group *Cc* with three molecules in the asymmetric unit with a calculated crystal density of  $\rho = 1.86$  g/cm<sup>3</sup> at 150 K. TTX is highly stable thermally ( $T_{dec} = 545$  K = 272°C) and has a pycnometric density of  $\rho = 1.82$  g/cm<sup>3</sup>. Both of these important parameters of TTX exceed those of RDX ( $T_{dec} = 477$  K = 204°C;  $\rho = 1.80$  g/cm<sup>3</sup>). The HOF was calculated to be +403.5 kJ/mol = 1.78 kJ/g.

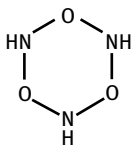
A triazolotriazine carbonitrile (**1**) was formed by diazotization of 3-amino-5-cyano-1,2,4-triazole followed by treatment with nitroacetonitrile [1270]. Cyclization of the nitrile  $C\equiv N$  bond with sodium azide results in 3-nitro-7-(1*H*-tetrazol-5-yl)-[1,2,4]triazolo[1,5-c][1,2,4]triazin-4-amine (**2**).



Compounds **(1)** and **(2)** were characterized by elemental analysis, IR spectroscopy,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and single-crystal XRD. Compound **(2)** has a density of  $\rho = 1.819 \text{ g/cm}^3$ , is thermally stable up to 578 K (305 °C), and is insensitive to impact, friction, or electrical discharge. The enthalpy of formation ( $\Delta H_f$ ) values for **(1)** and **(2)** were calculated and found to be 533 and 753 kJ/mol (127.5 and 179.9 kcal/mol), respectively. The detonation pressure and velocity of **(2)** were calculated to be 27.04 GPa and 8.312 km/s, respectively, making this a good 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) replacement candidate.

#### 19.8.1 1,3,5-Trioxa-2,4,6-triazine

A purely speculative compound that has never been synthesized but would make a good rocket propellant is 1,3,5-trioxa-2,4,6-triazine, 1,3,5,2,4,6-trioxatriazinane,  $\text{H}_3\text{N}_3\text{O}_3$  (note that there is no carbon in this heterocyclic compound).



1,3,5-Trioxa-2,4,6-triazine

The enthalpies of formation of the gas-phase species were computed according to the atomization energy method and found to be  $\Delta H_f^\circ(\text{G}) = +100.6 \text{ kcal/mol}$  [1271]. The enthalpy of sublimation for  $\text{H}_3\text{N}_3\text{O}_3$  was estimated as 74 kJ/mol = 17.7 kcal/mol according to Trouton's rule. With the estimated sublimation enthalpy, the enthalpy of forma-

tion for solid 1,3,5-trioxa-2,4,6-triazine was calculated to be  $\Delta H_f^\circ(\text{S}) = +347 \text{ kJ/mol} = +82.9 \text{ kcal/mol}$ . The density of  $\text{H}_3\text{N}_3\text{O}_3$  was calculated to be  $\rho = 1.60 \text{ g/cm}^3$  from the molecular volume.

## 19.9 Azotriazines

Preliminary information on azotriazines and hydrazotriazines was presented in the section on azidotriazines and detailed further in Table 74. Additional information is provided here.

4,4',6,6'-Tetra(azido)azo-1,3,5-triazine,  $\text{C}_6\text{N}_{20}$ , TAAT,  $M = 352.21 \text{ g/mol}$  with 79% N and 4,4',6,6'-tetra(azido)hydrazo-1,3,5-triazine (TAHT) and a set of computer-designed bridged triazines with similar bridges were studied theoretically to facilitate further laboratory developments [1272]. The molecular structure of TAAT has already been detailed in an earlier section of this chapter.

The gas-phase enthalpies of formation of TAAT and TAHT were predicted based on isodesmic reactions by using a DFT method. The estimates of the condensed-phase enthalpies of formation and heats of sublimation were estimated in the framework of the Politzer approach. Calculations showed that the method provided a good estimation for enthalpies in comparison with available experimental data for TAAT and TAHT. The crystal density was computed using molecular packing calculations. The calculated detonation velocities and detonation pressures indicated that  $-\text{NF}_2$ ,  $-\text{NO}_2$ ,  $-\text{N}=\text{N}-$ , and  $-\text{N}=\text{N}(\text{O})-$  groups would be effective structural units for improving the detonation performance of bridged triazines. The synthesized TAAT and TAHT were not preferred energetic materials due to their inferior detonation performance. The  $p \rightarrow \pi$  conjugation effect between the triazine rings and bridges makes the molecules more stable as a whole. An analysis of the BDE showed that these derivatives had good thermal stability over RDX and HMX, and the  $-\text{NH}-\text{NH}-$  bridge is more helpful for improving the stability than  $-\text{N}=\text{N}(\text{O})-$  and  $-\text{N}=\text{N}-$  bridges.

The enthalpies of formation, electronic structures, energetic properties, and thermal stabilities of a series of bridged 1,3,5-triazine derivatives with different substituents and linkages were studied using DFT methods [1273]. Azido groups and  $-\text{N}=\text{N}-$  azo bridges are effective structural units for improving the  $\Delta H_f$  values of di-1,3,5-triazine derivatives. The  $-\text{NH}_2$ ,  $-\text{N}_3$ ,  $-\text{NH}-$ , and  $-\text{CH}=\text{CH}-$  groups are effective structural units for increasing the thermal stabilities of the derivatives. Based on detonation performance and thermal stability, nine of the compounds are promising candidates for HEDMs with reduced sensitivity.

A detailed study on the structural, electronic, and thermodynamic properties of the solid polyazide 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT) under the hydrostatic pressure of 0-100 GPa was performed using a DFT computational method [1274]. The predicted crystal structure compared well with experimental results at

ambient pressure. The results showed that a pressure less than 40 GPa does not significantly change the crystal and molecular structures. When higher pressure is applied, the molecular geometry, band structure, and density of states change except at 48 and 90 GPa where the azide-tetrazole transformation occurs. At 48 GPa, the tetrazole rings are almost coplanar with the triazine rings, whereas it has a big deviation at 90 GPa. The azide cyclization for polyazido-1,3,5-triazine has not been observed in the gas phase or in polar solvents. An analysis of the density of states showed that the electronic delocalization in TAAT increases generally under the influence of pressure. This indicates that an applied pressure may increase the impact sensitivity.

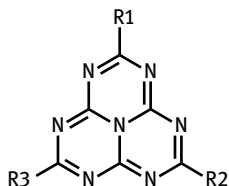
### 19.10 Hydrazotriazines

DFT calculations were performed to study hydrostatic compression effects on the structure, electronic, and thermodynamic properties of 4,4',6,6'-tetraazido-hydrazo-1,3,5-triazine (TAHT) in the range of 0–100 GPa [1275]. At ambient pressure, the relaxed crystal structure compared well with experimental results. The predicted heat of sublimation was 161.8 kJ/mol (38.68 kcal/mol), and the evaluated condensed phase enthalpy of formation ( $\Delta H_f = +1732$  kJ/mol = +414.04 kcal/mol) approximated the experimental value. The detonation velocity and detonation pressure for solid TAHT were predicted to be 7.44 km/s and 23.71 GPa, respectively. When examining the effect of pressure on molecular structure, at less than 35 GPa, the crystal structure and geometric parameters changed only slightly. However, at 36 GPa, the molecular structure, band structure, and density of states changed abnormally because of the azide-tetrazole transformation. This has not been observed in the gas phase or in polar solvents. The azido group cyclizes to form a five-membered tetrazole ring that is coplanar with the triazine ring and contributes to a larger conjunction system. An analysis of the electronic structure showed that an applied pressure would increase the impact sensitivity of TAHT.

### 19.11 Heptazine

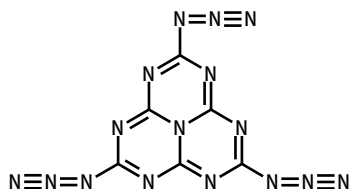
Heptazine,  $C_6N_7$ , 1,3,4,6,7,9b-heptaazaphenalene, which is also called tri-s-triazine or cyamelurine, consists of three fused triazine rings, typically with three substituents at the corners of the triangle [1276]. The name “hepta” initially conjures up the image of a seven-membered ring, however, this molecule is just a honeycomb of hexagonal rings with seven nitrogen atoms embedded, which explains the name hepta. Its skeleton structure is similar to that of the all-carbon phenalene, a polycyclic aromatic hydrocarbon. The parent compound  $C_6N_7H_3$ , where the three substituents are hydrogens, is called 1,3,4,6,7,9-hexaazacyclo[3.3.3]azine or tri-s-triazine proper. Heptazines

are used as flame retardants and have been proposed for applications in electronics materials, explosives, and gas generants.



Generic heptazine; R1, R2, R3 are arbitrary substituents

DFT techniques were used for the prediction of gas phase HOF of nitroheptazines, while crystal density was assessed by packing density calculations [1277]. The results revealed that nitro derivatives of heptazine possess a high HOF. Further enhancement was achieved by the substitution of nitrogen heterocycles. The crystal packing density of the designed compounds varied from 1.8 to 2 g/cm<sup>3</sup>, hence, of all the designed molecules, nitro derivatives of heptazine exhibit better energetic performance characteristics in terms of detonation velocity and pressure. 2,5,8-Tri(azido)-s-heptazine, 3,7,11-triazido-2,4,6,8,10,12,13-heptazatricyclo[7.3.1.0<sup>5,13</sup>]trideca-1(12),2,4,6,8,10-hexaene, 2,5,8-triazido-1,3,4,6,7,9,9b-heptaazaphenalene, C<sub>6</sub>N<sub>16</sub>, contains 75.67 mass-% N.



2,5,8-Triazido-s-heptazine, C<sub>6</sub>N<sub>16</sub> (TAH)

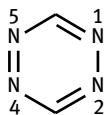
Derivatized s-triazine precursors can be used in the production of carbon nitride materials. Larger polycyclic molecular precursors, such as those containing an s-heptazine core (C<sub>6</sub>N<sub>7</sub> or tri-s-triazine), may improve stability and order in carbon nitride products. Synthesis of 2,5,8-triazido-s-heptazine was achieved from melon, an oligomeric s-heptazine synthesized by the pyrolysis of NH<sub>4</sub>SCN [1278]. Melon was converted to molecular 2,5,8-trichloro-s-heptazine, which was then transformed to triazide. The crystal structure of 2,5,8-triazido-s-heptazine was verified and showed that the s-heptazine is planar and that the azides adopt a pinwheel-like C<sub>3h</sub> arrangement around the periphery. 2,5,8-triazido-s-heptazine exhibits photoluminescence at 430 nm. It rapidly and exothermically decomposes upon heating at 458 K (185 °C) to produce a tan, thermally stable carbon nitride powder with a composition near C<sub>3</sub>N<sub>4</sub>.



2,5,8-Trihydrazino-*s*-heptazine  $C_6N_7(NHNH_2)_3$  can be obtained from melem  $C_6N_7(NH_2)_3$  or melon  $[C_6N_7(NH_2)NH]_n$  and hydrazine by an autoclave synthesis [1279]. Upon treatment with a 10% HCl solution, it can be transformed into the trihydrochloride  $[C_6N_7(NHNH_3)_3]Cl_3$ . These compounds were analyzed by  $^{13}C$  NMR,  $^{15}N$  NMR, XRD, FTIR, and Raman spectroscopy. The reaction of 2,5,8-trihydrazino-*s*-heptazine with  $NaNO_2/HCl$  yields triazido-*s*-heptazine,  $C_6N_7(N_3)_3$ .

## 20 Tetrazines

The most common tetrazine is the symmetrical 1,2,4,5-tetrazine,  $C_2H_2N_4$ , CAS RN [290-96-0],  $M = 82.064$  g/mol.



1,2,4,5-Tetrazine

Tetrazines have highly positive enthalpies of formation and high crystal densities. These are desirable properties for a HEDM backbone. Relatively few unsubstituted tetrazine compounds have been evaluated as rocket propellants. Most of the work was conducted with tetrazines that had amino, hydrazino, nitramino, or guanidino groups attached in the 3- and 6-positions [1012]. These amines form high-energy salts with oxygen-containing mineral acids. With strong nitric acid, tetrazine can also form tetrazinium(2+) dinitrate salts [1280]. There have been numerous efforts to develop and improve tetrazine-based molecular and ionic energetic compounds [1281], such as by linking or fusing tetrazine rings with furazan rings or pyrazole rings [1, 11, 1282–1284].

### 20.1 Molecular Structure of Tetrazines

The thermal decomposition pathways of the *s*-tetrazine molecule and five of its derivatives were simulated by an AIMD method to predict the possible decomposition pathways and identify their relative importance [1285]. The reaction channels were studied by DFT methods to locate the local minimum points and the transition structures. It was also used to verify the result of the AIMD method in terms of energy, with findings suggesting that the *s*-tetrazine molecule underwent concerted triple dissociation. The effect rules of five different substituents on the modes of the tetrazine ring-opening, the stability of the tetrazine ring, and the thermal decomposition mechanism of tetrazine derivatives were investigated. If the stability of the substituent is better than that

of the tetrazine ring, decomposition occurs first through the ring breaking. Otherwise, the substituent reactions first take place.

Dihydrotetrazine can undergo isomerization reactions. A study of the mechanism of hydrogen transfer isomerization reactions for dihydrotetrazine indicated that the reaction is an endothermic and unspontaneous process at room temperature [1286]. The obtained results indicated that the variational effects are small over the whole temperature range, while the tunneling effects are remarkable at low temperatures (200–500 K).

*s*-Tetrazine crystals are monoclinic, space group  $P2_1/c$ . The crystal unit cell has the following dimensions:  $a = 5.23 \pm 0.01 \text{ \AA}$ ,  $b = 5.79 \pm 0.01 \text{ \AA}$ ,  $c = 6.63 \pm 0.01 \text{ \AA}$ , and  $\beta = 115^\circ 30' \pm 15'$  [1287]. The *s*-tetrazine molecule is a planar distorted hexagon with the following bond lengths and angles: C–N 1.334 Å, N–N 1.321 Å,  $\angle$ C–N–N  $115^\circ 57'$ , and  $\angle$ N–C–N  $127^\circ 22'$  [1288].

Although theoretically possible, 1,2,3,4-tetrazine (vicinal) and 1,2,3,5-tetrazine (unsymmetrical) do not exist and only a few derivatives with the isomeric arrangement of the four nitrogens in the ring other than the symmetric 1,2,4,5 arrangement are known [1289].

## 20.2 Thermodynamic Properties of Tetrazines

Thermodynamic properties and the thermal stability of tetrazines vary with the type of substituents. These properties can be determined by experiment or can be predicted by computational chemistry. There has been a flood of computational studies on tetrazines and other heterocyclic energetic compounds but very few have tested the accuracy of the predicted performance by comparing it with actual experimental data.

Substituted *s*-tetrazine compounds were designed and investigated to find comprehensive relationships between the structures and explosive performance of high-nitrogen energetic compounds [1290]. DFT was used to predict the optimized geometries, electronic structures, HOFs, and densities, and the detonation properties were calculated. Calculation results showed that there are good linear relationships between enthalpies of formation, densities, detonation properties, and the number of N atoms in many designed high-nitrogen compounds. Furthermore, several envisioned high-nitrogen compounds showed good predicted detonation velocities and pressures compared with HMX.

The HOFs for a series of 1,2,4,5-tetrazine derivatives were calculated by using DFT, Hartree Fork (HF), and MP2, and semi-empirical methods were utilized also [1291]. The results showed that –CN or –N<sub>3</sub> groups play a very important role in increasing the  $\Delta H_f$  values of 1,2,4,5-tetrazine derivatives. An analysis of the BDE for the weakest bonds indicated that substitutions by –N<sub>3</sub>, –NH<sub>2</sub>, –CN, –OH, or –Cl groups were favorable for enhancing the thermal stability of 1,2,4,5-tetrazine,

however,  $-\text{NHNH}_2$ ,  $-\text{NHNO}_2$ ,  $-\text{NO}_2$ ,  $-\text{NF}_2$ , or  $-\text{COOH}$  group produced the opposite effects. The calculated detonation velocities and pressures indicated that the  $-\text{NF}_2$  or  $-\text{NO}_2$  groups are very helpful for enhancing the detonation performance for the derivatives but the contrary applied for  $-\text{CN}$ ,  $-\text{NH}_2$ , or  $-\text{OH}$  groups.

### 20.3 Ring-Substituted Tetrazines

Tetrazine(s) are the building blocks for a wide array of energetic materials with potential uses as explosives or rocket propellants [1292]. The most desirable substituents are explosophoric groups like nitro or nitramino groups. In addition, one or two nitrogens in the ring can be oxidized to form *N*-oxides.

### 20.4 Di-Substituted Tetrazines

#### 20.4.1 Diaminotetrazine

3,6-Diamino-1,2,4,5-tetrazine,  $\text{C}_2\text{H}_4\text{N}_6$ , DATZ, DATz, CAS RN [19617-90-4], is a symmetrical molecule and has a molecular mass of 112.0934 g/mol. It is a precursor for the synthesis of many more energetic molecules such as 3,6-diamino-1,2,4,5-tetrazine 1,4-dioxide.

The reaction of triaminoguanidinium chloride with 2,4-pentanedione produced 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine in 80–85% yield. Oxidation of bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine with nitric oxide or nitrogen dioxide leads to 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, followed by ammonolysis, which produced 3,6-diamino-1,2,4,5-tetrazine in good yields [1293–1295]. 3,6-Diamino-1,2,4,5-tetrazine melts at 477–478 K (204–205 °C) [1296]. 3,6-Diamino-*s*-tetrazine (DATz) and some other *s*-tetrazine high-nitrogen energetic compounds were synthesized and characterized by IR, elemental analysis, NMR, and DSC at different heating rates [1283].

The enthalpies of formation and densities of six mono-substituted and six di-substituted tetrazine derivatives were calculated using a DFT method [1297]. The values were then used to predict the detonation velocity and detonation pressure of these compounds. The substituents were amino, hydrazino, carbamido, semicarbazido, 2-semicarbazido, and carbohydrazido groups.  $-\text{NH}_2$ ,  $-\text{NHNH}_2$ ,  $-\text{NHCONH}_2$ , and  $-\text{NHCONHNH}_2$  groups showed a strong electrophilic effect when connected with the tetrazine, especially the  $-\text{NHCONH}_2$  group. The predicted properties of 3,6-diaminotetrazine and 3,6-dihydrazinotetrazine are listed in Table 75. The 3,6-dihydrazinotetrazine was predicted to have the worst thermal stability of the twelve compounds examined.

Table 74 demonstrates a predicted  $\Delta H_f^0_{298} = +319.29 \text{ kJ/mol}$  but other sources reported a  $\Delta H_f$  for 3,6-diaminotetrazine as  $+307 \text{ kJ/mol} = +73.37 \text{ kcal/mol}$  [1298]. More

**Table 75:** Predicted properties of 3,6-diaminotetrazine and 3,6-dihydrazinotetrazine.

| Compound name            | Nitro-<br>gen<br>content | $E_{\text{TOTAL}}$ | $\Delta H_f^0_{298}$ |          | Density           | Deto-<br>nation<br>velocity | Deto-<br>nation<br>pressure |
|--------------------------|--------------------------|--------------------|----------------------|----------|-------------------|-----------------------------|-----------------------------|
|                          | Mass %                   | kJ/mol             | kJ/mol               | kcal/mol | g/cm <sup>3</sup> | km/s                        | GPa                         |
| 3,6-Diaminotetrazine     | 74.97                    | -1067.97           | +319.29              | +76.3    | 1.26              | 5.89                        | 12.08                       |
| 3,6-Dihydrazinotetrazine | 78.84                    | -1358.18           | +425.56              | +101.7   | 1.64              | 7.36                        | 22.67                       |

Data source: [1297].

recent sources reported a HOF of  $71.2 \text{ kcal/mol} = +297.9 \text{ kJ/mol} = 635 \text{ kcal/kg}$ , which may be an experimentally measured value [1299].

3,6-Diamino-1,2,4,5-tetrazine (DATz) was synthesized in 500g batches with a yield of 98.7% using 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine as the starting material [1300]. The structure of DATz was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR, MS, and elemental analysis. The thermal decomposition behavior of DATz was studied by DSC, TGA-DTG, and *in-situ* RSFTIR. The crystal structure was determined by XRD. The crystals crystallized in orthorhombic shapes, space group *Cmcm*, with crystal unit cell parameters of  $a = 0.9431(4) \text{ nm}$ ,  $b = 0.7850(3) \text{ nm}$ ,  $c = 0.6267(3) \text{ nm}$ ,  $V = 0.464(3) \text{ nm}^3$ , and  $Z = 8$ ,  $\rho_c = 1.605 \text{ g/cm}^3$ . In the DSC, DATz had an exothermic decomposition peak with a peak at 615 K (342 °C) and had good thermal stability. The thermal decomposition of DATz starts by first breaking the tetrazine ring.

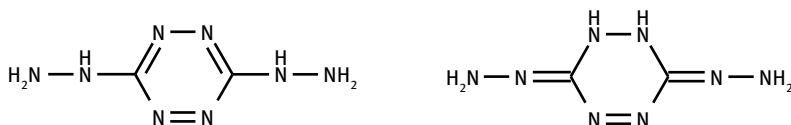
3,6-Diamino-1,2,4,5-tetrazine can be synthesized by nucleophilic substitution using 3,6-bis(3,5-dimethylpyrazol)-1,2,4,5-tetrazine as the precursor [1301]. As the next step, 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAATz) can be obtained by the oxidative coupling reaction of DATz and 3,3'-diazenebis(*N*-(2,2,2-trinitroethyl)-1,2,4,5-tetrazin-6-amino) (BATAT) can be synthesized from 2,2,2-trinitroethanol and DAATz. The structure of BATAT was determined by MS,  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR. The density, enthalpy of formation, detonation velocity, and detonation pressure of BATAT were calculated by a Monte Carlo method and the K-J equation. The predicted density, detonation velocity, and detonation pressure were  $1.827 \text{ g/cm}^3$ ,  $8.76 \text{ km/s}$ , and  $34.11 \text{ GPa}$ , respectively.

Oxidation of 3,6-diamino-1,2,4,5-tetrazine with peracids produced 3,6-diamino-1,2,4,5-tetrazine 1,4-dioxide as a major product [1302]. However, treatment of 3,6-diamino-1,2,4,5-tetrazine with peroxytrifluoroacetic acid produced only 3,6-diamino-1,2,4,5-tetrazine 1-oxide as a major product, along with a small amount of 3-amino-6-nitro-1,2,4,5-tetrazine 2,4-dioxide. All attempts to obtain 3,6-dinitro-1,2,4,5-tetrazine by this way failed.

3,6-Diamino-1,2,4,5-tetrazine-1,4-dioxide is also known under the code name LAX112. LAX112 has a very high detonation velocity of  $8300 \text{ m/s}$  and has been tested as an explosive in comparison to TNAZ and 2,4-DNI [104].

### 20.4.2 Dihydrazinotetrazine

3,6-Bis-(3,5-dimethylpyrazol-1-yl)-s-tetrazine (BDT) can be reacted with hydrazine and refluxed in acetonitrile to form 3,6-dihydrazino-s-tetrazine, also known as 3,6-dihydrazino-1,2,4,5-tetrazine; 1,2-dihydro-1,2,4,5-tetrazine-3,6-dione dihydrazone; 1,2,4,5-tetrazine, 3,6-dihydrazinyl-; dihydrazinotetrazine, 1,2-dihydro-1,2,4,5-tetrazine-3,6-dione hydrazone, (6-hydrazino-1,2,4,5-tetrazin-3-yl)hydrazine,  $C_2H_6N_8$ , DHT, CAS RN [5940-53-4],  $M = 142.13$  g/mol. DHT melts at 434–436 K (161–163 °C), has a density of  $1.667$  g/cm<sup>3</sup>, and has an enthalpy of formation of  $+535$  kJ/mol ( $+128.0$  kcal/mol =  $+901$  cal/g). Other sources gave the melting point as 410–411 K (137–138 °C). It can exist in two tautomeric forms.



3,6-Dihydrazino-1,2,4,5-tetrazine (DHT)

Some properties of DHT have already been listed in Table 75. 3,6-Dihydrazino-1,2,4,5-tetrazine is a very energetic molecule with a highly positive enthalpy of formation ( $+577$  kJ/mol) due to the N–N single bonds of the hydrazine moiety and the aromatic N–N bonds of the 1,2,4,5-tetrazine. The nitrogen content is 78.84 mass-% N. It can serve as a doubly charged cation to create 1:2 or 1:1 salts.

DHT is an example of a high-nitrogen, oxygen-free explosive that relies entirely on its HOF for sustaining a detonation. The density of DHT is  $1.69$  g/cm<sup>3</sup>. Other sources report a density of  $1.61$  g/cm<sup>3</sup> [1303, 1304] or  $1.667$  g/cm<sup>3</sup>. The predicted HOF of DHT in the gas phase is  $+640$  kJ/mol ( $+153$  kcal/mol). The heat of sublimation of DHT is  $105$  kJ/mol ( $25$  kcal/mol). The measured enthalpy of formation of solid DHT is  $+536$  kJ/mol ( $+128$  kcal/mol). The predicted detonation velocity is  $D = 8319$  m/s and the predicted C-J pressure is  $P = 30.41$  GPa [1305].

Other sources of DHT properties reported the following findings:  $\rho = 1.69$  g/cm<sup>3</sup>; auto-ignition temperature  $T_i = 437$  K =  $164$  °C;  $\Delta H_f = +535.5$  kJ/mol =  $+128$  kcal/mol =  $900$  kcal/kg; measured detonation velocity  $D = 7540$  m/s at a packing density of  $1.56$  g/cm<sup>3</sup> [1299]. The vapor pressure of DHT can be expressed by the equation

$$\ln p = 16.4 - 11410/T$$

where  $p$  is the vapor pressure in atm and  $T$  is the temperature in kelvin. The heat of sublimation is  $95$  kJ/mol ( $22.7$  kcal/mol). The dinitrate salt of DHT has a density of  $\rho = 1.80$  g/cm<sup>3</sup>, an auto-ignition temperature  $T_{ign}$  of  $429$  K ( $156$  °C), and an enthalpy of formation  $\Delta H_f$  of near zero. The diperchlorate salt of DHT has a density of  $\rho = 1.96$  g/cm<sup>3</sup>, an auto-ignition temperature of  $593$  K ( $320$  °C), an enthalpy of formation of  $\Delta H_f = +711$  kJ/mol ( $+170$  kcal/mol =  $685$  kcal/kg), and a detonation velocity of  $D = 7520$  m/s at a packing density of  $1.76$  g/cm<sup>3</sup>.

The thermal and EI ionization stabilities of eight 3,6-disubstituted-1,2,4,5-tetrazines were examined by tandem mass spectroscopy techniques to construct fragmentation pathways [1306]. Tetrazine ring structures were not maintained under EI ionization nor under conditions of thermal decomposition. Under EI ionization conditions, the tetrazines shared the same initial fragmentation pathways: elimination of two of the nitrogen atoms as  $N_2$  from the tetrazine ring and cleavage of the remaining N—N bond. This pathway was also applicable to thermal decomposition. However, the main route involved dissociation of the substituent group, in some cases assisted by proton transfer.

The thermal stabilities of 3,6-dihydrazino-1,2,4,5-tetrazine and its diperchlorate [ $Hz_2Tz(HClO_4)_2$ ], dinitrate [ $Hz_2Tz(HNO_3)_2$ ], bisdinitramidate [ $Hz_2Tz(HDN)_2$ ], and bisdinitroimidazolate [ $Hz_2TzBim$ ] salts have been examined and compared to other 3,6-disubstituted tetrazines [1307]. The neutral tetrazines exhibited two principal modes of decomposition. The elimination of  $N_2$  from the tetrazine ring was followed by cleavage of the remaining N—N bond and loss of the substituent group (in some cases, this was assisted by proton transfer). The salts undergo reversible equilibrium with the parent amine and the proton donor. Thus, in several cases, the decomposition rate of the parent tetrazine amine and the salt were essentially identical. For a comparison of DHT with other tetrazine derivatives, see also [1308].

1,4-Dihydrazinotetrazine (DHTz) along with 3,3'-diamino-4,4'-azoxyfuran (DAAF) and 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) were synthesized and characterized by IR, NMR, MS, TG-DTA, DSC, TG-FTIR, impact, and friction sensitivity tests [682]. DAAF is insensitive to mechanical stimuli whereas DAAT and DHTz are vulnerable to impact stimuli. The theoretical explosive power of DAAF, DAAT, and DHTz alone and their combinations with well-known IHE as well as that of propellants based on them were calculated.

3,6-Dihydrazino-1,2,4,5-tetrazine and several of its energetic salts were synthesized from readily available starting materials like triaminoguanidine and 2,4-pentanedione [1309]. The synthesis route described in the literature was scaled up safely. The synthesized compounds were characterized by IR, NMR, elemental analysis, and MS, and the explosive properties (impact and friction sensitivity) and thermal stability properties (TGA/DTG) were studied.

3,6-Dihydrazino-s-tetrazine (DHT) and several other s-tetrazine high-nitrogen energetic compounds were synthesized and characterized by IR, elemental analysis, NMR, and DSC at different heating rates [1283]. The results showed that DHT was stable up to 393 K (120 °C), with a maximum exotherm at 432 K (159 °C) and a heat of reaction  $\Delta H$  of 1843 J/g.

The thermal behavior of 3,6-dihydrazino-1,2,4,5-tetrazine was studied by DSC and TG-DTG [1310]. The decomposition process can be divided into two exothermic decomposition stages with apparent activation energy ( $E_a$ ) and pre-exponential constants ( $A$ ) of the two exothermic decomposition stages being 154.8 and 123.4 kJ/mol, and  $10^{16.63}$  and  $10^{9.48} s^{-1}$ , respectively. The critical temperature of thermal explosion

is 426 K. The specific heat capacity of DHT was determined by the micro-DSC method and a theoretical calculation method. The standard molar specific heat capacity was found to be  $183.6 \text{ J mol}^{-1} \text{ K}^{-1}$  at 298 K. The adiabatic time-to-explosion of DHT was calculated to be somewhere between 263 and 297 s.

3,6-Dihydrazino-1,2,4,5-tetrazine forms dimers in the vapor phase [1311]. DFT methods were used to predict the changes of thermodynamic properties from the monomers to dimers, with the temperature ranging from 200 to 800 K. It was found that the hydrogen bonds predominantly contribute to the dimers and that the binding energies are not determined by hydrogen bonding only.

The molecular structure of a single crystal of 3,6-dihydrazino-1,2,4,5-tetrazine (DHT) was determined by XRD [1312]. The crystal belongs to the monoclinic system with a  $P2_1c$  space group,  $a = 0.4032(4) \text{ nm}$ ,  $b = 0.5649(6) \text{ nm}$ ,  $c = 1.2074(14) \text{ nm}$ ,  $\beta = 99.32^\circ$ ,  $Z = 2$ , and  $V = 0.2714(5) \text{ nm}^3$ . The molecule is centrosymmetric. A three-dimensional herringbone-like pattern was formed with the extensive hydrogen bonds. The heat of combustion was  $1787 \text{ kJ/mol}$  and the autodecomposition explosion point was 454 K. The theoretical standard HOF calculated through an atomization energy method was  $1075 \text{ kJ/mol}$ , leading to a theoretical detonation velocity of  $9.27 \text{ km/s}$  and a detonation pressure of  $36.02 \text{ GPa}$ . Both are higher than those of either TNT or HMX.

The thermal stabilities of 3,6-dihydrazino-1,2,4,5-tetrazine (DHT) and 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylimino)-1,2,4,5-tetrazine (BTATz) were examined using isothermal and non-isothermal methods [1313]. The first stage of DHT decomposition is a redox process in which the tetrazine ring is reduced by the hydrazine group forming diaminodihydrotetrazine and molecular nitrogen. The reaction has a high activation energy of decomposition ( $240.6 \text{ kJ/mol} = 57.5 \text{ kcal/mol}$ ) in the temperature interval 523–607 K (250–334 °C).

3,6-Dihydrazino-1,2,4,5-tetrazine can be synthesized by hydrazinolysis of 3,6-bis-(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine or in four steps via triaminoguanidinium chloride and acetyl acetone, followed by oxidation with liquid  $\text{NO}_2$  in NMP or  $\text{NaNO}_2$  in  $\text{CH}_2\text{Cl}_2$ /glacial acid and substitution with hydrazine. Nine doubly protonated 1:1 and 1:2 bishydrazinium-tetrazine salts of highly energetic anions were synthesized and five of them were characterized by XRD, NMR, MS, IR and Raman spectroscopy, DSC, and elemental analysis [1314]. The energies of formation and the detonation parameters of the most promising candidates were calculated and compared to RDX. Sensitivity tests towards impact, friction, and ESD were carried out. These revealed that some of the compounds were more sensitive than RDX.

If one wants to formulate propellants with high-nitrogen compounds, it is important to know if the highly reactive chemicals are compatible with other constituents (e.g., binders) of the propellant. The interaction of 3,6-dihydrazino-1,2,4,5-tetrazine with the main components of solid propellant was studied by DSC and the interaction of DHT with a CMDB propellant was investigated by a curing experiment [1315]. The results revealed that there were no obvious interactions between DHT with HMX, CL-20, NC, aluminum powder, carbon black, polyethylene glycol, 2-nitrodianiline-

(2-NDPA), 1,3-dimethyl-1,3-diphenyl urea (C2), or diisocyanate (N100). There were strong interactions between DHT and NG, RDX, 3,4-dinitrofurazanofuroxan, *N*-guanylurea dinitramide (FOX-12), *N*-nitrodihydroxyethylamine-dinitrate (DINA), and resorcinol. The DHT/CMDB propellant mixture can catch on fire when the slurry of the propellant is cured at 343 K (70 °C) for about 40 min. DHT cannot be applied to double-base propellants where NG is the main component.

Dihydrazino-1,2,4,5-tetrazine was synthesized from 3,6-di(3,5-dimethylpyrazole)-1,2,4,5-tetrazine and combined with decahydrodecaboric acid [1316]. Dihydrazine-1,2,4,5-tetrazinium decahydrodecaborate was obtained by a neutralization reaction with a yield of 80% and characterized by IR,  $^1\text{H}$  NMR, and elemental analysis. The heat of combustion determined by oxygen bomb combustion was 37.5 kJ/g.

3,6-Dihydrazino-1,2,4,5-tetrazine (DHT) can be used as a burning rate modifier in solid propellants. The thermal decomposition characteristics of DHT and the influence of eight types of lead/copper compounds on the thermal decomposition of DHT were investigated by DSC and TGA-DTG [1317]. The results showed that there are two stages in the DHT decomposition process. The first stage is the main decomposition process, which is the ring opening of the tetrazine ring. The second stage is the decomposition of the condensed phase products of the first stage. The thermal decomposition peak temperature of DHT can be significantly decreased and the exothermicity of DHT can be increased by mixing DHT with lead or copper compounds. Copper compounds have a better effect on decreasing the decomposition temperature of DHT than lead compounds, while lead compounds are more effective in increasing the exothermicity of DHT than copper compounds. Compared with single lead or copper catalysts, a composite catalyst of both lead and copper can further reduce the decomposition temperature and increase the exothermicity of DHT decomposition.

3,6-Dihydrazino-1,2,4,5-tetrazine can be prepared via a hydrazine base substitution reaction using 3,6-bis(dimethylpyrazole)-1,2,4,5-tetrazine (BDT) as raw material [1318]. The conditions of DHT synthesis were optimized, resulting in a yield of 92% and purity of 98.5% (the literature yield was 77%). 3,6-Dihydrazino-1,2,4,5-tetrazinium(2+) dinitrate (DHTN) and 3,6-dihydrazino-1,2,4,5-tetrazinium(2+) diperchlorate (DHTP) were prepared and properties were determined. The yield of DHTN was 91%. The density  $\rho$ , decomposition peak temperature, detonation velocity  $v_{\text{det}}$ , drop weight impact sensitivity  $H_{50}$ , and friction sensitivity were  $\rho = 1.708 \text{ g/cm}^3$ ,  $377.6 \text{ K} = 104.5 \text{ °C}$ ,  $v_{\text{det}} = 8541.3 \text{ m/s}$ ,  $H_{50} = 38 \text{ cm}$ , and 4% for DHTN, and  $\rho = 1.765 \text{ g/cm}^3$ ,  $470.5 \text{ K} = 197.4 \text{ °C}$ ,  $v_{\text{det}} = 8882 \text{ m/s}$ ,  $H_{50} = 8 \text{ cm}$ , and 100% for DHTP, respectively.

Structures of the salts formed by 3,6-dihydrazino-1,2,4,5-tetrazine with  $\text{HNO}_3$ ,  $\text{HN}(\text{NO}_2)_2$ ,  $\text{HClO}_4$ , and  $\text{HC}(\text{NO}_2)_3$  were studied using dispersion-corrected DFT calculations [1319]. The intra-molecular hydrogen bond energies of the four salts were estimated using the quantum theory of atoms in molecules. The total hydrogen bond energies ( $\text{EH}_{\text{tot}}$ ) decreased in the order of  $\text{NO}_3^- > \text{N}(\text{NO}_2)_2^- > \text{ClO}_4^- > \text{C}(\text{NO}_2)_3^-$ .

The pressure dependence of the strand burning rates of DHT burning rate can be described by two laws for two pressure intervals, which are divided by a combustion



instability region [1299]. Pellets of DHT burn by themselves smoothly at pressures from 0.2 to 20 atm with a burning rate equation of

$$r_b = 3.63p^{0.69}$$

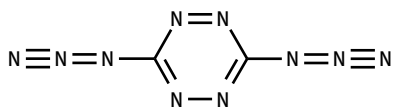
where  $r_b$  is the burning rate in mm/s and  $p$  is the pressure in atm. At 20 atm the burning rate becomes irregular but normal behavior resumes at pressures between 40 and 100 atm. The burning rate was expressed by the equation

$$r_b = 2.04p^{0.67}$$

where  $r_b$  is the burning rate in mm/s and  $p$  is the pressure in atm.

### 20.4.3 Azidotetrazines

3,6-Diazido-1,2,4,5-tetrazine, 3,6-bis(azido)-1,2,4,5-tetrazine; 1,2,4,5-tetrazine, 3,6-diazido-;  $C_2N_{10}$ , DiAT, DAT, CAS RN [5940-58-9],  $M = 164.088$  g/mol, is a high nitrogen content (85.36 mass-% N) heterocyclic compound. There is substantial interest in it as a propellant and gas generant ingredient. 3,6-Diazido-1,2,4,5-tetrazine melts at 403 K (130 °C) and had a density of 1.72 g/cm<sup>3</sup>. It contains no hydrogen; therefore the combustion products are water-free, which is of importance for applications such as in chemical or gas dynamic lasers where the infrared absorption of water would interfere.



3,6-Diazido-1,2,4,5-tetrazine (DiAT)

Carbon nitrides are of current interest due to their novel mechanical, optical, and tribological properties, including low density, extreme hardness, surface roughness, wear resistance, chemical inertness, and biocompatibility. These extremely hard diamond-like materials promise a variety of technological and biological applications. For example, they are used as biocompatible coatings on biomedical implants, battery electrodes, catalyst supports, gas separation systems, electronic materials, and humidity and gas sensors. Unlike carbon-based materials, applications of carbon nitrides are governed by their nitrogen content. As a consequence of this, extensive effort has been focused on the discovery of precursors along with the appropriate methods to control and increase the nitrogen content in carbon nitrides. Carbon nitrides  $C_3N_4$  (60.9 mass-% N) and  $C_3N_5$  (66.0 mass-% N) have been prepared using high-nitrogen 2,4,6-tri(azido)-1,3,5-triazine as the precursor. A different synthesis of the high-nitrogen compound 3,6-di(azido)-1,2,4,5-tetrazine (DiAT), from which carbon nano-spheres ranging from 5 to 50 nm and nitrogen-rich carbon nitrides  $C_3N_4$  and  $C_3N_5$  can be prepared, has been developed. This started with the readily

available 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, which rapidly reacted with hydrazine hydrate to produce 3,6-di(hydrazino)-1,2,4,5-tetrazine. This was diazotized in 3M HCl at 273K (0 °C) to yield 3,6-di(azido)-1,2,4,5-tetrazine [1320]. DSC revealed an onset of decomposition at 403K (130 °C), which coincided with the melting point. It is extremely sensitive to spark, friction, and impact.

The normalized HOF ( $\Delta H_f$ ) of 3,6-diazido-1,2,4,5-tetrazine, which was experimentally determined using an additive method, is the highest positive  $\Delta H_f$  compared to all other organic molecules [1282]. The calculated  $\Delta H_f$  of 3,6-diazido-1,2,4,5-tetrazine is +1101 kJ/mol. This is +91.75 kJ/atom, which is the highest positive  $\Delta H_f$  reported for all known organic molecules. Notably, the replacement of the first N<sub>3</sub> increases  $\Delta H_f$  by 19.21 kJ/atom, while the second N<sub>3</sub> increases  $\Delta H_f$  by an additional 54.45 kJ/atom. The unexpected azido-tetrazolo isomerizations and irreversible tetrazolo transformation of DiAT are remarkable compared to all other polyazido heteroaromatic high-nitrogen C—N compounds; e.g., 2,4,6-triazido-1,3,5-triazine; 4,4',6,6'-tetra(azido)hydrazo-1,3,5-triazine; 4,4',6,6'-tetra(azido)azo-1,3,5-triazine; and 2,5,8-tri(azido)-1,3,4,6,7,9b-heptaazaphenylene (heptazine).

3,6-Diazido-1,2,4,5-tetrazine has been synthesized from 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine by hydrazinolysis and diazotization [1321]. The molecular geometries, IR spectra, and thermodynamic properties were calculated using the DFT method. Contrary to observations by other investigators, Li et al [1321]. claim that IR spectra indicates that no azido-tetrazole tautomerism exists in solid DiAT. The thermodynamic parameters including heat capacities, entropies, and enthalpies were calculated according to IR spectra. The polynomial functions between thermodynamic parameters and temperature were determined also. The accurate enthalpy of formation of 1088 kJ/mol of DiAT in the gas phase was obtained via designed isodesmic reactions in which the tetrazine ring and the azide group have been kept intact. The data obtained from that study detailed a predicted detonation performance, with a detonation velocity of 8.45 km/s and detonation pressure of 31.3 GPa, both of which were higher than those of TNT and HMX counterparts. 3,6-diazido-1,2,4,5-tetrazine (DiAT) has the highest HOF (+966 kJ/mol = +231 kcal/mol) in comparison to those of DHT or DAAT.

The tautomerizations of polyazido-azine (ring-closure reaction) for 3,6-diazido-1,2,4,5-tetrazine (DiAT) and 2,4,6-triazido-1,3,5-triazine (TAT) were investigated by DFT methods [1322]. Enthalpies of formation were derived via isodesmic reactions. The changes of energies, geometries, and enthalpies of formation in the tautomerization showed that the enthalpies of formation increase in the process of cyclization, which makes this reaction less likely. The ring-closure reaction of TAT is thermodynamically more unfavorable in comparison to that of DiAT.

3,6-Bis(3,5-dimethylpyrazol-1-yl)1,2,4,5-tetrazine (BDT) was synthesized from guanidine nitrate, hydrazine hydrate, and acetylacetone as starting materials. Several high-nitrogen energetic compounds including 3-hydrazino-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, 3-azido-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, 3,6-di-hydrazino-1,2,4,5-tetrazine, 3,6-diazido-1,2,4,5-tetrazine, and 3,6-diguanidino-1,2,4,5-

tetrazine were synthesized by nucleophilic substitution reactions using BDT as a precursor and their structures were characterized by IR, MS, and NMR [1323].

The azido group attached to an aromatic heterocyclic ring can cyclize and isomerize to form a tetrazole fused ring. This does not happen with all azido groups attached to a ring; certain conditions must be met. The azido-tetrazole isomerization has caught many early investigators by surprise.

The azide-tetrazole isomerism in some diazido-1,2,4,5-tetrazines was investigated by *ab initio* quantum chemical methods to determine whether the polyazides are suitable starting materials for the synthesis of the isomeric tetrazoles [1250]. In the gas phase, polyazidoheterocycles do not cyclize to form tetrazoles. An electron-donating amino group favors the ring closure to tetrazoles, whereas an electron-withdrawing nitro group favors the linear azides. Solvation in polar solvents favors the formation of a tetrazole ring system due to higher charge separation in the tetrazole ring system. Diazidoazo- and hydrazotetrazines will readily cyclize to the tetrazoles in polar solvents.

A computational chemistry method was applied to study the molecular structures, electronic structures, and azido-tetrazole isomerization of azido-tetrazines [1324]. The results revealed that the reaction proceeds initially through the loss of the linearity of the azido group, with the terminal nitrogen N9 atom of the azide group approaching the nitrogen atom N2 of the ring. This step is followed by the attachment of the lone pair on N2 to the azido group, leading to the formation of the bond between N2 and N9. The bending of the N—N—N angle in the azido and the redistribution of electron density associated with these events gives rise to a large activation energy for the reaction.

The azido-tetrazolo tautomerization of 3,6-diazido-1,2,4,5-tetrazine (DiAT) in different solvents was investigated with HPLC and  $^{13}\text{C}$  NMR spectroscopy [1325]. The bicyclic compound 6-amino-tetrazolo[1,5-b]-1,2,4,5-tetrazine (ATTZ) was irreversibly formed as the final product by azido-cyclization following  $\text{N}_2$  elimination from one of the azido substituents at room temperature in DMSO. The structure of ATTZ was characterized by XRD, DSC, mass spectrometry, IR spectroscopy, and  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy. The crystal density was  $1.272\text{ g/cm}^3$ . The DSC result suggested that ATTZ with an m.p. of 357 K (84 °C) decomposed violently with explosion at 471 K (198 °C). It is so shock-sensitive that it can be regarded as a primary explosive.

DFT calculations were performed to study the molecular structures, HOFs, infrared spectra, detonation properties, and thermodynamic properties for five energetic 1,2,4,5-tetrazine derivatives [1326]. The results showed that 3,6-diazido-1,2,4,5-tetrazine is a promising candidate among HEDMs. NBO analysis indicated that the tetrazine compounds all have higher BDE when compared with RDX or HMX.

AIMD quantum chemical calculations were performed to study the thermal decomposition of isolated and crystal 3,6-diazido-1,2,4,5-tetrazine (DiAT) [1327]. During unimolecular decomposition, the three different initiation mechanisms predicted by the computer were N—N $\equiv$ N cleavage, ring-opening, and isomerization. The preferen-

tial initial decomposition step was the homolysis of the  $\text{N}-\text{N}\equiv\text{N}$  bond in the azido group. The release mechanisms of nitrogen gas were found to be very different in the early and later decomposition stages of crystal DiAT. In the early stages of decomposition, DiAT decomposed very quickly and drastically without forming any stable long-chains or heterocyclic clusters, and most of the nitrogen was released through the rapid rupture of nitrogen-nitrogen and carbon-nitrogen bonds. But in the later decomposition stages, the release of nitrogen gas was inhibited due to low mobility, long distances (from each other), and strong carbon-nitrogen bonds.

#### 20.4.4 Nitrotetrazines

Nitrotetrazines are multi-purpose energetic materials. In this group, there are examples for all classes of explosives: primary explosives, IHE, and gas generants. Starting with 3,6-diamino-1,2,4,5-tetrazine, three compounds of differing explosive behavior were prepared [303]. Physical data and small-scale explosive properties of the new substances were summarized in this publication.

To evaluate 3,6-dinitro-1,2,4,5-tetrazine (DNTAz), the geometries of this and two other compounds have been fully optimized using the DFT method [1221]. The accurate gas phase enthalpies of formation were obtained by using the atomization procedure and designing isodesmic reactions in which the parent rings are not destroyed. Based on calculated geometries and natural charges, the crystal structures have been predicted. Computed results revealed that extended conjugation exists over the parent rings of these compounds. More energy content was reserved in DNTAz than in other compounds investigated. The compounds were much more sensitive than 1,3,5-trinitrobenzene. The calculated detonation velocity of DNTAz reached 9.73–9.88 km/s, which is larger than that of CL-20.

The geometrical structures, NBOs, and enthalpies of formation of 23 different 1,2,4,5-tetrazine derivatives, including 3,6-dinitro-1,2,4,5-tetrazine, were calculated using theoretical MO methods. The predicted detonation properties (detonation velocity and detonation pressure) of the derivatives were estimated using the K-J equation [1328]. The predicted detonation velocities of these compounds were between 6.69 and 9.37 km/s. 3,6-Dinitro-1,2,4,5-tetrazine was one of the best performing explosives among the compounds studied. 3,6-Dinitro-1,2,4,5-tetrazine (DNTAz) has a density of  $\rho = 1.874\text{--}1.920\text{ g/cm}^3$ , a HOF  $\Delta H_f$  of +251 kJ/mol (+60 kcal/mol = +350 kcal/kg), and a predicted detonation velocity of  $D = 9730\text{--}9880\text{ m/s}$  [1299].

#### 20.4.5 Nitroalkyltetrazines

The DFT method was used to study the HOFs, energetic properties, and thermal stability for a series of trinitromethyl-substituted and tetrazine derivatives with different substituents [801]. It was found that the  $-\text{NO}_2$ ,  $-\text{NHNO}_2$ , or  $-\text{NF}_2$  groups play a very important role in increasing the HOFs of the derivatives. The calculated detonation velocities and pressures indicated that the group  $-\text{CF}_2\text{NF}_2$ ,  $-\text{NHNO}_2$ ,  $-1H$ -tetrazolyl,

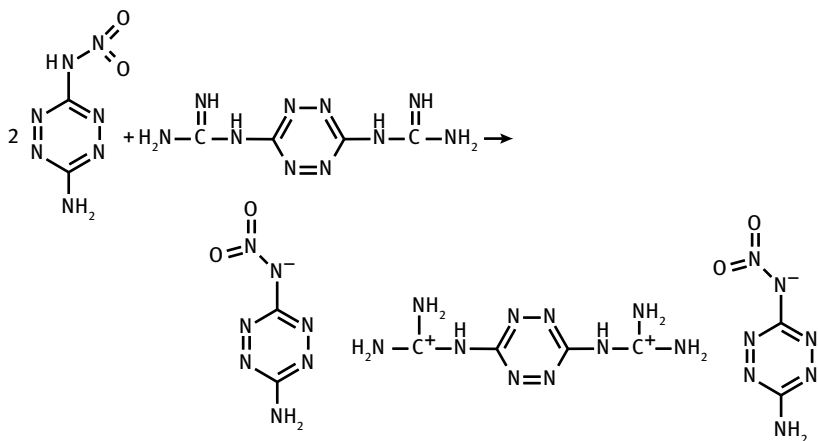
–2*H*-tetrazolyl, or –1,2,4,5-tetrazinyl are effective structural units for enhancing the detonation performance of the rings they are attached to. An analysis of the BDE for several relatively weak bonds indicated that incorporating the –NHNO<sub>2</sub> and –NH<sub>2</sub> group into the parent ring decreased their thermal stability. Taking detonation performances and thermal stability into account, 37 compounds in this study could be considered as potential high-energy compounds. Their oxygen balances were close to zero.

Combining oxygen-rich trinitroethyl groups with diaminotetrazine resulted in energetic compounds like 3,6-bis(trinitroethylamino)tetrazine (BTAT, BiTNEAT), which has an enthalpy of formation of +336 kJ/mol, a density of 1.886 g/cm<sup>3</sup>, a detonation velocity of 9261 m/s, and an impact sensitivity of 7 J [876]. The onset of exotherm in the DSC is only at 457 K (184 °C), which gives it good thermal stability.

Some of the most promising candidates for high-nitrogen compounds are the neutral compounds, N<sub>3</sub>,N<sub>6</sub>-bis-(2,2,2-trinitroethyl)-1,2,3,4-tetrazine-3,6-diamine (BiTNEAT), and the two promising ionic compounds triaminoguanidinium dinitramide (TAG-DN), triaminoguanidinium 1-methyl-5-nitriminotetrazolate (TAG-1-MeAtNO<sub>2</sub>), 5-nitriminotetrazole (H<sub>2</sub>AtNO<sub>2</sub>), and 5-aminotetrazolium dinitramide [840, 841].

#### 20.4.6 Nitroaminotetrazines (Nitraminotetrazines)

The synthesis and properties of several new high-nitrogen materials with 3-amino-6-nitroamino-tetrazine (ANAT) as the anion were synthesized and characterized by IR and NMR spectroscopy and elemental analysis [1329]. One of the most energetic examples was the dianion salt of 3,6-diguanidyl-1,2,4,5-tetrazine with two 3-amino-6-nitroamino-tetrazinate anions with an enthalpy of formation of +1088.8 kJ/mol.

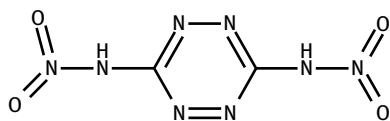


3-Amino-6-nitroamino-tetrazinate salt

3-Amino-6-nitroamino-tetrazine, *N*-nitro-3,6-diamino-1,2,4,5-tetrazine,  $C_2H_3N_7O_2$ ,  $M = 157.09$  g/mol, ANAT, has very attractive energetic properties. 3-Amino-6-nitroamino-tetrazine has a density of  $\rho = 1.71$  g/cm<sup>3</sup>, an auto-ignition temperature  $T_{\text{ign}}$  of 437 K (164 °C), a HOF  $\Delta H_f$  of +464 kJ/mol (+111 kcal/mol = +707 kcal/kg), and a detonation velocity of  $D = 8230$  m/s. In nitramines, the nitroamino group plays an important role because of the presence of an energetic site and an acidic proton, thus making it possible for nitroamino-containing compounds to form corresponding salts. The nitramino group substantially improves the oxygen balance of the corresponding derivatives and eventually results in a higher exothermicity of combustion and detonation processes. The syntheses of the nitrogen-containing cation 3-amino-6-nitroamino-tetrazinate salts were easily accomplished by reacting ANAT with one equivalent of guanidine carbonate, aminoguanidine bicarbonate, 3,6-diguanidine tetrazine, aqueous ammonia, or its silver salt with diaminoguanidine chloride or triaminoguanidine chloride [202]. All of the salts were recovered as highly crystalline materials with excellent yields and purities. DSC and TGA studies revealed a family of very stable salts that decomposed exothermically upon melting. All of the salts had relatively high melting points for simple heterocyclic salts. This most likely can be attributed to the high basicity of guanidine or ammonia as well as the extent of the crystalline phase hydrogen bonding. The HOFs, detonation pressures, and detonation velocities were calculated and are summarized in Table 76.

The calculated enthalpies of formation for 3,6-diguanidine tetrazine nitrate (**No. 172**) and 3,6-diguanidine tetrazine perchlorate (**No. 173**) were in good agreement with the experimental values of −255 kJ/mol and the estimated value of −125 kJ/mol, respectively. This is impressive considering that the enthalpy of formation of 3,6-diguanidine tetrazine itself is reported to be +197 kJ/mol, which is a clear indication of the degree of energy.

*N,N'*-Dinitro-3,6-diamino-1,2,4,5-tetrazine, 3,6-dinitroamino-1,2,4,5-tetrazine, *N*-(6-nitramido-1,2,4,5-tetrazin-3-yl)nitramide,  $C_2H_2N_8O_4$ ,  $M = 202.09$  g/mol, has a density of  $\rho = 1.83$  g/cm<sup>3</sup>, an auto-ignition temperature of  $T_{\text{ign}}$  of 383 K (110 °C), an enthalpy of formation  $\Delta H_f$  of +565 kJ/mol (+135 kcal/mol) = 670 kcal/kg, and a detonation velocity of  $D = 8890$  m/s at a packing density of 1.71 g/cm<sup>3</sup>.



*N,N'*-Dinitro-3,6-diamino-1,2,4,5-tetrazine

The extent of nitration of *N,N'*-dialkyl-1,2,4,5-tetrazine-3,6-diamines under acidic conditions depends on the concentration of nitric acid and the selection of the alkyl sub-

**Table 76:** Structure and properties of energetic salts with 3-amino-6-nitroamino-tetrazinate (ANAT) anion.

| Compound No. | Compound name                                                | $T_{\text{dec}}$ onset of decomposition |       | Density<br>g/cm <sup>3</sup> | $H_L^a$<br>kJ/mol | $H_{fm}^b$<br>kJ/mol | $P_{\text{det}}$<br>GPa | $v_{\text{det}}$<br>m/s |
|--------------|--------------------------------------------------------------|-----------------------------------------|-------|------------------------------|-------------------|----------------------|-------------------------|-------------------------|
|              |                                                              | K                                       | °C    |                              |                   |                      |                         |                         |
| 165          | 3-Amino-6-nitroamino-tetrazine                               | 437.1                                   | 164.0 | 1.82                         | —                 | +441.0 <sup>c</sup>  | —                       | —                       |
| 166          | 3,6-Diguanidinium tetrazine 3-amino-6-nitroamino-tetrazinate | 505.4                                   | 232.3 | 1.56                         | 1354.5            | +1088.8              | 20.9                    | 7546                    |
| 167          | Guanidinium 3-amino-6-nitroamino-tetrazinate                 | 521.2                                   | 248.1 | 1.62                         | 567.6             | +340.7               | 23.3                    | 8169                    |
| 168          | Aminoguanidinium 3-amino-6-nitroamino-tetrazinate            | 478.5                                   | 205.4 | 1.71                         | 494.8             | +443.2               | 28.9                    | 8898                    |
| 169          | Ammonium 3-amino-6-nitroamino-tetrazinate                    | 447.1                                   | 174.0 | 1.63                         | 526.3             | +370.0               | 26.6                    | 8448                    |
| 170          | Diaminoguanidinium 3-amino-6-nitroamino-tetrazinate          | 420.8                                   | 147.7 | 1.56                         | 475.4             | +564.2               | 23.9                    | 8258                    |
| 171          | Triaminoguanidinium 3-amino-6-nitroamino-tetrazinate         | 436.6                                   | 163.5 | 1.59                         | 470.5             | +671.5               | 26.1                    | 8582                    |
| 172          | 3,6-Diguanidinium tetrazine dinitrate                        | —                                       | —     | 1.72                         | 1555.0            | −252.5               | 25.6                    | 8160                    |
| 173          | 3,6-Diguanidinium tetrazine diperchlorate                    | —                                       | —     | 1.90                         | 1512.7            | −164.8               | 30.9                    | 8593                    |

<sup>a</sup> Calculated molar lattice energy.<sup>b</sup> Calculated molar enthalpy of formation.<sup>c</sup> Calculated HOF in the gas phase.

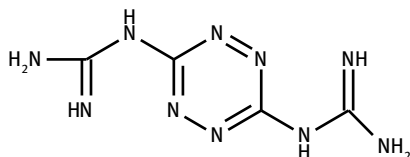
Data source: [202].

stituents at the exocyclic nitrogen atom [1330]. For instance, treating bis(alkylamino)-1,2,4,5-tetrazine with 98% HNO<sub>3</sub> produces the bis-alkylnitramino-1,2,4,5-tetrazine.

#### 20.4.7 Guanyltetrazines (Guanidinetetrazines)

3,6-Diguanidino-1,2,4,5-tetrazine, also known as; guanidine, *N,N'''*-1,2,4,5-tetrazine-3,6-diylbis-; *N,N'''*-1,2,4,5-tetrazine-3,6-diylbis[guanidine], 3,6-guanyl-*s*-tetrazine, bis(guanidinyl)tetrazine, 1-(6-guanidino-1,2,4,5-tetrazin-3-yl)guanidine, 1,1'-(1,2,4,5-tetrazine-3,6-diyl)diguanidine, 3,6-diguanidino-1,2,4,5-tetrazine, BGTz, C<sub>4</sub>H<sub>8</sub>N<sub>10</sub>, CAS RN [757961-08-3], *M* = 196.17 g/mol, can be converted to nitrate and perchlorate salts and to *N*-oxides. The guanidines are attached to the tetrazine ring at their 1-position

(end position) nitrogen and not at the 2-position (center position) nitrogen or the carbon atom.



3,6-Diguanidino-1,2,4,5-tetrazine

The nitrate and perchlorate salts of 3,6-diguanidino-1,2,4,5-tetrazine, as well as the nitrate and perchlorate salts of 3,6-diguanidino-1,2,4,5-tetrazine-1,4-di-*N*-oxide, 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine and its 1,4-di-*N*-oxide derivative, 3,3'-azobis(6-amino-1,2,4,5-tetrazine), provide high-energy materials and high-nitrogen compounds with attractive properties [1331]. The dinitrate salt of bis(guanidiny)tetrazine, BGTz-DN; BGTz-2HNO<sub>3</sub>, C<sub>4</sub>H<sub>10</sub>N<sub>12</sub>O<sub>6</sub>, CAS RN [757961-10-7], *M* = 322.199 g/mol, has a density of 1.72 g/cm<sup>3</sup> and an enthalpy of formation of -196.6 kJ/mol (-47.0 kcal/mol = -146 cal/g). It contains 52.17% nitrogen and has an oxygen balance of -34.8%. Other sources reported the properties of the dinitrate salt as density  $\rho = 1.72$  g/cm<sup>3</sup>, auto-ignition temperature  $T_{\text{ign}} = 527$  K (254 °C), enthalpy of formation  $\Delta H_f = -225$  kJ/mol (-53.8 kcal/mol), and detonation velocity  $D = 7310$  m/s at a packing density of 1.6 g/cm<sup>3</sup>. The diperchlorate salt of BGTz has a density of  $\rho = 1.977$  g/cm<sup>3</sup>, an auto-ignition temperature  $T_{\text{ign}}$  of 561 K (288 °C), an enthalpy of formation of  $\Delta H_f = -125.5$  kJ/mol (-30 kcal/mol), and a detonation velocity of  $D = 8070$  m/s at a packing density of 1.79 g/cm<sup>3</sup>.

3,6-Diguanidino-1,2,4,5-tetrazine (BDT) can be prepared by reaction of triamino-guanidinium nitrate with 2,4-pentanedione after condensation, oxidation, and neutralization [1332]. Using CH<sub>3</sub>COOH/NaNO<sub>2</sub> as the oxidizer and ethanol as the reactive medium, BDT was obtained with a yield of 85% at room temperature. This improvement reduced the cost of synthesis, raised the yield, and facilitated the experimental operation. Structures of BDT and its salts were confirmed by IR and NMR and thermal stability was measured by DSC.

3,6-Diguanidino-1,2,4,5-tetrazine dihydrate [(DGTz)(H<sub>2</sub>O)<sub>2</sub>] and its diperchlorate [(DGTz)(ClO<sub>4</sub>)<sub>2</sub>] were prepared and characterized by elemental analysis, FTIR, and XRD [1333]. The hydrogen atoms in the 3- and 6-positions of the tetrazine ring were substituted by two guanidino groups for (DGTz)(H<sub>2</sub>O)<sub>2</sub>, and two crystal water molecules were placed in the hydrate sphere. (DGTz)(H<sub>2</sub>O)<sub>2</sub> crystallized in the shape of monoclinic crystals, space group *C2/c*, with unit cell parameters of  $a = 1.3077$  nm,  $b = 0.36935$  nm,  $c = 1.9823$  nm,  $\beta = 95.158^\circ$ ,  $V = 0.9536$  nm<sup>3</sup>,  $Z = 4$ , and  $\rho_{\text{XRD}} = 1.618$  g/cm<sup>3</sup>. In the (DGTz)(ClO<sub>4</sub>)<sub>2</sub> crystal, two ClO<sub>4</sub><sup>-</sup> anions and one DGTz<sup>2+</sup>



cation were bonded together by electrostatic attraction and hydrogen bonds. The (DGTz)(ClO<sub>4</sub>)<sub>2</sub> crystals crystallized in the shape of monoclinic crystals, space group *P*2<sub>1</sub>/*c*, with unit cell parameters of *a* = 0.48581 nm, *b* = 1.3058 nm, *c* = 1.0519 nm, *β* = 91.159°, *V* = 0.6672 nm<sup>3</sup>, *Z* = 2, and *ρ*<sub>XRD</sub> = 1.977 g/cm<sup>3</sup>. The thermal decomposition process of the two compounds was investigated by DSC and TGA-DTG and the activation energy was derived. In the DTA-DSC with a heating rate of 10°/min, (DGTz)(H<sub>2</sub>O)<sub>2</sub> begins to lose water at 54 to 98 °C with a peak at 79 °C (endotherm). This is followed by a sharp exotherm starting at 273 °C that maxes at 297 °C. (DGTz)(ClO<sub>4</sub>)<sub>2</sub> decomposed directly without melting. In the DSC curve of (DGTz)(ClO<sub>4</sub>)<sub>2</sub>, there is only one sharp exotherm starting at 255.7 °C that maxes at 272.4 °C. The apparent activation energy of (DGTz)(H<sub>2</sub>O)<sub>2</sub> decomposition was 228.6 kJ/mol which was about 50 kJ/mol higher than the apparent activation energy of (DGTz)(ClO<sub>4</sub>)<sub>2</sub>, which was only 178.5 kJ/mol.

The molecular structures of three stable conformations of salts formed from 3,6-diguanidino-1,2,4,5-tetrazine-1,4-di-*N*-oxide (DTDO) and HNO<sub>3</sub> and HN(NO<sub>2</sub>)<sub>2</sub> were calculated using DFT methods and free energies. The total energies of the three conformations were compared to hydrogen bonding interaction, charge transfer, binding energy, dispersion energy, and the second-order perturbation energy [1334]. Aromaticities of tetrazine in different conformations were slightly different. Although the stabilities of the three conformations are different, their values were comparable.

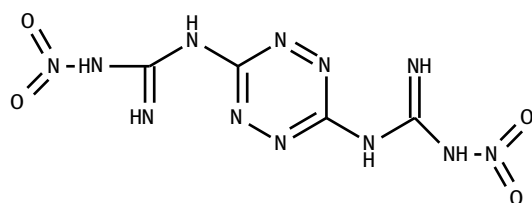
The strand burning rates of 3,6-diguanidino-1,2,4,5-tetrazinium nitrate (DGTN) and TAGN, their combustion wave structure, and the location and chemical nature of the leading reaction of combustion were determined and compared to each other [1335]. Burning rate measurements were carried out in a windowed 1.5-L constant-pressure bomb. The mixtures under investigation were placed in transparent acrylic tubes that were 7 mm in diameter and 12–15 mm long. Temperature profiles in the combustion wave were measured using thin tungsten-rhenium thermocouples. DGTN in the form of samples pressed into acrylic tubes can even sustain stable combustion at sub-atmospheric pressures. In the pressure range of 0.1–10 MPa, DGTN burns 1.5–2 times faster than HMX but 2–3 times slower than TAGN. The surface temperatures in the combustion of TAGN and DGTN are very close and are controlled by a dissociation process, just as they are for other onium salts,. The burning rates of both substances are governed by processes in the condensed phase.

3,6-Diguanidino-1,2,4,5-tetrazinium dinitroguanidinate salt can be prepared in 82.2% yield by using hydrazine hydrate, guanidinium nitrate, and nitroguanidine as raw materials under optimum synthetic conditions (reaction time and reaction temperature of 323 K/50 °C) [1336]. The thermal decomposition behavior was studied by DSC and TGA-DTG and its detonation properties were predicted using DFT methods. The compound decomposed at about 533 K (260 °C), demonstrating good thermal stability. The HOF of the compound obtained by Born-Haber cycle was 294.9 kJ/mol. The theoretical density predicted by a Monte-Carlo method was 1.69 g/cm<sup>3</sup>. The

predicted detonation velocity and detonation pressure calculated by the K-J equation were 7.67 km/s and 25.04 GPa, respectively.

#### 20.4.8 Nitroguanyltetrazines (Nitroguanidinotetrazines)

3,6-Diguanidino-1,2,4,5-tetrazine has served as an ingredient in several of the energetic materials already described in this chapter. Now, instead of just two plain guanidino groups attached to tetrazine, a more energetic compound can be made by attaching two nitroguanidino groups to tetrazine. This compound is no longer a base; it is an acid that can form salts with a variety of bases. 3,6-Bis(nitroguanidinyl)-1,2,4,5-tetrazine; guanidine, *N,N'*-1,2,4,5-tetrazine-3,6-diylbis[*N*-nitro-]; 1-nitro-3-[6-[(*N*-nitrocarbamimidoyl)amino]-1,2,4,5-tetrazin-3-yl]guanidine, (NQ)2Tz, NQ2Tz, DNGTz, CAS RN [756482-91-4],  $C_4H_6N_{12}O_4$ ,  $M = 286.168$  g/mol, melts at 501 K (228 °C) (decomp.) and has a density of 1.76 g/cm<sup>3</sup>. It is an energetic material. The enthalpy of formation is +389 kJ/mol (+93.0 kcal/mol = +325 cal/g). It contains 58.73% nitrogen and its oxygen balance is -39.1%.



3,6-Bis(nitroguanidinyl)-1,2,4,5-tetrazine

3,6-Bis(nitroguanidinyl)-1,2,4,5-tetrazine is a dibasic acid and forms salts with a variety of bases. The triaminoguanidinium salt of 3,6-bis(nitroguanidinyl)-1,2,4,5-tetrazine, also known as (TAG)2(NQ)2Tz, CAS RN [756482-94-7],  $C_6H_{22}N_{24}O_4$ ,  $M = 494.41$  g/mol, has a density of 1.610 g/cm<sup>3</sup>. Chemical Abstracts lists this compound as “3,6-bis(nitroguanidinyl)-1,2,4,5-tetrazine, bis(triaminoguanidinium) salt” or “carbonohydrazonic dihydrazide, compound with *N,N'*-1,2,4,5-tetrazine-3,6-diylbis-(*N'*-nitroguanidine) (2:1).” It is a high-nitrogen content (68% N) energetic material that melts at 439 K (166 °C) and has an enthalpy of formation of +1255 kJ/mol (+300 kcal/mol = +607 cal/g). Other literature sources gave the enthalpy of formation of (TAG)2(NQ)2Tz as  $\Delta H_f = +711$  kJ/mol (+170 kcal/mol = +345 kcal/kg).

Another salt formed with 3,6-bis(nitroguanidinyl)-1,2,4,5-tetrazine is the bis-(1-methyl-4,5-diaminotetrazolium) salt, (MAT)2(NQ)2Tz, with a molecular mass of 514.4 g/mol, but only a few properties are known. There are no known applications of this compound.

The synthesis of several high-nitrogen materials based on nitroguanyl-substituted tetrazines by reaction of tetrazine derivatives with the anion of nitroguanidine

(anionic heteroatom nucleophile) in the first stage led to a bis(nitroguanidiny)-tetrazine disodium salt that was prepared from 3,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2,4,5-tetrazine and nitroguanidine sodium salt (formed *in-situ*) [1337]. Treatment of this disodium salt with triaminoguanidinium hydrochloride produced a bis-(triaminoguanidinium) salt. Gas pycnometry of the triaminoguanidinium salt of 3,6-bis(nitroguanidiny)-1,2,4,5-tetrazine indicated a crystal density near 1.61 g/cm<sup>3</sup>. The HOFs were determined to be +1255 kJ/mol (+300 kcal/mol), making them an attractive candidate for energetic materials applications.

3,6-Bis-nitroguanyl-1,2,4,5-tetrazine (NQ2Tz) and its bis-triaminoguanidinium salt (TAG)2(NQ)2Tz exhibited very low pressure dependence in burning rate [1338]. Flash pyrolysis/FTIR spectroscopy provided some insight into this interesting burning behavior.

The reaction between acetyl acetone and TAGN at 343–348 K (70–75 °C) produced 1,3,6-bis-(3,5-bismethyl-pyrazole-*N*-yl)-1,2-dihydro-*s*-tetrazine; at 313–318 K (40–45 °C) it produced 2,α,α'-bis(3,5-bismethyl-pyrazole-*N*-yl)-carbene-acetyl-isopropenyl hydrazine [1339]. They were characterized by IR, MS and <sup>1</sup>H-NMR spectra, and XRD. The results of crystal structure determination showed that there exist intermolecular hydrogen bonds which stabilize the crystals.

TGA-FTIR was used in real-time to measure the thermal decomposition behavior of 3,6-bis-nitroguanyl-*s*-tetrazine dihydrate (DNGTz•2H<sub>2</sub>O) with constant rate-controlled heating (10 °C/min) [1340]. The thermal decomposition of DNGTz•2H<sub>2</sub>O can be divided into three stages. The first stage was an endothermic process with a mass loss of 10% for the loss of two molecules of water. The second stage was an exothermic stage that took place between 501 and 526 K (228 and 253 °C) with a mass loss of 68.66%. The third stage happened between 734 and 846 K (461 and 573 °C) with a mass loss of 17.46%. The FTIR spectra showed that the main products of the thermal decomposition of DNGTz•2H<sub>2</sub>O were NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, CO<sub>2</sub>, and N<sub>2</sub>.

3,6-Dinitroguanidino-1,2,4,5-tetrazine (DNGTz) was synthesized with a yield of 92.3% from 3,6-bis(3,5-dimethylpyrazole-1-yl)-1,2-dihydro-1,2,4,5-tetrazine through oxidation and substitution [1341]. The bis(triaminoguanidinium) salt of 3,6-dinitroguanidino-1,2,4,5-tetrazine (TGA-DNGTz) and a bisguanylylurinium salt of 3,6-dinitroguanidino-1,2,4,5-tetrazine (M-DNGTz) were synthesized and their structures were characterized by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. The conditions for the reactions of oxidation and substitution were optimized. The physico-chemical properties, detonation, and thermal stability of DNGTz, TGA-DNGTz, and M-DNGTz were measured. Their decomposition temperatures were 491.8, 463.3, and 476.8 K (218.7, 190.2, and 203.7 °C), respectively.

From the viewpoint of designing high-performance energetic materials, the most widely used strategy is to incorporate some energy-containing groups such as nitro, azido, azo, or *N*-oxide into the molecular backbone of the high-nitrogen heterocycles (especially the 1,3,5-triazine or 1,2,4,5-tetrazine ring). Nitroguanidyl-functional-

ized nitrogen-rich materials derived from 1,3,5-triazine and 1,2,4,5-tetrazine were synthesized through reactions between *N*-nitroso-*N'*-alkylguanidines and the hydrazine derivatives of 1,3,5-triazine or 1,2,4,5-tetrazine and were characterized by NMR and IR spectroscopy, elemental analysis, and DSC [1266]. The HOFs for all compounds were calculated and then combined with experimentally determined densities to calculate the predicted detonation pressures and velocities.

3,6-Bis-nitroguanyl-1,2,4,5-tetrazine (DNGTz) was synthesized by a similar method and its thermal behavior was studied by DSC and TGA-DTG [1342]. The DSC data were used to analyze the thermal decomposition mechanism and kinetics using the methods of Kissinger, Ozawa, and integral. The thermal kinetic parameters of the activation energy and pre-exponential factor were  $E_a = 187.23 \text{ kJ/mol}$  and  $A = 10^{15.01} \text{ s}^{-1}$ , respectively. The thermal safety of DNGTz and the density ( $\rho = 1.762 \text{ g/cm}^3$ ) and thermal conductivity ( $\lambda = 0.1856 \text{ W m}^{-1} \text{ K}^{-1}$ ) were estimated and the specific heat capacity ( $c_p$ ) was measured in a micro-calorimeter to obtain the dependence of  $c_p$  on  $T$  for the range  $287 \text{ K} < T < 352 \text{ K}$

$$c_p = -2.8805 + 2.1283 \times 10^{-2}T - 2.3132 \times 10^{-5}T^2 - 1.1689 \times 10^{-8}T^3$$

where  $c_p$  is the heat capacity in  $\text{J g}^{-1} \text{ K}^{-1}$  and  $T$  is the temperature in kelvin. The thermal decomposition kinetic parameters, mechanism function, and the equations of  $c_p$ ,  $\rho$ , and  $\lambda$  were combined to evaluate thermal stability of DNGTz. The adiabatic-time-to-explosion was 8.16 s. The self-accelerating decomposition temperature was  $T_{\text{SADT}} = 522.2 \text{ K} = 249.12^\circ\text{C}$ . The thermal ignition temperature was  $T_{\text{be}} = 535.4 \text{ K} = 262.3^\circ\text{C}$ . The critical temperature of thermal explosion was  $T_{\text{bp}} = 484.8 \text{ K} = 211.7^\circ\text{C}$ . The thermal sensitivity probability density function  $S(T)$  vs  $T$  for DNGTz was calculated for different geometries, including infinite cylindrical, spheroidal, or infinite platelike shapes with a radius of 1 m. The thermal safety of the spheroidal geometry was found to be better than that of the infinite cylindrical or infinite platelike geometry.

More recent literature sources gave the following properties for 3,6-bis-(nitroguanidinyl)-1,2,4,5-tetrazine (NQ2Tz): density  $\rho = 1.76 \text{ g/cm}^3$ , auto-ignition temperature  $T_{\text{ign}} = 501 \text{ K}$  ( $228^\circ\text{C}$ ), HOF  $\Delta H_f = +389 \text{ kJ/mol}$  ( $+93 \text{ kcal/mol} = +330 \text{ kcal/kg}$ ), and detonation velocity  $D = 7840 \text{ m/s}$  at a packing density of  $1.7 \text{ g/cm}^3$ , vapor pressure

$$\ln p = 30.4 - 22540/T$$

where  $p$  is the vapor pressure in atm and  $T$  is the temperature in kelvin [1299]. 3,6-Bis-(nitroguanidinyl)-1,2,4,5-tetrazine can burn at very low pressures. The strand burning rate for pressures between 0.02 and 10 MPa follows the equation

$$r_b = 5.04p^{0.42}$$

where  $r_b$  is the burning rate in mm/s and  $p$  is the pressure in MPa. NQ2Tz burning rate is very sensitive to impurities. This substance can burn at sub-atmospheric pressure. There is flameless combustion at low pressures and a luminous flame appears above 2 MPa. The strand burning rate of the triaminoguanidinium salt of NQ2Tz between 0.1 and 10 MPa can be expressed by the following equation:

$$r_b = 7.6p^{0.52}$$

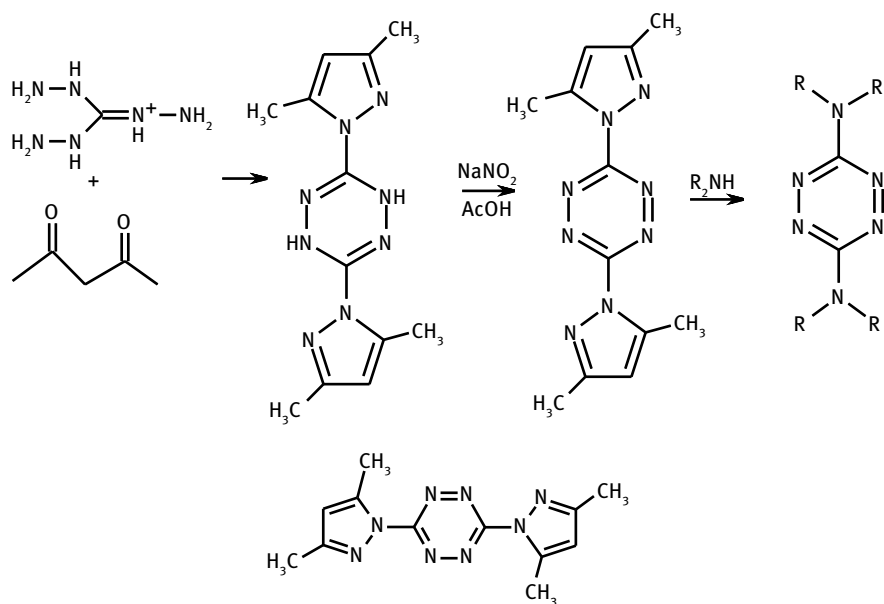
where  $r_b$  is the burning rate in mm/s and  $p$  is the pressure in MPa.

#### 20.4.9 Other Di-Substituted Tetrazine Derivatives

The properties of 3,6-dihydrazino-1,2,4,5-tetrazine (DHT), 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT), 3,6-bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz), and 5,5'-bitetrazole (BHT) were compared among the promising high-nitrogen energetic materials [1308, 1343]. Because of their highly positive HOFs and higher density, these high-nitrogen compounds are unique in their gas generating ability, having little or no smoke and a lack of residue. This makes them compounds of interest for applications in insensitive explosives, low signature propellants, gas generants, and low-smoke pyrotechnics. An excellent source of information on tetrazines as energetic materials is provided in [1299, 1344], with lecture slides accompanying one of the book chapters.

### 20.5 C—C-Linked, C-Bridged, and Fused Multi-Ringed Tetrazines

3,6-Bis-(3,5-dimethylpyrazol-1-yl)-*s*-tetrazine, 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, BDT,  $C_{12}H_{14}N_8$ ,  $M = 270.293$  g/mol, can be synthesized from triaminoguanidinium chloride and 2,4-pentanedione (= acetylacetone) followed by oxidation by atmospheric oxygen or nitrogen dioxide. Starting with the precursor 3,6-bis-(3,5-dimethylpyrazol-1-yl)-*s*-tetrazine (BDT), several useful energetic compounds based on the *s*-tetrazine system have been synthesized and studied [1345], including 3,6-diamino-*s*-tetrazine-1,4-dioxide (LAX-112), 3,6-bis-(1*H*-1,2,3,4-tetrazol-5-ylamino)-*s*-tetrazine, and 3,6-dihydrazino-*s*-tetrazine (DHT).



3,6-Bis-(3,5-dimethylpyrazol-1-yl)-s-tetrazine (BDT)

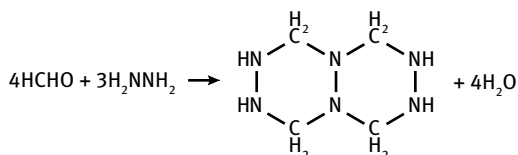
3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (BDT) was synthesized from guanidinium nitrate, hydrazine hydrate, and acetylacetone as starting materials [1323]. Several high-nitrogen energetic compounds, including 3-hydrazino-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, 3-azido-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine, 3,6-dihydrazino-1,2,4,5-tetrazine, 3,6-diazido-1,2,4,5-tetrazine, and 3,6-diguanidino-1,2,4,5-tetrazine, were synthesized by nucleophilic substitution reactions using BDT as a precursor. Their structures were characterized by IR, MS, and NMR.

3,6-Bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine was synthesized from guanidine hydrochloride and acetylacetone by an amazing multiple ring-closure reaction [1346]. Three additional 1,2,4,5-tetrazine derivatives were synthesized, starting from 3,6-bis(3,5-dimethyl-1*H*-pyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine by oxidation and substitution. These compounds were characterized by  $^1\text{H}$  NMR and MS. The single-crystal XRD study of N3,N6-bis(pyridin-2-ylmethyl)-1,2,4,5-tetrazine-3,6-diamine indicated that it belongs to the triclinic system, space group  $P_1$ . The unit cell parameters were:  $a = 8.0764(16) \text{ \AA}$ ,  $b = 9.5262(19) \text{ \AA}$ ,  $c = 10.243(2) \text{ \AA}$ ,  $\alpha = 86.08(3)^\circ$ ,  $\beta = 74.60(3)^\circ$ ,  $\gamma = 69.87(3)^\circ$ ,  $V = 713.1(2) \text{ \AA}^3$ , and  $Z = 2$  [303]. Physical data and small-scale explosive properties of new triazole and tetrazine derivatives were summarized in this publication.

The enthalpy of formation of 3,6-bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazine (BTT) is  $\Delta H_f^{298} = +933 \text{ kJ/mol} = +223 \text{ kcal/mol}$  [1347]. The thermal decomposition behavior of BTT and DAAT was thermo-analytically characterized. Both substances decomposed at surprisingly high temperatures of  $>473 \text{ K}$  ( $>200^\circ\text{C}$ ). The heats of decomposition released were among the highest ever measured for energetic materials under similar experimental conditions and were released over a relatively narrow temperature range. More recent sources of information listed the properties of BTT as  $\rho = 1.68 \text{ g/cm}^3$ , auto-ignition temperature  $T_i = 508 \text{ K} = 235^\circ\text{C}$ ,  $\Delta H_f = +937 \text{ kJ/mol} = +224 \text{ kcal/mol} = +1026 \text{ kcal/kg}$  [1299].

The enthalpy of formation, theoretical crystal density, and explosive performance of *s*-tetrazine derivatives, in which two different  $\text{O}_2\text{N}$ -,  $\text{H}_2\text{N}$ -, and  $\text{N}_3$ -substituted imidazoles, triazoles, or tetrazoles were attached to the tetrazine ring in the 3- and 6-positions, were calculated using DFT methods [1348]. The predicted results showed that azide groups increase all enthalpy of formation values of the *s*-tetrazine derivatives. The densities for the designed molecules were predicted by using crystal packing calculations. The introduction of  $-\text{NO}_2$  groups improved the density and, hence, the detonation performance was better than the  $-\text{N}_3$  or  $-\text{NH}_2$  groups. Amino derivatives are better candidates based on their insensitivity and thermal stability.

The reaction of hydrazine with the lowest member of the aldehyde family, formaldehyde, proceeds quite unexpectedly beyond the hydrazone, and results in the formation of tetraformaltrisazine, 1,2,3,4,6,7,8,9-octahydro-[1,2,4,5]tetrazino-[1,2-*a*][1,2,4,5]tetrazine, TFTA,  $\text{C}_4\text{H}_{12}\text{N}_6$ ,  $M = 144.18 \text{ g/mol}$ , CAS RN [1743-13-1], which is a white powder [1349, 1350].

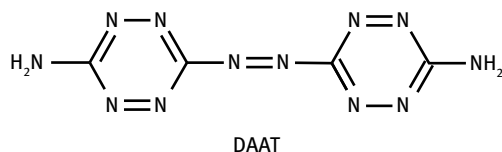


Tetraformaltrisazine polymerizes after a few minutes with excess formaldehyde to form a white gelatinous precipitate. The precipitate forms even if formaldehyde is reacted with the azine formed by reactions of hydrazine with an excess of acetone. Formaldehyde reverses the acetone-hydrazine reaction. 2,3-Diazabuta-1,3-diene (formalazine)  $\text{H}_2\text{C}=\text{N}=\text{CH}_2$  cannot be isolated but polymerizes [1351, 1352].

The enthalpy of formation of tetraformaltrisazine is  $+475 \text{ kcal/100 g} = +475 \text{ cal/g} = +68.5 \text{ kcal/mol} = +286 \text{ kJ/mol}$ , which is derived from heat of combustion measurements. The pyrolysis and combustion of TFTA leads to much nitrogen, hydrogen, carbon dioxide, some carbon monoxide, and only a little methane and ethylene [1353, 1354]. This makes it a good source of nitrogen for gas generator propellants and for blowing agents that are used in making plastic foams. TFTA can also be used as the fuel for hybrid rockets [1355].

## 20.6 —N=N—Linked Azo-s-tetrazines

While azo-s-tetrazine may have a few desirable properties, continued synthesis efforts have yielded a derivative of azo-s-tetrazine, 3,3'-azobis(6-amino-s-tetrazine), or DAAT, which has a very high positive enthalpy of formation [1347]. As far as the nomenclature is concerned, the prefix “bis” appears to be unnecessary. For instance, “azobenzene” describes a molecule consisting of a diazene group with two phenyl rings, and the prefix “bis” is not used.



3,3'-Azobis(6-amino-1,2,4,5-tetrazine), 6,6'-(1E)-azobis-1,2,4,5-tetrazin-3-amine, diaminoazotetrazine, 6-[[*(Z)*-aminomethylazo]-[methylene-(methyleamino)-λ5-azanyl]-methyl]azo-1,2,4,5-tetrazin-3-amine, DAAT,  $C_4H_4N_{12}$ , CAS RN [286472-58-0],  $M = 220.16$  g/mol, is a very sensitive high-nitrogen compound. This is surprising because it does not contain any oxygen and has a very high density of  $1.840$  g/cm<sup>3</sup>. 3,3'-azobis-(6-amino-1,2,4,5-tetrazine) was prepared starting from 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (DBT) [1356, 1357]. The energetic compound was characterized by spectroscopic methods, XRD, DSC, and combustion calorimetry. The pure material is thermally stable up to  $525$  K =  $252$  °C. The enthalpy of formation was measured to be  $+862$  kJ/mol ( $+206$  kcal/mol). The drop weight impact sensitivity value was  $70$  cm (for comparison, HMX is  $21$  cm) even though there are no oxygen atoms in the molecule. The compound is insensitive to initiation by spark ( $>0.36$  J) or friction (BAM  $>36$  kg) and the density was once reported as  $1.84$  g/cm<sup>3</sup>. However, later gas pycnometry measurements have placed the density more accurately at  $1.78$  g/cm<sup>3</sup>, which was very likely related to the densest C, H, N molecule known at that time [1358].

The properties of DAAT were compared to those of other energetic high-nitrogen compounds. These are leading candidates among other promising high-nitrogen energetic materials [1308, 1343]. Because of their highly positive HOFs and higher density, these high-nitrogen compounds are unique in their gas-generating abilities. They generate little to no smoke and lack any leftover residue.

3,3'-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT) along with 3,3'-diamino-4,4'-azoxyfurazan (DAAF) and 1,4-dihydrazino tetrazine (DHTz) were synthesized and characterized by IR, NMR, MS, TG-DTA, DSC, TG-FTIR, and impact and friction sensitivity tests [682]. DAAF was insensitive to mechanical stimuli whereas DAAT and DHTz were vulnerable to impact stimuli. The theoretical explosive power of DAAF, DAAT, and DHTz alone and their combinations with well-known IHE as well as that of propellants based on them were calculated.



3,3'-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT) can be synthesized from guanidinium nitrate and hydrazine hydrate via a seven-step reaction [1359]. The structure and composition were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and elemental analysis [1360, 1361]. Other sources of properties of DAAT reported  $\rho = 1.78 \text{ g/cm}^3$ ; auto-ignition temperature  $T_i = 592 \text{ K} = 319^\circ\text{C}$ ;  $\Delta H_f = +862 \text{ kJ/mol} = +206 \text{ kcal/mol} = 936 \text{ kcal/kg}$ ; measured detonation velocity  $D = 7400 \text{ m/s}$  at a packing density of  $1.65 \text{ g/cm}^3$  [1299].

3,3'-Azobis(6-amino-1,2,4,5-tetrazine) (DAAT) was included in a demonstration of DFT calculations for a group of energetic materials and used to check the validity of calculations because it was one of the few molecules for which experimental data were available [1305]. This source reported the density of DAAT as  $1.76 \text{ g/cm}^3$  (which is similar to the density reported by other sources). The predicted HOF of DAAT vapor was  $+1146 \text{ kJ/mol}$  ( $+274 \text{ kcal/mol}$ ). The heat of sublimation of DAAT was measured to be  $167 \text{ kJ/mol}$  ( $40 \text{ kcal/mol}$ ). The measured enthalpy of formation of solid DAAT is  $+979 \text{ kJ/mol}$  ( $+234 \text{ kcal/mol}$ ). The predicted detonation velocity is  $D = 8250 \text{ m/s}$  and the predicted CJ pressure is  $P = 31.14 \text{ GPa}$ . In this work, the reference molecules DAAT and DHT were studied to validate the theoretical approach and to facilitate further progress toward the development of previously unknown molecules (some of which were to be obtained by forming *N*-oxides of DAAT). The DAAT oxidation will preferably take place at N1, N'1, N3, N'3, N5, and N'5 positions rather than N2, N'2, N4, or N'4.

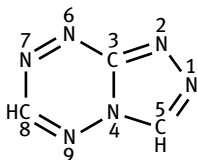
Nitrogen-bridged 1,2,4,5-tetrazine-, furazan-, and 1*H*-tetrazole-based polyheterocyclic compounds were prepared and characterized by HOFs, thermal stability, and detonation properties [1104]. This included 3,6-bis(1*H*-1,2,3,4-tetrazole-5-ylamino)-1,2,4,5-tetrazine, 3,6-bis(furazan-5-ylamino)-1,2,4,5-tetrazine, 3,4-bis(1,2,4,5-tetrazine-3-ylamino)-furazan, and 1,5-bis(1,2,4,5-tetrazine-3-ylamino)-1*H*-1,2,3,4-tetrazole.

The fast and precise modeling of the enthalpy of formation and the density of the HEDMs would simplify the design and selection process of these materials. Seven recently synthesized 1,2,4-triazine-based compounds were modeled by computer [1362]. For the validation of the model, a well-characterized molecule (DAAT) that is similar to the seven other ones was selected as a benchmark for comparing predicted and experimentally measured properties.

## 20.7 Triazolotetrazines and Tetrazolotetrazines

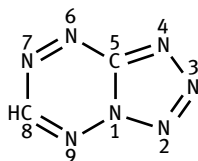
Attaching additional fused rings to tetrazine created a new category of heterocyclic compounds. Five- or six-membered nitrogen-containing heterocycles are traditional sources of energetic materials. Triazole, tetrazole, and tetrazine derivatives have been investigated extensively as HEDMs, both theoretically and experimentally. The desired properties are high densities, high enthalpies of formation, and high thermal stability (due to aromaticity). Of course, increasing interest in the chemistry of 1,2,4,5-tetrazine derivatives has stimulated research on 1,2,4,5-tetrazine-based compounds.

Among them, 1,2,4-triazolo-[4,3-*b*]-1,2,4,5-tetrazine (TTZ) and its substituted derivatives have been synthesized and investigated.



1,2,4-Triazolo-[4,3-*b*]-1,2,4,5-tetrazine (TTZ)

The first synthesis of this ring system was reported in 1968 [1363]. Chavez and Hiskey [1288] synthesized the parent TTZ ring and obtained its mono-substituted and di-substituted derivatives: 6-amino-1,2,4-triazolo-[3,4-*b*]-1,2,4,5-tetrazine (ATTZ) and 3,6-diamino-1,2,4-triazolo-[3,4-*b*]-1,2,4,5-tetrazine (AATZ). The melting points of TTZ, ATTZ, and AATZ are 483, 490, and 605 K (210, 217, and 332°C), respectively. The parent tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine (TETZ) ring was synthesized and its explosive properties were reported.

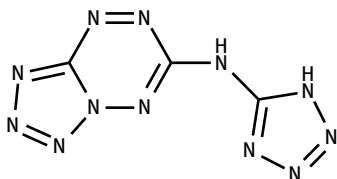


Tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine (TETZ)

The friction and shock sensitivity of 6-diamino-tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine (AATZ) were reported by [303]. One substituent can go into the 8-position in TETZ and one or two substituents can go into the 2- or 8-position in TTZ. A systematic design of TTZ- and TETZ-based more energetic compounds with higher performance and less sensitivity was supported by computational chemistry and a lot of imagination. The enthalpies of formation for a series of 40 different tetrazolo-[1,5-*b*]-1,2,4,5-tetrazine (TETZ) and 1,2,4-triazolo-[3,4-*b*]-1,2,4,5-tetrazine (TTZ) derivatives were calculated by using a DFT method [1364]. The results showed that the attachment of  $-N_3$  or  $-N(NO_2)_2$  groups on the TETZ or TTZ ring enhances their enthalpy values. In the case of mono-substituted derivatives, attachment of a substituent to the 8-position in the TETZ or TTZ ring will increase its energy gaps, although not for the derivatives with the  $-NO_2$  group. The substitution of the  $-NH_2$  group in the TETZ ring is favorable for enhancing its thermal stability. For the TTZ ring, different substituted positions and numbers of the substituent might affect its thermal stability. The calculated detonation properties indicated that incorporating the  $-NO_2$ ,  $-NF_2$ ,  $-ONO_2$ , or  $-N(NO_2)_2$  group into the TETZ or TTZ ring will enhance its detonation performance.

For the TETZ derivatives, the largest  $\rho$  value and the smallest were 1.96 and 1.68 g/cm<sup>3</sup>, respectively, whereas for the TTZ derivatives, the largest  $\rho$  value and the smallest were 2.05 and 1.60 g/cm<sup>3</sup>, respectively. Calculated BDE can be correlated to the thermal stability and impact sensitivity of these compounds. Calculated predicted explosive performance of 40 different compounds was compared to that of RDX and HMX calculated data, as reported in the literature.

6-Aminotetrazolo-[1,5-b]-1,2,4,5-tetrazine has a density of  $\rho = 1.68$  g/cm<sup>3</sup>, an auto-ignition temperature  $T_i$  of 476 K (203 °C), a HOF of  $\Delta H_f = +611$  kJ/mol (+146 kcal/mol = 1060 kcal/kg), a detonation velocity of  $D = 7970$  m/s at a packing density of 1.6 g/cm<sup>3</sup>, and its sensitivity is similar to that of other primary explosives [1299]. 6-Aminotetrazolo-[1,5-b]-1,2,4,5-tetrazine is thermally less stable than the related 6-aminotriazolo-[1,5-b]-1,2,4,5-tetrazine. 6-Aminoguanidino-tetrazolo-[1,5-b]-1,2,4,5-tetrazine, 2-tetrazolo[1,5-b]-1,2,4,5-tetrazino-6-hydrazinecarboxamide, 2-tetrazolo[1,5-b]-1,2,4,5-tetrazinyl-6-hydrazinecarboxamide (STTZ) has a density of  $\rho = 1.84$  g/cm<sup>3</sup>, an auto-ignition temperature  $T_{ign}$  of 488 K (215 °C), a HOF  $\Delta H_f$  of +477 kJ/mol (+114 kcal/mol = +584 kcal/kg) and a detonation velocity of  $D = 6080$  m/s at a packing density of 1.43 g/cm<sup>3</sup>. In the 2+1-ring structure of 6-(tetrazolyl-5-amino)-tetrazolo-tetrazine (TzATTz), the hydrogen atom at the —NH— bridge becomes acidic because electrons have been drained away from the bridge nitrogen into the adjacent aromatic ring structures.



6-(Tetrazolyl-5-amino)tetrazolo-tetrazine (TzATTz)

6-(Tetrazolyl-5-amino)tetrazolo-tetrazine, *N*-(1*H*-tetrazol-5-yl)tetrazolo[1,5-*b*][1,2,4,5]-tetrazin-6-amine, has a density of  $\rho = 1.98$  g/cm<sup>3</sup>, an auto-ignition temperature  $T_{ign}$  of 461 K (188 °C), an enthalpy of formation  $\Delta H_f$  of 925 kJ/mol (221 kcal/mol = 1077 kcal/kg), and a detonation velocity of  $D = 7390$  m/s at a packing density of 1.52 g/cm<sup>3</sup>. The triaminoguanidinium salt of 6-(tetrazolyl-5-amino)tetrazolo-tetrazine has a density of  $\rho = 1.49$  g/cm<sup>3</sup>, an auto-ignition temperature  $T_{ign}$  of 460 K (187 °C), an enthalpy of formation  $\Delta H_f$  of +1092 kJ/mol (+261 kcal/mol = +845 kcal/kg), and a detonation velocity of  $D = 6800$  m/s at a packing density of 1.49 g/cm<sup>3</sup>.

Combustion behavior, flame structure, and thermal decomposition of fused-ring compounds based on tetrazine, triazole, and furazan rings have been described [1365]. It was found that the introduction of a [1,2,4]triazolo[3,4-*b*][1,2,4,5] tetrazine core into the multi-ringed structure of energetic molecules allows energetic compounds with combustion rates greater than those of HMX or RDX to be obtained. These compounds

Table 77: Summary of high nitrogen organic compounds and their properties.

| Compound abbreviation                   | Chemical name                                                    | Chemical formula                                               | Mol. mass<br>g/mol | Nitrogen content<br>Mass-% | Density<br>g/cm <sup>3</sup> | Enthalpy of formation |       |          | References |
|-----------------------------------------|------------------------------------------------------------------|----------------------------------------------------------------|--------------------|----------------------------|------------------------------|-----------------------|-------|----------|------------|
|                                         |                                                                  |                                                                |                    |                            |                              | kJ/mol                | kJ/kg | kcal/mol |            |
| BTz                                     | Bis-tetrazolylaminotetrazine                                     | C <sub>4</sub> H <sub>4</sub> N <sub>14</sub>                  | 248.17             | 79.01                      | 1.76                         | +883                  | +3558 | +211     | [1367]     |
| DAAT-N-Ox                               | Diamino-azo-tetrazine-N-oxides                                   | C <sub>4</sub> H <sub>4</sub> N <sub>12</sub> O <sub>3.5</sub> | 276.16             | 60.86                      | 1.9                          | +636                  | +2303 | +152     | [1367]     |
| H <sub>2</sub> Tz                       | Dihydrazinotetrazine                                             | C <sub>2</sub> H <sub>6</sub> N <sub>8</sub>                   | 142.13             | 78.84                      | 1.68                         | +535                  | +3764 | +128     | [1367]     |
| GuzT                                    | Guanidinium azotetrazolate                                       | C <sub>4</sub> H <sub>12</sub> N <sub>16</sub>                 | 284.25             | 78.84                      | 1.54                         | +410                  | +1442 | +98      | [1367]     |
| DNAT                                    | Dinitro-azo-triazole                                             | C <sub>4</sub> H <sub>2</sub> N <sub>10</sub> O <sub>4</sub>   | 254.13             | 55.12                      | 1.88                         | +406                  | +1598 | +97      | [1367]     |
| BGTz•2HNO <sub>3</sub>                  | Bis(guanidinyl)tetrazine dinitrate                               | C <sub>4</sub> H <sub>10</sub> N <sub>12</sub> O <sub>6</sub>  | 322.2              | 52.17                      | 1.72                         | -197                  | -611  | -47      | [1367]     |
| TAGAT                                   | Triaminoguanidinium azotetrazolate                               | C <sub>4</sub> H <sub>18</sub> N <sub>22</sub>                 | 374.34             | 82.32                      | 1.6                          | +1071                 | +2861 | +256     | [1367]     |
| TAGzT                                   | Bis(triaminoguanidinium) 5,5'-azotetrazolate*                    | C <sub>4</sub> H <sub>18</sub> N <sub>22</sub>                 | 374.34             | 82.32                      | 1.60                         | +1089                 | +2908 | +260.2   | [1042]     |
| TAGzT                                   | Bis(triaminoguanidinium) 5,5'-azotetrazolate                     | C <sub>4</sub> H <sub>18</sub> N <sub>22</sub>                 | 374.34             | 82.32                      | 1.60                         | +1076                 | +2874 | +257.2   | [1051]     |
| (NQ) <sub>2</sub> Tz                    | 3,6-Bis-nitroguanyl-1,2,4,5-tetrazine                            | C <sub>4</sub> H <sub>6</sub> N <sub>12</sub> O <sub>4</sub>   | 286.17             | 58.74                      | 1.76                         | +389 ± 8              | +1539 | +92.97   | [1051]     |
| (TAG) <sub>2</sub> (NQ) <sub>2</sub> Tz | Bis(triaminoguanidinium) 3,6-bis-nitroguanyl-1,2,4,5-tetrazinate | C <sub>6</sub> H <sub>24</sub> N <sub>24</sub> O <sub>4</sub>  | 496.42             | 67.72                      | 1.61                         | +1255 ± 3             | +2528 | +300     | [1051]     |

have good thermal stability that depend on the substituent at the furazan ring (not on the triazolotetrazine core). The burning rates of nitrogen-rich compounds of this type are controlled by the decomposition kinetics at burning surface temperatures. The two-stage decomposition of these substances leads to the appearance of two regions in the burning rate-pressure dependency charts. These transition to each other through an instability region.

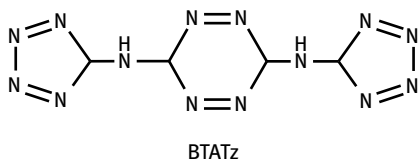
Nitrate ester derivatives of 1,2,4,5-tetrazine and 1,2,4-triazolo[3,4-b]-[1,2,4,5]-tetrazine ring systems had lower thermal stabilities relative to PETN, although they had slightly improved mechanical sensitivities [1366]. The presence of electron-rich amine donors leads to a cathodic shift of the tetrazine redox potentials, making them suitable as sensors for explosive vapor detectors.

Various high-nitrogen energetic materials, viz., dinitro-azo-triazole, triamino-guanidinium azotetrazolate (TAGAT), guanidinium azotetrazolate (GAT or GZT), bistetrazolylamino tetrazine (BTATz), dihydrazino tetrazine, bis(guanidinyl)tetrazine dinitrate, and diamino azobistetrazine *N*-oxide (DAAT-N-Ox) were investigated as additives in gun propellant formulation to reduce the barrel erosion [1367]. Table 77 provides a summary of the physical and thermodynamic properties of these and a few other materials.

## 20.8 —NH—Linked s-Tetrazyl Amines

### 20.8.1 3,6-Bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz)

3,6-Bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine, *N,N'*-bis(1*H*-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine; 1,2,4,5-tetrazine-3,6-diamine, *N*3,*N*6-bis(2*H*-tetrazol-5-yl)-; 1,2,4,5-tetrazine-3,6-diamine, *N,N'*-bis(1*H*-tetrazol-5-yl)-; *N*3,*N*6-bis(2*H*-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine, 3,6-bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine, 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylimino)-1,2,4,5-tetrazine, C<sub>4</sub>H<sub>4</sub>N<sub>14</sub>, CAS RN [254879-86-2], *M* = 248.17 g/mol, with a nitrogen content of 79.017%N, has a density of 1.76 g/cm<sup>3</sup>, melts at 537 K (264 °C), and has an enthalpy of formation of +883 kJ/mol (+211 kcal/mol).



#### 20.8.1.1 Preparation of BTATz

The synthesis and characterization of 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz) has been reported in [1368–1370]. It is most conveniently prepared by treating BDT with commercially available anhydrous 5-aminotetrazole in hot

sulfolane. The enthalpy of formation is +883 kJ/mol (+211 kcal/mol). BTATz is fairly stable, having a DSC onset of exotherm at 537 K (264 °C), and is friction insensitive. Although pure BTATz is fairly sensitive to spark initiation at 0.36 J of capacitive energy, it is easily desensitized through the addition of a binder such as Kel-F or polyethylacrylate.

3,6-Bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine was synthesized using triaminoguanidinium nitrate and 5-aminotetrazole as the starting materials. This synthesis was a four-step process, including cyclization, oxidation, and dehydrogenation followed by nucleophilic substitution [1371]. The structure of BTATz was identified by IR, <sup>1</sup>H and <sup>13</sup>C NMR, and elemental analysis. Some important properties of BTATz have been determined as follows: density of 1.76 g/cm<sup>3</sup>, melting point of 537–558 K (264–285 °C), detonation velocity of 7520 m/s, burning rate of 5.6 mm/s (at 101 kPa), pressure exponent 0.49, DSC exothermic peak temperature of 593 K (320 °C).

BTATz was synthesized by a condensation reaction of triaminoguanidine nitrate with 2,4-pentanedione. This was followed by oxidation and substitution reactions [1372]. The product was characterized by elemental analysis, IR, NMR, and DSC. Instead of nitrogen dioxide/*N*-methylpyrrolidone, acetic acid/sodium nitrite was an oxidation agent. This reduced the cost and simplified the process. The synthesis, characterization, and quantum chemistry study of 3,6-bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine provided additional information on this highly energetic compound. Quantum mechanical calculations provided stable geometric configuration and bond orders. It also predicted the vibrational frequencies, IR spectrum, and thermodynamic properties at different temperatures. The pyrolysis of BTATz proceeds via a transition state and the activation energy of the ring-opening reaction of the tetrazole was deduced.

The advantages of BTATz are that it is impact insensitive, non-explosive, non-pyrophoric, and it is an inflammable solid that decomposes rapidly without flame and produces mostly nitrogen as the main combustion product. BTATz is a solid compound that decomposes primarily to nitrogen gas once initiated by heat. The decomposition is rapid, self-sustained, flameless, and occurs readily over a wide range of chamber pressures. The nitrogen gas produced from BTATz can be used to displace oxygen near a flame, thus extinguishing a fire. Because of these qualities, BTATz has been identified as a component for fire suppression gas generants.

### 20.8.1.2 Properties of BTATz

The properties of 3,6-bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz) were compared to other promising high-nitrogen energetic materials [1308, 1343, 1373]. Because of their highly positive HOFs and higher density, these high-nitrogen compounds are unique in their gas generating ability, produce little to no smoke, and have no leftover residue.

BTATz may form dimers, where two molecules are held together by intermolecular forces. Six optimized stable BTATz dimer pairs were found on the potential energy sur-

face; their electronic structures have been obtained by using DFT calculations [1374]. The largest intermolecular interaction energy of the dimer calculated with BSSE and ZPE correction was  $-68.82 \text{ kJ/mol}$ . An NBO analysis was performed to reveal the origin of the intermolecular interaction. Based on the vibrational analysis, the changes of thermodynamic properties from the monomer to dimer in the temperature range of 200 to 800 K were obtained using statistical thermodynamics methods. The strong hydrogen bonds were found to effectively contribute to dimer formation. The dimerization process can occur spontaneously throughout the temperature range of 200 to 400 K.

Other sources for the properties of BTATz reported  $\rho = 1.76 \text{ g/cm}^3$ ; auto-ignition temperature =  $593 \text{ K} = 320^\circ\text{C}$ ; HOF  $\Delta H_f = +711 \text{ kJ/mol} = 170 \text{ kcal/mol} = 685 \text{ kcal/kg}$ ; measured detonation velocity  $D = 7520 \text{ m/s}$  at a packing density of  $1.76 \text{ g/cm}^3$  [1299]. The vapor pressure of BTATz can be expressed by the equation

$$\ln p = 21.1 - 18000/T$$

where  $p$  is the vapor pressure in atm and  $T$  is the temperature in kelvin. The heat of sublimation is  $150 \text{ kJ/mol}$  ( $35.8 \text{ kcal/mol}$ ). The thermal decomposition of BTATz is governed by the kinetic rate equation

$$k = 2.8 \times 10^{10} \exp(-32090/RT) \text{ s}^{-1}.$$

### 20.8.1.3 Thermal Decomposition of BTATz

The thermal decomposition of BTATz was investigated by using TGA, DSC, and *in-situ* thermolysis rapid-scanning FTIR [1375]. The results showed that the thermal decomposition of BTATz is insensitive to pressure. The thermal decomposition kinetic parameters and equation of BTATz, based on the Ozawa, Kissinger, and Coats-Redfern method, was  $E_a = 317.41 \text{ kJ/mol}$  and  $\log A = 28.07 \text{ s}^{-1}$ . The kinetic equation of BTATz decomposition can be expressed as

$$\frac{d\alpha}{dt} = 1.5 \times 10^{28.07} \exp\left(-3.8178 \times \frac{10^4}{T}\right) (1-\alpha) [-\ln(1-\alpha)]^{\frac{1}{3}}.$$

The primary step in the thermal decomposition of BTATz is the opening of the tetrazine and tetrazole ring. The solid residue after heating to  $738 \text{ K}$  ( $465^\circ\text{C}$ ) consisted of  $\text{NH}_4\text{N}_3$ , a polyamine, and melem, which is a triazine condensation product.

The thermal decomposition characteristics of triaminoguanidinium azotetrazolate (TAGZT), 3,6-bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz), and 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112) were studied using DTA, DSC, high-pressure DSC (PDSC), TGA-DTA, and T-jump/FTIR [1376]. The thermal decomposition kinetic parameters, the  $E_a$ , and  $\log A$  values of TAGZT, BTATz, and LAX-112 were 231.87, 317.41, and  $175.62 \text{ kJ/mol}$ , 25.01, 28.07, and  $16.20 \text{ s}^{-1}$ , respectively. Other TGA and DSC results suggested that BTATz decomposes in the range of  $538\text{--}623 \text{ K}$  ( $265\text{--}350^\circ\text{C}$ ) and the calculated energy of activation of BTATz decomposition was  $212.69 \text{ kJ/mol}$  [1370].

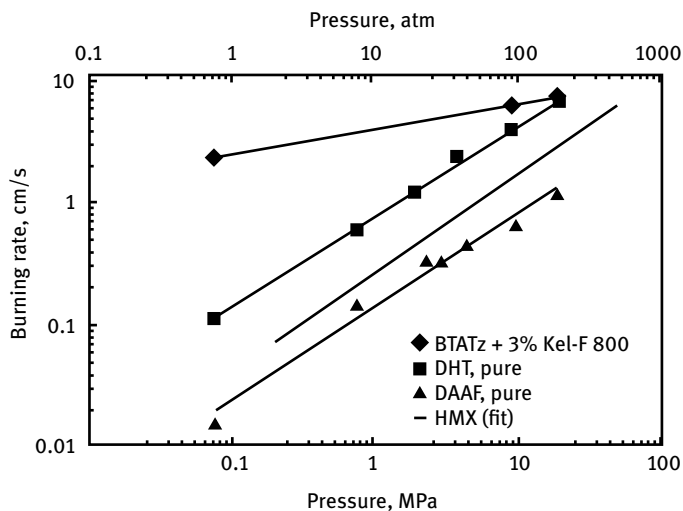
Based on a combination of the power of AIMD methods and DFT, a study of the thermal decomposition mechanisms of the *s*-tetrazine molecule and five of its derivatives suggested that the *s*-tetrazine molecule undergoes a concerted triple dissociation that is similar to its photolysis mechanism [1377]. The tetrazine ring in BTATz-type tetrazine derivatives may be broken by three modes: a concerted triple dissociation, a concerted double dissociation, or a single dissociation, where the concerted triple dissociation mechanism is generally dominant. The stability of the tetrazine ring can be strengthened by substituents like tetrazolyl. If the stability of substituents is better than that of the tetrazine ring, decomposition occurs first through tetrazine ring-breaking. Otherwise, the substituents decay first.

The thermal stability of 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylimino)-1,2,4,5-tetrazine (BTATz) was examined by isothermal and non-isothermal methods [1313]. In the case of BTATz, the decomposition begins with less thermostable tetrazole fragments that capture the tetrazine ring also. The presence of the preliminary reactions of isomerization during tetrazole ring decomposition is the reason for the large observable activation energy of decomposition (240 kJ/mol = 57.5 kcal/mol) in the temperature interval 523–607 K (250–334 °C). In the combustion wave at higher temperatures, the activation energy of BTATz decomposition had a considerably lower value (128 kJ/mol = 30.7 kcal/mol) that was close to a theoretically calculated one. The temperature distribution in the combustion waves of BTATz was measured at low pressures that allowed the surface temperature dependence vs. pressure to be obtained. The burning of these compounds can be explained by a combustion model with a leading reaction in the condensed phase.

#### 20.8.1.4 Strand Burning Rates of BTATz

BTATz burns at impressive rates and with lower than typical pressure effects [1368, 1369], (see Figure 27). At 1 atm, BTATz has a burn rate of 0.56 cm/s that increases to 7.5 cm/s at 191 atm. The pressure exponent over the same range of pressure calculates to 0.49. This has piqued interest in the propellant community. Like DHT, BTATz burns with little or no flame front. In measurements performed at Sandia Laboratory, BTATz was able to sustain a burn front when packed in capillary glass tubes as small as 250 μm in diameter. The compound and its salts can be used in a propellant composition, including an oxidizer, a binder, and 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine, or its ammonium, hydrazinium, or hydroxylammonium salts. BTATz has a high burn rate as shown in Figure 27, wherein the burn rate of BTATz (with 3 vol.-% of Kel-F 800 resin as a binder) is shown and compared with the burn rate of commonly known materials such as 3,6-dihydrazino-*s*-tetrazine (DHT), 3,3'-diamino-4,4'-azoxyfurazan (DAAF), and HMX. Besides a high burn rate, the plot of the burn rate for BTATz has an unexpectedly low slope that is desirable for some propellant applications.





**Figure 27:** Burning rates of BTATz and other high-nitrogen compounds. (Reproduced and modified from [1369].)

The strand burning rates of 3,6-bis(1*H*-1,2,3,4-tetrazol-5-amino)-2-tetrazine (BTATz) were determined in a windowed combustion bomb and compared to those of di-amino-azo-tetrazine (DAAT) *N*-oxides, DAAT, and hydrazinium nitroformate (HNF) [1378]. The effect of the synthesis procedure on the burning rate and burning rate pressure exponent was measured for a wide range of pressures. It appears that the use of DMF in the final synthetic step not only results in higher burning rate materials but also reduced burning rate pressure exponents. After characterizing the pure compound, the effect of BTATz on ADN burning rate was measured by preparing ADN/BTATZ mixtures and pelletizing them. Pellets of BTATz burn smoothly by themselves at pressures between 1 to 70 atm with a burning rate equation of

$$r_b = 5.6p^{0.49}$$

where  $r_b$  is the burning rate in mm/s and  $p$  is the pressure in atm [1299]. The tendency of tetrazines to form solvates (residual solvents) affects their strand burning behavior.

#### 20.8.1.5 BTATz Salts

BTATz is an acid that forms salts with a wide variety of bases. Salts with nitrogen-rich bases that have very high nitrogen contents are preferred. The 1,3-propane diamine salt of BTATz was synthesized by the reaction of 3,6-bis (1*H*-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (BTATz) with 1,3-propane diamine in DMSO [1379]. Single crystals suitable for XRD measurement were obtained by recrystallization. The

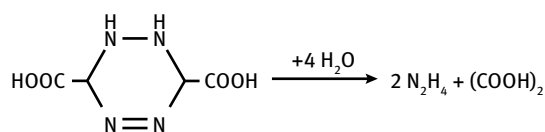
crystals belonged to the monoclinic system, space group  $Cc$  with crystal unit cell parameters of  $a = 2.2699(10)$  nm,  $b = 0.5098(2)$  nm,  $c = 1.6449(6)$  nm,  $\beta = 93.045(15)^\circ$ ,  $V = 1.9008(13)$  nm<sup>3</sup>,  $\rho_c = 1.504$  g/cm<sup>3</sup>, and  $Z = 4$ . The DSC showed that the thermal decomposition of the salt included only an exothermic process.

## 20.9 Other Tetrazine Derivatives

3,6-Dihydrazino-1,2,4,5-tetrazine would be a good constituent of gas generator propellants due to its high nitrogen content (79%) and high enthalpy of formation (519 kJ/mol). It can be prepared by reaction of 3,6-diamino-1,2,4,5-tetrazine with hydrazine [1380].

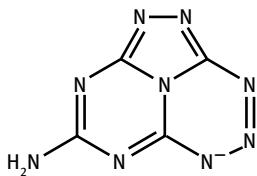
### 20.9.1 Other Single-Ringed Tetrazine Derivatives

When developing tetrazine-based HEDMs, the HOF as a performance parameter can be measured in a calorimeter bomb or predicted using theoretical calculations. The enthalpies of formation of six 1,2,3,4-tetrazine-based compounds were calculated using a DFT method and by using homodesmotic reaction combinations [1381]. The predicted detonation velocity and pressure were calculated. The detonation performances of two of the compounds were superior to those of CL-20. The detonation velocity, detonation pressure, and oxygen balance of 1,2,3,4-tetrazine-based oxo derivatives can be improved by the partial oxidation of the nitrogen atoms in the tetrazine ring. However, further oxidation causes a reduction of the enthalpies and the specific impulses of the *N*-oxide derivatives. The acidic hydrolysis of 1*H*,2*H*-1,2,4,5-tetrazine-3,6-dicarboxylic acid was instrumental in the discovery of hydrazine in 1889.



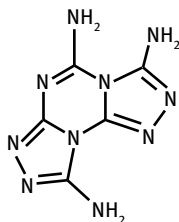
### 20.9.2 Other Multi-Ringed (Fused, Annulated) Tetrazine Derivatives

3-Amino-6-(3,5-dimethylpyrazol-1-yl)-*s*-tetrazine (ADMPT), 3-hydrazino-6-(3,5-dimethylpyrazol-1-yl)-*s*-tetrazine (HDMPT) and several other *s*-tetrazine-derived high-nitrogen energetic compounds were synthesized and characterized by IR, elemental analysis, and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra [1283]. The thermal stability was measured with a DSC at different heating rates. Energetic salts of a three-ringed structure containing triazole, *s*-triazine, and tetrazine rings have been patented [1382].



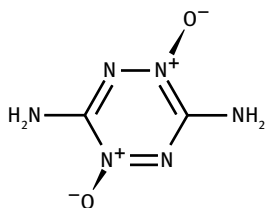
Triazinotriazolotetrazine

Similar derivatives were made from a di(triazolo)triazine three-ringed structure [1383]. These compounds are suitable as sources of nitrogen in gas generants.



### 20.9.3 Tetrazine *N*-Oxides

If 3,6-diamino-*s*-tetrazine is oxidized, *N*-oxides are formed at the 1- and 4-positions, producing 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide; 1,2,4,5-tetrazine-3,6-diamine, 1,4-dioxide; 1,4-dioxido-1,2,4,5-tetrazine-1,4-dium-3,6-diamine, DATZO\_2, LAX-112, CAS RN [153757-93-8],  $C_2H_4N_6O_2$ ,  $M = 144.092$  g/mol, with a density of  $1.860$  g/cm<sup>3</sup>, a melting point of  $539$  K ( $266$  °C), an oxygen balance of  $-44\%$ , and an enthalpy of formation of  $+164$  kJ/mol ( $+39.2$  kcal/mol =  $272$  cal/g).

3,6-Diamino-*s*-tetrazine-1,4-dioxide (LAX112)

LAX112 was once extensively studied as an insensitive explosive by Los Alamos National Laboratory (LANL) [1303]. More recent publications referenced its density as  $\rho = 1.86$  g/cm<sup>3</sup>, the auto-ignition temperature as  $T_{\text{ign}} = 463$  K ( $190$  °C), the HOF as  $\Delta H_f = +200.8$  kJ/mol ( $+48$  kcal/mol) =  $+330$  kcal/kg, and a detonation velocity of  $D = 8700$  m/s at a packing density of  $1.86$  g/cm<sup>3</sup>.

3,6-Diamino-1,2,4,5-tetrazine (DATZ), the raw material needed for the synthesis of LAX112, was synthesized from 3,6-bis(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine (BT)

with a yield of 95.3% [1384]. DATZ was oxidized with peroxyformic acid to form 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (DATZO\_2) with a yield of 60.2%. The effects of reaction conditions on the yield of DATZO\_2 were studied and the optimum reaction conditions were reported as being: DATZ 1.12 g (0.01 mol), formic acid 200 mL and hydrogen peroxide 4 mL, reaction time 1 h, and reaction temperature 298 K (25 °C). The structures of both DATZ and DATZO\_2 were identified and characterized by IR, NMR, DSC, MS, elemental analysis, and melting point determination.

3,6-Diamino-1,2,4,5-tetrazine-1,4-dioxide (DATZO\_2) was synthesized from 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine (BDT) using a two-step reaction sequence, with an overall yield of 46.8% at the 30-g scale [1385]. 3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (BT), which was an important synthesis intermediate, was obtained by using oxygen as the oxidizer without  $N_xO_y$ . A series of synthesis and recrystallization methods were developed to yield different particle sizes and crystal morphologies, and their sensitivities were tested. The thermal decomposition of DATZO\_2 was investigated, and the kinetic parameters of decomposition and some indications of governing decomposition mechanisms were obtained.

The thermal decomposition characteristics of 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112) were studied by DTA, DSC, PDSC, TGA-DTG, and T-jump/FTIR along with those of triaminoguanidinium azotetrazolate (TAGZT) and 3,6-bis(1*H*-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine (BTATz) [1376]. The thermal decomposition kinetic parameters, the  $E_a$ , and log A values of TAGZT, BTATz, and LAX-112 were 231.87, 317.41, and 175.62 kJ/mol and 25.01, 28.07, and 16.20 s<sup>-1</sup>, respectively.

An energetic tetrazine-1,3-dioxide, 5,7-dinitrobenzo-1,2,3,4-tetrazine-1,3-dioxide (DNBTDO), was synthesized and characterized as an energetic material in terms of performance ( $V_{det}$  8411 m/s;  $p_{CJ}$   $3.3 \times 10^{10}$  Pa at a packing density of 1.868 g/cm<sup>3</sup>), mechanical sensitivity (impact and friction as a function of grain size), and thermal stability ( $T_{dec}$  = 477 K = 204 °C) [1386]. DNBTDO exhibited a sensitivity slightly higher than that of RDX and a performance slightly lower (96%) than that of RDX.

Another high-energy tetrazine *N*-oxide is 1,4-diamino-2,3,5,6-tetrazine-2,5-dioxide (TZX). Despite a high detonation velocity and a predicted CJ pressure that is comparable to that of RDX, TZX performed relatively poorly in the cylinder test [1387, 1388]. Theoretical and computational analyses showed this to be the result of a low heat of detonation.

5-Amino-(*tert*-butyl-NNO-azoxy)-1,2,3,4-tetrazine-1,3-dioxide reacts with nitronium tetrafluoroborate to form 5-amino-6-nitro-1,2,3,4-tetrazine-1,3-dioxide [1389]. A plausible reaction mechanism involves the electrophilic substitution of the *tert*-butyl-NNO-azoxy group by the nitro group.

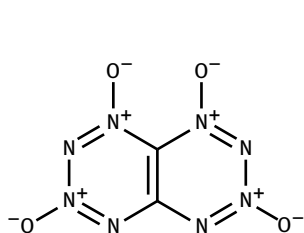
3-Amino-6-nitro-1,2,4,5-tetrazine-2,4-dioxide,  $C_2H_2N_5O_4$ ,  $M$  = 160.07 g/mol, has a very low auto-ignition temperature of 383 K (110 °C) and an enthalpy of formation  $\Delta H_f$  of +180 kJ/mol (+43 kcal/mol = +245 kcal/kg).

*N*-oxides of 3,3'-azo-bis(6-amino-1,2,4,5-tetrazine), diaminoazotetrazine poly(*N*-oxide), DAATO, DAATOx, can have 3.5–3.9 oxygen atoms per molecule. Those carrying an uneven number of oxygen atoms are called “DAATO-3.5.” The 3.5 represents the average oxygen atom content on the ring (5 is maximum). 3,3'-Azoxybis(6-amino-5-*N*-oxide-s-tetrazine), DAATO3.5, DAATO-3.5, is a high-nitrogen compound that derives its energy mostly from the high HOF rather than the oxidation of a carbon backbone. The high nitrogen content of the DAAT building block also results in a high density, and the low content of carbon and hydrogen allows for the easy achievement of a good oxygen balance. In one test, DAATOx was found to have the fastest strand burning rate of any known organic material and it sustained combustion even at very small diameters. For the 3.5-oxygen-per-molecule composition, the molecular mass would be 276.16 g/mol, and the enthalpy of formation for that composition would be +628 kJ/mol (+150.0 kcal/mol = +543 cal/g). Other literature sources gave the following properties for DAATO3.5: density  $\rho = 1.88 \text{ g/cm}^3$ , auto-ignition temperature  $T_{\text{ign}} = 450 \text{ K}$  (177 °C), enthalpy of formation  $\Delta H_f = +548 \text{ kJ/mol}$  (+131 kcal/mol = 440 kcal/kg).

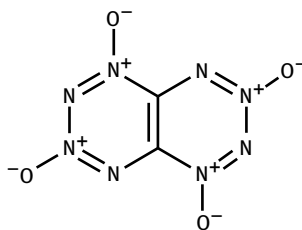
The initiation and secondary reactions from the decomposition of DAATO-3.5 were examined by DSC and TGA/MS [1390]. It was found that the stability of the oxidized compound reduces significantly compared to its building block. A rapid decomposition was observed to begin around 538 K (265 °C), with the release  $\text{N}_2$  and NO as the major species. It was believed that isocyanic acid (HNCO) is released in large quantities too, however, its relative concentration has not yet been quantified. Species observed in smaller quantities included HCN,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ . A significant amount of the residue is believed to be tetrazines, which are known to resist decomposition at the considered temperatures during the relatively short duration of the experiment.

#### 20.9.4 Ditetrazinetetroxide

Based on computations and similarity with other energetic compounds, it was predicted that di-1,2,3,4-tetrazine tetraoxide and its isomer should make good explosives. While, as of 2015, neither had yet been synthesized, it has been suggested that the semi-polar  $\text{N} \rightarrow \text{O}$  linkages on alternate nitrogens will have a stabilizing effect.



Di-1,2,3,4-tetrazine tetraoxide



*iso*-Di-1,2,3,4-tetrazine tetraoxide

The accurate, full-length name for di-1,2,3,4-tetrazine tetraoxide should be [1,2,3,4]tetrazino-[5,6-e]-[1,2,3,4]tetrazine-[1,3,5,7]tetraoxide. It is known as  $C_2N_8O_4$ , DTTO, TTTO,  $M = 200.07$  g/mol. The most stable conformation of TTTO is a planar structure with  $C_{2h}$  symmetry. Using various high-level *ab initio* methods together with DFT-based models, the enthalpies of formation of TTTO at 0 K and standard state were calculated [1391]. The predicted high HOF ( $>200$  kcal/mol), high density ( $>2.0$  g/cm<sup>3</sup>), planar non-polar electronic structure, and the perfect oxygen balance indicate that TTTO should be a HEDM with exceptional performance.

Theoretical quantum mechanical MO calculations were carried out for the isomeric di-1,2,3,4-tetrazine tetraoxides (DTTO and iso-DTTO) [1392]. Detonation pressure and detonation velocity of these compounds are dominated by the densities and not so much by the HOFs. By 2015, DTTO and iso-DTTO were still unknown. The crystal densities were predicted using several different methods resulting in similar densities and explosion parameters. Based on predicted density, DTTO and iso-DTTO could match, or substantially outperform, the best state-of-the-art explosives such as CL-20.

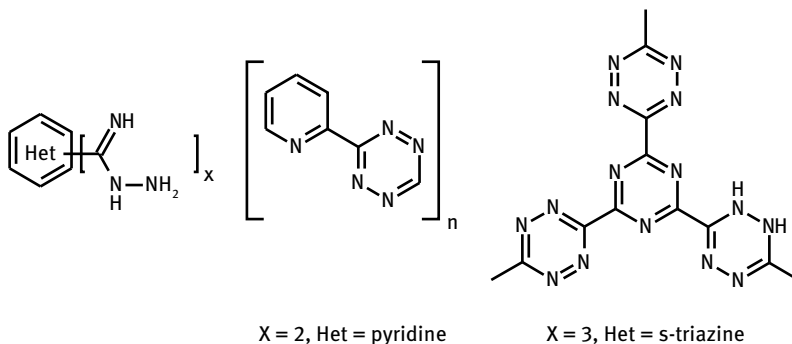
Attempts to prepare a similar molecule containing two carbon atoms that are not part of a phenyl ring, 6-phenyl-[1,2,3]triazolo[4,5-e]-1,2,3,4-tetrazine, PTAT, using a complex 15-step synthesis route had only mixed success [1393]. This compound was chosen as a model compound to test the hypothesis that alternating oxygen substitution on the nitrogen atoms results in a pronounced increase in thermal stability. Only the first ten of 15 steps were successfully completed, with an overall yield of 13%. Predicted properties of DTTO are: density  $\rho = 1.90$  g/cm<sup>3</sup>; HOF (liquid) = 874 kJ/mol = 209 kcal/mol; HOF (solid) = 862 kJ/mol = 206 kcal/mol; detonation velocity  $v_D = 9.71$  km/s; detonation pressure  $p_D = 43.2$  GPa = 432 kbar [1394].

Another model compound made by a four-step synthesis was 6-(tert-butyl-NNO-azoxy)-5-methylthio-1,2,3,4-tetrazine-1,3-dioxide, which was supposed to be a precursor of tetrazino-tetrazine-1,3,6,8-tetraoxide [1395]. Eventually, one group of chemists succeeded in the synthesis and characterization of [1,2,3,4]tetrazino-[5,6-e][1,2,3,4]tetrazine 1,3,6,8-tetraoxide (TTTO) [1396]. It was synthesized in a ten-step synthesis from 2,2-bis(tert-butyl-NNO-azoxy)acetonitrile. The synthetic strategy was based on the sequential closure of two 1,2,3,4-tetrazine 1,3-dioxide rings by the generation of oxodiazonium ions and their intra-molecular coupling with tert-butyl-NNO-azoxy groups. The molecular structure of TTTO was confirmed by single-crystal XRD.

### 20.9.5 Polymeric Tetrazines

In a search for high-nitrogen content polymers suitable as highly energetic binders for solid propellants, linked chains, or networks of triazine and tetrazine rings have been synthesized and tested. The synthesis of polyhetarylenes containing s-tetrazine and other nitrogen heterocycles (pyridine or s-triazine) involved the polymerization of di- or triamidrazones, leading to a linear or hyperbranched dihydrotetrazine-based

assembly [1397]. The poly-(triazinylene-tetrazinylene) material was described as one of the most nitrogen-rich polymers ever made.

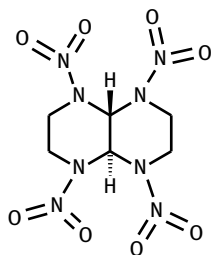


## 20.10 Fused Heterocyclic Ring Structures

### 20.10.1 Fused Heterocyclic Ring Structures with Two Rings

Quantum-chemical calculations of hypothetical molecules of octaazanaphthalene and its *N*-oxides were performed by a modified neglect of differential overlap (MNDO) method and with full geometry optimization [1398]. The paths of probable decomposition reactions of these compounds were outlined. Compounds with more pronounced alternation of charges on adjacent atoms (such as in triazine) were shown to be more thermodynamically favorable and thermally stable than molecules with identical charges on adjacent atoms [1399].

An intermediate in the synthesis of *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD), *trans*-1,4,5,8-tetraazadecalin, was first prepared from glyoxal and ethylenediamine and then nitrated to TNAD with  $\text{HNO}_3$  in acetic acid anhydride [1400, 1401]. The nitration was carried out in three steps.



1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin

*trans*-1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin, decahydro-1,4,5,8-tetranitropyrazino-[2,3-*b*]pyrazine; pyrazino[2,3-*b*]pyrazine, 1,4,5,8-tetranitro-2,3,4a,6,7,8a-hexahydro-

pyrazino[2,3-*b*]pyrazine, decahydro-1,4,5,8-tetranitro-, *trans*-; 1,4,5,8-tetranitro-1,4,5,8-tetraazadecahydronaphthalene,  $C_{10}H_{10}N_8O_8$ , TNAD, CAS RN [83673-31-8],  $M = 322.19$  g/mol, melts at 505–507 K (232–234 °C) and has a density of 1.80 g/cm<sup>3</sup> and an enthalpy of formation of +96.2 kJ/mol (+23.0 kcal/mol = +71 cal/g). This is a quadruple nitramine, and its synthesis and properties should also have been included in chapter “Nitramines” of *Encyclopedia of Liquid Fuels*.

Several possible pathways of the thermal decomposition of 1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin were examined using computational chemistry and DFT. The results were compared with experimental data, revealing the most probable pathway for TNAD thermal decomposition [1402].

A systematic study of the thermolysis mechanism and stability of a series of energetic cyclic nitramines (*trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin isomers) was performed using DFT and semi-empirical MO calculations [1403]. BDE and activation energies ( $E_a$ ) of the thermolysis processes were predicted. The effect of nitroamino groups on the thermal stability and pyrolysis mechanism of the bicyclic nitramines was evaluated by predicting the BDE and  $E_a$ . The results indicated that thermal stabilities and decomposition mechanisms of the bicyclic nitramines derived from the BDE, activation energy, and static electronic parameters were consistent. Homolysis of the N–NO<sub>2</sub> bonds is the initial step in the thermolysis of the bicyclic nitramines. The *meta*-isomers were more stable than the *para*-isomers, and the *ortho*-isomers were the most sensitive.

DFT calculations were performed to relate the structures to the properties of crystalline *trans*-1,4,5,8-tetranitrotetraazadecalin [1404]. The calculated crystal structure compared well with the experimental data. The crystal is an electric insulator. All the atoms of TNAD make up both the lower and the higher energy bands. The projection of the electron density of state demonstrated that the N–NO<sub>2</sub> bond is the most reactive region of the material. The lattice energy was predicted to be –155.13 kJ/mol, which is consistent with previous studies, whereas it was underestimated by the other methods (–70.41 and –74.33 kJ/mol, respectively). The optical properties under ambient conditions were investigated, including dielectric function, absorption coefficient, and reflectivity. The calculated absorption spectra showed several absorption peaks in the fundamental absorption region. These were believed to be associated with different exciton states in the crystal.

The kinetics and mechanism of thermal decomposition of *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD) have been studied using TGA, IR spectroscopy, and pressure differential scanning calorimetry [1405]. The IR spectra of TNAD have also been recorded, and the kinetics of thermolysis has been followed using non-isothermal TGA. Based on the activation energy of the solid-state process, the reaction mechanism of the exothermic process of TNAD decomposition was classified as a nucleation and nuclear growth reaction and a 2-D diffusion chemical reaction.  $E_a$  and  $\ln A$  of the two processes were 330.14 kJ/mol and 29.93, or 250.30 kJ/mol and 21.62, respectively.

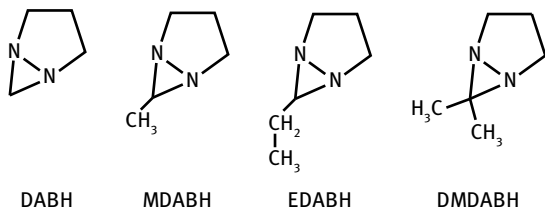


Tetraazadecalin (TAD), a precursor for the synthesis of TNAD, was made by aldehyde amine cyclization from glyoxal and ethylenediamine as the primary material. Tetraazadecalin hydrochloride was obtained via the acidification of TAD [1406]. Nitration of tetraazadecalin hydrochloride with a nitrating acid mixture of nitric acid and acetic anhydride formed 1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD). The overall yield of TNAD was >43%. The purity of TNAD was 98%. The structure of TNAD was characterized by IR, NMR, and elemental analysis.

## 20.10.2 Bridged and Caged Heterocyclic Ring Structures

### 20.10.2.1 Diazabicyclohexane

1,5-Diazabicyclo[3.1.0]hexane-type compounds (DABHs) were identified as promising liquid hypergolic fuels [1407]. The synthesis process and purification of DABHs, 1,5-diazabicyclo[3.1.0]hexane (DABH, CAS RN [13090-31-8]), 6-methyl-1,5-diazabicyclo[3.1.0]hexane (MDABH, CAS RN [6794-96-3]), 6-ethyl-1,5-diazabicyclo[3.1.0]hexane (EDABH), and 6,6-dimethyl-1,5-diazabicyclo[3.1.0]hexane (DMDABH, CAS RN [104518-69-6]) were optimized [20]. The densities of DABHs were greater than 1.0 g/cm<sup>3</sup> and the viscosities were about 2.40–2.63 mPa s. The DABHs are less volatile than methylhydrazines and the freezing points varied considerably for different degrees of alkylation.

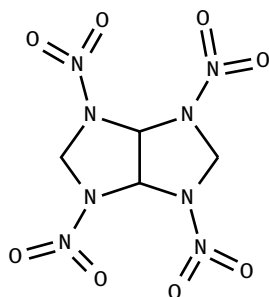


The enthalpies of formation of DABHs were calculated as 129.2–276.2 kJ/mol, which was higher than those of MMH, unsymmetrical dimethylhydrazine (UDMH), or hydrazine. The ignition delay time of DABH with dinitrogen tetroxide was 1 ms, and the ignition delay times of other alkyl-substituted DABHs was 4–11 ms, which indicated their merits as hypergolic fuels.

1,5-Diazabicyclo[3.1.0]hexane (DABH) was evaluated as a potential hypergolic liquid fuel [1408]. The physical and energetic properties of DABH were compared to those of 2-(dimethylamino)ethyl azide (DMAZ), and MMH. The ignition delay time of DABH with dinitrogen tetroxide was 1 ms, which was shorter than DMAZ and similar to that of MMH. A toxicology experiment showed that LD<sub>50</sub> of DABH was 621 mg/kg, which suggested that DABH was less toxic than the other liquid propellants. Thermal decomposition experiments showed that the apparent activation energy ( $E_a$ ) was about 66.3 kJ/mol and the pre-exponential factor was obtained.

### 20.10.2.2 Tetraazabicyclooctane

A DFT method was used to study the molecular geometry, electronic structure, IR spectrum, and thermodynamic properties of cage-tetranitrotetraazabicyclooctane [1409]. The HOF ( $\Delta H_f$ ) and calculated density were used to calculate the predicted detonation properties using K-J equations. The thermal stability of 3,5,7,10,12,14,15,16-octanitro-3,5,7,10,12,14,15,16-octaaza-heptacyclo [7.5.1.1<sup>2,8</sup>.0<sup>1,11</sup>.0<sup>2,6</sup>.0<sup>4,13</sup>.0<sup>6,11</sup>]hexadecane, also known as cage-tetranitrotetraazabicyclooctane, 1,3,4,6-tetranitro-2,3a,5,6a-tetrahydroimidazo[4,5-d]imidazole,  $C_4H_6N_8O_8$ , “bicyclo HMX,” CAS RN [473796-67-7], was investigated by calculating the BDE. Both the predicted detonation velocity of 9.96 km/s and the detonation pressure of 47.47 GPa are better than those of CL-20.



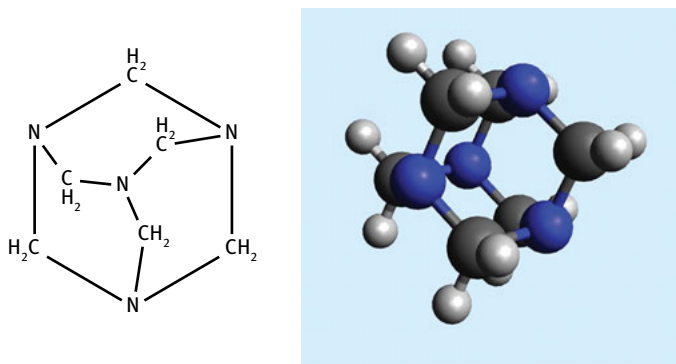
Tetranitrotetraazabicyclooctane

The calculated results showed that the N—NO<sub>2</sub> bond is a trigger during the thermolysis initiation process. The predicted crystal structure obtained by molecular mechanics methods belongs to space group  $Pna2_1$ , with cell parameters  $a = 12.840 \text{ \AA}$ ,  $b = 9.129 \text{ \AA}$ ,  $c = 14.346 \text{ \AA}$ ,  $Z = 6$ , and  $\rho = 2.292 \text{ g/cm}^3$ . However, this predicted crystal structure does not match the experimental measurements for *cis*-2,4,6,8-tetranitro-1*H*,5*H*-2,4,6,8-tetraaza-bicyclo-[3.3.0]-octane,  $C_4H_6N_8O_8$ , monoclinic,  $P2_1$ ,  $a = 8.5979(2) \text{ \AA}$ ,  $b = 6.9495(2) \text{ \AA}$ ,  $c = 8.9726(2) \text{ \AA}$ ,  $\beta = 101.783(2)^\circ$ ,  $V = 524.83(2) \text{ \AA}^3$ , and  $Z = 2$  [1410].

### 20.10.2.3 Hexamethylenetetramine (Urotropine)

Hexamethylenetetramine, also known as urotropine, hexamine, 1,3,5,7-tetraazatricyclo[3,3,1,<sup>3,7</sup>]decane, tetraazaadamantane, methenamine,  $C_6H_{16}N_4$ , CAS RN [100-97-0],  $M = 144.22 \text{ g/mol}$ , is a bridged heterocyclic amine formed from formaldehyde and ammonia. The structure of hexamethylenetetramine is shown in Figure 28.

It is a crystalline solid and forms monobasic salts with strong acids. Other urotropinium salts are formed as quaternary salts by methylation with methyl iodide. One or two amine groups in hexamethylenetetramine can be quaternized. The iodide ion(s) can then be replaced with more energetic (oxidizing) anions in



**Figure 28:** Molecular structure of hexamethylenetetramine.

**Table 78:** Physical properties of hexamethylenetetramine.

| Property                     | SI units                                     | Other units                                   |
|------------------------------|----------------------------------------------|-----------------------------------------------|
| Gross formula                | $C_6H_{12}N_4$                               |                                               |
| Molecular mass               | 140.19 g/mol                                 | 7.133 mol/kg                                  |
| Melting point                | 558–568 K (sublimes)                         | 285–295 °C (sublimes)                         |
| Density                      | 1.339 g/cm <sup>3</sup> (at 24 °C)           | —                                             |
| Molar heat capacity          | 152.38 J mol <sup>-1</sup> K <sup>-1</sup>   | 36.42 cal mol <sup>-1</sup> °C <sup>-1</sup>  |
| Enthalpy of formation, 298 K | +120.499 kJ/mol                              | +28.9 kcal/mol                                |
| Entropy of formation, 298 K  | 163.385 kJ mol <sup>-1</sup> K <sup>-1</sup> | 39.05 kcal mol <sup>-1</sup> °C <sup>-1</sup> |

a metathetical reaction with silver salts of the oxidizing acid. The physical properties of hexamethylenetetramine are summarized in Table 78.

### Physical Properties of Urotropinium Salts

Urotropine forms energetic salts when paired with energetic anions. The initial preparation of urotropinium salts was carried out in the 1950s and, subsequently, the syntheses of a variety of urotropinium salts were reported.

Urotropinium nitrate, *N*-methylurotropinium azide, dinitramide, and azotetrazolate salts have been prepared and characterized using analytical and spectroscopic (<sup>1</sup>H, <sup>13</sup>C, <sup>14</sup>N NMR, IR, Raman) methods [1411]. The structures of all four compounds have been determined using XRD. Hexamethylenetetramine dinitrate can be prepared from hexamethylenetetramine and nitric acid of medium concentration. It is an important precursor in the production of RDX using the Bachmann method, although it may not be isolated as such [1412].

Hexamethylenetetrammonium salts (formed from hexamethylenetetramine with energetic anions: 3,5-dinitropyrazolate, 4,5-dinitroimidazolate, 3,5-dinitro-1,2,4-triazolate, 5-nitrotetrazolate, perchlorate, nitrate, and azide) were synthesized

and characterized [1413]. The structure of *N*-methyl-hexamethylenetetrammonium 3,5-dinitro-1,2,4-triazolate, was confirmed by XRD. The standard enthalpies of formation for the new salts were calculated by using the computationally feasible DFT and MP2 methods in conjunction with an empirical approach based on the densities of the salts. The calculated values ranged from  $\Delta H_f^\circ = -30.6$  to  $+468.8$  kJ/mol where the experimental densities were  $>1.35$  g/cm<sup>3</sup>.

Urotropinium nitrate forms colorless crystals, m.p. 430–434 K (dec.) (157–161 °C) and density  $\rho = 1.47$  g/cm<sup>3</sup>. It can be prepared by the reaction of urotropine with nitric acid. *N*-methylurotropinium azide is a white solid, m.p. 438–443 K (dec.) (165–170 °C) and density 1.4 g/cm<sup>3</sup>. *N*-Methylurotropinium azotetrazolate forms yellow crystals, m.p. 181–184 °C (dec.) and density 1.46 g/cm<sup>3</sup>. These salts can be prepared from either the corresponding iodide or sulfate. Because of the high sensitivity and explosive nature of anhydrous silver azide, an alternative route using sodium azide with *N,N*-dimethylurotropinium diiodide was recommended. Tables 79 and 80 provide summaries of the properties of urotropinium salts. Other sources report the enthalpy of formation of urotropinium dinitrate as  $= -1417.7$  kJ/kg  $= -377.4$  kJ/mol  $= -338.8$  cal/g  $= -90.2$  kcal/mol.

### Chemical Properties of Urotropinium Salts

The oxygen balance of urotropinium dinitrate is  $-78.3\%$ . Hexamethylenetetramine forms complexes with metal salts. Those formed with metal perchlorates are of interest as energetic materials. The kinetics and mechanism of thermolysis of hexamine metal perchlorates have been investigated [1414].

**Table 79:** Physical properties of urotropinium salts.

| Compound name                               | Gross formula                                                   | Melting point  |                | Density<br>g/cm <sup>3</sup> | Enthalpy of formation |          | References |
|---------------------------------------------|-----------------------------------------------------------------|----------------|----------------|------------------------------|-----------------------|----------|------------|
|                                             |                                                                 | K              | °C             |                              | kJ/mol                | kcal/mol |            |
| Urotropinium nitrate                        | C <sub>6</sub> H <sub>13</sub> N <sub>5</sub> O <sub>3</sub>    | 430–434        | 157–161        | 1.47                         | —                     | —        | [1413]     |
| Urotropinium dinitrate                      | C <sub>6</sub> H <sub>14</sub> N <sub>6</sub> O <sub>6</sub>    | 431            | 158 (dec.)     | —                            | –345.2                | –82.5    | [1412]     |
| <i>N</i> -methylurotropinium azide          | C <sub>7</sub> H <sub>15</sub> N <sub>7</sub>                   | 438–443 (dec.) | 165–170 (dec.) | 1.35                         | +468.8                | +112.0   | [1413]     |
| <i>N</i> -methylurotropinium dinitramide    | C <sub>7</sub> H <sub>15</sub> N <sub>7</sub> O <sub>4</sub>    | 394–397 (dec.) | 121–124 (dec.) | 1.46                         | —                     | —        | [1413]     |
| <i>N</i> -methylurotropinium azotetrazolate | C <sub>16</sub> H <sub>30</sub> N <sub>18</sub>                 | 454–457 (dec.) | 181–184 (dec.) | 1.46                         | —                     | —        | [1413]     |
| <i>N</i> -methylurotropinium nitrate        | C <sub>7</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub>    | 467            | 194            | 1.42                         | –30.6                 | –7.31    | [1413]     |
| <i>N</i> -methylurotropinium perchlorate    | C <sub>7</sub> H <sub>15</sub> N <sub>4</sub> O <sub>4</sub> Cl | 473            | 200            | 1.47                         | +14.5                 | +3.46    | [1413]     |

**Table 80:** Properties of urotropinium salts.

| Compound name                                             | Gross formula                                                   | Molecular mass | $T_{\text{melt}}$ |     | $T_{\text{dec}}$ |     | Density | Nitrogen content | Oxygen balance |
|-----------------------------------------------------------|-----------------------------------------------------------------|----------------|-------------------|-----|------------------|-----|---------|------------------|----------------|
|                                                           |                                                                 |                | g/mol             | K   | °C               | K   |         |                  |                |
| Urotropinium 3,5-dinitropyrazolate                        | C <sub>9</sub> H <sub>14</sub> N <sub>8</sub> O <sub>4</sub>    | 298.26         | 453               | 180 | 457              | 184 | 1.56    | 37.57            | −112.7         |
| Urotropinium 4,5-dinitroimidazolate                       | C <sub>9</sub> H <sub>14</sub> N <sub>8</sub> O <sub>4</sub>    | 298.26         | 456               | 183 | 456              | 183 | 1.41    | 37.57            | −112.7         |
| Urotropinium 3,5-dinitro-1,2,4-triazolate                 | C <sub>8</sub> H <sub>13</sub> N <sub>9</sub> O <sub>4</sub>    | 299.25         | 450               | 177 | 455              | 182 | 1.72    | 42.13            | −98.9          |
| Urotropinium 5-nitrotetrazolate                           | C <sub>7</sub> H <sub>13</sub> N <sub>9</sub> O <sub>2</sub>    | 255.24         | 439               | 166 | 442              | 169 | 1.48    | 49.39            | −116.0         |
| <i>N</i> -Methylurotropinium 3,5-dinitro-1,2,4-triazolate | C <sub>9</sub> H <sub>15</sub> N <sub>9</sub> O <sub>4</sub>    | 313.28         | 443               | 170 | 475              | 202 | 1.45    | 40.24            | −109.8         |
| <i>N</i> -Methylurotropinium nitrate                      | C <sub>7</sub> H <sub>15</sub> N <sub>5</sub> O <sub>3</sub>    | 217.23         | 467               | 194 | 469              | 196 | 1.42    | 32.24            | −136.3         |
| <i>N</i> -Methylurotropinium perchlorate                  | C <sub>7</sub> H <sub>15</sub> N <sub>4</sub> O <sub>4</sub> Cl | 254.67         | 473               | 200 | 478              | 205 | 1.47    | 22               | −106.8         |

Data source: [482].

### Safety Properties of Urotropinium Salts

The impact sensitivity of urotropinium dinitrate is 15 N m. The friction sensitivity is defined as a reaction at 240 N pistil load. In the lead block test, a 10-g sample will enlarge the cavity by 220 cm<sup>3</sup>. Urotropinium dinitrate is an intermediate in the production of RDX.

#### 20.10.3 Bridged-Ring HMX Precursors

Dinitropentamethylenetetramine, 1,5-endo methylene-3,7-dinitro-1,3,5,7-tetrazacyclooctane, DPT, is a precursor or an intermediate of hexogen (RDX) and octogen (cyclotetramethylene tetramine, HMX) synthesis. Dinitropentamethylenetetramine (DPT) can be made by starting from urea (without the isolation of intermediates) by nitration, hydrolysis, and Mannich condensation, with a total yield of 63.2%. The reaction mechanism of one-pot synthesis of DPT was studied by isolating and capturing intermediates and by isotope tracing experiments [1415]. The stable intermediates dinitrourea, nitramide, and bis(hydroxymethyl)nitroamine were isolated, and the active intermediate 1-nitro-hexahydrotriazine was captured by benzenesulfonyl chloride. The <sup>2</sup>H (deuterium, which is also abbreviated as D) labeled DPT (DPT-D) was synthesized by the reaction of CD<sub>2</sub>O with NH<sub>3</sub> and bis(hydroxymethyl)nitroamine. The analysis results from <sup>1</sup>H NMR and MS of DPT-D indicated that, in the course of

the reaction, bis(hydroxymethyl)nitroamine decomposed into  $\text{CH}_2\text{O}$  and nitramide, and the small molecule species arranged themselves randomly to form triazine then DPT. DPT can be synthesized by a one-pot method starting with urea [1416]. Without isolation from intermediates, DPT was obtained by nitration, hydrolysis, and Mannich condensation. The yield of DPT was up to 65.2%.

Another process for the preparation of DPT used sulfuric acid, hexamine dinitrate, and formalin [1417]. The yield of crude product could be improved from 30% (literature value) to 60%. The purity of the product was better than 98% [1418].

The crystal structure of dinitropentamethylenetetramine, DPT, is monoclinic, space group  $P2_1/c$  with unit cell parameters of  $a = 9.345 \text{ \AA}$ ,  $b = 8.284 \text{ \AA}$ ,  $c = 11.566 \text{ \AA}$ ,  $\beta = 105.6^\circ$ ,  $Z = 4$ , and  $\rho = 1.682 \text{ g/cm}^3$  [1419]. The two  $\text{N}-\text{NO}_2$  groups in the DPT molecule are planar, with two nitramine carbons raised out of the plane.

## 21 Azacubanes, Azaquadricyclanes, and Azaadamantanes

Cubanoid structures called azacubanes, in which one or more CH groups in the corner of the cube have been replaced by nitrogen, have been synthesized and tested as energetic materials. Of special interest are those azacubanes that carry explosophoric groups, such as nitro groups or azido groups.

Cubane was first synthesized in 1964. However, as of 1990, its unsubstituted heterocyclic analog, 1,3,5,7-tetraazacubane, had not yet been synthesized. The presence of four nitrogen atoms in the cubane skeleton distorts the geometry of the cube, causing highly strained bond angles. This may be due to a combination of several factors such as non-bonding interactions and other repulsive effects of the nitrogen lone electron pairs.

Energetics and charge distributions in azacubanes ( $\text{C}_{8-x}\text{N}_x\text{H}_{8-x}$ ) have been calculated using *ab initio* and hybrid density functional methods and the topography of the molecular electrostatic potential and the electron density of azacubane conformers have been investigated [1420]. From diazacubane to hexaazacubane, the lowest-energy conformers have nitrogen atoms occupying the opposite face opposite corners of a cube. Electrostatic potential studies have shown that the successive insertion of nitrogen in place of CH groups of cubane engenders smaller and more localized electron-rich regions around the nitrogens of a cube. The bond ellipticity and the electron density at the bond critical point of the  $\text{X}-\text{N}$  bonds ( $\text{X} = \text{C}$  or  $\text{N}$ ) in a cubanoid increase from azacubane to octaazacubane. The HOFs of azacubanes calculated by an isodesmic reaction approach using different levels of theory correlated well with the electron density at the bond critical point of  $\text{X}-\text{N}$  ( $\text{X} = \text{C}$  or  $\text{N}$ ) bonds in a cubanoid.

The enthalpies of formation of several polynitrohexaazaadamantanes (PNHAA's) have been calculated by designing isodesmic reactions [1421]. The enthalpies of formation were found to correlate with the number ( $n$ ) and the spatial orientations of nitro groups. Detonation velocities ( $D$ ) and detonation pressures ( $P$ ) were estimated

for PNHAAs by using the K-J equations. It was found that  $D$  and  $P$  increase as  $n$  ranges from one to six, and PNHAAs with four to six nitro groups are very energetic. When  $n$  is over six, the density  $\rho$  of PNHAAs slightly increases; however, the chemical energy of detonation ( $Q$ ) decreases so greatly that both  $D$  and  $P$  decrease. The calculations on BDE suggest that the N—N bond would be the trigger bond during the pyrolysis initiation process of each PNHAA. As  $n$  increased, N—N BDE ( $E_{\text{N-N}}$ ) decreased on the whole, which means that the relative stability of PNHAAs decreases. All  $E_{\text{N-N}}$ (s) of PNHAAs were more than 125 kJ/mol (30 kcal/mol). Considering the synthesis difficulty and the performance as an energetic compound, 2,4,6,8,10-pentanitrohexaazaadamantane was recommended as the most promising candidate.

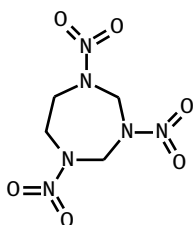
In the caged cubane molecule  $(\text{CH})_8$ , the replacement of CH groups by N atoms increases the content of nitrogen while reducing the content of hydrogen. A series of caged molecules  $(\text{CH})_x\text{N}_{8-x}$  ( $0 \leq x \leq 8$ ) were studied for: **(1)** molecular geometries and electronic structures, **(2)** the analysis of the electronic structure using NBO and atoms in molecules methods, and **(3)** some physico-chemical properties such as the dipole moments. IR vibrational spectra, NMR chemical shifts, HOFs, and relative specific impulses were calculated [1422]. The studies showed that these molecules should be useful energetic materials.

The gas phase enthalpies of the formation of highly nitrated azacubanes have been calculated via isodesmic reactions in which the azacubane cage skeleton is not destroyed [1423]. After the full nitration of 1,4-diazacubane or 1,3,5,7-tetraazacubane, the weakest C—N bond on the 1,3,5,7-tetraazacubane cage skeleton strengthens slightly. However, it weakens on the 1,4-diazacubane cage skeleton. For highly nitrated azacubanes, the introduction of  $-\text{NH}_2$  group results in the destabilization of the neighboring C—N bond on the cage skeleton. The shock stability of 2,4,6,8-tetranitro-1,3,5,7-tetraazacubane (TNTAzC) is superior to that of 2,3,5,6,7,8-hexanitro-1,4-diazacubane (HNDaZC). The detonation velocity and pressure for TNTAzC were predicted to reach 11 km/s and 101 GPa, respectively.

Studies have suggested that ONC is one of the most powerful HEDMs currently known. On the other hand, 2,4,6,8-tetranitro-1,3,5,7-tetraazacubane (TNTAC) may also be a promising HEDM due to its high nitrogen content and high crystal density. DFT and molecular mechanics methods were used to study the crystal structure, IR spectrum, electronic structure, thermodynamic properties, gas-phase and condensed-phase HOF, detonation performance, and the pyrolysis mechanism of TNTAC [100]. TNTAC has a predicted density of about 2.12 g/cm<sup>3</sup>, and its detonation velocity (10.42 km/s) and detonation pressure (52.82 GPa) are higher than those of ONC. The space group is  $P2_12_12_1$ , and the corresponding cell parameters are  $Z = 4$ ,  $a = 8.87 \text{ \AA}$ ,  $b = 8.87 \text{ \AA}$ , and  $c = 11.47 \text{ \AA}$ . Both the density of states of the predicted crystal and the BDE of the molecule in the gas phase showed that the cage C—N bond is the trigger bond during thermolysis. The activation energy of the pyrolysis initiation reaction obtained from calculations is 125.98 kJ/mol, which indicated that TNTAC should have good thermal stability.

## 22 Seven-Membered Ring Heterocyclic Compounds

Structure optimization and frequency calculation of six nitro derivatives of 1,3,5-triazepine (triazepane) were performed using a quantum chemical method [1424]. To obtain reliable energy data, single-point energy and the subsequent thermodynamic properties of the species considered were calculated at a fairly high level of theory. Solid-phase HOFs and the crystal density were determined using an electrostatic potential method, utilizing wave function analysis-surface analysis suite code. The result showed that all nitro derivatives possessed highly positive HOFs that increased with an increase in the number of nitro groups attached to the ring skeleton. The crystal densities were in the range of 1.67–1.90 g/cm<sup>3</sup>. Detonation properties of the compounds were estimated using the K-J equations. The results showed that detonation velocity and detonation pressure increased with an increase in the number of nitro groups attached to the ring structure. It was found that all six nitro derivatives of triazepine had better or comparable performance characteristics than the most widely used commercial explosives, such as TNT, RDX, or HMX. 1,3,5-trinitro-1,3,5-triazepine, 1,3,5-trinitro-1,3,5-triazepane, 1,3,5-trinitro-1,3,5-triazacycloheptane, C<sub>4</sub>H<sub>8</sub>N<sub>6</sub>O<sub>6</sub>, CAS RN [5790-78-3], *M* = 236.143 g/mol, yielded a predicted detonation pressure and a detonation velocity of 45.5 GPa and 9.23 km/s, respectively, at a loading density of 1.90 g/cm<sup>3</sup>, which are superior to HMX (*P* = 39.00 GPa and *D* = 9.11 km/s).



1,3,5-Trinitro-1,3,5-triazepine

Azacycloheptane forms a nitrate salt that melts at 393–396 K (120–123 °C). In the DTA, the maximum exotherm peak is 565 K (292 °C) [1202].

## 23 Eight-Membered Ring Heterocyclic Compounds

Heterocyclic compounds containing eight-membered rings with one or more heteroatoms in the ring are relatively rare compared to six-membered ring heterocyclic compounds. The main representative in this group is HMX, which is thermally more stable and a more powerful explosive than RDX.

As the structure of the book at hand evolved over two decades, the RDX and HMX sections were once contained in the chapter on energetic materials for solid propel-



lants, however, the properties of the pure compounds were eventually moved to chapter “Nitramines” in *Encyclopedia of Liquid Fuels*. Applications of solid energetic compounds will be discussed in future volumes on solid propellants.

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# Hydrocarbons

## Introduction

The *Encyclopedia of Liquid Fuels* contains eight chapters dealing with hydrocarbon fuels. The topic of hydrocarbon fuels had to be subdivided into several smaller chapters that were easier to arrange in alphabetical order in five subvolumes of equal size. The titles of the eight hydrocarbon chapters are: “Alkanes,” “Alkenes and Alkynes,” “Aromatic Hydrocarbons,” “Cycloaliphatic Hydrocarbons,” “Hydrocarbons,” “Jet Fuels,” “Kerosenes,” and “Ramjet Fuels.” The current chapter, “Hydrocarbons,” is a short introduction to the chemistry and applications of hydrocarbons, and is recommended reading before studying any of the more specialized chapters on hydrocarbons.

## 1 Hydrocarbons

Hydrocarbons are the main mode of energy storage for all modes of transportation, be it by land, sea, air, or space. The combustion of hydrocarbons in air or oxygen releases energy that can propel a vehicle, discharging nitrogen, carbon dioxide, and water or only carbon dioxide/carbon monoxide and water. Hydrocarbons retrieved from fossil fuel deposits in liquid or gaseous form are processed in oil refineries to obtain hydrocarbons in a purified state that are suitable to be burned in internal combustion engines, either reciprocating engines in automobiles or rotary turbines in air-breathing jet engines. We will not discuss the use of hydrocarbons as heating fuels or for generation of steam in stationary or mobile steam power plants here because there is not much chemistry involved in such applications and steam-powered rockets are a thing of the past.

Evaluation criteria for hydrocarbon fuels for air-breathing jet engines are quite different from those for rockets. Not every good jet engine fuel must also be a good rocket fuel. For air-breathing engines, the heat of combustion and the density are the main evaluation criteria. For rocket fuels, low-molecular-mass exhaust products are the most desirable property because this allows high exhaust velocities and specific impulses. Density is important only for the pressure-fed systems usually found in missiles and satellites. Pump-fed rocket propulsion systems can handle liquids with a wide range of densities. If density was important for all rocket fuels, liquid hydrogen, with its very low density, would never have made it onto the list of best rocket fuels.

## 1.1 Summary Publications on Hydrocarbon Fuels

The majority of summary publications on hydrocarbon fuels deal with fuels for air-breathing engines, and only very few deal specifically with hydrocarbon fuels for rockets. Since many of these fuels can be used for either application, we deal with them together here, in spite of the fact that this is a book on rocket fuels, not jet engine fuels. The main emphasis will be on the kerosenes RP-1 and RP-2, but we will also consider the growing interest in liquid methane as a rocket fuel. There are combined-cycle engines and air-breathing rocket engines in development which use fuels that were traditionally used only for jet engines (turbojet or ramjet engines). A complete summary of information on a wide range of hydrocarbon fuels is needed for all these applications.

The historic *CPIA/M6 Air-Breathing Propulsion Manual*, which is still available as a loose-leaf ring binder, describes air-breathing engine fuels (missile/ramjet, turbine/jet, and endothermic) and air-breathing engines (ramjets and small or expendable turbojets). It includes data on the chemical and physical properties of many different fuels. The same data are also available online, but to qualified subscribers only, and in a different format – as Liquid Propellant and Fuels Database (LPFD) Datacards. The complete *CPIA/M6 Air-Breathing Propulsion Manual* is available only to JANNAF ERG service subscribers [1]. As of 2020, it was available for \$300 (contains test facilities of air-breathing engines and is available in paper form only). A table of contents of Volume I is shown in Table 1. Several of the units are available for unlimited distribution (Distribution Statement A), which is why they are referenced here. Both CPIA/M6 Volume I and LPFD Datacards are out-of-date and need to be updated. Some distribu-

**Table 1:** Table of contents of the *CPIA/M6 Air-Breathing Propulsion Manual*, Volume I.

| Unit no. | Title   | Pages | Date     | Author                    | Distribution statement |
|----------|---------|-------|----------|---------------------------|------------------------|
| 01       | RJ-4    | 3     | Dec 1982 | Reedy                     | A                      |
| 02       | RJ-5    | 2     | Dec 1982 | Reedy                     | A                      |
| 03       | JP-4    | 3     | Dec 1983 | Reedy                     | A                      |
| 04       | JP-5    | 3     | Dec 1982 | Reedy                     | A                      |
| 05       | JP-9    | 3     | Dec 1982 | Reedy                     | A                      |
| 06       | JP-10   | 12    | Jan 2003 | McCoy, Edwards, and Reedy | C <sup>a</sup>         |
| 07       | RJ-6    | 3     | Feb 1986 | Reedy                     | A                      |
| 08       | JP-7    | 16    | Jan 2003 | Fry and Edwards           | C                      |
| 09       | MCH     | 20    | Jul 1996 | Fry and Reedy             | C                      |
| 10       | Decalin | 22    | Jul 1997 | Fry                       | C                      |
| 11       | JP-8    | 4     | Sep 2000 | Fry                       | C                      |
| 12       | T6      | 4     | Sep 2000 | Edwards                   | C                      |
| 13       | T15     | 4     | Sep 2000 | Edwards                   | C                      |

<sup>a</sup> Distribution Statement C: Distribution authorized to U.S. Government agencies and their contractors

tion limitations should be relaxed because most of the information contained therein is now also publicly available from other unlimited sources.

Some hydrocarbon fuels have been custom synthesized to meet specific requirements in terms of density and heat of combustion. High-energy-density liquid fuels are critical for volume-limited airbreathing vehicles as they can extend the flight range and increase the payload and can be used as an energetic additive for conventional fuels. Current multi-cyclic high-energy-density fuels were first introduced due to a focus on more efficient and environmentally compatible synthesis routes. A review paper summarized the synthesis, properties, and challenges (especially those that have become apparent in the past decade) of high-energy-density fuels [2].

The book by Zou, Zhang, and Pan on high-energy-density fuels for advanced propulsion contains chapters on the history and basics of aerospace fuels, high-density polycycloalkane fuels, high-density diamondoid fuels, high-energy strained fuels, nanofluid fuels, and hypergolic ionic liquid fuels [3].

More useful than books written on paper or ring-bound manuals would be an electronic database that provides search capabilities and instant access to reliable and verified property data for hydrocarbon fuels. Several publications have dealt specifically with hydrocarbon fuels for cruise missiles [4] or ramjets. See also [5–7].

## 2 Properties of Hydrocarbon Fuels

The volume occupied by missile propulsion systems on-board ships is a major consideration for sea-launched weapon systems, as the space available to house weapons under deck or above deck is minimal. By comparison, weight is of more significance in air-launched systems. A fuel of increased density for a given gravimetric heat of combustion will have an advantage in volume-limited systems. High-energy-density hydrocarbon fuels can be obtained either by synthesizing polycyclic and diamondoid hydrocarbons with cyclic or spherical structures to achieve high density or by synthesizing strained cyclic hydrocarbons, which have not only high density but also higher energy due to the additional strained energy in the molecules. In general, for hydrocarbon fuels, as the density is increased, the gravimetric heat of combustion decreases [8]. To utilize the density increase to its full advantage, the gravimetric heat of combustion should remain at least constant. However, thanks to the ingenuity of some chemists, the new generation of fuels possess increased gravimetric heat of combustion simultaneously with increased density. This is partly due to the strain energy in the molecules. The increased density ( $\rho = 1.2\text{--}1.3\text{ g/cm}^3$ ), and moderate strain energy of pentacyclic or tetracyclic hydrocarbons can contribute to an increased energy output during combustion. By breaking the molecular symmetries of some of these high-freezing fuels by attaching one or several methyl groups to the ring structure, the freezing and boiling points can be decreased significantly.

These three- or four-membered ring and caged ring fuels have distorted C—C bonds, and the strain energies of these strained rings are much higher than those of cyclopentane and cyclohexane rings. This chapter does not contain a separate section on hydrocarbons with strained rings. Instead, sections on hydrocarbons with strained rings are scattered throughout this volume, especially in the “Alkanes,” “Cycloaliphatic Hydrocarbons,” “Kerosenes,” “Jet Fuels,” and “Ramjet Fuels” chapters. Other books contain dedicated chapters that deal more specifically with hydrocarbons with high densities and high energy contents due to strained rings [9].

Hydrocarbon fuels still represent the largest mass fraction of all currently used liquid rocket fuels for boosters in space launch vehicles, although hydrogen (in spite of its low density) is slowly catching up. For rocket propellants, it is desirable to use hydrocarbon fuels that contain as much hydrogen as possible, which is why most hydrocarbon rocket fuels are saturated alkanes. Selection criteria for air-breathing engines and rocket engines differ in that air-breathing engines benefit more from the heat of combustion and high density than from low-molecular-mass exhaust gases. Nevertheless, many fuels that were originally intended for air-breathing jet engines have also been tested as rocket fuels, often only because they were readily available at the petroleum product tank farm next door.

Hydrocarbons are divided into groups according to their chemical structures. Aliphatic hydrocarbons include the alkanes, alkenes, and alkynes (acetylene and homologues), in order of increasing degree of unsaturation. Cycloaliphatic hydrocarbons are a group by themselves and are also of specific interest as fuels for air-breathing propulsion as well as rocket engines. Hydrocarbons containing benzene rings are called aromatic hydrocarbons. They have better thermal stability than most aliphatic hydrocarbons with similar molecular masses, but are rarely used as liquid rocket propellants. If we arranged this chapter on hydrocarbon fuels based on the number of carbon atoms in the molecule, then methane and the lower hydrocarbons would be discussed first, before dealing with hydrocarbons containing more than one carbon atom, such as kerosene.

Alkanes have the best hydrogen:carbon ratio, which is a desirable property for rocket propellants. The best hydrogen:carbon atom ratio is obtained with methane. The hydrogen:carbon atom ratio in methane is 4:1, which cannot be beaten. In spite of this advantage, methane has not been used as a rocket propellant until recently. Aromatic fuels have the lowest hydrogen:carbon ratios and are less suitable for use as rocket fuels.

Alkenes contain carbon-to-carbon double bonds that are characteristic of unsaturated compounds. An antiquated designation for alkenes is *olefins*. Alkenes with one or more double bonds are more susceptible to autoxidation and resin formation during storage, an undesirable property for jet engine fuels and rocket fuels alike. They are more reactive than either alkanes or aromatics, and their presence reduces the storability of liquid fuels because they may polymerize and autoxidize. Alkynes are

derivatives of acetylene and have unique fuel properties. Alkenes and alkynes will be discussed in the chapter “Alkenes and Alkynes.”

## 2.1 Physical Properties of Hydrocarbon Fuels

### 2.1.1 Vapor Pressures of Hydrocarbon Fuels

Vapor pressures of hydrocarbons can be calculated using a group additivity relationship [10]. For instance, plotting the vapor pressures of linear alkanes or cycloalkanes as a function of the number of carbon atoms gives a nearly linear relationship. Group values were derived from experimental vapor pressure data for 326 compounds. The vapor pressures thus predicted ranged from  $10^{-4}$  to 1000 kPa, and the temperature dependence of the group values was given for temperatures from 298 to 500 K.

### 2.1.2 Thermodynamic Properties of Hydrocarbon Fuels

The most important thermodynamic property of hydrocarbon fuels for airbreathing and for rocket propulsion applications is the enthalpy of formation, directly related to the heat of combustion. For the chemist, the architect of ever more energetic molecules, the design of hydrocarbons is a challenging task. Indeed, one can show some examples of the successful synthesis of fuels for which the molecular structures did not even exist on paper several decades ago. A key property that is common to many of these newer synthetic fuels is the strain energy inherent in alicyclic molecules with strained rings [8, 11].

The vibrational frequencies of selected alkylcyclohexanes and related polycyclic molecules consisting of chair- and boat-shaped six-membered rings were calculated using conventional Hartree-Fock theory with a hybrid density functional procedure [12]. The sums of zero-point energies (ZPE) and heat-content ( $H_T - H_0$ ) energies thus obtained were reproduced by an empirical formula featuring only the total number of carbon atoms, the number of tertiary carbons, the number of carbons in the cycle(s), and the number of rings, while the presence of boat rings or the occurrence of gauche-butane interactions play no role in the description of  $ZPE + H_T - H_0$ . Enthalpies of formation calculated on this basis agreed to within 1 kJ/mol (0.24 kcal/mol) with the experimentally determined numbers. Examples calculated included methylcyclohexane, ethylcyclohexane, propylcyclohexane, bicyclo[2.2.2]octane, adamantane, and decalin.

### 2.1.3 Enthalpies of Fusion of Hydrocarbon Fuels

A group additivity method was used for estimating enthalpies of fusion and entropies of fusion for a wide range of hydrocarbons [13]. The group additivity factors were based on experimental fusion enthalpy data for 191 hydrocarbons. The average deviation between experimental and predicted fusion enthalpies was  $\pm 2.34$  kJ/mol

( $\pm 0.56$  kcal/mol). This method was later expanded to include mono- and multi-substituted derivatives as well [14].

## 2.2 Chemical Properties of Hydrocarbon Fuels

### 2.2.1 Thermal Stabilities of Hydrocarbon Fuels

#### 2.2.1.1 Thermal Stabilities of Hydrocarbon Fuels for Combined Cycle Engines

Plans for launch vehicles with air-breathing first stages and rocket upper stages, mixed-mode propulsion, and dual-mode propulsion may benefit from a commonality of fuels on-board the vehicles [15]. Propellant combinations were evaluated for a variety of candidate engines for use in mixed-mode, single-stage-to-orbit applications. The ISTAR Rocket Based Combined Cycle (RBCC) propulsion system would use the same fuel for both modes of propulsion.

In RBCC engines, in addition to its obvious use as a fuel for propulsive purposes, liquid fuel is used to cool system structures regeneratively to temperatures commensurate with presently available structural materials used for leading edges and combustion chamber walls. Insufficient fuel thermal stability limits the use of some hydrocarbon fuels. In a study of the use of high-energy, high-density hydrocarbons in rocket and combined-cycle propulsion systems, the thermal stabilities of RP-1, JP-10, and quadricyclane were assessed using a system for thermal stability diagnostic studies [16, 17]. Whereas JP-10 and RP-1 exhibited reasonable thermal stability, the highly strained quadricyclane molecules rapidly degraded under high-pressure, condensed-phase thermal stress.

#### 2.2.1.2 Coke Deposition Due to Thermal Decomposition of Hydrocarbon Fuels

There are several other sections in this encyclopedia on coke deposition specifically those on coke deposition in kerosene, RP-1, and RP-3 (in the “Kerosenes” chapter). Coke deposition during pyrolysis of hydrocarbon fuel in a mini-channel reduced the effective diameter and increased the pressure drop. It also drastically reduced heat transfer between the flowing liquid and the tubing. A hydraulic resistance method was introduced to quantitatively evaluate coke deposition [18]. Pyrolysis of a hydrocarbon fuel was carried out during 30-min runs in an electrically heated mini-channel (heated length, 508 mm; inner diameter, 2 mm) at fuel temperatures up to 998 K (725 °C) and a supercritical pressure of 4 MPa. The post-test coke evaluation was non-destructive and performed by flowing at normal temperature and pressure. Through comparison with optical microscope visualization, the hydraulic resistance method was shown to be accurate. Experimental results showed that the thickness of coke deposit along the channel, which varied from several to about 130  $\mu\text{m}$ , was a function of film temperature (average of the wall and bulk fuel temperatures). The hydraulic resistance continuously increased, contributing to the coke deposition during fuel pyrolysis. However, the thermal effects of coke layer thickness will reduce the heat transfer.

### 2.2.1.3 Endothermic Fuels

The speed of a hypersonic air-breathing vehicle is limited by aerodynamic heating. While their lack of thermal stability is a detriment to the use of hydrocarbon fuels in rocket engines, for certain applications of hydrocarbon fuels in hypersonic air-breathing jet engines, the ability to use fuels that decompose endothermically as coolants for leading edges and other hot parts of the missile can be an advantage. Some hydrocarbon fuels have been developed specifically to be used as endothermic fuels [19–21]. Dehydrocyclization of normal alkanes to form saturated ring compounds is not highly endothermic and proceeds slowly on known catalysts, and in a subsequent reaction the saturated rings could be further dehydrogenated to form aromatics. Dehydrogenation of normal alkanes and ring fracture of aromatics and cycloalkenes generally require very high temperatures. Catalytic cracking of normal alkanes follows many different reaction routes and produces hydrogen and a medley of saturated and unsaturated hydrocarbon products.

The endothermic dehydrogenation of methylcyclohexane over a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst can approximately double the 2324 kJ/kg (1000 BTU/lb) cooling capability available from the sensible enthalpy of the fuel alone. This should provide cooling sufficient to allow flight speeds into the range of Mach 10 at optimum altitude. However, the application of cooling to the various portions of the aircraft may present formidable problems. Factors that are important in this consideration are thermal stability, reaction rate, reactor weight and volume, heat transfer, pressure drop, combustion characteristics, and the close mating of the cooling system to the aircraft [22].

Endothermic fuels were specifically developed for air-breathing hypersonic propulsion; however, many of the properties of the fuels developed and characterized under the endothermic fuels programs also apply to the design of regenerative cooling jackets in rocket engines. Although this is a book on rocket propellants, the scope of this chapter on hydrocarbon fuels has been expanded to include fuels that were primarily intended for air-breathing propulsion but may be used as rocket propellants as well.

The development of endothermic fuels has stimulated a wide range of hydrocarbon fuel syntheses and characterization. Early development work on endothermic fuels was conducted at Shell Development Company in Emeryville, CA [23]. Consideration of the effect of design parameters on the conditions under which endothermic reactions can be carried out led to the conclusion that space velocities of 50 or higher would be necessary due to volume limitations in high-speed aircraft. The investigation of the feasibility of using hydrocarbons as heat sink fuels for hypersonic aircraft studied both thermal and catalytic endothermic reaction at temperatures up to 1033 K (1400 °F), pressures up to 6.8 MPa (1000 psi), and liquid hourly space velocities up to 260 and 150, respectively. Kinetic rate considerations favor catalytic reactions. Preliminary studies of the dehydrogenation of propane to propene and of methylcyclohexane to toluene were made. Fuels were tested at temperatures up to at least 811 K (1000 °F). Thermal stability was found to decrease in the following order: *n*-dodecane, toluene,



methylcyclohexane. A 94 L/h (25 gallon/h) fuel system simulation test rig was used for determining heat transfer coefficients, heat sinks, and decomposition product compositions.

The dehydrogenation of methylcyclohexane to form toluene and hydrogen over a platinum-on-alumina catalyst is an effective heat sink [24]. Propane dehydrogenation may absorb about 3489 kJ/kg (1500 BTU/lb), but the reaction is neither as clean nor as rapid. The thermal stabilities of molecular types generally increase in the following order: monocyclic aromatic, monocyclic naphthene, bicyclic naphthene, *n*-paraffin. Exclusion of oxygen increases the critical thermal stability temperature by about 111 K (200 °F). The introduction of alkyl groups into either the cyclohexane or benzene rings increases thermal stability.

Both thermal and catalytic endothermic reactions of mono- and bicyclic naphthenes have been considered as heat sinks at temperatures up to 1033 K (1400 °F), pressures up to 6.8 MPa (1000 psi), and liquid hourly space velocities up to 260 and 150, respectively [25]. Using dehydrogenation to the corresponding aromatics over a platinum-on-alumina catalyst, reaction heat sinks of about 2324 kJ/kg (1000 BTU/lb) of feed should be achievable with the lower members of the series, such as cyclohexane, methylcyclohexane, dicyclohexyl, and decalin. Rates of reaction generally increased with alkyl substitution. Activation energies showed variable behavior. Selectivities for the corresponding aromatics were high.

A study of the supersonic combustion characteristics of the decomposition products of endothermic hydrocarbon fuels (propane and methylcyclohexane dehydrogenation fuel systems) was done in order to define the parameters that affect the combustion process and to establish the feasibility of burning these fuels in supersonic combustors [26].

Laboratory studies on the dehydrogenation over Pt/Al<sub>2</sub>O<sub>3</sub> of a number of mixtures of naphthenes included methyldecalin and dicyclohexyl as well as the pure components, along with additional studies on decalin [23]. About 220 dehydrogenation catalysts were prepared using a variety of metals and supports. The thermal stabilities of methylcyclohexane, decalin, and a naphthenic jet fuel were all critically, but uniquely, dependent on the dissolved O<sub>2</sub> concentration in the region below about 10 ppm.

The dehydrogenation of decalin over a platinum/Al<sub>2</sub>O<sub>3</sub> catalyst was studied on a laboratory scale in the temperature region up to 922 K (1200 °F) and at pressures to 10 atm in order to provide kinetic data for the construction of a mathematical model [24]. Testing has shown that catalysts which demonstrate improved activity with methylcyclohexane do the same with decalin, and it has confirmed the observation that improved catalyst stability is associated with a small pore size. Heat transfer studies in a simulated single-tube fuel system have confirmed the mathematical model for the catalytic dehydrogenation of methylcyclohexane up to a heat flux of 1891 kW/m<sup>2</sup> (600000 BTU h<sup>-1</sup> ft<sup>-2</sup>).

Calculations of the cooling requirement for a Mach 8 supersonic combustion ramjet engine under standard conditions indicated that this application would require about 4416 kJ/kg (1900 BTU per pound of fuel) [27, 28]. The possibility of utilizing the dehydrogenation of bridged-ring naphthenes to provide an additional heat sink has been studied, but no suitable catalysts have been found for this reaction. Studies on methods of accelerating the thermal cracking of paraffins by means of additives have shown some promise. In the dehydrogenation of naphthenes over supported platinum catalysts, the stability of the catalyst was found to be inversely proportional to the pore size of the support, and was also affected by the composition of the support. Efforts to induce the dehydrogenation of methylcyclohexane using dispersed catalysts have met with some success.

The endothermic decomposition of normal straight-chain alkanes (e.g., heptane) or methanol may offer more of a heat sink capability than methylcyclohexane or decalin, the two most commonly tested endothermic fuels.

Storable liquid hydrocarbon fuels such as JP-7, JP-8+100, and JP-10 that can undergo endothermic reactions may provide sufficient heat sink capability to enable hypersonic flight without having to resort to cryogenic fuels. A program to develop and demonstrate the endothermic potential of these fuels for hypersonic scramjet cooling used a high-pressure bench-scale reactor to determine the overall heat sinks (including endotherm), endothermic reforming products, and coking rates for the fuels [29]. A baseline fuel, *n*-octane, was also investigated for comparison. The tests were conducted in tubes that simulated a single passage in a practical catalytic heat exchanger/reactor under representative flow conditions. Performance evaluations were primarily based on endotherm measurements and coke deposition. Adequate heat sink capacities were demonstrated for JP-7 and JP-8+100 at elevated pressures using a simple, inexpensive zeolite cracking catalyst. Although JP-10 provided an attractive heat sink, its high carbon-to-hydrogen ratio led to significant coking/fouling problems and potential poisoning of the catalyst, even at relatively low temperatures.

The coking characteristics of the Chinese endothermic hydrocarbon fuel S-1 on Ni-Cr alloy was studied in a laboratory-scale continuous flow reactor system [30]. The carburization of the Ni-Cr alloy surface was examined by EDAX analysis. The coke composition was determined by elemental analysis, which showed that the ratio of hydrogen to carbon in the coke decreased with reaction time. The surface morphology of the coke was determined by SEM after heat treatment at 973–1473 K (700–1200 °C) with a heating rate of 20 K/min applied by a DSC. The results showed that temperature has an important effect on the structure of the coke. The analytical results for soluble coke deposits showed that the intermediate coking products consisted of aromatic compounds and paraffins.

The activities of catalysts for decomposition of endothermic fuels can be improved by depositing the active metal preferentially on the surfaces of catalyst granules or reactor wall coatings [31].

Catalytic cracking of China No. 3 aviation kerosene using a zeolite catalyst was investigated under supercritical conditions [32]. A three-stage heating/cracking system was designed to be capable of heating 0.8 kg kerosene to a temperature of 1050 K and a pressure of 7.0 MPa with a maximum flow rate of 80 g/s. The mass flow rate was found to correlate well with the extent of fuel conversion. The gaseous products obtained from fuel cracking under different conditions were analyzed using GC. Results showed that the average molecular weight of the resulting gaseous products and the fuel mass conversion percentage were strong functions of the fuel temperature and fuel pressure. The fuel conversion was shown to depend on the fuel residence time in the reactor, as expected. The heat sink levels due to sensible heating and endothermic cracking were determined and compared under varying operating conditions. It was found that at a fuel temperature of ~1050 K, the total heat sink reached ~3.4 MJ/kg, with the chemical heat sink accounting for 1.5 MJ/kg.

Nucleate boiling heat transfer may induce oscillation under near-boiling conditions in any fluid, including hydrocarbons and endothermic fuels. The thermo-acoustic instability and heat transfer coefficients of an endothermic hydrocarbon fuel were investigated in a horizontal mini-tube at supercritical pressure [33]. The test section was a CRES 316tube with a length of 240 mm and an inner diameter of 1.6 mm. Experiments were conducted at pressures of 2.5–4.0 MPa, mass fluxes of 800–1200 kg m<sup>-2</sup> s<sup>-1</sup>, and heat fluxes of 665–950 kW/m<sup>2</sup>. A correlation between the heat transfer coefficient and the oscillation intensity indicated that the periodic decrease in wall temperature was accompanied by synchronous increases in the outlet bulk temperature and the pressure drop during oscillation. The thermo-acoustic oscillation was more pronounced at a lower mass flux, lower pressure, or higher heat flux. The instability disappeared when the inlet bulk temperature exceeded a threshold value. A dimensionless criterion was obtained to evaluate the stability limit of thermal-acoustic oscillation.

*n*-Dodecane (C12) and decalin (decahydronaphthalene, DHN) were studied as model alkane and cycloalkane compounds, respectively. Pyrolysis of C12, DHN, and C12-DHN binary fuels with different mass ratios of C12 to DHN was performed on an experimental cracking apparatus equipped with a tubular reactor under supercritical conditions (3.5 MPa and 973 K = 700 °C) [34]. The amount of coke deposited on the inner surface of the tubular reactor was determined by weight. During a study of the effects of endothermic hydrocarbon fuel composition on the pyrolysis and anti-coking performance, it was observed that there were reciprocal inhibition and competition effects during the co-pyrolysis of C12 and DHN. Increasing the ratio of C12 to DHN exerted a positive effect on gas yields of endothermic hydrocarbon fuels, but hardly influenced the selectivities of H<sub>2</sub> and alkenes (≤ C<sub>4</sub>). The heat sink abilities of the endothermic hydrocarbon fuels depended largely on the gas yields, representing the thermal cracking level. The C12:DHN ratio greatly affected the amount of coke and the morphologies of the endothermic hydrocarbon fuels. The

alkane:cycloalkane ratio for advanced EHF's should not be less than 3/7 in order to minimize coking problems.

## 2.2.2 Safety Properties of Hydrocarbon Fuels

### 2.2.2.1 Flash Points of Hydrocarbon Fuels

Flash points of flammable liquids are determined in accordance with ASTM D 92–98a [35], ASTM 1998 (open cup) or ASTM D93 [36], ASTM 1993 or ASTM D3828 [37], ASTM 1994 or ASTM D56 [38], ASTM 1993 (closed cup) or ASTM D1310 [39], and ASTM 1993 (open cup). See also [40].

### 2.2.2.2 Autoignition Temperatures of Hydrocarbon Fuels

Autoignition temperatures of flammable liquids are determined in accordance with ASTM Method E659–78 (1994) [41]. An increase in molecular weight results in a decrease in spontaneous ignition temperature for both normal alkanes and normal alkenes. The spontaneous ignition temperatures for normal alkanes decrease with increasing molecular weight from 778 K (504 °C = 940 °F) for propane to 503 K (230 °C = 446 °F) for hexadecane (Table 2).

**Table 2:** Spontaneous ignition temperatures of *n*-alkanes.

| Hydrocarbon | Spontaneous ignition temperature |     |     | Time lag at last ignition |
|-------------|----------------------------------|-----|-----|---------------------------|
|             | K                                | °C  | °F  | min                       |
| Propane     | 778                              | 504 | 940 | 0.1                       |
| Butane      | 704                              | 431 | 807 | 0.1                       |
| Pentane     | 558                              | 284 | 544 | 0.4                       |
| Hexane      | 534                              | 261 | 501 | 0.5                       |
| Heptane     | 520                              | 247 | 477 | 0.5                       |
| Octane      | 513                              | 240 | 464 | 0.9                       |
| Nonane      | 507                              | 234 | 453 | 1.1                       |
| Decane      | 505                              | 232 | 449 | 0.9                       |
| Hexadecane  | 503                              | 230 | 446 | 1.1                       |

Data source: [42]

In general, increased branching increases the ignition temperatures of alkanes and alkenes. Aromatics have considerably higher spontaneous ignition temperatures than most alkanes or alkenes, with benzene having the highest value for any of the hydrocarbons tested [42]. The spontaneous ignition temperature of a substance has been defined as the lowest temperature at which that substance will ignite in air or oxygen without the application of an external source of ignition. Spontaneous ignition temperatures of fuels are of some significance in the performance of reciprocating engines

because, in general, fuels for spark-ignition engines should have high ignition temperatures and fuels for compression-ignition engines should have low spontaneous ignition temperatures. Rocket engines can operate with fuels with a wide range of autoignition temperatures. The spontaneous ignition temperature is a factor in rating the inflammability hazards in the handling of hydrocarbon fuels during their production, transportation, storage, and use as rocket fuels.

In another test series in a crucible apparatus, the spontaneous ignition temperature of hexadecane with dropwise addition was 505 K (232°C), and with spray injection it was 503 K (230°C) [43].

The autoignition temperature of an undecomposed endothermic fuel is an important safety criterion. The autoignition temperature of a decomposing endothermic fuel changes with progressing endothermic decomposition. The autoignition temperatures and ranges of flammability of hydrocarbons and other combustibles must be known when investigating fire and explosion accidents [44].

In order to study the importance of fuel cracking in the autoignition of endothermic fuel/product mixtures, both the autoignition temperatures and the ignition delay times of the hydrocarbon vapors and their endothermic pyrolysis products in air were studied in a shock tube [45]. The ignition delays of ethene and heptane, typical constituents of a reformed fuel, and simulated endothermic fuel products were measured in diluted air/fuel mixtures behind reflected shock waves at temperatures in the range 1100–1400 K, pressures of 5–8 atm, and equivalence ratios of 0.5 and 1.0. The experimental data were compared to literature-sourced correlations for pure hydrocarbons and hydrogen, and new ignition delay correlations were derived from the combined data sets and expressed as Arrhenius equations for each fuel mixture. The relative ignition delay times for the different fuels decreased in the order methane > heptane > reformed endothermic fuel > ethylene > hydrogen. These results support the general assumption that fuel cracking enhances ignition. However, autoignition of the endothermic reaction product mixture was not driven entirely by that of the constituent with the shortest ignition delay (i.e., ethylene or hydrogen). Small changes in the concentrations of the individual component species were not likely to cause large changes in the ignition delay time of the fuel.

The ignition temperatures of hydrocarbons can be lowered in the presence of heterogeneous or homogeneous catalysts. Homogeneous catalysts are soluble in kerosenes. For instance, a certain catalyst produced substantial improvements in combustion activity for both JP-10 and a surrogate, JP-5 [46]. The addition of only 5 ppm catalyst to the surrogate JP-5 reduced the temperature required to initiate combustion by about 300°C. These results demonstrate that a soluble catalyst has the potential to significantly reduce the ignition delay and to widen the range of stable flame operating conditions.

### 3 Production of Hydrocarbon Fuels

The primary source of hydrocarbon fuels is petroleum from crude oil. Petroleum is subjected to fractionated distillation in tall distillation columns. The fractions are characterized by their boiling ranges. The heavy residues from crude oil distillation are then cracked or hydro-cracked to create more of the more desirable lighter boiling fractions. Only a small percentage of synthetic hydrocarbon fuels is produced from natural gas or coal, or, more recently, from biomaterials (wood, grass, oily fruits, spent cooking oils).

The importance of the availability of hydrocarbon fuels and the impact of temporary shortages of these fuels on the automotive, air, and sea transportation economy have been well documented. A large proportion of petroleum fuels is used as heating oil, so it is just burned for its heating value – a very wasteful practice considering that we could be using clean nuclear energy instead. Hydrocarbons are much more difficult to replace as a feedstock for the chemical industry in the production of plastics, clothing, fertilizer, and pharmaceuticals than as heating oils, so the remaining fossil hydrocarbons should be reserved for use in the chemical industry and as rocket propellants.

#### 3.1 Purification of Hydrocarbon Fuels

The thermal stability of Jet A-1 fuel subjected to purification by clay treatment, desulfurization, or hydrogenation was determined in comparison to the untreated fuel using the Jet Fuel Thermal Oxidation Tester (JFTOT) thermal stability method [47]. Desulfurization increased the JFTOT breakpoint by 66–77 K, and desulfurization followed by hydrogenation increased the JFTOT breakpoint of the fuel by more than 83 K. A low-aromatic JP-4 type of fuel blended from a hydrogenated stock and a solvent-treated stock to remove aromatics was also tested and compared to a conventional JP-4 fuel. Desulfurization, hydrogenation, clay treatment, and aromatic solvent extraction were shown to be effective methods for upgrading the thermal stability of kerosene fuels.

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# Hydrogen

## Hydrogen

Thanks to its low molecular mass and high heat of combustion, hydrogen, typically liquid hydrogen, makes an excellent rocket propellant fuel. It is of interest and very educational to study the historical evolution of hydrogen as a rocket propellant, and therefore many older references are included in this book. In some respects this book is a book on the history of rocket propellants. Today's achievements in space travel would not be possible without the use of liquid hydrogen. In the following discussion, we'll frequently abbreviate liquid hydrogen as LH2 or LH<sub>2</sub>.

There were many sources of information on liquid hydrogen, most of those from the Cryogenics Laboratory in Boulder, CO, USA, operated by the National Bureau of Standards. Many of those references are now included in the current chapter on hydrogen, although some are already quite old.

To be accurate, the molecular hydrogen we use as a rocket fuel should be called dihydrogen in order to differentiate it from atomic hydrogen, which is also a potential rocket fuel but difficult to stabilize and store. In the following chapters, it is safe to assume that whenever a fuel is described as hydrogen that this is **dihydrogen** and not atomic hydrogen. It would be nice if we could add a chapter on atomic hydrogen as a rocket propellant, because that would be the most energetic rocket propellant we can imagine. Unfortunately, atomic hydrogen is difficult to store and it will be a long time before we can master it [1]. Another form of hydrogen we would dearly like to have in quantity and fly it in our rockets is metallic hydrogen. Again, it exists only in other worlds and if we can create it on Earth, it is only in tiny quantities and only for a short time.

Initially many technical obstacles prevented the application of liquid hydrogen as a rocket propellant [2]. Only few people were optimistic enough that it could ever be used as a transportation fuel. When the first edition of a book on rocket propellants went to press in 1968, only few upper stages had ever flown with liquid hydrogen. Now there are many books describing the history of the evolution of liquid hydrogen as a rocket propellant. The first CENTAUR upper stage was launched atop an Atlas booster in May 1962, and not all initial flights were successful [3]. Much progress was made by the time liquid hydrogen in the SATURN-V S-II second stage and S-IVB third stage enabled the APOLLO astronauts to reach the moon. The largest rocket ever to use liquid hydrogen was the ENERGIYA, the core stage of which had a lift-off mass of 905 tons and a dry mass of 85 tons, which contained 117 metric tons of liquid hydrogen at launch, even more than the Space Shuttle (103 tons) or ARIANE-V core stage (25 tons) or H-II core stage (14.5 tons) or DELTA-IV Heavy (28.5 tons in the first stage and 4.2 tons in the second stage). As of 2013, there were plans that Russia may revive the ENERGIYA launch vehicle to use it again for launching components for the next space station

into orbit. The US Space Launch System core stage, a derivative of the Space Shuttle external tank, will contain 144 tons ( $2033 \text{ m}^3 = 537000$  gallons) of liquid hydrogen.

First attempts to liquefy hydrogen using the same technique as for liquid air or liquid oxygen were wrought with difficulties. For one, hydrogen has a negative Joule-Thomson coefficient such that when compressed hydrogen expands isentropically at room temperature, it warms up instead of cooling down. Then, even after a jug full of liquid hydrogen has been obtained by precooling the gas before expanding it, the liquid will suffer evaporation losses due to the exothermic orthohydrogen-parahydrogen ( $o\text{-H}_2 \rightarrow p\text{-H}_2$ ) conversion, which continues at an unslowable rate, thanks to quantum mechanics [4]. This can be avoided by accelerating the conversion and aiming at complete orthohydrogen→parahydrogen conversion already during the stepwise liquefaction process (section “Catalysts for Orthohydrogen-Parahydrogen Conversion”).

Only history fans will find useful bits of information in the long list of publications that we referenced in the first edition of a book on rocket propellants. Most of these documents that were relatively new in 1968 are now hopelessly out of date because liquid hydrogen technology development in the second half of the last century moved much faster than even the most optimistic observers dared to hope for at mid-century of the 1900s. There were even voices of some pessimists who considered it impossible to use liquid hydrogen as a rocket propellant [5].

The early development of large-scale liquefaction and application of hydrogen as a rocket propellant was driven not only by its anticipated use as a chemical rocket fuel in combination with suitable oxidizers, but also by the demonstration of its use as a working fluid for nuclear thermal rockets and arcjets, plasma rockets, and magnetohydrodynamic rockets [6]. Table 1 contains a historical summary of publications on hydrogen as a working fluid for nuclear thermal rockets. This includes the KIWI-A, ROVER, and the NERVA nuclear thermal rocket projects, which are now only part of by-gone history.

**Table 1:** Historical descriptions of liquid hydrogen use in nuclear thermal rockets.

| Author              | Year | References |
|---------------------|------|------------|
| Saenger-Bredt       | 1957 | [7]        |
| Wyatt               | 1961 | [8]        |
| Edeskuty and Hammel | 1962 | [9]        |
| Hammel              | 1964 | [10]       |
| Edeskuty            | 1965 | [11]       |
| Ehrenkranz          | 1965 | [12]       |
| Ehrenkranz          | 1967 | [13]       |

By the early 1970s, NASA had ground-tested a series of nuclear thermal rocket engines at the Nevada test site. These systems generated up to 4500 megawatts of thermal power, produced 1.1 million Newtons ( $1.1\text{MN} = 250000$  pounds force) of thrust, about half the thrust of a space shuttle main engine, and accumulated 90 min of run time. Unfortunately, this promising NERVA, for Nuclear Engine for Rocket Vehicle Application, space propulsion system was discarded during the agency's precipitous post-APOLLO downsizing. Liquid hydrogen technology that was developed during these programs greatly benefited the later development of LOX/LH2 bipropellant rocket engines. One can only speculate if this nuclear thermal rocket technology will ever be revived to play a role in future rocket propulsion.

NASA awarded a contract in 2017 with the nuclear engineering firm BWXT to examine design and licensing requirements for a full-scale, full-thrust ground test of a nuclear thermal propulsion engine along the lines of the NERVA tests 50 years ago [14]. The US \$18.8 million contract included the conceptual design of a propulsion reactor that, because of its much higher rocket exhaust velocity, would be about twice as efficient as chemical rockets such as the LOX/hydrogen space shuttle main engine. Such a 500-megawatt (a measure of reactor power) nuclear thermal rocket might have a low-enriched uranium core to alleviate proliferation security concerns and ceramic/metallic fuel elements to deliver a specific impulse of 900–910 s.

Here we deal only with chemical rocket propellants, but hydrogen is a major player in both chemical and other rockets. In nuclear research, liquid hydrogen is used for bubble chambers, neutron moderators, and superconductors [15].

In the far distant future, hydrogen or deuterium could also be the fuel of choice for fusion nuclear reactors and fusion rockets. In the meantime, in the area of air-breathing engines, liquid hydrogen as a fuel in supersonic combustion scramjets has moved from the stage of computation and ground testing to the first flight demonstration in the X-43A in 2004. It is also being considered as a fuel for commercial passenger jet transports where it is used as fuel in fuel cells to generate electricity and electric motors drive the propellers [16]. Compressed hydrogen/air or liquid hydrogen/air fuel cells are advancing to the stage that they will be used in prototype automobiles and experimental airplanes with electric motors.

Automobiles operating on combustion engines fed with compressed hydrogen gas are already in use in several demonstration projects and promise a future free from hazardous emissions. Automobiles with liquid hydrogen storage have been considered, but of course safety considerations will prevent such an application for now [17]. We realize that not every person with a driver's license is a rocket engineer, and they might have difficulty in safely managing the fueling and the boil-off during idle periods. Supercritical oxygen and hydrogen storage was used to supply fuel cells on the APOLLO Service Module and on the Space Shuttle Orbiters, but that technology is also not suitable for the average consumer.

Liquid hydrogen technology borrowed from the space program is aiding the development of earth-based hydrogen-powered airplanes. Liquid hydrogen already powers fuel cells in electrically driven propeller airplanes. In 2013, a fuel-cell-powered unmanned aerial vehicle (UAV) developed by the US Naval Research Laboratory (NRL), *Ion Tiger*, flew 48 h using liquid hydrogen fuel in a new, NRL-developed, cryogenic fuel storage tank and delivery system. The liquid hydrogen-fueled *Global Observer* UAV made by AeroVironment can fly at 65000 ft for more than 1 week, letting it operate as a geosynchronous “satellite” system for regional communications coverage. A Fuel Cell Demonstrator Airplane is being developed by Boeing Research and Technology Europe in Madrid, Spain. *Phantom Eye* is a liquid hydrogen-fueled, high-altitude, and long-endurance unmanned aircraft system for persistent intelligence, surveillance, reconnaissance, and communications missions. The demonstrator aircraft is capable of maintaining its altitude for up to 4 days while carrying a 450-pound payload. Typical payloads include multiple sensor packages for monitoring, tracking, and communications. A full-size *Phantom Eye* variant is designed to stay aloft for up to 10 days and carry a payload of 2000 pounds.

## 1 Occurrence, Production, and Liquefaction of Hydrogen

### 1.1 Occurrence of Hydrogen

Weight-wise and the number of atoms-wise, hydrogen is the most abundant element of the universe (as we know it). It has been estimated that 75% of the cosmos consists of hydrogen. Our sun consists of about 84% hydrogen, and much of it will be converted to helium as the aging of our sun progresses. This thermonuclear process is the source of life-sustaining energy on our planet Earth. On Earth, hydrogen rarely occurs in elemental form. It mostly occurs in the form of water, mineral hydrates, and a precious small fraction occurs in the form of petroleum and natural gas (methane). The top-most crust of the Earth to a depth of 16 km contains about 0.88 mass-% hydrogen. The atmosphere at sea level contains hardly any dihydrogen gas. The upper reaches of the ionosphere contain a little dihydrogen and atomic hydrogen that is likely to escape Earth once it becomes accelerated or ionized by solar wind. A distant cloud of hydrogen atoms that makes up the outermost part of Earth's atmosphere extends up to 630000 kilometers (391464 miles) away, far enough to envelope the moon.

On Earth, hydrogen gas may form along with methane as the result of microbial decay of organic material. Fermentation gas accumulations and mixtures with air have been the cause of numerous fires and explosions.

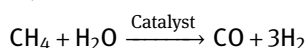
It has been theorized that on Jupiter, where interior pressures are millions of atmospheres, hydrogen may exist as a super-hot liquid metal. The density of metallic hydrogen is expected to be about ten times that of liquid H<sub>2</sub> at Earth atmospheric

pressure, which translates into great energy density, and metallic hydrogen would be a powerful propellant if we could tame it. In March 1996, the Lawrence Livermore National Laboratory (LLNL) observed the formation of metallic hydrogen at 1.4 megabars pressure (an unanticipated result of using a gas gun to compress liquid hydrogen). It is not known if metallic hydrogen could be stabilized long enough to be used as a solid rocket propellant ingredient at ambient pressure and temperature. Methods of using metallic hydrogen have been proposed, including entrapment in solid hydrogen, or suspended in a liquid cryogen like liquid helium [18].

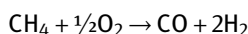
## 1.2 Production of Hydrogen

### 1.2.1 Production of Hydrogen from Carbon-based Fuels

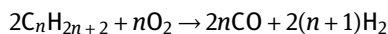
Hydrogen is mostly prepared by steam reforming of natural gas [19]:



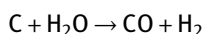
or partial combustion of natural gas



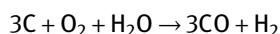
or other hydrocarbons



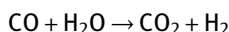
In earlier years, in a coal-based instead of oil-based economy, industrial hydrogen production, e.g. for the synthesis of ammonia, was often done by first producing synthesis gas (“water gas”) by passing overheated steam over coal (coke)



or



and then shifting the CO equilibrium in the water gas shift reaction



to a point where the carbon dioxide could be washed out and separated from unreacted CO and the desired H<sub>2</sub> product.

Hydrogen production by electrolysis of water is very energy-intensive and would be economical only in locations where due to cheap hydropower the off-peak capacity of the generating plant can be used to produce hydrogen. Often this electrolysis process is combined with isotope separation and production of deuterium and heavy water. Hydrogen gas is often a by-product of other industrial processes, such as the chlorine-alkali electrolysis.



### 1.2.2 Thermochemical Water Splitting Cycles

Thermochemical water splitting cycles, mostly based on solar energy, have been developed but have not advanced past the feasibility demonstration stage, [20–27]. It is possible to use solar heat directly to split  $\text{H}_2\text{O}$  into  $\text{H}_2$  and  $\text{O}_2$  or  $\text{CO}_2$  into  $\text{CO}$  and  $\text{O}_2$ . Such processes would be of interest for *in situ* resource utilization, producing propellants, and life-support on other planets or moons from indigenous resources; however, these single-step processes require operating temperatures above  $2000^\circ\text{C}$ , which places high demands on materials and process conditions. Alternative multi-step thermochemical cycles operate at lower temperatures and eliminate the need for high-temperature gas separation [28].

## 1.3 Liquefaction of Hydrogen

The first person to produce liquid hydrogen was Sir James Dewar in 1898. In the literature, liquid hydrogen may occasionally also be called “liquefied hydrogen.”

The ideal work required for liquefaction of normal hydrogen ( $n\text{-H}_2$ ) starting at 300 K and 101.3 kPa is 12019 kJ/kg (5167 BTU/lb). Conversion to parahydrogen requires additional energy. There are several other hydrogen liquefaction processes, but the Claude cycle is the only one of practical interest [29]. Large hydrogen liquefaction plants usually operate with multi-stage turbo compressors and turbine expanders [30, 31].

The hydrogen gas to be liquefied must be carefully purified and freed of all contaminants which might solidify at the temperature of liquid hydrogen and clog the apparatus. Carbon monoxide and nitrogen, which might still be present in the feed as residues from the steam reforming process, must first be removed. They could be condensed in a cold trap that is cooled with cold hydrogen in a separate circuit. Other contaminants are removed by washing the gas with liquid methane. Residual contaminants are removed by absorption on a bed packed with activated charcoal, silica gel or molecular sieves. That will reduce the contaminant concentration in the hydrogen to below 1 ppm by volume.

Not all liquid hydrogen is alike. In the freshly condensed state, without ortho-hydrogen-parahydrogen conversion during liquefaction, the normal hydrogen liquid would consist of a mixture of orthohydrogen and parahydrogen in a molar ratio of 3:1. This liquid is sometimes called normal hydrogen. Orthohydrogen contained in the normal hydrogen mix would slowly convert to parahydrogen and release the heat of conversion. This heat of orthohydrogen-parahydrogen ( $o \rightarrow p$ ) conversion would result in excessive evaporation losses from the vessel containing the liquid if one attempted to store normal hydrogen as a liquid. The heat of conversion ( $1411\text{ J/mol} = 337.2\text{ cal/mol}$ ) is 1.562 times bigger than the heat of evaporation of liquid hydrogen ( $903\text{ J/mol} = 215.9\text{ cal/mol}$ ), such that for every kg of orthohydrogen that converts,

1.562 kg of liquid hydrogen is lost. For quantum mechanical reasons, there is no pure orthohydrogen. Figure 58 (shown later in Section 5.4.1) illustrates the evaporation losses as a function of the initial orthohydrogen content in the freshly liquefied mixture.

In order to achieve the equilibrium composition corresponding to the momentary temperature and pressure, and in order to accelerate the rate at which the equilibrium is attained, the hydrogen gas is repeatedly passed over catalysts during the cooldown on its way to being liquefied. Catalytically active for this conversion are all paramagnetic materials. A paramagnetic catalyst can reverse the nuclear spins without breaking the H–H bonds. As a matter of fact, a test for paramagnetism in certain solids uses the rate of *o* – *p* conversion of natural cold hydrogen as an indication of the extent of paramagnetism in the sample. Active catalysts consist of chromium(III) oxide deposited on alumina, iron(II, III) oxides and oxygen adsorbed on activated charcoal. There are three conversion strategies, and they differ in the energy requirements during liquefaction:

1. Continuous conversion
2. Stepwise conversion initially at 65 K (typically achieved by lowering the pressure above a bath of LN<sub>2</sub>) and then completing the process at 20.4 K
3. Performing all conversion at 20.4 K

The production of liquid parahydrogen requires more energy than the production of liquid normal hydrogen. While the production of normal hydrogen requires typically 3.35 kWh/kg, the production of parahydrogen with only a trace (0.21%) of residual orthohydrogen requires the energy listed in Table 2, depending on the cooldown and equilibration sequence

**Table 2:** Energy requirements for hydrogen liquefaction.

|          | kWh/kg | kWh/L | Relative energy consumption, %, relative to Method 1 = 100% |
|----------|--------|-------|-------------------------------------------------------------|
| Method 1 | 3.9    | 0.28  | 100                                                         |
| Method 2 | 4.7    | 0.33  | 117                                                         |
| Method 3 | 5.3    | 0.38  | 137                                                         |

The energy consumption for liquefying hydrogen is much higher than that for liquefying air or oxygen. One can only appreciate the current advanced state of liquid hydrogen technology if one goes back and reads some of the historical references, written at a time when the scale of current liquid hydrogen operations could not be imagined [32–35]. Then, during the 1960s, liquid hydrogen technology slowly began to evolve [36].

With an average hydrogen feed of 150 ton/day, a cascade mixed refrigerant (CMR) precooling process with implemented chillers and integrated liquid expanders was predicted to be the most energy-efficient and exergy-efficient process, with an exergy efficiency calculated as above 45% [37].

The design of a proposed liquid hydrogen plant using a multi-component refrigerant (MR) refrigeration system capable of producing 100 tons of liquid hydrogen per day was analyzed [38]. The MR system can be used to cool feed normal hydrogen gas from 298 K (25 °C) to the equilibrium temperature of 80 K (−193 °C) with a high efficiency. For the transition from the equilibrium temperature of the hydrogen gas from 80 to 20 K (−193 to −253 °C), a four-stage H<sub>2</sub> Joule-Brayton cascade refrigeration system was recommended. The overall power consumption of the proposed plant was predicted to be 5.35 kWh/kg LH<sub>2</sub>, with an ideal theoretical minimum of 2.89 kWh/kg LH<sub>2</sub>. Thus, it could represent a plant with the lowest construction cost with respect to the amount of liquid hydrogen produced in comparison to today's plants, e.g., those in Ingolstadt and Leuna in Germany.

Today's hydrogen liquefiers are a mature technology for capacities up to 30 ton/day and with energy requirements of 30–40 MJ/kg LH<sub>2</sub>, while the world's capacity today is around 350 ton/day, which is an order of magnitude lower than the required capacity for fueling a future vehicle mobility largely based on hydrogen. Diverse investigations indicated that liquefier capacity as high as 900 ton/day as well as energy requirements as low as 18–25 MJ/kg may be achieved [39, 40].

### 1.3.1 Theory of Hydrogen Liquefaction

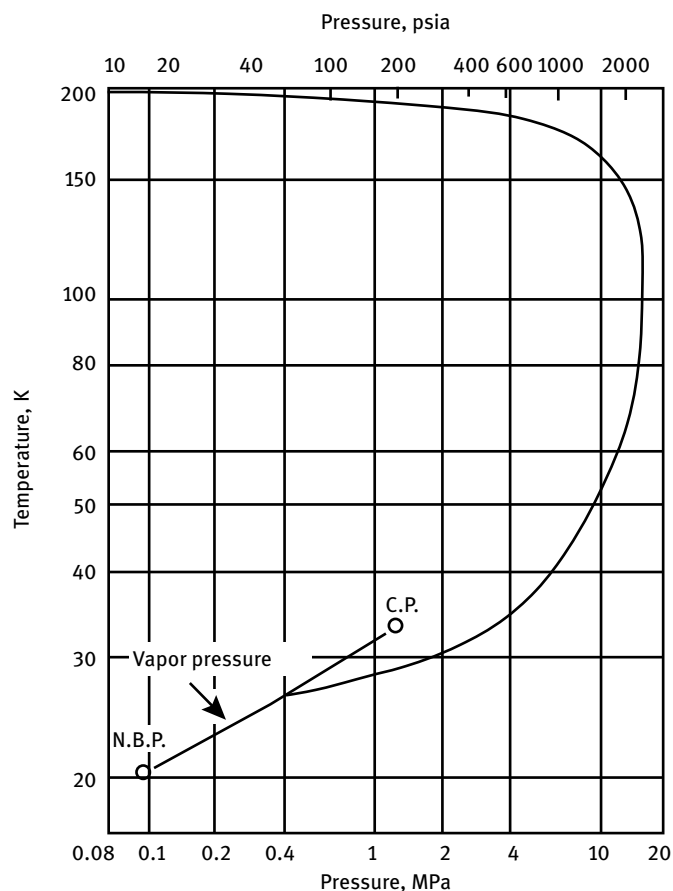
Most gases at ambient temperature are cooled by adiabatic expansion from high to low pressure. Hydrogen behaves differently. The temperature of hydrogen increases when it is expanded at a temperature and pressure outside the range of temperature and pressure conditions that define the Joule-Thomson inversion curve for hydrogen. The maximum inversion temperature for hydrogen is 202 K (−71 °C = −96 °F) at an absolute pressure of zero. At any temperature and pressure condition greater than this, the temperature of hydrogen will increase upon expansion.

Hydrogen cannot be liquefied like other permanent gases (air, nitrogen, oxygen) by the conventional LINDE liquefaction scheme because at room temperature it has a negative differential Joule-Thomson coefficient. The Joule-Thomson coefficient increases with decreasing temperature and reaches the value of zero at the inversion temperature of hydrogen, which is at 202 K. If one wants to liquefy hydrogen by compressing, cooling, and expanding it, one must first pre-cool the gas to below the inversion temperature. In most cases the hydrogen is pre-cooled in a heat exchanger with liquid nitrogen which takes it sufficiently below the inversion point.

The Joule-Thomson coefficient,  $\mu$ , is defined as

$$\mu = -C_P^{-1} \left( \frac{\partial H}{\partial P} \right)_T = \left( \frac{\partial T}{\partial P} \right)_H$$

The sign of  $\mu$  indicates whether a sudden gas expansion will cause an increase or decrease in the temperature of the gas. If  $\mu$  is positive, the expanding gas will be cooled. The locus of points where  $\mu = 0$  is called the Joule-Thomson inversion curve. This curve for parahydrogen is illustrated in Figure 1.



**Figure 1:** Joule-Thomson inversion curve for parahydrogen gas. (Reproduced and modified from [41].)

Values of the Joule-Thomson coefficient were calculated from compressibility isotherms for pressures up to 253 MPa (2500 atm) [42, 43]. The data were presented at integral values of pressure and temperature for the normal ortho-para concentrations.

The equations of state pressure-volume temperature (PVT) relations for hydrogen and several other gases were used to establish Joule-Thomson inversion curves for each fluid [44]. The principle of corresponding states was applied to the inversion curves, and a generalized inversion curve for fluids with small acentric factors was developed. The critical isenthalpic Joule-Thomson coefficient  $\mu_c$  was determined and a simplified approximation

$$\mu_c \approx \frac{T_c}{6P_c}$$

was found adequate, where  $T_c$  and  $P_c$  are the temperature and pressure at the thermodynamic critical point. The maximum inversion temperatures were obtained from the second virial coefficient (maximum  $B/T$ ).

### 1.3.2 Design of Hydrogen Liquefaction Plants

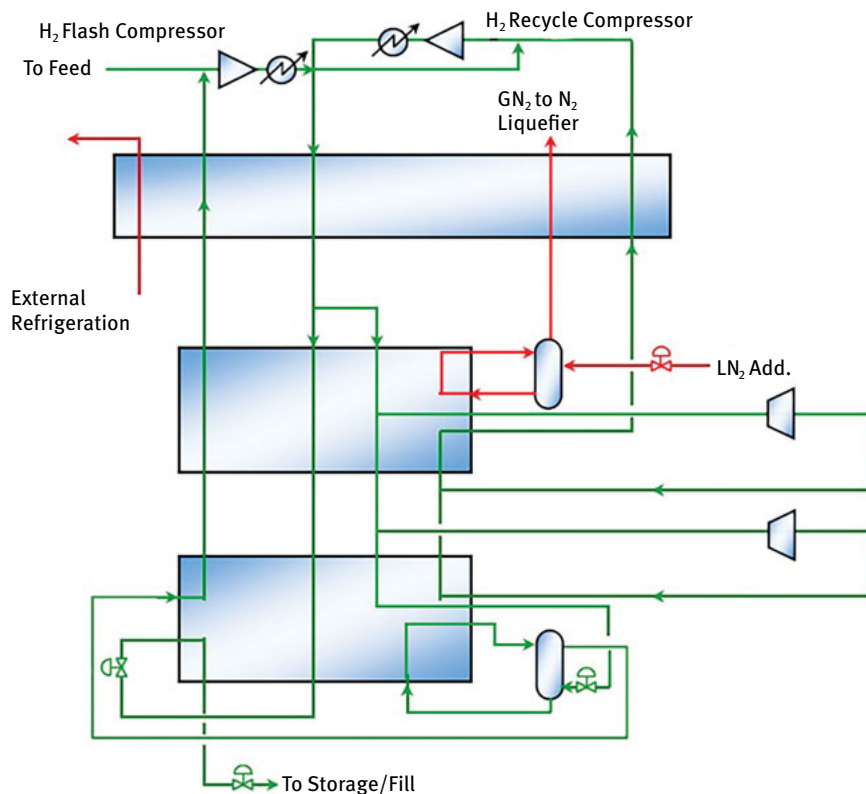
Liquefaction of hydrogen is a multi-step process as illustrated in Figure 2.

### 1.3.3 Catalysts for Orthohydrogen-Parahydrogen Conversion

In order to avoid evaporation losses due to orthohydrogen-parahydrogen conversion in the freshly liquefied hydrogen, the  $o \rightarrow p$  conversion must be achieved as close to the equilibrium composition as possible. The liquefaction is usually a multi-step process and each stage has its own catalytic converter [46]. Of the many parameters which must be considered in the design of an efficient orthohydrogen-parahydrogen converter, the most obvious is the choice of an effective catalyst. After this choice is made, there remain as variables the conditions of temperature, pressure, feed composition and space velocity (or contact time) under which the conversion proceeds. All these variables influence the kinetics of the conversion [47, 48]. Basically, any paramagnetic material will catalyze the  $o \rightarrow p$  conversion, but for an industrial installation, more active catalysts especially developed for this purpose are being used.

The  $o \rightarrow p$  conversion was investigated on a series of  $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$  catalysts by a static method at 77K and under various pressures in the gaseous and liquid states [49]. Chromia-alumina catalysts containing 1–2 mass-%  $\text{Cr}_2\text{O}_3$  on alumina were faster than commercial catalysts containing 20–35%  $\text{Cr}_2\text{O}_3$  [50]. The kinetics of the  $o \rightarrow p$  conversion is a first-order process and the rates of conversion depend on diffusion into and out of the pores of the catalyst [51]. The overall liquefaction cycle efficiency depends on efficient utilization of  $o \rightarrow p$  conversion catalysts [52].

Kinetic rate measurements were made of the low-temperature  $o \rightarrow p$  conversion reaction with a very active  $\text{NiO-SiO}_2$  catalyst [53]. The model matched experimental data over the temperature range 79–93K (142–168°R) and pressure range 0.69–10.3 MPa (100–1500 psia).



**Figure 2:** Hydrogen Liquefaction Process Flowchart. (Reproduced from [45] with permission from Linde 9 Feb 2021.)

Chromium(VI) oxide ( $\text{CrO}_3$ ) supported by silica gel is a highly efficient catalyst for ortho-para conversion at low temperatures [54]. The material is also less susceptible to poisoning than the commonly used ferric hydroxide gels.

### 1.3.4 Hydrogen Purification

Any gas other than helium as a contaminant in the hydrogen feed stock will interfere with the liquefaction process because the foreign gas would condense as solid crystals and clog orifices in the process equipment. Nitrogen can be removed by adsorption onto silica gel at low temperatures [55]. The adsorbed nitrogen would also inhibit the catalysts that are needed for  $o \rightarrow p$  conversion [56]. Any adsorbate which competes with hydrogen may be expected to reduce the catalyst effectiveness unless this competing adsorbate is also a catalyst.

One must avoid the formation of oxygen/hydrogen mixtures under any circumstances. Solid oxygen floating in liquid hydrogen will clog orifices and constitutes an explosion hazard. The specific concern is with the behavior of oxygen which is present as a trace impurity (concentration of a few parts per million) in a high-pressure hydrogen stream which is being cooled and liquefied. Oxygen crystallizes during the cooling process when the saturation concentration of oxygen is reached. The exact temperature depends upon the total pressure and the oxygen concentration. For low concentrations, the temperature is below the triple point temperature of oxygen ( $54.37\text{ K} = -218.78\text{ }^{\circ}\text{C} = -361.8\text{ }^{\circ}\text{F}$ ) [57]. The possibility always exists that solid oxygen may concentrate in heat exchangers and other process components which are at temperatures lower than the triple point. Even at very low concentrations, the oxygen may accumulate and cause hazardous conditions. The data on the solid/vapor equilibria of the oxygen/hydrogen system are important for the safe design and operation of hydrogen liquefaction equipment. Trace oxygen in hydrogen feed could be converted to water by first passing the gas mixture over a platinum catalyst and then water would be easier to remove and would not constitute an explosion hazard.

### 1.3.5 Hydrogen Liquefaction Capacity in the World

Table 3 shows a list of some of the hydrogen liquefaction plants in use around the world. Most of the liquid hydrogen plants are stationary, but there are also mobile hydrogen liquefaction machines [58].

The size and liquefaction and storage capacity of these liquid hydrogen production facilities continues to increase [40]. Using isentropic instead of isenthalpic expansion processes, cascading of refrigerating cycles, use of mixed refrigerants as working fluid of refrigeration cycles, and hybridization of renewable energy power cycles to refrigeration cycles are the main growing approaches in the large-scale hydrogen liquefaction market.

**Table 3:** Commercial hydrogen liquefaction plants worldwide.

| Continent/<br>Country | Location      | Operated by              | Capacity<br>tons<br>per day<br>(TPD) | Commis-<br>sioned<br>in | Still in<br>opera-<br>tion? (as<br>of 2009) |
|-----------------------|---------------|--------------------------|--------------------------------------|-------------------------|---------------------------------------------|
| America               |               |                          |                                      |                         |                                             |
| Canada                | Sarnia        | Air Products             | 30                                   | 1982                    | Yes                                         |
| Canada                | Montreal      | Air Liquide Canada, Inc. | 10                                   | 1986                    | Yes                                         |
| Canada                | Becancour     | Air Liquide              | 12                                   | 1988                    | Yes                                         |
| Canada                | Magog, Quebec | BOC                      | 15                                   | 1989                    | Yes                                         |
| Canada                | Montreal      | BOC                      | 14                                   | 1990                    | Yes                                         |
| French Guyane         | Kourou        | Air Liquide              | 5                                    | 1990                    | Yes                                         |

Table 3: (continued)

| Continent/<br>Country | Location         | Operated by               | Capacity<br>tons<br>per day<br>(TPD) | Commis-<br>sioned<br>in | Still in<br>opera-<br>tion? (as<br>of 2009) |
|-----------------------|------------------|---------------------------|--------------------------------------|-------------------------|---------------------------------------------|
| USA                   | Painsville       | Air Products              | 3 <sup>a</sup>                       | 1957                    | No                                          |
| USA                   | West Palm Beach  | Air Products              | 3.2 <sup>a</sup>                     | 1957                    | No                                          |
| USA                   | West Palm Beach  | Air Products              | 27 <sup>a</sup>                      | 1959                    | No                                          |
| USA                   | Mississippi      | Air Products              | 32.7 <sup>a</sup>                    | 1960                    | No                                          |
| USA                   | Ontario          | Praxair                   | 20                                   | 1962                    | Yes                                         |
| USA                   | Sacramento       | Union Carbide, Linde Div. | 54 <sup>a</sup>                      | 1964                    | No                                          |
| USA                   | New Orleans      | Air Products              | 34                                   | 1977                    | Yes                                         |
| USA                   | New Orleans      | Air Products              | 34                                   | 1978                    | Yes                                         |
| USA                   | Niagara Falls    | Praxair                   | 18                                   | 1981                    | Yes                                         |
| USA                   | Sacramento       | Air Products              | 6                                    | 1986                    | Yes                                         |
| USA                   | Niagara Falls    | Praxair                   | 18                                   | 1989                    | Yes                                         |
| USA                   | Pace             | Air Products              | 30                                   | 1994                    | Yes                                         |
| USA                   | McIntosh         | Praxair                   | 24                                   | 1995                    | Yes                                         |
| USA                   | East Chicago, IN | Praxair                   | 30                                   | 1997                    | Yes                                         |
| Subtotal              |                  |                           | 300                                  |                         |                                             |
| Europe                |                  |                           |                                      |                         |                                             |
| France                | Lille            | Air Liquide               | 10                                   | 1987                    | Yes                                         |
| Germany               | Ingolstadt       | Linde                     | 4.4                                  | 1991                    | Yes                                         |
| Germany               | Leuna            | Linde                     | 5                                    | 2008                    | Yes                                         |
| Netherlands           | Rosenburg        | Air Products              | 5                                    | 1987                    | Yes                                         |
| Subtotal              |                  |                           | 24.4                                 |                         |                                             |
| Asia                  |                  |                           |                                      |                         |                                             |
| China                 | Beijing          | CALT                      | 0.6                                  | 1995                    | Yes                                         |
| India                 | Mahendragiri     | ISRO                      | 0.3                                  | 1992                    | Yes                                         |
| India                 | India            | Asiatic Oxygen            | 1.2                                  | —                       | Yes                                         |
| India                 | Saggonda         | Andhra Sugars             | 1.2                                  | 2004                    | Yes                                         |
| Japan                 | Amagasaki        | Iwatani                   | 1.2 <sup>a</sup>                     | 1978                    | No                                          |
| Japan                 | Tashiro          | MHI                       | 0.6 <sup>a</sup>                     | 1984                    | No                                          |
| Japan                 | Akita Prefecture | Tashiro                   | 0.7                                  | 1985                    | Yes                                         |
| Japan                 | Oita             | Pacific Hydrogen          | 1.4                                  | 1986                    | Yes                                         |
| Japan                 | Tane-Ga-Shima    | Japan Liquid Hydrogen     | 1.4                                  | 1986                    | Yes                                         |
| Japan                 | Minamitane       | Japan Liquid Hydrogen     | 2.2                                  | 1987                    | Yes                                         |
| Japan                 | Kimitsu          | Air Products              | 0.3                                  | 2003                    | Yes                                         |
| Japan                 | Osaka            | Iwatani (Hydro Edge)      | 11.3                                 | 2006                    | Yes                                         |
| Japan                 | Tokyo            | Iwatani, built by Linde   | 10                                   | 2008                    | Yes                                         |
| Subtotal              |                  |                           | 30.6                                 |                         |                                             |
| Worldwide             |                  |                           | 355                                  |                         |                                             |

<sup>a</sup> Not included in the subtotal of the capacity for the year 2009.

Data source: [59]



#### 1.3.4.1 Hydrogen Liquefaction Capacity in the USA.

As of 2003, there were already 10 hydrogen liquefaction plants in North America. Train size ranged from 6 to 35 tons per day (TPD, 5400–32000 kg/day) [45]. In 1960, the first few liquid hydrogen plants were built to support the APOLLO program. In the beginning of the 1960s there was a liquid hydrogen demand for US space programs. The capacity installed up to 1965 was capable of supplying the demand of NASA and others until 1977. In this period, no additional plants were built, not least because of the reduction of NASA's space activities. Since 1977, further increase in capacity this time was mainly caused by the steadily increasing commercial demand for liquid hydrogen. As of 2015, there were more than 9 hydrogen liquefaction plants in the US with production rates of 5–34 tons per day (TPD). As of 2005, the Air Products plant at New Orleans had a liquefaction capacity of 54 metric tons/day and was considered the largest plant of its type in the world.

As of 2005, one of the plants operated by Air Products in Sacramento had a capacity of 5.4 metric tons/day and a storage capacity of 36 tons. Much of that hydrogen at that time was used in the semiconductor industry. Air Products supplies the largest quantity of liquid hydrogen in North America, followed by Praxair. As of 2009, Praxair had 5 hydrogen liquefaction plants in the US with production rates between 6 and 35 TPD LH<sub>2</sub>. Typical specific power consumptions were between 12.5 and 15 kWh/kg LH<sub>2</sub> [45].

A historical review of the development of large-scale hydrogen liquefaction processes throughout the world from 1898 to 2009 included a literature review, designs and a list of the capacity and location of every hydrogen liquefaction plant in the world [59]. It was found that every current hydrogen liquefaction plant is based on the precooled Claude system, which is still the same as was 50 years ago with little improvement. Redesigning of hydrogen liquefaction plants is done with the target of efficiencies of 40–50% and lowering energy usage of 10 kWh/kg LH<sub>2</sub> to around 5 kWh/kg LH<sub>2</sub>. This leads to predictions about the development and improvement potential of future large-scale liquid hydrogen liquefaction plants. Methods to resolve the challenges of the future plants include proposing completely new configurations and efficient systems coupled with improved efficiencies of the main system components, such as compressors, expanders, and heat exchangers. Hydrogen liquefaction plants would best be located at places where LNG tankers are off-loaded and the LNG is gasified for distribution to the pipeline network, because then the cold from the liquid LNG can be used to pre-chill the GH<sub>2</sub> to be liquefied.

#### 1.3.4.2 Hydrogen Liquefaction Capacity in Europe

As of 2009, there were 4 hydrogen liquefaction plants in Europe with capacities of 5–10 TPD, and 11 plants in Asia with capacities of 0.3–11.3 TPD. In 1987 L'Air Liquide started operation of a 5.4 metric tons/day liquefaction unit at Rozenburg in The Netherlands and a 10 metric tons/day unit at Waziers in North France. Up until that time, liquid

hydrogen was available only from a 1 ton/day plant at Fraiss-Marais near Waziers. The Rozenburg facility has 70-ton storage capacity.

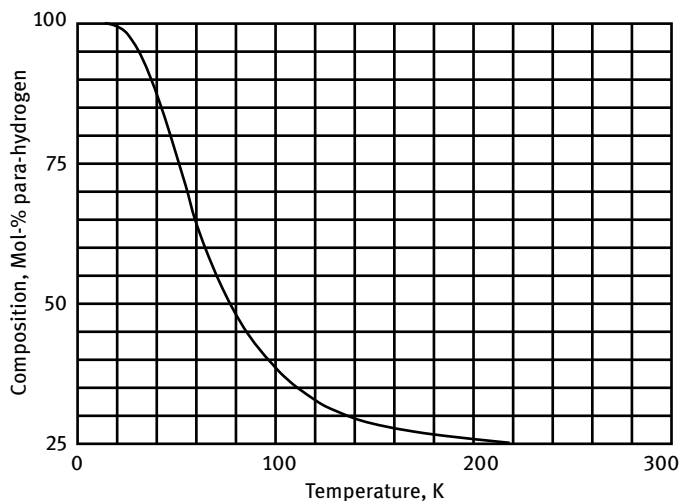
An example of a modified precooled Claude cycle is the hydrogen liquefaction plant in Ingolstadt near Munich, Germany, which has been in operation since 1992 [60]. The liquefier has a daily liquefaction capacity of 4.4 tons and is based on a Claude process with nitrogen precooling. Apart from the liquefier, the whole plant comprises a pressure-swing adsorption purification, a high-pressure hydrogen compressor station, a  $\text{LH}_2$  storage tank and filling stations for  $\text{GH}_2$  and  $\text{LH}_2$  trailers.

Linde opened a second hydrogen liquefaction plant in September 2007 in Leuna, Germany. As of 2009, it was the newest and largest  $\text{H}_2$  liquefier plant in Germany. The energy consumption of the Leuna plant was less than 14 kWh/kg  $\text{LH}_2$ .

## 2 Physical Properties of Hydrogen

### 2.1 The Orthohydrogen/Parahydrogen Equilibrium

The two ortho-para isomers of hydrogen have substantially different physical properties. Therefore, when physical properties are listed, one must specify if this property is for the equilibrium mixture at one particular temperature ("normal hydrogen" at room temperature) or for parahydrogen at its normal boiling point. The difference of physical properties of hydrogen is caused by the different orientation of spin in the two hydrogen atom nuclei that form the dihydrogen  $\text{H}_2$  molecule. The difference between orthohydrogen and parahydrogen is the relative orientation of the nuclear spin of the individual atoms. The nuclear spin is associated with the rotational motion of the nuclei about an axis perpendicular to the molecular axis (the line between the two atoms), and the spins in the two atoms forming the hydrogen molecule may be in the same direction (parallel), or in opposite directions (anti-parallel). The spin orientation relative to the individual nuclei of the molecule has a significant influence on the energy levels of the molecule. This would also occur with heavier atoms and molecules, but it is most noticeable with hydrogen. There are quantum numbers for the spin and the corresponding energy levels. The molecules with anti-parallel nuclear spins, called parahydrogen, have even rotational quantum numbers ( $J = 0, 2, \dots$ ) and are in the lowest energy states. The molecules with parallel nuclear spins, called orthohydrogen, have odd quantum numbers ( $J = 1, 3, \dots$ ) and are predominant at higher temperatures. The energy content of the two orientations is different, with the anti-symmetric being the lower state of energy. In parahydrogen the two spins are anti-symmetric, in orthohydrogen the two spins are parallel. Because of the low molecular mass of dihydrogen this quantum chemical effect causes observable differences in physical properties. Similar ortho-para isomerism occurs also in hydrogen isotopes such as deuterium, but it is not as pronounced as in dihydrogen itself. The ortho-para equilibrium is temperature dependent (Figure 3).



**Figure 3:** Ortho-para-hydrogen equilibrium as a function of temperature. (Reproduced and modified from [41].)

Measurements and quantum mechanical calculations show that normal hydrogen at room temperature consists of a mixture of orthohydrogen and parahydrogen in the mol ratio of 3:1. The equilibrium composition is temperature dependent. The equilibrium shifts toward the less energetic parahydrogen when the temperature is lowered. At the normal boiling point of hydrogen at 20.4 K, the equilibrium mixture contains only a small residual of 0.3% orthohydrogen. The effect of pressure on these equilibrium concentrations is considered to be negligible.

At high temperatures above room temperature one does not obtain pure orthohydrogen. The normal hydrogen at higher temperatures always contains a mixture of orthohydrogen and parahydrogen (Table 4).

Hydrogen physical properties can be divided into two groups; the first group of properties exhibits relatively large changes in value between orthohydrogen and parahydrogen [62]. The second group of properties exhibits only very small changes in value, if any, with differences in ortho-para concentration. The properties with significant ortho-para dependency include specific heat and properties related to specific heat, such as entropy, enthalpy, thermal conductivity, and velocity of sound. Properties are sought with significant differences that can be used for the quantitative analysis of the ortho-para composition of hydrogen at different temperatures, in particular the normal boiling point. The properties which are almost independent of ortho-para concentrations include density and viscosity. Property value differences due to ortho-para composition for density and viscosity may be expected to be of the same order of magnitude as the systematic experimental errors in their measurement.

**Table 4:** Orthohydrogen-parahydrogen equilibrium data for dihydrogen.

| Temperature, K | Mol-% para-H <sub>2</sub> |
|----------------|---------------------------|
| 10             | 99.9999                   |
| 20             | 99.821                    |
| 20.39          | 99.789                    |
| 30             | 97.021                    |
| 33.10          | 95.0340                   |
| 40             | 88.727                    |
| 50             | 77.054                    |
| 60             | 65.569                    |
| 70             | 55.991                    |
| 80             | 48.537                    |
| 90             | 42.882                    |
| 100            | 38.620                    |
| 150            | 28.603                    |
| 200            | 25.974                    |
| 250            | 25.264                    |
| 298.16         | 25.075                    |
| 300            | 25.072                    |
| 350            | 25.019                    |
| 400            | 25.005                    |
| 500            | 25.000                    |

Data source: [61]

The conversion from orthohydrogen to parahydrogen is exothermic. The heat of conversion in this temperature regime is 1417 J/mol (338.648 cal/mol). Liquid parahydrogen has been considered as a dump coolant to prevent boil-off of liquid oxygen in an adjacent tank during long-term in-space missions with cryogenic propellant storage for both oxidizer and fuel. The amount of heat dissipated by evaporating hydrogen can be increased (improved) by allowing conversion of parahydrogen back to orthohydrogen by passing it over a catalyst while it is warming up [63]. That conversion is an endothermic reaction and would allow more liquid oxygen to be kept at below its normal boiling point.

## 2.2 Computer Programs for Predicting Physical Properties of Hydrogen

There are a number of computer programs that give physical, thermodynamic, and transport properties of parahydrogen and equilibrium hydrogen and can be used as subroutines for modeling heat and mass flow phenomena in rocket propulsion systems [64, 65].

The pressure, temperature, and enthalpy of saturated liquid and vapor parahydrogen were presented in the form of two computer programs [66]. Using these routines and those in NBS Report 9288 “Computer programs for thermodynamic and transport properties of hydrogen” (Aug 1967), it is possible to obtain values of the saturated liquid and the saturated vapor for all of the properties given in NBS Report 9288 (density, entropy, thermal conductivity, viscosity, specific heat, and velocity of sound) [67]. Similar subroutines can be used to calculate fluid properties of normal and parahydrogen [68]. Physical properties of hydrogen and other propellants can be calculated on-line with REFPROP computer program and on-line database developed by NIST [69].

## 2.3 Physical Properties, General Information

In arranging physical properties of hydrogen in a user-friendly format, information was drawn from a multitude of sources. We are not in a position to verify the accuracy of the numbers or evaluate the reliability of one source compared to another. This results in information from multiple sources being listed in juxtaposition next to each other, usually in chronological order. This may result in some duplication of data that were referenced in one source and they in turn had drawn it from another source. Wherever possible, we have attempted to include the original, experimental source of the data.

Some surveys of information on physical properties of hydrogen are also including hydrogen isotopes [70]. Although deuterium is used as a chemical laser propellant, we have not included deuterium properties in this book. For summaries of the physical properties of hydrogen see also [41, 71–82]. Physical properties of hydrogen are summarized in Table 5.

## 2.4 Melting Point of Hydrogen

The melting point of frozen hydrogen is  $13.95\text{ K} = -259.21^\circ\text{C}$  and the triple point is at  $13.84\text{ K} = -259.32^\circ\text{C}$  at  $364\text{ kPa}$  ( $52.76\text{ Torr}$ ) [84]. Solid hydrogen as a rocket propellant would most likely be encountered in the form of hydrogen slush, a suspension of solid hydrogen in liquid hydrogen which has a higher density than liquid hydrogen. For this reason, physical properties of solid hydrogen are listed here.

For certain isotopic compositions, hydrogen may undergo a phase transition at low temperatures [70]. This transition has been studied by XRD, electron diffraction, neutron diffraction, NMR, and IR absorption. In general, all hydrogen isotopes solidify in the hexagonal close packed (hcp) structure, particularly if cooled from the liquid state. Parahydrogen appears to be stable in hcp down to the lowest temperatures in-

**Table 5:** Physical properties of hydrogen.

| Property                               | SI units                                            | Other units                                                            | References      |
|----------------------------------------|-----------------------------------------------------|------------------------------------------------------------------------|-----------------|
| Molecular mass                         | 2.01588 g/mol                                       |                                                                        | [83]            |
| Melting point                          | 13.95 K                                             | −259.21 °C                                                             | [84]            |
| Triple point                           | 13.84 K at 7.03 kPa                                 | −259.32 °C at 52.76 mm Hg                                              | [84]            |
| Boiling point, normal hydrogen         | 20.38 K                                             | −252.78 °C                                                             | [85]            |
| Boiling point, parahydrogen            | 20.27 K                                             | −252.89 °C                                                             | [61]            |
| Density, liquid                        | 0.07111 g/cm <sup>3</sup> at 20 K                   | 71 g/L = 71 kg/m <sup>3</sup>                                          | [86]            |
| Dynamic viscosity, liquid              | $1.344 \times 10^{-4}$ Ps at 20 K                   | 0.016 cPs at 17.15 K                                                   | NBS Report 3282 |
| Surface tension                        | 0.00191 N/m at 20.4 K<br>0.0023 N/m at 20.15 K      | 1.91 dyn/cm at −252.7 °C                                               | NBS Report 3282 |
| Thermal conductivity, liquid           | 11.8 W cm <sup>−1</sup> K <sup>−1</sup>             | 2.817 cal cm <sup>−1</sup> s <sup>−1</sup> °C <sup>−1</sup> at −253 °C | [87]            |
| Dielectric constant, liquid            | 1.2307 at 20 K                                      | —                                                                      | NBS Report 3282 |
| Critical temperature                   | 33.19 K                                             | −239.96 °C                                                             | [61]            |
| Critical pressure                      | 1.292 MPa                                           | 12.751 atm                                                             |                 |
| Critical density                       | 0.0291 g/cm <sup>3</sup>                            | —                                                                      |                 |
| Heat capacity, liquid, normal hydrogen | 12.2 J mol <sup>−1</sup> K <sup>−1</sup> at 20 K    | 2.92 cal mol <sup>−1</sup> °C <sup>−1</sup> at −253 °C                 |                 |
| Heat capacity, liquid, parahydrogen    | 19.7 J mol <sup>−1</sup> K <sup>−1</sup> at 20.45 K | 4.71 cal mol <sup>−1</sup> °C <sup>−1</sup> at −253 °C                 | [88]            |
| Heat of formation                      | −9012 J/mol                                         | −2154 cal/mol                                                          | [89]            |
| Heat of vaporization, normal hydrogen  | 917.6 J/mol at 20.26 K                              | 219.3 cal/mol at −252.89 °C                                            | [84]            |
| Heat of vaporization, parahydrogen     | 898.7 J/mol at 20.26 K                              | 214.8 cal/mol at −252.89 °C                                            |                 |
| Heat of fusion, parahydrogen           | 117.5 ± 0.6 J/mol at 13 K                           | 28.08 ± 0.15 cal/mol at −259 °C                                        | [84]            |

vestigated. In contrast, H<sub>2</sub> rich in the ortho component (>60%) and deuterium rich in para-deuterium undergo a transition to the face centered cubic (fcc) structure in the temperature range 1.2–4.2 K. The transition temperature is a function of ortho-para concentration as well as density or pressure. The volume change of the transition is small, 1.3%, but has been measured. The melting point of parahydrogen increases with pressure, as tabulated in Table 6.

Solid hydrogen under extreme compression, about 2.8 megabars, undergoes a phase transition to the metallic state, and may be superconducting. This state may exist in the core of some of the giant gas planets like Jupiter.

**Table 6:** Melting pressures of parahydrogen as a function of temperature.

| Temperature<br>K | Pressure |       |
|------------------|----------|-------|
|                  | atm      | MPa   |
| 14.1             | 8.57     | 0.87  |
| 14.1             | 8.63     | 0.87  |
| 14.4             | 17.75    | 1.79  |
| 14.4             | 17.84    | 1.80  |
| 14.6             | 24.01    | 2.43  |
| 14.6             | 24.03    | 2.43  |
| 14.8             | 30.33    | 3.06  |
| 14.8             | 30.36    | 3.07  |
| 14.8             | 30.4     | 3.07  |
| 15               | 36.79    | 3.72  |
| 15.2             | 43.24    | 4.37  |
| 15.4             | 49.93    | 5.04  |
| 15.4             | 49.94    | 5.04  |
| 15.4             | 49.96    | 5.05  |
| 15.8             | 63.33    | 6.40  |
| 15.8             | 63.33    | 6.40  |
| 16               | 70.19    | 7.09  |
| 16.2             | 77.06    | 7.78  |
| 16.4             | 84.09    | 8.49  |
| 16.4             | 84.13    | 8.50  |
| 16.6             | 91.17    | 9.21  |
| 17               | 105.65   | 10.67 |
| 17.2             | 112.95   | 11.41 |
| 17.4             | 120.33   | 12.15 |
| 17.6             | 127.96   | 12.92 |
| 17.8             | 135.48   | 13.68 |
| 17.8             | 135.51   | 13.69 |

Data source: [90,91]

The melting point of  $p\text{-H}_2$  was measured at high pressures up to 35.46 MPa (350 atm) [92, 93]. The melting curve of solid parahydrogen in Figure 4 can be expressed by the equation

$$(P - P_t)/(T - T_t) = \left[ A \exp\left(\frac{-\alpha}{T}\right) + BT \right]$$

where  $P_t$  is the triple point pressure 0.00704 MPa,  $T_t$  is the triple point temperature 13.803 K,  $A = 30.3312 \text{ atm/K}$ ,  $\alpha = 5.693 \text{ K}$ ,  $B = 2/3 \text{ atm/K}^2$  [41].

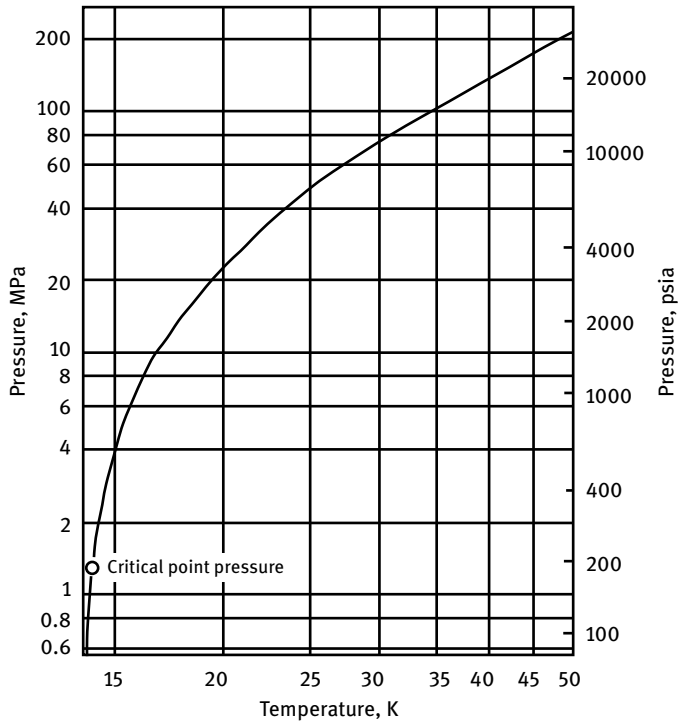


Figure 4: Melting line for parahydrogen at 0.6 to 200 MPa. (Reproduced and modified from [41].)

## 2.5 Boiling Point of Hydrogen

The boiling point of normal hydrogen is at  $20.38\text{ K} = -252.78^\circ\text{C}$  [85] and the boiling point of parahydrogen is at  $20.27\text{ K} = -252.89^\circ\text{C}$  [61].

## 2.6 Density and Molar Volumes of Hydrogen

### 2.6.1 Density of Gaseous Hydrogen

The real gas behavior of normal hydrogen gas at pressures up to 101 MPa was measured in order to create a PVT diagram covering a wide range of pressures and temperatures [94]. The PVT and thermophysical properties of compressed normal hydrogen (75% orthohydrogen and 25% parahydrogen) up to 100 MPa and its equation of state derived from the measurement data of the Burnett method, along with the measurement methods and correlation of viscosity and thermal conductivity for compressed hydrogen were summarized in [95].



### 2.6.2 Density of Condensed Phase Hydrogen

Density data for solid and liquid hydrogen under atmospheric ambient pressure are listed in Table 7.

**Table 7:** Density of solid and liquid hydrogen.

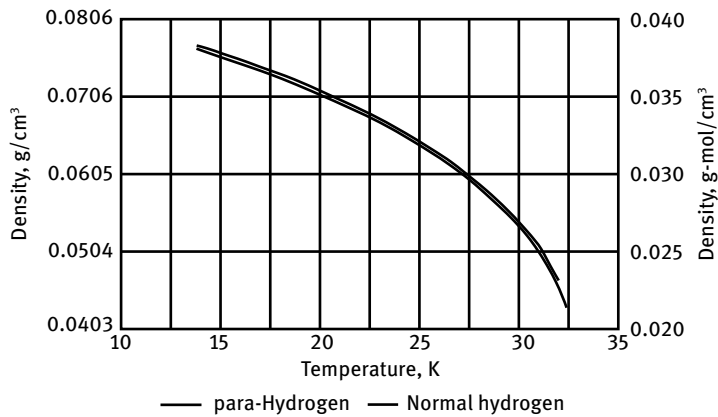
| State                                                  | Temperature, K              | Density $\rho^a$ , g/cm <sup>3</sup> | References |
|--------------------------------------------------------|-----------------------------|--------------------------------------|------------|
| Solid                                                  | 11.15                       | 0.08077                              | [96]       |
| Solid                                                  | 13.25                       | 0.0763                               |            |
| Liquid (parahydrogen, equilibrium composition at 20 K) | 13.803                      | 0.07702                              | [86]       |
|                                                        | 14.99                       | 0.07602                              |            |
|                                                        | 16.99                       | 0.07417                              |            |
|                                                        | 18.99                       | 0.07214                              |            |
|                                                        | 20.00                       | 0.07111                              |            |
|                                                        | 20.268 <sup>b</sup>         | 0.070781 <sup>b</sup>                |            |
|                                                        | 21.00                       | 0.06995                              |            |
|                                                        | 22.00                       | 0.06876                              |            |
|                                                        | 23.00                       | 0.06746                              |            |
|                                                        | 24.00                       | 0.06598                              |            |
|                                                        | 25.00                       | 0.06450                              |            |
|                                                        | 26.00                       | 0.06282                              |            |
|                                                        | 28.00                       | 0.05896                              |            |
|                                                        | 30.00                       | 0.05392                              |            |
|                                                        | 32.00                       | 0.04595                              |            |
| Critical                                               | 32.984 = $T_{\text{crit.}}$ | 0.03078 = $\rho_{\text{crit.}}$      |            |

Note: <sup>a</sup> Experimental values, except <sup>b</sup> which is calculated

If the critical density is known, the density of liquid parahydrogen from the melting point up to 31 K can be calculated from the following equation [86]:

$$\rho - \rho_{\text{crit.}} = 2.016 \left[ -0.001810 + 0.0092597 (T_{\text{crit.}} - T)^{\frac{1}{3}} \right]$$

where  $\rho_{\text{crit.}}$  is the critical density in g/cm<sup>3</sup> and  $T$  is the temperature in kelvin. The original equation was in gram-mols/cm<sup>3</sup> and in order to convert to g/cm<sup>3</sup> we had to multiply it by 2.016, the molecular mass of dihydrogen. As shown in Figure 5, the density of parahydrogen is slightly less than that of normal hydrogen.



**Figure 5:** Calculated density of saturated liquid parahydrogen and normal hydrogen. (Chart created by Schmidt 2016 based on data from [86].)

The density of subcooled liquid hydrogen is strongly dependent of the temperature and only slightly dependent of the pressure. A simplified state equation for this region was given as [97]

$$\ln \rho = b_0 + b_1 T^{\frac{9}{4}}$$

$$b_0 = -2.532955 + 3.588795 \times 10^{-2} P$$

$$b_1 = -1.694709 + 2.248987 \times 10^{-5} P$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$ ,  $T$  is the temperature in K, and  $P$  is the pressure in MPa.

The density of condensed-phase hydrogen was measured from 15 to 100 K at pressures up to 350 atmospheres [92, 93]. The accuracy of these measurements ( $\pm 0.03\%$ ) was insufficient to detect any difference between the densities of liquid normal and parahydrogen.

In a representation of pressure-density-temperature relations of fluid parahydrogen from 15 to 100 K at pressures to 350 atmospheres, the range of experimental densities was from 0.064 to 2.8 times the critical density [98]. This publication contains lots of numbers but no graphs.

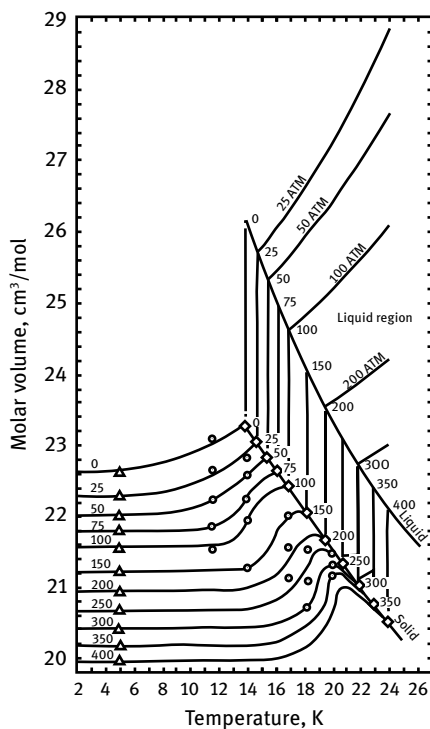
The molar volume of liquid  $p\text{-H}_2$  at the triple point is  $26.17 \text{ cm}^3/\text{mol}$ . Subtracting  $\Delta V$ , one obtains  $23.30 \text{ cm}^3/\text{mol}$  for the molar volume of solid  $p\text{-H}_2$  at the triple point. Density data for liquid and gaseous hydrogen from multiple sources were correlated in [99].

Two different curve-fit equations were given for the specific volume of solid  $p$ -H<sub>2</sub> as a function of temperature, a simple linear equation and a polynomial equation [100]:

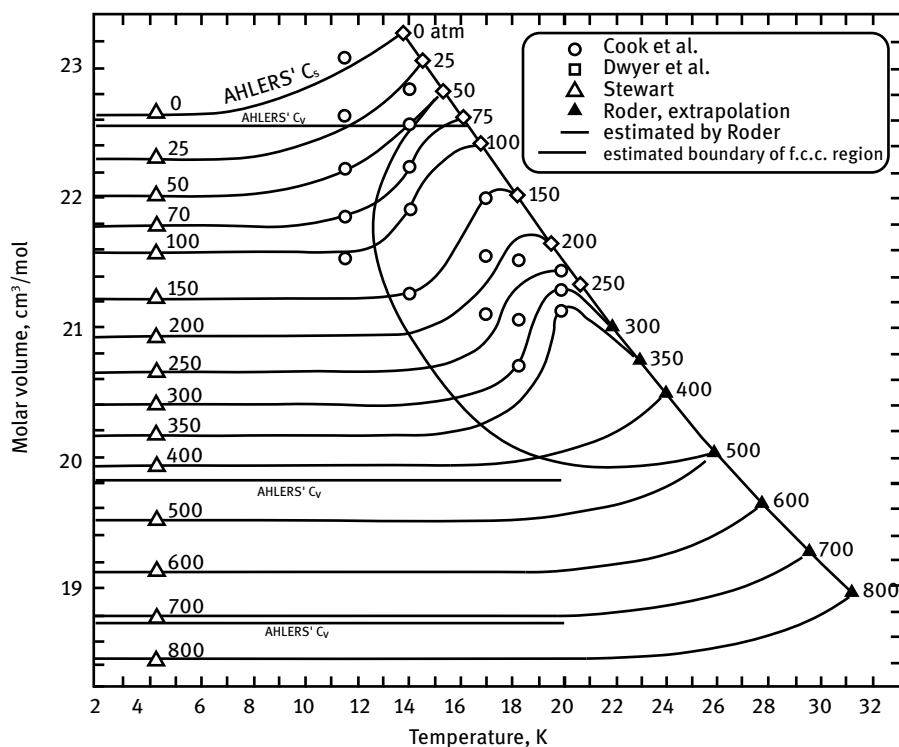
$$V_s = 27.1788 - 0.283044 T$$

$$V_s = 23.4469 + 0.376708 T - 0.0380559 T^2 + 0.000715738 T^3$$

where  $V_s$  is the molar volume in cm<sup>3</sup>/mol and  $T$  is the temperature in kelvin. The cubic polynomial equation is not much more accurate than the linear equation. Using the best data available, a PVT diagram for  $p$ -H<sub>2</sub> was constructed (Figure 6). On this diagram the molar volume (cm<sup>3</sup>/mol) of solid  $p$ -H<sub>2</sub> has been plotted vs. temperature in a series of isobars ranging from 0 to 400 atm pressure. Above the melting line on Figure 6 they have plotted the freezing line for the liquid and a few of the isobars for liquid  $p$ -H<sub>2</sub>. The lower part of this graph is similar to Figure 40a on page 5–43 of [41], shown here as Figure 7, except that the more recent graph contains data all the way up to 800 atm instead of only 400 atm.



**Figure 6:** PVT Diagram for liquid and solid parahydrogen. (Reproduced and modified from [100].)



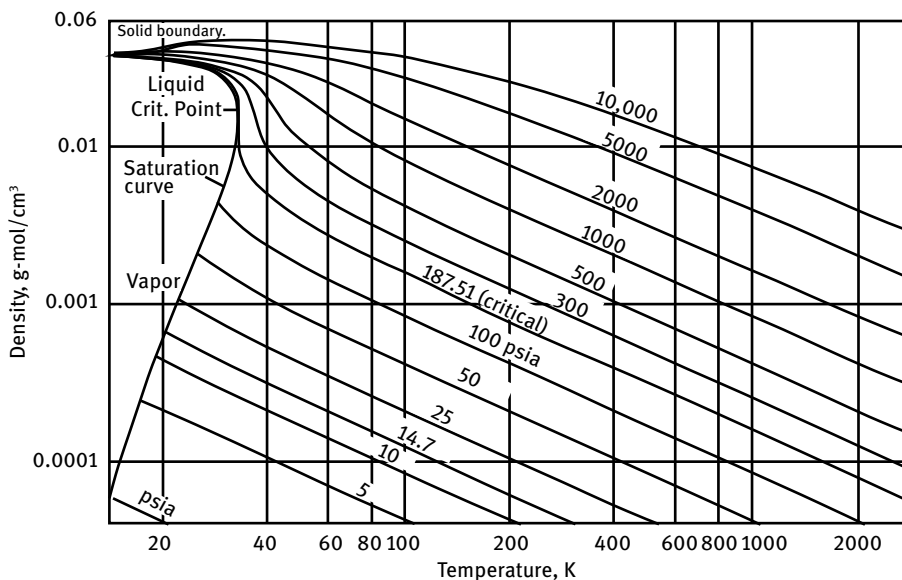
**Figure 7:** PVT diagram for compressed solid parahydrogen. (Reproduced and modified from [41].)

The most striking anomaly about the PVT diagram in Figure 6 is the shape of the isobars near the melting line. It is seen that at pressures above 150 atm there is a narrow temperature region in which the molar volume of solid  $p$ -H<sub>2</sub> increases as the temperature is lowered at constant pressure, instead of decreasing, as one would expect. The density of parahydrogen in a  $P$ – $\rho$ – $T$  diagram is illustrated in Figure 8.

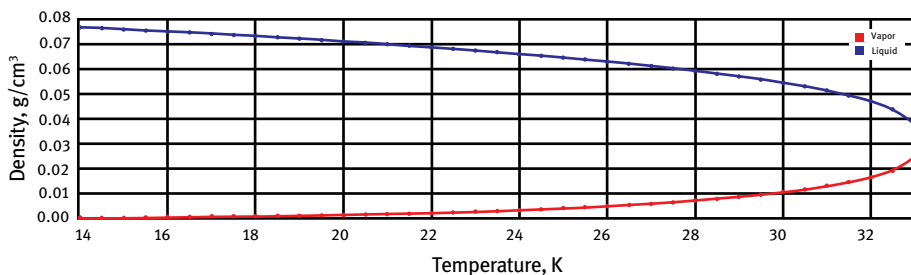
The density of liquid hydrogen as a function of temperature can be displayed graphically or printed out as a table by an on-line app on the NIST Chemistry Web-Book Fluids web page [101]. A sample calculation for saturated hydrogen  $14 < T < 33$  K is shown in Figure 9.

### 2.6.3 Density near the Critical Point

Closely spaced experimental data were used for defining a consistent set of values for critical constants that describe the two-phase boundaries between saturated liquid and saturated vapor [102]. The PVT properties of 20.3 K equilibrium hydrogen (0.21% orthohydrogen), herein simply called parahydrogen, were measured by Goodwin et al. [98]. The experimental runs were conducted at nearly constant



**Figure 8:**  $P$ – $\rho$ – $T$  density diagram of parahydrogen. (Reproduced and modified from [41].)



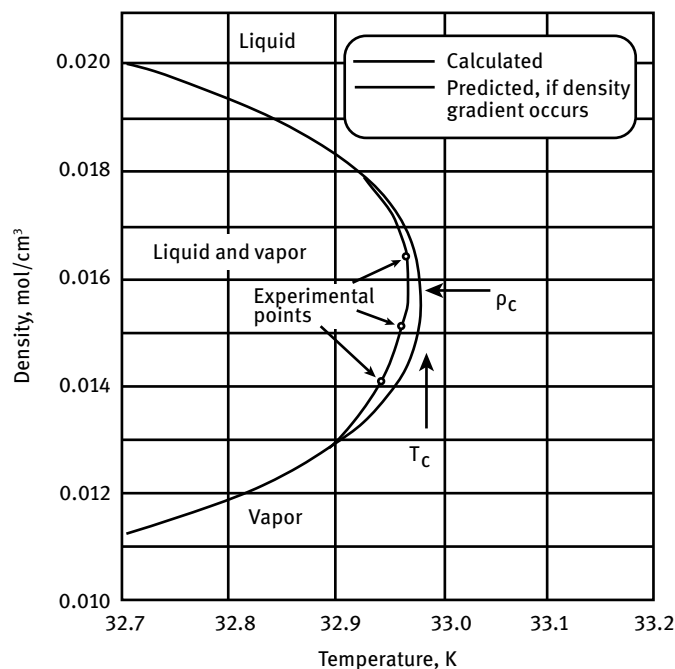
**Figure 9:** Density of liquid and gaseous hydrogen along the saturation line. (From [101].)

density (pseudo-isochores) by taking pressure measurements at numerous fixed temperatures. The density near the critical point can be expressed by the equation

$$\rho = \rho_c + A(T_c - T)^{0.370} + B(T_c - T) + C(T_c - T)^{0.7} + D(T_c - T)^{0.8}$$

where  $\rho$  is the density in mol/cm<sup>3</sup>,  $\rho_c$  is the critical density  $\rho_c = 0.01559 \pm 0.00005$  mol/cm<sup>3</sup>,  $T$  is the temperature in kelvin,  $T_c$  is the critical temperature  $T_c = 32.976 \pm 0.015$  K and  $A$ ,  $B$ ,  $C$  and  $D$  are constants ( $A = -0.71967724 \times 10^{-2}$ ,  $B = 0.14495527 \times 10^{-2}$ ,  $C = 0.32403120 \times 10^{-2}$ ,  $D = -0.44640177 \times 10^{-2}$ ). The experimental

configuration used yielded a flatter dome, shown in Figure 10 as the dashed line. The solid line represents the computed results, and circles represent the experimental values.



**Figure 10:** Density of hydrogen near the critical point. (Reprinted and modified from [102], with permission from ©1963 Elsevier; permission conveyed through RightsLink.)

#### 2.6.4 Density of Solid Hydrogen

The molar volume ( $V_s$ ) of solid parahydrogen along the melting line up to a temperature of about 24 K and a pressure of about 400 atm has been determined by two independent methods: direct measurement and computation from the heat of fusion and change in volume during melting [103]. Results obtained by the two methods agreed with each other within about  $\pm 0.2\%$ ; they were both referred to as “experimental.” The empirical linear equation

$$V_s = 27.1788 - 0.283044 T$$

where  $V_s$  is the molar volume in  $\text{cm}^3/\text{mol}$  and  $T$  is the temperature in kelvin, reproduced the experimental results with a mean deviation of about 0.15%. The molar volume of solid hydrogen at the triple point is  $22.561 \text{ cm}^3/\text{mol}$ .

The density of melting solid hydrogen as a function of the melting temperature under pressure along the melting line can be calculated from a curve-fitted linear equation [90]

$$\rho = 0.06924 + 0.00123T$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin. Note that the melting temperature increases with pressure, and thus the density increases with temperature and pressure along the melting line. Density data along with dielectric constants of solid hydrogen under pressure are shown in Table 38.

## 2.7 Compressibility of Hydrogen

### 2.7.1 Compressibility of Liquid Hydrogen

The isothermal compressibility is defined as

$$\beta_T = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_T$$

The isothermal compressibility is a negative quantity. The isothermal compressibility of liquid hydrogen is  $-1.10 \times 10^{-2} \text{MPa}^{-1}$  at the triple point and  $-1.99 \times 10^{-2} \text{MPa}^{-1}$  at the boiling point.

The adiabatic (isentropic) compressibility is defined as

$$\beta_S = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_S = \frac{C_V}{C_P} \beta_T$$

The adiabatic compressibility of liquid parahydrogen is  $0.00807 \text{MPa}^{-1}$  at the triple point and  $0.0119 \text{MPa}^{-1}$  at the boiling point. The adiabatic compressibility of gaseous parahydrogen is  $8.56 \text{MPa}^{-1}$  at the triple point and  $5.93 \text{MPa}^{-1}$  at the boiling point. Adiabatic compressibility and sonic velocity are closely related by the relationship

$$\beta_S = \frac{1}{\rho c^2}$$

where  $\rho$  is the density and  $c$  is the velocity of sound. Density, coefficient of thermal expansion, velocity of sound, and compressibility data of liquid parahydrogen at sea level pressure are summarized in Table 8.

Measured isotherms of liquid normal hydrogen from the boiling point to the critical point were tabulated for seven temperature intervals between 20.38 and 32.58 K at pressures up to 100 atm [105]. The compressibility can be derived from these data by plotting the isochors, which gives straight lines which can be expressed by a linear equation (Table 9).

**Table 8:** Density, velocity of sound, compressibility, and coefficient of thermal expansion of liquid parahydrogen.

| Temperature<br>K | Density<br>g/cm <sup>3</sup> | Velocity of<br>sound<br>m/s | Adiabatic<br>compressibility |                                         | Isothermal<br>compressibility |                                         | Coefficient<br>of thermal<br>expansion<br>1/K |
|------------------|------------------------------|-----------------------------|------------------------------|-----------------------------------------|-------------------------------|-----------------------------------------|-----------------------------------------------|
|                  |                              |                             | cm <sup>2</sup> /dyn         | m <sup>2</sup> /N<br>= Pa <sup>-1</sup> | cm <sup>2</sup> /dyn          | m <sup>2</sup> /N<br>= Pa <sup>-1</sup> |                                               |
| 14               | 0.07685                      | 1256                        | 82.5 × 10 <sup>-11</sup>     | 8.25 × 10 <sup>-8</sup>                 | 115.8 × 10 <sup>-11</sup>     | 1.16 × 10 <sup>-7</sup>                 | 1.083 × 10 <sup>-2</sup>                      |
| 16               | 0.07511                      | 1217                        | 89.9 × 10 <sup>-11</sup>     | 8.99 × 10 <sup>-8</sup>                 | 132.5 × 10 <sup>-11</sup>     | 1.32 × 10 <sup>-7</sup>                 | 1.222 × 10 <sup>-2</sup>                      |
| 18               | 0.07320                      | 1174                        | 99.1 × 10 <sup>-11</sup>     | 9.91 × 10 <sup>-8</sup>                 | 156.0<br>× 10 <sup>-11</sup>  | 1.56 × 10 <sup>-7</sup>                 | 1.397 × 10 <sup>-2</sup>                      |
| 20               | 0.07108                      | 1124                        | 111.4 × 10 <sup>-11</sup>    | 1.11 × 10 <sup>-7</sup>                 | 189.2 × 10 <sup>-11</sup>     | 1.89 × 10 <sup>-7</sup>                 | 1.628 × 10 <sup>-2</sup>                      |

Data source: [104]

**Table 9:** Compressibility of liquid normal hydrogen.

| Temperature |        | Pressure |       | Compressibility           |                         |                                      |
|-------------|--------|----------|-------|---------------------------|-------------------------|--------------------------------------|
| K           | °C     | MPa      | atm   | cm <sup>2</sup> /kg force | cm <sup>2</sup> /N      | m <sup>2</sup> /N = Pa <sup>-1</sup> |
| 20          | -253.2 | 0.202    | 2.0   | 1.86 × 10 <sup>-3</sup>   | 1.90 × 10 <sup>-4</sup> | 1.90 × 10 <sup>-8</sup>              |
| 20          | -253.2 | 1.01     | 10.0  | 1.59 × 10 <sup>-3</sup>   | 1.62 × 10 <sup>-4</sup> | 1.62 × 10 <sup>-8</sup>              |
| 20          | -253.2 | 5.05     | 50.0  | 1.03 × 10 <sup>-3</sup>   | 1.05 × 10 <sup>-4</sup> | 1.05 × 10 <sup>-8</sup>              |
| 20          | -253.2 | 10.1     | 100.0 | 0.76 × 10 <sup>-3</sup>   | 7.75 × 10 <sup>-5</sup> | 7.75 × 10 <sup>-9</sup>              |
| 33.2        | -240.0 | 5.05     | 50.0  | 2.97 × 10 <sup>-3</sup>   | 3.03 × 10 <sup>-4</sup> | 3.03 × 10 <sup>-8</sup>              |
| 33.2        | -240.0 | 10.1     | 100.0 | 1.40 × 10 <sup>-3</sup>   | 1.43 × 10 <sup>-4</sup> | 1.43 × 10 <sup>-8</sup>              |

Based on specific volume PVT data from [105]

The compressibility coefficient is defined as

$$C = \frac{P}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

This quantity may be easily obtained by forming the product of  $P$  times the isothermal compressibility. The compressibility coefficient of liquid hydrogen is  $7.79 \times 10^{-5}$  at the triple point and  $2.02 \times 10^{-3}$  at the boiling point. The compressibility factor is defined as  $Z = PV/RT$ . The compressibility factor of liquid hydrogen is 0.00161 at the triple point, 0.01712 at the boiling point and 0.3024 at the critical point.

The isothermal compressibility of liquid hydrogen has been listed as  $-1.10 \times 10^{-2} \text{ MPa}^{-1} = -1.10 \times 10^{-8} \text{ Pa}^{-1}$  at the triple point and  $-1.99 \times 10^{-2} \text{ MPa}^{-1} = -1.99 \times 10^{-8} \text{ Pa}^{-1}$  at the boiling point [79].



The compressibility of liquid and solid hydrogen has been measured up to very high pressures, trying to find the transition point to metallic hydrogen. Conditions like this may exist in the interior of the gaseous giant planets but are not likely to be encountered in rockets.

High explosives were used to shock liquid hydrogen to 39500 bar pressure, compress it to a specific volume of  $5.2 \text{ cm}^3/\text{g}$  and an estimated temperature of 1100 K from an initial state near the normal boiling point, 20.5 K and  $14.1 \text{ cm}^3/\text{g}$  [106]. The derived intermolecular potential between two hydrogen molecules was shown to be inadequately represented by the previously postulated Lennard-Jones 6–12 potential in the repulsive region between 2.0 and 2.7 Å. The power of the inverse intermolecular distance is shown instead to be 8.5 in that region if a purely repulsive potential is used. These experiments predated the discovery of metallic hydrogen. Liquid hydrogen was isentropically compressed to a density of  $1 \text{ cm}^3/\text{g}$  at 2 MPa by a combination of magnetic field constriction and explosive implosion [106].

### 2.7.2 Compressibility of Gaseous Hydrogen

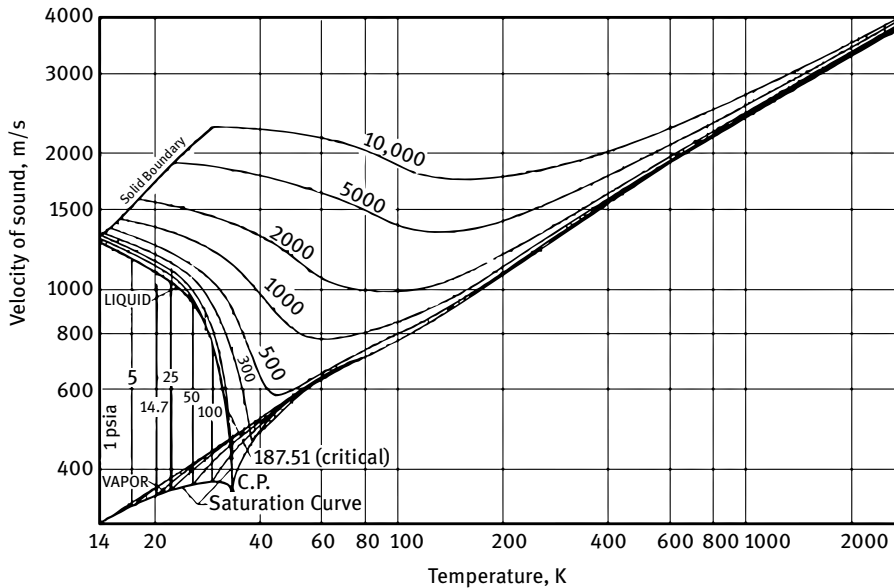
Compressibility isotherms of hydrogen were given at temperatures from 98 to 298 K (–175 to 25 °C) and at maximum pressure of 1000 atm, also at temperatures from 273 to 423 K (0–150 °C) and at maximum pressure of 2950 atm [107]. Values of the second and third virial coefficients of hydrogen were calculated from experimental PVT data with the method of least squares in the temperature range from 423 to 98 K (150 to –175 °C) [108]. Theoretical values of the second virial coefficient were calculated in the same temperature range, based on the Lennard-Jones potential field and on parameter values taken from the literature, with corrections for the non-spherical part of the potential and for a number of quantum effects. A comparison showed that a satisfactory representation of the experimental data with a Lennard-Jones potential was impossible, even after adjustment of the parameter values to the experimental results.

### 2.7.3 Compressibility of Solid Hydrogen

The isothermal compressibility of solid parahydrogen was measured in the temperature range of 6–14.5 K and at pressures of 0–180 atm on the basis of dielectric constant measurements [109].

## 2.8 Velocity of Sound in Liquid Hydrogen

The velocity of sound in liquid parahydrogen is 1264 m/s at the triple point and 1089 m/s at the normal boiling point. The velocity of sound in gaseous parahydrogen is 305.7 m/s at the triple point and 355 m/s at the normal boiling point. Figure 11 illustrates the velocity of sound in parahydrogen for a wide range of temperatures and pressures [41]. The unit of pressure on the auxiliary parameter curves is psia. Data for normal hydrogen are available from the same source but they are not much different.



**Figure 11:** Velocity of sound in parahydrogen. (Reproduced and modified from [41].)

Liquid hydrogen has been compressed in shock waves from explosive charges in an attempt to create metallic hydrogen [110]. High explosives were used to shock liquid hydrogen to 39500 bar,  $5.2 \text{ cm}^3/\text{g}$  and an estimated temperature of 1100 K from an initial state near the normal boiling point, 20.5 K and  $14.1 \text{ cm}^3/\text{g}$ . It was attempted to calculate the repulsive potential between two hydrogen molecules and two hydrogen atoms as they are squeezed together at high pressures. Hydrogen isotopes are subjected to very high pressures when they are packaged in targets for controlled nuclear fusion experiments.

Based on measured values of  $P$  vs.  $V$ , isotherms of normal liquid hydrogen were tabulated for 7 temperatures between 20.38 and 32.58 K [105]. Then the data were re-plotted as isochores, and a straight line relationship could be adequately described by

$$P = A_v + B_v T$$

$$B_v = -7.11 + 437 \left( \frac{1}{V} \right)$$

The velocity of ultrasonic waves in liquid hydrogen depends upon the orthohydrogen-parahydrogen concentration in the liquid. Between 14 and 20 K the velocity in a 99.8% parahydrogen mixture is about 8 m/s or about 0.6% smaller than in the non-equilibrated 25% mixture [111]. No influence of frequency on velocity of sound could be detected in the frequency range from 1 to 5 MHz. The adiabatic compressibility of the equilibrium mixture exceeds that of the normal hydrogen by about 2%.

It had been shown that the velocity of sound in liquid hydrogen is dependent on the orthohydrogen-parahydrogen concentration at temperatures between 13 and 20 K. These measurements were later extended to near the critical point [112].

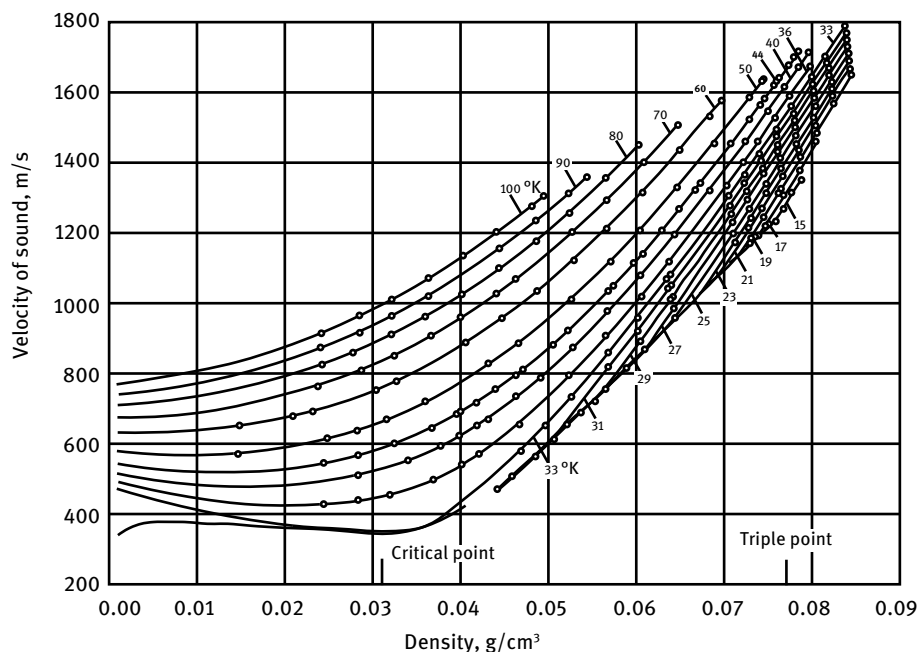
The specific heat  $C_p$ , the thermal expansion coefficient  $\alpha$  and the pressure coefficient  $\gamma_p$  are well known for liquid normal or parahydrogen in equilibrium with saturated vapor. Combining these data with experimental values of the velocity of sound, one is able to calculate other thermodynamic properties, e.g. the specific heats  $C_p$  and  $C_v$ , the compressibility coefficients  $\beta_S$  and  $\beta_T$ , the expansion coefficient  $\alpha$ , the pressure coefficient  $\gamma_p$ , and the derivative  $dp/dt$  [113].

The most comprehensive measurements of the velocity of sound in liquid hydrogen have been made by Younglove, Figure 12 [114]. The measurements cover temperatures from 15 to 100 K and pressures up to 300 atm. Calculations based on previous pressure density and temperature measurements of this laboratory provide the density corresponding to each experimental temperature and pressure. Prior to this work no known experimental velocities had been determined for compressed liquid parahydrogen above 21 K.

Figure 13 is taken from a later reference to illustrate the slight difference in velocity of sound between saturated liquid normal and parahydrogen. The two lines nearly fall on top of each other.

The difference in the velocity of sound between that of liquid normal and that of parahydrogen is emphasized in Figure 14. The difference increases with temperature past the normal boiling point of hydrogen.

The velocity of sound in highly compressed hydrogen was measured from Brillouin scattering in a diamond anvil cell at 1.2–5.0 GPa at 293 K and also at 4.6–13 GPa over a wider temperature range 300–530 K [115]. From these velocity of sound data together with previously reported volume and ultrasonic velocity data at low pressures



**Figure 12:** Velocity of sound as a function of density, showing isotherms. (Reprinted and modified from [114], with permission from ©1965 Acoustic Society of America; permission conveyed through RightsLink.)

Legend: The dashed lines are calculated values. The heavy lines are phase boundaries. For reference, the densities of the critical point and triple point are indicated on the abscissa.

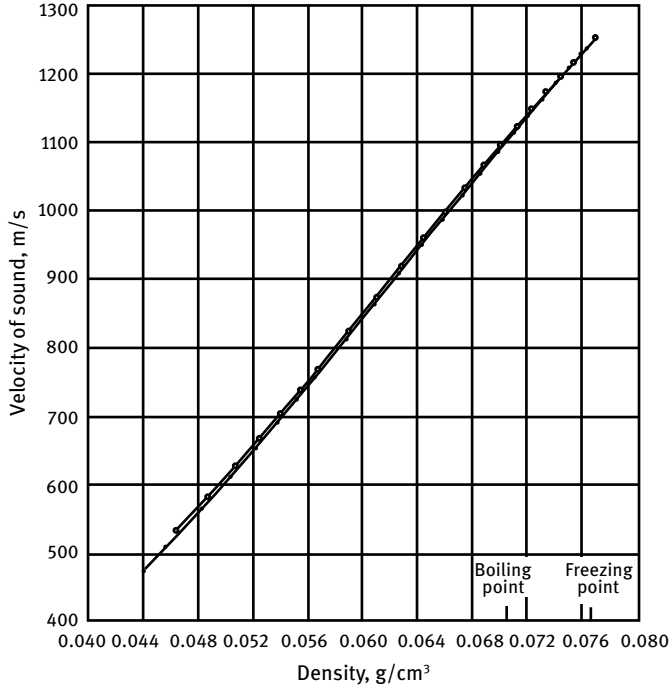
and temperatures, a Benedict type PVT equation of state was derived that is valid for fluid hydrogen up to the maximum pressures and temperatures with an average deviation of 1% from the new and previously published experimental data.

## 2.9 Vapor Pressure of Hydrogen

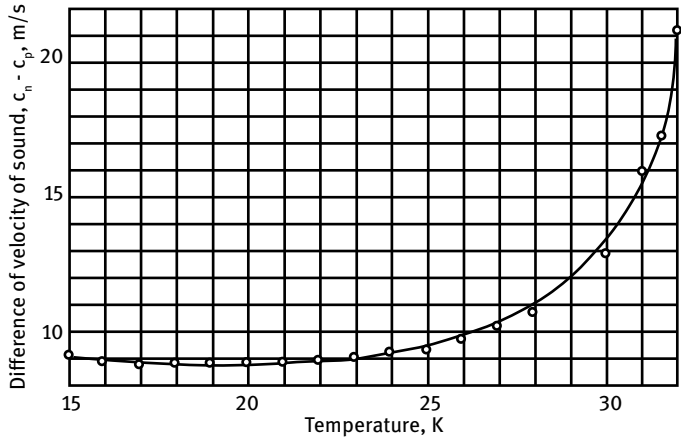
Table 10 is a summary of vapor pressure data for normal (75% *o*-H<sub>2</sub>, 25% *p*-H<sub>2</sub>) liquid hydrogen calculated using equation

$$\log_{10} p = 4.66687 - 44.9569/T + 0.020537T$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.



**Figure 13:** Velocity of sound in liquid parahydrogen and normal hydrogen. (Reproduced and modified from [70].)  
Legend: The open circles are for normal hydrogen.



**Figure 14:** Difference in velocity of sound between liquid normal and parahydrogen. (Reproduced and modified from [62]; based on data from Younglove 1965.)

**Table 10:** Calculated vapor pressure of normal liquid hydrogen.

| Temperature |         | Vapor Pressure |        |
|-------------|---------|----------------|--------|
| K           | °C      | kPa            | atm    |
| 14.00       | −259.16 | 7.38           | 0.0728 |
| 16.00       | −257.16 | 20.4           | 0.2018 |
| 18.00       | −255.16 | 46.1           | 0.4551 |
| 20.00       | −253.16 | 90.1           | 0.8891 |
| 22.00       | −251.16 | 158            | 1.564  |
| 24.00       | −249.16 | 258            | 2.545  |
| 26.00       | −247.16 | 395            | 3.899  |
| 28.00       | −245.16 | 577            | 5.695  |
| 30.00       | −243.16 | 812            | 8.010  |
| 32.00       | −241.16 | 1103           | 10.923 |
| 33.00       | −240.16 | 1280           | 12.632 |

Data source: [61]

A similar equation exists for solid normal hydrogen

$$\log_{10}p = 4.56488 - 47.2059/T + 0.03939T$$

where  $p$  is the vapor pressure in mmHg and  $T$  is the temperature in Kelvin. Corresponding equations for the equilibrium composition at 20.4 K which is mostly parahydrogen (actually, 99.79%  $p$ -H<sub>2</sub> and 0.21%  $o$ -H<sub>2</sub>) are for the liquid

$$\log_{10}p = 4.64392 - 44.3450/T + 0.02093T$$

and for the solid:

$$\log_{10}p = 4.62438 - 47.0172/T + 0.03635T$$

where  $p$  is the vapor pressure in mmHg and  $T$  is the temperature in Kelvin. Corresponding equations for normal hydrogen consisting of 75% orthohydrogen and 25% parahydrogen are for the liquid:

$$\log_{10}p = 4.66687 - 44.9569/T + 0.020537T$$

and for the solid:

$$\log_{10}p = 4.56488 - 47.2059/T + 0.03939T$$

Measured vapor pressure data for normal liquid hydrogen are presented in Table 11.

**Table 11:** Vapor pressure of normal liquid hydrogen, measured data.

| Temperature |         | Vapor pressure |         |
|-------------|---------|----------------|---------|
| K           | °C      | kPa            | atm     |
| 20.90       | −252.26 | 117.5          | 1.1596  |
| 22.65       | −250.51 | 184            | 1.8155  |
| 23.72       | −249.44 | 238            | 2.3493  |
| 24.73       | −248.43 | 299            | 2.9510  |
| 25.70       | −247.46 | 366            | 3.6126  |
| 26.74       | −246.42 | 448            | 4.4178  |
| 28.20       | −244.96 | 584            | 5.7618  |
| 30.19       | −242.97 | 817            | 8.0645  |
| 31.40       | −241.76 | 983            | 9.6981  |
| 32.36       | −240.80 | 1135           | 11.2065 |
| 33.14       | −240.02 | 1279           | 12.620  |
| 33.24       | −239.92 | 1297           | 12.797  |

Data source: [116]

These values can be represented by the following polynomial equation:

$$\log p_v = 3.068281 - 55.25642/T - 3.1282 \times 10^{-2} T + 6.6989 \times 10^{-4} T^2$$

where  $T$  is the temperature in kelvin and  $p_v$  is the vapor pressure in atm.

**Table 12:** Comparison of measured and interpolated vapor pressures of parahydrogen.

| Temperature, K | Vapor pressure, atm, measured | Vapor pressure, atm, calculated |
|----------------|-------------------------------|---------------------------------|
| 20.268         | 1.0000                        | 0.9999                          |
| 22.00          | 1.6124                        | 1.6127                          |
| 23.00          | 2.0688                        | 2.0691                          |
| 25.00          | 3.2462                        | 3.2453                          |
| 26.00          | 3.9826                        | 3.9818                          |
| 27.00          | 4.8285                        | 4.8285                          |
| 28.00          | 5.7920                        | 5.7939                          |
| 29.00          | 6.8863                        | 6.8869                          |
| 30.00          | 8.1162                        | 8.1176                          |
| 31.00          | 9.5005                        | 9.5006                          |
| 32.00          | 11.0516                       | 11.0513                         |
| 32.50          | 11.8988                       | 11.8984                         |
| 32.60          | 12.0742                       | 12.0745                         |
| 32.70          | 12.2526                       | 12.2529                         |
| 32.80          | 12.4330                       | 12.4340                         |
| 32.90          | 12.6183                       | 12.6177                         |

Data source: [117]

Table 12 is a comparison of measured and interpolated vapor pressures of parahydrogen (frozen equilibrium concentration at 20 K) by using the following equation [117]

$$\log p_v = 2.000620 - 50.09708/(T + 1.0044) + 1.748495 \times 10^{-2} T$$

where  $T$  is the temperature in kelvin and  $p_v$  is the pressure in atm. Vapor pressure and density of normal saturated liquid hydrogen are listed in Table 13.

The vapor pressure data for normal hydrogen from [118] in the range from 21.01 to 32.27 K can be expressed by the Antoine equation

$$\log p = 3.54314 - [99.395/(T + 7.726)]$$

where  $p$  is the pressure in bar and  $T$  is the temperature in kelvin.

**Table 13:** Saturation properties, normal hydrogen, liquid-vapor.

| Temperature | Pressure | Vapor pressure<br>slope $dP/dT$ | Density, sat.<br>liquid | Density, sat.<br>vapor |
|-------------|----------|---------------------------------|-------------------------|------------------------|
| K           | atm      | atm/K                           | g mol/cm <sup>3</sup>   |                        |
| 13.947      | 0.071    | 0.041                           | 0.03830                 | 0.000063               |
| 14          | 0.073    | 0.042                           | 0.03828                 | 0.000064               |
| 15          | 0.125    | 0.063                           | 0.03786                 | 0.000104               |
| 16          | 0.202    | 0.091                           | 0.03742                 | 0.000159               |
| 17          | 0.310    | 0.125                           | 0.03695                 | 0.000232               |
| 18          | 0.456    | 0.167                           | 0.03647                 | 0.000327               |
| 19          | 0.648    | 0.216                           | 0.03595                 | 0.000447               |
| 20          | 0.891    | 0.273                           | 0.03540                 | 0.000595               |
| 20.380      | 1.000    | 0.296                           | 0.03519                 | 0.000660               |
| 21          | 1.196    | 0.337                           | 0.03483                 | 0.000776               |
| 22          | 1.569    | 0.409                           | 0.03421                 | 0.000995               |
| 23          | 2.018    | 0.490                           | 0.03355                 | 0.001257               |
| 24          | 2.551    | 0.579                           | 0.03285                 | 0.001569               |
| 25          | 3.178    | 0.676                           | 0.03209                 | 0.001938               |
| 26          | 3.906    | 0.783                           | 0.03127                 | 0.002377               |
| 27          | 4.746    | 0.898                           | 0.03036                 | 0.002900               |
| 28          | 5.705    | 1.023                           | 0.02935                 | 0.003527               |
| 29          | 6.794    | 1.157                           | 0.02821                 | 0.004290               |
| 30          | 8.023    | 1.302                           | 0.02689                 | 0.005241               |
| 31          | 9.401    | 1.457                           | 0.02528                 | 0.006482               |
| 32          | 10.94    | 1.622                           | 0.02312                 | —                      |
| 33          | 12.65    | 1.800                           | 0.01903                 | —                      |
| 33.18       | 12.98    | 1.833                           | 0.01494                 | 0.01494                |

Data source: [70], p. 13



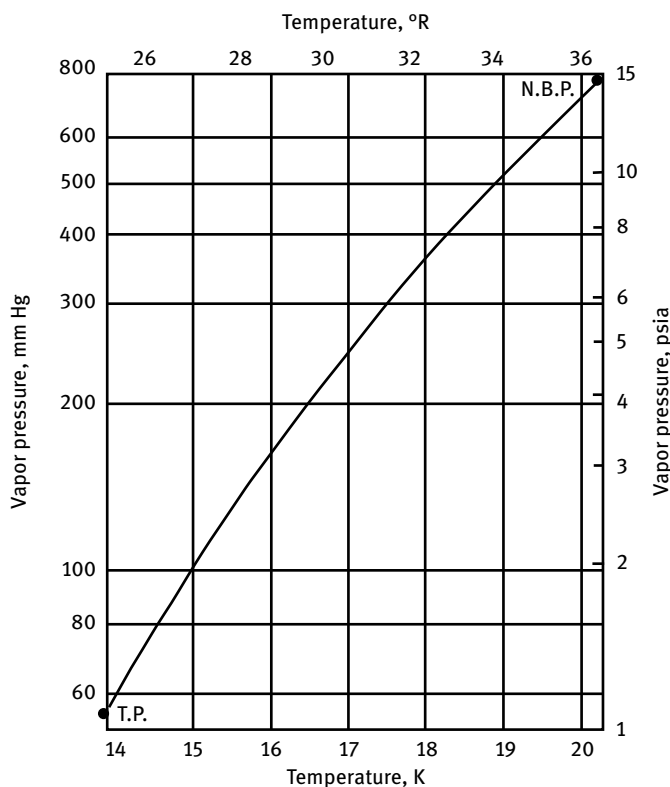
The NBS values for the vapor pressure of liquid  $p\text{-H}_2$  in the temperature range below the normal boiling point from 13.803 to 20.268 K are given by the simple equation [74]:

$$\log P = a + \frac{b}{T} + cT$$

where  $a = 1.772454$ ,  $b = -44.36888$ , and  $c = +0.02055468$  are constants,  $P$  is the pressure in atm, and  $T$  is the temperature in kelvin. Above the normal boiling point from 20.26 to 29.00 K a slightly different equation can be used:

$$\log P = A + B/(T + C) + DT$$

where  $A = +2.000620$ ,  $B = -50.09708$ ,  $C = +1.0044$ ,  $D = +0.01748495$  are constants,  $P$  is the pressure in atm, and  $T$  is the temperature in kelvin. These two equations reproduce experimental vapor pressures within 0.002 atm and are accurate enough for daily use.



**Figure 15:** Vapor pressure of parahydrogen below 0.101 MPa. (Reproduced and modified from [41].)

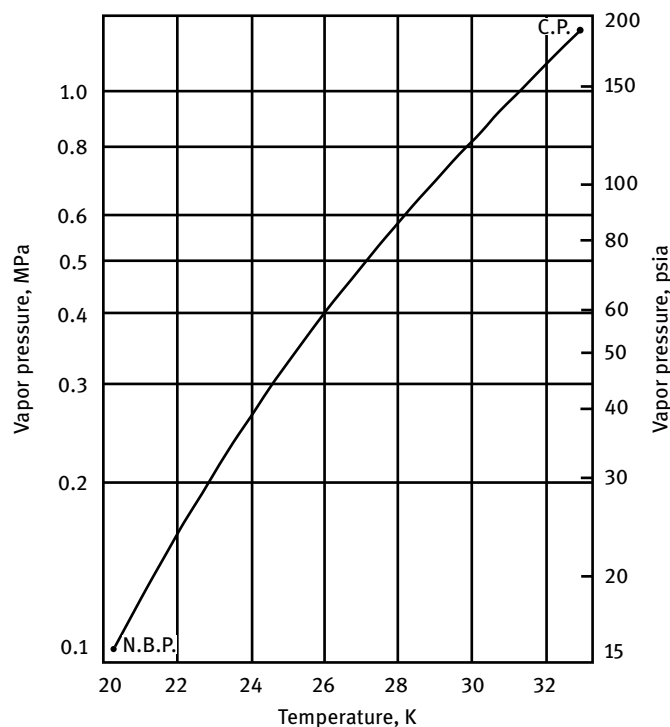
The vapor pressure of parahydrogen can be calculated from the very complex equation from [119]:

$$\ln\left(\frac{P}{P_t}\right) = n_1x + n_2x^2 + n_3x^3 + n_4(1-x)^{n_5}$$

where  $n_1 = 3.05300134164$ ,  $n_2 = 2.80810925813$ ,  $n_3 = -0.655461216567$ ,  $n_4 = 1.59514439374$ ,  $n_5 = 1.5814454428$ ,  $x = (1 - T_t/T)/(1 - T_t/T_c)$ , with  $T_t = 13.8$  K,  $T_c = 32.938$  K, and  $P_t = 0.007042$  MPa.

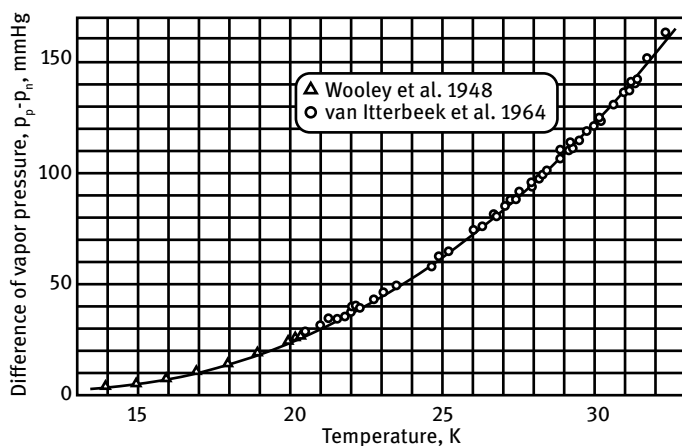
Vapor pressure of liquid parahydrogen as a function of temperature for temperatures below the normal boiling point is illustrated in Figure 15 and data for temperatures above the normal boiling point are illustrated in Figure 16. For additional (sometimes antiquated) vapor pressure data see also [120].

Vapor pressure data in the literature often lack information as to the temperature scale being used for calibration of thermometers. Other authors fail to correct for other deviations expected from pressure measurements. It would be difficult to decide if the *o-p* composition of liquid hydrogen has an effect on the vapor pressure. Such measurements would have to be made side by side with exactly the same equipment.



**Figure 16:** Vapor pressure of parahydrogen above 0.101 MPa. (Reproduced and modified from [41].)

Van Itterbeek, et al. [118] measured the difference in vapor pressure of normal and parahydrogen and the vapor pressure of normal hydrogen, simultaneously. The normal boiling points of normal and parahydrogen were determined to be 20.389 and 20.269 K, respectively. The vapor pressure results were reported as accurate to within  $\pm 0.004$  atm. The vapor pressure differences of the Wooley et al. 1948 and Itterbeek et al. 1964 measurements are illustrated in Figure 17 and seem to match each other in the range where they overlap. There is a substantial difference between the vapor pressures of normal and parahydrogen. The difference increases with increasing temperatures.



**Figure 17:** Vapor pressure difference between liquid normal and parahydrogen. (Reproduced and modified from [62].)

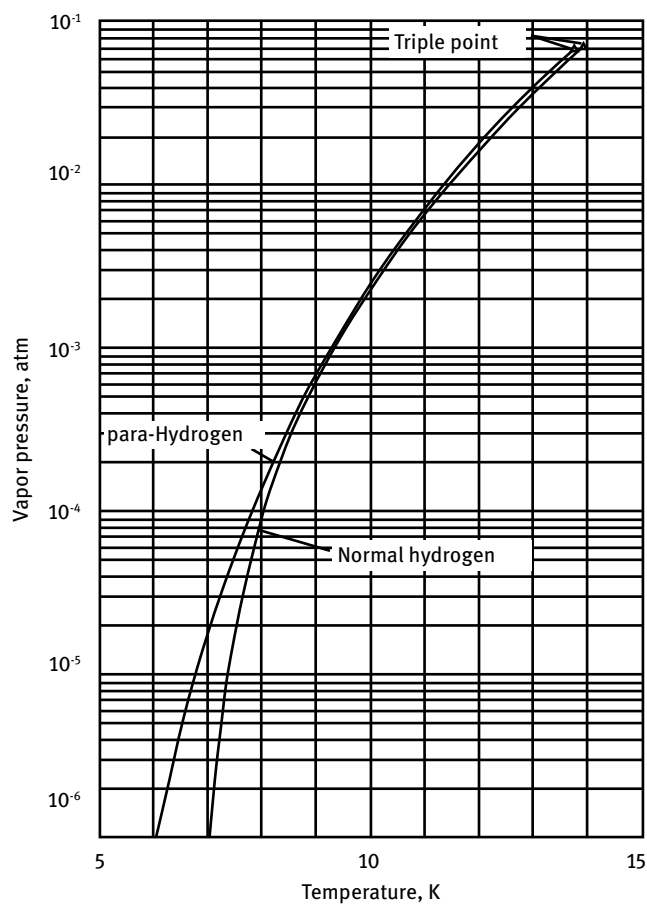
The sublimation vapor pressure of solid hydrogen below the triple point is very low, but it can still sublime. The vapor pressure of solid parahydrogen is somewhat higher than that of normal hydrogen (Figure 18). The line for parahydrogen in Figure 18 for temperatures below 10 K can be represented by the equation (based on data from [121]):

$$\log P = 43.39/T + 2.5 \log T + 2.047$$

The sublimation pressure of solid parahydrogen can be expressed by a Kirchoff-Rankine equation:

$$\log P = \frac{A}{T} + B \log T + C$$

where  $P$  is the sublimation pressure in mmHg,  $T$  is the temperature in kelvin, and  $A$ ,  $B$ , and  $C$  are constants, with  $A = -90.77568949$ ,  $B = 2.489830940$ , and  $C =$



**Figure 18:** Vapor pressure of solid hydrogen. (Reproduced and modified from [41].)

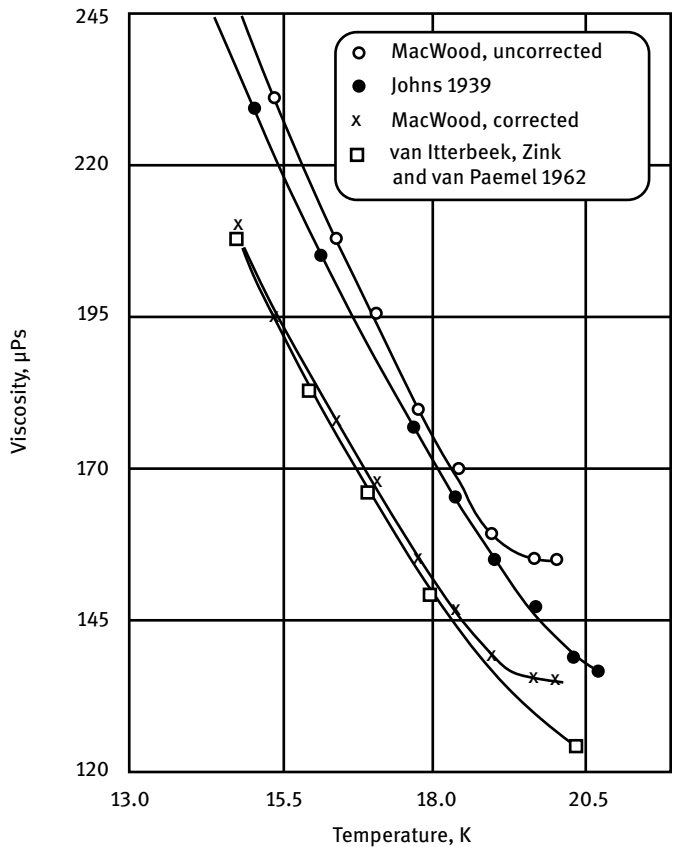
4.009857354 [122]. This equation has been forced to go through the triple point at  $P_t = 0.00704$  MPa (0.0695 atm) and,  $T_t = 13.80$  K. See also [123].

## 2.10 Viscosity of Hydrogen

The viscosity differences of gaseous orthohydrogen and parahydrogen are small, approaching 1% near the triple point [124, 125]. In all cases the para modification had the slightly higher viscosity. Liquid hydrogen viscosity values, however, differ by larger amounts with differences of about 5% at saturation near the triple point.

2.10.1 Viscosity of Liquid Hydrogen

The viscosity of normal liquid hydrogen was measured by observing its flow through a variety of capillary tubes and the data are listed in Table 14. The resulting viscosities were about 10% higher than those obtained by [126] using an oscillating disc. Figure 19 compares liquid hydrogen viscosity data from three different sources [127].



**Figure 19:** Viscosity of liquid hydrogen. (Reprinted and modified from [127], with permission from ©1962 Elsevier; permission conveyed through RightsLink.)

Table 15 lists the density and viscosity of liquid parahydrogen as a function of temperature. The measurable difference in viscosity of saturated liquid normal and parahydrogen is illustrated in Figure 20.

**Table 14:** Viscosity of normal liquid hydrogen.

| Temperature |        | Viscosity |         |
|-------------|--------|-----------|---------|
| K           | °C     | mPa s     | cPs     |
| 15.0        | −258.1 | 0.02293   | 0.02293 |
| 16.2        | −256.9 | 0.02046   | 0.02046 |
| 17.7        | −255.4 | 0.01772   | 0.01772 |
| 18.7        | −254.4 | 0.01600   | 0.01600 |
| 19.2        | −253.9 | 0.01519   | 0.01519 |
| 20.6        | −252.5 | 0.01362   | 0.01362 |

Data source: [128]

**Table 15:** Density and viscosity of saturated liquid parahydrogen as a function of temperature.

| Temperature |                              | Viscosity                                             |         |
|-------------|------------------------------|-------------------------------------------------------|---------|
| K           | Density<br>g/cm <sup>3</sup> | g cm <sup>−1</sup> s <sup>−1</sup> × 10 <sup>−6</sup> | cPs     |
| 14.0        | 0.07685                      | 250.7                                                 | 0.02507 |
| 14.5        | 0.07643                      | 234.1                                                 | 0.02341 |
| 15.0        | 0.07599                      | 221.3                                                 | 0.02213 |
| 15.5        | 0.07555                      | 207.3                                                 | 0.02073 |
| 16.0        | 0.07510                      | 197.5                                                 | 0.01975 |
| 16.5        | 0.07464                      | 185.6                                                 | 0.01856 |
| 17.0        | 0.07417                      | 177.7                                                 | 0.01777 |
| 17.5        | 0.07368                      | 168.5                                                 | 0.01685 |
| 18.0        | 0.07319                      | 160.5                                                 | 0.01605 |
| 18.5        | 0.07268                      | 153.8                                                 | 0.01538 |
| 19.0        | 0.07216                      | 147.0                                                 | 0.01470 |
| 19.5        | 0.07163                      | 141.3                                                 | 0.01413 |
| 20.0        | 0.07108                      | 135.4                                                 | 0.01354 |
| 20.5        | 0.07052                      | 130.6                                                 | 0.01306 |
| 21.0        | 0.06994                      | 125.3                                                 | 0.01253 |
| 21.5        | 0.06934                      | 120.6                                                 | 0.01206 |
| 22.0        | 0.06872                      | 116.1                                                 | 0.01161 |
| 23.0        | 0.06741                      | 108.1                                                 | 0.01081 |
| 24.0        | 0.06601                      | 100.8                                                 | 0.01008 |
| 25.0        | 0.06449                      | 93.5                                                  | 0.00935 |
| 26.0        | 0.06283                      | 87.2                                                  | 0.00872 |
| 26.5        | 0.06194                      | 84.1                                                  | 0.00841 |
| 27.0        | 0.06100                      | 81.0                                                  | 0.00810 |
| 27.5        | 0.06001                      | 78.1                                                  | 0.00781 |
| 28.0        | 0.05896                      | 75.2                                                  | 0.00752 |
| 28.5        | 0.05784                      | 72.4                                                  | 0.00724 |
| 29.0        | 0.05664                      | 69.6                                                  | 0.00696 |
| 29.5        | 0.05534                      | 67.0                                                  | 0.00670 |

Table 15: (continued)

| Temperature | Density           | Viscosity                                             |         |
|-------------|-------------------|-------------------------------------------------------|---------|
| K           | g/cm <sup>3</sup> | g cm <sup>-1</sup> s <sup>-1</sup> × 10 <sup>-6</sup> | cPs     |
| 30.0        | 0.05393           | 64.9                                                  | 0.00649 |
| 30.5        | 0.05236           | 61.2                                                  | 0.00612 |
| 31.0        | 0.05058           | 58.1                                                  | 0.00581 |
| 31.5        | 0.04852           | 55.7                                                  | 0.00557 |
| 32.0        | 0.04599           | 51.9                                                  | 0.00519 |
| 32.5        | 0.04248           | 47.5                                                  | 0.00475 |
| 32.7        | 0.04041           | 43.9                                                  | 0.00439 |

Data source: [129]

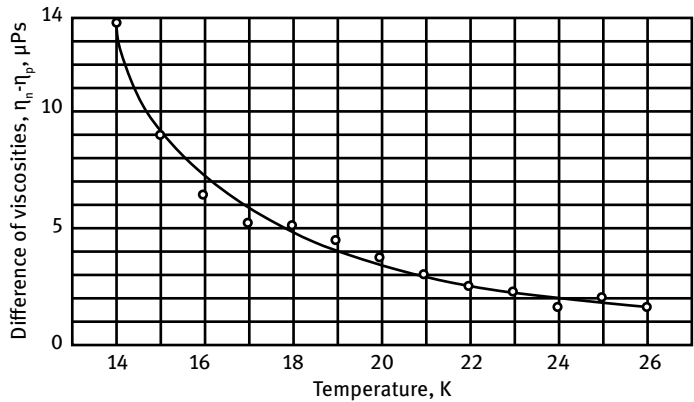
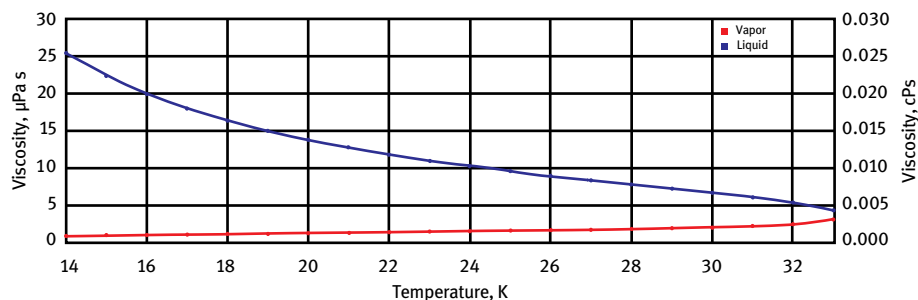


Figure 20: Viscosity difference between saturated liquid normal hydrogen and parahydrogen. (Reproduced and modified from [62]; based on data from Diller 1965.)

The viscosity of liquid hydrogen as a function of temperature can be displayed graphically or printed out as a table by an on-line app on the NIST Chemistry Web-Book Fluids web page [101]. A sample calculation for saturated hydrogen  $14 < T < 33$  K is shown in Figure 21.

The viscosity of liquid parahydrogen at just above the triple point is  $255.1 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}$  and at a temperature just below the boiling point it is  $132.0 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}$ . The viscosity of liquid hydrogen at the critical point is  $35.43 \times 10^{-7} \text{ kg m}^{-1} \text{ s}^{-1}$ .

A piezoelectric alpha quartz torsional oscillator technique was used to measure liquid hydrogen viscosity. There is only a minimal difference in the viscosity of liquid parahydrogen and non-equilibrium normal hydrogen at temperatures between 10 and 14 K [130].



**Figure 21:** Viscosity of liquid and gaseous hydrogen along the saturation line. (From NIST RefProp [101].)

The viscosity at 14 K of a liquid containing 68% orthohydrogen was 4% higher than that of a liquid containing only 28% orthohydrogen. Theoretical calculations predicted higher viscosity for gaseous orthohydrogen-rich equilibrium mixtures than for parahydrogen non-equilibrium gas, and the similar trend may be true for the liquid.

Fundamental transport properties of liquid parahydrogen ( $p\text{-H}_2$ ) including shear viscosity and bulk viscosity, have been evaluated over a wide temperature range, 14–32 K, by means of path integral centroid molecular dynamics (CMD) calculations [131]. For the bulk viscosity of liquid  $p\text{-H}_2$ , which was never known from experiments, the present CMD has given a clear temperature dependence. In addition, from the comparison based on the principle of corresponding states, it has been shown that the marked deviation of the transport properties of liquid  $p\text{-H}_2$  from the properties expected from the molecular parameters is due to the quantum effect.

A survey of experimental data for the viscosity of hydrogen, which is needed for many applications in system analysis and design, included an analysis of the current standard models for thermal conductivity and viscosity of normal hydrogen and parahydrogen, which are based on measurement and correlation work done before the mid-1980s, and collected more than 100 literature references on transport properties of hydrogen and a few on transport properties of parahydrogen [132]. Properties calculated with these models were analyzed and compared to all available experimental data for normal hydrogen and parahydrogen, and percent deviations of individual data sets from the computed mean were graphed.

A wide-ranging correlation for the viscosity of normal hydrogen covering the temperature range from the triple-point temperature to 1000 K and pressures up to 200 MPa was derived from literature data [133]. It can extrapolate to 2000 K with an estimated uncertainty of 4% for the saturated liquid from the triple point to 31 K, with larger deviations as the critical region is approached. The estimated uncertainty is 4% for the supercritical fluid phase at pressures to 200 MPa. For the limited range of 200–400 K at pressures up to 0.1 MPa, the uncertainty is 0.1%.



2.10.2 Viscosity of Gaseous Hydrogen

Table 16 lists viscosity data for gaseous hydrogen at atmospheric pressure.

Table 16: Viscosity of normal gaseous hydrogen.

| Temperature, K | Viscosity                       |                         |
|----------------|---------------------------------|-------------------------|
|                | $\text{N s}^{-1} \text{m}^{-2}$ | $\text{Ps} \times 10^7$ |
| 10             | $5.10 \times 10^{-7}$           | 51.0                    |
| 20             | $1.093 \times 10^{-6}$          | 109.3                   |
| 30             | $1.607 \times 10^{-6}$          | 160.7                   |
| 40             | $2.068 \times 10^{-6}$          | 206.8                   |
| 50             | $2.489 \times 10^{-6}$          | 248.9                   |
| 60             | $2.876 \times 10^{-6}$          | 287.6                   |
| 70             | $3.238 \times 10^{-6}$          | 323.8                   |
| 80             | $3.579 \times 10^{-6}$          | 357.9                   |
| 90             | $3.903 \times 10^{-6}$          | 390.3                   |
| 100            | $4.211 \times 10^{-6}$          | 421.1                   |
| 110            | $4.508 \times 10^{-6}$          | 450.8                   |
| 120            | $4.793 \times 10^{-6}$          | 479.3                   |
| 130            | $5.070 \times 10^{-6}$          | 507.0                   |
| 140            | $5.338 \times 10^{-6}$          | 533.8                   |
| 150            | $5.598 \times 10^{-6}$          | 559.8                   |
| 160            | $5.852 \times 10^{-6}$          | 585.2                   |
| 170            | $6.100 \times 10^{-6}$          | 610.0                   |
| 180            | $6.343 \times 10^{-6}$          | 634.3                   |
| 190            | $6.581 \times 10^{-6}$          | 658.1                   |
| 200            | $6.814 \times 10^{-6}$          | 681.4                   |
| 210            | $7.043 \times 10^{-6}$          | 704.3                   |
| 220            | $7.269 \times 10^{-6}$          | 726.9                   |
| 230            | $7.490 \times 10^{-6}$          | 749.0                   |
| 240            | $7.709 \times 10^{-6}$          | 770.9                   |
| 250            | $7.924 \times 10^{-6}$          | 792.4                   |
| 260            | $8.136 \times 10^{-6}$          | 813.6                   |
| 270            | $8.346 \times 10^{-6}$          | 834.6                   |
| 280            | $8.553 \times 10^{-6}$          | 855.3                   |
| 290            | $8.758 \times 10^{-6}$          | 875.8                   |
| 300            | $8.960 \times 10^{-6}$          | 896.0                   |
| 310            | $9.160 \times 10^{-6}$          | 916.0                   |
| 320            | $9.358 \times 10^{-6}$          | 935.8                   |
| 330            | $9.554 \times 10^{-6}$          | 955.4                   |
| 340            | $9.748 \times 10^{-6}$          | 974.8                   |
| 350            | $9.940 \times 10^{-6}$          | 994.0                   |
| 360            | $1.013 \times 10^{-5}$          | 1013                    |

Table 16: (continued)

| Temperature, K | Viscosity                      |                         |
|----------------|--------------------------------|-------------------------|
|                | $\text{Ns}^{-1} \text{m}^{-2}$ | $\text{Ps} \times 10^7$ |
| 370            | $1.032 \times 10^{-5}$         | 1032                    |
| 380            | $1.051 \times 10^{-5}$         | 1051                    |
| 390            | $1.069 \times 10^{-5}$         | 1069                    |
| 400            | $1.087 \times 10^{-5}$         | 1087                    |
| 420            | $1.124 \times 10^{-5}$         | 1124                    |
| 440            | $1.160 \times 10^{-5}$         | 1160                    |
| 460            | $1.195 \times 10^{-5}$         | 1195                    |
| 480            | $1.230 \times 10^{-5}$         | 1230                    |
| 500            | $1.264 \times 10^{-5}$         | 1264                    |
| 520            | $1.298 \times 10^{-5}$         | 1298                    |
| 540            | $1.331 \times 10^{-5}$         | 1331                    |
| 560            | $1.364 \times 10^{-5}$         | 1364                    |
| 580            | $1.397 \times 10^{-5}$         | 1397                    |
| 600            | $1.429 \times 10^{-5}$         | 1429                    |
| 620            | $1.461 \times 10^{-5}$         | 1461                    |
| 640            | $1.493 \times 10^{-5}$         | 1493                    |
| 660            | $1.524 \times 10^{-5}$         | 1524                    |
| 680            | $1.555 \times 10^{-5}$         | 1555                    |
| 700            | $1.585 \times 10^{-5}$         | 1585                    |
| 720            | $1.616 \times 10^{-5}$         | 1616                    |
| 740            | $1.646 \times 10^{-5}$         | 1646                    |
| 760            | $1.675 \times 10^{-5}$         | 1675                    |
| 780            | $1.705 \times 10^{-5}$         | 1705                    |
| 800            | $1.734 \times 10^{-5}$         | 1734                    |
| 820            | $1.763 \times 10^{-5}$         | 1763                    |
| 840            | $1.792 \times 10^{-5}$         | 1792                    |
| 860            | $1.820 \times 10^{-5}$         | 1820                    |
| 880            | $1.848 \times 10^{-5}$         | 1848                    |
| 900            | $1.876 \times 10^{-5}$         | 1876                    |
| 920            | $1.904 \times 10^{-5}$         | 1904                    |
| 940            | $1.932 \times 10^{-5}$         | 1932                    |
| 960            | $1.959 \times 10^{-5}$         | 1959                    |
| 980            | $1.986 \times 10^{-5}$         | 1986                    |
| 1000           | $2.013 \times 10^{-5}$         | 2013                    |
| 1020           | $2.040 \times 10^{-5}$         | 2040                    |
| 1040           | $2.066 \times 10^{-5}$         | 2066                    |
| 1060           | $2.092 \times 10^{-5}$         | 2092                    |
| 1080           | $2.118 \times 10^{-5}$         | 2118                    |
| 1100           | $2.144 \times 10^{-5}$         | 2144                    |

The viscosity of gaseous  $n\text{-H}_2$  at atmospheric pressure in the range from 13.97 to 1280 K can be represented by the following polynomial equation [134, 135].

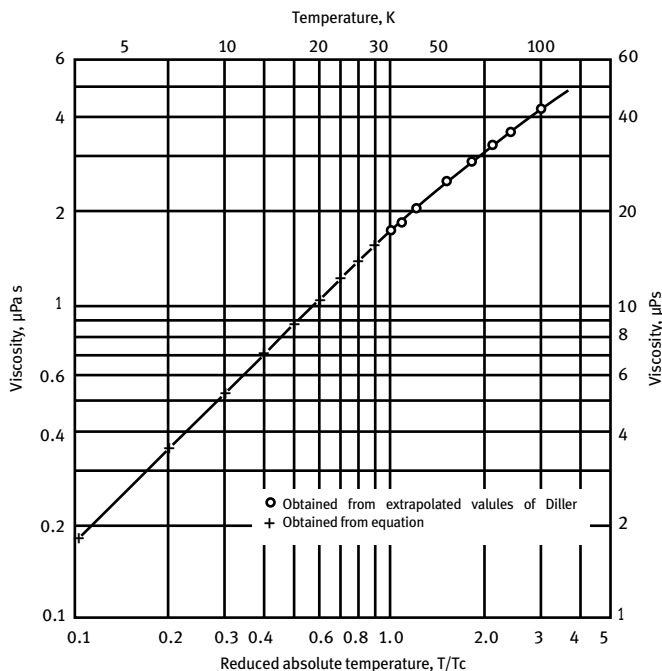
$$\eta = 2.105 + 0.4774 T - 9.9784 \times 10^{-4} T^2 + 1.61827 \times 10^{-6} T^3 \\ - 1.28024 \times 10^{-9} T^4 + 3.8164 \times 10^{-13} T^5$$

where  $\eta$  is the viscosity in micro Poise and  $T$  is the temperature in kelvin. The orthohydrogen-parahydrogen composition of gaseous hydrogen has no influence on the viscosity.

Plotting the logarithm of the viscosity of hydrogen versus the logarithm of the reduced temperature  $T/T_c$  gives almost a straight line, extending both below and above the critical point, expressed by the equation for temperatures up to 100 K

$$\mu_p^* = 1.004 \mu_n^{1.0019}$$

where  $\mu_p^*$  is the viscosity of gaseous parahydrogen at 1 atm and  $\mu_n$  is the viscosity of gaseous normal hydrogen at 1 atm, as shown in Figure 22, from [136]. The critical temperature used for these calculations was 32.976 K.



**Figure 22:** Viscosity of gaseous parahydrogen at atmospheric pressure and cryogenic temperatures. (Republished and modified from [136], with permission of ©1967 American Institute of Aeronautics & Astronautics; permission conveyed through Copyright Clearance Center Inc.)

Viscosity and density data of gaseous normal hydrogen at high pressures are listed in Table 17.

**Table 17:** Viscosity and density of gaseous normal hydrogen at high pressures.

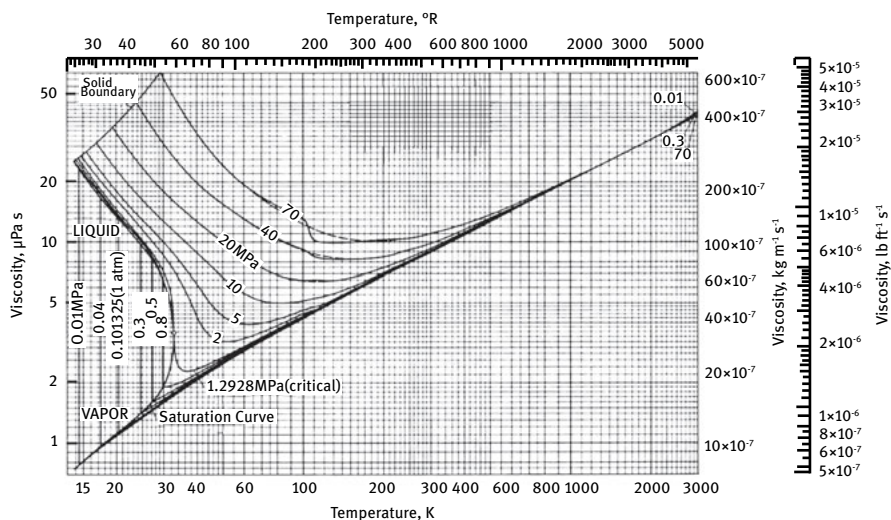
| Temperature |     | Pressure |       | Density           | Viscosity              |               |
|-------------|-----|----------|-------|-------------------|------------------------|---------------|
| K           | °C  | MPa      | atm   | g/cm <sup>3</sup> | Pa s × 10 <sup>7</sup> | micro-Poise   |
| 223         | −50 | 1.206    | 11.9  | 0.001299          | 72.81 ± 0.007          | 72.81 ± 0.007 |
| 223         | −50 | 3.293    | 32.5  | 0.003497          | 73.31 ± 0.03           | 73.31 ± 0.03  |
| 223         | −50 | 6.160    | 60.8  | 0.006417          | 73.91 ± 0.08           | 73.91 ± 0.08  |
| 248         | −25 | 1.115    | 11.0  | 0.001081          | 78.08 ± 0.10           | 78.08 ± 0.10  |
| 248         | −25 | 2.888    | 28.5  | 0.002768          | 78.62 ± 0.05           | 78.62 ± 0.05  |
| 248         | −25 | 4.882    | 48.18 | 0.004621          | 79.07 ± 0.07           | 79.07 ± 0.07  |
| 273         | 0.0 | 1.019    | 10.06 | 0.000899          | 83.76 ± 0.06           | 83.76 ± 0.06  |
| 273         | 0.0 | 2.933    | 28.95 | 0.002557          | 83.98 ± 0.03           | 83.98 ± 0.03  |
| 273         | 0.0 | 5.050    | 49.84 | 0.004345          | 84.35 ± 0.08           | 84.35 ± 0.08  |

Data source: [137], which contains data for pressures up to 200 atm

Experimental values for the viscosity of hydrogen at atmospheric pressure were gathered from the literature and plotted against the reduced temperature. A viscosity correlation for hydrogen has been developed for reduced temperatures up to  $T_R = 75$  (at which point dissociation becomes noticeable) and reduced pressures up to  $P_R = 100$ , see [138]. Experimental viscosities available in the literature for hydrogen at moderate pressures were used to establish the atmospheric pressure viscosity behavior of hydrogen. For each experimental high-density value, the residual viscosity,  $\mu - \mu^*$ , was determined from the atmospheric pressure relationship and plotted against reduced density to produce a continuous curve for both the gaseous and liquid regions. This information enabled a plot of viscosity against reduced temperature and reduced pressure to be developed for hydrogen. No significant difference exists between the viscosities of orthohydrogen and parahydrogen. Viscosity values of dissociating hydrogen for temperatures up to 5000 K were obtained from reported theoretical calculations and were plotted against temperature for constant pressures.

Measurements of the viscosity and thermal conductivity of gaseous parahydrogen and normal hydrogen from 15 to 5000 K, including the dissociation region, were critically evaluated and correlated by means of a dilute gas kinetic theory [139].

Figure 23 shows the viscosity of liquid and gaseous hydrogen over a wide range of temperatures and pressures. At the coarse scale of this graph, there is no noticeable difference in the viscosity of parahydrogen or normal hydrogen.



**Figure 23:** Dynamic viscosity of liquid and gaseous hydrogen at high pressures. (Reproduced and modified from [41].)

Using appropriate force constants and a collision integral for the Chapman-Enskog solution the viscosity of hydrogen gas can be estimated [140]. At high density, modification of Diller's extrapolation equation for excess viscosity gave good agreement with the available experimental data. A combination of the Chapman-Enskog solution and modification of Diller's excess viscosity gave estimated hydrogen gas viscosity within 2–4% deviation from the existing experimental data for the high-temperature and high-pressure region.

A capillary tube viscometer was used to measure the dynamic viscosity of hydrogen under high pressures and at high temperatures [141]. A differential pressure sensor for high pressures up to 100 MPa was not commercially available. Instead, a pair of accurate absolute pressure transducers was used as a differential pressure sensor and the pressure drop was calculated by subtracting the outlet pressure from the inlet pressure with a resolution of 100 Pa at 100 MPa. The apparatus provided viscosities of hydrogen from ambient temperature up to 400 K and for pressures up to 100 MPa with a maximum deviation of 2.2%. Another way to measure the viscosity of hydrogen gas is by a vibrating wire method [142]. The viscosity of hydrogen at temperatures of 296–573 K and under pressures of up to 0.7 MPa were measured by a vibrating wire method with an uncertainty of 1.4% [143].

### 2.10.3 Flow Properties of Slush Hydrogen

While it is relatively easy to measure flow properties of a homogeneous fluid, measuring viscosity of a two-phase heterogeneous suspension of solid hydrogen in liquid hydrogen is a more difficult task. Slush hydrogen pressurized expulsion tests were performed to provide experimental data on pressurant gas requirements, ullage and tank wall temperature distributions, and slush hydrogen density changes. The tests used gaseous hydrogen pressurant during the expulsion of normal boiling point liquid hydrogen and slush hydrogen from a 1.89-m<sup>3</sup> (500-gallon) spherical tank. Expulsion test data obtained for the slush hydrogen and normal boiling point hydrogen experiments were compared with predictions from an analytical model. A computer program (EXPL) was used to model pressurant gas requirements, 1-D wall and ullage gas temperatures, and slush hydrogen density changes during pressurized expulsion.

## 2.11 Surface Tension of Hydrogen

Surface tension data of liquid normal hydrogen are listed in Table 18 and illustrated in Figure 25.

**Table 18:** Surface tension of normal, liquid hydrogen.

| Temperature, K | Surface tension |        |
|----------------|-----------------|--------|
|                | N/m             | dyn/cm |
| 13.0           | 0.00349         | 3.49   |
| 15.0           | 0.00313         | 3.13   |
| 20.0           | 0.00223         | 2.23   |
| 25.0           | 0.00133         | 1.33   |

Data source: [144]

The surface tension as a function of temperature is a linear function and can be calculated from

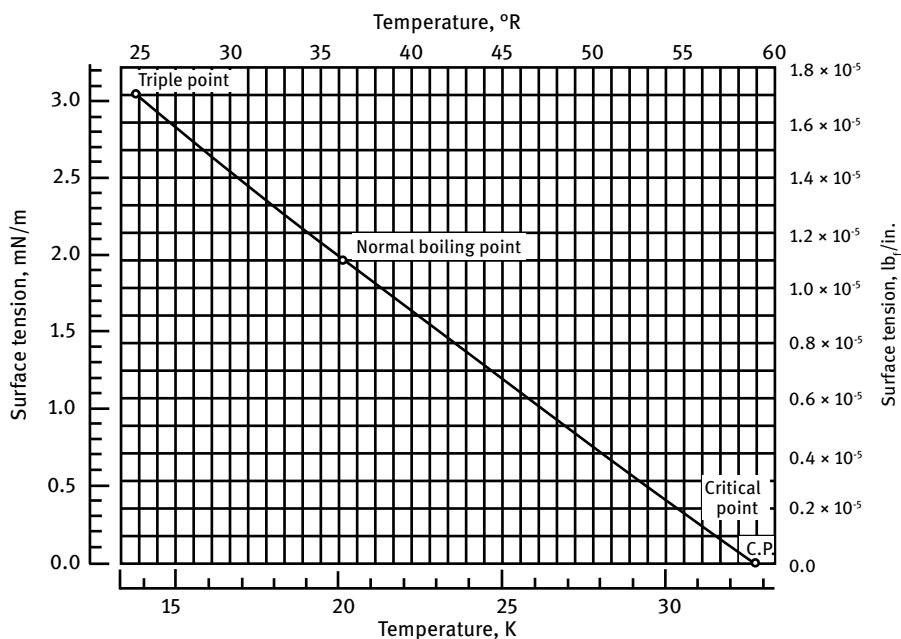
$$\sigma = 5.83 - 0.18 T$$

where  $\sigma$  is the surface tension in dyn/cm and  $T$  is the absolute temperature in kelvin. This equation is similar to

$$\sigma = \sigma_0 - \left(1 - \frac{T}{T_c}\right)$$

where  $\sigma$  is the surface tension in dyn/cm,  $\sigma_0$  is 5.328 for parahydrogen, and 5.369 for normal hydrogen,  $T$  is the temperature in kelvin, and  $T_c$  is the critical temperature.  $T_c$

is 32.976 K for parahydrogen and 33.18 K for normal hydrogen. The surface tension of liquid parahydrogen is 0.0029 N/m at the triple point and 0.00193 N/m at the normal boiling point. The surface tension of liquid normal hydrogen is 0.003 N/m at the triple point and 0.00195 N/m at the normal boiling point. The surface tension of parahydrogen is illustrated in Figure 24.



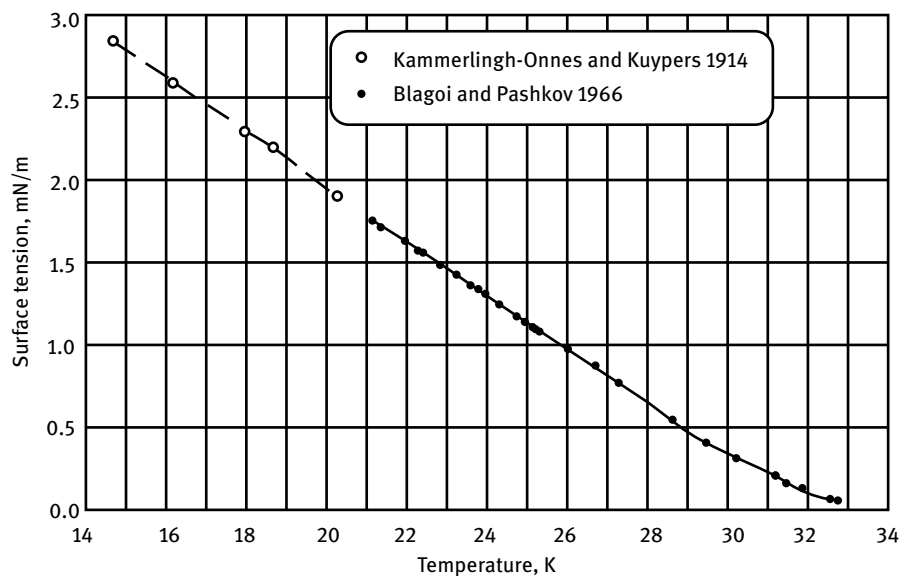
**Figure 24:** Surface tension of parahydrogen. (Reproduced and modified from [41].)

For temperatures higher than about 21 K only the measurements by Blagoi and Pashkov on normal hydrogen are available [145]. In the temperature range below 26–27 K, the surface tension can be calculated from

$$\sigma = 5.38 - 0.170T \pm 0.02$$

where  $\sigma$  is the surface tension in dyn/cm and  $T$  is the temperature in kelvin. These data are illustrated in Figure 25.

A comparison of the measurements by Blagoi and Pashkov on normal hydrogen with the equations proposed by Corruccini showed that extrapolation of the equations to temperatures above about 22 K leads to sizeable differences at the higher temperatures. Table 19 is a comparison of the Corruccini data and the Blagoi and Pashkov data. The Blagoi and Pashkov data are consistently about  $70 \times 10^{-6}$  N/m (0.07 dyn/cm) lower at all temperatures below 31.5 K than those calculated from the above equation and are considered not very accurate. See also [146].



**Figure 25:** Surface tension of hydrogen. (Chart created by Schmidt 2021 based on numerical data from [145].)

**Table 19:** Comparison of surface tension of hydrogen data.

| Data source                   | Corrucini [75]           |                          | Blagoi and Pashkov [145] |        |       |        |
|-------------------------------|--------------------------|--------------------------|--------------------------|--------|-------|--------|
|                               | <i>p</i> -H <sub>2</sub> | <i>n</i> -H <sub>2</sub> | <i>n</i> -H <sub>2</sub> |        |       |        |
| K                             | dyn/cm                   | dyn/cm                   | K                        | dyn/cm | K     | dyn/cm |
| 13.803 (triple point)         | 2.990                    | —                        | 21.15                    | 1.755  | 24.77 | 1.171  |
| 13.947 (triple point)         | 3.004                    | —                        | 21.40                    | 1.715  | 24.98 | 1.136  |
| 14                            | 2.958                    | 2.995                    | 21.98                    | 1.633  | 25.16 | 1.100  |
| 15                            | 2.792                    | 2.829                    | 22.13                    | 1.594  | 25.25 | 1.089  |
| 16                            | 2.627                    | 2.663                    | 22.31                    | 1.575  | 25.37 | 1.073  |
| 17                            | 2.462                    | 2.498                    | 22.43                    | 1.565  | 26.05 | 0.969  |
| 18                            | 2.298                    | 2.334                    | 22.65                    | 1.516  | 26.72 | 0.869  |
| 19                            | 2.135                    | 2.171                    | 22.83                    | 1.502  | 27.31 | 0.767  |
| 20                            | 1.973                    | 2.008                    | 22.84                    | 1.486  | 28.68 | 0.540  |
| 20.268 (normal boiling point) | 1.930                    | —                        | 22.86                    | 1.481  | 29.49 | 0.401  |
| 20.38 (normal boiling point)  | 1.946                    | —                        | 23.25                    | 1.431  | 30.27 | 0.303  |
| 23.28                         | 1.421                    | —                        | —                        | —      | 31.23 | 0.193  |
| 23.62                         | 1.361                    | —                        | —                        | —      | 31.49 | 0.149  |
| 23.80                         | 1.351                    | —                        | —                        | —      | 31.90 | 0.116  |
| 23.98                         | 1.307                    | —                        | —                        | —      | 32.57 | 0.053  |
| 24.33                         | 1.244                    | —                        | —                        | —      | 32.77 | 0.0459 |



## 2.12 Thermal Conductivity of Hydrogen

### 2.12.1 Thermal Conductivity of Solid Hydrogen

The thermal conductivity of solid hydrogen, similar to the heat capacity, is highly dependent on the orthohydrogen-parahydrogen composition. It also depends on crystal quality and on density for the compressed solid states. Most of the measurements were made at or near saturation pressure. The thermal conductivity of solid 99% parahydrogen with 1% orthohydrogen is at a maximum at 4 K. Some of the data reported in the literature differed by almost an order of magnitude. The thermal conductivity of solid hydrogen must be known to predict the behavior of hydrogen particles in hydrogen slush as they freeze or melt.

The thermal conductivity of solid  $p\text{-H}_2$  was measured under three sets of conditions, ranging from 8.92 MPa (88 atm) pressure at 15 K to 20.37 MPa (201 atm) at 17 K [100]. These thermal conductivity data, combined with values from the literature, are shown in Figure 26. From this figure it can be seen that the thermal conductivity of solid  $p\text{-H}_2$  changes very little with an increase of either temperature or pressure at temperatures above 11 K. All three measured values fall in the range 0.086–0.0100  $\text{W cm}^{-1} \text{K}^{-1}$ . It can be seen that the values in this range are about four times as high as those for liquid  $p\text{-H}_2$ . The curves in Figure 26 are similar to those

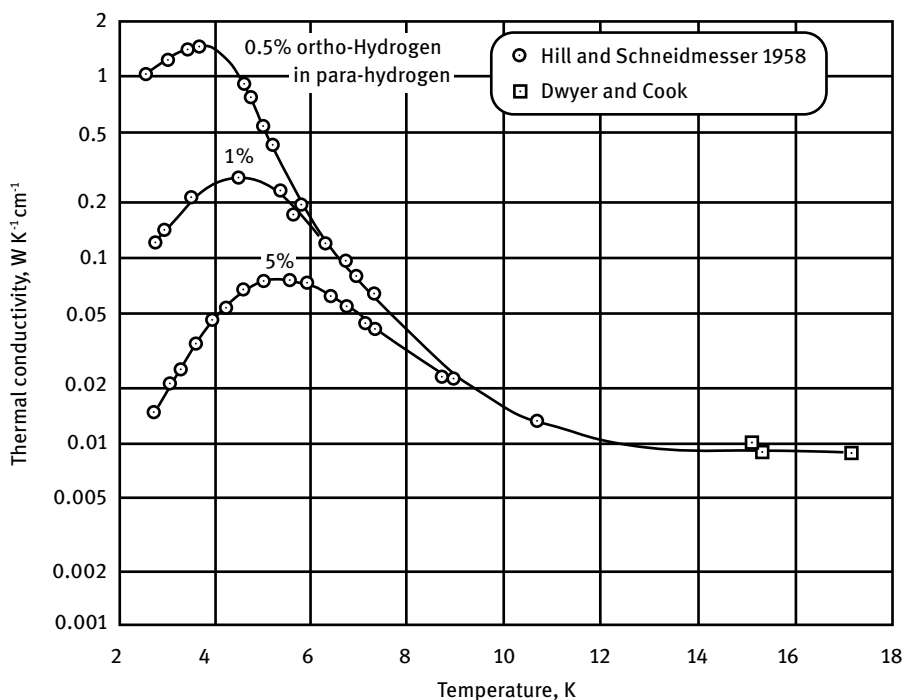
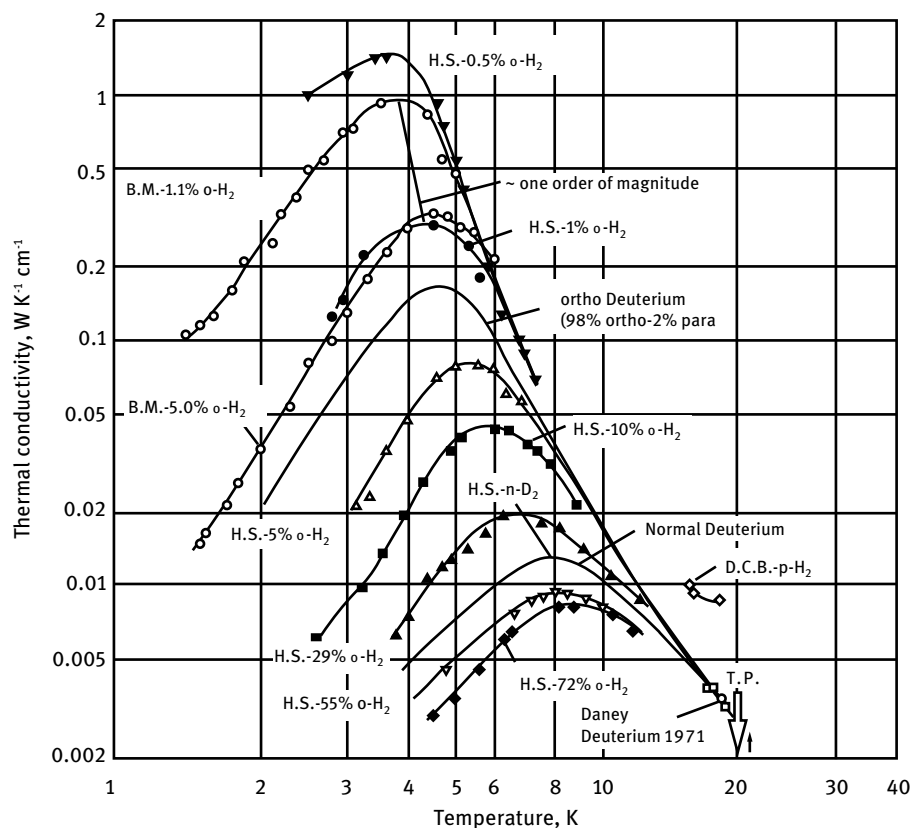


Figure 26: Thermal conductivity of solid hydrogen. (Reproduced and modified from [100].)

shown in Figure 42 on page 5–46 of [41], except that the graph also shows data for hydrogen containing 10, 29, 55, and 72% orthohydrogen and also for deuterium, as shown here in Figure 27. Deuterium is not used as a rocket propellant, but it may be used in chemical lasers. The two curves based on data from two different authors for hydrogen with 1% orthohydrogen differ by almost an order of magnitude. This chart is very busy and should have been separated into one for hydrogen and one for deuterium.



**Figure 27:** Thermal conductivity of solid hydrogen. (Reproduced and modified from [41].)

Legend: H.S. = Hill and Schneidmesser 1958; B.M. = Bohn and Mate 1970; D.C.B. = Dwyer, Cook, and Berwaldt 1966

Hill and Schneidmesser [147] published measurements of the thermal conductivity of solid hydrogen as a function of its  $o\text{-H}_2$  content. The  $o\text{-H}_2$  concentration was not determined analytically, but was inferred from the method of preparation; no further details were given.

The thermal conductivity of solid parahydrogen containing 0.2–5% orthohydrogen was measured over the temperature range 1.5–6 K [148]. On the low-temperature side of the conductivity maximum, the conductivity showed both a  $T^3$  dependence and a strong dependence on orthohydrogen concentration.

### 2.12.2 Thermal Conductivity of Liquid Hydrogen

The thermal conductivities of liquid normal and liquid parahydrogen have been measured over the temperature interval 13–27 K [87]. They were found to be independent of the orthohydrogen-parahydrogen composition and can be expressed by the equation

$$k = (1.702 + 0.05573T) \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^\circ\text{C}^{-1}.$$

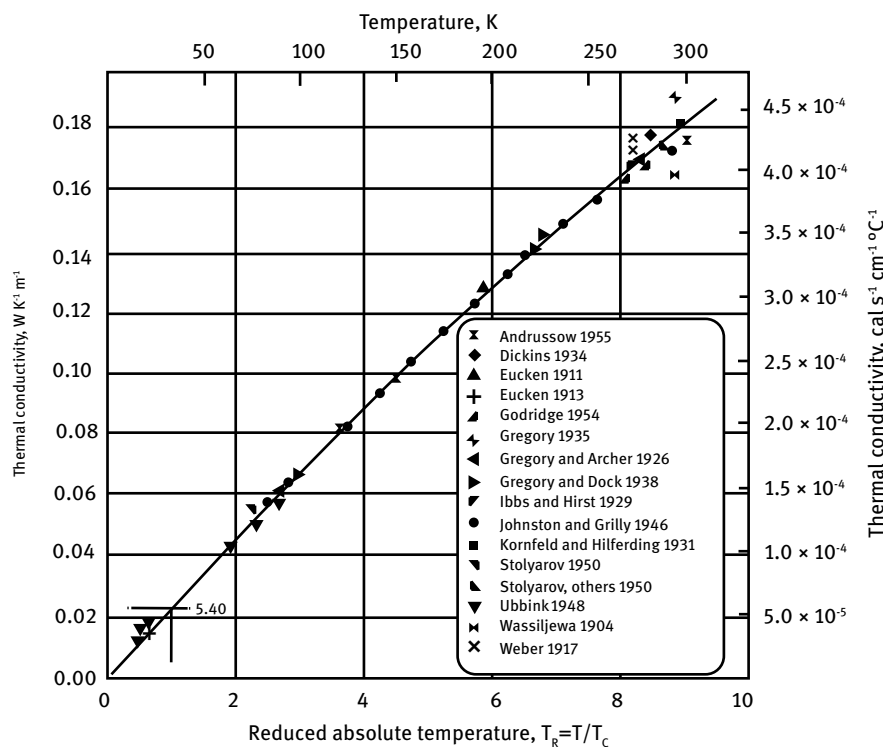
It was believed that the probable error was within 2%, but later examination showed that the Powers, Mattox, and Johnston 1954 [87] data were substantially higher than the more accurate numbers measured later.

Taking thermal conductivity data for liquid hydrogen from almost a dozen different quite antiquated sources and plotting them against the reduced temperature normalized by the critical temperature (33.3 K) gives an almost linear relationship as shown in Figure 28 [149].

For data on the thermal conductivity of liquid hydrogen see also [150]. The thermal conductivity of gaseous and liquid hydrogen has been measured with a guarded horizontal flat-plate calorimeter at temperatures between 17 and 200 K and at pressures up to 15 MPa [70, 151]. The data have been analyzed as a function of density at fixed temperatures and as a function of temperature at fixed densities. Outside the critical region the thermal conductivity of both the gas and the liquid increases continuously with temperature and density. In the compressed liquid the temperature derivative at fixed density is positive and unusually large compared to that for most other simple liquids. In the critical region the thermal conductivity increases rapidly with both temperature and density as these parameters approach their critical values.

The thermal conductivity of liquid hydrogen depends on temperature and is particularly sensitive to density. Its behavior is related to that of  $C_v$  and  $C_p$ . For temperatures up to the critical point the thermal conductivity shows very little dependence on orthohydrogen-parahydrogen composition. Values for the thermal conductivity of liquid hydrogen are uncertain by about 3%. Differences in experimental values reported by various investigators have been attributed to convection.

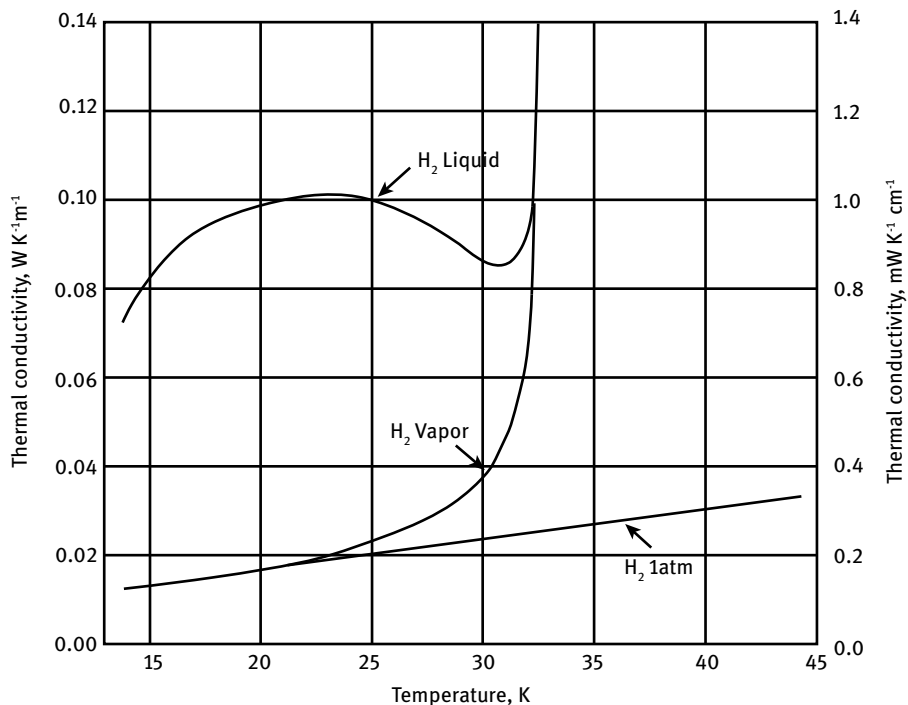
Surveys of information on hydrogen thermal conductivity also included hydrogen isotopes [70]. The thermal conductivities of liquid and gaseous hydrogen are illustrated in Figure 29. The difference between the two physical states diminishes as the temperature approaches the critical point. Similar data are available for the other two hydrogen isotopes.



**Figure 28:** Thermal conductivity of liquid hydrogen versus reduced temperature. (Reprinted and adapted from [149], with permission from ©1958 American Chemical Society; permission conveyed through RightsLink.)

The thermal conductivity of liquid parahydrogen was measured at temperatures from 15.4 to 21.4 K at pressures from below atmospheric to 21.8 MPa (215 atm), [100]. All measured thermal conductivities for liquid  $p$ -H<sub>2</sub> were in the range from 0.0014 to 0.0036 W cm<sup>-1</sup> K<sup>-1</sup>.

Fundamental transport properties of liquid paraparahydrogen ( $p$ -H<sub>2</sub>), i.e., thermal conductivity, diffusion coefficients, shear viscosity, and bulk viscosity, have been evaluated over a wide temperature range, 14–32 K, by means of path integral centroid molecular dynamics (CMD) calculations [131]. Although a relatively large deviation was found for the thermal conductivity, the calculated values are less than three times the amount of the experimental values at any temperature. From the comparison based on the principle of corresponding states, it has been shown that the marked deviation of the transport properties of liquid  $p$ -H<sub>2</sub> from the properties expected from the molecular parameters is due to the quantum effect.

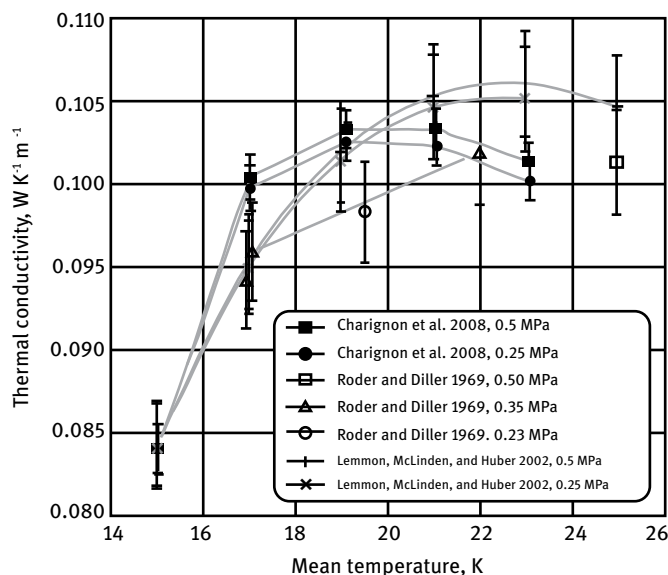


**Figure 29:** Thermal conductivity of liquid and gaseous hydrogen. (Reproduced and modified from [70].)

A survey of experimental data for the thermal conductivity and viscosity of hydrogen, physical properties which are needed for many applications in system analysis and design, included an analysis of the current standard models for thermal conductivity and viscosity of normal hydrogen and parahydrogen, which are based on measurement and correlation work done before the mid-1980s, and collected more than 100 literature references on transport properties of hydrogen and a few on transport properties of parahydrogen [132]. Properties calculated with these models were analyzed and compared to all available experimental data for normal hydrogen and parahydrogen, and percent deviations of individual data sets from the computed mean were graphed.

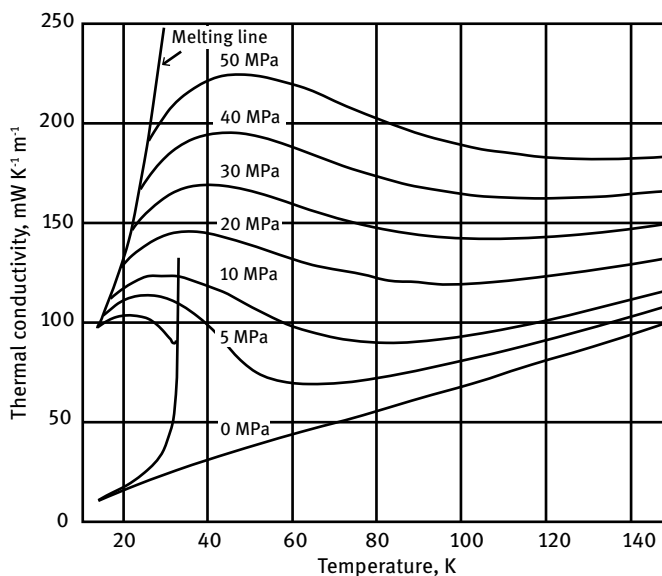
Thermal conductivity measurements of subcooled equilibrium liquid hydrogen in the temperature range from 15 to 23 K and under pressures up to 1 MPa were done in a horizontal, guarded, flat-plate calorimeter [152], Figure 30. One-dimensional heat transfer between the hot and the cold plates of the calorimeter was achieved by the placement of two thermal guards. Capacitance measurement between the calorimeter plates gave a precise and accurate value for the gap. Knowledge of the density

dependence on the thermal conductivity is useful for subcooled hydrogen transport processes. One should note that the distinction between equilibrium hydrogen and parahydrogen is insignificant in this case as equilibrium hydrogen is 99.8+% parahydrogen in the indicated temperature range. Writers often refer to liquid hydrogen with the implication that it is in the equilibrium state. The addition of uncertainty bars to Figure 30 makes it a little more difficult to read data.



**Figure 30:** Thermal conductivity of liquid hydrogen measurement results at constant pressures. (Reprinted and modified from [152] with the permission of ©2008 AIP Publishing)

A correlation of the thermal conductivity of liquid normal and parahydrogen from the triple point to 1000 K and up to 100 MPa contains a list of 13 primary data sources and 40 secondary data sources of thermal conductivity of hydrogen from the literature [153]. The literature data were fitted into a set of correlation equations and their deviations from the calculated mean were shown. The equations were based in part on a body of experimental data that has been critically assessed for internal consistency and for agreement with theory whenever possible. Figure 31 shows a plot of the thermal conductivity of normal liquid hydrogen values calculated by 7 different equations for the temperature range 14–150 K for pressures between 0 and 50 MPa. Note that the units on the abscissa scale shown in Assael et al. 2011 should be  $mW K^{-1} m^{-1}$  and not  $W K^{-1} m^{-1}$ .



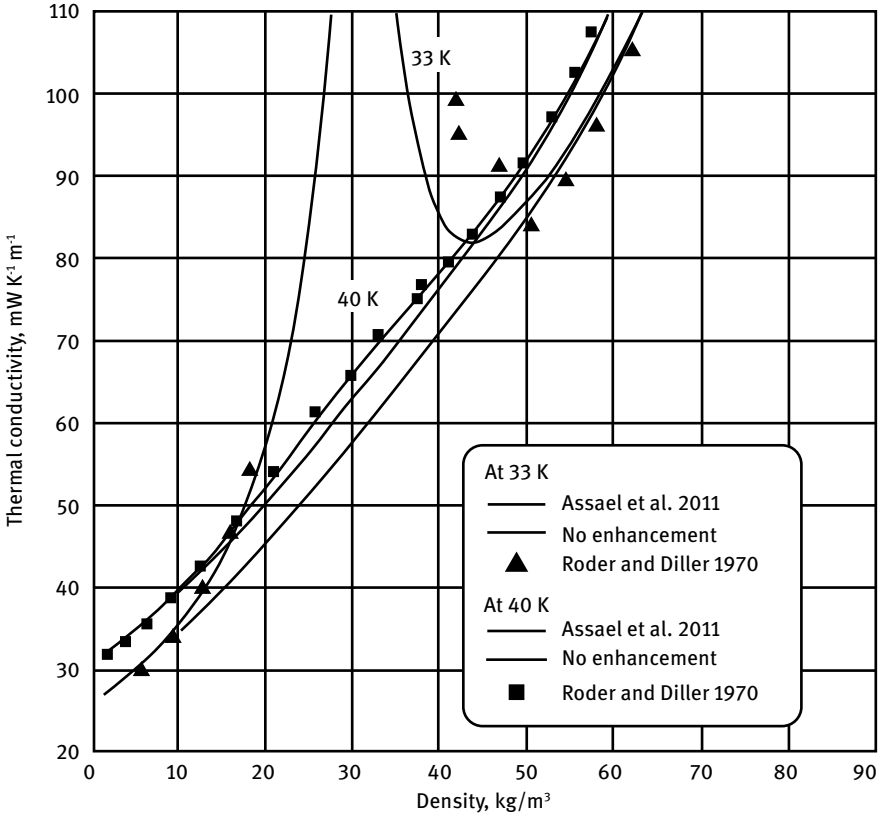
**Figure 31:** Thermal conductivity of normal hydrogen as a function of the temperature for different pressures. (Republished and modified from [153], with permission of ©2011 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

Figure 32 shows the thermal conductivity of liquid parahydrogen as a function of density for two isotherms that exhibit critical enhancement. The model is shown with and without the critical enhancement term. The experimental data of Roder and Diller 1970 are plotted at nominal isotherms of 33 and 40 K using the experimental values of temperature and density.

The thermal conductivity of a classical fluid is a function of the density  $\rho$  and the temperature  $T$ . Various molecular theories of thermal conductivity including those based on a pseudo-lattice model of the liquid state have been examined to determine whether they predict the sign and magnitude of the separation of the low-temperature isotherms [154]. They can only be applied to the dense fluid as the relevant deviations also occur at low temperatures and high densities. The lattice theories have been used to explain the thermal conductivities of simple liquids below the critical temperature, where they are relatively small.

### 2.12.3 Thermal Conductivity of Gaseous Hydrogen

The thermal conductivity of hydrogen gas depends primarily on temperature and on density or pressure (Table 20).



**Figure 32:** Thermal conductivity of parahydrogen as a function of density for 33 and 40 K isotherms. (Republished and modified from [153], with permission of ©2011 American Institute of Physics; permission conveyed through Copyright Clearance Center Inc.)

**Table 20:** Calculated thermal conductivity of gaseous hydrogen at 1atm.

| Temperature<br>K | Thermal conductivity             |                                                               |
|------------------|----------------------------------|---------------------------------------------------------------|
|                  | $\text{mW m}^{-1} \text{K}^{-1}$ | $\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1} \times 10^6$ |
| 10               | 5.98                             | 14.3                                                          |
| 20               | 14.48                            | 34.6                                                          |
| 30               | 22.38                            | 53.5                                                          |
| 40               | 29.58                            | 70.7                                                          |
| 50               | 36.19                            | 86.5                                                          |
| 60               | 42.43                            | 101.4                                                         |
| 70               | 48.58                            | 116.1                                                         |
| 80               | 54.73                            | 130.8                                                         |
| 90               | 61.04                            | 145.9                                                         |



Table 20: (continued)

| Temperature<br>K | Thermal conductivity             |                                                               |
|------------------|----------------------------------|---------------------------------------------------------------|
|                  | $\text{mW m}^{-1} \text{K}^{-1}$ | $\text{cal s}^{-1} \text{cm}^{-1} \text{°C}^{-1} \times 10^6$ |
| 100              | 67.49                            | 161.3                                                         |
| 110              | 74.06                            | 177.0                                                         |
| 120              | 80.71                            | 192.9                                                         |
| 130              | 87.36                            | 208.8                                                         |
| 140              | 93.97                            | 224.6                                                         |
| 150              | 100.6                            | 240.4                                                         |
| 160              | 107.1                            | 256.0                                                         |
| 170              | 113.6                            | 271.4                                                         |
| 180              | 119.9                            | 286.5                                                         |
| 190              | 126.0                            | 301.1                                                         |
| 200              | 132.0                            | 315.4                                                         |
| 210              | 137.9                            | 329.6                                                         |
| 220              | 143.7                            | 343.5                                                         |
| 230              | 149.5                            | 357.2                                                         |
| 240              | 155.1                            | 370.7                                                         |
| 250              | 160.7                            | 384.0                                                         |
| 260              | 166.1                            | 397.0                                                         |
| 270              | 171.4                            | 409.7                                                         |
| 280              | 176.6                            | 422.1                                                         |
| 290              | 181.7                            | 434.2                                                         |
| 300              | 186.7                            | 446.3                                                         |
| 320              | 196.6                            | 469.8                                                         |
| 340              | 206.2                            | 492.8                                                         |
| 360              | 215.5                            | 515                                                           |
| 380              | 224.7                            | 537                                                           |
| 400              | 233.9                            | 559                                                           |
| 420              | 242.7                            | 580                                                           |
| 440              | 251.5                            | 601                                                           |
| 460              | 260.2                            | 622                                                           |
| 480              | 269.0                            | 643                                                           |
| 500              | 277.8                            | 664                                                           |
| 520              | 286.2                            | 684                                                           |
| 540              | 295.0                            | 705                                                           |
| 560              | 303.3                            | 725                                                           |
| 580              | 311.7                            | 745                                                           |
| 600              | 320.5                            | 766                                                           |

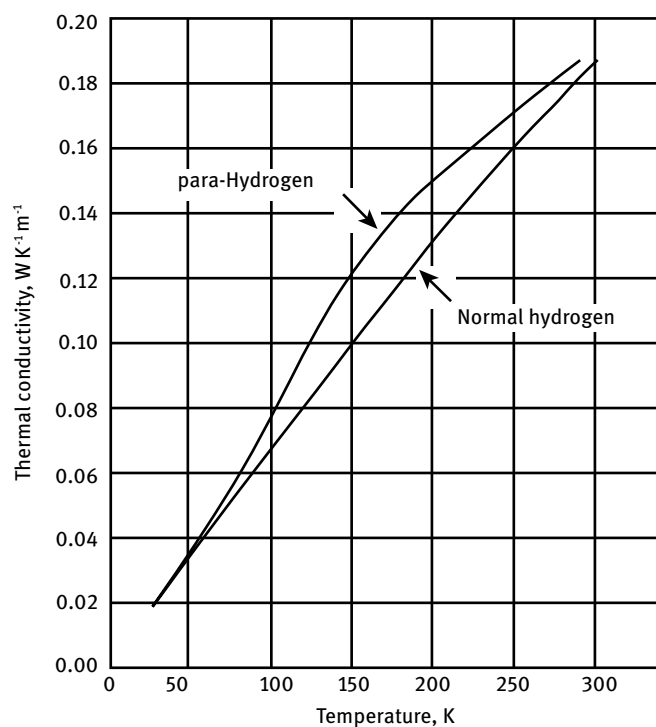
Data source: [61]

The thermal conductivity of gaseous normal hydrogen at 1 atm for the range from 20 to 2000 K can be calculated from the following equation [134]:

$$\lambda = \left( 1.8052 T - 1.4829 \times 10^{-3} T^2 + 1.2481 \times 10^{-6} T^3 - 4.195 \times 10^{-10} T^4 + 4.6302 \times 10^{-14} T^5 \right) \times 10^{-6}$$

where  $T$  is the temperature in kelvin and  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$ .

The thermal conductivity of gaseous parahydrogen and normal hydrogen diverge in the range from 100 to 250 K. The ratios of the two thermal conductivities are listed in Table 21 and illustrated in Figure 33.



**Figure 33:** Thermal conductivity of gaseous parahydrogen and normal hydrogen. (Reproduced and modified from [144], based on data from Farkas 1935.)

**Table 21:** Ratio of thermal conductivities of gaseous normal and parahydrogen

| Temperature, K | Ratio $\lambda_p/\lambda_n$ |
|----------------|-----------------------------|
| 40             | 1.001                       |
| 50             | 1.004                       |
| 75             | 1.051                       |
| 100            | 1.136                       |
| 125            | 1.196                       |
| 150            | 1.203                       |
| 175            | 1.175                       |
| 200            | 1.135                       |
| 225            | 1.096                       |
| 250            | 1.065                       |
| 275            | 1.044                       |
| 298            | 1.030                       |

Data source: [144]

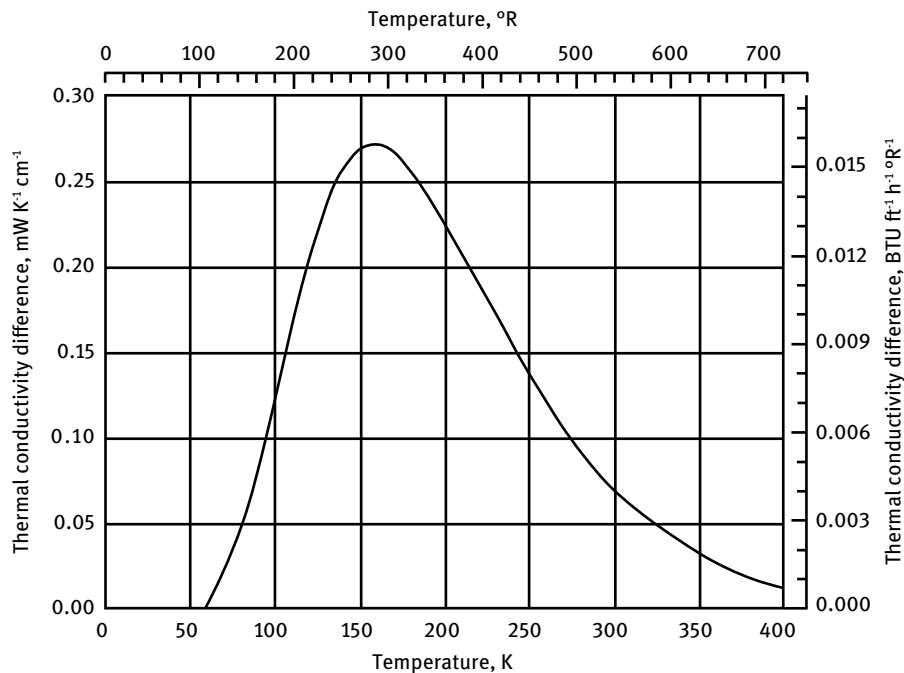
For temperatures below the critical point the dependence on orthohydrogen-parahydrogen composition is only very slight ~0.5%, but the difference reaches a maximum at 160 K (Figure 34). The difference in thermal conductivity can be used to analyze the parahydrogen content of hydrogen gas.

The difference in thermal conductivity between parahydrogen and normal hydrogen, noticeable only in a narrow range between 100 and 300 K, can be used for the determination of parahydrogen content in hydrogen gas samples. One must make sure that no catalysts are in the thermal conductivity measurement apparatus, otherwise the composition of the sample would change while the measurement is in progress. The gas flow could be measured first, then passed over a catalyst to allow it to equilibrate, and then measured again. This can be done with a pair of thermistors in a Wheatstone bridge circuit.

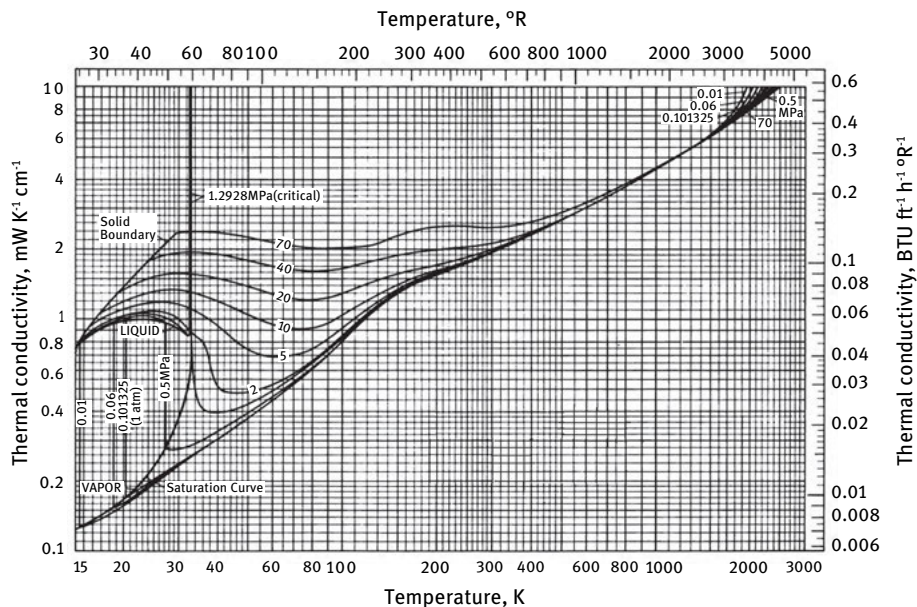
The thermal conductivity of hydrogen was determined indirectly from measured effective thermal conductivities of porous tungsten specimens in a pressurized hydrogen atmosphere. Measurements were made at pressures of 1.03, 0.69, 0.34, and 0.1 MPa (150, 100, 50, and 15 psia) and at temperatures to 2866 K (4700 °F) [155, 156].

The thermal conductivity of liquid hydrogen rises infinitely steep at the critical point (Figure 35). The auxiliary parameter shown in line with the curves is the pressure in MPa. The thermal conductivity of liquid parahydrogen at the triple point is  $0.7259 \text{ mW cm}^{-1} \text{ K}^{-1}$ , and it is  $0.9892 \text{ mW cm}^{-1} \text{ K}^{-1}$  at the normal boiling point. The thermal conductivity of normal liquid hydrogen is the same as that of parahydrogen. The thermal conductivity of gaseous hydrogen is  $0.1243 \text{ mW cm}^{-1} \text{ K}^{-1}$  at the triple point and  $0.1694 \text{ mW cm}^{-1} \text{ K}^{-1}$  at the normal boiling point.

Thermal conductivity measurements of normal, near normal, parahydrogen, and parahydrogen-rich hydrogen were made with a transient hot wire apparatus over the temperature range from 78 to 310 K with pressures to 70 MPa and densities from 0 to



**Figure 34:** Differences in thermal conductivity between parahydrogen and normal hydrogen. (Invariant with pressure, reproduced and modified from [41].)



**Figure 35:** Thermal conductivity of parahydrogen. (Reproduced and modified from [41].)

a maximum of 40 mol/L [157, 158]. For compositions normal and near normal, the isotherms covered the entire range of pressure, and the temperatures were 78, 100, 125, 150, 175, 200, 225, 250, 275, 294, 300, and 310 K. The  $p$ -H<sub>2</sub> measurements included eight isotherms at temperatures from 100 to 275 K with intervals of 25 K, pressures to 12 MPa, and densities from 0 to 12 mol/L. Three additional isotherms at 150, 250, and 275 K covered  $p$ -H<sub>2</sub>-rich compositions with parahydrogen percentages varying from 85 to 72%. The data for all compositions are represented by a single thermal conductivity surface.

Calculations of the viscosity and thermal conductivity coefficients of normal hydrogen in the limit of zero density as a function of temperature were based upon the semi-classical kinetic theory of polyatomic gases and a body of critically evaluated experimental data [159]. The available thermal conductivity data of high accuracy cover the much more restricted temperature range from 100 to 400 K and the correlation of this property is limited to that range. An attempt has been made to represent the viscosity data by means of a correlation universal among several other polyatomic gases but it has proven unsatisfactory for hydrogen. An extension of the temperature range of the thermal conductivity correlation based upon the Wang, Chang, and Uhlenbeck kinetic theory also failed to produce acceptable results.

The thermal conductivity for normal hydrogen gas was measured in the range of temperatures from 323 to 773 K at pressures up to 99 MPa using a transient short hot-wire method [160]. An existing thermal conductivity equation of state was modified to include the expanded range of conditions measure. The new correlation is applicable from 78 to 773 K with pressures to 100 MPa and is in agreement with the majority of the reported thermal conductivity measurements within  $\pm 2\%$ .

The thermal conductivities and thermal diffusivities of hydrogen gas were measured with a transient short hot-wire method for temperature range up to 573 K (300 °C) and pressure range up to 100 MPa [161]. The measured thermal conductivities showed good reproducibility and agreed with the existing values within a deviation of  $\pm 2\%$ . See also [71, 73].

#### 2.12.4 Thermal Diffusivity of Hydrogen

The thermal diffusivity,  $\alpha$ , is defined as

$$\alpha = \frac{\lambda}{\rho C_p}$$

where  $\alpha$  is the thermal diffusivity in m<sup>2</sup>/h,  $\lambda$  is the thermal conductivity in J s m<sup>-1</sup> K<sup>-1</sup>,  $\rho$  is the density in kg/m<sup>3</sup>, and  $C_p$  is the heat capacity in J kg<sup>-1</sup> K<sup>-1</sup>. The thermal diffusivity of liquid hydrogen at the triple point is 0.00053 m<sup>2</sup>/h and at the boiling point it is 0.00052 m<sup>2</sup>/h. The thermal diffusivity of hydrogen gas at the triple point is 0.034 m<sup>2</sup>/h and at the boiling point it is 0.0038 m<sup>2</sup>/h.

## 2.13 Heat Transfer Coefficient of Hydrogen

### 2.13.1 Heat Transfer Coefficient to Liquid Hydrogen

The heat transfer to hydrogen, in particular heat transfer to liquid hydrogen, which is important for the design of regeneratively cooled chemical combustion chambers or nuclear-thermal rocket heat exchangers, has been thoroughly studied during the past 70 years.

While the heat transfer characteristics of other cryogenic and non-cryogenic liquids such as ammonia or liquid oxygen have been known for a long time, the corresponding data for hydrogen only became available after the interest in hydrogen as a rocket propellant increased 70 years ago. Like so many other physical properties, the heat transfer properties of hydrogen are somewhat abnormal. The fundamentals of heat transfer are textbook knowledge and most third year chemical engineering students will master them. We may assume that this basic understanding pre-exists with most of the readers of this chapter.

Although this book deals mostly with chemistry and not the physics of propellants, we found it useful to compile references to design equations for rocket engines with regeneratively cooled chambers and nozzles. This should be a great help to the rocket designer. Thermal conductivity measurements try to eliminate gravity-dependent effects like convection. Heat transfer measurements depend on the conditions of convection and the absence or presence of gravity. We deal with free (density gradient) convection and forced convection [162]. A review of forced convection and natural convection processes in low-temperature (cryogenic) fluids placed the emphasis on forced convection, including turbulent forced convection, because more applications for that type of cooling are found. Transport properties of a near-critical fluid and the effects of curvature on the properties of near-critical hydrogen need to be known. Theoretical considerations in free and forced convection were examined. For stagnant fluids, we need to know the free heat transfer in varying gravitational fields, on Earth and in orbit. For forced convection, the flow velocity and its Reynolds number (laminar vs. turbulent flow) and the heat flux determine different regimes of heat transfer (nucleate and film boiling). The understanding of free convection heat transfer is needed to calculate the evaporation losses from stationary ground storage tanks and flight tanks during the pre-launch hold.

There are many publications which provide a good summary of heat transfer properties of liquid hydrogen, including [163–168]. Because the heat of evaporation of liquid hydrogen is relatively low, it does not take much heat input to convert liquid to gas. This occurs in many rocket engine cooling jackets and in specially designed gas generators where the liquid is injected into hot combustion products to generate hot gas to drive a turbine (which in turn drives the propellant pumps). In most rocket engines with hydrogen the hydrogen enters the combustion chamber in the gaseous or supercritical state.

In the early days of computers (main frame computers), a FORTRAN program (remember punch cards?) was written that permitted calculation of real fluid state relations, thermodynamic properties, and transport properties of molecular hydrogen in any fixed orthohydrogen-parahydrogen combination [169]. The program was to be used for numerical integration of heat transfer and fluid-flow calculations over the temperature range from melting to dissociation for pressures up to 34.4 MPa (340 atm = 5000 psia). A more recent computer program was developed for calculation of thermal and transport properties of parahydrogen from 20 to 10000 K and a pressure range from 10 kPa to 16 MPa [170].

A technique for obtaining the transient heating, cooling, and freezing heat transfer characteristics of liquid hydrogen is based on the magnetocaloric effect [171]. This method takes advantage of the reversible change in temperature exhibited by certain magnetic materials as they experience increasing or decreasing magnetic fields. A single crystal of paramagnetic gadolinium gallium garnet was placed in a temperature-regulated chamber which could be filled with liquid hydrogen. The temperature of the crystal was monitored as it experienced relatively rapid increasing or decreasing magnetic field strengths in vacuum or in the presence of liquid hydrogen. The results of a one-dimensional finite difference model were compared to the data to yield the transient heat transfer characteristics.

### 2.13.1.1 Heat Transfer in the Free Convection Regime

The graph showing heat flux per unit area ( $q/A$ ) as a function of the temperature differential between the wall and the liquid ( $T_w - T_s$ ) (the so-called boiling curve) passes through an initially flat zone (pure convection) and then traverses a steeper slope (bubble formation, nucleate boiling) and finally reaches a maximum at the upper limit of nucleate boiling. Above that is an unstable (oscillating) intermediate zone before the zone of stable film boiling is reached.

For calculating the evaporation losses of liquid hydrogen during storage in stationary tanks, we will initially only look at the first two regimes, those of pure convection and incipient nucleate boiling. For the regime of pure convection, the relationship between dimensionless numbers is as follows:

$$\text{Nu} = 0.54(\text{Gr Pr})^{1.25}$$

and

$$\text{Gr} = \frac{g\beta D^3 \Delta T}{\nu^2}$$

where Nu is the Nusselt number, Gr is the Grashof number, and Pr is the Prandtl number. Further,  $g$  is the gravity acceleration,  $\beta$  is the coefficient of thermal expansion (equal to approximately  $1/T$ , for ideal gases),  $D$  is the diameter,  $\Delta T$  is the difference in temperature, and  $\nu$  is the kinematic viscosity.

For the regime of incipient nucleate boiling different authors propose different equations, which differ in the definition of the characteristic diameter  $D$ . A good summary of these equations is given in a publication in which the discussion is extended to higher temperature differentials which are normally not encountered in liquid hydrogen storage tanks [166].

Natural convection heat transfer and heat transfer for the point of inception of vapor formation for liquid hydrogen and liquid nitrogen, and nucleate boiling heat transfer in liquid hydrogen were measured, and some data indicated a hysteresis effect with increasing and decreasing heat flux [172]. The variables studied were heater surface material, roughness, and orientation.

Instead of measuring heat transfer to cylindrical tank walls or tubes, it is easier to formulate the maths for heat transfer to and from a flat plate immersed in liquid hydrogen [173]. Equations derived from this geometry can be used for calculating evaporation losses from other more complex geometrical shaped tanks [174].

The start of bubble nucleate boiling in stagnant liquid hydrogen on a horizontal heater was observed visually as a function of pressure in the pressure range  $p = 7.2 \times 10^3$  to  $6 \times 10^5$  Pa and with heat fluxes of 640–2120 W/m<sup>2</sup> in an apparatus similar to that one used earlier by Coeling [172, 175].

### 2.13.1.2 Heat Transfer during Nucleate Boiling

Nucleate boiling does not start until the hot convecting fluid finds a seed which can be a dust particle or an irregularity in the wall. Until the first bubble forms, the liquid is in a locally superheated state [176]. The metastable superheat  $\Delta T$  attainable by a liquid above its saturation temperature is important in determining the onset of nucleate boiling. Aside from the boiling description, however, a knowledge of  $\Delta T$  also provides criteria for heat transport transition when bubble formation is entirely suppressed. A non-boiling liquid may be heated to the maximum metastable superheat before it disintegrates. As soon as the wall excess temperature increases beyond the limiting superheat value, the system will enter the Leidenfrost film boiling regime, within which liquid is converted into the completely disordered phase when it approaches the hot walls. Polished surfaces are more likely to lead to superheat and delayed nucleate boiling.

Various heat transfer mechanisms including convection, transient conduction, and evaporation contribute to the overall nucleate-boiling heat flux. A nucleate-boiling model was proposed that applies to any boiling liquid, including liquid hydrogen, and included elements of each of the aforementioned mechanisms. From a comparison of the model with experimental information on water and methanol, no single mechanism dominates over the entire boiling heat-flux range. The cyclic removal of heat from the surface into the liquid sublayer by conduction appears to be an efficient process compared with steady-state free convection [177].

With boiling of liquid hydrogen under increasing pressure one observes a shift of the  $q$ - $\Delta T$  curves to higher values of  $\Delta T$ , caused by a layer of immobilized gases,



the thickness of which increases continuously. The departure diameter  $D$  and the frequency  $f$  of bubbles were observed with discrete nucleate boiling under pressure [178]. The results can be described by the equation  $fD^2 = K$ . The constant  $K$  gets smaller with rising pressure and with increasing roughness of the surface.

### 2.13.1.3 Transition from Nucleate to Film Boiling

Early experimental studies on boiling heat transfer to liquid hydrogen involved the measurement of heat fluxes and wall temperatures only where they studied both the nucleate and film boiling regimes but did not correlate their data. Hendricks et al. [179, 180] studied the film boiling regime only and assumed an annular flow model and vapor-liquid equilibrium. In an attempt to use earlier correlations to predict fluid and wall and fluid qualities, significant discrepancies were found between observed and predicted values [181].

In order to measure the onset of nucleate and film boiling resulting from transient heat transfer to liquid hydrogen, thin carbon films and Pt foils submerged in liquid hydrogen received stepped inputs of power of 1–42 W/cm<sup>2</sup>, and the onset of nucleate or film boiling was obtained for each power level [182, 183]. A single device used as both heater and thermometer eliminates any temperature difference and time lags in heat transfer between the heater and thermometer. Devices constructed of  $4 \times 10^{-4}$  cm thick Pt foil, a well-characterized thermometric material, adhered to quartz and fiberglass-epoxy substrates, had good sensitivity and fast response at 20 K. The critical heat flux was found to be approximately 8 W/cm<sup>2</sup>, with the transition to film boiling occurring in times less than 1 ms. Premature film boiling can be related to the positive temperature coefficient of resistance and the narrowness of the heaters.

Heat transfer from a flat plate facing upward immersed in a liquid hydrogen pool was measured for pressures from atmospheric to 1.1 MPa [184]. Critical heat fluxes in saturated boiling increased with the increase in pressure up to around 0.3 MPa and then decreased with further pressure increase. The critical heat fluxes under subcooled conditions at each pressure increased with the increase in subcooling. The experimental critical heat fluxes were much smaller than those predicted for higher pressure up to critical pressure. The heater surface temperature was found to reach the critical temperature before the occurrence of hydrodynamic instability and transition to the film boiling regime at the lower heat flux in the higher pressure range.

Transient heat transfer from a horizontal flat plate in a pool of liquid hydrogen was measured under saturated and subcooled conditions at pressures from 104 to 700 kPa [185]. Transient heat transfer before the inception of boiling for exponential periods shorter than 100 ms was expressed well by the transient conduction heat transfer with no movement of liquid. Incipient boiling heat flux and temperature were higher for shorter transient periods. Transient critical heat flux was higher for shorter exponential periods and higher subcooling.

Film boiling heat transfer properties of LH2 under various pressure and subcooling conditions were measured by applying electric current to a horizontal PtCo wire

with a diameter of 1.2 mm submerged in LH2 to give an exponential heat input [186]. The heat transfer coefficient in the film boiling region was higher for higher pressure and higher subcooling. The experimental results were compared with predictions from literature equations for pool film boiling heat transfer, and good agreement was observed.

#### 2.13.1.4 Effect of Gravity and Acceleration on the Rate of Hydrogen Evaporation

Because liquid hydrogen is stored not only on the surface of Earth but at times is stored for short periods in space under conditions of complete or partial weightlessness, it is important to know heat transfer properties at reduced or non-existent gravity. At the other extreme of acceleration, heat transfer to hydrogen during periods of high acceleration during the launch of rockets must be understood. Initially, this concerned only liquid hydrogen that was carried in upper stages such as CENTAUR, the S-II or the S-IVB, but now liquid hydrogen is used in many booster stages (ARIANE, H-II, DELTA-IV, SLS) and it was carried in the Space Shuttle external tank.

#### 2.13.1.5 Heat Transfer in Zero $g$ and Low $g$

Visual observation of heat transfer to boiling liquid hydrogen in zero  $g$  showed that the heat transfer is very similar to that at 1  $g$ . Zero  $g$  nucleate boiling heat transfer tests were performed to study the action of boiling liquid hydrogen on the face of a heated surface and to determine the heat flux as a function of the temperature in both 1  $g$  and zero  $g$  environments [187]. Visual observation of boiling for a range of heat fluxes between 788.6 and 22082 W/m<sup>2</sup> (250 and 7000 BTU h<sup>-1</sup> ft<sup>-2</sup>) showed that the bubbles formed at the heated surface coalesced and the surface tension forces were sufficient to rewet the surface behind the bubble. Data indicated that the zero  $g$  nucleate boiling heat transfer is approximately the same as 1  $g$  boiling heat transfer results for the particular test specimen orientation used throughout the tests and for the zero  $g$  test duration times available.

It could be seen that bubbles separate from the surface and that the surface is immediately again wetted by liquid hydrogen [188]. These observations were made in a jet plane flying a parabolic flight path that provides near-zero gravity for only a few minutes.

More realistic heat transfer data were obtained during the flights of CENTAUR and SATURN S-IVB upper stages [189–192]. Theoretically one would expect a dependence of the heat transfer with free convection on the acceleration, be it gravity or flight-induced, because  $g$  enters into the Grashof number. In the absence of gravity, density gradients will no longer cause convection currents. These considerations apply not only to liquid hydrogen under zero  $g$ , but they are examining the behavior of liquid oxygen under zero  $g$  as well. See also [193].

Incipient and steady boiling of cryogenic liquids, both LN2 and LH2, under reduced gravity conditions was studied in a drop tower which had 9.7 m (32 ft) free fall distance, giving 1.34 s of free fall [194]. The parameters varied included the fluid used,

heater surface temperature, geometry, orientation, and fractional gravity. A transient calorimeter technique was used with a variety of geometries. This technique readily provided results in all of the boiling regimes. The transient calorimeter technique was adapted to flat surfaces to determine the influence of geometry and orientation on boiling of LN2 and LH2 at normal and reduced gravities. A vertical cylinder was used to simulate a vertical flat plate. Measurements of incipient boiling at normal and zero gravity were made in both LN2 and LH2, using a transient technique with a platinum wire. A step increase in power was applied, and from the transient wire temperature measurements it was possible to observe when nucleate boiling began. It was observed, in both LN2 and LH2, that the maximum heater superheat at nucleation was independent of the body forces present.

An existing gravity scaling analysis, proposed based on the experimental data of non-cryogenic fluids, was assessed using the boiling heat transfer data of hydrogen under different gravities [195]. A validation study showed that this scaling analysis is also acceptable in predicting the nucleate boiling heat transfer of hydrogen under low gravity conditions. Through this analysis, the heat flux at any gravity level can be obtained if data in a similar condition are available at a reference gravity. Another scaling analysis aiming at the film boiling regime was proposed, and its predictive accuracy was validated by comparing its predictions with hydrogen experimental data. The comparison showed that a reasonable agreement was obtained and the deviation was within 15%. Hydrogen boiling curves under normal gravity and microgravity conditions were constructed which showed that microgravity yields lower heat flux throughout the overall boiling range, and the influence of gravity on heat flux is most significant in the film boiling regime.

The flow boiling of liquid hydrogen during transfer in microgravity is very different from that under terrestrial conditions. A saturated flow boiling of LH2 in a horizontal tube has been modeled under microgravity conditions using coupled level-set and volume of fluid methods [196]. The validation of the developed model showed good agreement with experimental data from the literature. The changes of heat fluxes and pressure drops under different gravitational accelerations were analyzed. The variation of heat fluxes with different wall superheat and contact angle were compared between microgravity ( $10^{-4}g_0$ ) and normal gravity ( $1g_0$ ) conditions where the influence of surface tension under microgravity was considered. The numerical results indicated that the heat flux decreased with the decrease of gravitational acceleration. The heat transfer ratio decreased with the increase of wall superheat in the nucleate boiling regime. The heat transfer was slightly reduced when considering surface tension. The changes of contact angle may have a more significant impact on heat transfer under microgravity condition than surface tension alone.

#### **2.13.1.6 Heat Transfer at High Accelerations**

Heat transfer to boiling liquid hydrogen was measured with samples on a centrifuge at accelerations up to 10g [197–199]. The influence of gravity on nucleate boiling heat

transfer is not as strong as that of tank pressure; however, in the film boiling regime acceleration has a more pronounced effect than in the nucleate boiling regime.

### 2.13.1.7 Heat Transfer in the Regime of Forced Convection

The achievable heat fluxes in the regime of forced convection (e.g. flow through a heated pipe or a flat or annular channel) are several orders of magnitude higher than in free convection and are often encountered in the regenerative cooling channels of rocket engines. The shape of the boiling curve with its characteristic regimes of convection, nucleate boiling, partial film boiling and total film boiling is similar to that of free convection heat transfer, but the entire curve is shifted toward higher  $q/A$  fluxes. The dependence of heat transfer on the flow velocity is least in the regime of nucleate boiling.

A single-tube heat transfer apparatus was used to determine heat transfer coefficients to boiling liquid hydrogen [200]. The facility set-up allowed measurements to be made at pressures up to 276 kPa (40 psia) and flow rates up to about 2.26 kg/min. (5 lb<sub>m</sub>/min.) through a 6.3-mm (0.25-in.) ID test section at saturated liquid Reynolds numbers from 220000 to 660000 at pressures from 162 to 223 kPa (1.6–2.2 atm).

Boiling heat transfer to liquid hydrogen under conditions of forced flow inside a vertical tube under a wide range of operating variables (flow rate, pressure, liquid inlet subcooling, heating rate and tube geometry, i.e., length to diameter ratio), the mode of heat transfer and their relation to the value of the critical heat flux were compared to similar tests with liquid nitrogen [201], Table 22. The test apparatus consisted of a pressure-fed, once-through system with an electrically heated vertical tube of 14 mm (0.555 in.) internal diameter and 40.6 cm (16 in.) length. Subcooled liquid parahydrogen or liquid nitrogen flowed through the tube in vertical up-flow. Tube exit qualities ranged from essentially 0–1.0 (with superheat), and transition from a relatively high to a lower value of heat transfer coefficient occurred over a range of axial locations from tube entrance to exit. The critical heat flux corresponds to the local heat flux just upstream of the location of a sudden rise in wall temperature.

**Table 22:** Heat transfer conditions tested at NASA

|                                                       | Hydrogen        | Nitrogen       |
|-------------------------------------------------------|-----------------|----------------|
| Mass velocity, lb h <sup>-1</sup> ft <sup>-2</sup>    | 2850 to 17000   | 15000 to 56000 |
| Mass velocity, lb h <sup>-1</sup> m <sup>-2</sup>     | 264.8 to 1580   | 1394 to 5204   |
| Mass velocity, kg h <sup>-1</sup> m <sup>-2</sup>     | 120 to 716      | 631 to 2358    |
| Local heat flux, BTU h <sup>-1</sup> ft <sup>-2</sup> | 3600 to 40000   | 2300 to 40000  |
| Local heat flux, W/m <sup>2</sup>                     | 11356 to 126483 | 7255 to 126483 |
| Liquid inlet subcooling, °R                           | 0 to 9          | 1 to 6         |
| Liquid inlet subcooling, K                            | 0 to 5          | 0.5 to 3.3     |
| Inlet pressure, psia                                  | 30 to 74        | 47 to 56       |
| Inlet pressure, kPa                                   | 206 to 510      | 324 to 386     |

Data source: [201]

In the regime of non-boiling forced convection heat transfer in flowing liquid hydrogen, the heat flux can be expressed by a DITTUS-BOELTER equation [202, 203]

$$\text{Nu} = 0.016\text{Re}^{0.8}\text{Pr}^{0.4}$$

A comparison of heat transfer at nucleate and film boiling for free convection versus forced convection showed that boiling heat fluxes for vertical flow and horizontal flow at comparable pressures showed very little observable effect of the orientation [204]. Pool boiling data for the film boiling and nucleate boiling regimes were compared to other flux vs.  $T_W - T_L$  correlations and there was some similarity in the slope of the curves. For pool boiling on vertical surfaces the rising bubbles create turbulence that affects a larger area than the effect of bubbles forming on horizontal surfaces.

In the regime of nucleate boiling with forced convection the heat transfer remains independent of the bubble fraction in the fluid (quality of the fluid) only as long as there is sufficient liquid remaining to completely wet the hot surface. In cooling channels of rocket engines this condition is maintained only in the inlet portion. Shortly downstream of that zone there is a transition regime where nucleate boiling makes a transition to film boiling. The location of the transition zone is dependent on the cooling channel design and the operating conditions of the engine. This transition is a potential trouble spot and susceptible to burnout if the flame-side temperature of the chamber wall exceeds the melting point or softening point of the metal.

If one develops a formula for heat transfer to a liquid in a cooling channel, the bubble fraction or liquid quality must be carried along as an additional variable. The heat transfer to liquid hydrogen flowing through a cooling channel and partially evaporating along its path cannot be calculated using the conventional equations which assume an infinite supply of liquid. In any rocket propulsion system using a propellant stored in the liquid state, the existence of two-phase flow of the working fluid is of critical concern during start-up phase. It is generally required that the quality of the fluid at certain locations be predicted. But the behavior of single component, non-isothermal two-phase flow is not well understood. Fluid flow and heat transfer data under these conditions were lacking. An experimental program was undertaken to study forced convection, transient boiling heat transfer to hydrogen during cool-down of a metal test section [205]. The partial evaporation and heat transfer to a two-phase fluid are more difficult to express in mathematical equations than either nucleate boiling with sufficient liquid or complete evaporation in the film boiling mode [206].

NASA conducted very thorough investigations of heat transfer to liquid hydrogen. The test conditions covered liquid pressures between 208 and 481 kPa (2.05 and 4.75 atm), heat fluxes up to  $163 \text{ W cm}^{-2} = 1631760 \text{ W/m}^2 = 39 \text{ cal cm}^{-2} \text{ s}^{-1} = 390000 \text{ cal m}^{-2} \text{ s}^{-1}$  and temperature differences from 28 to 415 °C between the fluid and the wall [179]. Two different test-section geometries of 30-cm (1-ft) length were employed; one had a 15.9-mm (0.625-in.) outside diameter and 1.6-mm (0.065-in.) wall, and the other a 9.5-mm (0.375-in.) outside diameter and 0.8-mm (0.031-in.) wall. The wall temperature profile along the tube was radically different from that observed

in convective heat transfer with single-phase fluids. For the range of investigation, film boiling of the hydrogen and a resulting two-phase flow phenomenon occurred. Correlations were derived from heated tube data which apply to (1) film boiling of liquid hydrogen, (2) hydrogen at supercritical pressure just above and below critical temperature, (3) low temperature hydrogen (83–139 K) above the critical pressure [207, 208]. Heat transfer in the convective film boiling regime can be predicted by correlating the ratio of experimental to predicted Nusselt numbers with the Martinelli two-phase parameter. Experimental pressure drops varied greatly.

The question has been posed if under these conditions some of the parahydrogen may reconverted to orthohydrogen, an endothermic process. The rate of equilibrium adjustments in the absence of catalysts would be very slow. Iron would be catalytic, but gold would not. Since the para-ortho conversion is endothermic, it should help the heat transfer. A stainless steel tube would be expected to show a lower wall temperature than a gold-plated tube but the experimental data showed the gold-plated tube to give a lower wall temperature.

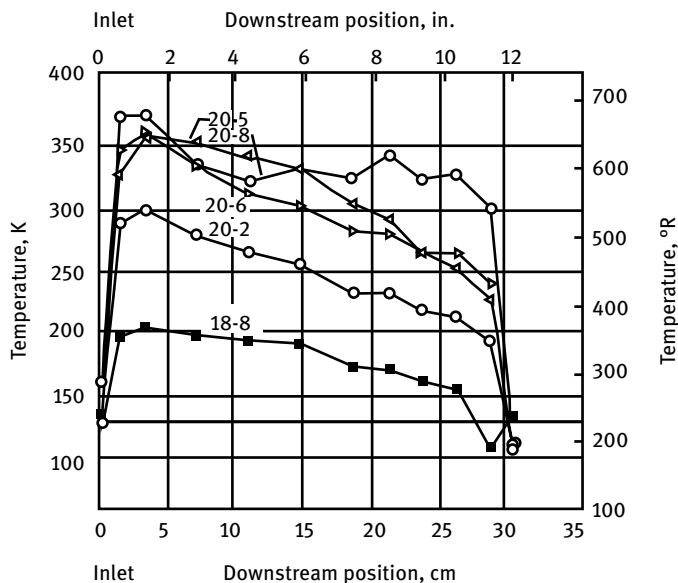
Heat transfer characteristics of cryogenic hydrogen flowing vertically upward in uniformly joule-heated straight tubes were assessed over the pressure range of 6.9–17.2 MPa (1000–2500 psia) [180]. The fluid appeared to exhibit gas-like behavior in this regime. Heat transfer data for the most part were predictable to  $\pm 20\%$  by the Nusselt-film correlation

$$\text{Nu}_f = C \text{Re}_f^p \text{Pr}_f^{0.4}$$

where  $C = 0.021$  and  $p = 0.8$ . A closer examination, however, of the data for each test section indicated that the Reynolds number exponent  $p$  can vary between 0.83 and 0.9 with the constant  $C$  changed correspondingly from 0.011 to 0.006. These correlations hold for heat fluxes up to  $1634 \text{ W/cm}^2$  ( $10 \text{ BTU in}^{-2} \text{ s}^{-1}$ ), wall-to-bulk temperature ratios to 11, mass flow rates to  $0.18 \text{ kg/s}$  ( $0.4 \text{ lb}_m/\text{s}$ ), film Reynolds number from  $10^5$  to  $4 \times 10^6$ , and inside tube diameters from 5.3 to 11.1 mm (0.21–0.438 in.).

Heat transfer studies with liquid hydrogen in the regime of film boiling with forced convection were conducted in a tube of stainless steel CRES-347 with an internal diameter of 14 and 0.89 mm wall thickness  $\text{s}^{-1}$  [209]. A length of 41 cm of the tube was heated in a furnace to different temperatures. The flow rate was up to  $12.7 \text{ kg/h}$  and the local maximum heat flux was  $12.5 \text{ W/cm}^2 = 3.0 \text{ cal cm}^{-2}$ . The transition from nucleate boiling to film boiling was evidenced by a steep increase of the wall temperature, similar to observations reported by other experimenters [210]. This group had flowed liquid hydrogen through a 30-cm (12-in.) electrically heated vertical Inconel tube with an outer diameter of 9.5 mm (0.375 in.) and a wall thickness of 0.8 mm (0.031 in.). The flow rate was  $13.6\text{--}86 \text{ g/s}$  and the pressure was  $206\text{--}482 \text{ kPa}$  ( $2\text{--}4.7 \text{ atm} = 30\text{--}70 \text{ psi}$ ). The temperature difference between the flowing fluid and the wall covered a range from 21 to  $550^\circ\text{C}$ . The maximum heat flux was  $130 \text{ W/cm}^2$  ( $31 \text{ cal cm}^{-2} \text{ s}^{-1}$ ). As illustrated in Figure 36, which shows data for a tube with an outside diameter of 0.95 cm (0.375 in.), it was noted that the wall temperature already reached its maximum value after only

1/10 of the length of the heated zone. The test conditions for the experiments shown in Figures 36 and 37 are listed in Table 23. The heat transfer coefficient, illustrated in Figure 37, at this point was at its minimum ( $3517 \text{ W cm}^{-2} \text{ K}^{-1} = 0.84 \text{ kcal m}^{-2} \text{ s}^{-1} \text{ }^{\circ}\text{C}^{-1} = 8.4 \times 10^{-5} \text{ kcal cm}^{-2} \text{ s}^{-1} \text{ }^{\circ}\text{C}^{-1} = 3024 \text{ kcal m}^{-2} \text{ h}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ). Apparently at this point the transition to film boiling has already occurred, and the heat capacity and thermal conductivity of the cold, gaseous hydrogen is still quite low. Additional degrees of freedom of vibration and oscillation in the  $\text{H}_2$  molecule still need to be thawed. At the end of the tube the heat transfer coefficient again reaches values close to those at the inlet of the tube. Hydrogen leaving the tube consisted of 80% vapor.

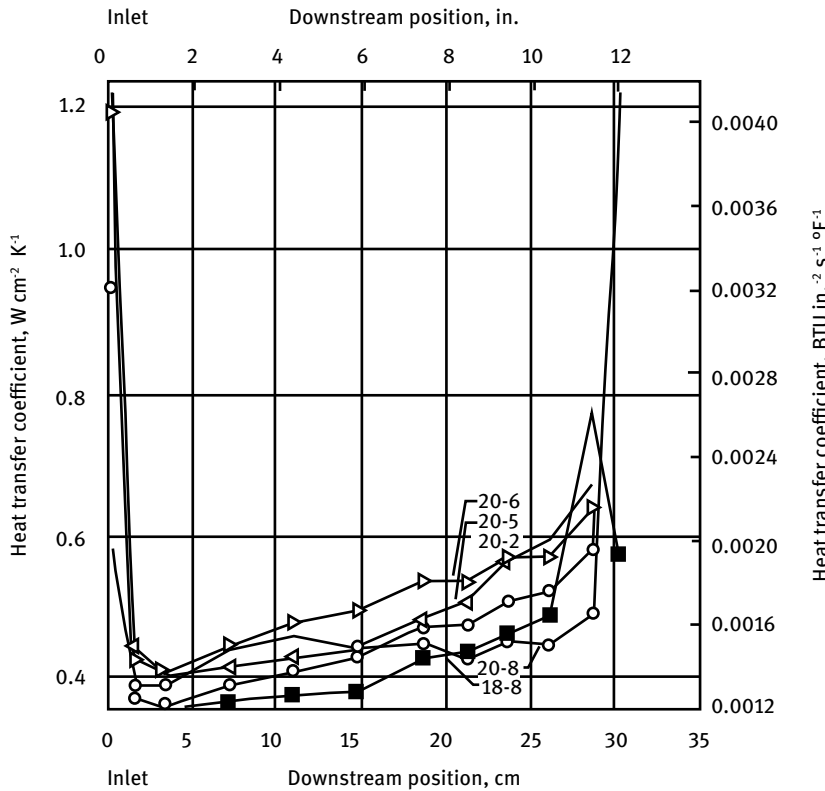


**Figure 36:** Internal wall temperature during forced convection heat transfer to liquid hydrogen. (Reprinted and adapted from [210], by permission from Springer Nature ©1961; permission conveyed through Copyright Clearance Center Inc.)

**Table 23:** Test conditions for experiments in Figures 36 and 37.

| Test Nr. | Heat flux<br>kcal/s | Flow rate<br>g/s | Supply tank temperature<br>K | Vapor fraction<br>Mass-% |
|----------|---------------------|------------------|------------------------------|--------------------------|
| 18-8     | 1.18                | 40               | 24.1                         | 31                       |
| 20-2     | 1.80                | 61               | 23.8                         | 24                       |
| 20-5     | 2.46                | 79               | 23.5                         | 22                       |
| 20-6     | 2.50                | 59               | 23.9                         | 36                       |
| 20-8     | 2.49                | 35               | 24.6                         | 69                       |

Data source: [210]



**Figure 37:** Heat transfer coefficient during forced convection heat transfer to liquid hydrogen. (Adapted from [210] by permission from Springer Nature ©1961; permission conveyed through Copyright Clearance Center Inc.)

A general equation was developed for forced convective film boiling heat transfer in liquid hydrogen [211]. Forced flow heat transfers of liquid hydrogen through a vertical tube with a diameter of 6 mm and length of 100 mm were measured at pressures of 0.4, 0.7 and 1.1 MPa for various inlet temperatures and flow velocities [212]. The heat fluxes at the inception of boiling and the departure from nucleate boiling heat fluxes were higher for higher flow velocity and subcooling. The departures from nucleate boiling heat fluxes under subcooled conditions were lower for higher pressure. The effects of tube diameter and subcooling on the departure from nucleate boiling heat flux were investigated. A new correlation of saturated and subcooled departure from nucleate boiling heat flux was established based on these data and the data for 3-mm diameter tubes already reported earlier.

The heat transfer from the inner side of a vertically mounted heated tube with a length of 200 mm and a diameter of 6 mm to a forced flow of liquid hydrogen was



measured for wide ranges of flow rate and liquid temperature [213]. The non-boiling heat transfer coefficients agreed well with the Dittus-Boelter equation. The heat fluxes at departure from nucleate boiling were higher for higher flow velocities and greater subcooling. The effect of the tube length on the departure from nucleate boiling heat flux was clarified through comparison with previous data.

The knowledge of departure from nucleate boiling heat flux of liquid hydrogen is necessary for designing and cooling analysis of high critical temperature superconducting devices. Departure from nucleate boiling heat fluxes of liquid hydrogen were measured under saturated and subcooled conditions at absolute pressures of 400, 700, and 1100 kPa for various flow velocities [214]. Round heaters made from Pt-Co alloy, 200 mm long and 0.7 mm in diameter were arranged in the central axis of a flow channel made of fiber reinforced plastic with inner diameters of 8 and 12 mm. These test bodies were vertically mounted and liquid hydrogen flowed upward through the channel. Correlations of departure from nucleate boiling heat flux data under saturated and subcooled conditions with the experimental conditions were made.

In order to calculate the transient temperature rise of hydrogen when precooled hydrogen is flowing and unavoidably heated through the wall of transfer ducting at a refueling station, like the umbilical at the launch pad, the filling equipment was assumed to be a simple and straight pipe, and the heat balance based on the thermodynamics for hydrogen flowing in the pipeline was analyzed [215]. The internal surface temperature of the pipeline wall was needed to calculate the heat flux into hydrogen. A solution to obtain the temperature distribution in the pipeline wall when hydrogen with lower temperature than the pipeline flows unsteadily was proposed. Based on the proposed solution, the heat flux and the hydrogen temperature were calculated. The hydrogen temperatures predicted by this approach were compared with experimental data for the temperature rise of hydrogen heated through actual filling equipment, and good agreement was achieved.

The thermal behavior of flowing liquid hydrogen inside the cooling channels of the regenerative cooling system of a scramjet was modeled and measured at different channel sizes [216]. In order to find the optimum design parameters, a 3-D model of coolant flow in terms of the fuel real properties was developed and validated through experiments under different conditions of flow area, channel aspect ratio, fin thickness and coolant inlet temperature. For the given cases, the wall temperature was decreasing when the channel aspect ratio increased from 1 to 8, but there exists an optimal channel aspect ratio at a relatively large value. The optimal channel aspect ratio increased when the flow area became smaller. Decreasing fin thickness can significantly reduce the wall temperature without resulting in a large increase of pressure drop.

### 2.13.2 Heat Transfer Coefficient to Gaseous Hydrogen

In order to successfully design cooling channels for rocket engines, heat transfer data for both liquid *and* gaseous hydrogen must be known. The heat transfer to gaseous hydrogen was measured at Reynolds numbers from 3670 to 62200 and gas pressures from 274 to 689 kPa (2.7–6.8 atm) in a tube that was 31 cm long and had an diameter of 7.75 mm [217]. The ratio of wall temperature to gas temperature was varied from  $T_w : T_i = 1.17$ –2.47. The heat transfer to gaseous hydrogen can be represented by the following equation:

$$\text{Nu}_f = 0.023 \text{Re}_f^{0.8} \text{Pr}_f^{0.4}$$

where the subscript f designates the conditions along the film next to the wall. This work was later expanded to conditions of higher heat fluxes ( $2428 \text{ W/cm}^2 = 580 \text{ cal cm}^{-2} \text{ s}^{-1}$ ) and higher pressures (up to 9.3 MPa = 92 atm) [218]. Those results can be represented by a more complex equation:

$$\text{Nu} = \frac{hd}{\lambda_a} = 0.023 \left( \frac{\rho_a v d}{\eta_a} \right)^{0.8} \text{Pr}_a^{0.4} \left( \frac{T_w}{T_a} \right)^{-0.8}$$

where

$h$  = heat transfer coefficient,  $\text{kcal h}^{-1} \text{ cm}^{-2} \text{ }^\circ\text{C}^{-1}$

$d$  = internal tube diameter, cm

$\lambda_a$  = thermal conductivity of hydrogen at  $T = a$ ,  $\text{kcal h}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1}$

$\rho_a$  = density of hydrogen at  $T = a$ ,  $\text{g/cm}^3$

$v$  = flow velocity, cm/s

$\eta_a$  = viscosity of hydrogen at  $T = a$ ,  $\text{g cm}^{-1} \text{ s}^{-1} = \text{Ps}$

$T_a$  = bulk temperature of hydrogen, K

For conditions in the boundary layer adjacent to the wall we can use a similar equation, where the subscript w indicates that this property must be taken at the wall temperature  $T_w$ :

$$\text{Nu} = \frac{hd}{\lambda_w} = 0.023 \left( \frac{\rho_w v d}{\eta_w} \right)^{0.8} \text{Pr}_w^{0.4}$$

These equations are valid for the following range of conditions:

|                                  |                         |
|----------------------------------|-------------------------|
| Reynolds number                  | 7800– $1.5 \times 10^6$ |
| Hydrogen gas initial temperature | 200–310 K               |
| Temperature ratio $T_w/T_a$      | 1.5–2.8                 |
| Wall temperature $T_w$           | 480–910 K               |
| Hydrogen bulk temperature $T_a$  | 310–406 K               |
| Hydrogen pressure                | 4.3–92 atm              |

Thermal conductivity and transport properties of hydrogen at extremely high temperatures, beyond the capabilities of experimentation, such as the temperatures expected

in some nuclear powered rocket engines from 300 to 10000 K can be calculated from theoretical considerations based on known thermodynamic properties [219]. In the upper end of this temperature regime molecular dihydrogen begins to dissociate. No experimental data exist for the transport properties of hydrogen in the dissociating region.

Transport properties were calculated for hydrogen in the pressure range from  $10^{-6}$  to  $10^2$  atm and at temperatures up to  $10^6$  K [220], also for heat transfer in rocket nozzles of gaseous-core nuclear rocket engines [221].

### 2.13.3 Heat Transfer to Hydrogen in the Supercritical State

#### 2.13.3.1 Heat Transfer to Hydrogen in the Near-critical State with Forced Convection

An experimental non-burnout study of heat transfer to hydrogen at near-critical temperatures flowing turbulently in resistance-heated straight and curved channels was made to evaluate the applicability of earlier heat transfer correlations to nozzle design [222]. Both straight and curved channels of circular cross-section were used, the latter being limited to simulating a single contour considered typical of a coolant passage in a rocket nozzle throat region. The fluid was heated asymmetrically by chemically milling the tube wall to reduce the metal thickness on one side. Inlet mass velocities ranged from 28.17 to 8618  $\text{kg m}^{-2} \text{s}^{-1}$  ( $62.2\text{--}19024 \text{ lb}_m \text{ m}^{-2} \text{s}^{-1} = 5.78\text{--}1768 \text{ lb}_m \text{ ft}^{-2} \text{s}^{-1}$ ). Local values of the pressure and bulk temperature ranged from 2.88 to 5.86 MPa (418–850 psia) and 28.2–161 K (50.9–290 °R) respectively, while local velocities ranging from 1.73 to 332 m/s (5.7–1095 ft/s) were obtained. The highest outer wall temperature measured was 1069 K (1925 °R), and the maximum inner wall temperature was computed as 610 K (1098 °R). The maximum local heat flux was 23.7  $\text{MW m}^{-2}$  (14.5  $\text{BTU in.}^{-2} \text{s}^{-1}$ ), and the highest value of the wall-to-bulk temperature ratio obtained was 18.5. Correlating equations were generated for the straight and curved tube geometries with fluid properties evaluated at the bulk temperature; however, analysis of the data indicated this simple correlation approach did not adequately express the data. A comparison of these equations with earlier correlations showed that the equation generated from straight tube tests was the most conservative and that generated from curved tube data was in general the most optimistic. Heat transfer to hydrogen flowing turbulently in straight asymmetrically heated tubes of circular cross-section was correlated by this equation, with fluid properties evaluated at the bulk temperature

$$\text{St}_b = 0.017 \text{Pr}_b^{0.96} \text{Re}_b^{-0.14} \left( \frac{T_w}{T_b} \right)^{-0.8}$$

Flow in curved tubes of circular cross-section was correlated by

$$\text{St}_b = 0.0346 \text{Pr}_b^{-0.3} \text{Re}_b^{-0.17} \left( \frac{T_w}{T_b} \right)^{-0.7}$$

A review of a method capable of including density fluctuations in the equations of turbulent transport indicated that the method may be used to predict heat transfer for the case of near-critical parahydrogen in turbulent upflow inside vertical tubes [223]. Wall temperatures, heat transfer coefficients and velocities obtained by coupling the equations of turbulent momentum and heat transfer with a perturbed equation of state showed good agreement with experiments for inlet reduced pressures of  $p/p_c = 1.28\text{--}5.83$ .

Four correlations which cover the ranges of liquid to gas transitions for turbulent flow convection of hydrogen were compared with computational fluid dynamics (CFD) analysis results over a range of expected design conditions for active cooling of hypersonic aircraft [224, 225]. The correlations compared here were those of Hess and Kunz, McCarthy and Wolf, Miller, Seader and Trebes, and Taylor. Analysis of hydrogen cooling in a typical cooling panel demonstrated how predicted design performance varies with the correlation used. The Taylor heat transfer coefficient correlation demonstrated the best overall agreement with the CFD results for constant heat flux over a wide range of pressure, temperature, mass flow, and heat load conditions. The McCarthy and Wolf correlation also agreed well with the CFD results. The CFD heat transfer coefficient results for a heat spike differed greatly from all four correlations. An acceptable heat transfer coefficient can be calculated at the heat spike location by ignoring the coefficient at the spike and averaging the coefficient before and after the spike.

### 2.13.3.2 Heat Transfer to Hydrogen in the Supercritical State with Forced Convection

Boiling point and critical point of hydrogen are so close together like no other gas used as a rocket propellant. The boiling point is at 20.27 K, and the critical temperature is at 33.3 K. The critical pressure is so low ( $1.297\text{ MPa} = 12.8\text{ atm}$ ), that it is easily exceeded with most rocket engine chamber pressures. In rocket engines operating at pressures above the critical pressure hydrogen can achieve supercritical conditions and enters the rocket engine or gas generator in the supercritical state [226–228]. In spite of this phase transition to supercritical conditions, hydrogen continues to be a good coolant for rocket engines over a wide range of temperatures and pressures.

Hydrogen heat-transfer data in the supercritical region has been compared with an analysis based on fully developed turbulent pipe flow with variable fluid properties [229]. The comparison indicated an additional variable property effect that was not included in the previous analysis. A new approach led to the correlation of the data over the full range of experimental conditions. These results indicated that the mechanism of supercritical heat transfer with hydrogen can be explained on the basis of variable fluid property effects without postulating a new mechanism for heat transfer, as was done in previous investigations. It was found that the pipe flow equation with fluid properties based on the film temperature can be made to correlate the data by correcting the calculated values with a simple function of wall to bulk kinematic

viscosity ratio. This method provided a rapid means for determining supercritical hydrogen heat transfer with an accuracy that was sufficient for most purposes.

Heat transfer to supercritical hydrogen is covered by mathematical equations which are quite different from the equations applicable to either gaseous or liquid hydrogen. Heat transfer by forced convection to cryogenic hydrogen at supercritical pressures has been studied experimentally, using a resistance-heated tubular test element [230, 231]. Test pressures were varied from 4.7 to 9.3 MPa (680–1344 psia) with fluid bulk temperatures at the test-section inlet ranging from 30 to 56 K (55–102°R). The maximum heat flux obtained was  $1307 \text{ W/cm}^2$  ( $8.0 \text{ BTU in.}^{-2} \text{ s}^{-1}$ ), while the maximum wall-to-bulk temperature ratio was 16.5. Heat transfer to hydrogen was found to be characterized by two mechanisms, each differing in its dependence on Reynolds number and the wall-to-bulk temperature ratio. Although mean residence times were only of the order of milliseconds, the data indicated that an appreciable fraction of the parahydrogen was converted to the ortho form, the degree of conversion increasing with wall temperature. In the neighborhood of the critical point the heat transfer coefficient of hydrogen passed through a minimum. Another minimum was observed at temperatures that were 28–40 K above the critical point temperature.

Heat transfer measurements reported in the early literature covered the range from 13 to 92 atm and 29 to 407 K. If one compares the heat transfer data for supercritical state hydrogen which were obtained experimentally under 14 different conditions, one will find that the measured numbers can be predicted with an accuracy of  $\pm 33\%$  by equations reported in the literature [232]. See also [207, 208, 233–236].

Turbulent flow of supercritical hydrogen through a uniformly heated circular tube for the range of  $4 \times 10^5 \leq \text{Re} \leq 3 \times 10^6$ ,  $5 \leq q_w \leq 10 \text{ MW/m}^2$ ,  $30 \leq T_{\text{in}} \leq 90 \text{ K}$ , and  $5 \leq P_{\text{in}} \leq 15 \text{ MPa}$  has been investigated using numerical methods [237]. The purpose was to validate a turbulence model and calculation method for the design of active cooling systems of hydrogen-fueled hypersonic aircraft, where the hydrogen fuel is used as coolant. The PHOENICS software package was used for the computations, which required special provision for evaluation of the thermophysical properties of the supercritical hydrogen, and a low Reynolds number form of the  $k$ - $\epsilon$  turbulence model. Pressure drop and heat transfer data were compared with experimental and existing correlations, and good agreement was demonstrated. For the pressure range considered, a “thermal spike” was observed and shown to be due to the secondary peak in specific heat, rather than the primary peak.

Heat transfer correlations for supercritical hydrogen and a study of the effects of uncertainties in hydrogen property data on the design of cooling channels showed that uncertainty due to property data alone can be as high as 10% [238]. Previous heated tube experiments with supercritical hydrogen were summarized, and data from a number of heated tube experiments were analyzed to evaluate conditions for which the available correlations are valid [239].

The transition from subcritical state to supercritical state severely influences the heat transfer of liquid hydrogen. In a numerical simulation study of the convective

heat transfer to supercritical hydrogen in a straight tube under high heat flux, the thermophysical properties and transport properties including the equation of state, specific heat capacity, viscosity, and thermal conductivity of hydrogen were evaluated first by comparison with the data from the National Institute of Standards and Technology (NIST) [240]. Then, the flow and heat transfer process was investigated using the Reynolds averaged Navier-Stokes (RANS) model, and the approach was validated by being able to successfully predict a behavior called “local heat transfer deterioration.” Further, the mechanism of heat transfer deterioration was analyzed based on detailed information of the flow field.

Wall temperature distribution and heat transfer coefficient during convective heat transfer to hydrogen flow are highly dependent on the heat flux profile imposed at the tube wall. The flow acceleration to a flat velocity profile contributes to the heat transfer deterioration [241].

The convective heat transfer to supercritical pressure hydrogen in a straight tube was investigated numerically by employing a computational model, which was simplified from experiments performed by Hendricks et al. [242]. During the simulation, the standard  $k-\epsilon$  model combining the enhanced wall treatment was used to formulate the turbulent viscosity, and the results validated the approach through successful prediction of wall temperature profile and bulk temperature variation.

### **2.13.3.3 Heat Transfer to Hydrogen in the Supercritical State without Forced Convection**

Both oxygen and hydrogen are commonly stored in cryogenic tanks under space zero- $g$  conditions, but not so much for rocket propulsion as for fuel cells for electricity generation. Therefore, the heat transfer to supercritical hydrogen under zero- $g$  conditions without external agitation poses a special problem that cannot be easily simulated on the ground [243]. Fuel cells with supercritical storage of fluids were used on GEMINI [244], APOLLO, and the Space Shuttle.

### **2.13.4 Practical Applications of Heat Transfer to Liquid Hydrogen**

Numerous rocket engines now use liquid hydrogen and heat transfer measurements on real-life operating rocket engines were made to validate the modeling that preceded their design. Nuclear thermal rockets with liquid hydrogen were tested briefly during the last century and posed unique heat transfer problems. One of the test series used the KIWI and ROVER reactors operated by the Los Alamos Scientific Laboratory [9, 11, 245]. Heat transfer experience gained during the operation of nuclear thermal rockets helped in the later design of large hydrogen-cooled chemical rockets.

In order to drive the liquid hydrogen pumps a peak power demand of 37 MW (50000 HP) was required that could not be drawn from the electric power grid in a remote area. Instead of storing electric power, the plant stored hot water and used it in heat exchangers to evaporate a portion of the liquid hydrogen to generate high

pressure hot hydrogen, which was used to drive a set of multi-stage turbines which in turn spun the liquid hydrogen pumps [246]. The expanded hydrogen was then dumped.

#### **2.13.4.1 Pressure Oscillations in Liquid Hydrogen**

At high heat fluxes to liquid or supercritical hydrogen at high stream velocities it is possible that the system will develop pressure oscillations which may propagate through the entire system, depending on the possible amplification by resonance in lines and cavities [247–249]. Such oscillations were disturbing enough in a stationary heat exchanger, but they would have been disastrous in a flight vehicle.

Thermal acoustic oscillations can occur whenever a long tube connects a region at cryogenic temperature with an ambient temperature, low pressure region where boiling occurs. Instrumentation lines and ports for fluid flow are examples where these conditions can exist. Thermal acoustic oscillations can occur without any net flow of fluid or any intended transfer of heat [250]. Thermal acoustic oscillations can lead to pressure surges in LH2 and slush hydrogen systems. Entry of LH2 into warmer instrument or discharge lines causes local vaporization and a pressure increase, which forces the LH2 and GH2 gas back to the bulk LH2, where cooling causes a reverse surge. Such back and forth oscillations can result in an increased heat input to the bulk LH2. This is related to geysering if it occurs in vertical tubes.

#### **2.13.4.2 Radiation Heating of Hydrogen**

In addition to conventional heat transfer from hot walls to liquid hydrogen flowing through an operating nuclear fission reactor (KIWI-A or NERVA type) the moving fluid may absorb neutrons and will pick up additional energy converted to heat [251, 252]. Unshielded nuclear radiation from an operating nuclear reactor absorbed into liquid hydrogen (which is a good neutron moderator) may result in nuclear heating of the unused propellant in the hydrogen storage tank adjacent to the reactor [253], potentially leading to premature cavitation in the inducer section of the hydrogen pump [254].

#### **2.13.4.3 Heat Transfer to Uninsulated Tanks**

In order to predict vaporization losses from an uninsulated tank, the heat transfer coefficients to an uninsulated copper plate at 20 K were investigated [255]. Data were taken over a range of air velocities, normal to the surface, of 0–9.3 m/s (0–21 miles/h), varying absolute humidity of air, and ambient air temperatures of 264–338 K (16–150 °F). A theoretical analysis, description of experimental apparatus and procedure, experimental results, discussion, and conclusions were presented. The results can be summarized as follows: **(1)** low ambient temperatures and absolute humidity inhibit and sometimes prevent frost accumulation on the test surface; **(2)** steady state frost thickness increases with air velocity and absolute humidity; **(3)** heat transfer coefficients exhibit a minimum point at all air velocities when plotted against absolute humidity; **(4)** the only theoretical analysis made was for the surface

covered with a liquid air film. No correlation between theory and experimental data was found to exist.

#### 2.13.4.4 Heat Transfer to Liquid Hydrogen in Nuclear Thermal Rockets

The understanding of heat transfer from a nuclear fission reactor to flowing liquid and gaseous hydrogen as measured during the NERVA, ROVER, and PHOEBUS experiments is also useful for the design of cooling channels in chemical rockets. The predicted pressure and temperatures at the exit of the cooling passages were compared with the measured values of EP-IV nuclear tests and were in good agreement with each other [256]. Incremental values of coolant temperatures and pressures, coolant passage wall temperatures, and heat flux to the coolant were calculated. A constant gas coefficient  $C$  of 0.026 yielded predicted values for coolant exit pressure and temperature that were in good agreement with measured values. Maximum wall temperature and heat flux were in good agreement with those calculated using the conventional varying coefficient.

Application of variable property heat transfer and friction equations to rocket nozzle coolant passages and comparison with nuclear rocket test results provided another set of data points [257]. Calculated local gas-side wall temperatures were compared with wall temperatures indicated by melting of selected braze alloys from NERVA nuclear tests. Several different heat transfer correlations were used to predict temperatures on the hot-gas side and wall temperatures.

### 2.14 Critical Constants of Hydrogen

The critical constants used for correlating density data near the critical point are listed in Table 24.

**Table 24:** Critical constants of hydrogen.

| Constant                                    | References |
|---------------------------------------------|------------|
| $\rho_c$                                    |            |
| 0.01559 $\pm$ 0.00005 g mol/cm <sup>3</sup> | [102]      |
| 0.01527 $\pm$ 2% g mol/cm <sup>3</sup>      | [258]      |
| 0.02909 g/cm <sup>3</sup>                   | [61]       |
| $T_c$                                       |            |
| 32.976 $\pm$ 0.015 K                        | [102]      |
| 32.984 $\pm$ 0.020 K                        | [258]      |
| 33.19 K                                     | [61]       |
| $P_c$                                       |            |
| 12.759 $\pm$ 0.028 atm                      | [102]      |
| 12.770 $\pm$ 0.04 atm                       | [258]      |
| 1292 kPa = 12.751 atm                       | [61]       |



## 2.15 Equation of State of Liquid Hydrogen

It was noticed very early that the equation of state of liquid hydrogen deviates substantially from the equations of state for other cryogenic liquids [105]. If the  $pV$  isotherms are known for a specific temperature and pressure condition, the compressibility can be calculated by differentiating the data. Detailed PVT tables are contained in a number of publications, including those by [61, 259]. See also [74, 260, 261].

A very simple, but approximate equation of state, while not adequate for computation of thermal properties, may, if valid over a wide range, be useful as a concise representation of the mechanical properties of a fluid like liquid hydrogen [262]. In particular, it would provide a continuous reference with which to compare experimental PVT data for purposes of smoothing, accomplished by examining differences.

The PVT surface presented by NBS covers both gaseous and liquid regions from the triple point to the critical point [93, 263]. Another equation of state gives qualitatively correct behavior in the critical region, i.e., “scaling-law” behavior [264].

A reasonably condensed table of PVT saturation properties and transport data of parahydrogen is offered in Table 2.2 on page 8 of [70].

Compressibility measurements and thermodynamic properties data for parahydrogen were extended to higher temperatures and pressures [265]. Results of an experimental program were presented in the form of pressure, volume, and temperature data in the temperature range 23–300 K at pressures up to 80 MPa (800 bar). Second and third virial coefficients can be calculated by two groups of polynomial equations, one for temperatures below 100 K and another for temperatures above 100 K. Tables for virial coefficients to be used in the standard equation of state are available in [41].

A truncated virial equation was based on the current parahydrogen equation of Younglove 1982 and is limited to low-density vapor states [266]. The density uncertainty for this equation is the same as that of Younglove 1982, but it has fewer terms making it suitable for engineering calculations.

A Benedict-type PVT equation of state was derived from high-pressure sound velocity data together with previously reported volume and ultrasonic velocity data at low pressures and temperatures, that is valid for fluid hydrogen up to the maximum pressures and temperatures with an average deviation of 1% from the new and previously published experimental data [115].

New fundamental equations of state for parahydrogen, normal hydrogen, and orthohydrogen were developed to replace existing, outdated property models [267]. To accurately predict thermophysical properties near the critical region and in liquid states, the quantum law of corresponding states was applied to improve the normal hydrogen and orthohydrogen formulations in the absence of available experimental data. All three equations of state have the same maximum pressure of 2000 MPa and an upper temperature limit of 1000 K.

## 2.16 Solubility, Miscibility, Mixtures, Solutions of Hydrogen

### 2.16.1 Solubility of Hydrogen in Other Fuels

Theoretically it should be possible to improve the performance of other rocket fuels by dissolving hydrogen in the liquid fuels. Unfortunately, the solubility of dihydrogen in other fuels is very poor.

### 2.16.2 Pressurant Gas Solubility in Liquid Hydrogen

There are numerous studies published on the phase diagrams of hydrogen/helium mixtures at very high pressures [268–272]. Hydrogen/helium mixtures would not be very practical as rocket propellants. At normal hydrogen storage pressures, the solubility of helium in liquid hydrogen is only very small. Helium is used as a pressurant in liquid hydrogen tanks to bring the tank pressure up to a point that it will prevent cavitation in the inlet section of propellant pumps. At the normal boiling point of helium, hydrogen has already frozen to a solid. There may even be a miscibility gap in a certain region. Experiments on phase behavior in hydrogen-helium mixtures have been carried out at pressures up to 9.3 kilobars, at temperatures from 260 to 1000 K [273]. Two distinct fluid phases were shown to exist at supercritical temperatures and high pressures. Both the trend of the experimental results and an analysis based on the van der Waals theory of mixtures suggest that this fluid-fluid phase separation persists at temperatures and pressures beyond the range of these experiments, perhaps even to the limits of stability of the molecular phases. The results confirmed earlier predictions concerning the form of the hydrogen-helium phase diagram in the region of pressure-induced solidification of the molecular phases at supercritical temperatures. This phase diagram may have implications for planetary interiors of giant gas planets.

The main reason for the study of hydrogen/helium mixtures at very high pressures is the indication that such mixtures may exist at very high pressures surrounding the cores of the giant gaseous planets, Jupiter and Saturn [274]. Models of Jupiter and Saturn postulate a central rock core surrounded by a fluid mixture of hydrogen and helium. These models suggest that the mixture is undergoing phase separation in Saturn but not Jupiter. State-of-the-art total energy calculations of the enthalpy of mixing for ordered alloys of hydrogen and helium confirm that at least partial phase separation has occurred in Saturn and predict that this process has also begun in Jupiter.

Equilibrium properties of hydrogen-helium mixtures under conditions similar to the interior of giant gas planets for densities between 0.19 and 0.66 g/cm<sup>3</sup> and temperatures from 500 to 8000 K were studied by means of first-principles density functional molecular dynamics simulations [275].

At very high pressures, hydrogen is more likely to turn into a metallic phase than helium with free mobility of electrons among the nuclei. At even higher pressures, it will fuse into helium as in the sun and in hydrogen atomic bombs. A good source of energy for rocket propulsion, but difficult to control.

Additional studies of the phase relationships of hydrogen/helium mixtures at high pressures in a pressure range from 15 to 75 kbar and at temperatures from 110 up to 360 K determined three-phase line solid-fluid-fluid and showed that the divergency of these lines persists up to the highest pressures and that the fluid-fluid equilibrium region extends to higher temperatures and higher pressures [276, 277].

Helium is the only pressurant for liquid hydrogen fuel tanks other than warm hydrogen gas. Precise composition measurements of this mixture are necessary for predictive models for propellant pressurization and transfer. Pressure-Volume-Temperature composition (PVT-x) measurements of cryogenic helium-hydrogen mixtures taken with a Rubotherm IsoSORP 2000 dual-sinker magnetic suspension microbalance that had been retrofitted for cryogenic service, measured the solubility of helium in liquid hydrogen. This system has been validated by direct comparison to previously published experimental data and extended the range of helium-hydrogen density measurements. The range of possible measurements extended from 10 to 288 K for pressures up to 275 bar.

Although NASA has used helium gas to pressurize liquid hydrogen propellant tanks for decades, little is known about the interactions between helium gas and liquid hydrogen. Traditionally, helium gas is injected into the liquid hydrogen propellant tank to maintain constant tank pressure. This method was used on the Space Shuttle and will continue to be used on the Space Launch System that is under development by NASA.

Tests using the Multipurpose Hydrogen Test Bed at NASA MSFC to evaluate the effects of helium pressurant on the performance of a spray bar thermodynamic vent system with an ambient heat leak of about 70–80 W and tank fill levels of 90, 50, and 25% successfully controlled the tank pressure within a  $\pm 3.45$  kPa ( $\pm 0.5$  psi) band with various helium concentration levels in the ullage [278]. Relative to pressure control with an “all hydrogen” ullage, the helium presence resulted in 10–30% longer pressure reduction durations, depending on the fill level. The time to opening the vent depended on activating the mixer in the tank to prevent stratification. Ullage stratification was present, and the ullage pressure was successfully controlled without the mixer operating. It was evident that the spray bar configuration, which extended almost the entire length of the tank, enabled significant thermal energy removal from the ullage even without the mixer operating.

Liquid hydrogen saturated with helium at atmospheric pressure contains 0.17 mol-% helium. The rate of self-pressurization of liquid hydrogen tanks is different for tanks containing pure hydrogen and tanks containing helium-saturated hydrogen [279]. The model compared the tank performance for the traditional model that assumes no helium pressurant dissolves into the liquid hydrogen propellant to an updated model that accounts for dissolved helium pressurant. Traditional NASA models have been unable to account for this dissolved helium due to a lack of fundamental property information. The self-pressurization model was run assuming

that the liquid propellant was pure liquid hydrogen and assuming helium dissolved into the liquid utilizing the new helium-hydrogen EOS. The analysis showed that having dissolved helium in the propellant does not have a significant effect on the tank pressurization rate for typical tank conditions (20.4 K and 206 kPa =  $-423^{\circ}\text{F}$  and 30 psia). The model predicted a  $0.2^{\circ}\text{F}$  difference in the propellant temperature over the course of a 10-h mission when accounting for dissolved helium pressurant. Calculations showed that dissolved helium slightly decreases the rate at which the propellant temperature rises [280, 281].

## 2.17 Thermodynamic Properties of Hydrogen

The publication by Woolley, Scott, and Brickwede [61] contains voluminous tables of the thermodynamic properties of hydrogen. Additional data on thermodynamic properties of hydrogen can be found in the publications listed in Table 25 which cannot all be reproduced here because they contain too much detailed information.

**Table 25:** Sources for data on thermodynamic properties of hydrogen.

| Properties                              | Author                     | Year | References |
|-----------------------------------------|----------------------------|------|------------|
| Thermodynamic properties                | Altman                     | 1956 | [282]      |
| Parahydrogen                            | Goodwin et al.             | 1964 | [74]       |
| Thermodynamic and transport properties  | Hilsenrath et al.          | 1960 | [73]       |
| Thermochemical tables                   | JANAF                      |      | [283]      |
| Thermodynamic properties                | Krascella                  | 1963 | [284]      |
| Thermodynamic properties from 1 to 22 K | Mullins, Ziegler, and Kirk | 1963 | [285]      |
| Thermodynamic properties up to 100000 K | Rosenbaum and Levitt       | 1962 | [286]      |
| Parahydrogen from 36 to 5400 °R         | Stephenson                 | 1965 | [287, 288] |
| Parahydrogen to 5000 °R and 10000 psia  | McCarty and Weber          | 1972 | [289]      |

Changes of temperature during isentropic expansion of normal hydrogen in nozzles were computed assuming equilibrium composition for chamber pressures from 0.96 kPa to 10 MPa, pressure ratios from 1 to 3000, and chamber temperatures from 600 to 5000 K [290]. Computed parameters included nozzle-exit pressure and temperature, enthalpy, molecular weight, isentropic exponent, specific heat at constant pressure, absolute viscosity, thermal conductivity, Mach number, specific impulse in vacuum, ratio of nozzle-exit to throat areas, thrust coefficient, specific impulse, equilibrium gas composition, characteristic velocity, and entropy. Additional properties of gaseous normal hydrogen, orthohydrogen, and parahydrogen were calculated for several pressures at temperatures below 600 K.

The report by [41] contains very detailed tables and graphs of the thermodynamic properties of hydrogen in various physical states as a function of temperature and pressure.

With the advances in computing power of computers, much of the work on thermodynamic properties of hydrogen is now not experimental, but computational, as indicated by relatively recent reviews of the status of thermodynamic properties of hydrogen [291, 292].

Many applications expose hydrogen to temperatures even higher than those encountered in chemical rockets. Thermodynamic properties of 20.4 K-equilibrium hydrogen for pressures between 6.9 kPa and 20.7 MPa (1 and 3000 psia) and temperatures between 14 and 2777 K (between 25 and 5000 °R) were tabulated, including temperature-entropy, enthalpy-entropy, pressure-enthalpy, temperature-enthalpy, and temperature-density diagrams [293]. At high temperatures a study of the gas properties must consider the effects of dissociation and non-ideal gas behavior.

Compressibility measurements and thermodynamic properties data for parahydrogen were extended to higher temperatures and pressures [265]. Tables contained thermodynamic properties on isobars to 100 MPa (1000 bar) including density, internal energy, enthalpy, entropy, specific heats at constant volume and constant pressure, velocity of sound, and surface derivatives.

The PVT properties of compressed normal hydrogen (75% orthohydrogen and 25% parahydrogen) up to 100 MPa and its equation of state (EOS) derived from the measurement data of the Burnett method, along with a correlation of viscosity and thermal conductivity for compressed hydrogen have been summarized [95, 294].

## **2.17.1 Heat Capacity of Hydrogen**

### **2.17.1.1 Heat Capacity of Solid and Liquid Hydrogen**

The heat capacity at constant pressure of liquid parahydrogen at the triple point is  $c_p = 6.36 \text{ J g}^{-1} \text{ K}^{-1}$  and at the boiling point it is  $9.66 \text{ J g}^{-1} \text{ K}^{-1}$ . For comparison, the heat capacity of gaseous parahydrogen at the triple point is  $10.52 \text{ J g}^{-1} \text{ K}^{-1}$  and at the boiling point it is  $12.15 \text{ J g}^{-1} \text{ K}^{-1}$ . Heat capacity data of solid and liquid normal and parahydrogen are listed in Tables 26 and 27.

Table 26: Molar heat capacity  $C_p$  and heat capacity  $c_p$  of solid and liquid hydrogen.

| Phase           | Temperature |         | Molar heat capacity                 |                                        | Heat capacity                     |                                      | Data source                        | References |  |  |
|-----------------|-------------|---------|-------------------------------------|----------------------------------------|-----------------------------------|--------------------------------------|------------------------------------|------------|--|--|
|                 | K           | °C      | J mol <sup>-1</sup> K <sup>-1</sup> | cal mol <sup>-1</sup> °C <sup>-1</sup> | J g <sup>-1</sup> K <sup>-1</sup> | cal g <sup>-1</sup> °C <sup>-1</sup> |                                    |            |  |  |
| Normal hydrogen |             |         |                                     |                                        |                                   |                                      |                                    |            |  |  |
| Solid           | 10          | -263.2  | 2.43                                | 0.58                                   | 1.20                              | 0.29                                 | Kit and Evered 1960                | [295]      |  |  |
| Solid           | 11          | -262.2  | 3.18                                | 0.76                                   | 1.58                              | 0.38                                 |                                    |            |  |  |
| Solid           | 12          | -261.2  | 3.97                                | 0.95                                   | 1.97                              | 0.47                                 |                                    |            |  |  |
| Solid           | 13          | -260.2  | 4.85                                | 1.16                                   | 2.41                              | 0.58                                 | Woolley, Scott, and Brickwede 1948 | [61]       |  |  |
| Solid           | 14          | -259.2  | 5.73                                | 1.37                                   | 2.84                              | 0.68                                 |                                    |            |  |  |
| Liquid          | 14          | -259.2  | 13.85                               | 3.31                                   | 6.87                              | 1.64                                 |                                    |            |  |  |
| Liquid          | 15          | -258.2  | 14.48                               | 3.46                                   | 7.18                              | 1.72                                 |                                    |            |  |  |
| Liquid          | 16          | -257.2  | 15.19                               | 3.63                                   | 7.53                              | 1.80                                 |                                    |            |  |  |
| Liquid          | 17          | -256.2  | 16.02                               | 3.83                                   | 7.95                              | 1.90                                 |                                    |            |  |  |
| Liquid          | 18          | -255.2  | 16.90                               | 4.04                                   | 8.38                              | 2.00                                 | Johnston et al. 1950               | [84]       |  |  |
| Liquid          | 19          | -254.2  | 17.87                               | 4.27                                   | 8.86                              | 2.12                                 |                                    |            |  |  |
| Liquid          | 20          | -253.2  | 18.83                               | 4.5                                    | 9.34                              | 2.23                                 |                                    |            |  |  |
| Parahydrogen    |             |         |                                     |                                        |                                   |                                      |                                    |            |  |  |
| Solid           | 12.71       | -260.45 | 4.18                                | 1.00                                   | 2.08                              | 0.50                                 | Smith, Hallett, and Johnston 1954  | [88]       |  |  |
| Solid           | 12.89       | -260.27 | 4.73                                | 1.13                                   | 2.35                              | 0.56                                 |                                    |            |  |  |
| Solid           | 13.2        | -259.96 | 5.23                                | 1.25                                   | 2.59                              | 0.62                                 |                                    |            |  |  |
| Solid           | 13.45       | -259.71 | 5.36                                | 1.28                                   | 2.66                              | 0.63                                 | Smith, Hallett, and Johnston 1954  | [88]       |  |  |
| Melting point   |             |         |                                     |                                        |                                   |                                      |                                    |            |  |  |
| Liquid          | 18.28       | -254.88 | 17.49                               | 4.18                                   | 8.68                              | 2.07                                 |                                    |            |  |  |
| Liquid          | 20.45       | -252.71 | 19.71                               | 4.71                                   | 9.78                              | 2.34                                 |                                    |            |  |  |
| Liquid          | 22.71       | -250.45 | 22.30                               | 5.33                                   | 11.06                             | 2.64                                 |                                    |            |  |  |
| Liquid          | 25          | -248.16 | 25.23                               | 6.03                                   | 12.52                             | 2.99                                 |                                    |            |  |  |
| Liquid          | 26.04       | -247.12 | 27.03                               | 6.46                                   | 13.41                             | 3.20                                 |                                    |            |  |  |
| Liquid          | 28.2        | -244.96 | 32.84                               | 7.85                                   | 16.29                             | 3.89                                 |                                    |            |  |  |
| Liquid          | 30.1        | -243.06 | 41.59                               | 9.94                                   | 20.63                             | 4.93                                 |                                    |            |  |  |
| Liquid          | 31.49       | -241.67 | 60.92                               | 14.56                                  | 30.22                             | 7.22                                 |                                    |            |  |  |

**Table 27:** Molar heat capacity  $C_p$  and heat capacity  $c_p$  of liquid parahydrogen.

| Physical state | Temperature<br>K | Molar Heat Capacity,<br>Measured  |                                           | Molar Heat Capacity,<br>Calculated |                                           | Heat Capacity,<br>Measured      |                                         |
|----------------|------------------|-----------------------------------|-------------------------------------------|------------------------------------|-------------------------------------------|---------------------------------|-----------------------------------------|
|                |                  | $\text{J mol}^{-1} \text{K}^{-1}$ | $\text{cal mol}^{-1} ^\circ\text{C}^{-1}$ | $\text{J mol}^{-1} \text{K}^{-1}$  | $\text{cal mol}^{-1} ^\circ\text{C}^{-1}$ | $\text{J g}^{-1} \text{K}^{-1}$ | $\text{cal g}^{-1} ^\circ\text{C}^{-1}$ |
| Liquid         | 14.83            | 13.71                             | 3.277                                     | 13.70                              | 3.274                                     | 6.80                            | 1.63                                    |
| Liquid         | 15.817           | 14.72                             | 3.519                                     | 14.74                              | 3.524                                     | 7.30                            | 1.75                                    |
| Liquid         | 16.753           | 15.68                             | 3.747                                     | 15.67                              | 3.746                                     | 7.78                            | 1.86                                    |
| Liquid         | 17.735           | 16.64                             | 3.976                                     | 16.64                              | 3.977                                     | 8.25                            | 1.97                                    |
| Liquid         | 18.701           | 17.61                             | 4.209                                     | 17.61                              | 4.21                                      | 8.74                            | 2.09                                    |
| Liquid         | 20.01            | 19.04                             | 4.551                                     | 19.02                              | 4.545                                     | 9.45                            | 2.26                                    |
| Boiling point  | 20.27            |                                   |                                           |                                    |                                           |                                 |                                         |
| Liquid         | 21.046           | 20.23                             | 4.835                                     | 20.22                              | 4.832                                     | 10.03                           | 2.40                                    |
| Liquid         | 23.952           | 24.16                             | 5.775                                     | 24.20                              | 5.785                                     | 11.99                           | 2.86                                    |
| Liquid         | 24.773           | 25.59                             | 6.116                                     | 25.56                              | 6.109                                     | 12.69                           | 3.03                                    |
| Liquid         | 25.563           | 27.07                             | 6.47                                      | 27.02                              | 6.457                                     | 13.43                           | 3.21                                    |
| Liquid         | 26.35            | 28.71                             | 6.863                                     | 28.66                              | 6.85                                      | 14.24                           | 3.40                                    |
| Liquid         | 27.614           | 31.86                             | 7.614                                     | 31.91                              | 7.627                                     | 15.80                           | 3.78                                    |
| Liquid         | 28.749           | 35.76                             | 8.546                                     | 35.85                              | 8.569                                     | 17.74                           | 4.24                                    |
| Liquid         | 29.484           | 39.27                             | 9.385                                     | 39.27                              | 9.386                                     | 19.48                           | 4.66                                    |
| Liquid         | 30.413           | 45.38                             | 10.847                                    | 45.25                              | 10.814                                    | 22.51                           | 5.38                                    |
| Liquid         | 31.228           | 53.11                             | 12.693                                    | 53.28                              | 12.734                                    | 26.34                           | 6.30                                    |
| Liquid         | 31.539           | 57.71                             | 13.792                                    | 57.61                              | 13.77                                     | 28.62                           | 6.84                                    |

Data source: [296]

### 2.17.1.2 Heat Capacity of Solid Hydrogen

Heat capacity data for solid parahydrogen are listed in Table 28. Specific heat, thermal conductivity, and thermal diffusivity of solid hydrogen are highly sensitive to actual ortho-para composition. A composite picture for the heat capacity of solid hydrogen containing varying amounts of ortho and parahydrogen is shown in Figure 38. This graph is similar to Figure 38 in [41].

The report by Roder et al. 1973 [70] also contains data for the heat capacity of compressed solid hydrogen under pressures of up to 400 atm. Heat capacity of solid hydrogen decreased with increasing pressure.

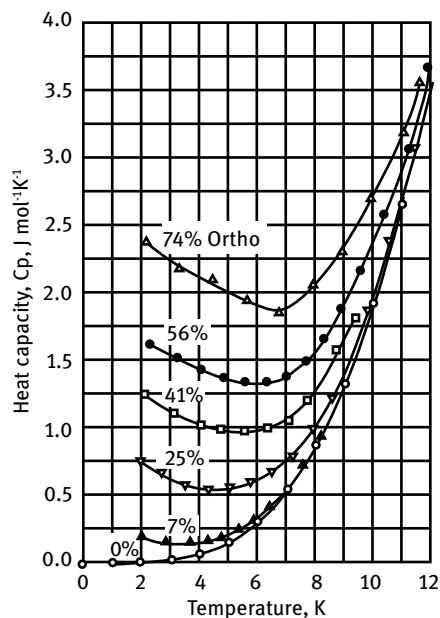
The lattice heat capacity of solid hydrogen was measured at zero pressure and at three constant volumes [297, 298], Table 26. The measurements extended from 2 K to the triple point for the zero pressure data, from 2 K to the melting temperature at  $22.56 \text{ cm}^3/\text{mol}$ , and from 4 to 20 K at  $19.83$  and  $18.73 \text{ cm}^3/\text{mol}$ . The isothermal compressibility at 16.35 K at the melting pressure is essentially the same as at 4.2 K at the same pressure. The thermal expansion coefficient at 8.31 MPa (82 atm) appears to have a maximum at about 12 K. At zero pressure the thermal expansion coefficient is approximately proportional to the temperature. For two of the samples there was an anomalous contribution to the heat capacity at low temperatures because the sam-

**Table 28:** Parahydrogen properties – saturated solid.

| Temperature<br>K | Pressure<br>mm Hg     | Spec. volume<br>cm <sup>3</sup> /mol | $C_S$<br>mJ mol <sup>-1</sup> K <sup>-1</sup> | $C_p$ est.<br>mJ mol <sup>-1</sup> K <sup>-1</sup> | Enthalpy<br>J/mol |
|------------------|-----------------------|--------------------------------------|-----------------------------------------------|----------------------------------------------------|-------------------|
| 0.00             |                       | 22.645                               | 0.0                                           | 0.00                                               | -758.0            |
| 1.00             | $8.3 \times 10^{-39}$ | 22.645                               | 1.03                                          | 1.03                                               | -758.0            |
| 2.00             | $4.0 \times 10^{-18}$ | 22.645                               | 8.57                                          | 8.57                                               | -758.0            |
| 3.00             | $4.8 \times 10^{-11}$ | 22.646                               | 30.7                                          | 30.7                                               | -758.0            |
| 4.00             | $2.1 \times 10^{-7}$  | 22.650                               | 78.7                                          | 78.7                                               | -757.9            |
| 5.00             | $3.6 \times 10^{-5}$  | 22.660                               | 168.5                                         | 168.5                                              | -758.8            |
| 6.00             | $1.2 \times 10^{-3}$  | 22.678                               | 318.8                                         | 318.8                                              | -757.6            |
| 7.00             | $1.6 \times 10^{-2}$  | 22.711                               | 551                                           | 551                                                | -757.2            |
| 8.00             | $1.1 \times 10^{-1}$  | 22.754                               | 882                                           | 882                                                | -756.4            |
| 9.00             | $5.3 \times 10^{-1}$  | 22.809                               | 1333                                          | 1333                                               | -755.3            |
| 10.00            | 1.97                  | 22.873                               | 1917                                          | 1917                                               | -753.7            |
| 11.00            | 5.68                  | 22.947                               | 2651                                          | 2652                                               | -751.5            |
| 12.00            | 14.0                  | 23.031                               | 3548                                          | 3550                                               | -748.4            |
| 13.00            | 30.4                  | 23.125                               | 4618                                          | 4622                                               | -744.3            |
| 13.803           | 52.8                  | 23.211                               | 5640                                          | 5646                                               | -740.2            |

Note:  $C_S$  is the heat capacity along the saturation line

Data source: [70, 297, 298]

**Figure 38:** Heat capacity of solid hydrogen containing varying amounts of ortho and parahydrogen. (Reproduced and modified from [70].)



ples contained some orthohydrogen. This contribution was subtracted and caused a small additional uncertainty where it was appreciable. The heat of melting at the triple point was  $118 \pm 1$  J/mol. The volume change on melting was estimated to be 4% or  $0.1 \text{ cm}^3/\text{mol}$ . The experimental values of the lattice heat capacity were plotted on large scale graphs in the form of  $C/T^3$  vs.  $T^2$ . These graphs were extrapolated to  $T^2 = 0$ . Other authors [299] had reported heat capacities of solid hydrogen that varied by as much as 14% at 3 K from the more recent data by Ahlers.

Measurements have been made in the temperature range 0.5–5 K of the specific heats of pure solid  $\text{H}_2$ , pure solid  $\text{D}_2$ , and four solid mixtures of  $\text{H}_2$  and  $\text{D}_2$  with  $\text{D}_2$  fractions between 15 and 95%, all of which systems had low concentrations of molecules in the rotational state  $J = 1$  typical for orthohydrogen [300]. The observed specific heats could be described as the sum of three terms: a lattice specific heat, a Schottky term with a maximum at about 1.3 K for solid  $\text{H}_2$  and a second anomalous term occurring at temperatures below about 0.8 K and, by extrapolation, having its maximum below 0.5 K.

### 2.17.1.3 Heat Capacity of Liquid Hydrogen

Values for the  $C_p$ ,  $C_v$ , and  $C_s$  of liquid parahydrogen are shown in Figure 39. Values for the graph were taken from the thermodynamic tables of Roder et al. which in turn were based on the measurements of  $C_v$  and  $C_s$  by Younglove and Diller [296]. Equally detailed and accurate tables of values for saturated liquid and compressed liquid states for parahydrogen from the freezing liquid line to 2700 K (5000 °R) for pressures to 69 MPa (10000 psia) were given [289]. Additional experimental measurements of hydrogen properties at pressures greater than 340 atm have been published [301].

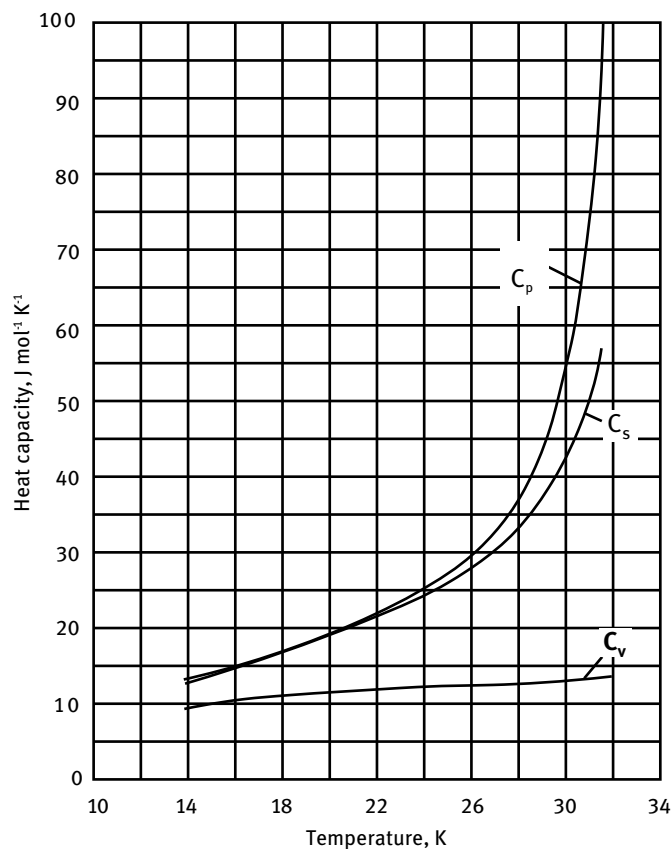
As mentioned above, the differences in specific heats for different orthohydrogen-parahydrogen compositions in the liquid state are very small [84, 88]. For additional heat capacity data see [302]. For additional heat capacity data  $C_v$  at constant volume and high pressure, see [296, 303].

### 2.17.1.4 Heat Capacity of Gaseous Hydrogen

The heat capacity of gaseous hydrogen between 298 and 6000 K can be calculated from a Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + \frac{E}{\tau^2}$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $\tau$  is the temperature in kelvin divided by 1000. The constants A through H are listed in Table 29 for three different temperature ranges.



**Figure 39:** Heat capacity of liquid parahydrogen. (Reproduced and modified from [70].)

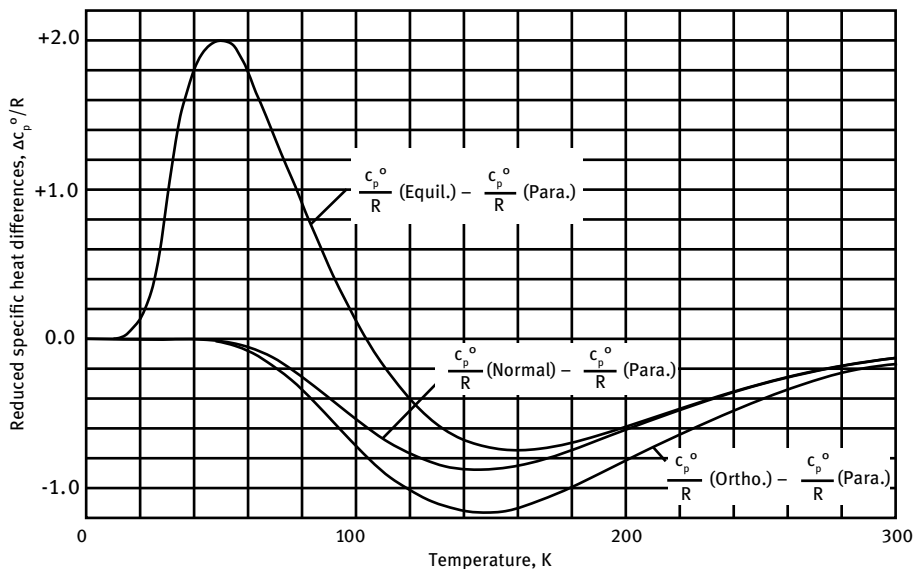
**Table 29:** Constants for Shomate equations for gaseous hydrogen

| Constant | Value      |            |            |
|----------|------------|------------|------------|
|          | 298–1000   | 1000–2500  | 2500–6000  |
| A        | 33.066178  | 18.563083  | 43.413560  |
| B        | −11.363417 | 12.257357  | −4.293079  |
| C        | 11.432816  | −2.859786  | 1.272428   |
| D        | −2.772874  | 0.268238   | −0.096876  |
| E        | −0.158558  | 1.977990   | −20.533862 |
| F        | −9.980797  | −1.147438  | −38.515158 |
| G        | 172.707974 | 156.288133 | 162.081354 |
| H        | 0.0        | 0.0        | 0.0        |

$H^\circ$  = standard enthalpy (kJ/mol)

Data source: [83]

Isentropic expansion of hydrogen gas is a key step in the liquefaction process and data for the isentropic heat capacity have been tabulated [304]. The difference in heat capacity of ortho, para and normal (equilibrium) hydrogen changes over a wide range of temperatures, as shown in Figure 40.



**Figure 40:** Reduced specific heat differences between equilibrium, normal, ortho and parahydrogen in the ideal gas state. (Reproduced and modified from [62]).

### 2.17.2 Enthalpy of Formation of Hydrogen

The reference state for enthalpy is zero for the ideal gas at zero kelvin absolute temperature. The reference state heat of formation of liquid parahydrogen at the triple point is  $-308.8\text{ J/g}$  and at the boiling point it is  $-256.3\text{ J/g}$ , this is more negative than the reference state heat of formation of normal hydrogen which is  $+218.3\text{ J/g}$  at the triple point and  $+270.9\text{ J/g}$  at the boiling point. The reference state enthalpy of parahydrogen gas at the triple point is  $140.3\text{ J/g}$  and at the boiling point it is  $189.3\text{ J/g}$ , compared to normal hydrogen gas which is  $667.4\text{ J/g}$  at the triple point and  $716.5\text{ J/g}$  at the boiling point.

By definition, the standard enthalpy of formation of hydrogen gas under standard conditions at  $298\text{ K}$  is zero ( $\Delta H_{298\text{ gas}} = 0.00\text{ kJ/mol}$ ). The enthalpy of formation of liquid parahydrogen, at the normal boiling point is  $-7.895\text{ kJ/mol} = -1.887\text{ kcal/mol}$ . The NASA CEC Thermo.inp list uses a heat of formation for LH2 of  $-9012\text{ J/mol}$  [89].

The differential enthalpy of formation of gaseous hydrogen in the temperature range 298–6000 K can be calculated from the equation

$$H^\circ - H^\circ_{298.15} = A\tau + \frac{B\tau^2}{2} + \frac{C\tau^3}{3} + \frac{D\tau^4}{4} - \frac{E}{t} + F - H$$

where  $H$  is the enthalpy of formation in J/mol and  $\tau$  is the temperature in kelvin divided by 1000. The constants were already shown in Table 29 above. This equation is shown in the NIST Chemistry WebBook [83].

The heat of conversion of hydrogen from normal hydrogen to parahydrogen is listed in Table 30. See also Figure A1.2 on page A4 of NASA Hydrogen Systems Safety Standard [305].

**Table 30:** Heat of conversion from normal to parahydrogen.

| Temperature<br>K | Heat of conversion |          |
|------------------|--------------------|----------|
|                  | J/mol              | cal/mol  |
| 10               | 527.139            | 253.9865 |
| 20               | 527.140            | 253.987  |
| 20.39            | 527.138            | 253.986  |
| 30               | 527.138            | 253.986  |
| 33.1             | 527.138            | 253.986  |
| 40               | 527.117            | 253.976  |
| 50               | 526.845            | 253.845  |
| 60               | 525.531            | 253.212  |
| 70               | 521.770            | 251.400  |
| 80               | 513.932            | 247.623  |
| 90               | 500.757            | 241.275  |
| 100              | 481.671            | 232.079  |
| 120              | 427.248            | 205.857  |
| 150              | 322.495            | 155.385  |
| 200              | 163.774            | 78.91    |
| 250              | 70.524             | 33.98    |
| 298.16           | 28.558             | 13.76    |
| 300              | 27.562             | 13.28    |

Data source: [61]

### 2.17.3 Heat of Combustion of Hydrogen

The heat of combustion of hydrogen per unit mass is higher than that of any other material, but hydrogen has a relatively low heat of combustion per unit volume. Thus, the combustion of a given volume of hydrogen will release less energy than the same volume of either natural gas or gasoline. Heat of combustion (lower)  $(\Delta H)_{\text{Comb}}$ , (gaseous at 298 K = 25 °C) 241.8 kJ/mol = 57.79 kcal/mol = 28.6696 kcal/g.

Heat of combustion (upper)  $(\Delta H)_{\text{Comb.}}$  (gaseous at 298 K = 25 °C) 285.8 kJ/mol = 68.31 kcal/mol = 33.89 kcal/g. Except for the different polarity sign, this number is identical with the standard enthalpy of formation of liquid water.

#### 2.17.4 Heat of Fusion of Solid Hydrogen

The heat of fusion of solid parahydrogen at the triple point was reported as  $118 \pm 1$  J/mol ( $28.2 \pm 0.2$  cal/mol) [297, 298]. The heat of fusion of parahydrogen at 13.95 K is  $117.5 \pm 0.6$  J/mol =  $28.08 \pm 0.15$  cal/mol [84]. This is the average of two measurements taken between 13.4 and 14.7 K. Data for the heat of fusion of solid hydrogen along the melting line over a wide range of temperatures and pressures are listed in Table 31.

**Table 31:** Parahydrogen properties along the melting line

| Temperature<br>K | Pressure<br>atm | Molar vol-<br>ume of the<br>liquid<br>cm <sup>3</sup> /mol | Molar vol-<br>ume of the<br>solid<br>cm <sup>3</sup> /mol | Enthalpy of<br>the liquid<br>J/mol | Heat of<br>fusion<br>J/mol | Enthalpy of<br>the solid,<br>J/mol |
|------------------|-----------------|------------------------------------------------------------|-----------------------------------------------------------|------------------------------------|----------------------------|------------------------------------|
| 13.803           | 0.0695          | 26.176                                                     | 23.31                                                     | -622.9                             | -117.3                     | -740.2                             |
| 14.0             | 5.89            | 26.062                                                     | 23.26                                                     | -606.9                             | -118.4                     | -725.3                             |
| 15.0             | 36.88           | 25.513                                                     | 22.97                                                     | -523.9                             | -124.1                     | -648.0                             |
| 16.0             | 70.19           | 25.006                                                     | 22.67                                                     | -436.2                             | -130.3                     | -566.5                             |
| 17.0             | 105.7           | 24.540                                                     | 22.36                                                     | -344.7                             | -136.9                     | -481.6                             |
| 18.0             | 143.2           | 24.103                                                     | 22.06                                                     | -249.6                             | -143.8                     | -393.4                             |
| 19.0             | 182.7           | 23.702                                                     | 21.76                                                     | -151.3                             | -151.1                     | -302.4                             |
| 20.0             | 224.1           | 23.328                                                     | 21.48                                                     | -50.1                              | -158.7                     | -208.8                             |
| 21.0             | 267.3           | 22.978                                                     | 21.20                                                     | +54.3                              | -166.7                     | -112.4                             |
| 22.0             | 312.2           | 22.654                                                     | 20.94                                                     | +161.1                             | -175.0                     | -13.9                              |
| 23.0             | 358.9           | 22.351                                                     | 20.69                                                     | +272                               | -183.6                     | +88.4                              |
| 24.0             | 407.2           | 22.065                                                     | 20.45                                                     | +387                               | -192.5                     | +194.5                             |

Data source: [70]

The latent heat of fusion of solid  $p$ -H<sub>2</sub> at constant pressure was measured at various temperatures and at pressures up to 34.25 MPa (338 atm) [100]. The data are well reproduced by the linear equation:

$$\Delta H_{\text{fus}} = 0.044149P + 28.041$$

where  $\Delta H_{\text{fus}}$  is the latent heat of fusion in cal/mol and  $P$  is the pressure in atm. Other sources give this equation as

$$\Delta H_{\text{fus}} = 0.044149P + 28.02693164$$

A generally accepted value for the heat of fusion of solid hydrogen at the triple point is 117.277 J/mol.

### 2.17.5 Heat of Vaporization of Liquid Hydrogen

The heat of evaporation decreases with increasing temperature and approaches zero as the temperature nears the critical point. In the following, heat of vaporization data from various sources dating back to the past century are assembled and some discrepancies in the data were noted. Some of the differences may be due to varying degrees of ortho→para conversion (Table 32).

The heat of vaporization between the triple point and the normal boiling point can be expressed by the equation

$$\Delta H = 219.7 - 0.27 (T - 16.6)^2,$$

where  $\Delta H$  is the heat of vaporization in cal/mol and  $T$  is the temperature in kelvin [306].

Raw, uncorrected calorimetric data for the heat of vaporization of parahydrogen are listed in Table 33. These early data do not match very well with data reported by other investigators which were mostly derived from vapor pressure measurements. The hydrogen was equilibrated at 20.4 K over a catalyst for several hours before the measurements were made, and thus should have contained only a very small amount of orthohydrogen.

The heat of vaporization as a function of temperature can be computed from the Clapeyron equation and a set of vapor pressure data. The heat of vaporization of parahydrogen derived from PVT data is listed in Table 34 from Reference [102]. These data were updated by the same author 10 years later.

**Table 32:** Heat of vaporization of liquid hydrogen.

| Ortho-para isomer | Temperature | Heat of vaporization ( $\Delta H$ ) <sub>evap.</sub> |                |       |       | Authors              | References |
|-------------------|-------------|------------------------------------------------------|----------------|-------|-------|----------------------|------------|
| Composition       | K           | J/mol                                                | cal/mol        | J/g   | cal/g |                      |            |
| Normal hydrogen   | 20.26       | 917.6                                                | 219.3          | 455.1 | 108.8 | Johnston et al. 1950 | [84]       |
| Normal hydrogen   | 20.4        | 915.0                                                | 218.7          | 453.9 | 108.5 | White,               | [116]      |
| Normal hydrogen   | 22          | 889.9                                                | 212.7          | 441.5 | 105.5 | Friedman             |            |
| Normal hydrogen   | 24          | 849.4                                                | 203            | 421.3 | 100.7 | and John-            |            |
| Normal hydrogen   | 26          | 797.9                                                | 190.7          | 395.8 | 94.6  | ston 1950            |            |
| Normal hydrogen   | 28          | 726.3                                                | 173.6          | 360.3 | 86.1  |                      |            |
| Normal hydrogen   | 30          | 620.9                                                | 148.4          | 308.0 | 73.6  |                      |            |
| Normal hydrogen   | 31          | 543.1                                                | 129.8          | 269.4 | 64.4  |                      |            |
| Normal hydrogen   | 32          | 427.6                                                | 102.2          | 212.1 | 50.7  |                      |            |
| Normal hydrogen   | 32.5        | 337.2                                                | 80.6           | 167.3 | 40.0  |                      |            |
| Normal hydrogen   | 33          | 168.6                                                | 40.3           | 83.6  | 20.0  |                      |            |
| Normal hydrogen   | 33.1        | 126.4                                                | 30.2           | 62.7  | 15.0  |                      |            |
| Parahydrogen      | 20.26       | 898.7                                                | 214.8<br>± 0.4 | 445.8 | 106.6 | Johnston et al. 1950 | [84]       |

**Table 33:** Experimental, calorimetric data for the heat of vaporization of parahydrogen.

| Temperature<br>K | $T/T_c$ | Heat of vaporization |       |         |       |
|------------------|---------|----------------------|-------|---------|-------|
|                  |         | J/mol                | J/g   | cal/mol | cal/g |
| 24.41            | 0.7344  | 858.6                | 425.9 | 205.2   | 101.8 |
| 26.33            | 0.7921  | 811.7                | 402.7 | 194.0   | 96.2  |
| 28.12            | 0.846   | 746.8                | 370.5 | 178.5   | 88.5  |
| 29.65            | 0.892   | 613.8                | 304.5 | 146.7   | 72.8  |
| 30.97            | 0.9317  | 495.4                | 245.7 | 118.4   | 58.7  |
| 31.85            | 0.9582  | 406.7                | 201.7 | 97.2    | 48.2  |
| 32.69            | 0.9835  | 244.3                | 121.2 | 58.4    | 29.0  |

Data source: [307]

**Table 34:** Heat of vaporization of parahydrogen as a function of temperature.

| Temperature<br>K | Calculated $\Delta H_{\text{vap}}$ heat of vaporization |         |       |       |
|------------------|---------------------------------------------------------|---------|-------|-------|
|                  | J/mol                                                   | cal/mol | J/g   | cal/g |
| 13.803           | 907.1                                                   | 216.8   | 450.0 | 107.5 |
| 13.99            | 908.3                                                   | 217.1   | 450.6 | 107.7 |
| 14.00            | 908.3                                                   | 217.1   | 450.6 | 107.7 |
| 14.99            | 913.4                                                   | 218.3   | 453.1 | 108.3 |
| 15.00            | 913.4                                                   | 218.3   | 453.1 | 108.3 |
| 15.99            | 914.6                                                   | 218.6   | 453.7 | 108.4 |
| 16.00            | 914.2                                                   | 218.5   | 453.5 | 108.4 |
| 16.99            | 913.8                                                   | 218.4   | 453.3 | 108.3 |
| 17.00            | 913.8                                                   | 218.4   | 453.3 | 108.3 |
| 17.99            | 911.7                                                   | 217.9   | 452.3 | 108.1 |
| 18.00            | 911.7                                                   | 217.9   | 452.3 | 108.1 |
| 18.99            | 907.1                                                   | 216.8   | 450.0 | 107.5 |
| 19.00            | 907.1                                                   | 216.8   | 450.0 | 107.5 |
| 19.99            | 900.8                                                   | 215.3   | 446.9 | 106.8 |
| 20.00            | 900.4                                                   | 215.2   | 446.7 | 106.8 |
| 20.268           | 898.7                                                   | 214.8   | 445.8 | 106.6 |
| 21.00            | 889.1                                                   | 212.5   | 441.0 | 105.4 |
| 22.00            | 876.5                                                   | 209.5   | 434.8 | 103.9 |
| 23.00            | 860.2                                                   | 205.6   | 426.7 | 102.0 |
| 24.00            | 840.1                                                   | 200.8   | 416.8 | 99.6  |
| 24.41            | 830.5                                                   | 198.5   | 412.0 | 98.5  |
| 25.00            | 815.9                                                   | 195.0   | 404.7 | 96.7  |
| 26.00            | 785.8                                                   | 187.8   | 389.8 | 93.2  |
| 26.33            | 774.9                                                   | 185.2   | 384.4 | 91.9  |
| 27.00            | 749.8                                                   | 179.2   | 371.9 | 88.9  |
| 28.00            | 705.8                                                   | 168.7   | 350.1 | 83.7  |
| 28.12            | 700.0                                                   | 167.3   | 347.2 | 83.0  |
| 29.00            | 651.9                                                   | 155.8   | 323.4 | 77.3  |
| 29.65            | 610.4                                                   | 145.9   | 302.8 | 72.4  |

**Table 34:** (continued)

| Temperature<br>K | Calculated $\Delta H_{\text{vap}}$ heat of vaporization |         |       |       |
|------------------|---------------------------------------------------------|---------|-------|-------|
|                  | J/mol                                                   | cal/mol | J/g   | cal/g |
| 30.00            | 586.2                                                   | 140.1   | 290.8 | 69.5  |
| 30.97            | 504.2                                                   | 120.5   | 250.1 | 59.8  |
| 31.00            | 501.2                                                   | 119.8   | 248.6 | 59.4  |
| 31.85            | 402.1                                                   | 96.1    | 199.5 | 47.7  |
| 32.00            | 379.9                                                   | 90.8    | 188.5 | 45.0  |
| 32.40            | 309.2                                                   | 73.9    | 153.4 | 36.7  |
| 32.69            | 236.0                                                   | 56.4    | 117.1 | 28.0  |
| 32.70            | 232.6                                                   | 55.6    | 115.4 | 27.6  |
| 32.90            | 141.8                                                   | 33.9    | 70.4  | 16.8  |

Data source: [70]

The data in Table 34 were compared to older literature data and the deviations were less than 0.2% below the boiling point but approached 6–8% near the critical point. A more recent set of data gave the heat of vaporization of normal and parahydrogen as summarized in Table 35. The heat of vaporization of parahydrogen at the triple point is 448.2 J/g and at the normal boiling point it is 445.5 J/g. The heat of vaporization of normal hydrogen at the triple point is not much different from that of parahydrogen, it is 449.1 J/g at the triple point and 445.6 J/g at the normal boiling point. The heat of vaporization of parahydrogen as a function of temperature is illustrated in Figure 41.

Data for latent heat of vaporization of parahydrogen from [102] and latent heat of vaporization of normal hydrogen were compiled from numbers calculated by Roder et al. (1963) from the Clausius-Clapeyron equation and were compared and the resulting differences in heat of vaporization between the two modifications of hydrogen are illustrated in Figure 42 [30, 308].

### 2.17.6 Entropy of Hydrogen

Entropy data for liquid and gaseous hydrogen are listed in Table 36. The entropy of gaseous hydrogen in the temperature range 298–6000 K can be calculated from the polynomial equation

$$S^\circ = A \ln(\tau) + B\tau + \frac{C\tau^2}{2} + \frac{D\tau^3}{3} - E/(2\tau^2) + G$$

where  $S^\circ$  is the standard entropy in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $\tau$  is the absolute temperature in kelvin divided by 1000. The constants were already shown in Table 29 above. This equation is shown in the NIST Chemistry WebBook [83].



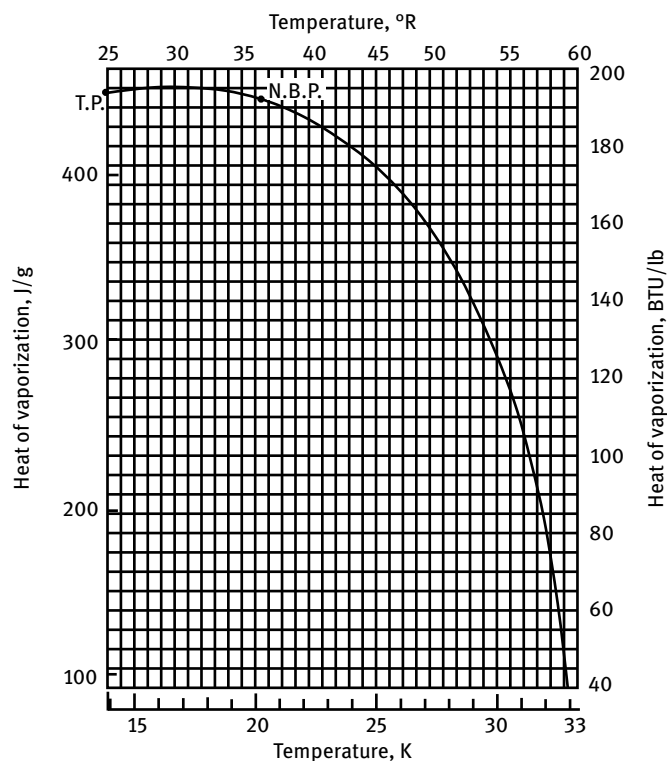
**Table 35:** Enthalpy of vaporization of normal and parahydrogen.

| Temperature<br>K | Latent heat of vaporization<br>Normal hydrogen |       |       |       | Parahydrogen |       |       |       | Difference<br>cal/mol |
|------------------|------------------------------------------------|-------|-------|-------|--------------|-------|-------|-------|-----------------------|
|                  | cal/mol                                        | J/mol | cal/g | J/g   | cal/mol      | J/mol | cal/g | J/g   |                       |
| 14               | 219.9                                          | 920.1 | 109.1 | 456.4 | 217.1        | 908.3 | 107.7 | 450.6 | 2.8                   |
| 15               | 220.7                                          | 923.4 | 109.5 | 458.1 | 218.3        | 913.4 | 108.3 | 453.1 | 2.4                   |
| 16               | 221.1                                          | 925.1 | 109.7 | 458.9 | 218.5        | 914.2 | 108.4 | 453.5 | 2.6                   |
| 17               | 221.1                                          | 925.1 | 109.7 | 458.9 | 218.4        | 913.8 | 108.3 | 453.3 | 2.7                   |
| 18               | 220.6                                          | 923.0 | 109.4 | 457.9 | 217.9        | 911.7 | 108.1 | 452.3 | 2.7                   |
| 19               | 219.6                                          | 918.8 | 108.9 | 455.8 | 216.8        | 907.1 | 107.5 | 450.0 | 2.8                   |
| 20               | 218                                            | 912.1 | 108.1 | 452.5 | 215.2        | 900.4 | 106.8 | 446.7 | 2.8                   |
| 21               | 215.7                                          | 902.5 | 107.0 | 447.7 | 212.5        | 889.1 | 105.4 | 441.0 | 3.2                   |
| 22               | 212.7                                          | 889.9 | 105.5 | 441.5 | 209.5        | 876.5 | 103.9 | 434.8 | 3.2                   |
| 23               | 208.9                                          | 874.0 | 103.6 | 433.6 | 205.6        | 860.2 | 102.0 | 426.7 | 3.3                   |
| 24               | 204.2                                          | 854.4 | 101.3 | 423.8 | 200.8        | 840.1 | 99.6  | 416.8 | 3.4                   |
| 25               | 198.5                                          | 830.5 | 98.5  | 412.0 | 195.0        | 815.9 | 96.7  | 404.7 | 3.5                   |
| 26               | 191.5                                          | 801.2 | 95.0  | 397.5 | 187.8        | 785.8 | 93.2  | 389.8 | 3.7                   |
| 27               | 183.1                                          | 766.1 | 90.8  | 380.0 | 179.2        | 749.8 | 88.9  | 371.9 | 3.9                   |
| 28               | 173                                            | 723.8 | 85.8  | 359.1 | 168.7        | 705.8 | 83.7  | 350.1 | 4.3                   |
| 29               | 160.6                                          | 672.0 | 79.7  | 333.3 | 155.8        | 651.9 | 77.3  | 323.4 | 4.8                   |
| 30               | 145.2                                          | 607.5 | 72.0  | 301.4 | 140.1        | 586.2 | 69.5  | 290.8 | 5.1                   |
| 31               | 125.4                                          | 524.7 | 62.2  | 260.3 | 119.8        | 501.2 | 59.4  | 248.6 | 5.6                   |
| 32               |                                                |       |       |       | 90.8         | 379.9 | 45.0  | 188.5 |                       |

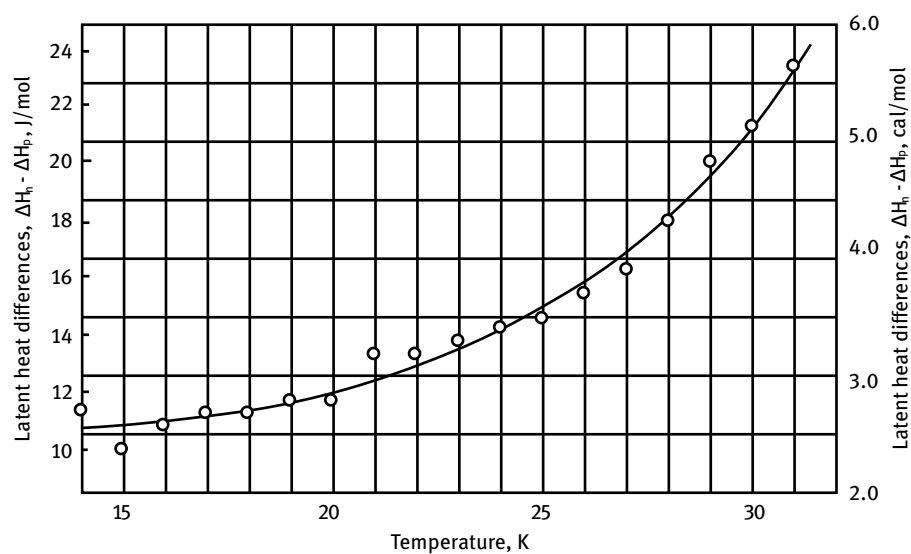
Data source: [70]

**Table 36:** Entropy of hydrogen

| State                 | Temperature |         | Pressure<br>atm | Entropy                             |                                        | References |
|-----------------------|-------------|---------|-----------------|-------------------------------------|----------------------------------------|------------|
|                       | K           | °C      |                 | J mol <sup>-1</sup> K <sup>-1</sup> | cal mol <sup>-1</sup> °C <sup>-1</sup> |            |
| Liquid                | 20.26       | −252.90 | 1.0             | 16.71 ± 0.29                        | 3.995 ± 0.07                           | [88]       |
| At the critical point | 33.24       | −239.92 | 12.8            | 71.96                               | 17.2                                   |            |
| Parahydrogen          |             |         |                 |                                     |                                        |            |
| Ideal gas             | 20.26       | −252.90 | 1               | 62.05 ± 0.4                         | 14.83 ± 0.1                            | [84]       |



**Figure 41:** Heat of vaporization of parahydrogen. (Reproduced and modified from [41].)



**Figure 42:** Difference in latent heat of vaporization of normal and parahydrogen. (Reproduced and modified from [62].)

Additional data on enthalpy and entropy of parahydrogen are summarized in [309]. The report by McCarty, Hord, and Roder 1981 [41] contains very detailed tables and graphs of the entropy of hydrogen in various physical states as a function of temperature and pressure.

The temperature-entropy diagram for parahydrogen three-phase region at and near the triple point was presented on the graphical coordinates of temperature and entropy [310]. Isobars from 10 mm Hg to 340 atmospheres, temperatures from 11 to 230 K and specific volumes covering the range of from 10.5 to 15000 cm<sup>3</sup>/g were included.

## 2.18 Molecular Structure of Solid Hydrogen

Typical crystal structures for solid parahydrogen, are hexagonal close packed structure with  $a = 3.75\text{--}3.761\text{ \AA}$ ,  $c = 6.105\text{--}6.14\text{ \AA}$ , and the  $c/a$  ratio = 1.623 – 1.633. There were some discrepancies in the literature about the exact crystal structure of solid hydrogen and its isotopes [311].

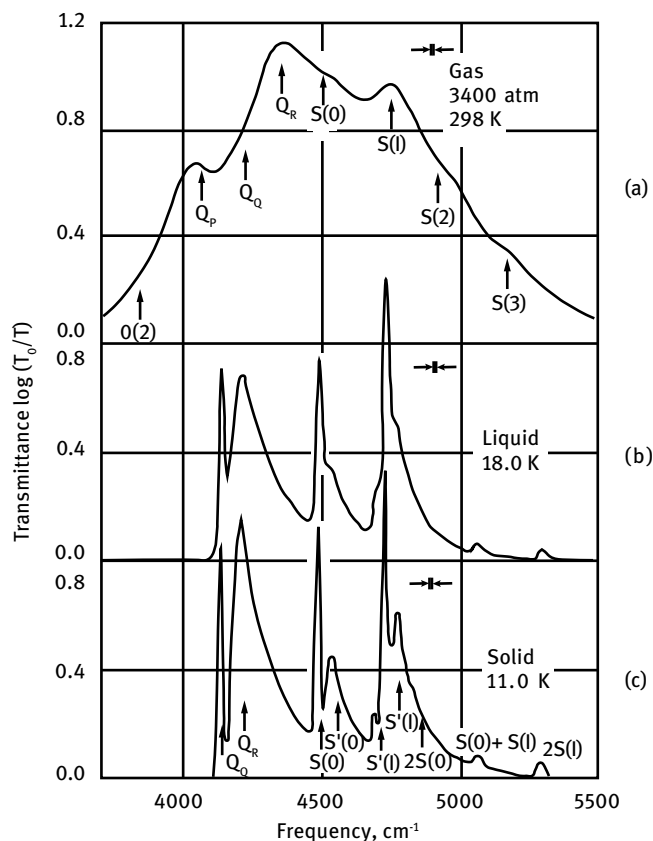
## 2.19 Optical Properties of Hydrogen

### 2.19.1 Infrared Spectra of Hydrogen

Infrared analysis of contaminants in liquid hydrogen would be difficult because hydrogen is a poor solvent and all contaminants would be suspended as particulate solids. While the Raman spectra of ortho and parahydrogen are sufficiently different to allow analysis of the parahydrogen content in gas mixtures, the IR spectra are not.

Induced infrared absorption of hydrogen is caused by the asymmetric distortion of the absorbing molecule by intermolecular forces. In crystalline hydrogen asymmetric distortion can be produced both by the random orientations of the freely rotating molecules and by the vibrational motion of the crystal lattice. The experimental results indicated that the first type of distortion occurs for quadrupole interactions, and that both types are operative for overlap interactions [312, 313]. IR spectra of high-pressure gaseous, liquid, and solid hydrogen show an increasing sharpness of the absorption bands as shown in Figure 43. In solid parahydrogen the lines become very sharp, and the double transition, Q1(0) + S0(0), shows a complex structure.

The induced infrared fundamental absorption band of liquid and solid hydrogen was investigated over a range of para-H<sub>2</sub> concentrations from 25 to 100% with a prism spectrometer and, in part, with a grating spectrometer at a resolution of  $\sim 0.2\text{ cm}^{-1}$  [314]. The spectrum of the solid showed **(a)** comparatively sharp lines due to quadrupole interaction, **(b)** broad bands interpreted as combination tones of the molecular frequencies with the lattice frequencies (phonon spectra), and **(c)**



**Figure 43:** Infrared absorption of hydrogen induced by intermolecular forces. (Reprinted and modified from [312], with permission from ©1955 American Physical Society; permission conveyed through SciPris)

weak double transitions. In solid parahydrogen the lines became very sharp and the double transition showed a complex structure.

A rich spectrum composed of hundreds of sharp features has been observed in the fundamental Q-branch of normal solid  $H_2$  using laser spectroscopy [315]. These features were interpreted as splitting of ortho- $H_2$  pairs.

### 2.19.2 Raman Spectra of Hydrogen

Raman spectra of ortho and parahydrogen differ sufficiently such that this method can be used to analyze the parahydrogen content of gas samples [316, 317].

### 2.19.3 Index of Refraction of Hydrogen

The refractive index of a non-polar fluid depends on the wavelength of the incident light, the density of the fluid and, to a lesser extent, the temperature. The dependence of the refractive index on temperature is usually small enough to be neglected.

The index of refraction of liquid hydrogen was determined at five wavelengths for saturated liquid at 745.52 mm Hg pressure corresponding to a temperature of 20.316 K [318]. The determination was made by measuring critical angles. The experiment was very similar to that of Johns and Wilhelm [319]; however, because of the way in which the optical cell was constructed, the measurements gave the ratio of the refractive indices of saturated liquid and vapor, whereas the refractive indices by Johns and Wilhelm were referenced to vacuum. Augustin obtained the refractive indices of the liquid from the above ratios by using estimated values of the refractive index of the vapor.

The refractive indices of liquid oxygen, nitrogen, and hydrogen at temperatures ranging from the normal boiling point to the normal freezing point of the liquefied gases were determined by means of a Wollaston cell for the wavelengths 6939 Å, 5461 Å, and 4358 Å. The values obtained at the normal boiling point for  $\lambda = 5461$  Å were: oxygen, 1.2242; nitrogen, 1.1990; hydrogen, 1.1120 [319]. Results from measurements on normal hydrogen from the triple point to the normal boiling point at the wavelengths 4358, 5461, and 6939 Å are shown in Table 37. The specific refractions, as calculated using the densities of Kamerlingh Onnes and Crommelin, showed no dependence on temperature or density. These have later been recalculated using modern density data.

Belonogov and Gorbunkov [320, 321] determined the refractive index of saturated liquid parahydrogen from about the normal boiling point (nbp) to 30.5 K and at the wavelengths, 4360, 5460, and 5790 Å. They also determined the refractive index of saturated liquid normal hydrogen over the same temperature range but at 5460 Å only. Their temperature range meets that of the other investigators at about the nbp but does not overlap it. As of 1965, these were the only data for the refractive index of parahydrogen or the para-normal difference.

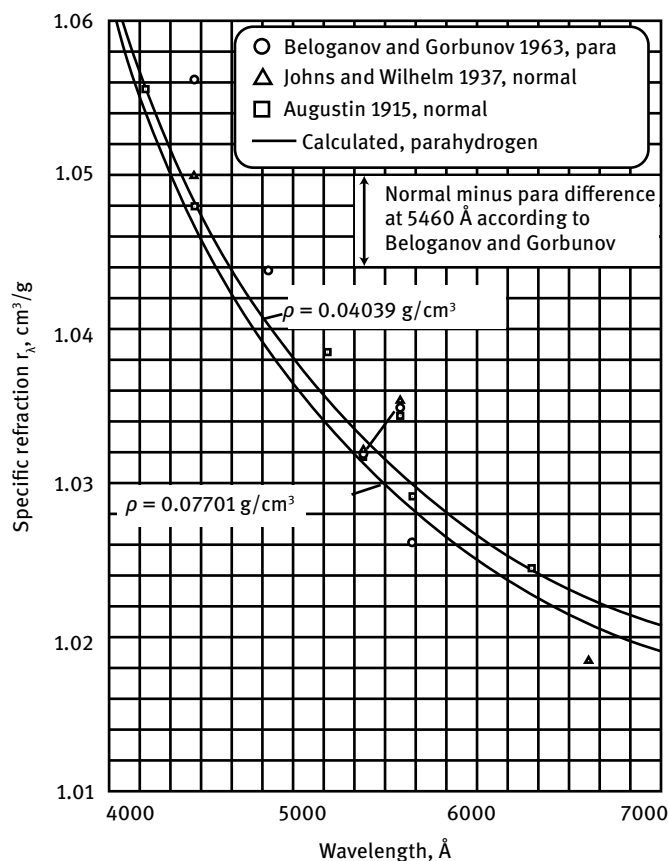
**Table 37:** Index of refraction for liquid hydrogen.

| Temperature<br>K | °C     | Wavelength, nm | Index of refraction |
|------------------|--------|----------------|---------------------|
| 19.8             | -253.3 | 435.8          | 1.1142              |
| 17.2             | -255.9 | 435.8          | 1.1199              |
| 13.9             | -259.2 | 435.8          | 1.2440              |
| 19.8             | -253.3 | 546.1          | 1.1121              |
| 17.4             | -255.7 | 546.1          | 1.1169              |
| 13.9             | -259.2 | 546.1          | 1.1221              |
| 19.8             | -253.3 | 693.9          | 1.1108              |
| 19.5             | -253.6 | 693.9          | 1.1121              |

Data source: [319]

The published experimental values of the refractive index of liquid hydrogen from four different sources have been correlated by calculating and comparing the values of the Lorentz-Lorenz ratio as a function of wavelength [322]. The data from Augustin were judged to be the most accurate ones (0.7% deviation) and those by Belonogov and Gorbunkov the least accurate ones (–1.8% deviation). Because of the scatter found by this analysis, it was proposed that more accurate values can be calculated from available data of other types, namely, the dielectric constants and the optical dispersion determined for the gas at STP. Formulas for this calculation were given and the results are shown in Figure 44.

The two curves in Figure 44 above show the extremes given by various computational methods for saturated liquid hydrogen. The lower one is for the triple point density. The upper one is for the density at which  $p$  and  $r$  are maximum. This is near to



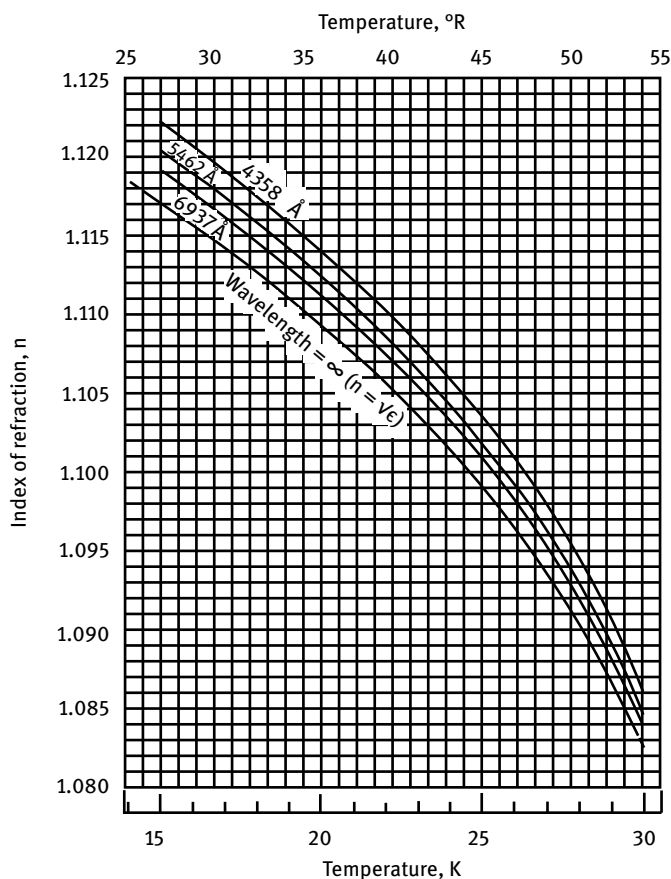
**Figure 44:** Specific refraction of liquid hydrogen as a function of wavelength. (Reproduced and modified from [322].)

the critical density. With further decrease of density,  $p$  and  $r$  decrease again towards the lower curve. See also [323].

The refractive index of gaseous and liquid hydrogen has been measured by an interferometric method at temperatures between 15 and 298.15 K and at pressures up to 23.3 MPa (230 atm) [324, 325]. The measurements have been analyzed in terms of the density and temperature dependence of the Lorentz-Lorenz function,

$$L-L \equiv \frac{n_{\lambda}^2 - 1}{n_{\lambda}^2 + 2} \rho^{-1}$$

where  $n_{\lambda}$  is the refractive index at  $\lambda = 5462 \text{ \AA}$  and  $\rho$  is the fluid density in  $\text{g/cm}^3$ . The precision and reproducibility of L-L is better than 0.05% in most cases. L-L for gaseous parahydrogen first increased with increasing density to a maximum and then decreased to values below the low-density limit. L-L is also slightly temperature dependent; the low-density limit increased with increasing temperature;



**Figure 45:** Index of refraction of saturated liquid parahydrogen. (Reproduced and modified from [41].)

the maximum on the L-L isotherms decreased with increasing temperature. L-L for saturated liquid parahydrogen decreased with increasing density by about 0.1% at temperatures between 15 and 32 K. The difference in L-L for normal and parahydrogen is consistent with previous theoretical and experimental estimates of the molecular polarizability difference. The temperature dependence of the refractive index of parahydrogen is illustrated in Figure 45. Data for refractive index of fluid hydrogen at high pressures between 1 and 9 GPa and temperatures between 293 and 490 K were measured in a diamond anvil [115].

## 2.20 Electrical and Magnetic Properties of Hydrogen

### 2.20.1 Electrical Conductivity of Hydrogen

Data from the organic chemicals and petroleum industries indicated that flowing fluids with conductivities in the  $10^{-11}$ – $10^{-15}$  mho/cm range could present electrostatic potential build-up and discharge hazards, particularly in situations of large volume storage and high flow rates. Liquid hydrogen, because of the possible explosion hazard, was of particular concern [326]. When trying to measure the electric conductivity of liquid hydrogen, the boiling of the liquid hydrogen introduced a large noise signal which made measurements very difficult [327]. Flowing non-conductive liquids can cause build-up of electrostatic charges. Such potentials are generated by flow of insulating fluids in the  $10^{-11}$ – $10^{-15}$   $\Omega^{-1} \text{ cm}^{-1}$  range. It was established that the conductivity of liquid hydrogen was below this range but the actual conductivity was not measured.

Measurements of the electrical conductivity of LH2 gave a typical resistivity of about  $10^{19}$   $\Omega \text{ cm}$  at 25 V and seemed to be a linear function of applied voltage. It was suggested that this current can be explained in terms of charge carriers formed by background radiation. Thus, the current carrying capacity is small and more or less independent of the imposed voltage. Some investigators suggested that electric charge build-up in flowing high-purity LH2 is not a great concern [328].

### 2.20.2 Dielectric Constant of Hydrogen

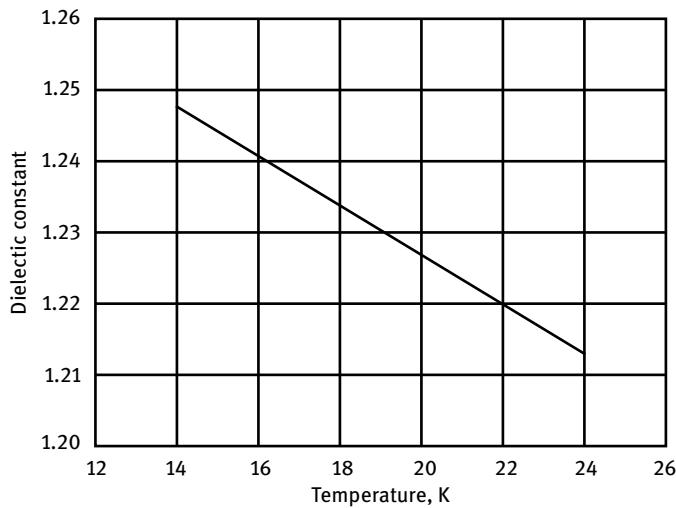
Early data on dielectric constant of gaseous hydrogen were inconsistent and one critical investigator stated “In a majority of, cases, values of the dielectric constant measured at radio frequencies do not appear to be of sufficient accuracy to provide useful information for reference purposes.” Some investigators derived a dielectric constant from index of refraction measurements [329].

The dielectric constant of liquid hydrogen is a linear function of temperature as shown in Figure 46 and represented by equation

$$\epsilon = 1.296 - 0.00345T$$

where  $\epsilon$  is the dielectric constant (dimensionless) and  $T$  is the temperature in kelvin.





**Figure 46:** Dielectric constant of liquid hydrogen as a function of temperature. (Chart created by Schmidt 2018, based on data from [144].)

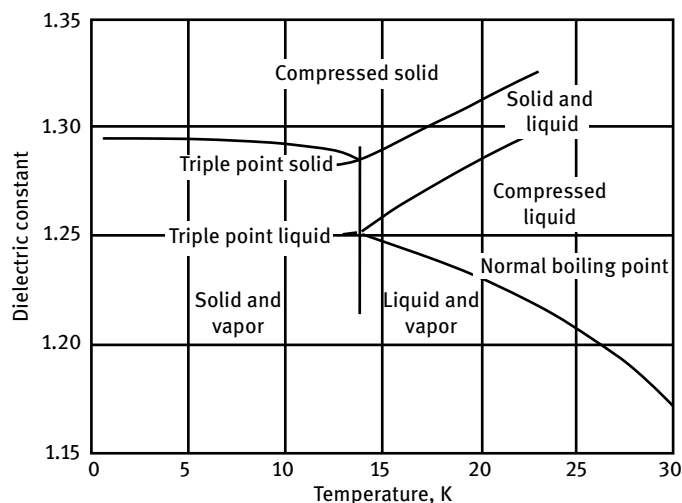
Polarizabilities, calculated from measurements of the dielectric constant, were reported for solid parahydrogen along the melting line between 18 and 320 atm (14.4–22.2 K) [90, 91]. The data for density, polarizability, and dielectric constant of solid hydrogen under pressure are summarized in Table 38.

**Table 38:** Polarizability and dielectric constant of liquid parahydrogen as a function of density and temperature or pressure of the compressed fluid.

| Density<br>g/cm <sup>3</sup> | Polarizability<br>cm <sup>3</sup> /g | Dielectric constant<br>ε | Temperature<br>K | Pressure<br>atm |
|------------------------------|--------------------------------------|--------------------------|------------------|-----------------|
| 0.08109                      | 1.0039                               | 1.26585                  | 17.0             | 87.49           |
| 0.08114                      | 1.0033                               | 1.26586                  | 22.0             | 138.82          |
| 0.08212                      | 1.0031                               | 1.26931                  | 22.0             | 156.21          |
| 0.08212                      | 1.0037                               | 1.26949                  | 17.0             | 105.05          |
| 0.08322                      | 1.0029                               | 1.27320                  | 22.0             | 177.03          |
| 0.08374                      | 1.0027                               | 1.27498                  | 21.0             | 176.81          |
| 0.08375                      | 1.0029                               | 1.27509                  | 21.0             | 176.94          |
| 0.08470                      | 1.0026                               | 1.27841                  | 22.0             | 207.68          |
| 0.08537                      | 1.0025                               | 1.28078                  | 22.0             | 222.19          |
| 0.08596                      | 1.0026                               | 1.28293                  | 21.0             | 224.65          |
| 0.08635                      | 1.0026                               | 1.28434                  | 21.0             | 223.60          |
| 0.08727                      | 1.0021                               | 1.28749                  | 23.0             | 278.49          |
| 0.08797                      | 1.0021                               | 1.29005                  | 23.0             | 296.35          |
| 0.08867                      | 1.0020                               | 1.29253                  | 23.0             | 315.01          |

Data source: [90,91]

The slight decrease in polarizability with pressure on the melting line is much less than the decrease for the liquid over the same pressure range. Since the dielectric constant is proportional to density, a plot of  $\epsilon$  vs.  $T$  is very similar to a density-temperature phase diagram. For parahydrogen, liquid and solid boundaries are shown in Figure 47.



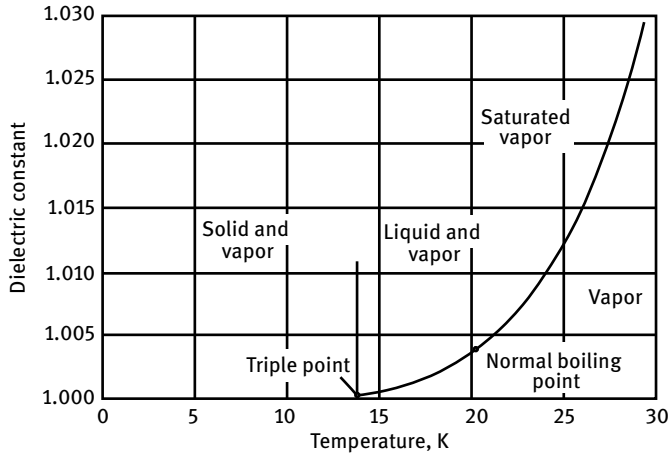
**Figure 47:** Dielectric constant of saturated solid and liquid parahydrogen as a function of temperature. (Reproduced and modified from [70].)

The measured dielectric constant of solid and liquid parahydrogen as a function of temperature is illustrated in Figure 48. The dielectric constant for fluid parahydrogen may be calculated from the equation

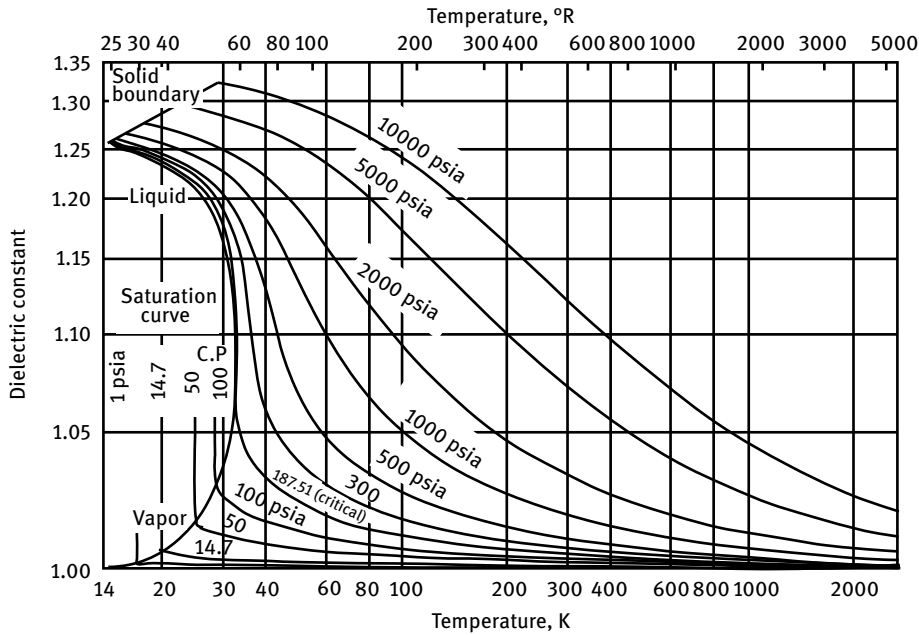
$$\frac{\epsilon - 1}{\epsilon + 2} = A\rho + B\rho^2 + C\rho^3$$

where  $\epsilon$  is the dielectric constant (dimensionless),  $\rho$  is the density in  $\text{g/cm}^3$  and  $A$ ,  $B$ , and  $C$  are constants ( $A = 0.99575$ ,  $B = -0.09069$ ,  $C = 1.1227$ ). This equation is valid from the freezing liquid line to 3000 K and 100 MPa, as illustrated in Figure 49. The dielectric constant of liquid hydrogen is 1.252 at the triple point, 1.229 at the boiling point and 1.00025 at the critical point. The dielectric constant of solid hydrogen is 1.285 at the triple point. The dielectric constant of gaseous hydrogen is 1.00038.

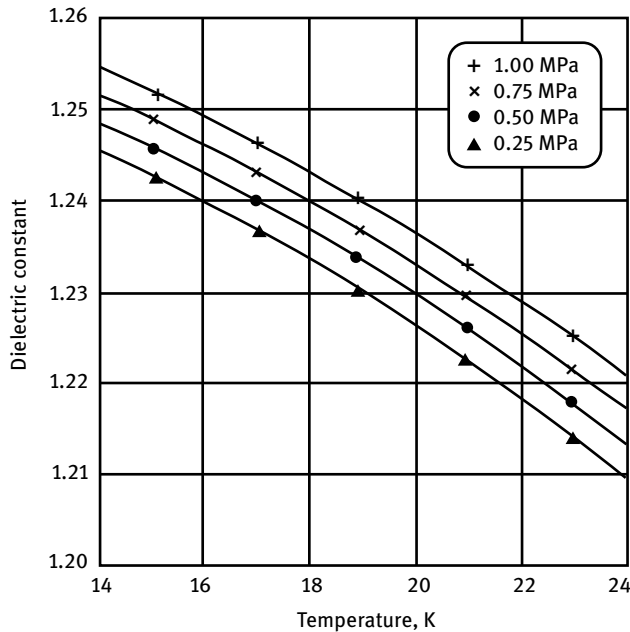
The dielectric coefficient is determined from the ratio of the capacitance of a three-terminal, flat plate capacitor when it is filled with liquid hydrogen to that when the capacitor is in vacuum at the same temperature. Precision dielectric coefficient measurements of subcooled equilibrium liquid hydrogen in the temperature range from 15 to 23 K and under pressures up to 1 MPa were performed using a three-terminal flat plate



**Figure 48:** Dielectric constant of parahydrogen vapor at the saturated vapor-liquid boundary as a function of temperature. (Reproduced and modified from [70].)



**Figure 49:** Dielectric constant of parahydrogen at high pressures. (Reproduced and modified from [41].)



**Figure 50:** Measured dielectric coefficient of compressed liquid hydrogen at different pressures. (Reprinted and modified from [97], with permission from ©2007 Elsevier; permission conveyed through RightsLink.)

capacitor and a single-frequency, ultra-precision capacitance bridge, Figure 50 [97]. The results were combined with previously published data to express the dielectric coefficient in the form of the Clausius-Mossotti relation with a new correlation which covers both liquid and gaseous hydrogen and is only a function of the density. Capacitance/dielectric coefficient measurements are useful for measuring fluid hydrogen liquid level, mass gauging, and void fraction in two phase flow. A new equation of state gives the density as a function of pressure and temperature for the subcooled liquid phase.

The density of liquid  $p$ -H<sub>2</sub> over the density range 0.066–0.080 g/cm<sup>3</sup> (4.1–5.9 lb/cu.ft.) can be determined by measurement of the dielectric constant ( $\epsilon$ ) by use of the equation:

$$\rho = 0.29503 + 17.936(\epsilon - 1)$$

where  $\rho$  is the density in lb/cu.ft. and  $\epsilon$  is the dielectric constant (dimensionless), or, better, in metric units

$$\rho = 4.72591 + 287.304(\epsilon - 1)$$

where  $\rho$  is the density in mg/cm<sup>3</sup> and  $\epsilon$  is the dielectric constant (dimensionless).

### 3 Chemical Properties and Analysis of Hydrogen

#### 3.1 Reactions of Hydrogen with Inorganic Compounds

In order to achieve energy release from hydrogen it has to be combusted with a suitable oxidizer. The most commonly used oxidizer for this purpose is oxygen. Hydrogen will begin to react with oxygen only if preheated to above the ignition temperatures or in the presence of catalysts which significantly lower the activation energy of this reaction and allow ignition to take place at room temperature. The most frequently used catalysts for this purpose contain platinum. For instance, two centuries ago, prior to the invention of safety matches and flint striker sparkers, it was common practice for smokers to carry or have on their desk a small zinc/sulfuric acid hydrogen generator and the hydrogen was ignited in air on a platinum sponge (Döbereiner lighter), such that the smokers could satisfy their craving for nicotine.

If oxygen gas and hydrogen gas are pre-mixed, they could be stored for a long time without reaction. It would not be very safe to store such a mixture because once ignited (on purpose or accidentally) it would burn rapidly with explosive force (“Knallgas” in German, literally translated as “bang gas” in English).

The use of hydrogen as a fuel in rocket engines with oxygen or fluorine as the oxidizer will be discussed in future *Encyclopedia of Rocket Propellant* sets on Bipropellant Combinations.

Fluorine is a stronger oxidizer than oxygen and will ignite most other fuels hypergolically, but in mixture with hydrogen at room temperature and at lower temperatures near that of liquid fluorine it will not always ignite, which is surprising. The reaction of fluorine gas with hydrogen gas is often delayed and inhibited by an uncontrollable and unpredictable impediment and is difficult to explain [330–332]. Some experimenters have been able to mix fluorine gas with hydrogen gas at room temperature without ignition [333]; however, once ignition takes place, the mixture will burn or detonate with the same explosive hazard as the better-known oxygen/hydrogen mixtures. Metal surfaces may act as catalysts and facilitate ignition of  $F_2/H_2$  at room temperature.  $F_2/H_2$  combinations as rocket propellants will be discussed in more detail in a future *Encyclopedia of Rocket Propellant* set on Bipropellant Combinations. This reaction, also with deuterium instead of hydrogen, is of interest as a propellant for chemical lasers.

The Material Safety Data Sheet (MSDS) lists lithium metal as being incompatible with hydrogen. Is it possible that the reaction between lithium metal and hydrogen forming lithium hydride starts on its own and it is exothermic?

##### 3.1.1 Kinetics of $O_2/H_2$ Reactions

The reaction of hydrogen with oxygen is a fundamental reaction and has been thoroughly investigated both as a flame and as a flameless or catalyzed reaction. At one

point or another, be it on Earth or in the depth of space where water-bringing comets once formed, this reaction has formed all the water that now fills the oceans of our planet. In the upper atmosphere of Earth, water vapor is photolyzed by sunlight and the recombination reaction allows some water to form, but the rest of the hydrogen is carried away with the solar wind. One can design a rocket without exact knowledge of hydrogen oxidation kinetics, but kinetics will control certain aspects of hydrogen combustion, such as combustion instabilities, that can have a pronounced effect on the safe operation of a rocket engine. Accidental ignition of hydrogen leaks and the rates of propagation of hydrogen flames are determined by kinetics.

This section on kinetics of hydrogen oxidation is only a random sampling of the literature on this subject and does not claim to be a complete overview of this subject. There are better and more complete literature sources available to consult for the academic researcher in need of kinetic data for combustion reactions.

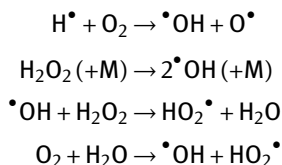
A detailed kinetic mechanism was developed to simulate the combustion of  $O_2/H_2$  mixtures over a wide range of temperatures, pressures, and equivalence ratios [334]. A series of experimental data taken from various sources with temperatures ranging from 298 to 2700 K, pressures from 0.05 to 87 atm, and equivalence ratios from 0.2 to 6 was compared to the predictions of the kinetic model. Ignition delay times, flame speeds, and species composition were simulated only with varying success. A sensitivity analysis was carried out to determine which reactions were dominating the  $O_2/H_2$  system at particular conditions of pressure, temperature, and fuel/oxygen/diluent ratios. Overall, good agreement was observed between the model and the wide range of experiments simulated.

A revised chemical kinetic mechanism model of hydrogen combustion was validated against a wide range of experimental conditions, including those found in shock tubes, flow reactors, and laminar pre-mixed flames [335]. Excellent agreement of the model predictions with experimental measurements demonstrated that the mechanism was comprehensive and had good predictive capabilities for different experimental systems, particularly high-pressure laminar flame speed and shock tube ignition results. The reaction  $H + OH + M$  was found to be primarily significant only to laminar flame speed propagation predictions at high pressure. All experimental hydrogen flame speed observations can be adequately fitted using any of the several transport coefficient estimates presently available in the literature for the  $O_2/H_2$  system simply by adjusting the rate parameters for this reaction within their present uncertainties.

An analysis of the performance of an updated hydrogen combustion mechanism paid particular attention to different channels of reaction between H atoms and  $HO_2$  radicals, to pressure dependence of the recombination of  $HO_2$  radicals, and to the anomalous rate constant of reaction between OH and  $HO_2$  radicals [336]. The contemporary choice of the reaction rate constants is presented with the emphasis on their uncertainties. The model predicted ignition, oxidation, flame burning velocities and flame structure of oxygen/hydrogen/inert mixtures. The modeling range covered ignition experiments from 950 to 2700 K and from subatmospheric pressures up to 87 atm,

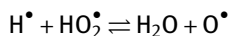
hydrogen oxidation in a flow reactor at temperatures around 900 K from 0.3 to 15.7 atm, flame burning velocities in oxygen/hydrogen/inert mixtures from 0.35 up to 4 atm and hydrogen flame structures at 1 and 10 atm. A comparison of the model predictions and experimental results revealed the remaining limitations in terms of the range of applicability of this detailed mechanism.

An updated  $O_2/H_2$  reaction mechanism incorporated reaction rate determinations in shock tubes [337]. These experiments used UV and IR laser absorption to monitor species time-histories and have resulted in improved high-temperature rate constants for the following reactions:



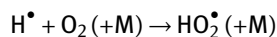
The updated mechanism also took advantage of the results of other rate coefficient studies, and incorporated the most recent thermochemical data for  $\bullet OH$  and  $HO_2^\bullet$ . The mechanism was tested (and its performance compared to that of other  $O_2/H_2$  mechanisms) against recently reported  $\bullet OH$  and  $H_2O$  concentration time-histories in various  $O_2/H_2$  systems, such as  $H_2$  oxidation,  $H_2O_2$  decomposition, and shock-heated  $H_2O/O_2$  mixtures. The mechanism was validated against a wide range of standard  $O_2/H_2$  kinetic targets, including ignition delay times, flow reactor species time-histories, laminar flame speeds, and burner-stabilized flame structures.

An updated  $O_2/H_2$  kinetic model based on that of Li et al. [335] was tested against a wide range of combustion targets, incorporating improvements in rate constant treatment and resolving discrepancies between experimental data and predictions using published kinetic models in dilute, high-pressure flames [338]. Attempts were made to identify major remaining sources of uncertainties, in both the reaction rate parameters and the assumptions of the kinetic model, affecting predictions of relevant combustion behavior. With respect to model parameters, uncertainties in the temperature and pressure dependence of rate constants for  $HO_2$  formation and consumption reactions substantially affect predictive capabilities at high-pressure, low-temperature conditions. With respect to model assumptions, calculations were performed to investigate several reactions/processes that had not received much attention previously. Results from *ab initio* calculations and modeling studies imply that inclusion of



in the kinetic model might be warranted, though further studies may be necessary to ascertain its role in combustion modeling. In addition, it appears that characterization

of non-linear bath-gas mixture rule behavior for

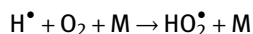


in multi-component bath gases might be necessary to predict high-pressure flame speeds within ~15%. The updated model was tested against all of the previous validation targets as well as new targets from a number of other studies. Predictions using this model adequately reproduced various targets and substantially improved agreements with high-pressure flame speed and shock tube speciation measurements.

Nine chemical reaction models for equilibrium schemes and six chemical models for non-equilibrium ones for the reaction of oxygen and hydrogen were studied, considering different conditions found in real liquid oxygen/liquid hydrogen rocket engines [339]. Comparisons between two eight-species models have shown that the most complex is also the best one. Besides, it was also verified that the most complex model has been the fastest among six-species and eight-species models. Both combustion temperature and thermochemical and transport properties depend only on the chemical species considered by the used model. Analyses have shown that mass generation rates are very dependent on third body reaction equations and forward reaction constants.

Termolecular reactions  $\text{H} + \text{O}_2 + \text{R}$  may significantly affect kinetic pathways under common combustion situations and require careful analysis, since, if included in contemporary kinetic mechanisms, these reactions will affect global reactivity and calculated burning velocities of laminar pre-mixed flames [340]. In view of their impact, a detailed kinetic scheme for hydrogen combustion was revisited to elucidate how to counterbalance enhanced chain termination caused by chemical termolecular reactions in an attempt to maintain or improve model performance. Experimental and theoretical kinetic studies of hydrogen reactions were compared. In the new mechanism, four new reactions were introduced and three rate constants were updated. These changes, however, significantly reduced calculated burning velocities of air +  $\text{H}_2$  flames as compared to experimental data and earlier model predictions with the major impact from chemically termolecular reactions. It was then found that implementation of a new theoretical transport properties database significantly improved the performance of the updated kinetic model. The new kinetic mechanism for hydrogen combustion, which included updated kinetics and new transport properties was found to be in good agreement with the consistent dataset of the burning velocity measurements for hydrogen flames obtained using the heat flux method at atmospheric pressure for which the accuracy of the previous model was not satisfactory.

The reaction rate of



in the low-pressure limit was determined in the temperature range of 1450–2000 K, with argon, nitrogen, and carbon dioxide as the third-body collision partners, by mea-



asuring the  $\bullet\text{OH}$  time-history after the induction time during lean oxidation of hydrogen [341]. A strong transition in the spectrum of  $\bullet\text{OH}$  was used as the probing wavelength for the diagnostics. Calibration measurements were performed prior to the experiments to estimate the effects of pressure shift and collision broadening on the absorption coefficient of  $\bullet\text{OH}$  for each of the gas species, which enabled a reduction in the uncertainty in the absorption cross-section of  $\bullet\text{OH}$ . Aided by the calibrated and improved  $\bullet\text{OH}$  diagnostics, the reaction rate constants were determined at high temperatures, with low scatter, and tight uncertainty bounds. The measured rate constants agreed with the extrapolation of previous investigations at lower temperatures. Combined rate constant expressions were proposed, which are valid over the temperature range of 1000–2000 K

### 3.2 Combustion of Hydrogen

Basically this entire section is devoted to the combustion of hydrogen, dealing mostly with academic and safety studies. Actual applications of hydrogen combusting rocket and ramjet engines will be presented in a future *Encyclopedia of Rocket Propellant* set on Bipropellant Combinations.

#### 3.2.1 Burning Velocity of Air/Hydrogen Flames

This section on flame speed (i.e., burning velocity) of hydrogen flames is closely related to Section 7.2 on Fire Hazards of Hydrogen and Section 5.5 on the design of flare stacks for the disposal of surplus hydrogen gas.

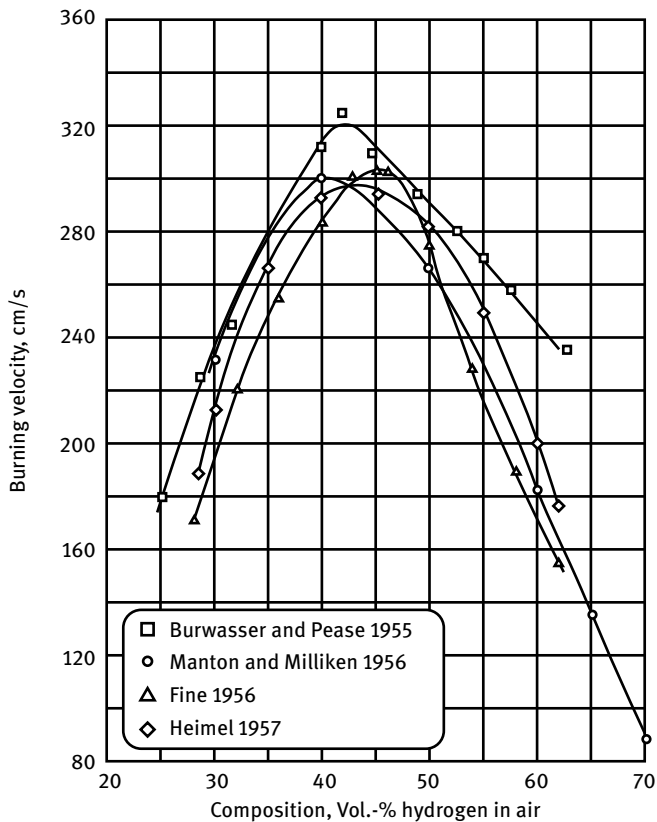
##### 3.2.1.1 Burning Velocity of Air/Hydrogen Flames at Sea-Level Pressure

The high burning velocity of hydrogen, approximately 6–7 times faster than that of hydrocarbon fuels, indicates its high explosive potential and explains the difficulty of preventing, confining or arresting hydrogen flames and explosions.

Burning velocities of air/hydrogen mixtures were measured by the Bunsen burner method [342]. A modified angle technique applied to the dark outer edge of the shadow cone was used in calculating the burning velocities. An attempt was made to correlate the experimental results with approximate diffusion and thermal theories of flame propagation. It was found that diffusion theory predicted a maximum in burning velocity at a much leaner hydrogen composition than was observed experimentally, whereas thermal theory produced the opposite situation by predicting a maximum at a richer composition (29 vs. 42 vs. 55 vol.-%  $\text{H}_2$ ).

The laminar burning velocity is defined as the velocity of unburned gas with given composition, pressure, and temperature that flows normal to the stationary flame surface. The measurement of laminar burning velocity must be performed to

obtain a physical constant free of the effects of geometry, fluid flow, and external heat sources or heat sinks [343]. The flame speed, a function of the frame of reference, is a combination of the burning velocity and the translational velocity of the bulk flow. Combustion behavior for scenarios in which hydrogen, released in the open, forms a flammable mixture, may be compared to the characteristics of laminar burning behavior. The hazard associated with laminar burning is the propagation of a high-temperature flames throughout the region where a flammable mixture persists. Without confinement of the reaction products, high flame velocities do not occur, nor is there any overpressure. Burning velocities reported for sensitive air/hydrogen mixtures under ambient conditions range between 1 and 3.5 m/s, with peak velocities observed for mixtures fuel-rich than stoichiometry, approximately 40 vol.-% (Figure 51).



**Figure 51:** Burning velocity of hydrogen in air. (Reproduced and modified from [343].)

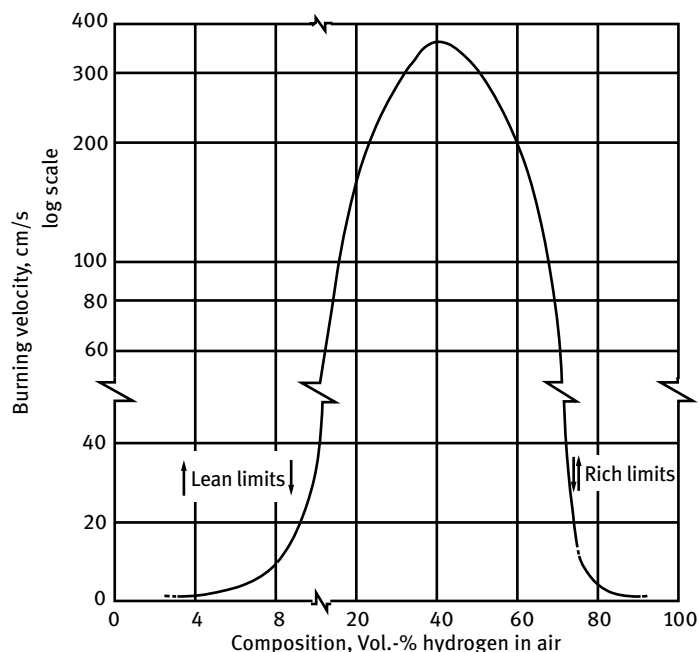
The burning velocity of air/hydrogen mixtures and mixtures of methane, ethane, propane, *n*-butane, acetylene, ethylene, propylene, and *n*-butylene with air as a function of the fuel:air ratio has been measured in an apparatus capable of measuring the burning velocity of gas-air mixtures with an accuracy of about 5% [344].

Conical air/hydrogen flames have been stabilized on a 10.3-mm diameter water-cooled nozzle burner designed so as to minimize the flashback tendency and to maintain laminar flow at very high rates [345]. Measurements of the cone half-angle,  $\theta$ , by schlieren optical techniques and the unburned gas velocity,  $V$ , by particle-tracking techniques have been used to determine burning velocity from the equation  $S_u = V \sin \theta$ . A burning velocity of 296 cm/s was obtained for a 50% hydrogen-air flame, whereas others reported the burning velocity to be approximately 250 cm/s. This discrepancy was attributed to errors in the earlier measurements caused by the use of averaging methods with very small burners. There was good agreement between the present experimental value of burning velocity and the value computed for a 50% air/hydrogen flame by others.

A method for the prediction of one-dimensional laminar flame propagation, using the time-dependent equations, used a very simple flame, that of hydrazine decomposition, to demonstrate the usefulness of the method [346]. This procedure was then used for an oxygen/hydrogen/nitrogen flame which can be characterized by reaction mechanisms for which an abundant number of adequate chemical kinetic data exists. As well-documented experimental studies of this flame showed, a critical comparison of predicted and measured flame characteristics can be used to explain some details of the reaction more accurately than previously possible. The results of two investigations were presented: the first concerned the effect of excluding some of the possible reactions from a very full reaction scheme on the prediction of flame speed; the second investigation resulted in recommendations for reaction rates of some of the reactions, for which there was still some uncertainty in the existing data.

A mathematical solution of the conservation equations governing a freely propagating laminar flat flame has been performed for the oxygen-hydrogen-nitrogen system [347, 348]. A reaction mechanism with rate constants from recent reviews was given which reproduced within the limits of experimental errors flame velocities in oxygen/hydrogen and oxygen/hydrogen/nitrogen mixtures between 10 and 1000 cm/s.

The difference in modes of flame propagation that occurs between the upward lean limit at 4%  $H_2$  and the downward lean limit near 8%  $H_2$  is quite anomalous for any flammable gas. Upward propagation from a convectively rising flame kernel involves propagation into a velocity gradient induced by buoyancy forces and at a slow but finite propagation velocity, the flame is blown out by its own buoyancy-induced flow [349]. Data for the laminar burning velocity of air/hydrogen mixtures obtained from such a nearly adiabatic burner system are shown in Figure 52.



**Figure 52:** Burning velocity of hydrogen in air. (Reproduced and modified from [349].)

The solid lines represent measured burner data and the dashed lines represent theoretical estimates but are not real data. There is no combustion beyond these limits. The arrows at lean limits and rich limits indicate the direction of flame propagation. This figure contains a vertical scale change, from linear to logarithmic at velocities above 50 cm/s. It also contains a horizontal scale discontinuity (scale compression) at concentrations above 10% H<sub>2</sub>.

The burning velocities of hydrogen-air and hydrogen-air-steam mixtures as a function of the temperature and composition of the unburned gases have been measured by laser-Doppler anemometry and schlieren photography using a constant velocity nozzle burner [350, 351]. A two-cyclone in-series particle generator was designed to provide a suitable particle seeding rate for the laser-Doppler anemometer. The overall method was checked by comparing measurements for air/methane mixtures with published data, which were obtained from both hot wire measurements in spherical propagating flames and double-ignition measurements in a closed vessel. Excellent agreement was observed. Burning velocities of air/hydrogen mixtures measured at room temperature agreed well with those reported by others. New data have been obtained for the burning velocity as a function of unburned gas temperature. The addition of steam to an air/hydrogen mixture noticeably decreased the burning velocity. A correlation equation has been derived from the observed

burning velocities covering a hydrogen concentration range of 18–65 vol.-%, a steam concentration range of 0–15 vol.-%, and a temperature range of 296–523 K (23–250 °C).

Laminar and turbulent burning velocities of air/hydrogen mixtures have been determined in a 17-L vessel using the double-kernel technique for a range of hydrogen concentrations between 9 and 70% by volume [352]. Over the range of mixtures investigated, simple empirical correlations were derived that predicted laminar burning velocities that were in good agreement with those measured. A turbulent-burning-velocity correlation that included the flame-generated turbulence produced burning velocities in good agreement with the values measured experimentally. The data and correlations for the hydrogen burning velocity were used in models to predict hydrogen combustion behavior in enclosures containing hydrogen-air-diluent mixtures and in combustion systems that employ hydrogen as the fuel.

The burning behavior of air/hydrogen fast deflagrations and detonations was investigated in an explosion tube for pre-mixed flames, partially diluted with additives [353]. The flames were accelerated after ignition by means of a cascade of obstacles. The structure of the reaction zone was determined by means of planar laser-induced predissociation fluorescence, whereas the shape of both flame front and shockwaves was investigated by means of color-schlieren technique in the unblocked tube section. On the basis of the obtained experimental results, quantitative criteria for the onset of slow and fast deflagrations as well as shock-induced combustion phenomena (spin/marginal detonations, planar cellular detonations) were obtained. The maximum pressure spikes were observed at the end of the tube for fast deflagrations.

Laminar burning velocities of air/hydrogen flames were measured at ambient temperatures for variable equivalence ratios [354]. The apparatus consisted of a 250-mm long cylindrical stainless steel explosion bomb enclosed at one end with a stainless steel plug which housed an internal stirrer to allow mixing. The other end was sealed with a 120-mm diameter round quartz window. Optical access for filming flame propagation was afforded via two diametrically opposed quartz windows in both sides. Flame speeds were determined within the bomb using a high-speed Schlieren photographic technique. This method is an accurate way to determine the flame speed and the burning velocities were then derived using a CHEMKIN computer model to provide the expansion ratio. The design of the test facility ensured the flame is laminar, which resulted in a spherical flame which was not affected by buoyancy.

Very rich near-limiting air/hydrogen flames were studied in a constant volume bomb equipped with a pressure sensor and a schlieren system for optical registration of the flame front movement [355]. The mixtures contained 70 and 75 vol.-% of hydrogen, the rest being air. The measurements were conducted at pressures from 101 to 404 kPa (1–4 atm) for the 70 vol.-% H<sub>2</sub> + air mixture and from 71 to 142 kPa (0.7–1.4 atm) for the 75 vol.-% H<sub>2</sub> + air mixture. Two methods for determination of the laminar burning velocity were used: from the temporal evolution of the flame front movement and

from the pressure records. These methods were compared and discussed in terms of accuracy and implicit assumptions behind them. Markstein lengths were calculated and compared with literature data by using different extrapolation models. The critical radius is an important parameter for extraction of the burning velocity and Markstein length. Experimental data were compared to three models for hydrogen combustion.

The flame burning velocities of unconfined air/hydrogen gas explosions depend on the cloud size and the distance from the initiating source, related to turbulence generated by the propagating flame front [356]. The molecular absorption bands in the flame front are exposed to continuously increasing radiation intensity of water emission bands from the interior of the reaction product fire ball. The air/hydrogen flame propagation in 1-m diameter balloons was observed by high-speed video techniques including time resolved spectroscopy in the UV-Vis-NIR spectral range with a time resolution up to 3000 spectra/s. Ignition, flame head velocity, flame contours, reacting species and temperatures were evaluated. Flame front velocities were found to be between 16 and 25 m/s.

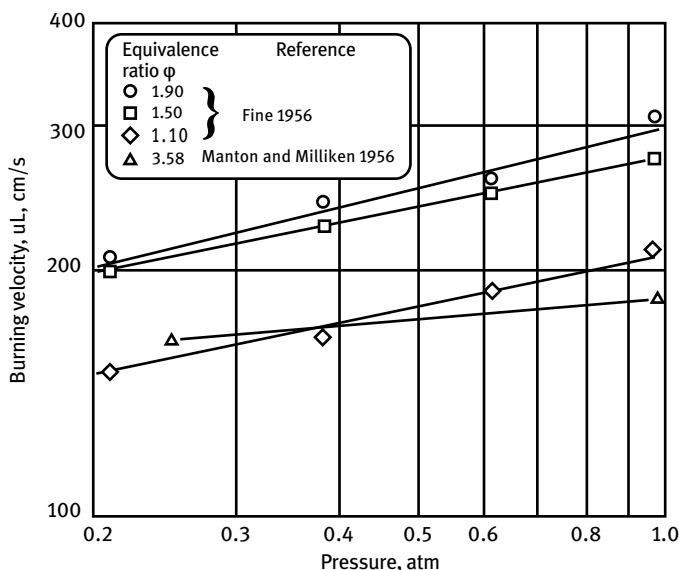
Outwardly propagating spherical hydrogen/air flames were examined theoretically and experimentally with respect to flame propagation speed and the onset of instabilities which develop due to thermal expansion and non-equal diffusivities [357]. Instabilities increase the surface area of the spherical flame, and hence the flame propagation speed. The theory applied here accounted for both hydrodynamic and diffusive thermal effects, incorporating temperature-dependent transport coefficients. Experiments were performed in a spherical combustion chamber over a wide range of equivalence ratios (0.6–2.0), initial temperatures (298–423 K), and initial pressures (1 atm–15 bar). The evolution of the flame propagation speed as a function of flame radius was compared to predictions from theory and showed good agreement. The wrinkling of air/hydrogen flames was examined under increased pressure and temperature for various equivalence ratios. Critical flame radii, defined as the point of transition to cellular flames, were extracted from high-speed schlieren flame imaging. Overall, the critical radius was found to decrease with increasing pressure. Experimental flame radii, as expected, were underpredicted by the theoretical findings. Experimental data were fitted to an empirical formula.

Flame flashback is a major challenge in pre-mixed flame studies and the design of flare stacks. The prediction of the minimum flow velocity to prevent boundary layer flashback is of high technical interest. An analytic approach to predicting boundary layer flashback limits for channel and tube burners developed a model which was based on an experimentally observed flashback mechanism and consisted of a local and global analysis [358]. Based on a local analysis, the flow velocity at flashback initiation was obtained depending on flame angle and local turbulent burning velocity. The local turbulent burning velocity was calculated in accordance with a predictive model for boundary layer flashback limits of duct-confined flames. The flame angle of the stable flame near flashback conditions can be obtained by various methods. An

approach based on global mass conservation was applied and was validated using Mie-scattering images from a channel burner test rig at ambient conditions. The predicted flashback limits were compared to experimental results and to literature data from preheated tube burner experiments.

### 3.2.1.2 Burning Velocity of Air/Hydrogen Flames at Reduced Pressures

It would be desirable to operate jet engines with hydrogen at high altitudes. During the ignition phase, flames have to propagate at low ambient pressure. Measurements of burning velocity at pressures other than atmospheric are difficult. This is especially true for reduced pressures. The experimental difficulties are reflected in large discrepancies in the literature data of the few workers who have studied combustion of air/hydrogen mixtures at low pressures. One ancient source [359] reported nearly constant burning velocity at total pressures from 1 to 4 atmospheres. Another source [360] gave burning velocity values of 164 cm/s at 0.393 atm and 140 cm/s at 1 atm for a mixture with  $\phi = 4.78$ . The burning velocity of a mixture with  $\phi = 3.58$  increased when the pressure was raised from 0.25 to 1.0 atm [361]. The same trend was shown between  $\phi$  of 1.10 and 1.90 [362, 363]. The data of Manton and Milliken 1956 are probably most correct, because the spherical bomb technique is not subject to some of the important sources of error that affect results obtained by other methods. The cause of the discrepancy between these two data sources is not known. Figure 53 shows burning velocities from two sources plotted logarithmically against pressure for four rich equivalence ratios. The data from Fine 1956 were obtained by a Bunsen



**Figure 53:** Effect of pressure on burning velocity of air/hydrogen flames. (Reproduced and modified from [343].)

burner total area method, and care was taken to avoid quenching effects from too-small burner tube.

Stability limits for laminar and turbulent air/hydrogen burner flames were measured as a function of pressure, burner diameter and composition [363, 364]. The average pressure exponent of the critical boundary velocity gradient for turbulent flashback was 1.31, which was not significantly different from the laminar value. The use of a simple flame model and measured turbulent flame speeds indicated that turbulent flashback could involve a smaller effective penetration distance than laminar flashback. Turbulent blow-off velocity was nearly independent of pressure and varied about as the inverse square root of the burner diameter. Of several theoretical treatments, none satisfactorily predicted the observed dependence of blow-off on pressure and burner diameter. The quenching pressure was inversely proportional to burner diameter. The actual pressures were higher than those obtained by other quenching measurements.

Effects of positive flame stretch on the laminar burning velocities of  $O_2/H_2/N_2$  flames at normal temperatures and various pressures and nitrogen dilutions were studied both experimentally and computationally [365]. Measurements and numerical simulations considered freely (outwardly) propagating spherical laminar pre-mixed flames at both stable and unstable preferential diffusion conditions with fuel/equivalence ratios in the range 0.45–4.00, pressures in the range 0.35–4.00 atm, and oxygen concentrations in the non-fuel gas in the range 12.5–21 vol.-%. Measured Markstein numbers were in the range  $-4$  to  $+6$ , implying strong flame/stretch interactions. For air/hydrogen flames, the neutral preferential diffusion condition shifted toward fuel-rich conditions with increasing pressure. Predictions of stretch-corrected laminar burning velocities and Markstein numbers, using typical contemporary chemical reaction mechanisms, were in reasonably good agreement with the measurements.

An apparatus used for the study of expanding spherical flames in  $O_2/H_2$ /inert mixtures was able to extend the initial unburnt sample pressure to 60 atm [366]. Results substantiated previous observations of the propensity of cell formation over the flame surface due to hydrodynamic and diffusive thermal instabilities and provided convincing evidence that wrinkled flames are the preferred mode of propagation in air/hydrogen mixtures at pressures above only a few atmospheres. It was shown that by using helium as the diluent and by reducing the oxygen concentration of the combustible, diffusional thermal instability can be mostly suppressed and the hydrodynamic instability delayed. Stretch-free laminar flame speeds were determined for smooth flames starting at up to 20 atm and were compared with the calculated values, allowing for detailed interpretation of chemistry and transport data. It is remarkable that, as shown in Figure 5 of this paper, the mass burning rate increased with pressure both in the range 1–3 and 10–30 atm, while the fundamental flame speed  $S_u$  increased only in the range 1–3 atm, but decreased at higher pressures of 10–30 atm.



An experimental and numerical study on laminar burning velocities of air/hydrogen flames was performed at low pressures, room temperature and different equivalence ratios [367]. Flames were generated using a small contoured slot-type nozzle burner ( $5 \times 13.8$  mm). Burning velocities were measured using the angle method combined with schlieren photography. Numerical calculations using existing detailed reaction mechanisms and transport properties and an analysis of the intrinsic flame instabilities of hydrogen/air flames at low pressure were performed. Results showed that the behavior of the laminar burning velocity was not regular when the pressure was decreased and that it depended on the equivalence ratio range. The behavior of the laminar burning velocity with decreasing pressure can be reasonably predicted using existing reaction mechanisms; however, changes in the magnitude of the laminar burning velocity were underestimated. It has been found experimentally and confirmed analytically that the intrinsic flame instabilities are reduced when decreasing the pressure to sub-atmospheric conditions.

Laminar flame speeds of air/hydrogen mixtures at sub-atmospheric pressures were measured in a spherical explosion chamber with a volume of 8.2 L and a high-speed camera combined with a schlieren system for flame visualization [368]. Laminar flame velocities were obtained in the range of 4–80% hydrogen in air at initial pressures of 25–1000 mbar. Laminar burning velocity and flame length were correlated with overall reaction order and activation energy.

The validation of available kinetic schemes is of great importance for predicting laminar burning velocities of air/hydrogen flames as a function of pressure and equivalence ratio. Experimental measurements of laminar flame speeds and modeling studies were performed for air/H<sub>2</sub> pre-mixed flames over a wide range of equivalence ratios (0.5–4.0) and pressures (0.2–3 bar) [369, 370]. The wide range in mixture and thermodynamic conditions studied allowed a better understanding of the peculiar behavior of hydrogen flame speeds with pressure. Two detailed chemical kinetic mechanisms for hydrogen combustion were selected. Excellent agreement was observed between calculations and experimental results, confirming the validity of the kinetic schemes selected. The kinetic analyses offered an explanation for the non-monotonic variation of air/hydrogen flame speed with pressure observed in the experiments.

### 3.2.1.3 Burning Velocity of Air/Hydrogen Flames at Elevated Pressures

The laminar burning velocity of pre-mixed air/hydrogen mixtures was measured in a fan-stirred combustion bomb [371]. Unstretched laminar burning velocities and Markstein lengths were obtained at 0.10 MPa for equivalence ratios of 0.4, 0.6, 0.8, and 1.0 using high speed flame imaging. There were difficulties which arose while trying to obtain similar measurements at 0.25 and 0.50 MPa. The turbulent burning velocity was measured at equivalence ratios of 0.4 and 0.8 from explosions carried out at 0.10 MPa with turbulence intensities of 0.8 and 1.6 m/s. Higher turbulent burning velocity ratios were observed for mixtures which yielded lower Markstein lengths in the laminar combustion experiments.

Laminar burning velocities of air/H<sub>2</sub> mixtures have been measured in a spherical explosion bomb with central ignition [372]. Pre-ignition pressures ranged from 0.1 to 1.0 MPa, with equivalence ratios between 0.3 and 1.0. Many of the flames soon became unstable, with an accelerating flame speed, due to thermal diffusive instabilities. This effect increased with increasing pressure. The flame wrinkling arising from the instabilities enhanced the flame speed. A method was described which allowed for measurement of this effect, based on measurements of the flame radii at which the instabilities increased the flame speed. This enabled burning velocities and Markstein numbers to be obtained, devoid of the effects of instabilities. With increasing pressure, the time interval between the end of the ignition spark and the onset of flame instability, the short period during which stable stretched flame propagation occurred, became increasingly short and very high camera speeds were necessary for accurate measurement. Eventually this time interval became so short that first Markstein numbers and then burning velocities could no longer be measured. Such flame instabilities throw into question the utility of for high pressure very unstable flames. The measured values were compared with those predicted by detailed chemical kinetic models of one-dimensional flames.

Modeling of air/hydrogen flames at elevated pressures and temperatures was extended to initial pressures and temperatures up to 8.0 MPa and 950 K, respectively [373]. Laminar burning velocities and Markstein lengths were obtained at the elevated pressures and temperatures. Sensitivity and flame structure analyses showed good agreement between the computed results and experimental data. The study showed that laminar burning velocities were increased with an increase of initial temperature, and they decreased with an increase of initial pressure. With an increase of initial pressure, the onset of cellular instability advanced and the Markstein length was decreased, indicating an increase of flame instability with the increase of initial pressure. Flame instability was insensitive to initial temperature. Laminar burning velocity was dependent on the competition between the main chain branching reactions and the chain termination reaction. The chain branching reactions are the temperature-sensitive reactions, while the termination reaction is a temperature-insensitive reaction. Through the extraction of the overall reaction orders, it was demonstrated that with increasing pressure, the overall reaction orders gave a decreasing trend and then an increasing trend. On the basis of the numerical data, an empirical formula for laminar burning velocity was correlated for the air/hydrogen pre-mixed mixture at elevated pressures and temperatures. The correlated laminar burning velocities were in good agreement with the known experimental results and simulated results with CHEMKIN. The correlation can be used in the calculation of laminar burning velocities at elevated pressures and temperatures.

### 3.2.1.4 Burning Velocity of Air/Hydrogen Flames at Increased Temperatures

The effect of initial temperatures from about 300 to 700 K on the laminar burning velocity of air/hydrogen mixtures was determined from schlieren photographs of open flames [374]. The temperature was raised in two ways: **(1)** by preheating of the hydrogen-air mixtures and **(2)** by simulated adiabatic preburning of part of the hydrogen in air at 300 K so that initial temperatures of 600 and 700 K would be attained for the resulting mixtures of hydrogen, air, water vapor and nitrogen. The following empirical equations for burning velocity  $u$  were determined: For air/hydrogen mixtures, at initial temperatures with preheating to  $T_0$  of 287 to 700 K, with 29.6 vol.-% hydrogen (stoichiometric mixture),

$$u = 0.01011 T_0^{1.721}$$

where  $u$  is the burning velocity in cm/s and  $T_0$  is the pre-ignition temperature, and with 45.0 vol.-% hydrogen (maximum burning velocity mixture),

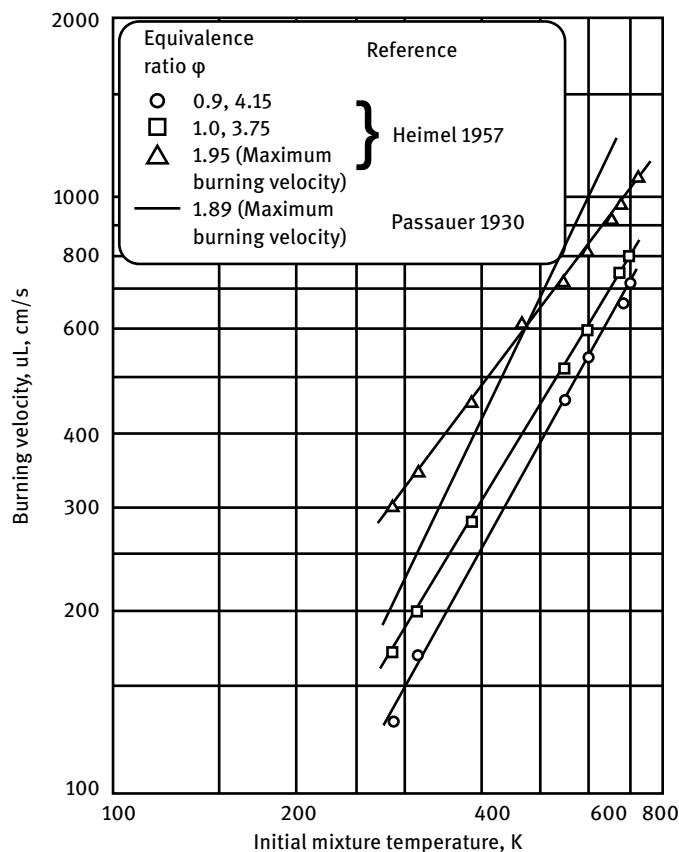
$$u = 0.09908 T_0^{1.413}$$

The effect of initial unburnt gas temperature on burning velocity of hydrogen flames in air is illustrated in Figure 54. Note that both scales are logarithmic scales which gave a nearly linear relationship with straight lines. This graph is based on data from [375] and [374].

The publications [350, 351] contained a graph showing the burning rate as a function of composition with temperatures as the auxiliary parameter. Those graphs covered a temperature range from 298 to 523 K (25–250 °C). The older publication from [374] covered a wider temperature range from 287 to 700 K and, although it is the older graph, this graph was preferred for illustrating the effect of initial temperature on burning rate in our book. The dependence of burning rates of air/hydrogen flames on initial unburnt gas temperature is illustrated in Figure 55.

The effect of temperature on the adiabatic burning velocities of diluted hydrogen flames has been analyzed using an updated version of the Konnov detailed reaction mechanism for hydrogen [376]. The rationale in selecting the reaction rate constants was provided with emphasis on their unfortunate uncertainties, and the performance of the updated mechanism was compared to a previous version for a wide range of validation cases: **(1)** jet-stirred and flow reactors; **(2)** oxidation, decomposition, and ignition in shock waves; **(3)** ignition in rapid compression machines; **(4)** laminar burning velocities and flame structures. An overall improvement of the mechanism performance was observed, particularly for the shock tube and flow reactor studies. Temperature dependence of the burning velocity,  $S_L$ , is commonly interpreted using the correlation

$$S_L = S_{L0} \left( \frac{T}{T_0} \right)^\alpha.$$

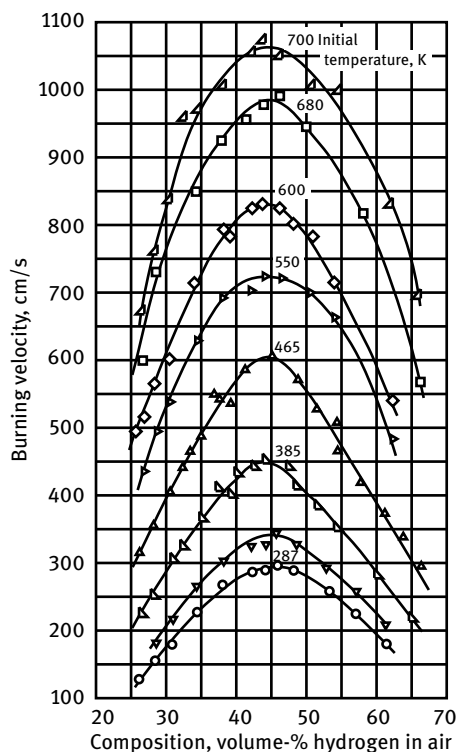


**Figure 54:** Burning velocity of hydrogen in air at elevated temperatures. (Reproduced and modified from [343].)

The updated mechanism was applied to study the behavior of the power exponent  $\alpha$  for  $O_2 + H_2 + N_2$  flames in a wide range of stoichiometry and dilution ratios. The simulations were compared to the available experimental results, either taken from the literature or from the existing burning velocity data. The equivalence ratio and  $N_2$  content in the mixture were found to have significant influence on the temperature power exponent. The dependence of the temperature exponent on the fitting temperature range was observed and discussed. This effect was found to cause significant discrepancies in the burning velocities at high temperatures, if it was based on an empirical correlation.

### 3.2.1.5 Burning Velocity of Air/Hydrogen/Diluent Flames

Measurements of laminar burning velocities of oxygen/hydrogen/inert gas systems have been made using the nozzle burner/schlieren/cone angle method in which un-



**Figure 55:** Temperature effect on burning rate of air/hydrogen flames. (Reproduced and modified from [374].)

burned gas velocity is determined by laser Doppler velocimetry [377]. The nozzle diameters of the burners were 7 or 10 mm. Nitrogen, argon or helium were used as the inert diluent gases. The oxygen mol fraction in oxygen-inert gas mixture,  $X_{OA}$ , was set at 0.209, 0.150, and 0.090. Equivalence ratio,  $\phi$ , was varied between 0.9 and 4.4. The laminar burning velocity of air/hydrogen was obtained in reasonable agreement with previous data. Under conditions of constant  $X_{OA}$  and  $\phi$ , the laminar burning velocity was the highest when helium was used as an inert diluent, followed by argon and nitrogen. The maximum burning velocities under constant  $X_{OA}$  conditions were experienced at  $\phi$  of about 1.8 in all cases of  $X_{OA}$  and inert gases. The variations of the maximum burning velocity with  $X_{OA}$  were essentially linear for every inert gas system.

Laminar flame speeds of  $O_2/H_2/N_2$  mixtures have been determined in the stoichiometric range of ultra-lean to moderately rich, oxygen concentration range of 7.4–30 mol-% of the oxidizer, and pressure range of 0.2–2.25 atm by using a counterflow flame technique [378]. The results were compared with calculated values obtained by using several existing  $O_2/H_2$  kinetic schemes. The results showed that while these kinetic schemes accurately predicted the propagation speeds of high-temperature flames, they substantially underpredicted those of low-temperature flames. While the experimental pressure exponents of the mass burning rates exhib-

ited a minimum point, parabola-like behavior with increasing pressure, indicating the initial, negative influence of the  $\text{H} + \text{O}_2$  termination reaction and the subsequent availability of a positive channel which facilitates radical production, the calculated results failed to predict the increasing trend in the pressure range investigated. It was suggested that existing kinetic schemes may require revision in the intermediate temperature regime strongly influenced by the  $\text{HO}_2^\bullet$  and  $\text{H}_2\text{O}_2$  chemistry.

Laminar adiabatic burning velocities of flames propagating in diluted oxygen/hydrogen/nitrogen mixtures were measured at atmospheric pressure [379]. The oxygen mol fraction in the oxidizer (an oxygen/nitrogen mixture) was varied between 0.07 and 0.1 (7–10 vol.-%) at an equivalence ratio of  $\phi = 1.058$ . Besides the variation in oxygen content, a variation in equivalence ratio from  $\phi = 0.7 - 3.1$  and from  $\phi = 0.7 - 0.95$  was tested at oxygen mol fractions of 0.077 and 0.1077, respectively. The heat flux method was used to determine burning velocities under conditions where the net heat loss of the flat stretchless flame to the burner was zero. A significant difference was noted when comparing the results with experimental data from the literature.

### 3.2.1.6 Effect of Water (Steam) on the Burning Velocity of Air/Hydrogen Flames

One diluent that is always present in air/hydrogen or oxygen/hydrogen flames is water in the form of steam, the combustion product [380]. The effect of water on the burning velocity of air/hydrogen flames was investigated mostly in connection of nuclear reactor meltdown accidents and flammable or explosive hydrogen mixtures accumulating inside the containment shell.

The effect of adding nitrogen, excess hydrogen, and steam on the burning velocity of a pre-mixed stoichiometric air/hydrogen flame at 0.25 atm pressure and an initial gas temperature of 800 °F (720 K) was measured [381]. Whereas addition of nitrogen caused a reduction in burning velocity proportional to the nitrogen added (as expected), the addition of excess hydrogen produced increases in the burning velocity. Water caused only about one-third of the reduction produced by an equivalent volume of nitrogen. On replacing the nitrogen in the air by water vapor on a mol-for-mol basis, the burning velocity increased. (From around 700 cm/s initially) by about  $6 \text{ cm s}^{-1} \text{ mol}^{-1} \text{ mol}^{-1}$  water in the overall mixture.

The burning velocities of air/hydrogen-air and air/hydrogen/steam mixtures as a function of the temperature and composition of the unburned gases were measured by laser Doppler anemometry and schlieren photography using a constant velocity nozzle burner [351]. A two-cyclone in-series particle generator was used to provide a suitable particle seeding rate for the laser Doppler anemometer to measure the flow velocity of the unburnt gas. Burning velocities of air/hydrogen mixtures measured at room temperature agreed well with those reported in the literature. The burning velocity was measured as a function of unburned gas temperature. The addition of steam to an air/hydrogen mixture noticeably decreased the burning velocity. A correlation equation has been derived from the observed burning velocities covering a hydrogen

concentration range of 18–65 vol.-%, a steam concentration range of 0–15 vol.-%, and a temperature range of 296–523 K (23–250 °C).

Laminar burning velocities of lean air/H<sub>2</sub>/steam mixtures near the lower flammability limit were measured by using the pressure-time history of an expanding flame kernel [382]. Although flames in these mixtures are inherently unstable, this difficulty was avoided by using the early pressure rise of the burn. A comparison of results from that method with burning velocities determined from schlieren photographs of the expanding flame kernel gave good agreement. Despite the difficulties, it was believed that the pressure trace method gives results that are useful in modelling nuclear reactor accident scenarios.

The kinetic effects of water vapor addition on the burning rates of H<sub>2</sub> from 1 to 10 atm at flame temperatures between 1600 and 1800 K were measured experimentally and computed numerically [383]. Burning rates were measured using outwardly propagating spherical flames in a nearly constant pressure chamber. Results showed good agreement with other kinetic models for H<sub>2</sub> flames. Both experiments and model simulations showed that water vapor addition caused a monotonic decrease in mass burning rate and the inhibitory effect was more pronounced with pressure. For hydrogen flames, water vapor addition reduced the critical pressure above which a negative pressure dependence of the burning rate was observed. Water vapor addition had the same effect as a pressure increase for H<sub>2</sub> flames, shifting the reaction zone into a narrower window at higher temperatures. For all fuels, water vapor addition increased OH formation via H<sub>2</sub>O + O while reducing the overall active radical pool for hydrogen flames.

Nitrogen dilution and very fine water mist fogs have been suggested as possible methods of mitigating the overpressure rise, should a hydrogen deflagration occur in a vented enclosure in a nuclear power plant. A numerical CFD gas explosion code has been used to simulate the pressure-time curves and the rate of pressure rise generated following the ignition of different oxygen/hydrogen/nitrogen mixtures in a small-scale vented cylindrical explosion rig [384]. The experimental results suggested that total explosion suppression can be achieved.

A mathematical model was fitted and used to estimate the burning velocity of hydrogen diluted with water fog and/or nitrogen. Burning velocities of hydrogen diluted with water fog and/or nitrogen were measured using a cylindrical explosion rig for both unmitigated and mitigated hydrogen-air deflagrations with nitrogen diluted (oxygen depleted) atmospheres and water fog present [385]. The experimental data examined covered both lean and rich hydrogen mixtures and a range of nitrogen dilution levels and water fog densities. The results suggested that a combination of high-density water fog and nitrogen dilution can be extremely effective in reducing the estimated burning velocity especially for hydrogen-rich O<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub> mixtures with equivalence ratios  $\varphi > 1$ , even at relatively modest dilution levels where the oxygen index is reduced to 16%.

It is not possible to safely operate a traditional gas turbine on hydrogen, due to the high risk of flashback. In particular, it is challenging to retrofit conventional gas turbines to enable an efficient and clean usage of hydrogen. In order to use hydrogen as an efficient and clean gas turbine fuel, steam is added at nearly stoichiometric conditions directly into the combustion process, which significantly reduces the flame temperature. The pre-mixed combustion of pure hydrogen diluted with varying amounts of steam for gas turbine applications was modeled using detailed chemical kinetic rate data of the complex oxidation reactions [386]. The effect of steam influenced the third-body reactions with a significant increase of some key radical concentrations. For the assessment of turbulent flames, it was shown that as the heat release spreads, the flame front thickens and the flame extends slightly further downstream with the addition of steam.

The laminar flame speeds of air/hydrogen flames with steam dilution (up to 33 vol.-%  $\text{H}_2\text{O}$ ) were measured over a wide range of equivalence ratios (0.9–3.0) at atmospheric and elevated pressures (up to 5 atm) by an improved Bunsen burner method [387]. Kinetic schemes taken from the open literature were used to calculate the laminar flame speeds and analyze different effects of steam addition. Four mechanisms all underestimated the laminar flame speeds of air/ $\text{H}_2$ / $\text{H}_2\text{O}$  mixtures at medium equivalence ratios while one mechanism provided the best estimates. When the steam concentration was lower than 12 vol.-%, increasing pressure first increased and then decreased the laminar flame speed, the inflection point appeared at 2.5 atm. When the steam concentration was greater than 12 vol.-%, increasing the pressure monotonously decreased the laminar flame speed. The chemical effect was amplified by elevated pressure and it played an important role for the inhibiting effect of the pressure on the laminar flame speed. The fluctuations of the chemical effect at 1 atm were mainly caused by three-body reactions, while the inversion at 5 atm was mainly caused by the direct reaction effect. Elevated pressure and steam addition amplified the influences of uncertainties in the rate constants for elementary reactions, which might be the cause of disagreement between experimental and simulation results.

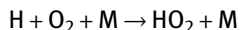
The combustion properties of hydrogen-based mixtures diluted by nitrogen and steam in spherical expanding flames in a spherical bomb have been studied over a wide range of equivalence ratios, initial temperatures and dilutions at an initial pressure of 100 kPa ( $T_{\text{ini}} = 296363413 \text{ K}$ ;  $\text{N}_2/\text{O}_2$  volume ratio = 3.76, 5.67, 9; vol.-% steam = 0, 20, 30) [388]. From these experiments, the laminar flame speed, the Markstein length  $L'$ , the activation energy  $E_a$  and the Zeldovich number  $\beta$  have been determined. These parameters were also simulated by a computer program in order to verify the validity of the kinetic mechanism. Other parameters such as the laminar flame thickness  $\delta$  and the effective Lewis number  $\text{Le}_{\text{eff}}$  were also simulated. These results will be very useful in the hydrogen combustion hazard assessment for nuclear reactor power plant new designs.



### 3.2.1.7 Burning Velocity of Air/Hydrogen Flames in Zero-*g* or Reduced Gravity

Burning hydrogen or any other combustible in air on the International Space Station or on the Moon or on Mars (remember the Martian making water?) with lack of buoyancy of hot gases would have burning velocities quite different from those on Earth. Experimental observations indicated that regardless of fuel type the gravity effects may be neglected for laminar burning velocities of 20 cm/s and greater.

A combination of microgravity experiments and computational simulations were used to study effects of diluents on the near-limit properties of laminar, pre-mixed air/hydrogen flames under reduced gravity [389]. One of the objectives of this study may have been to identify diluents that are effective as fire suppressants on space stations. The experiments were conducted in a short-drop free-fall laboratory facility that provided at least 450 ms of  $10^{-2}g$  conditions. Outwardly propagating spherical flames were used to measure near-limit laminar burning velocities at various equivalence ratios and pressures with reactants containing varying concentrations of He, Ar, N<sub>2</sub> or CO<sub>2</sub> as fire suppressants. Burning velocities were also computed using a pre-mixed flame code PREMIX with detailed chemical kinetics, transport properties and radiative heat loss based on optically thin flames. Measured and computed results both showed the suppressant effectiveness of diluent gases to increase in the order He < Ar < N<sub>2</sub> < CO<sub>2</sub>. This was attributed to both the increasing specific heats and the decreasing transport rates of the gases. The agreement between measured and computed laminar burning velocities was better than it was near the limit. Sensitivity analyses suggested that inaccuracies in three-body termination rates for



reactions and in mass diffusion coefficients for H<sub>2</sub> diffusion are the most likely explanation for the near-limit differences. Corresponding calculations of laminar burning velocities considered variable transport and thermodynamic properties, a radiation model, and a detailed O<sub>2</sub>/H<sub>2</sub> chemical kinetic mechanism.

## 3.2.2 Burning Velocity of Oxygen/Hydrogen Flames

### 3.2.2.1 Burning Velocity of Oxygen/Hydrogen Flames at Sea-Level Pressure

It is nearly impossible to measure burning velocities of oxygen/hydrogen flames at atmospheric pressure because the flames will transition to a detonation on the first opportunity.

The flame temperature of a stoichiometric flame of oxygen/hydrogen is very hot, which is why this combination of gases is sometimes used in welding torches. However, in rocket engines this combination is always used with a large excess of hydrogen, which suppresses the flame temperature. The burning velocity of oxygen/hydrogen flames goes through a maximum at 25 mol-% O<sub>2</sub>, which is on the fuel-rich side of the stoichiometric composition (33 mol-%).

The maximum burning velocity of ozone/hydrogen flames is about 2.5 times faster than that of oxygen/hydrogen flames.

Small amounts of nitrogen dioxide when added to an oxygen/hydrogen mixture have a marked catalytic effect on both the slow reaction and ignition. Concentrations of the order of 0.05 vol.-%  $\text{NO}_2$  may depress the ignition temperature by several hundred degrees.

### 3.2.2.2 Burning Velocity of Oxygen/Hydrogen Flames at Reduced Pressures

Composition and temperature profiles were measured for lean, near-stoichiometric and rich, low-pressure oxygen/hydrogen flames at 7 and 14 mm Hg [390, 391]. Gas samples were withdrawn from the flame with quartz microprobes having orifice diameters ranging from 50 to 100  $\mu\text{m}$ . Infrared spectroscopic measurements were made searching for  $\text{HO}_2$  and  $\text{H}_2\text{O}_2$  in the wavelength region 1–15  $\mu\text{m}$  on a rectangular  $40 \times 10$  cm burner.  $\text{HO}_2$  concentration was below the detection limit of 0.01 mol-% but  $\text{H}_2\text{O}_2$  was found at 0.02 mol-%. A kinetic mechanism was proposed consisting of 6 bimolecular and 4 trimolecular reactions for which rate constants and activation energies were known.

### 3.2.2.3 Burning Velocity of Oxygen/Hydrogen Flames at Increased Pressures

A mechanism consisting of 18 elementary chemical reactions was demonstrated to give a complete quantitative description of the concentration, temperature, and pressure dependence of the flame velocity in  $\text{O}_2/\text{H}_2/\text{N}_2$  mixtures [392]. Whereas concentration and temperature dependence showed the expected behavior, the pressure dependence was determined by two different chain reaction mechanisms occurring simultaneously. At low and at high pressures the pressure exponent of the flame velocity was positive in agreement with simple flame theory. In between there was a transition region with negative pressure exponents due to the change of the chain reaction mechanism, which does not contradict simple flame theory as sometimes asserted in the literature. The partial equilibrium assumption was shown to be valid only at temperatures  $T > 1700$  K, whereas at lower temperatures this hypothesis failed by orders of magnitude.

A study of a similar reaction mechanism consisting of 25 elementary reactions included a sensitivity analysis of the influence of individual elementary reactions involved in the mechanism [393].

## 3.2.3 Effect of Diluents on the Burning Velocity of Oxygen/Hydrogen Flames

Laminar flashback was studied for hydrogen-argon-“air” and hydrogen-helium-“air” systems over a range of pressures [364]. These data contributed toward a general consideration of the pressure dependence of flashback for several fuel-oxidant systems. No relation was found between the critical boundary velocity gradient at 1 atm and its pressure exponent. However, the critical flashback gradient at a pressure of 1 atm and

an equivalence ratio of 1 decreased exponentially with the reciprocal of the adiabatic flame temperature in the manner of a chemical reaction rate.

### 3.2.3.1 Effect of Water (Steam) on the Burning Velocity of Oxygen/Hydrogen Flames

One diluent that is always present in air/hydrogen or oxygen/hydrogen flames is water in the form of steam, the combustion product [380]. The effect of water on the burning velocity of oxygen/hydrogen and air/hydrogen flames was investigated.

Radiolysis of water in the cooling loop of nuclear power reactors during normal operation of the reactor forms a mixture of oxygen, hydrogen, and steam. The radiolysis gas consisting of a stoichiometric hydrogen-oxygen mixture diluted with steam at different temperatures and pressures is a typical gas composition for the closed loop system of Boiling Water Reactors (BWR). There are occasional radiolysis gas explosions relevant to BWR operating conditions: initial pressures up to 70 bar and temperatures up to 570 K [394]. The gas has to be vented periodically on the low-pressure side of the turbine after the effluent has passed the cooling tower.

In the case of accidental meltdown of nuclear reactors, the hydrogen is formed by reaction of hot steam with the zirconium cladding of the fuel rods, and the containment vessel may be filled with a mixture of air, hydrogen, and steam. In certain postulated loss of coolant nuclear reactor accidents, hydrogen gas from zirconium-steam reactions in the reactor core can leak into the containment building to form a combustible mixture. If the hydrogen mixes with air and is ignited, the resulting explosion pressure could pose a threat to the integrity of containment structures and other essential equipment. The overpressure developed in such accident scenarios depends on the burning rate of the combustible mixture and the presence or absence of steam, usually expressed in terms of its laminar burning velocity.

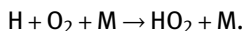
The exhaust of gas generators in closed cycle LOX/LH2 engines consists of steam and unburnt hydrogen that is then fed into the main engine. The burning velocities of  $O_2/H_2/H_2O$  steam mixtures were measured repeatedly under a wide range of conditions.

A comparative study of the effects of diluents on the burning velocity of  $O_2/H_2$  mixtures has been carried out, focusing on the effect of steam on burning velocity and flame structure [395]. Burning velocities were measured by the nozzle burner, cone angle method with particle tracking by laser doppler anemometry for a range of stoichiometries and diluent fractions (He, Ar,  $N_2$ , steam) for air/ $H_2$  mixtures containing up to 50% steam. An empirical correlation was obtained which accurately predicted the physical effects of diluents (flame cooling and heat transport) on burning velocity:

$$S_u \left( \frac{\alpha_0}{\alpha} \right)^{\frac{1}{2}} = S_{u0} \left( 1 - \frac{X}{X_L} \right)$$

where  $S_u$  is the laminar burning velocity,  $\alpha$  is the thermal diffusivity,  $X$  is the mol fraction of diluent,  $X_L$  is the diluent fraction sufficient to inert the mixture and suffix 0 denotes the undiluted mixture. This correlation underestimated the burning velocity for

steam diluent by 20%, indicating that steam influences the burning velocity by mechanisms other than flame cooling and heat transport. Using a one-dimensional flame model, the changes to the flame structure caused by the addition of steam were calculated and indicated that steam effects a redistribution of heat release in the flame. This is caused by the high third-body efficiency of steam in the exothermic reaction



Steam increases the rate of this reaction and, subsequently, the rates of a cycle of exothermic reactions involving  $\text{HO}_2$  in the preheat region of the flame. The result is a steeper temperature profile (i.e., a thinner flame) and an increased burning velocity. Sensitivity analysis indicated this mechanism produces the same effect on burning velocity as is observed experimentally upon adding steam.

The burning velocities of stoichiometric  $\text{O}_2/\text{H}_2$ /steam mixtures with steam concentrations up to 70 vol.-% at elevated pressures and temperatures have been measured and the results compared with numerical calculations [396]. The influence of thermal radiation and kinetic mechanisms on the burning velocity and the detonability of such mixtures at high initial pressure and temperature was evaluated.

The radiolysis gas consisting of a stoichiometric oxygen/hydrogen mixture diluted with steam at different temperatures and pressures is a typical gas composition and a potential hazard for the closed loop system of BWR. There are significant gaps in the experimental data on radiolysis gas explosions relevant to BWR operating conditions. Critical conditions for the flame acceleration and detonation onset of stoichiometric hydrogen-oxygen-steam mixtures at pressures up to 70 bar and temperatures up to 573 K have been calculated. A problem was that critical conditions for the flame acceleration and deflagration to detonation transition (DDT) were only based on experimental data obtained at initial pressures up to 3 bar. Flammability limits, flame acceleration limits and DDT limits at the characteristic scale  $L = 100$  mm were calculated for hydrogen-oxygen mixtures at the initial temperature of 573 K (300 °C) and for two different initial pressures with and without addition of steam [397]. The experiments have been performed with hydrogen-oxygen mixtures at pressures up to 72 bar and temperatures of 383, 423, 473, and 573 K (110, 150, 200, and 300 °C) in a 121-mm I.D., 8-m long tube, and also in a 24-mm I.D., 4-m long tube.

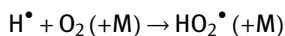
Stoichiometric oxygen/hydrogen mixtures diluted with steam up to 85 mol-% have been tested in a spherical explosion chamber with an inner diameter of 25 cm using the pressure method and high-speed shadow cinematography [398]. The experimental data on the laminar burning velocity were compared with numerical calculations that used different H/O reaction mechanisms based on the Lutz, GRI-Mech 3.0, Li and Warnatz kinetic schemes. Non-monotonic pressure dependence and strong suppressing effect of steam dilution on laminar flame velocity was found both experimentally and numerically. The best consistency with the experimental measurements of the laminar flame velocity at elevated pressures and temperatures in the presence of high steam concentrations was found for the Lutz H/O mechanism.

### 3.2.3.2 Flame Speed of Oxygen/Hydrogen/Diluent Flames

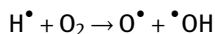
One ternary oxygen/hydrogen/inert gas diluent mixture of particular interest as a rocket propellant is the  $O_2/H_2/He$  mixture also known as Tridyne (see *Encyclopedia of Monopropellants*, chapter “Other Monopropellants”).

This mixture is formulated to avoid the flammable range. In order to safely formulate Tridyne-like gas mixtures, the flammable range and the flame speed of  $O_2/H_2/He$  mixtures have to be known.

Experimental and calculated laminar burning velocities of  $O_2/H_2/He$  mixtures with equivalence ratios of 0.6–4.0, initial pressures of 0.1–0.5 MPa, initial temperature of 373 K, and dilution ratio of 7.0 were compared [399]. Laminar burning velocities changed non-monotonically with the increasing initial pressures at equivalence ratios of 1.0–3.0. The decrease of overall reaction orders can explain the non-monotonic relationship between the laminar burning velocities and initial pressures. Consumption and production rates of both  $H^\bullet$  and  $HO_2^\bullet$  radicals were obtained to explain the decrease of overall reaction order. The three-body reaction



gained more  $H^\bullet$  radicals in competition with



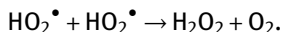
producing more  $HO_2^\bullet$  radicals. Through the reaction pathway analysis, the restraint in production of both OH and H lead to a reduced radical pool. The lower reaction pool would restrain the overall reaction and lead to the reduction of overall reaction order and the non-monotonic behavior of the laminar burning velocity.

### 3.2.4 Radiation Emission Spectra of Oxygen/Hydrogen Flames

Hot flames of oxygen/hydrogen combustion emit a wide range of radiation, although not as luminescent in the visible range as oxygen/hydrocarbon flames. Radiation emissions from oxygen/hydrogen flames have been studied as a diagnostic tool, to identify reactive species in the combustion reaction, to develop fire sensing apparatus and to protect fire-fighting crews from unseen hazards.

Experiments were conducted to study the establishment of equilibrium in  $O_2/H_2$  detonations, especially with respect to the rotational and vibrational degrees of freedom [400]. For this purpose, the emission spectra of different detonations were recorded both photographically and electronically with a photomultiplier tube and a moving slit. Temperatures of rotation and vibration were calculated where possible. In all these experiments, the initial gas mixtures were at room temperature and atmospheric pressure. The spectra were studied in three different spectrographs. A comparison of the spectra of burner with spectra of detonations showed that detonation spectra were less resolved than the burner flame spectra. Transitions with higher quantum numbers were stronger in detonations than in flames.

The emission spectra of oxygen/hydrogen and air/hydrogen flames at 0.1–1 atm exhibit a system of bands between 852 and 880 nm, which were assigned to the  $\text{H}_2\text{O}_2$  molecule vibrationally excited into the overtone region [401]. This molecule results from the reaction



The overtone region also contains bands at 670 and 846 nm, which were assigned to the vibrationally excited  $\text{HO}_2^\bullet$  radical. This radical results from the reaction between  $\text{H}^\bullet$  and  $\text{O}_2$ . The  $\text{HO}_2^\bullet$  radicals resulting from  $\text{H}_2$  combustion inhibited by small amounts of propylene as a free radical scavenger were initially in vibrationally excited states.

There are two dominant types of radiation from hydrogen flames under rocket engine combustion conditions: ultraviolet and blue radiation [402]. The intensity of the spectral lines is pressure dependent [403]. The hyperfine structure of the OH emission lines is useful for combustion and plume diagnostics [404].

### 3.3 Analysis of Hydrogen

The preferred method for the analysis of contaminants in hydrogen gas is by gas chromatography, in particular with flame ionization detectors for organic contaminants (methane, oil).

The other analytical task is the determination of the orthohydrogen: parahydrogen ratio which changes with the conditions during liquefaction and changes with storage time if the mixture has not achieved equilibrium at the normal boiling point of hydrogen. One must know the orthohydrogen: parahydrogen ratio for predicting evaporation losses from large hydrogen tanks. The thermal conductivity of orthohydrogen and parahydrogen gas is quite different, so that this property can be used for determining the orthohydrogen: parahydrogen ratio. The difference in thermal conductivity is most pronounced at 150 K. The method uses a thermal conductivity bridge detector similar to the katharometers used in the first generation of gas chromatographs [405–407].

Parahydrogen content in  $\text{GH}_2$  can be determined by thermal conductivity type in-stream analyzers typically already installed in the manufacturer's liquefaction plant system. Analyzers must be calibrated integrally by the appropriate use of temperature-controlled catalyst beds.

The output of a thermal conductivity cell to measure the parahydrogen concentration in a mixture of para and orthohydrogen gas had been previously assumed to be linear, but this assumption can lead to systematic errors of up to 5.6% in the determination of the parahydrogen concentration. This requires separate calibration procedures [408, 409].

Raman spectroscopic measurement of the ratio of the first two rotational bands of hydrogen at 355 and 586 cm<sup>-1</sup> corresponding to parahydrogen and orthohydrogen, respectively, has been used to determine the parahydrogen content during a production process and a reaction [317]. The results obtained using Raman spectroscopy were compared to those obtained by low-field nuclear magnetic resonance (NMR) spectroscopy. While the results were in good agreement, Raman analysis had several advantages over NMR for this application. The Raman method does not require a reference sample, as both spin isomers (ortho and para) of hydrogen can be directly detected, which simplifies the procedure and eliminates some sources of error. This offers the potential of an industrially compatible method for determining parahydrogen content in applications that require the storage and usage of hydrogen.

### 3.3.1 Specification Requirements for Hydrogen

Military Specification MIL-PRF-27201D covers both gaseous (type I) and liquid (type II) hydrogen [410]. The purity requirements for hydrogen are listed in Table 39.

**Table 39:** Purity requirements for hydrogen per MIL-PRF-27201D

| Constituent                             | Composition                      | Analytical method           |
|-----------------------------------------|----------------------------------|-----------------------------|
| Hydrogen assay                          | 99.995% by volume, min.          | As recommended by CGA G-5.3 |
| Parahydrogen                            | 95% by volume, min. <sup>a</sup> | Thermoconductivity detector |
| Impurities                              | 50 ppm by volume, max.           | As recommended by CGA G-5.3 |
| Nitrogen, water, and total hydrocarbons | 9 ppm by volume, max.            | As recommended by CGA G-5.3 |
| Oxygen and argon                        | 1 ppm by volume, max.            | As recommended by CGA G-5.3 |
| Helium                                  | 39 ppm by volume, max.           | As recommended by CGA G-5.3 |
| Carbon monoxide and carbon dioxide      | 1 ppm by volume, max.            | As recommended by CGA G-5.3 |

<sup>a</sup> Applies to liquid hydrogen only

CGA = Compressed Gas Association

### 3.3.2 Gas Chromatographic Analysis of Hydrogen

Gas chromatographic analysis of hydrogen in gas mixtures using helium as the carrier gas will give erroneous results because the thermal conductivity of the two gases is so similar. More accurate results can be obtained by using argon as the carrier gas, but sensitivity for all other gases is then reduced and the katharometer can only be operated at a lower current.

Catalytic conversion of parahydrogen to normal hydrogen is essential to improve the accuracy of gas chromatographic determination of impurities in LH2 [411]. Fe<sub>2</sub>O<sub>3</sub> or Ni catalysts were used for the conversion.

### 3.3.3 Hydrogen Gas Detectors

Hydrogen from undetected leaks has a tendency to collect under roofs where there may be ignition sources leading to a fire or an explosion. Hydrogen gas detectors would typically be mounted under the ceilings of buildings where hydrogen is handled.

There are hydrogen gas detectors that can trigger an alarm to detect hydrogen leakage or spillage near storage areas. Two hydrogen gas detectors were evaluated in experiments simulating likely operating conditions [412]. Both units were console types sampling by diffusion and convection. When exposing the instrument to increasing concentrations from 4 to 100% hydrogen in air, followed by exposure to decreasing concentration, the calibration had shifted by a substantial amount.

One type of flammable vapor in an air detector uses catalyst coated beads. In the presence of flammable vapors even below their lower flammable limit, the warming of the catalyst bead is sensed by a series of thermistors and triggers an alarm [413, 414]. These sensors work for hydrogen or hydrocarbon vapors. In a catalytic sensor, a palladium and/or platinum catalyst is used to facilitate the combustion of hydrogen with oxygen. A sensing element detects the heat of combustion.

In electrochemical sensors, liquid or solid electrolytes are surrounding a sensing electrode and a counter electrode and in contact with the air to be monitored. Reaction with hydrogen produces an electric current. The air containing the hydrogen gas must flow through a gas permeable membrane to reach the electrolyte. In semiconducting hydrogen gas sensors the gas reacts with chemisorbed oxygen in an oxide semiconductor material, such as tin oxide, and changes the resistance of the material.

In thermal conductivity sensors similar to those used in gas chromatography detectors, the rate of heat conduction from a heat source into the surrounding environment is dependent on the thermal conductivity of that gas environment. Hydrogen has a much higher thermal conductivity than air.

In mass spectrometer monitors, the gas is ionized and then accelerated through an electric field along a curved path. The amount of curvature induced by the electric field is dependent on the mass of the particle and is used to separate the particles by mass. A detector is placed in the path of the desired gas to be measured. Various other sensor techniques for hydrogen leakage and fire detection are available [415, 416]; Table 40.

A solid-state potentiometric hydrogen gas sensor based on hydronium Nasicon, a hydrogen ion conducting solid electrolyte, incorporated a silver-based reference electrode and a palladium working electrode [417]. The sensor was robust, simple, fast, and capable of detecting hydrogen concentrations from at least 0.01 to 100%, a range of four orders of magnitude, in oxidizing and non-oxidizing atmospheres.

A review of electrochemical hydrogen sensors included amperometric, potentiometric, and conductometric sensors [418]. There are sensors with liquid electrolytes and sensors with polymer electrolytes. There are solid-state sensors for hydrogen, but some of those need to be heated all the time.



**Table 40:** Sensitivity limits of hydrogen detectors.

| Minimum detection limits, average values |                    |                    |       |                    |                    |                   |
|------------------------------------------|--------------------|--------------------|-------|--------------------|--------------------|-------------------|
| Principle                                | In air             |                    |       | In nitrogen        |                    |                   |
|                                          | atm-cc/s           | % Hydrogen         | % LEL | atm-cc/s           | % Hydrogen         | Distance (ft)     |
| Catalytic combustion                     | 8.0                | 0.02               | 0.5   | 80                 | 0.2 <sup>a</sup>   | 2000 <sup>b</sup> |
| Bubble testing                           | $1 \times 10^{-4}$ | NA                 | NA    | $1 \times 10^{-4}$ | NA                 | NA                |
| Sonic-Ultrasonic                         | $1 \times 10^{-2}$ | NA                 | NA    | $1 \times 10^{-2}$ | NA                 | 100 <sup>c</sup>  |
| Thermal conductivity                     | $1 \times 10^{-3}$ | $5 \times 10^{-4}$ | 0.01  | $1 \times 10^{-3}$ | $5 \times 10^{-4}$ | —                 |
| Gas density                              | $1 \times 10^{-2}$ | $5 \times 10^{-3}$ | 0.1   | $1 \times 10^{-2}$ | $5 \times 10^{-3}$ | NA                |
| Hydrogen tapes                           | 0.25               | 1.5                | 35    | —                  | —                  | (d)               |
| Scott-Draeger tubes                      | —                  | 0.5                | 13    | —                  | —                  | NA                |
| Electrochemical                          | —                  | 0.05               | 1.2   | —                  | 0.05               | 1000b             |
| Optical interferometer                   | —                  | 0.2                | 5     | —                  | 0.2                | NA                |

LEL = Lower Explosive Limit

<sup>a</sup> Only one commercial catalytic instrument has claimed to detect hydrogen in nitrogen.

<sup>b</sup> The sensing head is remote from readout.

<sup>c</sup> For pressure differential of 25 psi with orifice of 0.20 inch.

<sup>d</sup> Tape can be placed on suspected leak site and visually checked periodically.

Dashes indicate information is not available.

Data source: [415].

There are numerous sensors reported in the literature for hydrogen detection. In one review, these sensors were classified into eight different operating principles [419]. Characteristic performance parameters of these sensor types, such as measuring range, sensitivity, selectivity, and response time were reviewed and the latest state of technology was reported. Testing and validation of sensor performance were described in relation to standardization and use in potentially explosive atmospheres specifying the requirements on hydrogen sensors for practical applications.

## 4 Materials of Construction for Hydrogen

This chapter summarized the choice of materials of construction for handling of liquid and gaseous hydrogen, both structural materials and insulating materials to keep the cold in and to keep the heat out. The main problem in the selection of materials of construction for cryogenic hydrogen systems is the embrittlement of materials that can lead to fractures under moderate loads and vibrations. The same problems could be encountered with other cryogenic liquids.

There are many sources of information on the selection of materials (metallic and non-metallic materials) for operation at cryogenic temperatures, foremost of all the Cryogenic Material Properties Database [420]. This database is a critical evaluation

of existing experimental measurements on the properties of engineering materials at cryogenic temperatures. Equations are given for the recommended property value as a function of temperature. There were many sources of information on materials of construction for liquid hydrogen, most of those from the Cryogenics Laboratory in Boulder, CO, USA operated by the National Bureau of Standards. During the period 1998–1999, the Chemical Propulsion Information Agency (CPIA) released four versions of the Cryogenics Information Retrieval System in CD form, including the NBS Cryogenics Database and a wide range of other literature sources, eventually containing 133000 citations [421].

Since the book at hand is mostly a chemistry book and not a materials science book, these sources are offered just as references recommended for further study, but the technical details cannot be provided in this book. Those mechanical considerations in the selection of cryo-capable materials are essentially the same for LH<sub>2</sub> or LOX, LN<sub>2</sub>, and LNG.

## 4.1 Metals for Hydrogen Service

Compared to natural gas transmission lines and storage tanks, composition, heat treatment, and weldability requirements are more severe for materials for hydrogen transport [422, 423]. Some pressure vessel steels are susceptible to hydrogen embrittlement and thus seamless vessels and/or protective liners are required. High-strength resistant steels must be developed for compressors, valves, and related equipment.

The embrittlement of metals exposed to hydrogen is not only due to the low temperature (all materials become brittle at low temperatures) but also due to hydrogen embrittlement where hydrogen diffuses into the metal and forms interstitial hydrides. The formation of interstitial hydrides causes some metals to swell and fall to powder once they are exposed to hydrogen. This is very catastrophic for structural materials but has been used with advantage for storage of compressed hydrogen in iron/titanium alloys.

### 4.1.1 Metals Acceptable for Hydrogen Service

Hydrogen is not corrosive and does not have special requirements in the selection of materials; however, hydrogen embrittlement of materials and loss of elasticity at the very low temperatures will present unique problems that are not usually observed with other rocket propellants.

One will look for metals which retain some elasticity even at the very low temperatures of boiling liquid hydrogen at 20 K. Metals accepted for tanks and components for liquid hydrogen service include stainless steel CRES-321, CRES-347, and CRES-304, in addition to Inconel, monel, nickel, and aluminum. Carbon steels become very brittle

at low temperatures. Aluminum/magnesium alloys Al-5052, Al-5083, Al-5086, Al-5164, and Al-5456 have been used for liquid hydrogen tanks.

Titanium alloys combine good strength with light weight [424]. A large 26000-L (7100 gallon) tank was made from titanium [425–427]. The oxygen, carbon, nitrogen, and iron content of titanium alloys for cryogenic hydrogen service must be very low. Best results were obtained with a Ti-5Al-2.5Sn alloy, which allows a weight saving of 30–35% compared to aluminum or steel vessels [428]. Tantalum and columbium alloys have been evaluated for liquid hydrogen service [429]. Various coatings were tested as hydrogen barriers. It is desirable that materials for construction of hydrogen facilities (tanks, lines, valves) should have a low heat capacity such that the component can cool down quickly and not so much liquid hydrogen is lost by evaporation during cooldown.

The evaporation losses during storage are reduced mostly by surrounding a tank with an insulating material with very low thermal conductivity (see section “Insulating Materials for Liquid Hydrogen Service”). In addition to using a thermal insulation with low thermal conductivity, it helps to select materials with low thermal conductivity for the design of the tanks and lines. In particular, support structures (struts, brackets) which carry the load through the thermal insulation (which is usually not load-carrying) should be made of materials with low thermal conductivity so they do not act as a bridge for heat flow.

The coefficient of thermal expansion should be low to prevent excessive stretching and shrinking during thermal cycles, causing microscopic thermal internal stress and macroscopic local stress concentrations in structures and container walls. The temperature fluctuations and material strains during filling and emptying of LH<sub>2</sub> tanks are more severe than with any other cryogenic rocket propellant [430, 431].

#### **4.1.2 Low Temperature Phase Changes**

Some metals undergo phase changes at low temperatures and changes of the crystal lattice structure with subsequent loss of mechanical strength. This is just a temperature problem and would occur with any cold fluid, not just with liquid hydrogen. Such phase changes take place very slowly and are often noticeable only after repeated temperature cycling. A martensitic transformation occurs in austenitic stainless steels when they are strained and the amount of the ferromagnetic phase appearing is particularly important when the deformation is produced at low temperatures [432]. The phase change from a gamma to an alpha phase is quite distinctly observable with a steel of the 18-10 type [433].

#### **4.1.3 Tensile Strength of Metals at Low Temperatures**

Tensile tests of 20 different metal coupons at room temperature, 200, 77, and 20 K (–100, –320, and –423 °F) temperature were conducted on a 60000-lb<sub>f</sub>-capacity Baldwin-type hydraulic-operated tensile machine in accordance with Method 211.1

of Federal Test Method Standard No. 151A, which is essentially identical with ASTM Specification E8-61T [434].

#### 4.1.4 Shear Strength of Metals at Low Temperatures

The following references give additional information on materials of construction for liquid hydrogen installations and flight vehicles: [435, 436].

#### 4.1.5 Hypervelocity Projectile Impact on Cryogenic Tank Walls

Orbital debris and micrometeorites constitute an omnipresent hazard for anything that moves in orbits in space. An experimental and analytical investigation was conducted to determine the structural behavior of cryogenic tank wall materials under simulated meteoroid environments and to develop engineering methods defining tank working stresses under the impact of hypervelocity projectiles [437]. The boundary limits between safe fracture and catastrophic fracture were established for 2219-T87 aluminum and Ti-5Al-2.5Sn (ELI) titanium alloy used in cryogenic propellant tanks. Safe fracture boundary limits were established for a wide range of meteoroid masses and velocities. Hypervelocity projectiles of known mass were launched by a light-gas gun to simulate meteoroid impacts. Impact tests were conducted with the tank walls at 77 K (−320 °F) and numerous tests were conducted at 20 K (−423 °F).

### 4.2 Metals Not Acceptable for Hydrogen Service

#### 4.2.1 Hydrogen Embrittlement of Metals

Hydrogen embrittlement causes a decrease in the fracture toughness or ductility in certain metallic materials due to the mobility of atomic hydrogen. Hydrogen must first permeate within a metal for hydrogen embrittlement to occur. Permeation of hydrogen gas in metals begins with the absorption of a hydrogen molecule upon the metal surface and dissociation into atomic hydrogen. Once hydrogen ions (H<sup>+</sup>) form, they readily diffuse through interstitial spaces in the metal crystal lattice. The interaction between hydrogen and metals can result in the formation of solid solutions of hydrogen in metals, solid compounds as hydrides, reforming into molecular hydrogen, or gaseous compounds with other elements in the metal. Some metals undergo noticeable swelling at this point. There are several types of hydrogen embrittlement: **(1)** hydrogen environmental embrittlement, **(2)** hydrogen internal embrittlement, and **(3)** hydrogen reaction embrittlement. Hydrogen embrittlement of metals may be the result of one or a combination of these three processes.

Sensitivity to hydrogen embrittlement is influenced by numerous parameters, including plastic deformation, cyclic loading, hydrogen purity, temperature, and pressure. Hydrogen embrittlement is a major concern for ferritic steels and occurs at ambient temperatures and elevated pressures. The problem is exacerbated when

the steel is subjected to mechanical stresses. The embrittlement processes take place more quickly on freshly generated metallic surfaces that are likely to form at surface defects or other stress raisers as a result of stress-induced local plastic deformation processes.

#### **4.2.2 Hydrogen Permeation of Metals**

Iron-titanium alloys are known to absorb hydrogen as intermetallic hydrides and are used as hydrogen storage media. In view of this property, it should not be surprising that hydrogen can permeate titanium metal. While titanium has proved to be a good material for containers for liquid hydrogen, calculations of the rates of permeation of gaseous hydrogen through titanium indicate that there may be practical limits of temperature, pressure, and time that must be recognized in designing pressure containers for hydrogen. On the basis of reported data, titanium and its alloys cannot be recommended as container materials for hydrogen for long-term service much above 366 K (200 °F) [438, 439]. For short-term service, the permeation to hydrogen may be low up to temperatures near 533 K (500 °F) and at low pressures.

#### **4.2.3 Metals Fatigue at Cryogenic Temperatures**

Metals need to maintain a certain flexibility to yield to stresses and deformations resulting from uneven thermal expansions and shrinking during their service life in a liquid hydrogen system. Many metals suffer fatigue during repeated flexing [440, 441]. This problem is not unique for metals at liquid hydrogen temperatures but affects all metals in all cryogenic environments. Strain-cycling fatigue behavior of 10 different structural alloys and metals was investigated in liquid helium (4 K), in liquid nitrogen (78 K), and in ambient air (300 K) [442]. At high cyclic lives, fatigue resistance increased with decreasing temperature for all the materials investigated. At low cyclic lives, fatigue resistance generally decreased with decreasing temperature for the materials investigated. Only for Inconel 718 did fatigue resistance increase with decreasing temperature over the entire life range investigated.

### **4.3 Composite Materials for Liquid Hydrogen Tanks**

Hydrogen tanks made of polymer-matrix composite material have been advertised as an enabling technology for reducing the dry weight of launch vehicles. For many decades it has been attempted to replace metal in cryogenic tanks by lightweight organic polymers, usually reinforced with inorganic fibers (glass or carbon fiber reinforced composites). The advantage of plastics over metal would be not only lighter weight but also reduced thermal conductivity [443]; however, most plastics become very brittle at the low temperatures and are susceptible to cracking. Remember the

science fair trick where a tennis ball soaked in liquid nitrogen and dropped on the floor shatters in many pieces like glass!

First evaluation of composite materials for liquid hydrogen tanks started in the 1960s, measuring thermal expansion [444], tensile strength at temperatures down to 20 K [445] and hydrogen gas permeability and vapor barrier materials [446]. Development has started on composite-overwrapped pressure vessels for cryogenic service [447, 448], but in the half century that has passed since it has unfortunately not yet progressed to a flight-ready design.

One difficulty with the use of composites is the gas permeability. Hydrogen diffuses readily through organic polymers. Organic polymers have to be laminated with metal foil as diffusion barriers [446, 449].

Composite liquid hydrogen flight tank development had been underway for several years. It began with the National Aerospace Plane (NASP) program, continued several years with work for Single-Stage-to-Orbit (SSTO) Reusable Launch Vehicle (RLV) studies and technology development, including the production of a complex, multi-lobed composite tank for the X-33 program, and continuing for 2<sup>nd</sup> Gen RLV applications under NASA's Space Launch Initiative (SLI).

#### 4.3.1 Hydrogen Permeability of Composite Tank Wall Materials

A fundamental issue for composite liquid hydrogen tanks is the hydrogen permeability of the composite material. Hydrogen permeability was studied in the early days of NASP and results were encouraging enough to proceed with unlined tank development. Then permeability work was relatively dormant for several years under the erroneous assumption that the unlined composite materials were sufficiently impermeable. The high-profile ground test failure of the X-33 hydrogen tank, however, is believed to be a direct result of excessive hydrogen permeation into the honeycomb cells of the sandwich tank wall. As the tank warmed after it was drained, the hydrogen that had permeated into the sandwich from the inside of the tank plus, perhaps, some air that had been cryopumped in from the outside, expanded, and the pressure inside the cells increased, eventually causing a debonding of the core and inner composite face sheet. The failure and subsequent investigation then brought the permeability issue back to center stage [450]. Some of the cryogenic permeability studies referenced here may apply to other cryogenic propellants in addition to liquid hydrogen.

A key development task for composite propellant tanks is to prevent the leakage of hydrogen through the composite material, which is a function of the tank manufacturing method, mechanical load, internal damage in the material due to thermal stresses (microcracks), and the temperature at which the tank must operate. A method was developed for measuring leakage through a geometrically complex shape at cryogenic temperatures and under mechanical load and used to measure helium and hydrogen leakage through the X-33 liquid hydrogen tank wall [451]. Both hydrogen and helium leak tests that were performed on two specimens taken from a discarded segment of

the X-33 tank structure and results showed that the leak rate varied with the applied mechanical load. The level of hydrogen leakage was shown to be significantly higher than the helium leakage and to exceed the acceptable leak rate for a vehicle like the X-33 liquid hydrogen tank by an order of magnitude. After the expensive lesson of the X-33 tank failure, studies of composite liquid hydrogen tanks ("cryotanks") resumed for a second-generation RLV [452].

Leak characteristics of carbon fiber reinforced plastic (CFRP) cross-ply laminates were experimentally investigated under biaxial loadings using an in-plane biaxial testing system [453]. Permeability through the damaged laminate under biaxial stresses was measured with a leak detection system and ultrasonic C-scan was used to inspect the matrix cracking in the specimens. Experimental results revealed that leakage through the damaged laminate is in correlation with the amount of damage and depended not only on load levels but also on biaxial load ratios.

Helium permeability in CFRP cross-ply laminates was measured in relation to crack density and applied biaxial loads [454]. The results of the experiments indicated that stacking sequences of CFRP laminate influenced not only matrix crack development but also leakage prevention. Permeability through the damaged laminates increased in accordance with damage development and increasing rate of permeability in connection with the strains was dominated by the external biaxial loads.

A computational fluid dynamics (CFD) model was developed to predict leakage through a damaged laminate [455]. Leakage under combined thermal and biaxial mechanical loadings was predicted with the estimated delamination length.

Thermal residual stresses, internal pressure stresses and acceleration stresses during launch were evaluated and quantified for cryogenic composite fuel tank designs [456]. Both failure initiation and progression of a graphite/epoxy laminate system and a graphite/BMI laminate system were investigated using the non-isothermal classical laminate and plate theory and the maximum stress failure criterion. The thermal residual stresses in the transverse direction are the dominant stresses on each ply in the launch stage. After initial ply cracking, through-the-thickness temperature change of a laminate related to fuel leakage as well as a laminate stiffness matrix change was applied to the progressive failure analysis. The fuel leakage-based progressive failure analysis showed a higher number of initial ply cracking does not necessarily mean a higher chance of matrix cracking in all plies at an initial exposure to 20 K (−253 °C) and 1500 kPa. In terms of complete laminate matrix cracking, however, the graphite/epoxy laminate was more resistant to transferring stresses to other plies than the graphite/BMI laminate.

A test system has been assembled to accurately measure the hydrogen permeability of laminates with microcracks and to establish a correlation between damage state and hydrogen gas permeability [457]. The test environment used to induce the microcrack damage consisted of mechanical cycles at both room temperature and at cryo-

genic temperature. Permeability was found to be clearly dependent on both applied mechanical loads and test temperature with the highest leak rate occurring at the cryogenic temperature condition.

Another experimental study of the correlation between damage state and hydrogen gas permeability of laminated composite materials under mechanical strains and thermal loads examined a composite material specimen that had been mechanically cycled at room temperature to induce microcrack damage [458]. Crack density and tensile modulus were observed as functions of number of cycles. Damage development was found to occur most quickly in the off-axis plies near the outside of the laminate. Permeability measurements were made after 170000 and 430000 cycles. Leak rate was found to depend on applied mechanical strain, crack density and test temperature [459].

In order to develop a correlation between thermal fatigue-generated networks of transverse microcracks and the permeability of carbon fiber, polymer matrix composites with epoxy and bismaleimide polymer matrices were cycled between liquid nitrogen temperature (77 K = -196 °C) and elevated temperature [460]. The samples were then optically examined for microcracks and evaluated for their tendency for low-pressure helium gas leakage in a fluid containment application.

A new composite concept that can be used to create CFRPs with high hydrogen gas barrier performance for applications in the cryogenic tanks of fully reusable space transportation systems consists of a non-metallic crystal layer, which is actually a dense and highly oriented clay crystal laminate [461]. Preliminary test results showed that the hydrogen gas barrier characteristics of this material after cryogenic temperature shocks and cyclic loads were still better than those of other polymer materials by approximately two orders of magnitude.

Hybrid fiber composites with carbon and Kevlar<sup>®</sup> fabric were explored as means to reduce the influence of thermal gradients and in order to enhance the material performance when cryogenic propellant fuels are stored in space launch vehicle applications [462]. Preliminary studies of tensile and flexural strength had indicated that carbon and Kevlar<sup>®</sup> woven fiber composites are suitable materials for cryogenic temperatures. The pristine mechanical properties of carbon composites changed within a maximum of 3–4% after initial cryogenic exposure during the fueling stage, while Kevlar<sup>®</sup> composites changed 17%.

#### 4.3.2 Insulation of Composite Propellant Tanks

Insulation can be applied either internally or (more commonly) externally. If the insulation is internal to the tanks, the outside load-bearing shell remains at higher temperatures and remains more flexible and hopefully will not embrittle due to the cold.

The use of fiber-glass-reinforced plastics as a structural material surrounding internally located foam insulation for liquid hydrogen propellant tanks was investigated



and experimentally evaluated in a sub-scale cryogenic tank [463]. The tank consisted of three main components: a structural shell of filament-wound fiber glass, an internal insulation system of polyurethane foam encapsulated in a vacuum-tight jacket of aluminum-Mylar-aluminum foil laminate, and an impermeable liner of the same laminate. Liquid-hydrogen boil-off tests were used to determine the thermal performance and pressure-cycling tests were used to evaluate structural performance. Hydrogen gas should not be allowed to diffuse into pores in internal insulation. Hydrogen gas has a very good thermal conductivity and would ruin the thermal insulation quality.

It was the failure of the composite LH2 tank in the X-33 which eventually killed the project. One of the tanks cracked when it was cooled down with LH2. Lockheed Martin X-33 was an unmanned reusable spaceplane sub-scale technology demonstrator for the VentureStar with a height of 20 m (69 ft), a launch mass of 130000 kg, powered by 2J-2S Linear Aerospike engines with a thrust of 1.82 MN each. The VentureStar was planned to be a next-generation, commercially operated RLV. The X-33 would flight-test a range of technologies that NASA believed it needed for SSTO RLVs, such as metallic thermal protection systems, composite cryogenic fuel tanks for liquid hydrogen, the aerospike engine, autonomous (unmanned) flight control, rapid flight turn-around times through streamlined operations, and its lifting body aerodynamics. Most importantly, through the use of the lifting body shape, composite liquid fuel tanks, and the aerospike engine, NASA and Lockheed Martin hoped to test fly a craft that would demonstrate the viability of a SSTO design. An SSTO craft would not require external fuel tanks or boosters to reach low-earth orbit. Doing away with the need for “staging” with launch vehicles, such as with the Shuttle and the APOLLO rockets, would lead to an inherently more reliable and safer space launch vehicle. Testing of twin Linear Aerospike XRS-2200 engines, originally built for the X-33 program, was performed on 6 August 2001 at NASA’s Stennis Space Center, Mississippi.

The unmanned craft would have been launched vertically from a specially designed facility constructed on Edwards Air Force Base, and have landed horizontally on a runway at the end of its mission. Initial suborbital test flights were planned from Edwards AFB to Dugway Proving Grounds southwest of Salt Lake City, Utah. Once those test flights were completed, further flight tests would be conducted from Edwards AFB to Malmstrom AFB in Great Falls, Montana, to gather more complete data on aircraft heating and engine performance at higher speeds and altitudes. The X-33 was never intended to fly higher than 100 km altitude nor faster than 1/2 orbital velocity. Risky extrapolation would have been necessary to apply the results of successful tests (if these had ever occurred) to an orbital vehicle.

Construction of the prototype was some 85% assembled with 96% of the parts and the launch facility 100% complete when the program was canceled by NASA in 2001, after a long series of technical difficulties including flight instability and excess weight. In particular, the composite liquid hydrogen fuel tank failed during testing in November 1999. The tank was constructed of honeycomb composite walls and inter-

nal structures to lower its weight. A lighter tank was needed for the craft to demonstrate necessary technologies for SSTO operations. A hydrogen-fueled SSTO craft's mass fraction requires that the weight of the vehicle without fuel be 10% of the fully fueled weight. This would allow a vehicle to fly to low earth orbit without the need for the sort of external boosters and fuel tanks. NASA had invested \$912 million in the project before cancellation and Lockheed Martin a further \$357 million. Due to changes in the space launch business, including the challenges faced by companies such as Globalstar, Teledesic, and Iridium and the resulting drop in the number of anticipated commercial satellite launches per year, Lockheed Martin deemed that continuing development of the X-33 privately without government support would not be profitable.

## 4.4 Insulating Materials for Liquid Hydrogen Service

### 4.4.1 Selection of Insulating Methods

Although this book is dealing mostly with the chemistry of rocket propellants, some information is provided on the equipment needed to safely store, transport, and handle these propellants. Storage tanks, flight tanks, and pipes for liquid hydrogen must be properly insulated. There are at least four different methods for insulating LH<sub>2</sub> tanks and lines:

One can build double-walled tanks and lines with a vacuum jacket, double-walled tanks and lines with powder-filled and evacuated jackets, multiple foil insulation ("superinsulation") or one can insulate tanks and lines by surrounding them with rigid foam. The latter two types of insulating material can be applied either internally or externally.

Double-walled tanks with evacuated interspace are usually possible only with very small tanks because the atmospheric pressure exerts a substantial load on the evacuated walls. Internal supports to prevent the double-walled structure from collapsing are unwanted thermal paths and should be minimized. It is better to fill the void space between the two walls with a rigid powder with poor thermal conductivity, such as kieselguhr, diatomaceous earth, perlite [464] or Santocel<sup>®</sup>™. Santocel is a porous silica aerogel manufactured by the Monsanto Chemical Company. The grade used for thermal insulation (Santocel A) is a granular material.

If the small double-walled containers are made from glass, the surfaces are usually mirror-plated to reduce heat transfer by radiation ("Dewar flasks"); however, the reflectivity of the walls does not significantly reduce heat transfer when porous or fibrous insulation is used to fill the interstices. It has been suggested to add shiny, reflective aluminum flakes to the porous insulation to reduce heat transfer by radiation.

The pressure in the vacuum jacket (regardless if filled with porous materials or not) at room temperature should be below 0.01 Pa ( $10^{-4}$  mm Hg). It must be checked

from time to time and if necessary the jacket needs to be pumped down and re-sealed. Good tanks should hold their vacuum for at least 5 years.

Additional information on thermal insulation for liquid hydrogen tanks is to be found in the references listed in Table 41. This is a random collection of historical references relating to insulation for liquid hydrogen tanks, a good starting point for additional studies. The documents referenced here do not specify if the insulation is intended for stationary or flight tanks and what type of insulation (powder or multi-layer or foam) is being considered.

**Table 41:** Information on thermal insulation for liquid hydrogen tanks.

| Author                       | Year | References |
|------------------------------|------|------------|
| Black, Fowle, and Glaser     | 1960 | [465]      |
| Gray et al.                  | 1960 | [466]      |
| Frainier                     | 1961 | [467]      |
| Wilkins                      | 1961 | [468]      |
| Smolak, Knoll, and Wallner   | 1962 | [469]      |
| Glaser                       | 1962 | [470]      |
| Kropschot and Burgess        | 1963 | [464]      |
| Lindquist and Niendorf       | 1963 | [471]      |
| Merrill and Murphy           | 1963 | [472]      |
| Ishaghoff and Canty          | 1964 | [473]      |
| Perkins, Colaluca, and Smith | 1964 | [474]      |
| Eyles                        | 1965 | [431]      |
| Perkins                      | 1965 | [475]      |

Tables 42 and 43 give a comparison of the efficiency of various insulating materials:

**Table 42:** Thermal conductivity and poured density of insulating materials.

| Insulating material <sup>a</sup> | Thermal conductivity            |                                                   | Poured density  |
|----------------------------------|---------------------------------|---------------------------------------------------|-----------------|
|                                  | $\text{W m}^{-1} \text{K}^{-1}$ | $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$ | $\text{g/cm}^3$ |
| Santocel-A                       | 0.00208                         | $4.97 \times 10^{-6}$                             | 0.096           |
| Perlite                          | 0.00156                         | $3.73 \times 10^{-6}$                             | 0.128           |
| Santocel                         | 0.00038                         | $9.12 \times 10^{-7}$                             | 0.176           |
| Laminated superinsulation SI-12  | 0.00019                         | $4.56 \times 10^{-7}$                             | 0.040           |
| Laminated superinsulation SI-4   | 0.000045                        | $1.08 \times 10^{-7}$                             | 0.075           |

<sup>a</sup> Vacuum  $10^{-2}$  mm Hg, ambient temperature 299.8 K = +26.7 °C, inner temperature 90.3 K = −182.8 °C

Data source: [34]

**Table 43:** Comparison of material and installation cost of various insulating materials.

|                                                                                         | Perlite               | Microcel T2           | Microcel T2 +<br>30% Al-Powder | Multi-layer<br>insulation |
|-----------------------------------------------------------------------------------------|-----------------------|-----------------------|--------------------------------|---------------------------|
| Thermal conductivity,<br>$\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$ <sup>a</sup> | $2.69 \times 10^{-6}$ | $1.45 \times 10^{-6}$ | $1.04 \times 10^{-6}$          | $1.24 \times 10^{-7}$     |
| Thermal conductivity, $\text{W cm}^{-1} \text{K}^{-1}$ <sup>a</sup>                     | $1.13 \times 10^{-5}$ | $6.07 \times 10^{-6}$ | $4.35 \times 10^{-6}$          | $5.17 \times 10^{-7}$     |
| Required thickness of insulating<br>layer, cm                                           | 22.8                  | 12.3                  | 8.8                            | 1.05                      |
| Bulk density, $\text{g/cm}^3$                                                           | 0.128                 | 0.304                 | 0.240                          | 0.144                     |
| Material cost, \$/L (1961)                                                              | 0.014                 | 0.067                 | 0.180                          | 0.94                      |
| Installation cost, \$/L (1961)                                                          | 0.008                 | 0.020                 | 0.021                          | 1.06                      |
| Total cost, \$/L                                                                        | 0.024                 | 0.087                 | 0.201                          | 2.00                      |

<sup>a</sup> At a constant heat flux of  $2.26 \times 10^{-5} \text{ cal cm}^{-2} \text{ s}^{-1}$  and a vacuum of better than  $10^{-2} \text{ mm Hg}$   
 Data source: [34]

#### 4.4.2 Multi-Layer Insulation

The best thermal insulation can be achieved by alternating layers of corrugated (waffle-patterned, dimpled) poorly insulating (organic polymer) and highly reflective (mirrored metal foil), often called “superinsulation” [476]. This can be used both internally and externally. Aluminized Mylar<sup>®</sup> is highly reflective and well insulating but needs to be evacuated to remove all gas [477, 478]. It takes substantially more skilled labor work to install multi-layered insulation than filling a fluffy powder into the space between two tank walls. Therefore, multi-layer insulation is used mostly in flight vehicles and not in ground service installations.

There are other multi-layered insulating layer designs which are sealed against intrusion of air but not evacuated. Whatever gas is in the layer will condense and create a vacuum as long as the tank is cold. Such insulating layers can be used for upper stages which are exposed to aerodynamic heating while traversing the atmosphere [479, 480]. Their insulating quality is not as good as that of evacuated layers but they only weigh a fraction of evacuated double-layer systems.

The outer surface of tank installations should have high reflectivity, in particular in the infrared regime, in order to minimize heat absorption in bright sunshine. Polished aluminum surfaces have good reflectivity.

An improvement of external insulation in SATURN-V SII second stage was a multi-layer insulation (MLI) in which aluminized Mylar<sup>®</sup> alternated with honeycomb profiles from phenolic resin [481]. The inner honeycomb cells were hermetically sealed, and the outer layers were purged with cold helium which was supposed to prevent air intrusion. The SIVB third stage had internal insulation. This insulating layer weighed  $253 \text{ g/m}^2$  and had a thermal conductivity of  $0.043 \text{ W m}^{-1} \text{K}^{-1}$  ( $0.025 \text{ BTU h}^{-1} \text{ft}^{-1} \text{°F}^{-1}$ ).

A subscale LH2 storage facility test article for instrumented steady-state and transient thermal tests was designed and a two-stage gaseous helium refrigerator was integrated with the test article and used to reduce boil-off and/or decrease the time required between passive test configuration steady-state conditions. Predictions of a computer program for calculation of space-based liquid hydrogen storage boil-off losses from multi-layer insulated tanks were conservative and consistently high compared to actual measurements [482].

#### 4.4.3 Foam Insulation

The last of the four methods listed at the introduction to this section, applying an external insulation of plastic organic (combustible) foam, was initially considered inappropriate for liquid hydrogen service, because it was feared that air would be sucked into the foam (“cryopumping”) and continue to condense, saturating it with liquid oxygen (which creates an explosive hazard) [483, 484].

The problems of safety associated with the design of a casing enclosing hydrogen process equipment at cryogenic temperatures are somewhat more complex than those of a typical oxygen-nitrogen plant, and several additional factors must be considered. It is necessary to keep air out of the insulation and provide a safe means for venting process fluids from the casing in the event of a large leak. An inert blanketing atmosphere such as nitrogen or helium may have to be kept in the casing, the gas would be selected depending on the process operating temperatures [485]. If the foam layer is not hermetically sealed, the condensation of air on the outside of the tank causes additional evaporation losses [480, 486]. The intrusion of air could be avoided if the foam was continuously purged with cold helium gas, which would be an added complication. In a launch vehicle, if the hydrogen level can be maintained during countdown by topping off the tank through the umbilical until a few minutes before launch, an external foam insulation may be sufficient and internal insulation is not required [487, 488].

History, in particular the history of the development of the external tank of the Space Shuttle, has shown that external foam insulations can provide good thermal insulation, even if the mechanical integrity of the foam during the boost phase leaves a lot to be desired and the impact of breakaway chunks of foam onto the leading edge of Space Shuttle Columbia wings led to the second Space Shuttle disaster with a loss of spacecraft and crew.

Selecting the right insulating material is a matter of optimizing thermal conductivity versus weight. Some insulating materials may also have sufficient rigidity that they support the tank wall against buckling such that the tank wall can be made a bit thinner [489]. The other optimization is dependent on the decision to use internal or external insulation. Internal insulation has the advantage that the insulating layer is not penetrated by support struts that act as undesirable heat leakage paths.

The SATURN S-IV and S-IVB upper stages hydrogen tanks employed internal insulation [490]. It was assembled from contoured foam tiles, which were later covered by a fiber glass-reinforced layer of epoxy resin and sealed with six layers of polyurethane sealant. In spite of this sealant, there were indications that hydrogen diffused into the insulating layer and caused some unexpected evaporation losses. If the S-IVB stage had evolved into a true interplanetary stage with long coasting periods between burns, such as doing a lunar orbit insertion burn, then it would have to be wrapped with additional layers of superinsulation [491].

A quasi steady-state model for the comparison of the thermal performances of foam and multi-layer insulation for a cryogenic liquid hydrogen tank during the ascent and on-orbit phase calculated the corresponding parameters within the temperature range from 55 to 700 K, and pressure range between  $10^{-6}$  and  $10^5$  Pa during the whole process [492]. The model was validated by the experimental results and turned out to have good prediction accuracy. Thermal resistance distributions of foam and multi-layer insulation were compared in detail, and their contributions to reduce the heat leakage and vaporization losses were analyzed and would help to optimize the future design of foam/MLI for cryogenic storage tanks.

## 4.5 Other Materials for Handling of Liquid Hydrogen

### 4.5.1 Sealants for Liquid Hydrogen Service

As sealants for gaskets and valve seats there are only few elastomers that are still elastic at the very, very low temperature of liquid hydrogen. Teflon has been used because no other material was available, but even Teflon becomes brittle at 20 K.

The search for polymers suitable for low-temperature service continued for a long time [493]. In many cases one will make provision for multiple seals, one at the cold temperature and a secondary seal at a higher temperature closer to the outside.

Extreme conditions were encountered in the KIWI, NERVA, and ROVER nuclear thermal rockets. At the transition between the reactor and the expansion nozzle the flanges were tightened with metal seals [494]. Diverse materials were tested as adhesives, foils, thermal insulation, and electrical wire insulation that had to withstand hot/cold cycles, nuclear radiation, and the vacuum of space in nuclear thermal rockets, although they never left the ground [495].

### 4.5.2 Adhesives for Liquid Hydrogen Service

Fifteen different adhesives were evaluated for their ability to provide a hermetic seal in lap joints between thin metallic foils and plastic films in the presence of gaseous and liquid hydrogen [496]. The lap joints were tested in a manner that provided a pressure difference of 20 psi through the adhesive bond line but did not subject the joint to any

mechanical stresses or loads. Each adhesive was tested at room, liquid nitrogen and liquid hydrogen temperatures. The adhesives tested were commercially available and included epoxy-polyamines, nylon-filled epoxies, urethanes, polyesters, and rubber-based adhesives. In general, the most satisfactory adhesives system for sealing aluminum to aluminum, Mylar to Mylar, and Mylar to aluminum at cryogenic temperatures were the epoxies.

#### **4.5.3 Lubricants for Liquid Hydrogen Service**

Most commonly used lubricants are useless at the low temperature of liquid hydrogen because they freeze solid. Dry bearings made from graphite or graphite-filled polymer-impregnated composites which can usually be used over a wide temperature range begin to fail at liquid hydrogen temperatures because friction increases significantly at low temperatures.

## **5 Handling of Liquid Hydrogen**

The handling of liquid hydrogen at rocket test stands and at launch sites requires a special set of precautions that exceed those required for other propellants. For many launch sites around the world, handling of liquid hydrogen has already become routine. The literature referenced here reflect some of the learning the early propellant handlers had to go through when liquid hydrogen was first used as a rocket propellant during the past century. Most of the following publications are only a historical summary and have been superseded by more modern handling and crew training manuals. Additional information on safe handling and potential hazards of liquid hydrogen can be found in the publications listed in Table 44. This listing was not kept up to date but is a good start for further study.

As the most important precaution, liquid hydrogen should not be allowed to come in contact with air, because oxygen and nitrogen will condense into it and form explosive mixtures. Whereas transfer lines in ground service equipment which are in use for only short periods of time sometimes remain without insulation where liquid oxygen or liquid nitrogen has to be transferred, corresponding lines for liquid hydrogen are always insulated and sealed from the surroundings to prevent condensation of air and to reduce hydrogen evaporative losses during cooldown and operations. One of the first commercial rocket engine test sites for LOX/LH<sub>2</sub> engines was the test site of Pratt & Whitney in West Palm Beach, FL, where much experience with the handling of liquid hydrogen was gained [524]. See also [525].

**Table 44:** Literature on handling of hydrogen.

| Author                               | Year  | References |
|--------------------------------------|-------|------------|
| Cassutt, Maddocks, and Sawyer        | 1958  | [497]      |
| A. D. Little                         | 1959  | [498]      |
| Cassutt, Maddocks, and Sawyer        | 1960  | [499]      |
| Jewett and Fowle                     | 1960  | [500]      |
| van der Arend                        | 1960b | [33]       |
| Smith, Wilson, and Scully            | 1962  | [501]      |
| Cloyd                                | 1965  | [502]      |
| NASA HQ                              | 1968  | [503]      |
| Balthasar and Schoedel               | 1983  | [504]      |
| Edeskuty and Stewart                 | 1996  | [250]      |
| Coplen                               | 1952  | [505]      |
| Wintersteen and Mathewson            | 1955  | [506]      |
| Bailey and Benedict                  | 1959  | [507]      |
| Bailey and Benedict                  | 1960  | [508]      |
| Cassutt                              | 1960  | [509]      |
| Laquer                               | 1960  | [510]      |
| A. D. Little Inc.                    | 1960  | [511]      |
| Perkins and Frainier                 | 1960  | [512]      |
| Adkins and Black                     | 1961  | [513]      |
| Adkins and Black                     | 1961  | [514]      |
| Parmley                              | 1962  | [515]      |
| von Elbe and Scott                   | 1962  | [516]      |
| Inst. Intl. du Froid                 | 1965  | [517]      |
| Weintraub.                           | 1965  | [518]      |
| Hernandez                            | 1967  | [519]      |
| Edeskuty and Reider                  | 1968  | [520]      |
| Maes                                 | 2006  | [521]      |
| Beeson and Woods                     | 2003  | [522]      |
| AIAA Hydrogen Committee on Standards | 2018  | [523]      |

### 5.1 Liquid Hydrogen Logistics

Liquid hydrogen (and liquid oxygen) is a volatile commodity and procurement and demand forecast require careful planning [526]. One of the trade-offs is between production plant capacity, separation distance between source and point of end use and storage capacity.

As of 2002, tank trucks hauled more than 804000 kg of liquid hydrogen fuel about 965 km from New Orleans to NASA KSC for every Shuttle launch. Each time the Shuttle was fueled, about 260000 kg of hydrogen would burn off in a flare stack or evaporate. NASA had to bring in a third more fuel than the Shuttle actually used. In 2002, NASA



Glenn Research Center (GRC) awarded an 8M\$ contract to a group of Florida universities to study hydrogen logistics.

## 5.2 Storage of Liquid Hydrogen

The best summary of information on liquid hydrogen storage and transmission is now available in [527]. This book contains a photo of a very large liquid hydrogen storage tank (Figure 56). See also [528].



**Figure 56:** A 2 million liter liquid hydrogen storage tank. (Reproduced from [527], by permission of ©2018 Taylor & Francis Group.)

### 5.3 Design Considerations for Liquid Hydrogen Storage Facilities

#### 5.3.1 Regulatory Requirements for Liquid Hydrogen Storage Facilities

Various government agencies and commercial organizations have issued regulations, industry standards and recommendations for the safe storage of liquid hydrogen. Storage and transportation of hydrogen within the US is governed by 29 CFR-1910.103 Hydrogen. § 1910.103, paragraph (c), pages 229–237 of this section applies to the installation of liquefied hydrogen systems on consumer premises. 14 CFR, Chapter III – Commercial Space Transportation, Federal Aviation Administration, Department of Transportation, Part 420 – License to Operate a Launch Site; Subpart D – Responsibilities of a Licensee; Section § 420.66 contains separation distance requirements for storage of liquid hydrogen and any incompatible energetic liquids stored within an intraline distance.

DoD 6055.09-STD [529] sets requirements for siting LH2 storage and piping in relation to facilities and other propellants and chemical storage and for personnel monitoring. Although DoD 6055.9-STD does not address piping design, construction, or testing, it is recommended by this guide that all vessel and piping systems for propellant hydrogen service be designed, constructed, and tested in accordance with ASME B31.3 and Compressed Gas Association (CGA) G-5.4. NASA Standard, “Safety Standard for Explosives, Propellants and Pyrotechnics.”

Liquid hydrogen is in the DoD Storage Hazard Class 2.1 (LB). Group LB includes “Energetic liquids that are readily combustible when exposed to, or ignited in the presence of an oxidizing agent, but that are not strong reducing agents.” Table C9.T22 establishes Quantity-Distance (QD) Criteria for Liquid Hydrogen and Bulk Quantities of Hydrazines.

NASA-STD-8719.12A [530] incorporates the requirements from DoD 6055.9. Table 5.33 is identical with Table C9.T22 of DoD 6055.09-STD.

NFPA 50B describes “Liquefied Hydrogen Systems at Consumer Sites.” The QD requirements of NFPA 50A and 50B are based on the concept that the effects of fire, explosion, and detonation can be reduced to tolerable levels if the source of the hazard is kept far enough from people and other facilities. The NFPA hazard diamond for liquid hydrogen has a 3 for health hazard (frostbite) and a 4 (worst possible) for fire hazard (Figure 57).

#### 5.3.2 Design of Liquid Hydrogen Storage Tanks

In order to minimize evaporation losses, the thermal insulations in stationary tanks are usually thicker and heavier than those in flight vehicles. Evaporation losses are a function of the surface to volume ratio. This ratio is the most favorable for a sphere. For this reason large hydrogen storage tanks are often designed and built in spherical shapes.

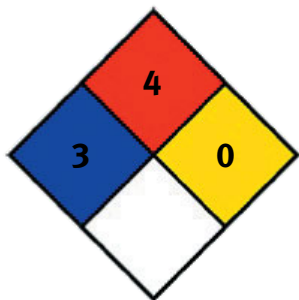


Figure 57: NFPA hazard diamond for liquid hydrogen

Some of the observations and recommendations on the storage of hydrogen reported here apply equally well to storage any of cryogenic liquid, including liquid helium or liquid oxygen. We are discussing this topic here in more detail for liquid hydrogen because much of the new cryogenic technology was developed specifically for this rocket propellant. There have been many conferences devoted specifically to the cryogenic technology for liquid hydrogen.

Hydrogen storage tanks should be kept under a slight overpressure to prevent intrusion of air. The evaporating hydrogen escapes through a pressure relief valve and is fed into a manifold that is constantly purged with nitrogen. The manifold leads away from the tank and in a safe distance into a vent and flare stack. The top of the vent stack carries a check valve and explosion barrier (metal foam, wire mesh) to prevent flashback of the combustion into the vent duct [531, 532].

Liquid hydrogen storage tanks, like all hazardous chemical storage areas, are usually surrounded by a berm and a catch basin that is intended to collect any leakage and restrict its overflow and travel to adjacent storage areas.

In order to avoid fires, all electrical installations must be spark-proof and must be grounded. Electrostatic charges are a serious threat when pumping non-conductive liquids.

Warm hydrogen gas rises in air and may collect underneath roofs and awnings, forming explosive mixtures. Hydrogen storage or test areas that are covered must be well ventilated. See also [533].

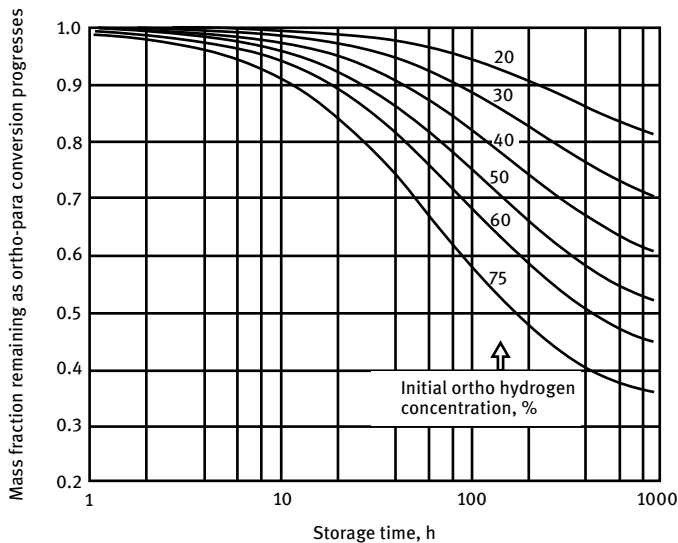
#### 5.4 Evaporation Losses from Stationary Liquid Hydrogen Storage Tanks

Evaporation losses are higher from cylindrical containers than from spherical containers with equal volume and same construction and thermal insulation. In spite of this disadvantage there are many cylindrical tanks in use for liquid hydrogen, mostly for tank cars and in rockets, where not only the surface to volume ratio, but also the

cross-sectional area is important to fit under bridges and through tunnels and have a small cross-section to reduce aerodynamic drag in flight.

#### 5.4.1 Influence of ortho-para Conversion on Evaporation Losses

The rate of evaporation losses during storage depends on the completeness of the conversion of orthohydrogen to parahydrogen during the liquefaction which should be as close to the equilibrium composition as possible. Figure 58 illustrates the evaporation losses as a function of ortho to para conversion and time. In order to prevent excessive evaporation losses during storage, one will want to achieve as complete as possible conversion of the room temperature equilibrium composition hydrogen to parahydrogen.



**Figure 58:** Evaporation losses of liquid hydrogen due to ortho-para conversion as a function of initial composition. (Reproduced and modified from [41].)

The evaporation of liquid hydrogen caused by the heat of reaction of the ortho-para conversion has been measured as a function of the orthohydrogen concentration [534].  $o \rightarrow p$  and  $p \rightarrow o$  conversion rates were measured within the entire range of existence of the liquid phase and in the gas for temperatures up to 120 K and pressures up to 700 bar [407, 535, 536]. All measurements were made under careful exclusion of catalytic (paramagnetic) materials and the containers were only glass or beryllium. Tests with different surface: volume ratios in the beryllium containers gave identical results, verifying that there was no surface catalysis of the conversion. Measurements were made of natural ortho-para conversion rates in  $H_2$  in a wide

range of fluid states: in the liquid at temperatures 16.65, 20.4, 24.15, 28.06, and 32.15 K and pressures up to 500 bar (densities from 0.05 to 0.09 g/cm<sup>3</sup>) and in the gas at temperatures 40, 51.15, 77.5, 90, and 120 K and pressures from 20 to 700 bar (densities from 0.019 to 0.085 g/cm<sup>3</sup>). The low-temperature ( $T > 4.2$  K) ortho-to-para conversion in hydrogen occurs according to the following equation, established in experiments on liquid and solid H<sub>2</sub>

$$\frac{dc}{dt} = -kc^2 + k'c(1-c)$$

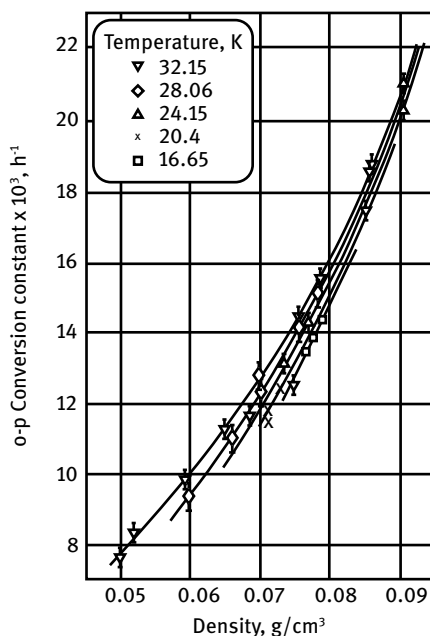
where  $k$  and  $k'$  are the  $o \rightarrow p$  and  $p \rightarrow o$  conversion constants and  $c$  is the orthohydrogen concentration. The conversion constants are calculated from

$$k = \frac{1}{ta} \ln \frac{(c_f - c_e)c_i}{(c_i - c_e)c_f} \quad a = \frac{k'}{k} = \frac{c_e}{1 - c_e}$$

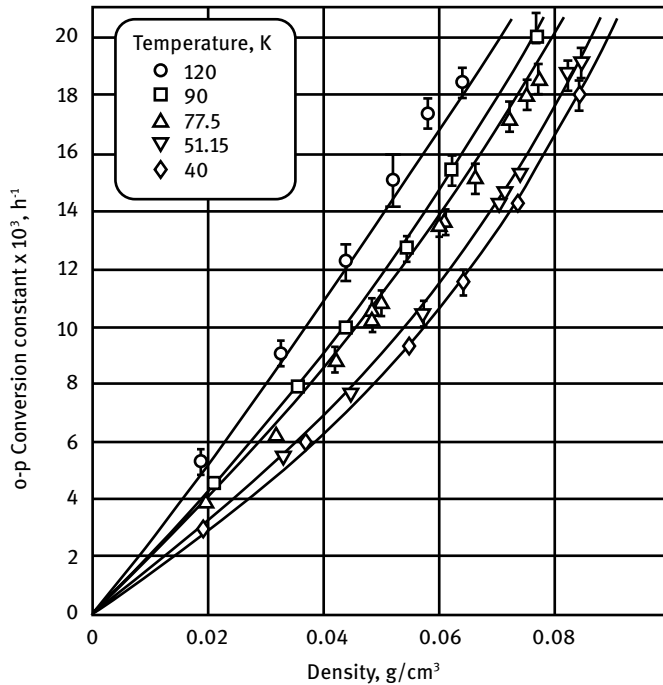
where  $k$  is the kinetic constant in h<sup>-1</sup>,  $c_i$  is the initial concentration,  $c_f$  is the final concentration, and  $c_e$  is the equilibrium concentration of orthohydrogen. The interpolation formula for the entire range of fluid phases has the form

$$k = A(T)\rho + C(T)\rho^p$$

where  $p = 3.6$ ,  $k$  is in units 10<sup>-3</sup> h<sup>-1</sup>, the temperature in K, and  $\rho$  is in g/cm<sup>3</sup>, then  $A(T) = A_0 T^n$ ,  $A_0 = 18.2 \pm 1.6$ ;  $n = 0.56 \pm 0.02$  and  $C(T) = 5 \times 10^4 (C_0 + DT^{-m})$  with  $C_0 = 0.77 \pm 0.03$ ;  $D = 921 \pm 91$ ;  $m = 2.5 \pm 0.2$ . Figure 59 shows the  $o \rightarrow p$  conversion constant



**Figure 59:**  $o \rightarrow p$  Conversion constant of liquid hydrogen as a function of density. (Republished and modified from [536], with permission of ©1997 Springer New York LLC; permission conveyed through Copyright Clearance Center, Inc.)



**Figure 60:**  $o \rightarrow p$  Conversion constant of gaseous hydrogen as a function of density. (Republished and modified from [536], with permission of ©1997 Springer New York LLC; permission conveyed through Copyright Clearance Center, Inc.)

of liquid hydrogen as a function of the density with the temperature as the auxiliary parameter. Figure 60 shows a similar graph for the  $o \rightarrow p$  conversion constant of gaseous hydrogen as a function of the density with the temperature as the auxiliary parameter.

A tank storing liquid hydrogen at 20 K and containing only 90% parahydrogen instead of the equilibrium concentration will lose an additional 0.25% of its content per day, in addition to the loss due to unavoidable heat leakage through the walls of the container. In the presence of catalysts, traces of oxygen or steel, the conversion and evaporation loss may occur even faster [4].

Evaporation losses from storage tanks are size dependent. Larger tanks are more economical for long-term storage. Very large tanks containing 1900000 L have demonstrated evaporation losses of only 0.06%/day in comparison to 0.24%/day in a 94000-L container. It is more economical to store liquid hydrogen in one large tank than in several small ones.

#### 5.4.2 Active Cooling to Prevent Evaporation Losses

It is possible to condense the evaporating hydrogen and return it to the storage volume if it is not permissible to vent the boil-off. The extra energy expenditure and the capital cost of the extra installation will have to be subject to an economic analysis [537]. The benefit of recondensation depends on the tank size. In many cases it will be less expensive to just purchase more liquid hydrogen and make an allowance for evaporation losses.

Evaporation losses occurring during liquid hydrogen transfer operations to cool down the lines and the receiving vessels are much faster and usually cannot be captured by recondensation or temporarily storing the large amount of gas in a gasometer for later use and reliquefaction at a slower rate [538]. Each storage facility will have to have a vent stack with a flare to handle these high flow conditions. Sometimes it is possible to precool the equipment by a recirculating flow of cold helium gas. That would reduce the vaporization losses when the tank is first filled with hydrogen. Precooling the liquid hydrogen to near slush formation temperature would also reduce the vaporization losses during cooldown of the equipment.

### 5.5 Hydrogen Flare Stacks

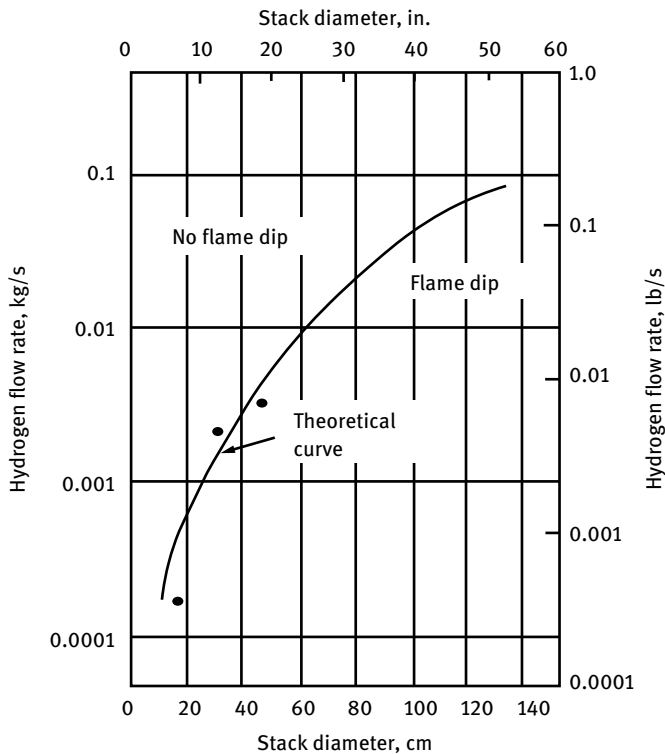
A design guide for hydrogen vent systems includes pressure relief valves and other safety devices [539]. The nitrogen purge of the vent duct should be turned off before venting cold hydrogen gas, otherwise nitrogen might solidify in the duct and clog the vent duct. If the vented hydrogen is always very cold, the vent duct may have to be purged with helium instead of nitrogen.

This publication presents design guidelines for hydrogen vent systems used in gaseous and liquid hydrogen systems at user sites and provides recommendations for safe operation of these vents. It begins at the discharge port of safety devices and other components that control the release of hydrogen and ends at the point where hydrogen concentration in the atmosphere is below the lower flammable limits. It also provides information on the production, transportation, handling, and storage of compressed hydrogen, cryogenic liquid hydrogen, and related products.

Boil-off from liquid hydrogen storage tanks or gas released during chilldown of equipment has to be collected in a duct and fed to a flare stack for safe disposal. The duct manifold leads away from the gas source and at a safe distance leads into a vent and flare stack. The top of the vent stack carries a check valve and explosion barrier (metal foam, wire mesh) as flashback arrestors [531, 532]. Under certain adverse conditions, explosions may occur in flare stacks if air can enter before the flare is ignited [540]. It is best to keep the pilot flame burning all the time to prevent this from happening.

Experiments showed that ambient air may enter the top of a hydrogen flare stack and cause problems when the hydrogen flowrate is too low [541, 542]. Diffusion flames burning in air on a wide, upright pipe (stack) and fed with slow, upward flows of buoyant gas may induce a downward flow of air along the interior walls of the pipe that can support combustion within the pipe. Predicted flame dip limits agreed roughly with experimental values determined on 6, 12 and 18-in. diameter stacks and increased with increasing stack diameter. Measurements were made of the limiting flow at which a hydrogen diffusion flame blows out in still air. Burning rates of large hydrogen diffusion flames ranging from about 1 to 30 cm/s (0.03–1 ft/s) were used to predict approximate flame heights on flare stacks (Figure 61).

There is concern that strong crosswinds may snuff out the flame on top of the flare stack [543]. Crosswinds do not strip significant amounts of unburned hydrogen from its diffusion flame. Flames held on bluff bodies in ducts owe their stability to the recirculation zone behind the flame holder. This zone may be thought of as a pilot flame that keeps the main flame established as long as it is able to ignite the mixture flowing



**Figure 61:** Dip limits of hydrogen diffusion flames into flare stack. (Reproduced and modified from [542].)



past. Blow-off occurs if the main stream flows so fast that sustained ignition cannot be achieved. The flow velocity at which this condition arises depends on the size and shape of the flame holder as well as on the temperature, pressure, and composition of the incoming mixture. Water-cooled flare stacks are not likely to be damaged when the flame is blown back into them by opposing winds.

## 5.6 Examples of Liquid Hydrogen Storage Facilities

### 5.6.1 USA

As of 1968, the largest tank built in the western world was a spherical tank containing 2650000 L of liquid hydrogen. The inner sphere with a diameter of 17.4 m was made from Al-5083, the outer shell was from steel. Smaller containers were made from titanium alloys [425].

At the KIWI test site of the Atomic Energy Commission there were initially two liquid hydrogen tanks with 190000 L contents, each of which could be pressurized to 6.8 atm [9, 10]. The thermal insulation consisted of a 91-cm thick layer of perlite. The evaporation losses ran at only 0.2%/day.

Later the AEC started testing a larger nuclear thermal rocket engine attached to the PHOEBUS nuclear fission reactor which delivered 5000 MW thermal. This effort required an increase of the liquid hydrogen storage capacity by a factor of 10. Toward the end of the program there were two spherical tanks with a net volume of 1900000 L each (allowing for 10% ullage) at the test site. The larger tanks were also insulated with perlite and could be pressurized to 7 atm overpressure.

While the test duration during KIWI-A testing was limited to 500 s (a supply of 380000 L consumed at a flow rate of 2700 L/min.), later tests with a flow rate of 130000 L/min. were extended to 2000 s. The suction line had an internal diameter of 40 cm and the feed line had a diameter of 25 cm and was rated for a feed pressure of 135 atm gauge.

In the foreground in front of the Space Shuttle launch pad is the liquid hydrogen storage tank used during the Space Shuttle era (Figure 62). In 2018 NASA started construction of a new spherical liquid hydrogen storage tank at KSC with a capacity of 4730 m<sup>3</sup> (1.25 million gallons) and a diameter of 25 m. Instead of evacuated Perlite insulation, the new tank will have evacuated glass bubble insulation. Liquid hydrogen losses through boil-off can be reduced by as much as 46% by using the different insulation fill material. The new tank will have a refrigeration system allowing control of the fluid inside the storage tanks. This approach provides direct removal of heat energy using an integrated heat exchanger together with a cryogenic refrigeration system.



**Figure 62:** Liquid Hydrogen Ground Storage Tank at NASA Kennedy Space Center. NASA Photo No: KSC-05pd-1569 (14 July 2005).

### 5.7 Stratification Problems with Liquid Hydrogen

Heat leak to cryogenic propellant tank causes buoyancy-driven liquid stratification, resulting in formation of a warm liquid layer at the top of the liquid free surface. This warm stratum may be further heated by the admission of warm pressurant gas for tank pressurization during engine operation. Since stratified layer temperature has a direct bearing on the cavitation-free operation of turbo pumps integrated into cryogenic rocket engines, it is necessary to model the thermal stratification for predicting stratified layer temperature and mass of stratified liquid in the tank at the end of engine operation. These inputs are required for estimating the minimum pressure to be maintained by the tank pressurization system and for the net positive suction head. If a tank containing initially well-mixed liquid hydrogen (or any other cryogenic fluid) is pressurized, as is often done for pressure-feeding or to prevent cavitation on the suction side of a pump, the boiling and mixing stops, and the liquid comes to rest for a while. If the heat influx to the tank comes uniformly from all sides, the warmer fluid will rise and collect in the top layer while the colder fluid remains at the bottom. The pressure in a stratified tank will rise faster than in a well-mixed tank. This stratifica-

tion is highly undesirable and can cause several types of operational problems. This problem has been extensively described and discussed in the cryogenic engineering literature, see the list of publications in Table 45.

**Table 45:** List of publications on stratification in liquid hydrogen.

| Author                            | Year | References |
|-----------------------------------|------|------------|
| Bailey and Fearn                  | 1964 | [544]      |
| Robbins and Rogers                | 1964 | [545]      |
| Tatom et al.                      | 1964 | [546]      |
| Vliet et al.                      | 1964 | [547]      |
| Barnett, Winstead, and McReynolds | 1965 | [548]      |
| Clark                             | 1965 | [549]      |
| Segel                             | 1965 | [550]      |
| Robbins and Rogers                | 1966 | [551]      |
| Bourgarel and Segel               | 1967 | [552]      |
| Fan                               | 1967 | [553]      |
| Hurd and Harper                   | 1968 | [554]      |

One way to avoid stratification is to allow heat leakage through support structures mainly at the bottom of the tank. In a gravity field, the upwelling and convection would then assure continued mixing even after pressurization. This works only in a gravitational field and not in outer space. Another method is the installation of a chimney in the tank which facilitates circulation by convection; however, in a zero-g environment all anti-stratification methods depending on convection will lose their effectiveness.

An experimental investigation was made to determine the behavior of liquid hydrogen in a 473 L (125 gallon) scale model of a propellant tank subjected to a range of wall heat flux from 13.6 to 93 W/m<sup>2</sup> (0.0012–0.0082 BTU ft<sup>-2</sup> s<sup>-1</sup>) and a range of bottom heat flux from 5.7 to 111 W/m<sup>2</sup> (0.0005–0.0098 BTU ft<sup>-2</sup> s<sup>-1</sup>) while discharging from the tank at a rate of 18 g/s (0.04 lb/s) under a constant tank pressure of about 202 kPa (2 atm) [555]. Increasing temperature stratification in the liquid was encountered with increasing wall heat flux. A decrease in stratification was experienced with increasing bottom heat flux. An available analysis partially predicted the increase in temperature stratification.

A thermal model was developed for a foam-insulated LH2 tank subjected to heat leak and pressurization with hydrogen gas at 200 K during liquid outflow at 38 L/s for engine operation [556]. The model considers buoyancy flow in a free-convection boundary layer caused by heat flux from the tank wall and energy transfer from warm pressurant gas to predict temperature of the liquid stratum and the mass of stratified liquid in a 30 m<sup>3</sup> tank at the end of engine operation in a cryogenic upper stage qualification stationary ground test firing.

Cryogenic liquids stored in a tank generally show different thermodynamic behaviors because of the heat ingress from the outside. Compared with those predicted by the homogeneous model, experimental results indicated different behaviors because of thermal stratification. The results particularly showed that thermal stratification is highly correlated with the thermal aspect ratio [557]. The top layer results in faster pressure increases, which is in contrast with the result predicted by the homogeneous model. The boil-off gas rate generated is significantly less than that predicted by the general calculation in the homogeneous model even if much boil-off gas is generated in the early stage in a system with a warmer top layer. It was shown that the thermodynamic behaviors resulting from thermal stratification are significantly different from those predicted by the homogeneous model.

For a liquid hydrogen tank in zero-g, stratification can be destratified by spinning the spacecraft. A method was presented for determining the onset of a thermally induced convective mixing motion in a model of a cylindrical space-storage tank subjected to a constant heat flux at its outer boundary. The model simulated a completely filled liquid cryogen tank with shear-free ends rotating in a low-gravity environment [558].

## 5.8 Self-Pressurization of Locked-up Liquid Hydrogen Tanks

The pressure rise rate in a locked-up, quiescent, stratified tank is different from that of a well-mixed tank and depends on the presence or absence of gravity [559–560]. Self-pressurization of liquid hydrogen tanks under conditions of reduced gravity is discussed at the end of this section.

The rate of pressure increase following the closure of the vent line in a tank and the pressurization gas requirements depend significantly on the amount of stratification in the tank [549, 550]. The temperature difference between the top layer and the bottom layer can amount to several degrees K. The temperature fluctuations of the propellant taken from the tank cause irregular deviations in the other physical properties of the propellant as it wends its way through the system. The properties will vary depending on which layer of the liquid the propellant was taken from.

The self-pressurization of a tank following closure of the vent line will occur faster with stratification than with a uniformly mixed liquid. Stratification is closely related to the rate of self-pressurization of liquid hydrogen in a tank once the vent is closed and the tank is allowed to come up to a safe operating pressure without adding any pressurant gas [561].

A non-venting 23-cm (9-in.) diameter spherical tank partially filled with liquid hydrogen was subjected to 4 uniformly heated self-pressurization tests [562]. These tests were conducted with various combinations of liquid filling levels, heat-transfer rates and either top heating, bottom heating or uniform heating.

A non-venting 56-cm (22-in.) diameter spherical tank partially filled with liquid hydrogen was subjected to 4 uniformly heated self-pressurization tests [563]. These tests were conducted with various combinations of liquid filling levels (approximately 30–80% by volume) and heat transfer rates (approximately  $53\text{--}202\text{ W/m}^2 = 17\text{--}64\text{ BTU h}^{-1}\text{ ft}^{-2}$ ). These data were compared with data from a similar study performed on a 23-cm (9-in.) diameter, uniformly heated, spherical tank and with the self-pressurization of a 189000L (50000 gallon) spherical liquid-hydrogen storage tank. The data from the 23-cm (9-in.) and 56-cm (22-in.) diameter spherical tank tests verified the analysis which predicted that the effect of size on self-pressurization of hydrogen tankage can be expressed as a simple geometric relation involving the heat added per unit volume. The conclusion was supported by the fact that the pressure data, plotted as a function of heat added per unit volume, fell within a narrow band. The pressure rise rate increased almost linearly with increasing heat transfer rate; however, as the heat transfer rate was increased, the contents of the 23-cm (9-in.) tank became slightly less homogeneous while the contents of the 56-cm (22-in.) tank remained essentially the same. This difference was attributed to the thicker wall of the 22-inch (56-cm) tank which absorbed a larger proportion of the incoming energy at the higher heat transfer rates and caused a change to more bottom heating. For both the 23-cm (9-in.) and 56-cm (22-in.) tanks the pressure rise rate was only slightly affected by varying the percent filling with a trend toward increasing pressure rise rates at higher fillings. The 189000L (50000 gallon) spherical liquid-hydrogen storage tank described in earlier work had a much greater rate of pressure rise, when compared with the homogeneous analysis, than either of the smaller tanks. This difference was attributed to a different mode of heat transfer in the liquid. At the low heat fluxes encountered in the earlier experiment ( $1.9\text{ W/m}^2 = 0.6\text{ BTU h}^{-1}\text{ ft}^{-2}$ ), heat was transported in the liquid by laminar natural convection rather than by turbulent convection as was the case for the tests on the smaller tanks so that larger temperature gradients and non-homogeneous conditions resulted.

A computer program was developed for calculating the thermal stratification and the associated self-pressurization of a closed liquid hydrogen tank [564]. The historical FORTRAN-IV programming language was used and runs were made on IBM 360/65 and CDC 3600 computers. Comparisons were made between the program calculations and test results from both ground and orbital coast tests of a CENTAUR upper stage.

Self-pressurization and thermal stratification tests of a  $4.89\text{-m}^3$  liquid hydrogen storage tank subjected to low-heat flux ( $0.35, 2.0, \text{ and } 3.5\text{ W/m}^2$ ) under normal gravity conditions were performed at fill levels of 83–84% (by volume) [565]. The LH2 tank was representative of future spacecraft tankage, having a low mass-to-volume ratio and high performance multi-layer thermal insulation. Results showed that the pressure rise rate and thermal stratification increased with increasing heat flux. At the lowest heat flux, the pressure rise rate was comparable to the homogeneous rate, while at the highest heat flux, the rate was more than three times the homogeneous rate. It was found that initial conditions had a significant impact on the initial pressure rise rate.

The quasi-steady pressure rise rates were nearly independent of the initial condition after an initial transient period had passed.

Tests of self-pressurization and thermal stratification of a  $4.89\text{-m}^3$  liquid hydrogen storage tank subjected to low heat flux ( $2.0$  and  $3.5\text{ W/m}^2$ ) in normal gravity, which was representative of future spacecraft tankage, having a low mass to volume ratio and high performance multi-layer thermal insulation, were performed at fill levels of 29 and 49% (by volume) and complement previous tests at 83% fill [566]. As the heat flux increased, the pressure rise rate at each fill level exceeded the homogeneous rate by an increasing ratio. This ratio did not exceed a value of 2. The slowest pressure rise rate was observed for the 49% fill level at both heat fluxes. This result was attributed to the oblate spheroidal tank geometry which introduces the variables of wetted wall area, liquid-vapor interfacial area, and ratio of side wall to bottom heating as a function of fill level or liquid depth. Initial tank thermal conditions were found to affect the initial pressure rise rate.

Three different pressure rise models were employed to calculate the self-pressurization and boil-off rates in cryogenic vessels [567]. These were a homogeneous model, a surface evaporation model and a thermal stratification model. The first two models were based on the assumption that no temperature gradients exist in the tank, while the thermal stratification model takes the temperature distribution into account. Employing the thermal stratification model, temperature gradients and their effect on the pressure rise rates in liquid hydrogen tanks were analyzed.

The rate of vaporization losses in a cryogenic tank has important design consequences for propellant and LH2 support systems planned for long duration space missions. The amount of liquid in the tank and the heat leak rate and distribution can all have an effect on the pressurization rate. A model fluid experiment was performed in normal gravity [568]. Experimental results showed that after undergoing an initial transient, the tank pressure rose at a uniform rate. The thermal inertia of the tank wall cannot be neglected and a thermodynamic model of the wall effects was developed. Comparisons showed good agreement between the pressurization rate predicted by the thermodynamic model and the obtained pressurization rate when the heat was added to the liquid but discrepancies arose when heat was added directly to the vapor.

At stationary conditions the pressurizing period is expected to be shorter because the contents of the tank will slowly stratify, so that the heat capacity of the stored fluid cannot be used completely [569]. From a thermodynamic point of view, an isochore change of state takes place and the heat flux into the vessel rises the internal energy of the fluid.

The effect of surface evaporation on stratification in large liquid hydrogen storage tanks of different aspect ratios was represented by a homogeneous two-phase model and the continuity, momentum and energy equations for the two phases were solved [570]. Evaporation at the liquid-vapor interface was incorporated through a source term for mass transfer. The amount of stratification was seen to progressively

increase as the aspect ratio of the tanks increases; however, the surface evaporation brings down the differences in the amount of stratification with changes of aspect ratio. The model gave predictions for stratification in the pre-evaporation and evaporation phases.

In optimizing the design of cryogenic storage facilities for future in-orbit or on-surface applications, the boil-off and the self-pressurization rates must be accurately predicted for different  $g$ -levels and for a variety of heat loads and distributions. A two-phase CFD model was developed that described the self-pressurization behavior of a flight weight partially full LH2 tank in normal gravity [571]. Existing experimental data at different fill levels were used to assess the predictive capability of the model. The model's predictions indicated good agreement with the experimentally measured pressure histories. Small deviations were observed for the median fill level cases where it was suggested that a non-uniform heat load may be the source of this discrepancy.

Cryogenic vaporization, caused by heat leakage into the tank from the surrounding environment, is one of the main causes of mass loss and leads to self-pressurization of the storage tanks. Many publications on self-pressurization and stratification of cryogenic tanks mainly focused on the convection and surface evaporation influences. Because large superheats increase the likelihood of evaporation in the liquid, the evaporation and its effect on vapor pressure under microgravity were studied and the effects of reduced gravity, contact angle of the vapor bubble, and surface tension were investigated [572]. The computations were carried out by using the CFD software package, ANSYS Fluent, and an in-house developed code to calculate the source term associated with the phase change. A coupled level set and the volume-of-fluid method was used to solve a single set of conservation equations for the whole domain and the interface between the two phases was tracked or captured. A heat and mass transfer model was implemented into the Fluent code for solving problems involving evaporation or condensation. Results showed that tiny vapor regions caused by the evaporation process change the pressure rise. Vortices were observed due to the vapor dynamics.

The commercially available computer program ANSYS Fluent was again used for simulation and analysis of self-pressurization of a flight weight, cryogenic, liquid hydrogen tank in 1- $g$  and the results were compared with experimental data, in particular, pressure evolution and temperature measurements at a 3-D set of sensors [573]. The simulations can be analyzed to identify and quantify heat flows in the tank. Heat flows change over time and influence the self-pressurization process. The initial rate of self-pressurization is sensitive to the initial temperature profile near the interface. Uncertainty in saturation pressure data and the accuracy of experimental measurements complicated the simulation of self-pressurization. The cryogenic hydrogen tank simulated is the same as that used in the K-Site experiment performed at the Cryogenic Propellant Tank Facility at NASA Plumbrook research center in the 1990s. This large, flight weight, 2219 aluminum tank with MLI insulation was tested in vacuum condi-

tions at 350 K shroud temperature and 1-g. The 2.2-m diameter tank consisted of two elliptical domes and a very small barrel section. Although the tank was tested for self-pressurization at 29, 49, and 83% fill levels, the simulations were focused on the 49% fill level.

A transient analytical, multi-phase, thermodynamic model of foam insulated liquid hydrogen tanks was developed to explain the effect of insulation thickness on the evolution of tank pressure and liquid thermal stratification [574]. The model was validated with experimental data reported in the literature. Analyses were carried out for pressurization considering two scenarios: first case with tank vent port closed after pressurization to study the pressure evolution and the second case for a constant tank pressure of 3.0 bar to study the growth of liquid thermal stratification. Both cases were investigated for different tank insulation thicknesses of 10, 20, 30, and 40 mm, and with a pressurization gas temperature of 50 K. Effects of variations in ambient atmospheric wind velocity and presence of solar flux on an asymmetric self-pressurization profile of the tank were also analyzed. The calculation showed that the reduction in insulation thickness would lead to an increase in stratified mass. The calculations predicted a significant increase in pressure rise when the tank was insulated with thinner insulation thickness. The rate of self-pressurization is of course related to the level of pre-pressurization that existed at the moment when the tank was locked up [575].

For studying the self-pressurization of locked-up liquid hydrogen tanks in reduced gravity, at first a series of self-pressurization tests was conducted to determine the thermodynamic history of a 23-cm- (9-in.-) diameter sphere under normal gravity conditions. Various combinations of the variables: percent liquid filling, heat-transfer rate, and heat-transfer distribution were studied. Next the tests were repeated at reduced gravities [576]. The rate of pressure rise in the hydrogen container was lower under reduced-gravity conditions than under normal gravity conditions because of the increase in the liquid-wetted wall area and the increased boiling. The location of the sources of heat input relative to the hydrogen liquid and vapor was the most important factor in determining the rate of pressure rise. Self-pressurization of a spherical liquid hydrogen storage tank in a microgravity environment occurs at a different rate than in a normal 1-g environment on the ground [577].

A method was developed for computing boil-off losses and the self-pressurization rate along with estimating the growth of the stratified layer for different levels of gravity in a cryogenic hydrogen storage system [578]. The factors that might have an impact on the system include the total heat leak, fill level, axial variation of the heat flux, gravity, and tank size and shape. The model is an extension of the model originally developed by Arnett and Voth. The current model differs from that used by the aforementioned authors in that constant thermophysical properties have been replaced by dynamic properties.

The self-pressurization of large cryogenic storage tanks under microgravity conditions was investigated by coupling a lumped thermodynamic model of the vapor



region with a complete solution of the flow and temperature fields [579]. The results indicated that in microgravity both buoyancy and natural convection are important and play a role in phase distribution and tank self-pressurization. A spherical vapor bubble placed at the center of the tank deforms and moves to one side of the tank before any significant pressure rise. Long-term results obtained with the vapor region near the tank wall showed that, even in microgravity, natural convection leads to thermal stratification in the liquid and alters the pressure rise rate. The final rate of pressure rise agreed with a lumped thermodynamic parameter model of the entire system, but the final pressure levels departed from predicted levels because of initial transients.

Modeling the thermal stratification of cryogenic propellants within the upper stage of a launch vehicle is necessary for mission planning and successful execution. During orbital transfer the upper stage may coast for several hours during which time the propellants are heated by solar radiation. For orbital insertion at the conclusion of the coast the propellants must be within a narrowly defined range of temperature and pressure to ensure engine restart. Several simplified models of thermal stratification were developed which included the low accelerations and thermal conditioning roll ("rotisserie mode") of the upper stage during the transfer coast. These models were used to assess the impact of thermal stratification within generic liquid hydrogen or liquid oxygen tanks over a range of accelerations, spin rates, and incident solar heat fluxes for cylindrical tank geometries [580].

## 5.9 Geysering Problems with Liquid Hydrogen

Geysering is the sudden gushing of a two-phase mixture of liquid and gaseous hydrogen if the liquid that was already near the boiling point but prevented from boiling by the hydrostatic pressure of the liquid column above it suddenly works its way to the surface and starts boiling, similar to geysers observed in geothermal springs. Geysering occurs in vertical pipes or tanks with a high L/D ratio and can occur with any liquid but is troublesome if it occurs unexpectedly with liquid hydrogen or liquid oxygen. Geysering can be prevented by subcooling the cryogenic fluids sufficiently before pumping them through vertical pipes. Vertical pipes are typically encountered at launch sites where the service tower plumbing connects to the umbilical that transfers propellant to the launch vehicle [581, 582].

## 5.10 Sloshing of Liquid Hydrogen

Sloshing of liquids in propellant tanks is a problem with all liquid propellants and not unique with hydrogen. Sudden center of gravity shifts may cause rockets to go unstable. Many propellant tanks have anti-slosh baffles to restrict liquid motion under the effect of lateral forces [583].

Experimental data on the dynamics of liquid hydrogen sloshing in the 6.6-m (260 in.) diameter tank of a SATURN S-IVB stage during boost, at S-IVB stage cut-off, and in orbit indicated that for the boost phase of flight, the amplitude of the sloshing liquid decreased from approximately 0.25 m (10 in.) at the beginning of S-IVB stage boost to a minimum of about 0.038 m (1.5 in.) as the liquid level moved past the baffle [584]. The frequency during the S-IVB stage engine burn increased from approximately .44 cycles per second to .70 cycles per second and showed good agreement with predicted values. During orbital coast phase, periods of the liquid hydrogen oscillation were measured through a range of accelerations from  $8 \times 10^{-5} g_0$  to  $4.4 \times 10^{-4} g_0$ . Period data taken while the acceleration was varying with time did not agree with either the predicted natural or coupled periods. Nearly steady-state conditions existed for the  $8 \times 10^{-5} g_0$  acceleration and the 300–330 s slosh periods measured at this acceleration were close to the predicted value of 315 s. The good agreement between experiment and “high- $g$ ” theory (i.e., a theory neglecting surface tension and contact angle effects) at this very low acceleration tends to verify the validity of the Bond number as a criterion for defining “high- $g$ ” conditions with regard to liquid sloshing.

Similar studies were done for sloshing in a CENTAUR upper stage hydrogen tank [585]. An experiment was conducted to investigate the process of liquid reorientation from one end of a small scale-model CENTAUR liquid-hydrogen tank to the other end by means of low-level accelerations. Prior to reorientation, the liquid was stabilized at the top of the tank at a Bond number of 15. Tanks both with and without ring baffles and with tank radii of 5.5 and 7.0 cm were used in the study. Reorientation acceleration values were varied to obtain Bond numbers of 200 and 450. Liquid fill levels of 20 and 70% were used. From the data in this study, relations were developed to estimate reorientation event times in unbaffled tanks through the point of final liquid clearing from the top of the tank. The insertion of ring baffles drastically changed the reorientation flow profiles but resulted in only minor differences in the times of tank-top uncovering and liquid collection.

Understanding the behavior and response of cryogenic propellants during spacecraft flight operations (e.g., engine restart and fluid transfer) is an extremely important aspect of vehicle design. Accurate predictions of fluid motion and slosh amplification are needed to ensure proper settling prior to engine burn and effective vehicle control throughout all phases of the mission [586].

The technology necessary for acquisition or controlled positioning of liquid and vapor within a tank in reduced gravity to enable single-phase liquid outflow or vapor venting depends on slosh wave excitation induced by the resettling flow field activated by impulsive reverse gravity acceleration during the course of liquid fluid reorientation, disturbed by geysering for liquid filled levels of 30, 50, and 80%, creating slosh waves with various frequencies [587].

Liquid hydrogen that was free-floating in a partially filled tank during the coast phase of an upper stage needs to be settled in a bubble-free condition over the outflow

pipe leading to the pump inlet. Propellant settling is achieved by firing small reaction control thrusters. If the thrust developed by the RCS thrusters is too low, not all propellant may collect at the bottom of the tank. If the RCS thrust is too high and too sudden, the propellant will splash all over and slosh and it will take a long time before it comes to rest. Propellant may enter the outlet duct and geyser back-out, spreading it all over the tank.

### 5.11 Liquid Hydrogen Propellant Management in Zero-*g* and Reduced Gravity

As with all liquid propellants, it is a problem to separate the liquid phase and the gas phase of liquid hydrogen and gaseous hydrogen in a zero-*g* environment to avoid bubble ingestion into liquid going through the pumps and loss of liquid when the ullage gas space needs to be vented. Boil-off during the coast phase has to be vented such that only gas is vented and no liquid is wasted. In most cases where upper stages using liquid hydrogen have to be started more than once, a propellant settling burn performed by a storable propellant auxiliary propulsion RCS system precedes the main engine re-ignition. For longer coast phases, the upper stage may be spun up to achieve phase separation with a bubble along the axis of the rotating tank and direct the propellant toward the galleys along the walls.

Positive expulsion propellant management devices like flexible bladders and diaphragms that can be used with storable propellants are out of the question for cryogenic propellants because all materials become too brittle at the liquid hydrogen temperature [588]. In spite of the embrittlement, bladders made from multiple layers of Mylar, Kapton, and a polyester film were tested for the expulsion of liquid hydrogen, and several filling/expulsion cycles were completed before the bladders started leaking [589].

Alternative methods for propellant management of liquid hydrogen in zero-*g* have been evaluated but have not yet flown. Passive propellant management devices depend on surface tension. Surface tension propellant management devices have been tested for liquid hydrogen. The surface tension and the wetting angle is sufficient that tank walls and wire mesh structures are completely wetted by liquid hydrogen in zero *g* [188, 190, 191].

It has also been attempted to collect non-conductive cryogenic liquids like LH2 in a zero-*g* environment by electrostatic fields and dielectric forces between the two plates of a capacitor [590, 591]. These propellant containment methods are also called “electrohydrodynamic propellant containment systems” or “dielectrophoretic propellant orientation systems.” This method would also work for other, non-conductive liquids other than liquid hydrogen. A converging plate system was designed to operate at 100 kV [592, 593]. For a tank containing 5400 kg (1200 lb<sub>m</sub>) of LH2, the power consumption would be 10 W. This method has been tested with LH2 and it was noted that evaporative losses were reduced by 20% because the liquid was levitated between the

capacitor plates at the location of the highest field strength and less of it was in direct contact with the walls. Concern is that electrical discharges could upset this propellant management scheme. The voltage applied to the capacitor plates must remain below the breakthrough voltage of hydrogen. It is not clear if the electrostatic forces are strong enough to keep the propellant in position once it starts boiling again.

The fourth and eighth ATLAS-CENTAUR upper stages (AC-4 and AC-8) were launched to study cryogenic propellant management during orbital coast phases in zero- $g$  [594]. The AC-4 flight showed that propellant management cannot be defined solely by the Bond number (ratio of acceleration to surface tension forces). On the AC-4 flight, kinetic energies imparted to the liquid hydrogen at first engine cut-off caused excessive liquid motion within the hydrogen tank, resulting in subsequent venting of liquid hydrogen rather than gaseous hydrogen. The vented liquid impinged on the vehicle causing it eventually to tumble out of control. The AC-8 vehicle was modified to reduce and/or control the energies transmitted to the propellant at cut-off. Energy dissipators were installed on the hydrogen tank pressurization line and boost pump return flow lines. A balanced thrust hydrogen vent system was installed to reduce vehicle disturbances. A slosh baffle was installed in the hydrogen tank.

A CFD model was used to study the effect of reduced gravity on the thermal performance in a liquid hydrogen tank [595]. Four gravity levels ( $1g$ ,  $10^{-1}g$ ,  $10^{-2}g$ , and  $10^{-3}g$ ) were compared to identify the influence of the reduced gravity on fluid thermal stratification. The results showed that with the increasing gravity level, the vapor temperature distribution becomes more uniform, and the liquid stratum layer develops faster. Comparing the CFD results with the results of two stratification theoretical models, the stratum thickness calculated by CFD model was close to the values of other models. Under the influence of surface tension in reduced gravity, liquid close to the tank wall moves up with the interface becoming curved. The interface area rises with the decrease of gravity.

A computational model for the liquid-vapor phase change was developed to investigate the thermal physical process in a liquid hydrogen (LH2) tank in reduced gravity [596]. Viscous flow was considered in the model with natural convection. The stratified layer parameters, the tank pressure rise rate, and the interface phase change were studied, and the influence of the initial liquid height, the initial ullage temperature and the tank wall heat flux on the development of thermal stratification was estimated. The results showed that the stratified layer thickness increased with the initial liquid height. While the initial liquid height is large, it takes more time for the complete development of fluid thermal stratification. Largely influenced by the temperature of the stratified layer, both tank pressure and phase change capacity increase with the initial liquid height. It seems that the initial ullage temperature has a weak effect on the development of fluid thermal stratification. Both the tank pressure and the phase change quality increase with the initial ullage temperature. The external tank wall heat flux promotes the development of thermal stratification. The stratified layer

has a larger thickness and develops faster for the larger heat flux. Both tank pressure and phase change capacity increase with the external heat flux.

A study on fluid flow and heat transfer of liquid hydrogen in a zero boil-off cryogenic storage tank in a microgravity environment used a storage tank that was equipped with an active cooling system consisting of a heat pipe and a pump-nozzle unit [597, 598]. The pump collected the cryogen liquid and discharged it through a nozzle onto the evaporator section of the heat pipe in order to prevent the cryogen from suffering boil-off losses due to the heat leaking through the tank wall from the surroundings. A three-dimensional finite element model was used in a set of numerical simulations to solve the velocity and temperature fields of liquid hydrogen under steady-state conditions. Parametric study results from both models predicted that as the speed of the cryogenic fluid discharged from the nozzle increased, the mean or bulk cryogenic fluid speed increased linearly, but the maximum temperature within the cryogenic fluid decreased.

#### **5.11.1 Venting of Hydrogen Boil-off in Zero-g**

Vapor venting to relieve tank pressure can be accomplished easily on the Earth's surface or during powered flight because the liquid and vapor occupy predictable positions within the tank and a simple vent pipe can be employed; however, under low-gravity conditions the vapor/liquid distribution in the tank can shift unpredictably as the result of small disturbing forces. Prior to re-igniting the main engine(s), small RCS thrusters are usually fired to re-orient the liquid and vapor and settle the liquid in one end of the tank, but the thruster firing affects vehicle orbital parameters. The thrusters consume propellant for any but very low acceleration levels and long settling times. It is important, therefore, to develop more efficient methods for venting vapor [599]. While a propellant settling maneuver, typically done for only one or a few restarts, would solve the ullage gas venting problem at the same time, it requires more propellant from the small RCS thrusters than when gas venting only is desired. Gas venting for longer coast phase missions can be achieved without settling all the propellant near the drain hole and with less propellant consumed by the RCS thrusters. Several methods to achieve venting without liquid propellant loss have been evaluated [600]. In a CENTAUR upper stage, a center vent tube was supposed to allow gas venting with a minimum of RCS thruster firing [601].

It was found to be feasible to vent a partially filled liquid hydrogen tank in an orbiting SATURN S-IVB stage in space continuously or intermittently by applying a small acceleration to keep the liquid hydrogen settled at one end of the tank [602]. Results of venting liquid hydrogen tanks in reduced gravity can be compared to venting tests performed under normal gravity [603].

Zero-gravity venting and surface tension screen baffle integration for orbital storage and transfer of liquid hydrogen were examined by analytical and experimental methods [604]. A full wall-screen liner was supposed to keep the liquid puddled in

the desired location. The screen bubble point, flow-through pressure loss and pressure loss along rectangular channels lined with screen on one side were measured for LH<sub>2</sub> saturated at 344 kPa (50 psia).

Instead of venting and losing the hydrogen boil-off while in orbit around the Earth, a solar-thermal rocket was proposed that would maintain the tank at a temperature such that all hydrogen withdrawn from the tank is used for active propulsion, in this case a solar-heated heat exchanger in the focal point of a collector mirror to provide rocket propulsion during a 30-day mission for LEO-GEO transfer [605].

### 5.11.2 Venting of Liquid Hydrogen Boil-off in a Vacuum

Assuming that the boiling liquid and the evolved gas can be separated, the boil-off during a coasting phase must be vented to outer space without causing uncontrolled thrusting (must use a pair of thrust-neutralizing nozzles) or disturbing the required orientation of the spacecraft with regard to the Sun or Earth. When the pressure of a liquid drops below its triple point, a phase transformation occurs forming both solid and gas phases with no remaining liquid. Liquid cryogenics vented from launch vehicles, such as the CENTAUR upper stage, will undergo such a transformation when exposed to pressures below their triple points. Solids thus formed may accumulate in the overboard vent, restricting flow and possibly blocking the vent.

When venting boil-off from cryogenic propellants in outer space, one must be aware that expanding gases near their boiling point can cool adiabatically to the point where they condense and freeze. Solid hydrogen might clog the lines or the valves through which it is expanded into vacuum [606, 607].

A test program was conducted to determine if solid hydrogen would form, adhere to the walls, and block the RL-10 engine vent ducts during a CENTAUR upper stage retro maneuver [608]. Results showed that solid hydrogen forms in the ducts and adheres to the interior surfaces of the vent tube, intermittently building up and breaking off into the gas stream. Approx. 80% of the vent tube exit area was choked by frozen hydrogen.

If liquid hydrogen stored at 1 atm is flashed into vacuum and allowed to go to triple point conditions, about 80% of it will solidify in the form of solid hydrogen “snow” [609]. In a similar situation with LOX, about 70% of it will solidify to oxygen “snow.”

An investigation of vent blockage was performed using saturated liquid argon as a substitute for LOX or LH<sub>2</sub> [610]. Observations of solid adherence and accumulation were recorded for various argon delivery pressures. Wall adherence and vent blockage was strongly dependent on delivery pressure, with accumulation increasing for decreasing pressure. For low delivery pressures, relative to the triple point, vent blockage was immediate and complete. In addition, solid formation was observed to propagate into the liquid, against the direction of flow, revealing the porous nature of the solid as well as the impact on the flow.

## 5.12 Chillover of Cryogenic Equipment

The calculation of evaporative losses during chillover of cryogenic equipment would apply to liquid oxygen systems just as well as liquid hydrogen systems. It is just that with liquid oxygen systems it is easier to vent the gases than with vented hydrogen or liquid methane that has to be ducted to a vent stack and flared off. One can minimize or avoid altogether evaporative losses by using chilled helium to precool the receiving equipment before dropping liquid propellant into it, but this is a very expensive option.

Measurements on the chillover and steady-state boil-off losses of a 189-m<sup>3</sup> (50000 gallon) evacuated perlite insulated liquid-hydrogen storage Dewar at the Nuclear Rocket Development Station in Nevada showed that this tank required less liquid hydrogen for chillover and the steady-state heat flux was less than by a factor of 2 from what conservative calculations had predicted [611, 612].

Results of these observations are directly applicable to large Dewar storage vessels currently being designed, built, or being placed into service. These results should assist the designer and planner in estimating the cryogen quantities required for chillover and may even in some cases aid in evaluating the relative merits of different types of insulation systems available.

A computer model was used to perform an analysis of non-vented fill techniques on a 4.96 m<sup>3</sup> light weight liquid hydrogen tank (which was similar in size and shape to the tankage planned for a COLD-SAT liquid hydrogen flight experiment), and was used to select one of two injection systems for non-vented fills of this tank at design flow rates between 220 and 450 kg/h [613]. The first system used multiple nozzles spraying from the top of the tank through the ullage space. This system should be capable of liquid fill levels in excess of 95%. The second system injected the liquid through a submerged nozzle and should produce fill levels on the order of 80% liquid.

A series of no-vent fill experiments were conducted on a 4.96-m<sup>3</sup> (175-cu. ft.) flight weight hydrogen tank using two different inlet systems (top spray and bottom spray) at different tank initial conditions and inflow rates [614]. Nine tests were completed of which six filled the tank to better than 94%. The experiments demonstrated a consistent and repeatable ability to fill the tank in excess of 94% using the non-vented fill technique.

Liquid hydrogen no-vent fill tests were performed using various size spray nozzles and a spray bar with different hole sizes in a 142-L (5-cu. ft.) receiver tank [615]. Fill levels of 90% by volume or greater were achieved while maintaining a receiver tank pressure below 207 kPa (30 psia). Spray nozzles were mounted at the top of the tank, whereas the spray bar was centered in the tank axially. Both liquid injection techniques tested were capable of filling the receiver tank to 90% under variable test conditions. The spray nozzle injection technique was more effective in minimizing the receiving tank pressure throughout a no-vent fill compared to the spray bar under normal gravity conditions.

For best results in a cryogenic pipeline and minimum propellant lost during chill-down, high vacuum is used as the insulation in the annulus between two concentric tubes with the cold fluid flowing through the center tube [616].

A facility was designed for cold-flow development testing of the M-1 LOX/LH2 rocket engine fuel and oxidizer turbopump assemblies based on thermal and stress analysis of initial chilldown of large diameter cryogenic piping systems [617]. Various methods were considered for chilldown of cryogenic piping systems. Consideration was given to LH2 and LOX propellant systems that utilize the cryogenic boil-off gases at a predetermined rate to achieve system chilldown. The use of this technique reduces or eliminates the problem of thermal stress concentrations in the system materials during chilldown. The transient chilldown of a single thick-walled tube by liquid and gaseous hydrogen was measured and parameterized for future designs of larger pipes carrying liquid hydrogen [618].

It would be very costly to keep a cryogenic pipeline cold all the time between uses. Cryogenic pipelines see a lot of transient operating conditions during pre-use chilldown and post-use thawing. An uncooled pipeline which is used to transfer a cryogenic fluid from one point to another must go through a period of cooling down from ambient temperature to near the liquid boiling temperature. During most of the cooldown period the liquid boils and the pipeline delivers only warm gas. The time required to achieve bubble-free flow can be estimated from a dimensionless parameter read from a graph based on knowledge of the fluid and pipe enthalpy, density, and velocity of sound in the warm gas [619]. The predictions from this method were compared to experimental results.

Two finite difference computer models, aiming to predict no-vent fill either in normal gravity and or in microgravity environments, were developed to investigate the filling performance in a liquid hydrogen tank [620]. In the normal gravity case model, the tank/fluid system was divided into five control volumes including ullage, bulk liquid, gas-liquid interface, ullage-adjacent wall, and liquid-adjacent wall. In the microgravity case model, the vapor-liquid thermal equilibrium state is maintained throughout the process, and only two nodes representing fluid and wall regions were applied. To predict the liquid-wall heat transfer accurately, a series of heat transfer mechanisms were considered and modeled successively, including film boiling, transition boiling, nucleate boiling and liquid natural convection. The two models were validated by comparing their predictions with experimental data, which showed good agreement. Then the two models were used to investigate the performance of no-vent fill under different conditions. It was showed that in the normal gravity environment the no-vent fill experiences a continuous pressure rise during the whole process and the maximum pressure occurs at the end of the operation, while the maximum pressure of the microgravity case occurs at the beginning stage of the process. Reducing inlet liquid temperature by subcooling can improve the filling performance in normal gravity but cannot significantly reduce the maximum pressure in microgravity.



### 5.13 Reliquefier and Condensers on Hydrogen Storage Tanks

If weight and power requirements permit, boil-off from hydrogen tanks can be condensed and returned to the tank. Such systems are called “reliquefiers.” They depend on a source of cold provided by cryocoolers. This would enable zero boil-off storage and would extend or even enable some missions. This would not only reduce or prevent boil-off vaporization losses, but it would also subcool and densify the propellants. Densified and slush propellants are discussed in section “Subcooled and Slush Hydrogen.” The reliquefaction and cooling systems described here for liquid hydrogen would work for extending the storage time of liquid oxygen on long-term missions as well.

Reliquefaction would be very useful in combination with propellant scavenging of unused propellants from upper stages before they are sent into a destructive re-entry and burn up in the atmosphere. At one time it was considered to bring the Space Shuttle external tank with the orbiter all the way up into orbit and transfer the unused propellant to a propellant depot. The orbital propellant depot would have needed a reliquefaction and cryocooling system to maintain its stockpile of liquid hydrogen and liquid oxygen.

Reliquefaction of all or part of the boil-off hydrogen vapor is being considered as a means of reducing or eliminating boil-off losses from propellant tanks during long-term missions in Earth orbit [621]. Both closed and open cycle reliquefier systems can offer weight savings and make certain missions possible that previously were not. Furthermore, the reliquefier can be optimized in conjunction with superinsulation for optimum results. For short missions, insulation would be more economical. For very long-duration missions, reliquefaction becomes more economical. The optimum insulation mass will be less for a system with a reliquefier than for a system without a reliquefier providing that certain conditions are met.

Partial hydrogen reliquefiers, having certain estimated mass and power requirements, can produce significant payload improvements in space missions requiring long-term storage of liquid hydrogen [622].

Five different cooling methods were evaluated for closed cycle reliquefaction long-term cryogenic storage: Stirling cycle, Vuilleumier refrigerator, separable component systems, Brayton refrigerator, Claude refrigerator, and Joule-Thomson refrigerator [623–625].

Cryocooler and passive insulation technology advances have substantially improved prospects for zero-boil-off cryogenic storage [626]. A large-scale, zero-boil-off demonstration at the NASA MSFC Multipurpose Hydrogen Test Bed used a commercial cryocooler with an existing spray bar mixer and insulation system in a manner that enabled a balance between incoming and extracted thermal energy.

Long duration space missions with liquid hydrogen depend on reducing boil-off losses. One way to control tank pressure and minimize boil-off losses involves the use of a subcooled axial liquid jet to both thermally destratify the bulk liquid and remove

energy from the tank. This method is called “jet mixing” [627]. The effectiveness of using subcooled jet mixing as a pressure control scheme was analyzed by performing a small-scale experiment in a normal gravity environment with a refrigerant [628]. Following a period of self-pressurization, the jet’s speed and degree of subcooling were parametrically varied so that relevant trends could be identified. Experimental results showed that mixing the bulk liquid is not sufficient to control pressure. To sustain any pressure reduction, substantial subcooling of the mixing jet is necessary. The rate of pressure and vaporization losses reduction is greater for increased jet speeds and subcooling. Analytical and computational models were developed in order to predict the self-pressurization behavior. Model comparisons revealed that generally a thermodynamic model underpredicts the self-pressurization and depressurization rates. The lack of agreement was primarily attributed to the homogeneity assumption inherent in the model. To improve model predictions, a zonal model was developed which avoids the global homogeneity assumption. Comparisons between the experimental data and the zonal model predictions were excellent for moderate to high jet flow rates. For slower jet speeds, buoyant flow in the bulk liquid adversely affected the effectiveness of a subcooled mixing jet and a more detailed computational model would be required to capture this intraphase phenomenon.

In order to avoid venting during liquid hydrogen storage and in order to decrease propellant vaporization loss in space application, a numerical study was performed of the thermal performance of a hydrogen storage tank with nozzle injection and a new improvement, a guide tube [629]. Compared with the previous storage tank design without a guide tube, the chilling performance of the new storage system was enhanced since the guide tube improved the heat transfer and reduced the stagnant region to meliorate the flow circulation. Distribution profiles of temperature and velocity in the storage tank have been attained to evaluate the chilling and mixing performance. The key geometric parameters were further optimized by analyzing a series of cases under different geometry settings, from which the optimized ranges of dimensionless parameters have been obtained and studied.

A series of tests was performed to demonstrate the capability of using integrated refrigeration and storage to remove energy from a liquid hydrogen (LH2) tank and control the state of the propellant [630]. A primary test objective was the keeping and storing of the liquid in a zero boil-off state, so that the total heat leak entering the tank is removed by a cryogenic refrigerator with an internal heat exchanger. The LH2 is therefore stored and kept with zero losses for an indefinite period of time. The LH2 tank in this case was a horizontal cylindrical geometry with a vacuum-jacketed, multi-layer insulation system and a capacity of 125000 liters. The closed-loop helium refrigeration system was a Linde LR1620 capable of 390 W cooling at 20K (without any liquid nitrogen precooling). Three different control methods were used to obtain zero boil-off: temperature control of the helium refrigerant, refrigerator control using the tank pressure sensor, and duty cycling (on/off) of the refrigerator as needed.

Cryocooler technology is needed at 20 K to achieve zero boil-off of liquid hydrogen and at 90 K to achieve zero boil-off of liquid oxygen or liquid methane as well as to liquefy oxygen or methane that is produced by *in situ* resource utilization on the surface of Mars [631]. Progress has been achieved with reverse turbo-Brayton cycle cryocoolers, where the specific power and specific mass have dropped, decreasing the mass and power requirements of these cryocoolers.

Thermoelectric refrigeration and thermomagnetic refrigeration were considered as a means to preserve solid hydrogen on board of interplanetary space vehicles so it could be used for the return trip back to Earth [632].

#### 5.14 Supercritical Storage of Hydrogen

Boiling point and critical point of hydrogen are very close together, unlike the properties of any other gas used as a rocket propellant. The boiling point is at 20.27 K, and the critical temperature is at 33.3 K. In addition, the critical pressure is so low (1.297 MPa = 12.8 atm) that it is easily exceeded with moderate storage tank pressures.

Supercritical storage of hydrogen (and oxygen) has been used to supply hydrogen (and oxygen) to fuel cells operating in zero-*g* environments during the GEMINI, APOLLO, and Space Shuttle missions. The advantage of supercritical storage is that the tank contains neither liquid nor gaseous phases and that one no longer has to worry about the physical state if propellant is drawn from the tank in a zero-*g* environment. Several companies, including Beech Aircraft Corp., developed supercritical storage tanks for hydrogen [244].

Conceptual space transportation vehicles and their orbital facilities, which may use single-phase, supercritical cryogenic propellants, have been compared with conventional subcritical, two-phase orbital propellant storage concepts. The study was motivated by the desire to avoid fluid-management problems associated with the storage, acquisition and transfer of subcritical liquid oxygen and hydrogen propellants in the low-gravity environment of space. Although feasible, the supercritical concepts suffer from weight and propellant resupply system power requirements that make the concepts impractical [633, 634].

#### 5.15 Cavitation of Liquid Hydrogen

Cavitation of liquid hydrogen in the inlet section and on the propeller tips of hydrogen pumps is a serious design problem and various techniques to prevent cavitation have been discussed here. Cavitation is defined as the formation, caused by a reduction in pressure, of a vapor phase within a flowing liquid or at the interface between a liquid and a solid. Since the formation and collapse of vapor cavities alters flow patterns, cavitation may reduce the efficiency of pumping machinery, and reduce the precision of

flow measuring devices. Collapse of these vapor cavities can also cause serious erosion damage to fluid-handling equipment. Cavitation can occur in any flow passage. The best way to study and visualize cavitation is in transparent cavitating venturi [635]. Conventional cavitation-inception parameters and head-velocity curves in liquid hydrogen were derived over a range of experimental temperatures (20.3–22.8 K = 36.5–41°R) and inlet velocities (21–56 m/s = 70–185 ft/s). Minimum local wall pressure at incipience was calculated to be less than bulk stream vapor pressure by as much as 100 m (328 ft) of hydrogen head in some inception tests.

## 5.16 Subcooled and Slush Hydrogen

Evaporative losses during transfer of liquid hydrogen can be minimized if the liquid is cooled to below the boiling point or even to near the freezing point. The designation “supercooled” hydrogen is not correct, because it would apply only to a liquid that has been supercooled to below its natural freezing point, but it failed to crystallize and instead supercooled and remained in a metastable state due to a lack of condensation nuclei. We prefer to call the condition of cold hydrogen at temperatures between its natural boiling point and its freezing point “undercooled” or “subcooled” instead of “supercooled” hydrogen. Undercooled, single phase liquid hydrogen is not in a metastable state and is in equilibrium with its surroundings. Undercooled, two-phase hydrogen is called “slush hydrogen” and it will be discussed later in this section. The density increase for densified hydrogen is 8%, and the density increase for slush hydrogen is 15%.

Supercooled hydrogen may exist when hydrogen is cooled to temperatures below the freezing point in a very clean, particle-free environment free of condensation nuclei. It has been speculated that it may be possible to supercool liquid H<sub>2</sub> and keep it as a liquid below its normal freezing temperature [636]. It was theorized that there is a significant prospect that H<sub>2</sub> could be supercooled to arbitrarily low temperatures, and that in this way superfluid H<sub>2</sub> might be produced.

### 5.16.1 Subcooled Homogeneous Liquid Hydrogen

In the early years of hydrogen cryogenics, the application of subcooled hydrogen was mostly directed towards specific vehicle systems. The use of hydrogen in its subcooled state, however, should be considered for any system anticipating the need for hydrogen. A trade-off must be made between whether one should be using subcooled or slush hydrogen for a specific mission. One must decide whether the primary effort should be directed toward the application of liquid hydrogen, subcooled liquid hydrogen or slush hydrogen [637, 638]. Ground handling of subcooled hydrogen is not much different from that of liquid hydrogen. Undercooled (subcooled) liquid oxygen [639] is

already used routinely by SpaceX on its Falcon launch vehicles, so the next step would be to use this technology with liquid hydrogen as well.

In the cryogenic engineering literature it is sometimes not quite clear if the term “densification” includes a phase change to frozen hydrogen or if it only means to cool the liquid hydrogen to near its triple point. Unless the term “solid hydrogen” or “slush hydrogen” is used in the title or abstract, we assume that densification papers deal only with subcooled hydrogen.

The X-33 project, NASA’s short-lived technology demonstrator for the next Reusable Launch Vehicle (RLV), revived interest in densified cryogenic propellants [640–642]. Densified hydrogen was also planned to be used for its sequel, the full-scale Venturestar, a SSTO RLV [643]. The heat exchanger for subcooling the hydrogen was developed based on an analytical model [644, 645].

A test program was conducted to demonstrate the ability to load densified (DLH2) into a subscale propellant tank [646]. The multi-lobe tank, which was made from composite materials similar to that to be used on X-33, was formed from two lobes with a center septum. Test results were compared to analytical predictions. Data collected for this test series agree well with analytical predictions of the environmental heat leak into the tank and the thermal stratification characteristics of the hydrogen propellant in the tank as it was filled with DLH2. The results from the recirculation tests with liquid oxygen have confirmed the mathematical model [647].

Densification of both LOX and LH2 was considered for the STS Space Shuttle, but was never implemented [648, 649]. It remains to be seen if it can be used for the Space Launch System.

Subcooling LOX has now become a routine operation for the Falcon-9 launch vehicle, allowing more propellant to be loaded into a given tank volume and reducing the flow rate at which the tank has to be topped off from an umbilical cryogenic line during countdown until immediately prior to launch. Using a similar subcooling technology for hydrogen is the next step.

### 5.16.2 Slush Hydrogen

The technology for undercooling liquid hydrogen and making slush hydrogen was developed in the late 1960s and various types of equipment were offered for this purpose (Table 46).

#### 5.16.2.1 Production of Slush Hydrogen

The slush hydrogen production methods include evaporative cooling processes, such as the freeze-thaw process [670] and the spray technique [671] and refrigeration processes, such as auger [672] and magnetic refrigeration [673, 674].

There are several recognized methods of producing slush hydrogen [675]. One is the auger method. An auger rotating inside a brass tube refrigerated with liquid helium

**Table 46:** Literature summary for slush hydrogen technology.

| Author                             | Year | References |
|------------------------------------|------|------------|
| Dempster and Olivier               | 1962 | [650]      |
| Elrod                              | 1963 | [637]      |
| Carney                             | 1964 | [651]      |
| Dwyer and Cook                     | 1965 | [652]      |
| Sindt and Ludtke                   | 1965 | [653]      |
| Cook and Dwyer                     | 1966 | [654]      |
| Chelton et al.                     | 1967 | [655]      |
| Keller, Lockheed Miss. & Space Co. | 1967 | [76]       |
| Keller                             | 1967 | [656]      |
| Ludtke and Sindt                   | 1969 | [657]      |
| Chain                              | 1970 | [658]      |
| Daney, Steward, and Voth           | 1973 | [659]      |
| de Witt et al.                     | 1990 | [660]      |
| Hardy and Whalen                   | 1991 | [661]      |
| Ohira, Matsuo, and Furumoto        | 1994 | [662]      |
| Cady                               | 1994 | [663]      |
| Miyake et al.                      | 1995 | [664]      |
| Fajardo and Tam                    | 1998 | [665]      |
| Tomsik                             | 2000 | [666]      |
| Brunnhofer                         | 2002 | [667]      |
| Brunnhofer et al.                  | 2006 | [668]      |
| Park                               | 2010 | [669]      |

was used to produce liquid-solid (slush) mixtures of hydrogen and of oxygen [672, 676]. The auger produced small particles from the cryogenics so that the resulting slush mixture could be transferred and stored. The auger could produce slush continuously in an appropriate system; it could produce slush at pressures higher than the triple point pressure of the cryogen, and the energy required to produce the slush was less than the energy required to produce slush using the freeze-thaw process.

The auger method simply uses an auger rotating inside an externally insulated refrigerated cylinder that is submerged in liquid hydrogen. Hydrogen freezes on the internal walls of the cylinder and is continuously shaved or scraped off by the auger. The auger method with a 178-mm (7-in.) diameter auger type hydrogen slush generator can be used in a continuous production mode and produces slush hydrogen at superatmospheric pressures so that the slush can be pressure-transferred to storage containers [677].

Similar auger methods are described in [678]. It was observed that the particle size of slush hydrogen produced by the auger method was smaller than that obtained with a freeze-thaw process. A propeller was installed at the bottom of the inner vessel to mix solid with liquid thoroughly and keep the solid in suspension [679].

Another method for making slush hydrogen is the freeze-thaw method. The freeze-thaw method has been used to generate small and relatively large quantities of slush hydrogen [680]. This production technique requires that the ullage over a fixed volume of liquid is vacuum pumped until a solid layer forms at the liquid-vapor interface. The vacuum pumping is then stopped and the solid layer melts (thaws) and settles into the liquid. This cycle is repeated until the desired solid content has been formed. The solid is then mixed with the liquid by stirring to form a homogeneous mixture of solid and liquid. The porosity of the solid formed in this manner is a function of the pumping rate. Slow pumping rates produce a dense solid which when broken forms large particles of solid and will not form a homogeneous mixture with the liquid. Higher pumping rates produce a porous solid which is easily broken into much smaller particles and is easily mixed with the liquid to form a homogeneous mixture, which may be defined as slush. Disadvantages of the method are: **(1)** not all cryogenic tanks are designed to operate at negative pressure. A safety hazard exists because the required triple point low ullage pressures (0.0061 MPa) invite air leakage into the slush container and oxygen/hydrogen mixtures are an explosive hazard, and **(2)** transfer of slush into a storage container requires ullage pressurization or pump-transfer. **(3)** This is a batch process and not easily scaled up to continuous operation. Maximum solid fractions achieved to date are 60%, with 40 to 50% solid content being practical and easily accomplished.

Subcooled liquid hydrogen can be produced by several different methods:

- a. By pumping off the gas space above liquid hydrogen, additional liquid hydrogen must evaporate and the heat of evaporation is extracted from the liquid, which can theoretically cool all the way down to the triple point [609].
- b. By passing cold helium through an external cooling jacket or a cooling coil that is immersed in the liquid hydrogen tank.
- c. Liquid hydrogen can be compressed isothermally and expanded isentropically.
- d. By passing cold helium gas directly through the liquid hydrogen (if the dilution of  $\text{LH}_2$  by dissolved He can be tolerated).

The concept of subcooled hydrogen was demonstrated by using method **(a)** in a laboratory test [681]. About 9 kg liquid hydrogen can be cooled from 20.4 to 13.9 K by sucking off 1 kg hydrogen as vapor at low pressure. If one wants to prepare slush hydrogen, an additional 130 g of hydrogen must be vaporized for each kg of solid hydrogen desired. If one wants to make 100 kg hydrogen slush with a solids content of 50%, one must start with 117 kg of liquid hydrogen. The hydrogen gas that is pumped off does not have to be discarded but can be fed to a liquefaction plant and recycled.

It would be most energy efficient and avoid an additional heat exchanger to pump cold gas, but it is difficult to operate a vacuum pump at 13–25 K. A cold pump would be more compact than a warm pump. If the gas is allowed to warm before it is pumped, the pump has to be bigger and has to perform more work because a larger volume of gas needs to be moved. If hydrogen slush is made by passing liquid helium through

a cooling jacket or an internal cooling coil (method **b**) and allowing the helium to evaporate, one will need 1 kg of liquid helium for each kg of solid hydrogen. The hydrogen would have to be well stirred to prevent the build-up of solid hydrogen crusts on the cooling coils. A crust of solid hydrogen would impede all further heat exchange. The concept of cyclic compression-expansion (method **c**) is theoretically promising, but has not yet been demonstrated.

The direct injection of cold helium gas into liquid hydrogen was tested in a laboratory experiment [682]. One has to remember that some of the helium will dissolve in the hydrogen. The direct injection method has been used for subcooling LOX [639].

Liquid-solid mixtures of hydrogen (slush hydrogen) were produced by vacuum pumping, gaseous He injection with vacuum pumping, and by cooling with liquid He in a low-heat-leak apparatus that permitted visual observation of the experiments through a periscopic device [683].

At one time, the large-scale slush hydrogen facility at Wright Patterson Air Force Base was the largest of its kind in the US [684]. The purpose of the facility was to simulate operational scale equipment while maintaining the flexibility of small-scale research apparatus.

A slush preparation method by intermittent vacuum pumping was developed [685]. Slush was aged 100 h during which time solid particle size and structure were observed for eventual particle growth by agglomeration. The solid particle structure changed dramatically during aging, even though the particle size changed insignificantly. The solid particles were observed to change from particles with irregular rough edges to particles with smooth edges. The smaller particles would tend to combine with the larger particles to form a particle of higher density. Slush with over 50% solid content can be transferred and pumped with losses similar to losses in triple-point liquid hydrogen if Reynolds numbers are high. Transfer losses in a smooth pipe were 10% less with slush of 30% solid content than with triple-point liquid when the Reynolds number was  $7 \times 10^5$  or greater. Although some special techniques are required for handling slush hydrogen, after some practice it has the characteristics of a simple cryogenic fluid for most applications.

The spray-freeze method creates hydrogen slush with very small particle sizes that can be pumped with a minimum of pressure loss. This produces a better slush product than the freeze-thaw technique, which continuously injects liquid hydrogen at or near its triple-point temperature into a slush hydrogen generator, forming solid hydrogen by removing hydrogen vapor from the slush hydrogen generator [686]. By alternately adjusting the pressure in the slush hydrogen generator to a pressure below the triple-point of hydrogen and then to a pressure slightly above the pressure at the triple-point causes the formation and dispersion of solids on the surface of the liquid hydrogen. To obtain finely grained hydrogen slush suitable for use in a rocket engine, it is necessary to destroy the crystalline surface solid by stirring, but this gives a very coarse



particle size slush. A finely grained slush can be obtained by expanding high pressure liquefied gas through a spray nozzle into a chamber ultimately to a pressure below the pressure of the triple-point in the gas-solid range and then to a pressure above the pressure of the triple point in the gas-liquid range. A high production rate, continuous production, slush hydrogen generator included a tank, a vacuum pump, and delivery of triple-point liquid hydrogen spray to the tank [687].

A handbook of physical and thermal property data for hydrogen in the region between the triple point and the critical point is available and is needed for study of hydrogen slush utilization [76]. The properties are given in both English engineering and SI units. The application of triple-point and slush hydrogen to three space missions was studied. These three space vehicles were the SATURN V S-IVB, a Lunar Mission Landing Vehicle, and a 120-day Earth Orbital Hydrogen Tanker. The SATURN V S-IVB application was based on performance of an advanced lunar logistics mission. In this concept, the S-IVB would be modified from the existing SATURN V APOLLO booster stage to a lunar cargo-landing vehicle. This would require a much longer duration for in-space storage of hydrogen slush turning to liquid [688].

A mission study looked at the use of subcooled liquid and hydrogen slush in a SATURN SIVB stage for a manned Mars fly-by mission [689]. It was concluded in the initial hydrogen slush study program that experimental work was needed on a scale larger than that conducted by the Cryogenic Engineering Laboratory of the National Bureau of Standards at Boulder, Colorado, to determine the practical aspects of applying slush hydrogen to existing or new space vehicles. To perform this experimental work, Lockheed provided a Cryogenic Vehicle Flight Simulator, a slush hydrogen manufacturing Dewar, a slush hydrogen storage Dewar, a 41.5-in. insulated flight-type propellant tank, and the necessary plumbing and controls located at the Lockheed Santa Cruz Test Base to provide realistic tools to conduct an experimental program [690].

Slush hydrogen offers certain advantages for transportation and storage on Earth as well as in space. In the last century, liquid hydrogen was transported between Florida and California in 107000-L tank cars filled to 95% of the tank volume. The trip took 9 days and the evaporation losses were 5.2%. If the hydrogen had been cooled to the point where it consisted of 75% solid and 25% liquid hydrogen, not only would there not have been any evaporation losses during transport, but the tank could also have been kept idle for another 62 days before the tank pressure exceeded the pressure rating the pressure relief valve started venting. Another advantage is that the density of the subcooled hydrogen is higher, such that the same tank volume can hold 16% more propellant. But one must allow for space if the propellant warms up and expands again.

That would be a significant advantage for upper stages where propellant tanks have to be fitted into a limited envelope. That advantage applies only for the trans-

port of hydrogen into orbit where it is stored at an orbital refueling station. There is currently no way to feed slush hydrogen into a rocket engine.

Slush hydrogen may offer certain advantages, but some practical problems have not yet been solved. If hydrogen slush must be transferred from one storage tank to another tank, or from a flight tank into a combustion chamber, one must first develop a pump capable of pumping hydrogen with a certain solids content. It was assumed that current design centrifugal pumps will be capable of pumping LH<sub>2</sub> with up to 20% solids content without too much difficulty. If one uses pressure-fed instead of pump-fed transfer, it might be possible to transfer hydrogen slush with up to 60% solids as long as the hydrogen crystals are finely dispersed and do not cake together.

Before hydrogen slush technology can advance to the next stage, one must develop fast analysis methods that allow the operator to monitor the progress of solidification and verify the solids content of a propellant even after it has been sitting around for several days. One way to predict the amount of solid hydrogen in the slush is to measure the mass fraction of gas pumped off and the rate of heat leaking into the container [691, 692].

Ground service equipment and flight vehicle system requirements were evaluated for the use of densified cryogenic propellants in advanced space transportation systems [693]. Propellants studied were slush and triple-point liquid hydrogen, triple-point liquid oxygen, and slush and triple-point liquid methane. Areas of study included propellant production, storage, transfer, vehicle loading, and system requirements. A saving of approximately  $8.2 \times 100000$  kg was predicted in single stage to orbit gross liftoff mass for a payload of 29484 kg by utilizing densified cryogenics in place of normal boiling point propellants.

A 178-mm diameter auger-type hydrogen slush generator with a supercritical helium flow loop, which simulates the performance of a helium refrigerator and cools the generator was modeled [677]. The coolant temperature was assumed to vary down to 5 K and the flow was assumed to vary about the 1.4 L/s (3 cfm) design point. The computer model of the auger-type generator showed that coolant temperature and auger speed have the greatest influence on slush production rate, although coolant flow rate and auger radial clearance are also important. Three slush hydrogen production methods were tested in the laboratory and compared: the spray method, the freeze-thaw method, and the auger method [694].

An excellent summary of the thermophysical properties, freeze-thaw and auger methods for production, measurement techniques for density and mass flow meters, pressure drop reduction and heat transfer deterioration in pipe flow, and nucleate pool boiling heat transfer properties associated with slush and liquid hydrogen is given in [695].

A demonstration of advanced liquid hydrogen storage techniques included the production of large quantities of densified liquid and slush hydrogen in a 125000-L

tank [696]. Densified hydrogen was produced at three different liquid levels and LH2 temperatures were measured by 20 silicon diode temperature sensors. Overall densification performance of the system was explored, and solid mass fractions were calculated. Experimental data indicated that hydrogen temperatures dropped well below the triple point during testing and were continuing to trend downward prior to system shutdown. Sub-triple-point temperatures were seen to evolve in a time-dependent manner along the length of the horizontal, cylindrical vessel. The phenomenon was observed at two different fill levels.

#### 5.16.2.2 Heat Transfer to Slush Hydrogen

Heat transfer to slush hydrogen was measured in a small laboratory apparatus [697]. Four types of tests were conducted using three different orientations of the heater surface. The four test types were: **(1)** heat transfer at 1 atm pressure in liquid at the normal boiling point temperature, **(2)** heat transfer at the triple-point pressure in liquid hydrogen, **(3)** heat transfer at the triple-point pressure in settled slush hydrogen (estimated solid fraction of 0.45), and **(4)** heat transfer in settled slush hydrogen at 1 atm pressure using helium as the pressurizing gas. The three orientations of the surface were horizontal facing up, vertical, and horizontal facing down.

Densification (subcooling) of liquid hydrogen and oxygen propellants offers potential reductions in size and mass of space launch vehicles. Oxygen densification is easily accomplished by heat exchange with a bath of boiling liquid nitrogen. Parahydrogen presents a more difficult problem because the cooling bath temperature is limited by its 13.8 K triple-point value. To achieve a high degree of densification, the parahydrogen cooling bath must be held close to its triple point and the heat exchanger exit  $\Delta T$  must be small. A parahydrogen heat exchanger was designed to remove approximately 60 kW from a 0.8165 kg/s (1.8 lb/s) flow with an exit  $\Delta T$  of 0.6 K with respect to a bath held at 14.4 K or lower [698]. Test results were compared with design model predictions.

Nucleate boiling heat transfer characteristics of slush hydrogen and slush nitrogen were studied by visual observation of heat transfer states using a heat transfer unit that was placed in a glass Dewar designed to minimize the heat loss from an atmospheric environment [699]. The heat transfer unit used was a circular flat plate 2.5 cm in diameter made of electrolytic copper. During testing, three different orientations of the heat transfer surface were used: horizontal facing up, vertical, and horizontal facing down. Heat transfer data for the normal boiling point of liquid hydrogen and the triple point of liquid hydrogen were obtained up to the critical heat flux (burnout). These data for slush hydrogen and nitrogen, including the results of observation of the heat transfer surface were compared. This provided data for the nucleate boiling heat transfer characteristics of slush hydrogen and slush nitrogen.

A numerical model was built based on the Eulerian model and the kinetic theory of granular flow to investigate the hydraulic and heat transfer characteristics of slush

hydrogen in a circular pipe under both terrestrial and microgravity conditions [700]. The numerical model was validated by experimental results reported in the literature. The flow of slush hydrogen with different inlet velocities and solid fractions was numerically studied to investigate the solid fraction distribution and particle velocity profile (lag) of the outlet cross-section. Considering the transportation of slush hydrogen in practical applications, the hydraulic characteristics of slush hydrogen in an inclined pipe under terrestrial conditions and in a horizontal pipe under microgravity were investigated. The results showed significant influence of the gravity on the solid fraction distribution and pressure drop of slush hydrogen. The heat transfer of slush hydrogen showed that the temperature of fluid can be locally decreased sufficiently using slush hydrogen such that the vaporization of liquid hydrogen can be suppressed. Solid hydrogen particles with small diameters can improve heat transfer between the solid phase and liquid phase, and the melting of solid hydrogen is accelerated. This explains that the increases of both the inlet velocity and solid volume fraction have positive effects on an increase of the local heat transfer coefficient.

### 5.16.2.3 Rheologic and Flow Properties of Slush Hydrogen

The heat of fusion, density, and thermal conductivity of solid  $p\text{-H}_2$  and thermal conductivity of liquid  $p\text{-H}_2$  were determined experimentally to pressures of several hundred atmospheres [100, 652]. Experiments were also carried out on the extrudability and hardness of solid  $p\text{-H}_2$ , heat capacity of solid  $p\text{-H}_2$  calculated over the temperature range 0–15 K and at pressures up to 400 atm. The enthalpy was calculated at saturation and along the melting line.

The pumping characteristics of slush hydrogen were investigated with a SATURN S-IVB liquid hydrogen chilldown pump [701]. As would be predicted from theory, pump performance and cavitation for slush and liquid hydrogen are the same when the difference in fluid density was considered. No pump wear or damage could be attributed to operating the pump with slush instead of liquid hydrogen. A nuclear radiation attenuation densitometer was installed on the 450-L slush generator. The precision of the densitometer was comparable to the accuracy of the pycnometric density determination methods to which it was compared. Flow data were taken in the flow loop for triple-point liquid and slush hydrogen.

The friction losses determined from flow data with hydrogen slush were compared to losses predicted for Newtonian fluids [670]. Liquid-solid mixtures of hydrogen with solid fractions of 0.5 were transferred through three types of flow restrictions, a globe valve, an orifice, and a venturi and the developed head, efficiency, cavitation constant and net positive suction head were measured. When pumped through a pipe network, slush hydrogen behaves as a conventional Newtonian fluid [697, 702–704].

Slush hydrogen was intended to be used as fuel in the National Aerospace Plane, where it would be recirculated in the tank to keep the solids in suspension and pre-

vent them from settling during the launch preparations and the countdown [705, 706]. As part of the National Aerospace Plane Project, an analytical model was developed to perform heat transfer and fluid dynamics calculations for in-line transfer of hydrogen slush [707]. This code, called FLUSH, calculates pressure drop and solid fraction loss for the flow of slush hydrogen through pipe systems. The model can solve the steady-state, one-dimensional equation of energy to obtain slush solids loss by melting estimates. Sample results showed the anticipated degradation of slush hydrogen solid content for various piping systems.

A series of 14 pressurization and expulsion tests were performed with triple-point and slush hydrogen in a horizontally positioned 1.9 m<sup>3</sup> (500 gallon) cryogenic tank [708]. The tank was instrumented to determine temperature distribution in the ullage gas and liquid/slush. The pressurization gas was nominally 80 K gaseous helium (GHe) and/or 300 K gaseous hydrogen (GH<sub>2</sub>). The test results showed that there were marked differences in pressurization performance between GHe and GH<sub>2</sub>, and with liquid or slush hydrogen. Pressurization of slush hydrogen with warm GH<sub>2</sub> was much more rapid and efficient than with cold GHe. In addition, GHe pressurization of slush hydrogen took twice as long as pressurization of triple-point hydrogen, while GH<sub>2</sub> pressurization of triple-point and slush hydrogen took about the same time. Pre-pressurization and expulsion pressurization using GH<sub>2</sub> resulted in substantial ullage pressure collapse at initiation of expulsion (possibly due to surging in the warm outflow line leading to interface disruption and ullage condensation). Conversely, pre-pressurization with cold GHe, followed by expulsion pressurization with warm GH<sub>2</sub>, appeared to suppress GH<sub>2</sub> condensation and eliminate ullage pressure collapse at expulsion. The test data were correlated using a multi-node one-dimensional pressurization/stratification computer code which accounts for real fluid properties, ullage/liquid condensation/evaporation, stratification and heat transfer [661, 709, 710].

If it is too difficult to pump slush hydrogen, slush hydrogen can be pressure-fed to the engine instead. The pressurization gas requirements for expelling slush hydrogen from a storage tank were calculated [711]. A multi-dimensional computational model of the pressurization process in a slush hydrogen propellant storage tank was developed and its accuracy evaluated by comparison to experimental data measured for a 1.5-m (5-ft) diameter spherical tank. The fluid mechanic, thermodynamic and heat transfer processes within the ullage were represented by a finite-volume model. The heat and mass fluxes at the ullage boundary were computed in auxiliary analyses and specified as input to the finite-volume model. Predictions by the model were shown to be in reasonable agreement with the experimental data.

Numerical simulations have been performed using the STAR CD numerical code in order to study the thermofluidynamic behavior of slush hydrogen in straight ducts [712]. For simplicity of the modeling, three straight ducts of same length but different diameter were selected for the simulations. A solid fraction of 35% was

assumed for slush hydrogen. This lower value had to be chosen in order to not override the code's upper limit for a single numerical cell. The analysis performed was mainly aimed at the solid fraction loss due to melting and at pressure drop. The results of the analysis for the solid fraction loss have been compared with the results obtained by previous simulations using FLUSH as numerical code, while the results for the pressure drop have been compared with the results obtained applying the Darcy-Weisbach equation.

The observation of a slight fluctuation in the distribution of solid hydrogen particles in slush hydrogen, i.e., slush hydrogen density, led investigators to place capacitance-type densimeters at two locations along the piped flow to measure the density and to detect density fluctuations [713, 714]. The flow velocity was calculated from the densimeter distance and delay time when the cross-correlation function of the two density signals was at a maximum. This capacitance-type flowmeter has no moving mechanical parts and no probe in the flow stream. A prototype slush hydrogen capacitance-type flowmeter was developed, built, and the accuracy of its output was confirmed by other flow measurements.

Slush hydrogen flowing at low-flow rates has a higher viscosity than the liquid; however, at higher velocities it approaches the viscosity of neat liquid. For the entire range of natural convection and nucleate boiling, the heat transfer at the triple-point temperature and pressure is nearly the same for the liquid and slush [669].

The use of slush in propulsion systems, its flow in pipes and orifices, the design of slush capable turbopumps and injection of slush into combustion chambers require a complete understanding of the flow properties of slush hydrogen [715, 716]. Numerical modeling tools for supporting future technical activities, the development of models of hydrogen slush flows has been split in two parts: the simple engineering model for slush flows in straight pipelines and the development of more complex models. The different issues in terms of modeling related to slush hydrogen have been identified and a potential model for future computational fluid dynamics calculations has been selected.

A three-dimensional numerical simulation code (SLUSH-3D), including the gravity effect based on a thermal non-equilibrium, two-fluid model was used to describe the flow and heat-transfer characteristics of cryogenic slush fluids in a horizontal circular pipe [717]. The calculated results of slush nitrogen flow predicted using the numerical code were compared with experimental results. As a result of these comparisons, the numerical code was validated, making it possible to analyze the flow and heat-transfer characteristics of slush nitrogen with sufficient accuracy. The numerical results obtained for the flow and heat-transfer characteristics of slush nitrogen and slush hydrogen clarified the effects of the pipe inlet velocity, solid fraction, solid particle size and heat flux on the flow pattern, solid-fraction distribution, turbulence energy, pressure drop and heat-transfer coefficient. The differences of the flow and heat-transfer characteristics between slush nitrogen and slush hydrogen were caused

to a large extent by their thermo-physical properties, such as the solid-liquid density ratio, liquid viscosity, and latent heat of fusion.

A numerical simulation based on a finite-volumes discretization using the software library OpenFOAM was carried out on solid-liquid multi-phase flows (slurry) and slush flows inside a typical pipe geometry, very common in propulsion pipelines [718]. A benchmark in comparison with previous experiments and simulations was established to assess the degree of accuracy of the code in predicting pressure drops and solid phase fraction dispersion. The study included the effects of particle size, inlet velocity, and particle concentration on heat transfer and fluid dynamics.

A two-phase mixture was modeled using a separated flow model in which the mathematical equations were written separately for each phase where different properties and velocities are considered for each phase [719]. Mass, momentum, energy equations, and interfacial phenomena equations were developed with the inclusion of drag force, virtual mass force, mass and momentum transfer, and interfacial shear stress. Turbulence effects were treated and multi-particle drag correlations were included. Results for pressure drop across a 38-mm (1.5-in.) Schedule 5S vacuum-jacketed pipe showed good agreement when comparing them with earlier experimental data.

An improved three-dimensional numerical model based on Euler-Euler two-fluid model has been built to predict the flow characteristics of slush hydrogen in a horizontal pipe [720]. In this model, an effective viscosity of mixture, which takes the particle shape and size into consideration, is adopted to modify the drag law for interphase momentum exchange, and the wall boundary conditions for the solid phase are based on Johnson-Jackson model which involves the friction and collision between the particle and the wall. The performance of the model has been validated by a comparison between the calculated results and experimental data from the literature, and it is now considered to be effective for calculations of slush hydrogen flow. The improved model was used to analyze the effects of inlet velocity, solid fraction, and particle size on the flow characteristics, including pressure gradient, solid volume fraction distribution, and velocity distribution. The numerical results indicated that the pressure drops for subcooled liquid hydrogen, under some operating conditions, can be greater than those of slush hydrogen, for which data can be found in some published experimental work.

A numerical model was developed based on the kinetic theory of granular flow to investigate the hydraulic and heat transfer characteristics of slush hydrogen flows in a circular pipe under both terrestrial and microgravity conditions [700]. The numerical model was validated by experimental results reported in the literature. The flow of slush hydrogen with different inlet velocities and solid fractions was numerically studied to investigate the solid fraction distribution and particle velocity profile (lag) of the outlet cross-section.

### 5.16.3 Mission Analyses for Missions Enabled by Slush Hydrogen

Using slush cryogenics instead of saturated liquid at the normal boiling point, cryogenics can be mission enabling or mission extending. The ability of slush and subcooled cryogenics to absorb and tolerate more heat leakage input can enhance space vehicle design and operations through: **(1)** increased storability for long-term missions; **(2)** reduced tank insulation (quantity or quality); **(3)** reduced tank venting frequency and **(4)** reduced tank size and operating pressure [721].

The potential benefits of using densified hydrogen have been quantified for Earth-to-orbit transportation vehicles (space shuttle STS) and space shuttle cargo (STS-C), space exploration mission transfer vehicles (lunar outpost missions), and cryogenic depots in low-Earth orbit. A mission analysis study was performed to quantify the benefits of using slush hydrogen instead of normal boiling-point liquid hydrogen as a fuel for several types of space missions [722]. Vehicles considered in the study included the Space Shuttle/Shuttle-C, LEO to GEO transfer vehicles, Lunar and Mars transfer vehicles, and cryogenic propellant depots in low Earth orbit. The advantages of using slush hydrogen were expressed in terms of initial mass savings at a constant payload, payload differences at a constant tank volume, and increases in fuel storage time for cryogenic depots. Both chemical oxygen/hydrogen and hydrogen nuclear thermal rocket propulsion were considered in the study. The results indicated that slush hydrogen offers the potential for significant decreases in initial mass and increases in payload for most missions studied. These advantages increase as the mission difficulty or energy increases. See also [723,724].

### 5.16.4 In-Space Evaporation Losses and Their Impact on Mission Profiles

For flight tanks which store liquid hydrogen for several hours in outer space, the weight of the insulation becomes a significant burden. One has to optimize the increased thickness and weight of the insulation versus the reduction of evaporative losses. Design properties of various insulations were already summarized in Section 4.4. Now it comes to the point where the optimum amount of insulation has to be determined to minimize evaporative losses with a minimum weight penalty of the dry weight of a spacecraft.

Storability studies of liquid hydrogen and mission analyses have been performed for Earth orbit [725, 726], for trans-Mars orbits [727], for Mars sample return missions [728] and for other space operations. The rate of propellant loss by evaporation and venting depends on the quality of insulation, the albedo of the surface, and the intensity of solar radiation [729–731]. Evaporation losses during space flight can be reduced by optimizing the thickness of multi-layer insulation [732].



## 5.17 Gelled Hydrogen

Gelling hydrogen would reduce sloshing during launch vehicle motions and would allow the suspension of specific impulse-increasing metal additives (lithium, beryllium) or metal hydrides (lithium hydride, beryllium hydride, aluminum hydride) in the liquid fuel. Finely divided, atomized frozen methane could be used as a gelling agent and it would contribute to the heating value of the fuel.

Lithium metal and lithium borohydride were prepared by several methods in the form of ultrafine particles suitable for gelling liquid hydrogen. Lithium-gelled hydrogen and lithium borohydride-gelled hydrogen produced a storable liquid hydrogen gel [733, 734]. A gel was obtained at 61 mass-% (17 vol.-%) lithium. Repeatable yield stresses of about 1250 dyn/cm<sup>2</sup> and shear stresses of about 1400 dyn/cm<sup>2</sup> at a shear rate of 1000 cm<sup>-1</sup> were obtained. Gelled liquid hydrogen was cold-flowed through test components with negligible restrictions due to gellant deposition under normal operating conditions. Liquid hydrogen gels based on lithium were stable to moderate levels of shock and vibrational acceleration. Another gel contained 58.8 mass-% (13.3 vol.-%) LiBH<sub>4</sub>. Another gel was prepared using pyrogenic ("fumed") silica as the gelling agent. The gel formed with 36.1 mass-% SiO<sub>2</sub> had a yield stress greater than 500 dyn/cm<sup>2</sup>.

Gelling of slush hydrogen with pyrogenic silica was accomplished with solid fractions from 0 to 0.2 [670]. The amount of gelling agent required to gel slush was found to be proportional to the liquid volume of the slush. One method for reducing the amount of gelling agent was found in the gelation of slush hydrogen, since only the liquid portion of the slush requires a gelling agent. Gelled slush combines most of the desirable features of both gel and slush. The semi-solid fluid has a high density [735, 736]. Alkoxides and silica were tested as gelling agents for suspending aluminum metal particles in liquid hydrogen and liquid hydrocarbons [737].

A mixture of gelled liquid hydrogen and solid methane has a mixture density approximately two times that of liquid hydrogen alone [738]. This increase in density is partially offset by a loss in  $I_{sp}$  of about 8%, compared to that of liquid hydrogen alone, with liquid oxygen. Increased fuel density reduces fuel tank size, mass and aerodynamic drag.

## 6 Equipment for Use of Liquid Hydrogen

### 6.1 Spark-proof Electrical Equipment in Liquid Hydrogen Storage Areas

Electrical equipment in areas where liquid hydrogen is stored and transferred must be spark-proof. The requirements for hydrogen atmospheres are more stringent than those for other flammable atmospheres because hydrogen can diffuse through many membranes and gaskets that are impermeable to larger hydrocarbon molecules [739].

## 6.2 Liquid Hydrogen Flight Tanks

### 6.2.1 Liquid Hydrogen Flight Tanks for Launch Vehicles

The design of flight tanks has to satisfy special requirements with respect to mass, rigidity, and thermal insulation. The design criteria are a compromise between tolerable evaporation losses and the allowed and affordable thickness and mass of thermal insulation [740, 741].

For upper stages of launch vehicles, it is important to know how long liquid hydrogen can be stored before the rated operating pressure is exceeded and gas must be vented. If the ullage is too small, the vent point will be reached too soon. If the ullage is larger, one is wasting valuable space that could be occupied by propellant. Aerodynamic heating during the first stage operation and the traverse of the lower, denser atmosphere makes this condition worse. Evaporation losses prior to ignition of the second (or upper) stage engine can be calculated from a detailed computer model. Insulation in upper stages is at a premium, so it is economically acceptable to use the more expensive superinsulation for upper stage tanks with cryogenic propellants [742]. The magnitude of tolerable heat flux, avoidance of stratification and the choice of insulation determine the design of flight tanks for liquid hydrogen [743].

### 6.2.2 Surface Tension Propellant Management Devices for Liquid Hydrogen

Surface tension Propellant Management Devices (PMDs) are also called Liquid Acquisition Devices (LADs). Hydrogen has a very low surface tension and thus it is difficult to contain it in a screen basket in low-g environments [744, 745].

The pores in the wire mesh have to be very small to effectively retain the liquid hydrogen in locations where it is supposed to be at the moment when the engine starts firing again. A multi-burn upper stage can afford to fire its small RCS thrusters for propellant settling before re-igniting the engine(s), but an orbital propellant depot is supposed to remain in a pre-assigned orbit and needs other methods for propellant management, such as surface tension screens. Different types of wire mesh weave patterns have been evaluated for this purpose [746]. Results indicated that a  $450 \times 2750$  Dutch Twill mesh may be the optimal screen weave for a future LH2 orbital fuel depot.

The  $325 \times 2300$  mesh screen has a bubble point of 6.1 kPa (46 mm Hg = 24.5 inches of water) in isopropyl alcohol, 2.6 kPa (20 mm Hg = 10.7 inches of water) in liquid nitrogen and 0.46 kPa (3.4 mm Hg = 1.83 inches of water) in liquid hydrogen [747]. These values were in good agreement with results reported in the literature.

The main criterion in designing surface tension propellant acquisition devices is the bubble point under varying gravitational conditions. Surface tension screen development tests will measure the bubble point pressure with different fluids [748]. Test parameters typically include the screen mesh size, type of liquid cryogen, liquid temperature and pressure, and type of pressurant gas. Bubble point data were collected using three fine mesh 304 stainless steel screens in two different liquids (hydrogen and

nitrogen), over a broad range of liquid temperatures and pressures in subcooled and saturated liquid states, using both a non-condensable (helium) and autogenous (hydrogen or nitrogen) gas pressurization scheme. Bubble point pressure scales linearly with surface tension but does not scale inversely with the fineness of the mesh. Bubble point pressure increased proportional to the degree of subcooling. Higher bubble points were obtained by using non-ondensable pressurant gases over the condensable vapor.

Higher bubble points are achieved by using a finer mesh screen and pressurizing and subcooling the liquid with gaseous helium [749]. Once a bubble point pressure is exceeded and control of the whereabouts of the propellant blob is lost, the reseal pressure can be measured that will allow the liquid to re-enter the screen cage [750].

An experiment was carried out that provided measurements of the velocity and pressure fields in a screen channel LAD and compared to the predictions of a hydrodynamic model, which accounts for non-uniform injection through the screen [751].

A passive zero boil-off hydrogen storage system for extended space missions was designed without good thermal insulation system around the liquid hydrogen tank, and it would allow the radiation heat to leak into the space environment from the tank [752]. The theories of heat conduction and radiation heat transfer have been utilized to study the rate of heat absorption for a hydrogen storage tank in space. The model has been simplified by taking several aspects of heat transfer into account, which contains the radiation heat into the storage tank from the sun and spacecraft, the radiation heat into the space environment from the tank, the heat conduction into the tank from the support structure, and the heat conduction into the tank from the liquid oxygen tank. By establishing the function relationship between the rate of heat absorption and the temperature of the liquid hydrogen and oxygen tank, it was theorized that liquid hydrogen can be stored for 2 years without evaporation losses.

### 6.2.3 Liquid Hydrogen Flight Tanks for Airplanes

Liquid hydrogen is being evaluated as the fuel for air-breathing scramjets (Hyper-X and X-43) or even conventional jet engines in commercial transports. Lockheed-Martin P-3 Orion is a four-engine turboprop anti-submarine and maritime surveillance airplane considered for conversion to operation on liquid hydrogen [753]. The fuel tank would take up 65% of the aircraft's internal volume. Despite the large LH2 tank weight, due to the low fuel weight the aircraft's take off gross weight would be only 80% of the current petroleum-fueled P-3. Hydrogen is used as the fuel in fuel cells for electrically driven UAV airplanes that have established record times for staying aloft. Development of liquid hydrogen tanks that were to be flown in aircraft testing ramjets and scramjets started already in the 1950s, but it has not yet led to widespread use of this fuel in air-breathing flight vehicles [754].

### 6.3 Transportation and Transfer of Liquid Hydrogen

Transportation of hydrogen within the USA. on interstate highways is governed by 49 CFR Subtitle B, Volume 2, Chapter 1, Parts 171–180 Hydrogen, specifically 49 CFR Part 173.306, Part 173.316 and Part 173.318.

In anticipation that hydrogen will one day play a major role in the energy sector of industrialized nations, the infrastructure for hydrogen transportation and transfer is already beginning to take shape [45]. As of 2003, there were already ten hydrogen liquefaction plants in North America. Train size ranged from 6 to 35 TPD (5400–32000 kg/day). This is another example where space technology, once derogated as a waste of taxpayers' money, is transferred to use by the general public to the benefit of society.

### 6.4 Trade-off between Pipelines versus Tank Cars

Short-distance transfer operations of liquid hydrogen within tank farms or from a tank farm to an adjacent test or launch site will usually be made by pipelines. But if the production and use point are further apart, of the order of 3–10 km, there comes a point where it is more economical to transport liquid hydrogen by tank car instead of building and maintaining a pipeline. Obviously, the breakeven point depends on the total volume of liquid hydrogen that must be moved and how frequently the pipeline is used. A mathematical method has been developed that would allow the logistics planner to decide between pipeline transport and tank car transport [755]. For best results in a cryogenic pipeline, high vacuum is used as the insulation in the annulus between two concentric tubes with the cold fluid flowing through the center tube [616].

The petroleum processing industry has a network of hydrogen gas pipelines which extends over hundreds of miles. There are already 245 miles of hydrogen gas pipelines connecting refineries in the US. But a network of liquid hydrogen pipelines has not yet been realized or even planned. A design for an LH2 pipeline was based on a single-phase flow regime of LH2 with a certain degree of supercooling [756]. A design for a 200-m long transfer line of LH2 service was calculated. Vacuum-jacketed, double-walled pipelines for liquid hydrogen are expensive to build and would only be used for short distances [757].

Tank cars for transportation of liquid hydrogen come in different sizes. A frequently used rail tank car used to hold 107000 L. The internal container had a diameter of 2.71 m, a length of 20.4 m, was made of stainless steel and surrounded by a 2.54-cm thick insulating double-walled layer that was evacuated to below 0.013 Pa ( $10^{-4}$  mm Hg). The evaporation losses from a railroad tank car like this were approximately 0.3%/day (without any contributions by *o-p* conversions). Liquid hydrogen has been transported in such railroad tank cars all across the American continent [758].



**Figure 63:** Liquid hydrogen tanker truck. (Photo: courtesy of Linde Gas Division-Hydrogen Solutions)

For transport by road tank cars holding 29500 L liquid hydrogen have been used and are still being used (Figure 63). Evaporation losses from these tank cars are 0.5%/day.

The quick dispersion of the boil-off from these tank cars is a critical problem. The escaping gas has to be diluted quickly to avoid formation of explosive gas clouds in the vicinity of the tank car. The tank car is under a slight overpressure and the gas is released through a relief valve. Instead of venting the gas directly, it passes through a small turbine which drives a fan which aspirates an airstream that dilutes the vented hydrogen quickly to below 2 vol.-% to below the lower flammable limit.

At one time in the early 1960s there was a smaller tank car on the road which held 6000 L and had evaporation losses of the order of 1.7%/day [759]. There are smaller tanks holding 1000 L available that can be skid-mounted and moved by a fork lift. The evaporation losses from a small tank like this are typically 1%/day. The insulation of one type of these containers was of the SI-62 type.

## 6.5 Transfer and Pumping of Liquid Hydrogen

Ground service equipment for fueling of rockets with liquid hydrogen depends on reliable transfer procedures between the stationary supply tank and the vehicle standing on the launch pad [501].

Liquid hydrogen ground service facilities for the SATURN-C1 rocket were thoroughly tested before the first flight vehicle was loaded with liquid hydrogen [760]. Liq-

liquid hydrogen can be transferred by pressurization or by pumps. Gravity-fed transfer is rarely used (at least there are no published designs).

### 6.5.1 Pressure-fed Transfer of Liquid Hydrogen

Only two gases can be used for pressure feeding hydrogen from pressurized tanks: warm hydrogen and helium. If warm gas pressurization is used, the entry points in the ullage need to be through multiple diffusers so that the hot gas does not impinge on the liquid surface and cool down, increasing the pressurization gas requirements [761].

Warm hydrogen for pressurization of liquid hydrogen tanks can be stored in compressed gas cylinders or can be generated *in situ* by evaporating some liquid hydrogen in a vaporizer. If helium is used as a pressurant gas for liquid hydrogen, one must consider that helium is partially soluble in liquid hydrogen [762, 763].

The solubility of helium in liquid hydrogen at 17.4, 20.39, and 21.8 K, and pressures of 2.9–32 atm (43–475 psia) is summarized in Table 47.

**Table 47:** Solubility of helium in liquid hydrogen.

| Temperature, K | Pressure, atm | Liquid phase  |                 | Gas phase     |
|----------------|---------------|---------------|-----------------|---------------|
|                |               | Helium, mol-% | Hydrogen, mol-% | Helium, mol-% |
| 17.4           | 3.36          | 0.20          | 99.80           | 83.5          |
| 17.4           | 5.64          | 0.22          | 99.78           | 89.7          |
| 17.4           | 6.52          | 0.27          | 99.73           | 91.0          |
| 17.4           | 9.60          | 0.45          | 99.55           | 93.5          |
| 17.4           | 14.1          | 0.74          | 99.26           | 94.6          |
| 17.4           | 21.5          | 1.08          | 98.92           | 95.1          |
| 20.39          | 4.28          | 0.59          | 99.41           | 73.7          |
| 20.39          | 12.0          | 1.53          | 98.47           | 87.3          |
| 20.39          | 15.1          | 2.04          | 97.96           | 88.9          |
| 20.39          | 17.4          | 2.16          | 97.84           | 89.6          |
| 20.39          | 20.8          | 2.48          | 97.52           | 90.0          |
| 20.39          | 24.4          | 2.77          | 97.23           | 90.0          |
| 20.39          | 26.9          | 3.01          | 96.99           | 90.0          |
| 20.39          | 27.6          | 3.06          | 96.94           | 90.1          |
| 20.39          | 32.3          | 3.44          | 96.56           | 90.1          |
| 21.8           | 2.92          | 0.18          | 99.82           | 60.8          |
| 21.8           | 5.57          | 0.29          | 99.71           | 73.4          |
| 21.8           | 10.7          | 1.36          | 98.64           | 83.3          |
| 21.8           | 15.4          | 1.49          | 98.51           | 87.9          |
| 21.8           | 20.8          | 2.44          | 97.56           | 88.2          |
| 21.8           | 26.2          | 3.06          | 96.94           | 88.3          |

Data source: [764,765]

The measured 1952 data were not in agreement with thermodynamic theories. It took a new approach incorporating the fugacity of hydrogen to derive a set of equations that was in agreement with the measured data [765]. See also [268].

The helium effect on the pressurization behaviors of cryogenic propellant tanks was represented by an enhanced computational fluid dynamic (CFD) approach, which could simultaneously account for the species transfer as well as its effect on phase change [766, 767]. Two transient pressurization events, including depressurization after an active helium pressurization and pressurized discharge process, were selected as examples, and the pressure responses, species concentration distribution, as well as mass transfer rates were analyzed. The results showed that the influence of species transfer on pressure behavior is strongly related to the pressurization time. For the depressurization performance after a pre-pressurization operation, the residual helium leads to a continuous liquid evaporation in the depressurization, while a pure hydrogen case experiences a vapor condensable process. The helium and hydrogen could sufficiently diffuse into each other within the depressurization period. For a typical pressurized discharge process, the species diffusion affects the distribution to a certain degree but a weak influence on the general pressurization performance remains. The species concentration along radial direction of the tank caused a distinguishable radial temperature gradient.

### 6.5.2 Pressurant Gas Requirements for Pressurized Transfer of Liquid Hydrogen

Because the only possible pressurant gas (other than hot hydrogen) for pressurized transfer of liquid hydrogen is helium, the pressure in a freshly pressurized tank decays because the gas cools off and because some of the helium gas dissolves in liquid hydrogen. The density and other properties of liquid hydrogen change as the result of dissolved helium contained in it. Therefore, it is important to have knowledge of the solubility, rate of diffusion and pressure-temperature-density behavior of the hydrogen/helium system. The solubility of helium in liquid hydrogen was already described in this book in Section 2.16.2. The PVT-X and  $P\Delta T$ -X phase behavior of helium/hydrogen mixtures was already described in Section 2.16.2.

The pressurant gas consumption for pressure-feeding of cryogenic liquids can be calculated using a variety of different equations. Table 48 is a summary of literature on pressurant gas requirements.

If the pressurant gas hydrogen is preheated, there is a 0.8% reduction in pressurant gas requirements for each 5.5 K increase in pressurant gas temperature [782]. The use of a straight-pipe injector decreased the pressurant gas requirements by 9 to 35% compared to that of a diffuser-type injector. Pressurization efficiency depends on the extent of gas mixing in the ullage. The gas mixing depends on the type of injector. Certain types of injectors can reduce the gas-wall heat losses and improve the performance of heated gas pressurization systems [783].

**Table 48:** Summary of literature on pressurant gas requirements.

| Author               | Year  | References |
|----------------------|-------|------------|
| Laquer               | 1958  | [768]      |
| Bowersock and Reid   | 1961  | [769]      |
| Coxe and Tatom       | 1962  | [770]      |
| Gluck and Kline      | 1962  | [771]      |
| Epstein              | 1965  | [772]      |
| Epstein and Georgius | 1965  | [773]      |
| Nein and Thompson    | 1966  | [774]      |
| Thompson and Nein    | 1966  | [775]      |
| Johnson              | 1967  | [776]      |
| Lacovic              | 1969  | [777]      |
| Stochl et al.        | 1969a | [778]      |
| Stochl et al.        | 1969b | [779]      |
| Stochl et al.        | 1970a | [780]      |
| Stochl et al.        | 1970b | [781]      |

A double-walled 2360-L tank insulated with a powder/vacuum jacket and instrumented with a liquid level sensor, a range of pressure gauges and numerous thermocouples was used to measure pressurant gas requirements for transfer of liquid hydrogen. The thermocouples gave a spatial profile of vertical and horizontal temperature gradients in a tank after it was pressurized [559, 784]. Following pressurization, the liquid may stratify and the temperature of the liquid gradually rises. The hotter, upper layer may feign a higher vapor pressure when in reality the bottom liquid is still cold. It takes a while until the temperature of the stagnant liquid at the interface to the gas space and in the bulk of the liquid has equilibrated. During this time, temperature differentials can cause thermal stresses in the container wall material.

A multi-dimensional computational model of the pressurization process in a liquid/slush hydrogen tank was developed and used to study the influence of heat flux rates at the ullage boundaries on the process [785, 786]. The model computed these rates and performed an energy balance for the tank wall, whereas previous multi-dimensional models required *a priori* specification of the boundary heat flux rates. Analyses of both liquid hydrogen and slush hydrogen pressurization were performed to expose differences between the two processes. Parameters of interest are the ullage boundary heat flux rates and pressurant mass flow rate. Detailed velocity fields and temperature distributions were presented for selected cases to further illustrate the pressurization process. It was demonstrated that ullage boundary heat flux rates do significantly effect the pressurization process and that minimizing heat loss from the ullage and maximizing pressurant flow rate minimizes the mass of pressurant gas required to pressurize the tank. Additional information on pressurized transfer of liquid hydrogen can be found in [787, 788].



### 6.5.3 Pressurization to Increase Net Positive Suction Head of Liquid Hydrogen in Pump-fed Systems

Low pressure at the suction side of a pump can cause the fluid to start boiling, resulting in reduced energy efficiency, cavitation, and damage to the pump impellers. Boiling starts when the pressure in the liquid drops to below the vapor pressure of the fluid at the actual temperature.

**Cavitation** means **cavities** or bubbles in the liquid. Cavitation is the forming and collapsing of bubbles. Bubbles take up more space than the liquid so the capacity of a pump drops once it starts cavitating. Collapsing bubbles may cause shock waves that can damage the impeller and volute. The violent collapse of cavitation bubbles creates a shock wave that can erode material from internal pump components (usually the leading edge of the impeller) and creates noise and vibrations. Vibration can cause other mechanical failures in the pump and associated equipment. This makes cavitation a problem for both the pump and the mechanical seal.

These problems can be avoided by providing sufficient Net Positive Suction Head (NPSH) at the inlet to the pump. The suction head in the fluid close to the impeller can be expressed as the sum of the static and the velocity head. The suction head is increased by pre-pressurizing the liquid in the supply tank from which it is drawn. For flight vehicles, the gas required to maintain the NPSH while the propellant tank is drained is typically not carried as compressed gas (it would be very heavy to carry compressed gas tanks), but it is generated on board large rockets by vaporizers fed with a side-stream of the liquid to be pressurized [513]. The pressurant liquid fed to these high-pressure vaporizers first has to be boosted by a high-pressure pump [789].

The National Aerospace Plane was designed to use slush hydrogen as the fuel. Pressurization of the fuel tank in preparation for launch would result in some of the pressurant gas condensing on the cold liquid if hydrogen was used for pressurization instead of helium. A multi-dimensional computational model of the pressurization process in a slush hydrogen propellant storage tank was developed and its accuracy was evaluated by comparing it to experimental data measured for a 1.5-m (5-ft) diameter spherical tank [790].

If left undisturbed, the ullage gas would thermally stratify. As part of the National Aero-Space Plane (NASP) project, the multi-dimensional effects of gravitational force, initial tank pressure, initial ullage temperature and heat transfer rate on the 2-D temperature profiles in the tank ullage were studied [791, 792]. These effects were examined on the basis of previous liquid hydrogen experimental data with gaseous hydrogen as the pressurant.

## 6.6 Zero-*g* Transfer of Liquid Hydrogen

Orbital propellant depots will require long-term storage of cryogenic propellants in space and transfer of liquid hydrogen between supply and user tanks under conditions of zero or microgravity [793].

The problem of the expulsion of liquid cryogenics from a partially filled orbital depot tank involves tracking the motion of a floating, mobile and expanding vapor ullage as fluid is expelled from a tank. A simulation of the interface movement of the vapor ullage in a volume of confined liquid under zero gravity was carried out by solving the Navier-Stokes equations in the transformed boundary-fitted curvilinear co-ordinate system using a finite difference approach [794].

A thermal model of an orbital propellant depot was used to examine the effects of passive and active thermal management strategies [795]. Results showed that an all-passive thermal management strategy would result in significant boil-off for both hydrogen and oxygen. Zero boil-off of propellant is achievable only with the use of active cryocoolers; however, the cooling power required to produce zero boil-off is an order of magnitude higher than current state-of-the-art cryocoolers. The study showed a zero boil-off cryocooler minimum power requirement of 80–100 W at 80 K for liquid oxygen, and 100–120 W at 20 K for liquid hydrogen.

A CFD model, verified by experimental data, is capable of accurately simulating the no-vent filling process with good flexibility [796]. No-vent filling processes under different gravities were compared and the effects of four factors including inlet configuration, inlet liquid temperature, initial wall temperature and inlet flow rate, were studied, concluding that: **(1)** compared to the situations in normal gravity, the no-vent filling in microgravity experiences a more adequate liquid-vapor mix, which results in a steadier pressure response and better filling performance. **(2)** Inlet configurations seem to have negligible effects on the no-vent filling performance under microgravity since liquid could easily reach the tank wall and then cause a sufficient fluid-wall contact under any inlet condition. **(3)** Higher initial tank wall temperature may directly cause a higher pressure rise in the beginning. Sufficient precooling and reasonable inlet liquid subcooled degree would assure the reliability and efficiency of the no-vent fill under microgravity.

## 6.7 Liquid Hydrogen Pumps

The design of centrifugal pumps for liquid hydrogen required special technologies, which were developed mostly as an offshoot of the use of liquid hydrogen as a rocket propellant. Similar pumps had to be designed for other cryogenic fluids [797].

### 6.7.1 Liquid Hydrogen Pumps for Flight Vehicles

Lubrication of bearings in liquid hydrogen pumps is very difficult because there are no known lubricants to prevent galling of metal-to-metal rotary seals. It was a major breakthrough when it became possible to lubricate the shafts of liquid hydrogen pumps used on the CENTAUR or SATURN S-IV upper stages with a stream of liquid hydrogen [798]. The shafts were suspended hydrodynamically in flowing hydrogen. Such pumps have achieved very long operating times under cryogenic conditions. Other cryogenic fluid pumps have been using impregnated carbon seals in the shaft seals and bearings [799].

An early model of a liquid hydrogen pump had a flow rate of 2.73 kg/s at 26.5 atm and was spinning at 35000 RPM. The flow rate was not very susceptible to fluctuations in the back pressure [800].

Both propellant pumps in a cryogenic propellant rocket should be able to feed the full flow rate as soon as the start signal is given. This is not quite possible with liquid hydrogen without special prearrangements. Without such precautions, the first hydrogen entering the warm pump would evaporate and two-phase flow would cause low overall pumping. Initially, pumps in the CENTAUR upper stage were flushed for 20–30 s after stage separation and before engine ignition with liquid hydrogen which resulted in a substantial waste of fuel. Later the pumps were pre-cooled with liquid helium on the ground before launch [801]. That reduced the flush time after stage separation by 75%, and the payload could be increased by more than 12.7 kg. Lubricating mechanism, cage design, and heat generation of ball bearings for liquid hydrogen turbopumps were studied [802].

Pressure of liquid hydrogen fed to a vaporizer that generates hydrogen gas for pressurizing propellant tanks while liquid is withdrawn must be boosted by a high-pressure pump [789]. In designing LH2 pumps, the most critical part is the inlet (suction side) of the pump where one must avoid cavitation [803]. Three different helical inducers were tested in liquid hydrogen for their ability to induce or prevent cavitation [804]. The tip helical angles were 78, 80.6, and 84°. The pressure requirements as well as the thermodynamic effects of cavitation for a head-rise coefficient ratio of 0.70 were the greatest for the 84° inducer and least for the 78° inducer for a given flow coefficient ratio. The non-cavitating flow range was the widest for the 78° inducer and the narrowest for the 84° inducer.

A finite element method was used to calculate the transient temperature field distribution during hydrogen pump chilldown in a liquid rocket engine before the engine starts [805]. The chilldown flow rate and chilldown time are both related to the wasteful consumption of liquid hydrogen that is dumped. If the chilldown flow rate or time is not adequate, it may jeopardize the engine start reliability.

### 6.7.2 Liquid Hydrogen Pumps for Ground Service Equipment Low-pressure Transfer

Pumps for transferring liquid hydrogen between tanks on the ground do not have to operate at such high pressures as pumps in rocket engines. They do not have to come up to full operating pressure as fast as pumps in flight vehicles.

Pumps for ground service equipment can even be designed as immersion pumps and thus they are precooled all the time as long as the tank is full. Unlike liquid oxygen, most liquid hydrogen is transferred from storage to propellant tanks by means of pressurization. For higher flow rates, a liquid-hydrogen transfer system was designed based on a Dewar-mounted liquid-hydrogen booster pump [806].

### 6.7.3 Liquid Hydrogen Facility Pumps for Rocket Test Stands

Liquid propellants for rocket engine tests of individual engines as opposed to tethered all-up live stage ground testing is usually done with facility pumps which are more rugged than flight pumps and designed for longer operating times. The test facilities for nuclear-thermal rockets with liquid hydrogen operated by the US Atomic Energy Commission (AEC) required very large pumps, bigger than any liquid hydrogen pumps that had been built up to that time. One of the pumps used by the AEC was driven by a 5000-HP motor and was capable of feeding 27 kg/s at a back pressure of 29.3 atm gauge [9]. Some facility pumps can be used for liquid nitrogen or liquid hydrogen [807].

In order to prevent cavitation in the suction (inlet) side of the pump, the tank is usually pressurized or the liquid is subcooled. Either method will prevent cavitation only for a short time due to continuing heat leaking into the tank [808]. See also [809].

### 6.7.4 Slush Hydrogen Pumps

Extrapolation of relationships for pumping water slurries indicated that the pumping characteristics of liquid and slush hydrogen should be the same when the difference in density is considered [702, 810]. This difference to water slurry pumping behavior is due to the similar flow losses for liquid and slush hydrogen.

### 6.7.5 Gaseous Hydrogen Compressors for Stationary Facilities

Electrochemical compression of hydrogen (and oxygen) is the reverse of high-pressure fuel cells. If additional electrical energy is available, hydrogen can be compressed from atmospheric pressure to higher pressures by feeding it to a fuel cell electrode at moderate pressure, boosting the voltage and discharging it in an electrolyzer at higher pressure [811, 812]. At the same time, hydrogen is purified. The oxygen created at the same time at the opposing electrode can be expanded to lower pressure and recycled.

## 6.8 Liquid Hydrogen Transfer Lines and Pipelines

Sections of double-walled straight pipe can be considered as small tanks with a high L/D ratio with two open ends and often use the same types of thermal insulation. Each section is surrounded by its own separate vacuum jacket. A specification describes low pressure vacuum jacketed pipelines with 1/2-in. through 16-in. diameter and a maximum internal operating/service pressure of 1.9 MPa (275 psig) [813].

The main difficulties with double-walled pipelines are encountered at Ts, bends, and joints. Instead of plain vacuum jackets, pipes are often insulated with powder-filled vacuum jackets. Powder-filled vacuum jackets do not need to be evacuated to the very low pressures required for plain vacuum jackets. Plain vacuum jackets require vacuum of  $10^{-5}$  mm Hg, whereas a vacuum of 0.05 mm Hg suffices for powder-filled insulations [814].

It has also been proposed to fill the jacket with a condensable gas instead of evacuating it. Once the condensable gas (e.g., carbon dioxide) condenses, it creates a vacuum [815]. Such units have the advantage that during idle periods they are not losing their vacuum since no ambient air will leak into the system. There are also couplings for flexible cryogenic lines [816, 817].

Due to large circumferential temperature differentials the thermal stresses in double-walled lines for liquid hydrogen transport during uneven cooldown can be substantial and destructive [818]. A line that initially was straight can distort like a snake. In particular, if the line is not filled to its full cross-section, with only the lower half filled with liquid, the temperature differential between top and bottom is critical and can cause permanent distortions and damage.

The experiences gained and lessons learned during the design of pipelines for the ROVER program were summarized in [819]. They report temperature differentials of up to 230 K between the top and the bottom of large pipelines.

In spite of the low viscosity of the liquid, the pressure drop of liquid hydrogen flowing through a long system of lines can be measurable and has to be figured in the design of plumbing systems, either with single-phase flow [820] or with two-phase flow. In particular, two-phase flow will increase the pressure drop significantly above that of the pure liquid flow [821, 822]. The two-phase flow condition is observed mostly during the cooldown of lines and equipment. Two-phase flow is also called “mist flow” [823]. Rotameters would no longer indicate the true volume flow rate of liquid passing through the line. The quality of the liquid (its unwanted content of bubbles, expressed as the vapor:liquid ratio) can be measured by a measurement of the dielectric constant of the mixture filling a known capacitance flow-through cell [824]. Similar instruments were even used in the heat exchanger inside of a KIWI nuclear reactor to monitor the state of phase change from liquid to gas [825].

Propellant transfer through double-walled plastic hoses has been proposed. The hoses are made from aluminized Mylar [826]. The hoses could be transferred to remote locations (space stations, lunar bases) rolled flat like a fire hose, then inflated

at the point of use and the jacket would be filled with polyurethane foam (similar to polyurethane used for foaming in place of delicate instruments prepared for shipping).

If liquid hydrogen is transferred through uninsulated lines, substantial evaporation losses during cooldown and also during transfer must be taken into account [827]. Short lines between tanks and pumps and pumps and engines in flight vehicles are not always insulated to save weight.

## **6.9 Instrumentation and Equipment for Liquid Hydrogen Service**

Sensors and transducers for use with liquid hydrogen must be qualified to operate at extremely low temperatures and may be subjected to steep temperature transients [828].

### **6.9.1 Fluid Flow Control Components**

The measurement and control of fluid flow and physical properties is an important part of designing either a ground service system or a flight system using liquid hydrogen or any other liquid rocket propellant. Whereas for liquid nitrogen or liquid oxygen systems most components are available off-the-shelf from a variety of vendors worldwide, that is not always the case for liquid hydrogen components. In many cases the components offered are modified variants of components sold for liquid nitrogen or liquid oxygen systems. One may still have to test the components under actual use conditions to make sure they work as intended at the much lower temperature.

During the development phase, there were several closed-loop liquid hydrogen circulation component test sites in use at various places in the US, including those at Pratt & Whitney [829], Aerojet [830], and General Dynamics [831].

### **6.9.2 Valves for Liquid Hydrogen Service**

Valves and pumps have so many moving parts that they are usually not designed with a double-walled jacket for insulation purposes. Many valves have only clamshell-type insulation that is easy to remove when the valve needs to be serviced.

Evaluation criteria for liquid hydrogen are the same as for any other propellant valves. In addition, they should not have a high heat capacity, so that they cool down quickly and do not cause too much boil-off.

#### **6.9.2.1 Flow Control Valves**

Valves of different design types have been used for ground service equipment with liquid hydrogen: Either ball valves or sliding gate or sliding cone valves have been used. Low pressure drop and high flow coefficient are desirable [832]. Ice accumulation along the valve stem may make valve operation difficult at times. Therefore, the

valve stem must be made of a material with low thermal conductivity. While it is relatively easy to block thermal leakage along pipes, valves are likely paths of heat leakage. A foam-encapsulated 10-cm I.D. valve can leak as much as 75 kcal/h. If the same design was surrounded by a vacuum jacket, the heat leak would still run as high as 55 kcal/h. Smaller (5 cm I.D.) valves may have heat leak rates between 33 and 43 kcal/h. Materials selection for valves for liquid hydrogen service is described on pages I-95 through I-97 of [833] and page 3-83 through 3-85 of [834].

#### 6.9.2.2 Pressure Relief Valves

Because of continuous boil-off losses, pressure relief valves are an essential part of liquid hydrogen storage tanks. Ice accumulation must be avoided to keep them in working order [835].

#### 6.9.3 Liquid Level Gauges for Liquid Hydrogen Service

The liquid level in a stationary liquid hydrogen storage tank may be difficult to determine while the liquid is boiling and sloshing around. Floats cannot be used for liquid hydrogen level sensing because liquid hydrogen has such a low density. Sight glasses are out of the question because they would ice up within seconds.

Electric capacitance measurements are being used for liquid level sensing both in LOX and in LH<sub>2</sub> service installations. They measure the difference of the dielectric constant for the liquid phase and the gas phase. There are at least two different designs: one consists of a long capacitor where the fluid fills the space between the electrodes to give a continuous readout proportional to the liquid level. The other design gives incremental liquid level signals by arranging a large number of small capacitors with individual leads in an array [524].

A capacitive liquid level meter working at low temperatures measured capacitance between parallel electrodes immersed in the liquid [836]. The meter was tested for liquid nitrogen, hydrogen, and helium. The operation was successful using an AC capacitance bridge. The estimated accuracy of the instrument was better than 0.2 mm for liquid hydrogen.

An optical-fiber-based liquid level detection system for applications in cryogenic environment consisted of a multiplexed array of point liquid probes [837]. Two different designs of the probe were fabricated and tested. The multiplexing of multiple liquid probes using an optical time domain reflectometer (OTDR) device was successfully demonstrated.

A sensor consisting of a vertical linear array of 140 highly sensitive optical fiber refractometric transducers with a measurement range of 1.6 m with a resolution of up to 5 mm can be used for measuring the level of any cryogenic liquid, such as liquid oxygen or liquid hydrogen [838].

Other liquid level gauges measure the difference in the thermal diffusivity in the vicinity of a hot wire [839]. The difference is mostly due to the difference in heat ca-

capacity of the two fluids: The heat capacity of liquid parahydrogen at its natural boiling point is  $9.66 \text{ J g}^{-1} \text{ K}^{-1}$ , whereas the heat capacity of gaseous hydrogen a few degrees above the boiling point is  $12.15 \text{ J g}^{-1} \text{ K}^{-1}$ . The liquid : gas ratio of these two properties for hydrogen is 1 : 1.26 whereas the same properties for LOX are  $1.699 \text{ J g}^{-1} \text{ K}^{-1}$  for the liquid and  $0.910 \text{ J g}^{-1} \text{ K}^{-1}$  for the gas, with a gas : liquid ratio of 1 : 1.87, giving a more distinct reading.

Because of continuing boil-off, liquid level measurement is a constantly changing readout. Liquid level gauges are mounted in different positions of both ground service equipment and flight tanks. The upper sensors are supposed to make sure that a flight tank is full enough just prior to launch and to meter in the make-up flow of fresh propellant to replace evaporation losses during the countdown and launch hold [840].

The liquid level measurements based on thermal diffusivity are made with heated platinum wires. The sensor design uses a very fine platinum sensing element tensioned within a ceramic housing and brazed to gold plated contacts. The platinum wire liquid hydrogen level sensors in the Space Shuttle external tank have been the cause of many launch aborts. In spite of the fact that already four multiple sensors were installed for redundancy, quite often more than two of the sensors failed during actual use conditions in spite of the fact that the tank had been tested before it was attached to the stack. Both liquid hydrogen and liquid oxygen systems each utilized four sensors and used the same logic to trigger an engine cut-off. The 13 July 2005 mission STS-114 of Space Shuttle Discovery was scrubbed when a low-level fuel cut-off sensor for the liquid hydrogen tank inside the external tank failed a routine prelaunch check during the countdown, causing mission managers to scrub Discovery's first launch attempt. The sensor protects the Shuttle's main engines by triggering their shutdown in the event fuel runs unexpectedly low (you do not want to operate these engines on a stoichiometric or oxygen-rich mixture ratio). The sensor was one of four inside the liquid hydrogen section of the external tank [841, 842]. Similar problems were encountered during STS-115, STS-121, and STS-122, and the cause was later traced to the connector pins at the feed-through through the tank wall.

Liquid level sensing is more difficult in a zero-g condition in outer space when the liquid is floating around throughout the tank, not knowing where is up or down [843]. In an effort to develop and evaluate zero-gravity propellant quantity gaging system concepts suitable for application to large, on-orbit cryogenic oxygen and hydrogen tankage, 18 potential quantity gaging approaches were investigated for their merit and suitability for gaging two-phase cryogenic oxygen and hydrogen under zero-gravity conditions [844]. These approaches were subjected to a comprehensive trade study and selection process, which found that the RF modal quantity gaging approach was the most suitable for both liquid oxygen and liquid hydrogen applications.

Summaries of liquid level sensing for liquid hydrogen are given in [845–847]. It is difficult enough to measure liquid levels in liquid hydrogen, but it is even more difficult to measure liquid levels in slush hydrogen [848].



Platinum hot wire liquid level sensors were used in an early version of the CEN-TAUR upper stage. In looking for most probable causes of an explosion, the catalytic action of platinum in its ability to ignite oxygen/hydrogen mixtures was blamed for the explosion after suspected air intrusion into the tank. It was attempted to poison the catalytic activity of the platinum wire to eliminate it as a potential source of ignition if air should intrude into the tank again [849].

The testing of liquid-vapor detectors in zero gravity in LH2 was done in a sealed glass Dewar system to eliminate any chance of mixing H<sub>2</sub> and air [850]. Most of the tests were performed with the leads to the sensor horizontal and some were done with rapid cycling when immersing it in LH2.

Most of the instrumentation intended for density measurement of cryogenic liquids can also be used for liquid level sensing [851]. This includes dielectric constant/capacitance, resonant cavity, nuclear radiation attenuation, acoustic reflection, and forced harmonic oscillation.

The Helmholtz resonance technique was applied to a liquid level gauge for liquid hydrogen [852]. A Helmholtz resonator with a small loudspeaker was installed in a glass cryostat. A swept frequency signal was supplied to the loudspeaker, and the acoustic response was detected by measuring the electrical impedance of the loudspeaker's voice coil. The penetration depth obtained from the Helmholtz resonance frequency was compared with the true value, which was read from a scale. There are still certain problems with regards to practical applications of this instrument.

#### 6.9.4 Flow Meters for Liquid Hydrogen Service

The flow of liquid hydrogen can be measured by differential pressure measurement before and behind an orifice, by cavitating venturi or by turbine flowmeters [524]. The difficulty with turbine flow meters is that they are often accidentally overspun during the cooldown of the system when large amounts of gas rush through the lines [853].

The calibration of flowmeters with liquid hydrogen is difficult because of evaporative losses while the measurement is in progress. For calibration of flow meters for non-cryogenic fluids, it is common practice to weigh the mass of the fluid that has passed through the meter. For hydrogen this method is not very accurate because hydrogen weighs only a small fraction of the dry weight of the receiving vessel. Differential weighing methods were developed that were supposed to measure even small weight differences of hydrogen tanks with an accuracy better than  $\pm 0.3\%$ . Calibration of these flow meters can be achieved within  $\pm 0.17$  mass-% or  $\pm 0.28$  vol.-% by the method described in [854].

Many turbine flow meters for other fluids are often calibrated with water at room temperature and the readings are then extrapolated to fluids with other densities and viscosities; however, the dimensions of the flowmeters at room temperature and at operating temperature are quite different due to thermal contraction of all parts [855].

It was attempted to establish a correlation between the readings with water at room temperature and with liquid hydrogen below 20 K. The goal was an accuracy of better than 2%.

Other methods for calibration of flowmeters for liquid hydrogen in use at NASA see [856, 857]. The main difficulty during such calibrations is to maintain a constant liquid flow for a certain time to obtain a reproducible reading. In order to prevent boiling of the fluid in the line, the entire assembly may have to be immersed in a bath of liquid hydrogen. Preliminary tests of an orifice plate and a nozzle indicated that the same correlation of discharge coefficient with Reynolds number applies for liquid hydrogen as for water. Preliminary tests of several commercially available turbine-type meters showed that the calibration constant (pulses per unit volume) for liquid hydrogen may differ on average by about 1.0% from the value for water [858, 859].

A group of 14 turbine-type flowmeters of 2.5 and 4-cm nominal size were operated for 100 or more hours at an average fluid speed in the unobstructed, upstream pipe of 20 m/s for the smaller meters and 9 m/s for the larger meters [860]. Calibration shifts over a 6.1 range of calibration flow rates varied from 0.5 to 1% after 50 h of operation. It was concluded that use of ball bearings with glass-filled Teflon retainers is most likely to produce minimal calibration shift with protracted use. 100 h was recommended, depending on accuracy requirements, for flowmeters used at the fluid speeds of these tests. Other calibration methods for liquid hydrogen flowmeters were described in [861–863].

Venturi orifices can be used to both measure and stabilize the flow of liquid hydrogen. One of the throttleable venturis was capable of regulating liquid hydrogen flow in the range from 34 to 1000 L/min.

Density measurements under flow conditions are generally more difficult than a density measurement in a static tank. A two-phase density meter for the flow case should have a rapid response and a wide range in order to cover both liquid and gaseous hydrogen, and it should also present a minimal obstruction to the flow. A device that possesses these desirable features is an open-ended microwave cavity. The shift in the resonant frequency when a gas is introduced into an evacuated microwave cavity gives a measure of the dielectric constant of the gas. Hydrogen density measurements obtained by using a microwave cavity were taken under **static** conditions. The density of the hydrogen in the vessel was determined by using the microwave cavity to measure the dielectric constant and then computing the density from Böttcher's equation, and by measuring the pressure and temperature of the hydrogen and then using an equation of state for parahydrogen developed by the National Bureau of Standards to compute the density [864, 865]. Resonant frequency measurement systems were used in conjunction with an open-ended microwave cavity to continuously monitor density of liquid hydrogen in a flow system [866, 867].

A prototype slush hydrogen capacitance-type flowmeter was developed, built, and the accuracy of its output was confirmed by other flow measurements. This capacitance-type flowmeter has no moving mechanical parts and no probe in contact

with the flow stream [713, 714]. The flow velocity was calculated from the densimeter distance and delay time when the cross-correlation function of the two density signals was at a maximum.

### 6.9.5 Temperature Sensors for Liquid Hydrogen Service

Temperature measurements are not so critical for liquid hydrogen in a vented storage vessel but are very important for subcooled and slush hydrogen.

The temperature of cryogenic fluids is usually measured with resistance thermometers. A ruggedized system was developed that will, with individual calibration, provide measurement accuracy of  $\pm 0.1^\circ\text{F}$  [868]. Besides metals, also graphite can be used as the conductor in low-temperature resistance gauges [869].

### 6.9.6 Pressure Transducers for Liquid Hydrogen Service

Pressure transducers in liquid hydrogen must be capable of measuring not only static pressures, but also pressure oscillations with response frequencies up to 5 kHz [869, 870].

A summary of pressure measuring instrumentation for cryogenic service is given in [871]. All transducer types of pressure transducers, such as strain gage, capacitance, potentiometric, or piezoelectric, were included and their uses with gaseous or liquid oxygen were reviewed.

## 6.10 Density of Slush Hydrogen Measurement

A hydrogen slush density reference system calibration of field-type instruments was based on the buoyancy principle of Archimedes [872, 873]. The solids were weighed in a low-mass container so arranged that solids and container are buoyed by triple-point liquid hydrogen during the weighing process. Several types of hydrogen slush density transducers, including beta ray attenuation, gamma ray attenuation, capacitance method, microwave method for dielectric measurement and velocity of sound were developed and tested for possible use as transfer standards. The most successful transducers found were those which depend on change in dielectric constant, after which the Clausius-Mossotti function is used to relate dielectric constant and density.

A wide range of instrumentation is available to characterize slush hydrogen during its production, storage, transfer and use [874, 875]. Slush hydrogen density gages intended for the National Aerospace Plane would have had to survive extreme temperatures and needed to be protected from high temperatures during the re-entry phase of the vehicle [876, 877].

As part of a study to demonstrate the suitability of an X-ray or gamma ray probe for monitoring the quality and flow rate of slush hydrogen, mass attenuation coefficients for Cd-109 X-ray and gamma radiation in five chemical compounds were mea-

sured [878]. It was shown that the mass attenuation coefficient for the selected radiations was independent of the phase of the test fluids or phase ratios in the case of mixed phase fluids.

The density of slush hydrogen can be measured by using the phase shift that takes place when microwaves are propagated through slush hydrogen, i.e., using the change in the specific dielectric constant [714, 879]. This technique, unlike the conventional method using a waveguide and horn antenna, features a coaxial cable and patch antenna that can be used at cryogenic temperatures, leading to the development of a slush hydrogen densimeter with a high accuracy of within  $\pm 0.5\%$ .

## 6.11 Storage of Gaseous Compressed Hydrogen

It is obvious that for large rocket engines, hydrogen will be used only in the form of liquid (or possibly slushed) hydrogen; however, for small thrusters, gaseous hydrogen has been evaluated as well, also in combination with electrolysis of water on board of satellites or crewed spacecraft. The compressed gaseous hydrogen will have to be stored between the point and time of manufacture and the point and time of use in a GOX/GH<sub>2</sub> rocket engine. Various methods for storage of gaseous hydrogen have been evaluated. Compressing the gas for storage is very energy intensive and may be prohibitively expensive in some locations with only limited electrical energy. Compressed gas cylinders are heavy and bulky, but at least they do not require permanent attention like a liquid hydrogen tank.

Storage of gaseous compressed hydrogen would also be useful for non-rocket applications of hydrogen such as for fuel cells or combustion engines in automobiles. Temporary storage of gaseous hydrogen boiloff from liquid hydrogen storage facilities instead of venting it would be one way to preserve a potential energy source for later use instead of wasting it in a flare stack.

### 6.11.1 Adsorption on Metal Hydrides

Hydrogen is the ideal, clean fuel for a variety of applications, but storability is difficult. Many methods have been evaluated for storage of hydrogen at room temperature instead of under cryogenic or supercritical conditions. Iron/titanium alloys will become saturated with hydrogen and form intermetallic hydrides, causing the metal particles to swell. This process is readily reversible. There have been entire conferences devoted to hydrogen storage and books have been written on hydrogen storage [880].

### 6.11.2 Hydrogen Storage in Intermetallic Metal Hydrides

Storage of hydrogen gas adsorbed on metal hydrides allows storage at lower pressures compared to the storage of the same amount of gas by simply compressing it in an empty tank that does not contain any absorbing metal hydride; however, the release

of hydrogen from the metal hydride is endothermic and requires additional heating. Metal hydrides have been evaluated for both mobile and stationary storage installations, but if they ever find any actual use, it would be more likely for stationary installations such as fuel cell batteries. Storage of hydrogen in metal hydride tanks as part of an electrolysis/fuel cell battery for load leveling of electric utilities has been evaluated. Metal hydrides are too heavy for hydrogen storage for rocket propulsion use. Reversible adsorption of hydrogen on metal hydrides can also be used for purification of hydrogen and isotope separation.

#### **6.11.3 Hydrogen Storage in Catalyzed Complex Covalent Metal Hydrides**

Hydrogen storage in catalyzed complex covalent metal hydrides undergoing reversible reactions is unlikely to be suitable for rocket propulsion [881].

#### **6.11.4 Hydrogen Storage by Adsorption on Nanotubes**

Storage of hydrogen by adsorption on carbon nanotubes would result in some weight savings compared to storage in iron-titanium hydrides, but it is most likely not suitable for rocket propulsion.

## **7 Safety and Hazard Properties of Hydrogen**

If hydrogen fuel cell cars become more widely accepted, hydrogen will most likely be transported from large, central hydrogen synthesis and liquefaction plants to distribution centers and refueling stations in the form of liquid hydrogen. The causes and consequences of potential accident scenarios in this distribution network have been reviewed [882]. Gas accumulation and explosion hazards were well studied, including experimental studies at full scale in refueling station geometries and unconfined explosions in congested regions; however, there was little information related to gas accumulation and explosions arising from a spill of LH<sub>2</sub> in a confined space. NASA has issued safety standards for the safe handling of liquid hydrogen [883–886].

### **7.1 Liquid Hydrogen Transportation Accident History**

This section is limited to accident histories involving moving vehicles carrying liquid hydrogen. Other accidents, occurring at stationary locations, will be reviewed in Section 9 below.

A web site <https://h2tools.org/lessons> offers a timely summary of lessons learned from accidents with hydrogen. Most of the accidents involved compressed gaseous hydrogen and only very few liquid hydrogen accidents were reported in that database.

The cause and lessons learned from accidents/incidents with hydrogen in NASA operations were reviewed [887]. The cause factors for the mishaps were reviewed and it was shown that although few accidents occurred, the number could have been further reduced if the established NASA rules and regulations had been strictly followed. The report included a compilation of 96 hydrogen mishaps, a description of the accidents and their causes.

## 7.2 Fire Hazards of Hydrogen

The following sections on ignition, combustion, explosion, and detonation of hydrogen in mixtures with air or oxygen are dealing with more academic studies, not directly relating to application of hydrogen in rocket engines. Many of these studies were motivated by applications of hydrogen as an energy storage medium other than in rocket propellants.

There is an international professional society exclusively devoted to the safety of hydrogen use [888]. The mission of the International Association for Hydrogen Safety, also called “HySafe,” is to facilitate the international coordination, development and dissemination of hydrogen safety knowledge by being the focal point for hydrogen safety research, education and training. Table 49 is a comparison of physical and safety properties of hydrogen with those of methane and gasoline.

There are numerous studies of the hazards associated with the production and handling of liquid hydrogen, and the repeated message is that ignition sources must be avoided anywhere near where hydrogen is stored and transferred [889, 890]. A quantity-distance table for the storage of liquid hydrogen was developed. The vaporization of liquid hydrogen from a surface was treated as a problem in heat transfer theory. Two extreme cases were considered: **(1)** the transfer of heat occurs at constant temperature drop between the boiling liquid and the hot surface, and **(2)** the transfer of heat is limited by the rate at which it can flow to the surface from a hot insulating medium. The available data indicated that the former case **(1)** is applicable when vaporizing from a conducting surface and, initially, when vaporizing from an insulating medium; the latter case **(2)** is applicable after initial flash vaporization has occurred from the insulating medium. The vaporization rate determines in part the rate at which flammable hydrogen vapor-air mixtures are formed above a spill area; however, the rates at which heat is transferred to the vapor, and air is brought in contact with it also are of importance. The distribution of flammable mixtures above a spill area was determined experimentally. In general, flammable mixtures were found to be both above and within the visible vapor cloud.

Federal regulations applicable to the manufacture and maintenance of hydrogen equipment and to the distribution of gaseous and liquid hydrogen in the United States were summarized and presented in a table of regulatory references [891]. A similar

**Table 49:** Safety properties of hydrogen in comparison to methane and gasoline.

| Property                                          | Units                               | Hydrogen     | Methane      | Gasoline   |
|---------------------------------------------------|-------------------------------------|--------------|--------------|------------|
| Triple-point pressure                             | atm                                 | 0.0695       | 0.1159       | —          |
| Triple-point temperature                          | K                                   | 13.803       | 90.68        | ~180–220   |
| Normal boiling point (NBP)                        | K                                   | 20.268       | 111.632      | ~310–478   |
| Critical pressure                                 | atm                                 | 12.759       | 45.387       | 24.5 to 27 |
| Critical temperature                              | K                                   | 32.976       | 190.56       | 540 to 569 |
| Density at critical point                         | g/cm <sup>3</sup>                   | 0.0314       | 0.1604       | 0.23       |
| Density of liquid at triple point                 | g/cm <sup>3</sup>                   | 0.0770       | 0.4516       | —          |
| Density of solid at triple point                  | g/cm <sup>3</sup>                   | 0.0865       | 0.4872       | —          |
| Density of liquid at NBP                          | g/cm <sup>3</sup>                   | 0.0708       | 0.4226       | ~ 0.70     |
| Density of vapor at NBP                           | g/cm <sup>3</sup>                   | 0.00134      | 0.00182      | ~0.0045    |
| Heat of fusion                                    | J/g                                 | 58.23        | 58.47        | 161        |
| Heat of vaporization at NBP                       | J/g                                 | 507.39       | 602.44       | —          |
| Upper heat of combustion                          | kJ/g                                | 141.86       | 55.53        | 48         |
| Lower heat of combustion                          | kJ/g                                | 119.93       | 50.02        | 44.5       |
| Viscosity of liquid at NBP                        | g cm <sup>-1</sup> s <sup>-1</sup>  | 0.000132     | 0.001130     | 0.002      |
| Thermal conductivity of liquid at NBP             | mW cm <sup>-1</sup> K <sup>-1</sup> | 0.99         | 1.86         | 1.31       |
| Surface tension at NBP                            | N/m                                 | 0.00193      | 0.01294      | 0.0122     |
| Limits of flammability in air, upward propagation | Vol-%                               | 4.0 to 75.0  | 5.3 to 15.0  | 1.0 to 7.6 |
| Stoichiometric composition in air                 | Vol-%                               | 29.53        | 9.48         | 1.76       |
| Minimum energy for ignition in air                | mJ                                  | 0.02         | 0.29         | 0.24       |
| Autoignition temperature                          | K                                   | 858          | 813          | 501 to 744 |
| Burning velocity at 101 kPa and 293 K             | cm/s                                | 265–325      | 37–45        | 37–43      |
| Detonation velocity at 101 kPa and 293 K          | km/s                                | 1.48 to 2.15 | 1.39 to 1.64 | 1.4 to 1.7 |
| Vaporization rate of liquid pools without burning | cm/min.                             | 2.5 to 5.0   | 0.05 to 0.5  | 0.005      |
| Burning rate of spilled liquid pools              | cm/min.                             | 3 to 6.6     | 0.3 to 1.2   | 0.2 to 0.9 |

table of references was presented for non-mandatory standards and guidelines pertinent to hydrogen safety and hydrogen facilities/equipment specifications. These two tables summarized information that had been published in industry, universities and government agencies for the safe production, storage, and handling of hydrogen.

NASA has developed a Hydrogen Systems Safety Standard, which establishes a uniform process for hydrogen system design, materials selection, operation, storage, and transportation of hydrogen [305]. This is an expanded version of the NASA Hydrogen Safety Handbook originally prepared by P.M. Ordin. The guidelines include suggestions for safely storing, handling, and using hydrogen in gaseous (GH<sub>2</sub>), liquid (LH<sub>2</sub>), or slush (SLH<sub>2</sub>) form, whether used as a propellant or non-propellant. The safety standard handbook contains 9 chapters detailing properties and hazards, facility design, design of components, materials compatibility, detection, and transportation. The appendices include assessment examples, scaling

laws, explosions, blast effects and fragmentation, codes, standards, NASA directives, design of pressure relief devices along with a list of tables and figures, abbreviations, a glossary, and an index for ease of use. There is also a companion document, Safety Standard for Oxygen and Oxygen Systems (NSS1740.151996). See also [892].

While initially prompted by the use of liquid hydrogen as a rocket propellant, the experience gained will in the future benefit the average consumer through the planned use of hydrogen as automotive (mostly compressed hydrogen, not liquid hydrogen) fuel and possibly even airplane fuel.

### 7.3 Liquid Hydrogen Spill Hazards

If liquid hydrogen is accidentally spilled, all potential sources of ignition must be removed and the spill site should be evacuated. One can then observe from a safe distance until all hydrogen is evaporated and it has warmed sufficiently that it will rise in air like a balloon [890, 893].

One unit volume of LH<sub>2</sub> converts to 845 times its volume of gas (at room temperature) as it evaporates and 1 kg of LH<sub>2</sub> creates a cloud of 11.1 m<sup>3</sup> of GH<sub>2</sub> at room temperature.

If a liquid hydrogen leak or spill occurs, a cold hydrogen cloud could flow horizontally for some distance or even downward, depending on the terrain and weather conditions. Cold hydrogen will travel some distance before it has warmed enough that it becomes buoyant in air.

Various investigations of the occurrence of detonations in the case of spillage and evaporation of liquid hydrogen have been carried out but they did not yield an unambiguous answer to the question what conditions lead to detonable mixtures in air. There have been studies of the laws governing the formation and floating buoyancy of a cloud of air/hydrogen mixtures when there are instantaneous emissions of small quantities of gaseous hydrogen, trying to calculate the TNT equivalent of such explosions, and the laws of combustion when evaporation takes place and the jet escape of hydrogen under pressure from pipe systems. There have been estimates of the coefficients of turbulent diffusion and of the velocities of uplift of air/hydrogen mixtures and the mass of hydrogen capable of taking part in the detonation when there is an instantaneous spillage and evaporation of liquid hydrogen. Only few measurements of the concentration and temperatures for the case of prolonged evaporation of hydrogen from spilled pools had been made until 1981. The distribution of hydrogen concentrations was calculated in an axisymmetric stationary regime of evaporation of liquid hydrogen including the convective uplift of turbulent vortices in free space [894].

The evaporation rates of liquid hydrogen spilled onto the ground were measured in laboratory tests [895]. To simulate the ground where the spill occurred, samples of concrete, dry sand, and wet sand layers were placed into a see-through vacuum-insulated cylindrical glass vessel. Based on the temperature variations within the layer and



detailed observation through the side of the vessel, the heat transfer modes controlling the evaporation phenomenon were visualized. When a wet sand layer was used, the liquid hydrogen did not soak into the layer, because the frozen layer of water between the liquid and the sand layer acted as a barrier. When a concrete layer was used, the liquid vaporized above the layer. In these cases, the evaporation rates were inversely proportional to the square root of the time, except in the early stage just after the start of vaporization. This relationship could be predicted by a simple calculation of heat conduction within the layer. When a dry sand layer was used, liquid hydrogen did not soak into the dry sand layer, and the evaporation mechanism seemed to be the same as that for the wet sand layer, because the air contained within interparticle cavities in the dry sand layer solidified at the boiling point of liquid hydrogen and clogged the pores.

The most important issues to be resolved in the safety assessment of accidental massive LH2 spills are the position, the size, and the hydrogen concentration of the vapor clouds formed after the spills. The multi-phase hydrodynamics analysis code (CHAMPAGNE) was used to calculate the behavior of hydrogen during the experiment in which 5100-L quasi-instantaneous LH2 spills were performed at the NASA White Sands Test Station [896].

In a study of worst-case accident scenarios with liquid hydrogen tanks, explosions of 125-L liquid hydrogen tanks with different fill pressures and fill levels were cut open by a linear shaped charge, which immediately ignited the released liquid and gas [897]. The fireball spread to 75% of its maximum size within 0.2 s. After 1–2 s the fireball began to separate from the ground level and rose to 10–20 m within another 1–2 s. The whole event lasted 3–4 s. The radiation emitted from the fire was measured.

A 3-D time dependent finite volume code was used to model liquid hydrogen release experiments [898]. The experiments were performed by Batelle Ingenieurtechnik for the Federal Institute for Materials Research and Testing (Bundesanstalt für Materialforschung und Prüfung, BAM), Berlin and they mainly deal with LH2 near ground releases between buildings. The simulations illustrated the complex behavior of LH2 dispersion in the presence of buildings, characterized by complicated wind patterns, plume back flow near the source, dense gas behavior at near range and significant buoyant behavior at the far range. The simulations showed the strong effect of ground heating in the LH2 dispersion. The model also revealed major features of the dispersion that had to do with the “dense” behavior of the cold hydrogen and the buoyant behavior of the “warming-up” gas as well as the interaction of the building and the release wake. Such a predicted behavior was in qualitative and even quantitative agreement with the experiment.

In earlier work a 3D time-dependent fully compressible CFD code was applied against large-scale LH2 release experiments in the vicinity of buildings. Subsequently the code was applied to simulate large-scale LH2 spill tests in open, unobstructed environments [899]. A series of simulations were performed to investigate the effects of the source model (jet or pool), the modeling of the earthen sides of the pond around

the source and the inclusion of a contact ground heat transfer. The predicted hydrogen concentrations (% by vol.) were compared against the experimental data at the available sensor locations. In addition, the predicted structure of the concentration field was compared against the experimental, which was originally derived from temperature measurements. Modeling the source as a two-phase jet pointing downwards, including the modeling of the earthen sides of the pond as a fence and the contact heat transfer to the ground gave the best agreement with respect to experimental behavior.

The understanding of cryogenic pool spreading and its vaporization is require to analyze an accident sequence with an inadvertent spillage of LH<sub>2</sub>, e.g., after failure of a transport container tank or the rupture of a pipeline [900]. This stage of an accident scenario is the source term for the subsequent analysis steps of atmospheric dispersion and, in the presence of an ignition source, the combustion of the hydrogen-air vapor cloud. A computer model has been developed which was able to simulate the spreading and vaporization of a cryogenic liquid under various conditions such as different grounds (solid, water). It was based on the so-called shallow-layer differential equations taking into account physical phenomena, such as ice formation if the cryogen is spilled on a water surface. One can compare an LH<sub>2</sub> spillage to the corresponding release of other cryogens, such as liquid natural gas or liquid oxygen.

Experiments were made to investigate spills of liquid hydrogen at a rate of 60 L/min. Measurements made on both unignited and ignited releases included concentration of hydrogen in air, thermal gradient in the concrete substrate, liquid pool formation, and temperatures within the pool, flame velocity within the cloud, thermal radiation, IR and visible spectrum video records and sound pressure measurements [901]. The tests which impinged hydrogen onto the ground all produced a pool of liquid once the ground had cooled sufficiently, usually about 2 minutes into the release. In addition, a large solid deposit, which had the appearance of “snow,” was produced. Both the liquid and the “snow” persisted for several minutes after the release ended. The thermocouple measurements showed a step near 77 K in the temperature traces as the temperature increased after the LH<sub>2</sub> release had ended. This was indicative of the melting and boiling of the condensed air. The release of liquid hydrogen at a rate consistent with the failure of a 1-in. transfer line produced a flammable mixture at least 9 m downwind of the release point.

The hazards arising from an accidental release of hydrogen from cryogenic liquid storage or compressed gas storage tanks and the subsequent damage consequences were compared, including hydrogen cold cloud, fire ball, jet fire, flash fire, and vapor cloud explosions [902]. The severity of cold effect, thermal effects, and explosion overpressures were evaluated using certain damage criteria. Results showed that for instantaneous releases of liquid hydrogen, the sequence of damage effect distances is: vapor cloud explosion>flash fire>cold cloud> fireball. For continuous releases of liquid hydrogen, the order of damage effect distances is: vapor cloud explosion>jet fire>flash fire>cold cloud. The vapor cloud explosion is the leading consequence of both instantaneous and continuous releases and may be used for the determination

of safety distances of a liquid hydrogen tank. The damage effect distances of liquid hydrogen tanks were compared with those of compressed hydrogen storages with equivalent mass. Results showed that the liquid hydrogen storage may be safer than 70 MPa gaseous storage in case of leak scenario but may be more dangerous than 70 MPa storage in case of a catastrophic rupture.

Several CFD models for predicting the movement of liquid releases, both two-phase flashing jets and pool spills, have been developed [903, 904]. The release of liquid hydrogen in the atmosphere may induce partial condensation or even freezing of the oxygen and nitrogen present in the air. In computations of two-phase jets it was assumed that the dispersed and continuous phases are in thermodynamic and kinematic equilibrium. A pool model was used to compute the spreading and vaporization of liquid hydrogen depositing on the ground and also the partial condensation or freezing of oxygen and nitrogen was taken into account. Simulations with these models were compared against selected experiments.

The different boiling regimes film boiling, transition boiling, and nucleation boiling after a release of liquid hydrogen into a pool were modeled by means of a code for wall heat transfer evaporation, which was implemented in a commercial CFD code and validated against LH2 spill experimental data [905].

A review of the data and detailed modeling of cryogenic releases in the scientific literature showed a dearth of validated models, or appropriate data to validate these models [906]. Challenges associated with modeling cryogenic hydrogen releases stem from the multi-phase flows and phase change behaviors encountered during these releases. In a reduced-order model that breaks stream-wise flow regimes for cryogenic releases into discrete zones, zones furthest from the release are expected to perform well where the jet has warmed to temperatures more characteristic of gaseous releases; however, in the zones near the release, complex thermodynamic state modeling and multi-phase flows require assumed models for relevant behavior, that had not yet been properly validated. A cryogenic hydrogen integral jet and plume model, COLDPLUME, has been updated for choked flows for cryogenic fluids.

A 3D model has been built for the simulation of liquid hydrogen spills on the ground, where the source of LH2 was modeled as a jet and placed near the ground [907]. The model was validated by the experimental results from the large-scale test of LH2 spill carried out by NASA in New Mexico in 1981, and then used to analyze the vaporization time of LH2 and the spreading range of gaseous hydrogen. The variation of hydrogen concentration distribution at different time nodes and different environmental conditions was presented as a function of wind velocity, wind temperature, and ground temperature. The flammable vapor cloud was found to undergo three different evolution stages, namely the initial stage, the quasi-steady spread stage, and the disappearance stage [908]. The composition differences between the cloud and undisturbed air play a major role in vertical turbulent fluctuation, while the wind will dominate with the increment of height in streamwise direction.

A 3D CFD model for large-scale liquid hydrogen spills was developed and validated by comparing it to the experiments carried out by NASA [909]. The effect of humidity on the development of hydrogen vapor cloud was quantified with the modified expressions of a model accounting for the phase changes of water and hydrogen. The results showed that the numerical prediction is more consistent with the experiment considering the presence of air humidity. The condensation of water in the atmosphere increases the buoyancy of the vapor cloud and promotes the diffusion of the cloud in a vertical direction. The dimension of the cloud in a streamwise direction changes little under conditions of different humidities due to the balance between the height-dependent wind speed and the induced buoyancy. The scope of visible cloud indicated by the condensed water vapor expands with the increasing air humidity, and still lies within the flammable domain when the relative humidity is approaching 75%.

#### 7.4 High Pressure Liquid Hydrogen Leak Jet Release Hazards

A model for computing hydrogen dilution distances for cold hydrogen releases was presented for leaks of room temperature gas and 80K high-pressure hydrogen gas [910]. The model accounted for a series of transitions that occurs from a stagnate location in the tank to a point in the leak jet where the concentration of hydrogen in air at the jet centerline has dropped to 4% by volume. The leaking hydrogen is assumed to be a simple compressible substance with thermodynamic equilibrium between hydrogen vapor, hydrogen liquid and air. It is assumed that further downstream the jet develops into an atmospheric gas jet where the thermodynamics are described as a mixture of ideal gases (hydrogen-air mixture). Simulations were presented for dilution distances in underexpanded high-pressure leaks from the saturated vapor and saturated liquid portions of a liquid hydrogen storage tank at 10.34 bar gauge (150 psig).

Venting of liquid hydrogen from lower stage propulsion systems can lead to two-phase flows, evaporation of the fuel and condensation of air [911, 912]. In a study of the non-equilibrium behavior associated with the injection of two-phase hydrogen jets into air, the air was treated as a binary mixture that condenses in equilibrium. The condensed hydrogen, however, was assumed to form a dilute suspension of spherical particles that evaporate at a finite rate. This partial equilibrium process was considered to take place under constant pressure in a one-dimensional inviscid stream tube configuration.

The hazard of cryogenic and combustible liquid rocket fuels (hydrogen and methane) leakage caused by spontaneous damage to tanks or rupture of pipelines is a potential problem for both applications. Numerical simulations have been performed to predict the differences in leakage and dispersion rates of the two fuels [913]. Based on liquid hydrogen release tests, a mixture four-phase flow model

considering the liquid hydrogen and air phase transitions has been developed. The liquid phase movements in the near field, combustible clouds and cold effect clouds movement in the far field were investigated. The Froude number is a dimensionless number defined as the ratio of the flow inertia to the external gravity field. With Froude number increases from 0.47 to 3.72, liquid hydrogen represents a downward trend while liquid methane shows a downwind trend. For combustible clouds, the movements of hydrogen are larger than those of methane in both downwind and vertical direction on a quasi-stable state. For cold effect clouds, the dispersion of methane is greater than that of hydrogen in Froude numbers of 0.47, 0.93, or 1.86, but then smaller in a larger Froude number of 3.72.

## 7.5 Hydrogen Plume Dispersion in the Atmosphere

Hydrogen spill and vapor cloud dispersion experiments were performed by NASA to obtain basic information regarding the physical phenomena governing the dispersion of flammable clouds formed as the result of spills of large quantities of liquid hydrogen [914, 915]. The experiments consisted of ground spills of up to 5.7 m<sup>3</sup> (1500 gallon) of liquid hydrogen, with spill durations of approx. 35 s. Instrumented towers, located downwind of the spill site, gathered data on the temperature, hydrogen concentration and turbulence levels as the hydrogen vapor cloud drifted downwind. Visual phenomena were recorded by motion picture and still cameras. Preliminary results of the experiments indicated that, for rapid spills, thermal and momentum-induced turbulences cause the cloud to disperse to safe concentration levels and become positively buoyant long before mixing due to normal atmospheric turbulence becomes a major factor. An adiabatic mixing model has been developed to deduce hydrogen-air mixture ratios for temperature measurements obtained within the cloud formed by liquid hydrogen spills. The model should be a useful tool for describing the hydrogen concentrations within the plume.

A large-scale experiment was set up to study the mechanisms of the formation of an unconfined gas cloud resulting from liquid hydrogen spillage and the associated mixing process and turbulence effects [916]. Dispersion tests were performed with cryogenic helium instead of hydrogen, presenting dispersion characteristics similar to liquid hydrogen (buoyancy). Flow rates up to 3 kg/s have been investigated and the instrumentation allowed the observation and quantification of buoyancy effects including internal turbulence. Those results constitute an original set of data which can be used as a basis for the development of dispersion software and reinterpretation of other existing databases resulting from LH2 spill tests.

Experiments and simulations were performed to evaluate the potential hazards of a liquid hydrogen spill accident [917, 918]. A CFD code was used to simulate the liquefied hydrogen spill experiments conducted. In these tests, LH2 was spilled at a fixed rate of 60 L/min. in several directions and for several durations. Factors that influ-

enced the vapor dispersion under cryogenic release conditions were: the air humidity, the wind direction, and the slip effect of droplets formed by both the cryogenic liquid and the condensation of air humidity. Two horizontal releases, one along the ground and the other one at a distance above the ground, and one vertical release were examined with spill rates of 60 L/min. The presence of humidity in the atmosphere has a distinct effect on the vapor dispersion. When humidity is present and it is cooled, it condenses and freezes due to the low prevailing temperature ( $\sim 20$  K near the release), and releases heat. In addition, during the release hydrogen droplets are formed due to mechanical and flashing break-up, and water droplets and ice crystals are formed due to humidity condensation. Two models were tested: a hydrodynamic equilibrium model, which assumed that the phases are in thermodynamic and kinematic equilibrium and the non-hydrodynamic equilibrium model (slip model), which assumed that the phases are in thermodynamic equilibrium but they can obtain different velocities. The computational results were compared with experimental measurements, and it was concluded that humidity along with the slip effect influences the buoyancy of the cloud to a great extent. The effect of each variable on the rate and shape of vapor cloud dispersion was examined.

A non-homogeneous equilibrium model (NHEM) was used to model flammable cloud dispersions following liquid hydrogen spills under various weather conditions and validated by a large scale LH2 spill experiment [919]. The predicted data were in good agreement with the experiment. Three primary questions of the hydrogen dispersion process were addressed: the maximum spreading range, the minimum distance above the ground, and the duration time of the flammable cloud in the atmosphere. Three major influence factors were selected to simulate various weather conditions, including ambient temperature (coupled with ground temperature), wind speed, and atmospheric pressure. The hydrogen dispersion can be increased with increased wind speed and be impeded by increased atmospheric pressure. The hydrogen dispersion process in four seasons of a year appears to follow a different trend.

The flashed vapor fraction at the pipe exit of liquid hydrogen leaking into air at sea-level pressure was estimated assuming isenthalpic expansion combined with the NIST equation of state [920]. Modeling the condensation of ambient air humidity and air components and imposing transient wind profile were part of a homogeneous equilibrium model (HEM) and then compared to the NHEM to account for slip effects of the non-vapor phase. A comparison of the momentum slip model with the algebraic slip model showed that the latter overestimated the slip velocity for large particles and thus it should be used only with precaution.

One study revealed that humidity can reduce the longitudinal distance of the zone within the lower flammability limit (LFL) [921]. Simulations with liquid methane release have been performed and compared to the liquid hydrogen simulations in order to identify the differences in the behavior of the two fuels as far as the humidity effect is concerned. It was shown that in methane spills the buoyancy effect in presence of humidity is smaller than in hydrogen spills and it can be considered almost negligible.

The dilution of hydrogen vapor clouds formed by liquid hydrogen spills under different conditions of spill amount, spill rate, and liquid mass fraction were numerically investigated by three-dimensional CFD simulations [922]. Time variation of the moment of maximum hydrogen concentration was most sensitive to the liquid mass fraction, followed by the spill rate, and finally the spill amount. The dilution process was nearly unaffected by the spill amount. With the increment of spill rates, the dilution speed first decreased and then remained approximately unchanged, which can be attributed to the combined effects of the gaseous hydrogen generated per unit time and the source disturbances generated by the spill and evaporation process. The turbulence induced by the evaporation of liquid hydrogen promotes the mixing and dilution processes, while the temperature drop in the ground and the ambient air due to liquid evaporation has little influence on the overall dilution of the vapor cloud.

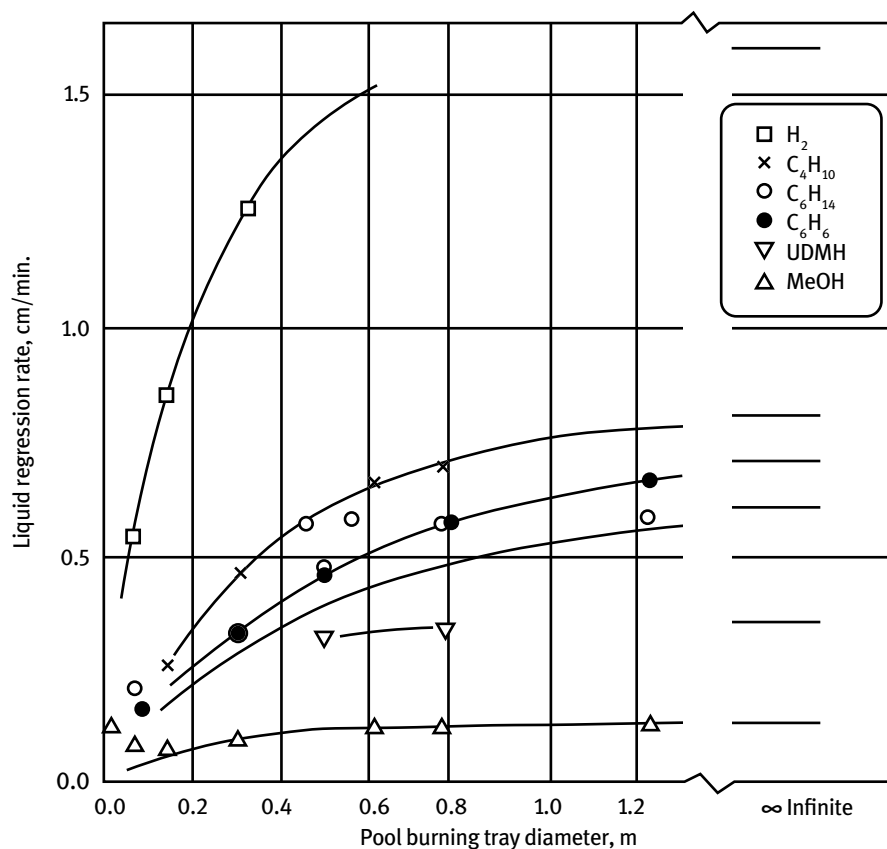
Venting of hydrogen to depressurize the receiving storage tanks is a routine part of the LH2 delivery and transfer process. The behavior of cold hydrogen plumes has not been well characterized because of the sparsity of empirical field data, which can lead to overly conservative safety requirements from the government regulators [923]. A prototype hydrogen analyzer was field deployed during an actual LH2 venting process and the data were used to characterize the hydrogen plume formed during LH2 storage tank venting. Hydrogen above the LFL was detected as much as 2 m lower than the release point, which is not predicted by any of the existing models. Some hydrogen was detected at ground level, although only at levels below the LFL.

## 7.6 Open Air Buoyancy of Hydrogen Flames

Hydrogen gas by itself and in the absence of flames will rise in air as soon as it is warm enough. If a bubble of hydrogen gas is ignited, the updraft caused by hot gases will accelerate the upward transposition of the hydrogen cloud and the surrounding flame. The average burning rate and expansion of burning hydrogen clouds was studied by rupturing hydrogen-filled balloons and igniting the released cloud of gas [924]. The maximum burning rate of the cloud was 2.5 m/s and occurred near stoichiometric dilution near the cloud center. The maximum flame propagation rate (19 m/s) occurred at higher hydrogen concentrations.

## 7.7 Pool Burning of Liquid Hydrogen Spills

In controlled spill and pool burning experiments with liquid hydrogen in containers with different diameters it has been noted that liquid hydrogen pools burn much faster than any other spilled rocket propellant or commercially used fuel (Figures 64 and 65) [889, 925, 926].



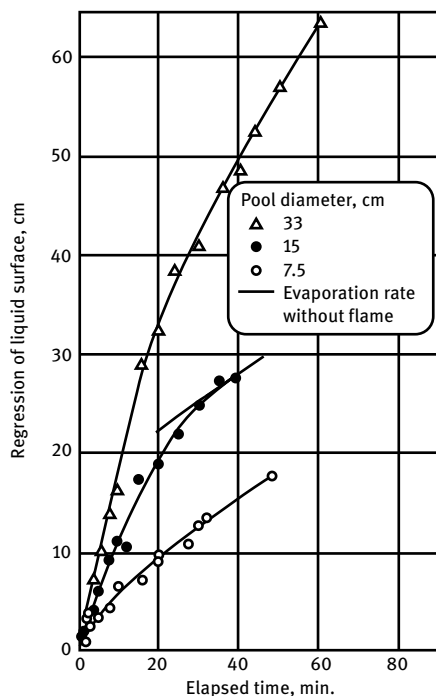
**Figure 64:** Dependence of pool burning rate on pool diameter. (Reproduced and modified from [889].)

When conducting this type of experiment, one must make sure that the spilled liquid is ignited before air has a chance to condense on top of it and form explosive mixtures. The effect of air condensation on pool burning is described at the end of this section.

Pool burning tests with spilled liquid hydrogen and immediate ignition led to the following conclusions [497, 499, 927]:

1. Unconfined mixtures of air and hydrogen will not explode, but burn quietly if the ignition is by a spark or a flame.
2. The heat radiation of an air/hydrogen flame is only 1/10 of the radiation intensity of a hydrocarbon flame. Firefighting crews can operate closer to a hydrogen fire without getting scorched by heat radiation. A hydrogen fire does not expand as rapidly to adjacent combustible structures as a hydrocarbon fire. A pool of burning liquid hydrogen is consumed in 1/10 of the time of a pool of gasoline or kerosene of the same volume.





**Figure 65:** Regression of liquid surface of liquid hydrogen burning in metal Dewars of different diameters. (Reproduced and modified from [889].)

The emissivity of a hydrogen flame is only 0.09 compared to the emissivity of a black body radiator which is close to 1.0. Hydrogen escaping from a pipe or at the top of a flare stack gives a cleaner, nearly invisible flame than liquid hydrogen spilled on the ground and burning with entrained contaminants. Radiation measurements showed that persons could approach a large hydrogen fire for 30 s to as close as 54 m without suffering heat burns [497, 499]. For kerosene JP-4 the safety distance would have to be 205 m, 4 times as much as for hydrogen. Tests with liquid hydrogen poured into a pan and delayed ignition showed that initially air does not condense into liquid hydrogen because the boiling liquid is surrounded by a cushion of cold hydrogen gas. Atmospheric moisture absorbs thermal energy radiated from a hydrogen fire and can reduce the radiation values recorded from laboratory experiments in dry air.

In order to measure the hydrogen spill hazards, 4.7 L of liquid hydrogen was poured into a concrete-lined basin and ignited after different delay times. In each case the gas above the pool and then the liquid burned without detonation. Pressure gauges showed some pressure build-up in deep pools that were surrounded by four walls. The pressure was higher than with a pool on flat ground. It was recommended to place hydrogen storage facilities on flat terrain without confining walls to avoid overpressure during combustion. The regression rate due to evaporation (not burning) of liquid hydrogen is initially 13–18 cm/min. After about 3 min. and after the walls of the pool have cooled down, the regression rate is only 4 cm/min. If liquid

hydrogen is poured onto porous ground or onto a bed with river pebbles instead of into a concrete-lined basin, it evaporates much faster.

In a series of LH2 spill tests, spills were first investigated experimentally as large-scale unignited spills of LH2 at a rate of 60 L/min by measuring the concentration of hydrogen in air, thermal gradients in a concrete substrate, liquid pool formation and temperatures within the pool [928]. Later, three different conditions of jet-fires in high and low wind conditions, “burn-back” of ignited clouds and secondary explosions after “burn-back” representing a realistic ignited spill of LH2 were tested and flammability limits of an LH2 vapor cloud, flame speeds through an LH2 vapor cloud and radiative heat levels after ignition were measured [929]. An attempt was made to estimate the overpressure of an explosion that occurred during one of the LH2 releases.

## 7.8 Firefighting of Liquid Hydrogen Fires

It is extremely difficult to extinguish liquid hydrogen fires. The first step should be to interrupt the source of hydrogen if it is a local leak.

Carbon dioxide fire extinguishers can knock down hydrogen fires only if the carbon dioxide is applied very rapidly so that it cuts off the supply of air. When feeding CO<sub>2</sub> into an air/hydrogen fire there is the potential that some of the CO<sub>2</sub> will be reduced to CO which then constitutes an inhalation toxicity hazard.

Applying water to a hydrogen fire has very little effect. Water is only useful to cool the surrounding area and prevent the spread of the fire. The hydrogen flame itself cannot be extinguished by water spray. It has been recommended to use a combination of nitrogen-filled aqueous foam and bicarbonate-filled dry powder fire extinguishers to fight hydrogen fires [930, 931]. Many chemicals have been evaluated as potential inhibitors for air/hydrogen explosions. One of the chemicals tested was iron pentacarbonyl but this compound is extremely toxic and will never be used. Confined liquid hydrogen combustion was effectively suppressed by air-halogenated hydrocarbon mixtures with 13–65% of inhibitor.

Fighting hydrogen fires is made difficult by the fact that hydrogen flames are not very luminous and are hard to see during daytime (see section “Radiation from Hydrogen Flames”). It has been recommended to equip firefighting crews with night vision goggles in which the infrared emission of hydrogen flames is better visible [932].

## 7.9 Ignition Hazards in the Vicinity of Hydrogen Facilities

As the Hindenburg dirigible disaster and other industrial accidents have shown, hydrogen in air has a very low ignition energy threshold and is quite susceptible to ignition by electrostatic discharges. For this reason, electrostatic accumulation of electric charges in the vicinity of hydrogen operations in air must be avoided. Electrostatic dis-

charges, even small ones like you encounter when bending down to the water drinking fountain after walking on synthetic fiber carpet, are sufficient to ignite a hydrogen fire or even a hydrogen explosion. Electrostatic charges may also accumulate when liquid hydrogen flows through pipes or if gaseous hydrogen is vented to the air [326].

Because of the very low electrical conductivity of hydrogen electrostatic charges in liquid hydrogen in an electrically insulated tank last a thousand times longer than in kerosene, but they do not reach as high values because the breakthrough voltage in hydrogen is lower than in kerosene: Hydrogen 10 V/cm; kerosene JP-4 800 V/cm. Electrostatic charges develop in particular during two-phase flow of liquid hydrogen through a line. This has also been observed with other cryogenic liquids.

In order to prevent the build-up of electrostatic charges and the potential for accidental ignition, all ground service equipment for liquid and gaseous hydrogen should be grounded in accordance with NFPA regulations.

### **7.9.1 Accidental Ignition Hazards**

Most people handling hydrogen and other flammable gases are fully aware of the ignition hazard due to electrostatic discharges. Only few people are aware of the potential of self-ignition if high-pressure hydrogen gas escapes into air.

Pressurized hydrogen released into the air can undergo spontaneous ignition [933]. Previous research had been limited to conduct tests at the pressure conditions below about 200 bar due to the experimental difficulties and danger. Experimental studies were now conducted to observe the spontaneous ignition of hydrogen released at pressures above 200 bar. The ignition and flame were detected using a photodiode inside the tube and a high-speed camera outside the tube. The spontaneous ignition limits were established with various internal tube diameters and lengths of the tube at the high-pressure conditions.

### **7.9.2 Electrostatic Discharge Sensitivity of Hydrogen**

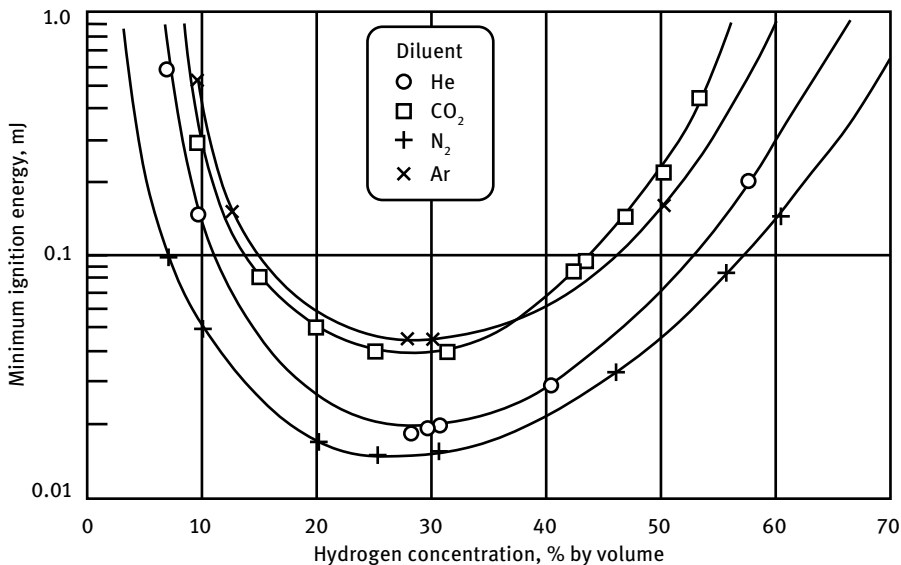
The minimum spark energy required for ignition of hydrogen in air is about an order of magnitude less than that for methane or gasoline. A discharge of static electricity from a human body may be sufficient to ignite any of these fuels in air. Sparks with 10 mJ energy may be produced in such electrostatic discharges from well-insulated bodies walking on carpets or coming into contact with moving machinery. The minimum ignition energy of hydrogen in air is 0.017 mJ, compared to 0.274 mJ for methane in air.

Because of the very low ignition energy requirements and wide range of flammability for mixtures of hydrogen and air (or oxygen), extreme care must be taken to remove all possible ignition sources from hydrogen facilities. Special concern is about the potential charge build-up in storage tank and transfer equipment during the flow of liquid hydrogen and charge build-up during venting of boil-off gases from missile and storage tanks [326]. The friction of high-pressure hydrogen gas exiting (venting)

into air can build up sufficient static charges to ignite the jet of gas. This mechanism of accidental ignition is reviewed in Section 7.9.2.3 “Spontaneous Ignition of High-pressure Hydrogen Gas Leaks.”

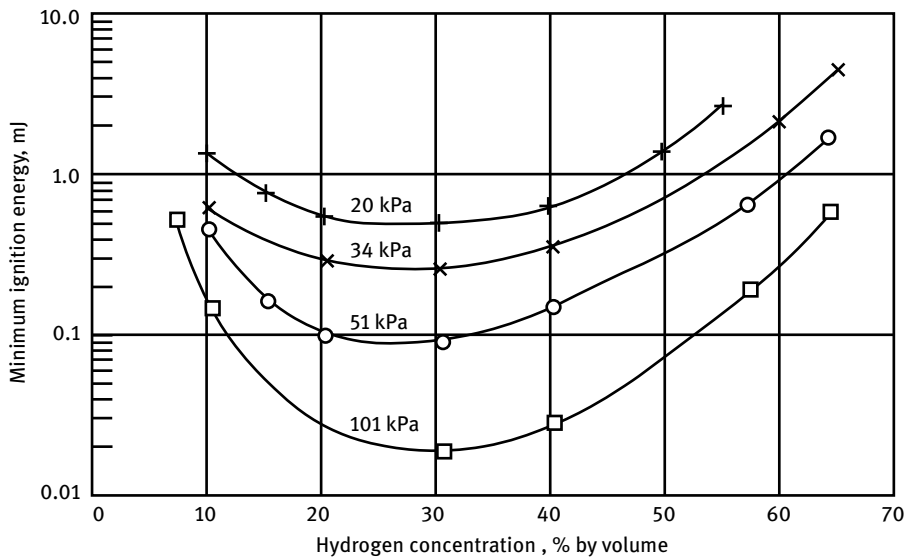
### 7.9.2.1 Minimum Ignition Energy of Air/Hydrogen Mixtures

The minimum ignition energies for hydrogen in air and in mixtures of 21 vol.-% oxygen, 79 vol.-% diluent (other than nitrogen) at 101 kPa (14.7 psia) are shown in Figure 66 from [934]. The lowest ignition energies occur for stoichiometric concentrations of hydrogen (29 Vol.-% in these mixtures). The ignition energies in Figure 66 are lowest for diluents with small heat capacities and low thermal conductivities, and highest for helium, which has a relatively high thermal conductivity. The minimum ignition energy for hydrogen in oxygen is significantly lower than for hydrogen in air. The lowest value found in the literature is  $1.2\mu\text{J}$  [935]; the lowest value for hydrogen in air is  $19\mu\text{J}$ .

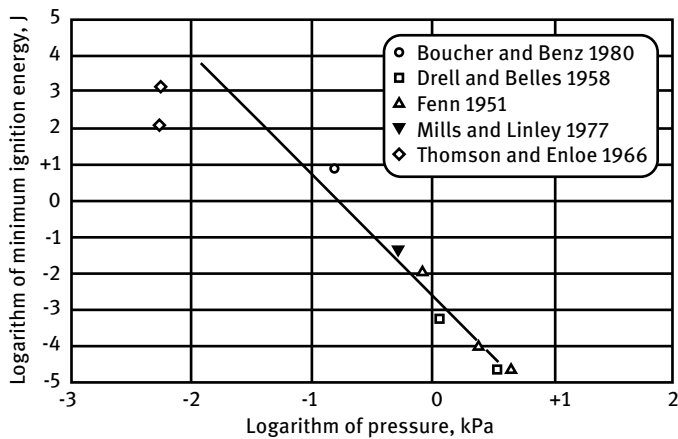


**Figure 66:** Minimum ignition energies for hydrogen in air and in mixtures of 21 vol.-% oxygen, 79 vol.-% diluent gas. (Reproduced and modified from [934].)

Figure 67 shows the effect of pressure on the minimum ignition energy of hydrogen in air. The minimum required ignition energy increased with decreasing pressure. Plotting the logarithm of the minimum required ignition energy versus the logarithm of the pressure gives a near-linear relationship, Figure 68. See also [936].



**Figure 67:** Effects of pressure on the minimum required ignition energy for hydrogen in air. (Reproduced and modified from [934].)



**Figure 68:** Effect of reduced pressure on the minimum required ignition energy for stoichiometric air/hydrogen mixtures. (Reproduced and modified from [934].)

### 7.9.2.2 Autoignition of Hydrogen in Air

Although hydrogen has a higher autoignition temperature than methane or gasoline, its low ignition energy makes it more readily accidentally ignitable than either of the hydrocarbon fuels. Ignition can occur on hot surfaces or by contact with hot air. These ignitions occur with a certain delay, unlike spontaneous ignition observed with high pressure hydrogen gas leaks.

The autoignition of hydrogen in air should be determined in accordance with ASTM E659, but many reports in the literature used different methods, resulting in a wide scatter of reported autoignition temperatures. It is assumed that those reports are for stoichiometric air/hydrogen mixtures which are most likely to ignite. The hot surface that is brought into contact with air/hydrogen as part of this test must be chemically inert and non-catalytic.

Other sources listed the autoignition temperature of hydrogen on inert surfaces in air as 793 K (520 °C), compared to 903 K (630 °C) for methane. A temperature of 858 K (585 °C) was reported as autoignition temperature of hydrogen in air in [521]. The Praxair MSDS for hydrogen gives an autoignition temperature of 839 K (566 °C).

One hydrogen safety manual gave the range of reported autoignition temperatures for stoichiometric hydrogen in air at 101.3 kPa (14.7 psia) as 773–850 K (932–1070 °F). For comparison, in stoichiometric mixtures with oxygen, the autoignition temperature is 773–833 K (932–1039 °F).

### 7.9.2.3 Spontaneous Ignition of High-pressure Hydrogen Gas Leaks

Accidental spontaneous ignition or self-ignition or autoignition of high-pressure hydrogen gas leaking into surrounding air has been observed on several occasions. Autoignition of flowing hydrogen was reported as early as 1918. Hydrogen flowing through an aspirator in the presence of air would occasionally autoignite. It was observed that an electric charge built up when the hydrogen/air mixture passed over a wire which was placed perpendicular to the direction of flow, but electrically insulated from the aspirator. Sparks 7 in. long were observed jumping to the aspirator. Various phenomena such as friction-induced ionization or electrostatic charge accumulation, test section surface irregularities, boundary layer effects, acoustic resonance, thermodynamic non-equilibrium, and diaphragm rupture have been considered as the cause of low-temperature ignition. While most of these phenomena can cause low-temperature ignition, it is not known which one of them or which combination of them is actually responsible for the low-temperature ignitions [937]. The resulting fire of the high-velocity stream of hydrogen has been described as “jet fire.”

During a compressed hydrogen gas high-pressure venting experiment conducted to make acoustic measurements the vented hydrogen autoignited and an explosion ensued that caused substantial building damage [938, 939]. At the moment of ignition, the hydrogen cloud was about 30 feet wide and 150 feet high.

While self-ignition of hydrogen is undesirable for accidental high-pressure gas releases, self-ignition of supersonic air/hydrogen mixtures is desirable in scram-jets [940]. A correlation of self-ignition data for supersonic air/hydrogen mixtures in configurations representative of scramjet combustors examined injection from transverse fuel jets on walls, transverse jets behind swept and unswept steps, and transverse injection ahead of swept and unswept steps and strut bases. The results provided useful guidance for predicting self-ignition in a variety of applications. The likely regions for self-ignition in a combustor were identified. See also [941].

Hydrogen releases from a high-pressure chamber were modeled to investigate the real gas effects at high pressures [942]. In the first method, an analytical model was developed to simulate time histories of stagnation properties of hydrogen inside the chamber as well as sonic properties of hydrogen at the orifice. Thermodynamic relations describing the specific heat, internal energy and velocity of sound were derived based on Beattie-Bridgeman state equation. In the second approach, a 3-D unstructured tetrahedral finite volume Euler solver was applied to numerically simulate the hydrogen release.

A large-scale hydrogen jet experiment was performed in which 27 kg of hydrogen was released vertically into the open atmosphere in a period of about 30 s to simulate the bursting of interconnecting piping between large high-pressure storage tanks [943]. The hydrogen plume spontaneously ignited early in the release.

The various autoignition mechanisms have been investigated, but the resulting conclusions arrived at by various investigators do not always match [944, 945]. Mechanisms which have been proposed in the past are the reverse Joule-Thomson effect, electrostatic charge generation, diffusion ignition, sudden adiabatic compression and hot surface ignition. Of these, some have been characterized by means of computer simulation rather than by experiment, and hence are not validated. There are discrepancies between the theories, releases known to have ignited, and releases which are known to have not ignited [946, 947]. Compression ignition, Joule-Thomson expansion, diffusion ignition, and hot surface ignition are unlikely ignition mechanisms for most accidental releases of hydrogen at ambient temperature. It is possible that some form of electrostatic charging is a part of the mechanism where spontaneous ignition of leaks of hydrogen from high pressure has occurred at ambient temperature. There is the possibility that when hydrogen does ignite on release, two or more of the postulated mechanisms are responsible together [948, 949].

An appreciable difference between the calculated and measured values of delay of self-ignition upon injection of pre-mixed air/hydrogen mixture into a preheated volume was revealed in the experiments of Ciccarelli et al. who studied the effect of initial temperature on the initiation of gas detonation [950, 951]. It was noted that conventional calculations by standard kinetic schemes predicted delay times much longer than those measured.

A numerical and experimental investigation of hydrogen self-ignition as a result of the formation of a primary shock wave in front of a cold expanding hydrogen gas

jet showed that temperature increase, as a result of this shock wave, leads to the ignition of the air/hydrogen mixture formed on the contact surface [952, 953]. The required condition for hydrogen self-ignition is to maintain the high temperature in the area for a time long enough for hydrogen and air to mix and inflammation to take place. Calculations of the self-ignition of a hydrogen jet were based on a physicochemical model involving the gas-dynamic transport of a viscous gas, the kinetics of hydrogen oxidation, the multi-component diffusion, and heat exchange. It was found that the reservoir pressure range, when a shock wave formed in the air during depressurization, has sufficient intensity to produce self-ignition of the air/hydrogen mixture formed at the front of a jet of compressed hydrogen.

Self-ignition of air/hydrogen gas mixtures was measured behind reflected explosive pressure waves at moderate (below 1200 K) temperatures and elevated pressures [954]. The experiments were performed in a modified shock tube which provided generation of explosive pressure waves. The explosive waves were characterized by a jump of parameters of shock-compressed gas (pressure, temperature) at the front with their subsequent continuous decrease. This explains hypothetical pre-explosion preheating of combustible mixtures by compression waves. The experiments involving standard shock waves (with constant pressure/temperature levels) revealed a significant deviation (by a factor of 10 and more) of measured values of the delay of self-ignition from the calculated values.

Releases of  $\text{GH}_2$  into atmospheres with no restrictive and reflective downstream geometry present resulted in no ignitions up to a burst pressure of 831 bar. No ignitions were observed below a cavity pressure of 8.8 bar (gauge). Ignitions always occurred above a cavity pressure of 27 bar (gauge) [955].

A large-eddy simulation model was used to describe the spontaneous ignition dynamics in a tube with a non-inertial rupture disk separating the high-pressure hydrogen storage and the atmosphere [956].

High-pressure hydrogen releases in the range of initial pressures from 20 to 275 bar and with nozzle diameters of 0.5–4 mm have been investigated using glass tubes and a high-speed CCD camera [957]. The problem was theoretically considered in terms of contact discontinuity for the case when spontaneous ignition of pressurized hydrogen due to the contact with hot pressurized air occurred. The effects of boundary layer and material properties were considered in order to explain the minimum initial pressure of 25 bar leading to the self-ignition of hydrogen with air.

The effects of the diaphragm shape and boundary layer near walls on autoignition induced by high-pressure hydrogen release in air in a real size tube were numerically studied using Navier-Stokes equations with multi-component gases [958]. The numerical results showed that there is a grid dependency that provides the optimal grid system via a comparison of the theoretical boundary layer thickness. The validity of the numerical system was confirmed by comparing the numerical and experimental precursor shock wave velocities. The initial diaphragm shape affects the hydrogen release flow structure and its autoignition mechanism. Two different autoignition styles were



observed from the numerical results: one occurred near the boundary layer owing to the induction time effect and Kelvin-Helmholtz instability and another may occur near the center axis owing to a Rayleigh-Taylor instability.

Self-ignition behavior of highly transient jets from hydrogen high pressure tanks were investigated at pressures up to 26 MPa [959]. The jet development and related ignition/combustion phenomena were characterized by high-speed video techniques and time-resolved spectroscopy, providing information on ignition region, flame head jet velocity, flame contours, pressure wave propagation, reacting species, and temperatures. On burst of the rupture disc, the combustion of the jet starts close to the nozzle at the boundary layer to the surrounding air. Combustion velocity decelerated in correlation to an approximated drag force of constant value which was obtained by analyzing the head velocity. The burning at the outer jet layer developed to an explosion converting to a nearly spherical volume at the jet head; the movement of the centroid was nearly unchanged and followed the jet front in parallel. The progress of the nearly spherical explosion could be evaluated by assuming an averaged flame ball radius. An apparent flame velocity was estimated to be about 20 m/s and it seemed to increase slightly with the pressure in the tank or the related initial jet momentum. Self-initiation was nearly always achieved especially by induced interaction of shock waves and their reflections from the orifice. The combustion process is composed of shell combustion of the jet cone at the bases with a superimposed explosion of the decelerating jet head volume.

High-pressure hydrogen can ignite spontaneously when it is abruptly released into the air. Numerical simulations were conducted for a cylindrical tube, initially filled with air, with various burst conditions and the predictions were validated by comparison with previous experimental data [960]. A maximum burst pressure of 40 MPa was simulated for two pressure boundaries characterized by spherical and flat diaphragm shapes. The results showed that there is a significant relevance between the ignition features and the burst conditions. The shock interactions induced by a spherical pressure boundary can play a role in the ignition by two separate mixing and reaction regions appearing in the core and boundary layer of the tube. The reaction in the core region can assist in the formation of a complete flame when the burst pressure is relatively low, whereas when the burst pressure is higher, it is possible to initiate the ignition by the reaction region near the boundary layer alone, even without the reaction in the core region when the burst pressure is high. The ignition patterns can differ according to the change of burst conditions and diaphragm shape.

An experimental investigation of spontaneous ignition and flame propagation at high-pressure hydrogen release used cylindrical tubes with different cross-sections: **(1)** local contraction, **(2)** local enlargement, **(3)** abrupt contraction, and **(4)** abrupt enlargement. The results showed that the presence of the varying cross-section geometries can significantly promote the occurrence of spontaneous ignition [961]. Com-

pared to a tube with constant cross-section, the minimum pressure release needed for spontaneous ignition for the varying cross-sections tubes was considerably lower. The initial ignition location was closer to the disk in the presence of varying cross-section geometries in comparison to a straight channel. As the flame emerged from the outlet of the tube, the velocity of the flame front in the vicinity of the nozzle increased sharply. Then, a deflagration developed across the mixing zone of the hydrogen/air mixture. The maximum deflagration overpressure increased linearly with the release pressure. Subsequently, a hydrogen jet flame was produced and evolved in different shapes at different release stages. A fireball was formed after the jet flame spouted into open air at the exit of the tube. Later, the fireball developed into a jet flame which drifted upward and continued to burn with updraft in the vertical direction.

Hydrogen diffusing into hot air caused by a shock wave from diaphragm rupture and entering the hydrogen-oxidizer mixed region is heated enough to start a chemical reaction. Flow visualization studies looked at spontaneous ignition in a rectangular tube [962]. The results confirmed the presence of a flame at the wall of the tube when the shock wave pressure reached 1.2–1.5 MPa in more than 9 MPa burst pressure and confirmed that ignition occurred near the wall, followed by multiple ignitions as the shock wave propagated, with the hot spots eventually combining to form a flame front.

Diaphragms with several membrane thicknesses and score patterns were ruptured in a controlled test by high-pressure hydrogen, and the formation of a shock wave in the tube was observed during a study of self-ignition of high-pressure hydrogen that was released into air through a ruptured diaphragm [963–965]. The behavior of the ruptured diaphragm and the subsequent self-ignition was photographed using a high-speed camera, while the self-emission intensity from a flame was measured using a photomultiplier. The experimental results showed that the diaphragm rupturing condition is one of the main factors affecting the self-ignition. The self-ignition caused a ring-shaped cylindrical flame that traveled downstream, along a boundary between the hydrogen jet and the shock-heated air.

In studying the effects of hydrogen additions on spontaneous ignition of high-pressure hydrogen released into hydrogen-air mixture, hydrogen and air were premixed with different volume concentrations (0, 5, 10, 15, and 20%  $H_2$ ) in the tube before high-pressure hydrogen was suddenly released [966]. Pressure transducers in the tube detected the shock waves, measured the shock wave speed and overpressure. Light sensors were used to detect the occurrence of high-pressure hydrogen spontaneous ignition in the tube. A high-speed camera was used to capture the flame propagation behavior outside the tube. It was found that only 5% hydrogen addition could decrease the minimum storage pressure required for spontaneous ignition from 4.4 to 2.8 MPa. When 10, 15 or 20% hydrogen were added to the air, the minimum self-igniting storage pressure decreased to 2.8, 1.8, and 1.8 MPa, respectively.

The self-ignition of hydrogen gas released from a high-pressure tank using discharge tubes with different diameters, the processes of flame transition at a nozzle

and jet flame development were characterized using a high-speed camera [967]. The results indicated that the intensity of a shock wave and the Mach number decay faster in a 10-mm diameter tube than that in a 15-mm diameter tube. The pressure in a 15-mm diameter tube was weaker than that in a 10-mm diameter tube at the initial stage; however, it became higher during the later stage. Spontaneous ignition was more likely to happen in a 15-mm diameter tube. The formation of a stabilized flame at the tube exit and Mach disk were observed during the transition of the flame to a jet fire. The stabilized flame showed a triangular shape because of the influence of a Prandtl-Meyer flow when a hydrogen jet entered a suddenly expanding environment. The formation and separation of a spherical flame were recorded during jet flame development. Large vortices were formed in front of the flame because of the Kelvin-Helmholtz instability, which resulted in the separation of the spherical flame. The vortices stopped rotating until the separated flame disappeared.

#### 7.9.2.4 Ignition by Adiabatic Compression

Hydrogen is unlikely to be used as a diesel fuel with compression-ignited reciprocating engines, but rapidly compressed air/hydrogen gas mixtures will ignite like diesel fuel. The spontaneous ignition of hydrogen at pressures between 3.5 and 7 MPa has been investigated in a free-piston compressor which rapidly increased the temperature and pressure of a mixture of oxygen, hydrogen, and helium [968]. Explosions occurred during the compression stroke and were detected by a piezoelectric pressure transducer. The temperature at ignition was independent of pressure, and was calculated to be approximately 1150 K. The results of a chemical kinetic analysis were in good agreement with the experiments. The kinetics analysis indicated that the ignition is most likely initiated by the breakdown of  $\text{H}_2\text{O}_2$  to the highly reactive radical  $\cdot\text{OH}$ .

#### 7.9.2.5 Autoignition of Flowing Propellant

It is unlikely that LOX and LH2 or LOX and RP-1 would autoignite upon rapid mixing, but various flow conditions potentially contributing to autoignition of flammable mixtures were investigated. An electrostatic charge might build up as a result of relative fluid motion between immiscible fuel and oxidizer [969]. A hypothesis was proposed based on two simultaneous processes: (1) mixing of the propellants, and (2) development of electrostatic charges sufficient to cause ignition sparks. This investigation included electrostatic charging effects at interfaces of mixing liquids, cosmic radiation, and heat from orthohydrogen→parahydrogen conversion. Neither of the latter two processes was considered a significant ignition mode compared to electrostatic phenomena.

## 7.10 Limits of Flammability

Limits of flammability, flammability limits may sometimes also be called limits of inflammability. They are closely related to limits of explosion and limits of detonation.

For mixtures of any particular combustible gas and air (or oxygen) there are, under given physical conditions, certain limits of composition within (but not outside of) which self-propagation of flame will occur indefinitely after ignition has once been effected. These limits, usually referred to as the “lower” and “upper” limits of flammability, respectively, at given temperature and pressure vary somewhat **(1)** with the position of the source of ignition, since the progress of the flame may be assisted or retarded by convection currents accordingly as it has to propagate in an upward, horizontal or downward direction, and **(2)** according to the size and material and wall-coating of the containing vessel.

### 7.10.1 Methods for Determination of Limits of Flammability

The limits of flammability of combustible gases and vapors in air are usually determined using the apparatus described in [970] and [971], but there are many other experimental set-ups in use. The limits of flammability will depend on the size and shape of the combustion chamber, on the direction of flame propagation, and on the ignition energy of the ignitor (Table 50).

**Table 50:** Explosion limits of hydrogen in air measured at room temperature and atmospheric pressure.

|                                               | Test method                       |             |             |            |
|-----------------------------------------------|-----------------------------------|-------------|-------------|------------|
|                                               | DIN 51649                         | EN 1839 (T) | EN 1839 (B) | ASTM E 681 |
| Gas mixture                                   | Composition, mol-% H <sub>2</sub> |             |             |            |
| LEL (Air/H <sub>2</sub> )                     | 3.8                               | 3.6         | 4.2         | 3.75       |
| UEL (Air/H <sub>2</sub> )                     | 75.8                              | 76.6        | 77          | 75.1       |
| LEL (Air/H <sub>2</sub> /40% N <sub>2</sub> ) | 3.6                               | 3.6         | 4.4         | 3.65       |
| UEL (Air/H <sub>2</sub> /40% N <sub>2</sub> ) | 38.2                              | 38.4        | 38.2        | 37.3       |

LEL = Lower Explosive Limit, UEL = Upper Explosive Limit

Data source: [974]

NASA has a standard procedure for determination of flammability, offgassing, and compatibility, but that is mostly for combustibility of solid materials in oxygen-enriched atmospheres [972]. Other countries have similar specifications for the determination of flammable limits in air [973].

Table 50 shows that the explosion limits measured according to the 4 standard test methods show differences, which are most pronounced with the diluted (40% N<sub>2</sub>) mixtures. The procedures according to DIN 51649 and EN 1839(T) yield comparable results because the test apparatus used for both methods is very similar. The explosion range of EN 1839(T) is a little bit wider because the diameter of the explosion tube is larger so that flame quenching effects are eliminated better. The ASTM method shows a similar LEL but a lower UEL. DIN 51649, ASTM E 681, and EN 1839(T) are so-called open vessel methods. The pressure inside the test vessel during the reaction is nearly constant at atmospheric pressure and burned gases can escape through a gas outlet. The closed vessel method according to EN 1839(B) shows the largest deviations. The LEL is higher compared to the other three methods. The reason might be the pressure threshold criterion for reaction indication. It is obviously less sensitive than the visual criterion.

### 7.10.2 Limits of Flammability of Hydrogen in Air

The limits of flammability of hydrogen in air are listed in a large number of publications, often in comparison to flammable limits of other combustible gases [343, 975, 976]. Other studies examined the limits of flammability and at the same time measured the speed of flame propagation and the quenching distance of hydrogen flames. Quenching distance of hydrogen flames are discussed in Section 7.10.3.5 “Quenching Distance and Critical Diameter for Propagation of Air/Hydrogen Flames.” Transition from hydrogen combustion to hydrogen detonation is discussed in Section 7.12.7 “Deflagration-to-Detonation Transitions.”

The limits of flammability of hydrogen in air are extremely wide, from 4.0 to 74.2 vol.-% for upward propagation at room temperature and sea-level atmospheric pressure. Hydrogen has a much wider range of flammability in air (4–75% by volume) than methane (5–17% by volume), propane, or gasoline, and the minimum ignition energy (for a stoichiometric mixture) is about an order of magnitude lower (1/16th that of methane). The transition from a combustion to an explosion and eventually a detonation depends on the amount of confinement and the energy of the ignition source. In confined spaces, such as in tanks or pipes, air/hydrogen mixtures will explode or even detonate, but not in unconfined open spaces [516, 890]. The flammability properties of hydrogen are unique and different from those of any other flammable gas.

A summary on thermal hazards of selected aerospace fluids contains a detailed section on flammability hazards of gaseous hydrogen [934]. Limits of flammability were summarized for test results obtained under a wide range of conditions, including direction of flame propagation, moisture content of air, pressure, dimensions of test chamber, diluents, inhibitors, gravity or oxygen content in diluents. Also, flammability in gas mixtures with other oxidizing atmospheres was tabulated and graphed.

**Table 51:** Flammability limits of hydrogen in oxidizing atmospheres

| Conditions                                                      | Hydrogen content, vol.-% |             |                         |             |                        |             |
|-----------------------------------------------------------------|--------------------------|-------------|-------------------------|-------------|------------------------|-------------|
|                                                                 | Upward propagation       |             | Downward propagation    |             | Horizontal propagation |             |
|                                                                 | Lower limit              | Upper limit | Lower limit             | Upper limit | Lower limit            | Upper limit |
| <b>Hydrogen in air at 101 kPa (14.7 psia):</b>                  |                          |             |                         |             |                        |             |
| Tubes                                                           | 4.1                      | 74.8        | 8.9                     | 74.5        | 6.2                    | 71.3        |
| Spherical vessels                                               | 4.6                      | 75.5        | —                       | —           | —                      | —           |
| <b>Hydrogen oxygen at 101 kPa (14.7 psia):</b>                  |                          |             |                         |             |                        |             |
| H <sub>2</sub> + oxygen                                         | 4.1                      | 94.0        | 4.1                     | 92.0        | —                      | —           |
| <b>Hydrogen plus inert gas mixtures at 101 kPa (14.7 psia):</b> |                          |             |                         |             |                        |             |
| H <sub>2</sub> +He+21 vol.-% O <sub>2</sub>                     | 7.7                      | 75.7        | 8.7                     | 75.7        | —                      | —           |
| H <sub>2</sub> +CO <sub>2</sub> +21 vol.-% O <sub>2</sub>       | 5.3                      | 69.8        | 13.1                    | 69.8        | —                      | —           |
| H <sub>2</sub> +N <sub>2</sub> +21 vol.-% O <sub>2</sub>        | 4.2                      | 74.6        | 9.0                     | 74.6        | —                      | —           |
| <b>Hydrogen in air at reduced pressure:</b>                     |                          |             |                         |             |                        |             |
| Pressure                                                        | 2.5 cm Tube <sup>a</sup> |             | 2 L Sphere <sup>b</sup> |             |                        |             |
| kPa                                                             | Lower limit              | Upper limit | Lower limit             | Upper limit |                        |             |
| 20                                                              | ~4                       | ~56         | ~5                      | ~52         |                        |             |
| 10                                                              | ~10                      | ~42         | ~11                     | ~35         |                        |             |
| 7                                                               | ~15                      | ~33         | ~16                     | ~27         |                        |             |
| 6                                                               | 20–30                    | 20–25       | —                       | —           |                        |             |

Note: Dashes indicate no information available. ~ indicates that tabulated values were obtained by visual interpolation of values from original graph curves.

<sup>a</sup> Tungsten electrodes were employed, but the energy of initiation was not published (Elston and Laffitte 1947).

<sup>b</sup> 45 mJ (47.5 BTU) ignition source was applied (Mills and Linley 1977).

Data source: [523, 934, 975]

Flammability limits of hydrogen in air are summarized in Table 51. This table may contain data for dry air as well as moisture-saturated air. The difference in modes of flame propagation that occurs between the upward lean limit at 4% H<sub>2</sub> and the downward lean limit near 8% H<sub>2</sub> is quite anomalous for any flammable gas. Upward propagation from a convectively rising flame kernel involves propagation into a velocity gradient induced by buoyancy forces, and at a slow but finite propagation velocity, the flame is blown out by its own buoyancy-induced flow [349].

The type of combustion of hydrogen-air mixtures near the flammability limits for different initial temperatures (from 298 to 423 K) and pressures (100 and 250 kPa) relevant was re-examined using a spherical vessel equipped with a pressure transducer to monitor the pressure increase subsequent to the combustion and with two optical windows to record the flame propagation [977]. From the schlieren images, different

regimes of flame propagation could be identified depending on the temperature and pressure. The maximum post-combustion pressure obtained experimentally has been compared to the theoretical maximum pressure for adiabatic combustion at constant volume. The flammability limits of air/hydrogen have been determined for different temperatures and pressures and were compared to the data reported in the literature.

### 7.10.3 Effect of Pressure on Limits of Flammability

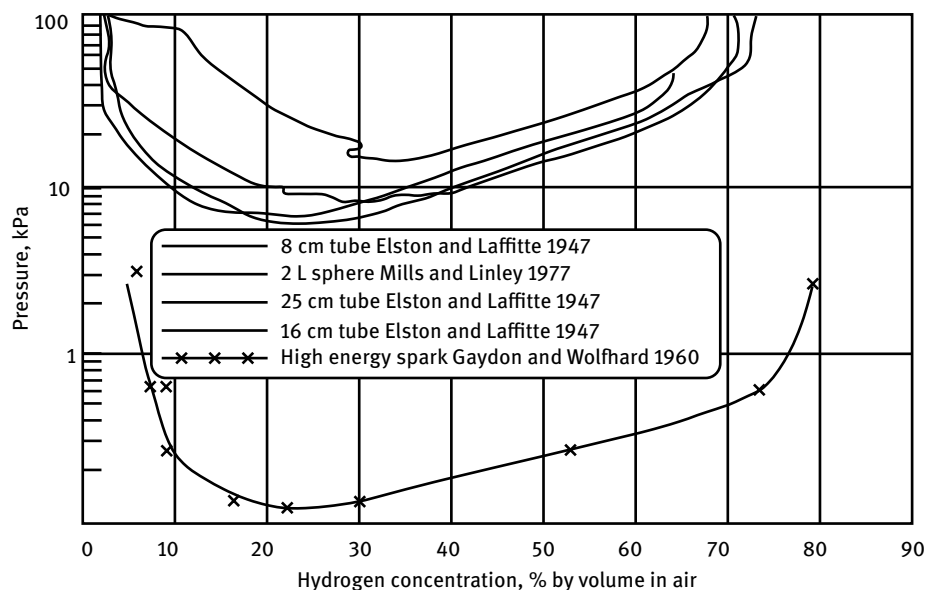
#### 7.10.3.1 Effect of Reduced Pressure on Limits of Flammability in Air

The flammability of hydrogen in air at reduced pressures was studied using tubes with lengths of 96 cm (38 in.) and with diameters of 8 cm (3.2 in.), 16 cm (6.3 in.), and 25 cm (9.8 in.) [978]. An electrical spark, positioned to promote upward flame propagation, was used as the ignition source. Similar flammability tests were performed in a 2-L (122-in.<sup>3</sup>) hemispherical chamber, using a 45 mJ spark discharge at the geometric center of the hemisphere as the ignition source [979].

Reduced pressure flammability tests were performed in two cylindrical chambers, one of length 1.83 m (72 in.) and diameter 0.61 m (24 in.), and another of length 3.66 m (144 in.) and diameter 1.23 m (48 in.) [980]. The direction of flame propagation was not specified. The ignition source was a spark discharged from a capacitor bank with a maximum storage capacity of 2700 J; approximately 60–70% of the energy was delivered to the gas. The results of these investigations are shown in Figure 69.

The lowest pressure for which a low energy ignition source produced ignition was approximately 6 kPa (0.9 psia), at a hydrogen concentration of between 20 and 30 vol.-% [934]. This value was obtained in a 25-cm tube and a 2-L hemispherical chamber. The low-pressure limits were greater in the small diameter tubes.

The upper flammability limits (UFL) of air/hydrogen, air/methane, air/ethane, air/*n*-butane, and air/ethylene were determined experimentally at room temperature (293 K = 20 °C) and initial pressures of 1.0, 0.7, 0.5, 0.3, 0.1, and 0.05 atm [981]. Experiments were conducted in a closed cylindrical stainless steel vessel with an internal diameter of 10 cm and a length of 100 cm with upward flame propagation. The UFL of hydrogen was observed to be inversely proportional to the initial pressure in the range from 1.0 to 0.3 atm and proportional to the initial pressure from 0.3 to 0.05 atm. In contrast, the UFLs of the lower alkanes and ethylene decreased with the initial pressure. The average flame propagation velocities at UFL concentrations of hydrogen, methane, ethane, *n*-butane, and ethylene in air at reduced pressures were also examined. It was found that the flame propagation velocity of hydrogen was larger than those of the hydrocarbons, increased when the initial pressure decreased from 1.0 to 0.3 atm, and then decreased with further decrease of pressure. Flame propagation velocities at UFL concentrations of the hydrocarbons decreased with the initial pressure. In a parallel series of experiments, the lower flammability limits (LFLs) of

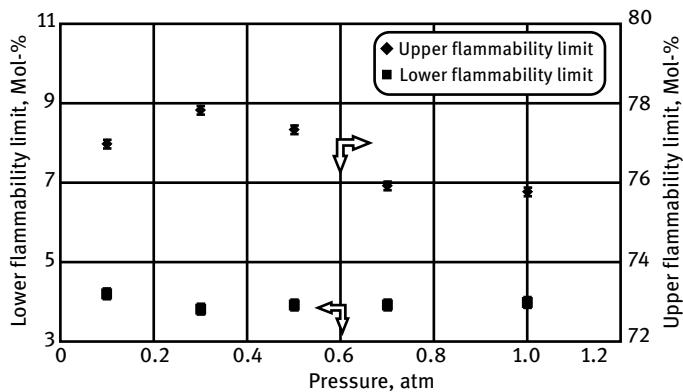


**Figure 69:** Effect of reduced pressure on limits of flammability of hydrogen in air. (Reproduced and modified from [934].)

air/hydrogen, air/methane, air/ethane, air/*n*-butane and air/ethylene were also measured in the same closed cylindrical vessel (inner diameter 10 cm, length 100 cm) under the same conditions with upward flame propagation, at room temperature (293 K = 20 °C) and initial pressures of 1.0, 0.7, 0.5, 0.3, and 0.1 atm [982, 983]. The LFL of hydrogen initially decreased with pressure from 1.0 to 0.3 atm, but then the LFL increased with further decrease of pressure. In contrast, the LFLs of the hydrocarbons increased when the pressure decreased from 1.0 to 0.1 atm, except for methane for which the LFL did not change with pressure. The adiabatic constant volume flame temperatures at the new measured LFL concentrations of hydrogen and the hydrocarbons were calculated at subatmospheric pressure conditions. The behaviors of the adiabatic flame temperatures of hydrogen and the hydrocarbons were similar to those of the LFLs under the influence of low pressures.

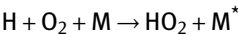
Under the influence of pressure, the UFL of hydrogen in air changes more than the LFL. For example, when the initial pressure decreased from 1.0 to 0.1 atm, the maximum change of the LFL was 0.2 mol-%, which is much smaller than that of the UFL which was 2.1 mol-%. For hydrogen, when the initial pressure decreases below 1.0 atm, the flammability region widens (LFL decreases and UFL increases), see Figure 70.





**Figure 70:** Flammability region of hydrogen at sub-atmospheric pressures and room temperature in air. (Reproduced and modified from [983], with permission from Dr. Thuy Minh Hai Le dated 9 March 2021.)

The region is the widest at 0.3 atm where the LFL decreases by 0.2 mol-% and the UFL increases by 2.1 mol-%. The region starts to narrow when the pressure decreases below 0.3 atm. The widening of the flammability region when the pressure decreases can be attributed to the reaction mechanism of hydrogen in which the influence of the three-body reaction



becomes weaker with decreasing pressure (Table 52). See also [984].

**Table 52:** Flammability limits of pure hydrogen and light hydrocarbons in air at atmospheric and subatmospheric pressures and room temperature.

| Initial pressure, atm |            | 1.0   | 0.7   | 0.5   | 0.3   | 0.1   |
|-----------------------|------------|-------|-------|-------|-------|-------|
| Hydrogen              | LFL, mol-% | 3.95  | 3.85  | 3.85  | 3.75  | 4.14  |
|                       | UFL, mol-% | 75.73 | 75.88 | 77.30 | 77.80 | 76.95 |
| Methane               | LFL, mol-% | 5.35  | 5.35  | 5.35  | 5.35  | 5.35  |
|                       | UFL, mol-% | 15.40 | 14.85 | 14.65 | 14.50 | 14.35 |
| Ethane                | LFL, mol-% | 2.85  | 2.85  | 2.90  | 3.00  | 3.75  |
|                       | UFL, mol-% | 14.00 | 13.64 | 12.86 | 12.37 | 11.76 |
| Ethylene              | LFL, mol-% | 2.85  | 2.90  | 2.95  | 2.95  | 3.45  |
|                       | UFL, mol-% | 30.61 | 29.49 | 27.50 | 23.39 | 19.26 |

Data source: [983]

Fundamental safety properties of air/hydrogen mixtures, such as flammability limits and laminar flame speed at subatmospheric pressures were measured in a spherical

explosion chamber with a volume of 8.2L and a high-speed camera combined with a schlieren system for flame visualization [368]. Upper and lower flammability limits and laminar flame velocity were obtained in the range of 4–80% hydrogen in air at initial pressures of 25–1000mbar. Laminar burning velocity and flame length were correlated with overall reaction order and activation energy.

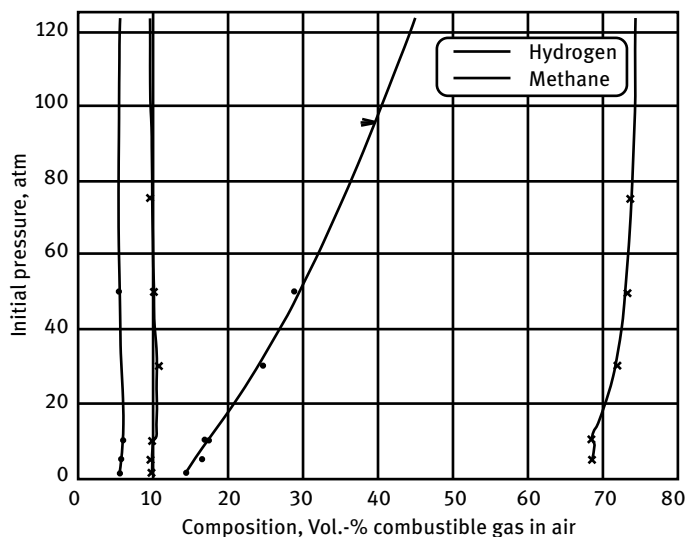
The flammability of hydrogen was tested in a 20-L vessel from the pressure at sea level up to 180 mbar corresponding to an altitude of 12.2km (40000 feet) [985]. The lower and upper flammability limits were found first and compared with previous data. Then, peak explosion pressure was measured across all flammable hydrogen and oxygen concentrations. The oxygen concentration started from the concentration found in air and was reduced by adding additional nitrogen. These tests were performed up to the point where the limiting oxygen concentration was reached for each altitude. In general, as the altitude increased, the limits of flammability for hydrogen and oxygen widened, and the peak explosion pressures decreased.

### 7.10.3.2 Effect of Increased Pressure on Limits of Flammability in Air

In the early years there were some reports that increased pressure would narrow instead of widen the range of flammability of hydrogen in air for downward propagation and the results were compared to those obtained with methane instead of hydrogen. Some investigators had reported that the lower limit for hydrogen-air mixtures, which started at 7.0 vol.-% at atmospheric pressure, rose steeply with pressure up to 10.8 vol.-% at 21atm, after which it fell gradually to 8.4 vol.-% at 210 atm, with some variation depending on the intensity of the source of ignition.

In one series of experiments, the “explosion-limits” at room temperature of air/hydrogen, air/methane and air/CO mixtures have been determined from initial pressures of 1, 5, 10, 30, 50, 75, and 125 atm [986]. These early (ancient) experiments showed that the general effect of increased pressure is to widen the explosion limits of air/hydrogen, shown as solid lines in Figure 71, also in comparison to methane (dashed lines). The effect of pressure on widening the explosive limits was more pronounced for methane than for hydrogen. Pressures up to 10atm were tested in a cylindrical explosion chamber 75cm long  $\times$  5cm diameter with a capacity of 2L, fitted at each end with a quartz window, so that the explosion could be visually observed and pressures above 10atm were tested in a 240-mL spherical chamber. The source of ignition was a melting platinum fuse wire. These early experiments failed to detect the anomaly which occurs in air/hydrogen and oxygen/hydrogen mixtures at pressures below 20 bar and is shown in subsequent figures in this chapter.

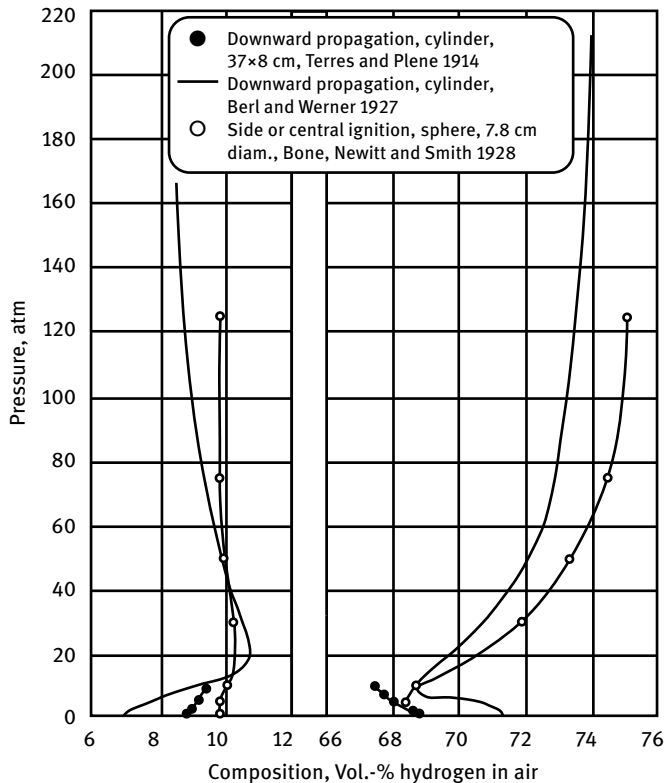
The effects of elevated pressures on the flammability of hydrogen in air are shown in Figure 72 for downward propagation in tubes, and side or central ignition in a spherical chamber. The shapes of the flammability curves changed with the direction of flame propagation, and the flammable range first decreased and then increased as pressure was increased above ambient pressure. This variability was



**Figure 71:** Limits of flammability of air/hydrogen and air/methane at elevated pressures. (Republished and modified from [986], with permission of ©1928 The Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

attributed to a combination of kinetic and thermal effects [975]. Figure 72 shows the effect of increasing pressure on lower and upper limits of flammability of hydrogen in air. This image consists of two graphs with the center section omitted because it did not contain any data. This graph is based on data obtained from three different sources with equipment of different dimensions and different ignition methods. If one plots the upper limit of flammability data as a function of pressure, all three curves have a minimum in the range 1.0–1.5 MPa, regardless of the apparatus in which the measurements were made.

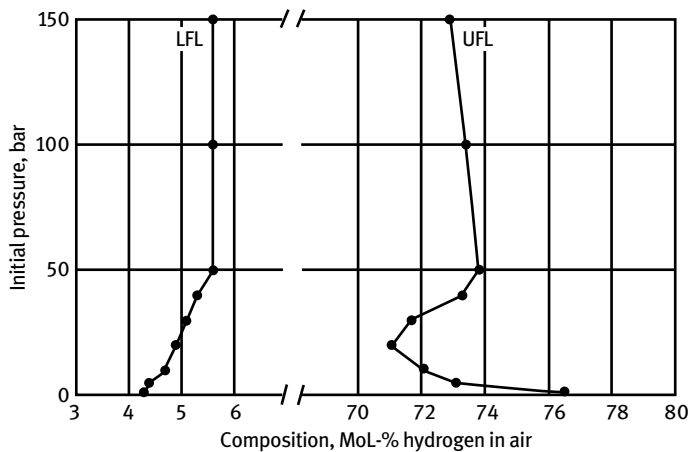
The upper limit of flammability is more sensitive to the type of diluent gas used than the lower limit. The upper limit of flammability of hydrogen in air, oxygen, oxygen-helium, oxygen-neon, oxygen-argon and oxygen-carbon dioxide mixtures was measured at room temperature and pressures between 98 and 2938 kPa (0.97 and 29 atm) in two cylindrical bombs with volumes of 1.5 and 5.2 L [987]. The limit in ternary mixtures was determined in 20, 40, 60, and 80% helium, 20% neon, 20% argon, and 10% carbon dioxide concentrations. The  $O_2/H_2/He$  experiments were carried out with oxygen-hydrogen-helium mixtures of 0, 20, 40, 60, and 80% helium at 0.97, 1.94, 2.98, 4.84, 9.7, 19.4, and 29.0 atm pressure. The critical oxygen concentration represents the maximum percentage of oxygen which will be safe in any unknown mixture of hydrogen with oxygen and helium at room temperature. The maximum safe percentage of oxygen in a oxygen-hydrogen-helium mixture was calculated for pressures between 98 and 2938 kPa (0.97 and 29 atm).



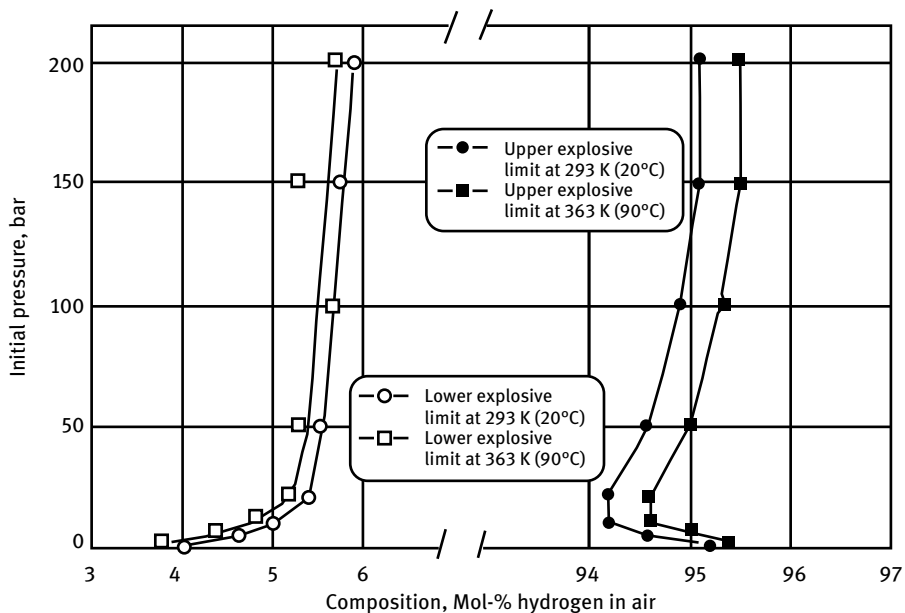
**Figure 72:** Limits of flammability of hydrogen in air at elevated pressures. (Reproduced and modified from [975].)

The flammability of hydrogen in air was measured at pressures up to 15 MPa (150 bar) and ignition by glow wires or sparks and the results in Figure 73 show the unusual behavior of the upper limit at pressures below 20 bar [988].

The discussion of explosion limits of oxygen/hydrogen in comparison to those of air/hydrogen may be repeated in Section 7.12.5 “Detonability Range of Hydrogen Gas in Air,” but it is started here by a juxtaposition of the explosion limits as a function of pressure graphs for the two mixture conditions with and without the presence of nitrogen. The explosion limits of oxygen/hydrogen mixtures were measured at pressures up to 200 bar and compared to the results discussed above, which were obtained with air/hydrogen at pressures up to 150 bar [988]. The upper limit of explosion for both mixtures initially goes down with increasing pressure and the lower limit of explosion goes up, resulting in a narrowing of the explosive range with increasing pressure at pressures below 20 bar [974, 989, 990]; however, once the pressure exceeds the regime of this anomaly, the opposite seems to be the case (Figure 74). The shape of the explo-



**Figure 73:** Explosion limits of air/hydrogen mixtures at elevated pressures. (Republished and modified from [988], with permission of ©1995 John Wiley & Sons; permission conveyed through RightsLink.)



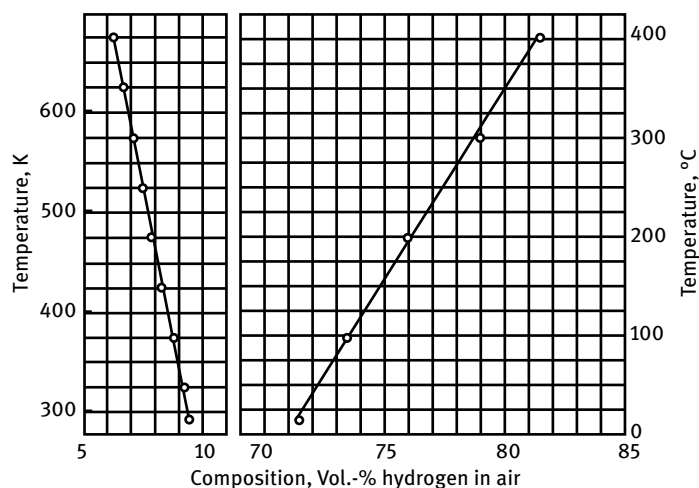
**Figure 74:** Flammability of oxygen/hydrogen at elevated pressure. (Republished and modified from [974], with permission from Bundesanstalt für Materialforschung und -prüfung dated 30 March 2021.)

sion limit curves is the same for initial gas temperatures of 293 and 353 K (20 and 80 °C). The explosive range is wider at the higher temperature, as expected.

Air/hydrogen combustion at initial pressures of up to 3 MPa and initial temperatures of 295 K was measured in a high-pressure bomb with windows which allowed recording the UV/Vis and NIR spectra of the flames [991]. Peak pressures up to 20 MPa were recorded with a piezoelectric transducer. The pressure-time and flame radius-time curves gave the burning velocity. The burning velocity had a pressure exponent of 0.23.

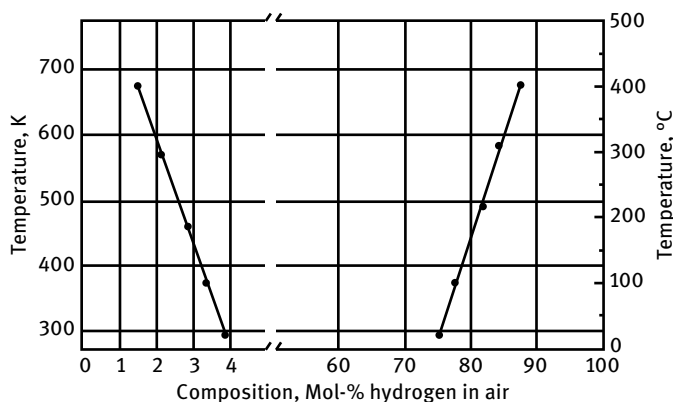
### 7.10.3.3 Effect of Increased Temperature on Limits of Flammability

A study of the effects of temperature on the flammability limits for downward propagation in air/hydrogen mixtures using an electrical spark as the ignition source in a 2.5-cm (1-in.) diameter tube showed that the LFL for downward propagation decreases from 9.4 to 6.3 vol.-% and the UFL increases from 71.5 to 81.5 vol.-% as the temperature was increased from 290 to 673 K (63 to 752 °F), as illustrated in Figure 75 [992]. This figure is essentially two graphs with the center section omitted because it did not contain any data.



**Figure 75:** Effect of increased temperature on limits of flammability with downward propagation of flame. (Reproduced and modified from [975].)

When studying the effect of initial gas temperature on explosive limits (initiation in the center of a high-pressure bomb with flame propagation in all directions), the shape of the two curves (lines) is similar to those shown in Figure 75 above, but the width of the flammable range is wider, Figure 76.

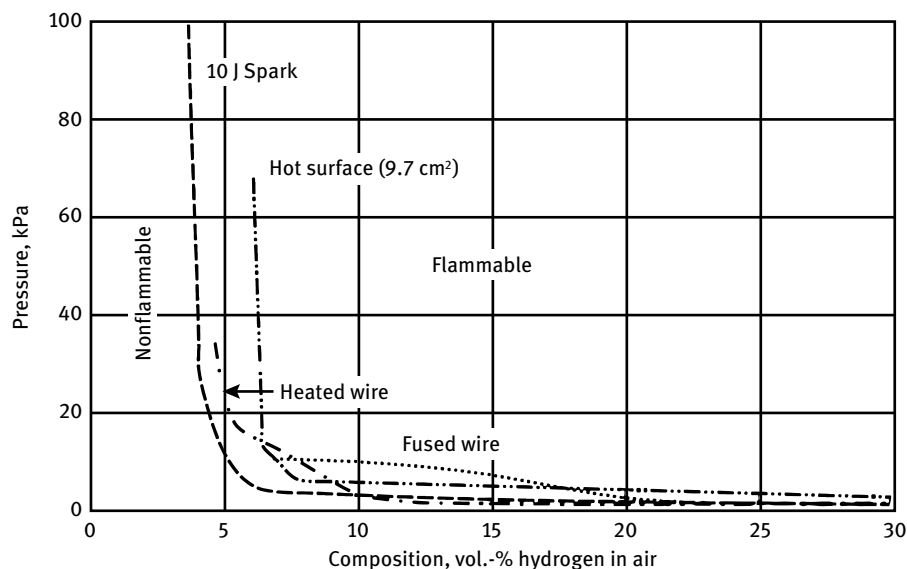


**Figure 76:** Influence of the temperature on the explosion limits of air/hydrogen mixtures, measured at atmospheric pressure according to DIN 51649. (Republished and modified from [974], with permission from Bundesanstalt für Materialforschung und -prüfung dated 30 March 2021.)

#### 7.10.3.4 Influence of Type of Ignition Sources on Flammability of Hydrogen in Air

In a study of the effects of different igniters on the flammability limits for oxygen-hydrogen-nitrogen mixtures at reduced pressures, two test chambers were fabricated out of 304 stainless steel, cylindrical in configuration, with volume displacements of 0.28 and 6.9 m<sup>3</sup> (10 and 240 ft<sup>3</sup>). The ignition sources were electrical spark discharge, electrically heated wire, electrically fused wire, and an electrically heated surface [993, 994]. The results indicated that the ignitability of hydrogen decreased as pressure was decreased. The ignitable pressure limits obtained in the 0.28 m<sup>3</sup> chamber were essentially the same as obtained in the 6.9 m<sup>3</sup> chamber; however, the lower flammability limits observed in the 6.9 m<sup>3</sup> chamber were significantly lower than those observed in the 0.28 m<sup>3</sup> chamber. The electrically heated wire igniter produced the lowest ignitable pressure limits at the higher hydrogen concentrations, whereas the spark igniter produced the lowest ignitable pressure limits at the lower hydrogen concentrations. The lowest ignitable hydrogen quantity was 4.25 vol.-% whereas the lowest oxygen quantity that supported an ignition was 4 vol.-%. Increasing the electrical spark discharge energy from 10 to 5000 joules resulted in a decrease of the ignitable pressure limit. Increasing the initial temperature of the gas mixture from -40 to 300 °F also produced a decrease in the ignitable pressure limit.

The oxygen concentration in these mixtures was 6 vol.-% for hydrogen concentrations of 10 vol.-% or less, and 6/10 of the hydrogen concentration at higher concentrations. This procedure ensured that the oxygen concentration always exceeded that required for stoichiometric oxidation. Figure 77 shows the lower flammability limit observed for each igniter as a function of pressure.



**Figure 77:** Effects of type of ignition source and pressure on the LFL for oxygen-hydrogen-nitrogen. (Reproduced and modified from [934].)

At hydrogen concentrations just below the observed lean limits, the heated wire and heated surface, which deliver their energy over a relatively long period of time, produced hydrogen burning at the igniters; however, the flames did not propagate and self-extinguished when the power to the ignition source was discontinued. This type of non-propagating burn was observed at the lean limits for pressures above 1.4 kPa (0.2 psia). A similar phenomenon has been observed when heated surfaces (glow plugs) were used to burn hydrogen in a controlled preventive manner at concentrations below the LFL, thus preventing leaks in enclosed areas from attaining flammable or explosive concentrations.

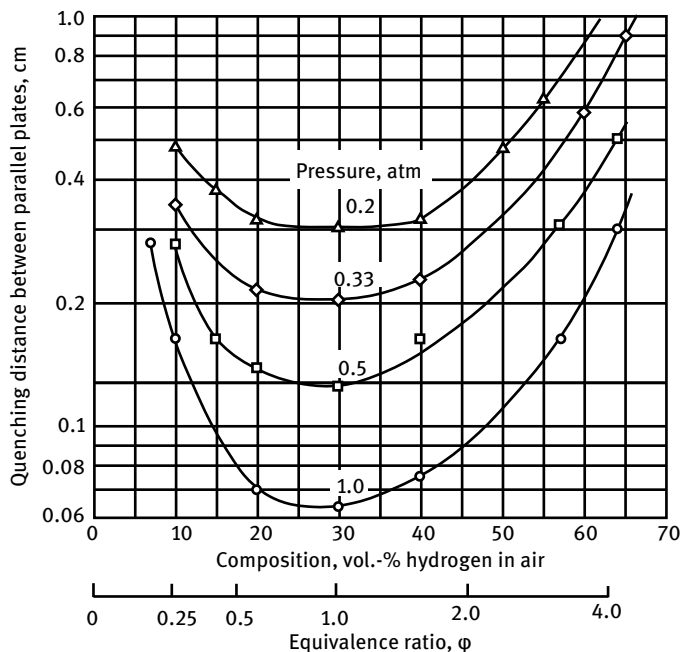
#### 7.10.3.5 Quenching Distance and Critical Diameter for Propagation of Air/Hydrogen Flames

Flames are quenched by excessive loss of heat or active particles or both, to adjacent walls. Experiments have shown that flames in a mixture of given temperature, pressure, and composition cannot pass through openings smaller than some minimum size. This size is the quenching distance. Its actual magnitude depends on the geometry; for instance, the minimum diameter for a cylinder is greater than the minimum separation distance of parallel plates. The geometrical relations among quenching distances for ducts of various shapes have been worked out theoretically and agree quite well with experimental results (From Refs. 35 and 36 in [343]).



### Effect of Mixture Composition on Quenching Distance

In Figure 78 quenching distances (minimum separation of parallel plates) are plotted against fuel concentration [343]. The data were obtained in connection with measurements of ignition energy. The curves show minimum quenching distances at or near stoichiometric composition. The minimum quenching distance at 1 atmosphere and room temperature is 0.063 cm. The knowledge of quenching distances is important for the design of flashback arrestors and detonation traps in air/hydrogen or oxygen/hydrogen gas mixtures.



**Figure 78:** Effect of hydrogen concentration on quenching distance of air/hydrogen mixtures. (Reproduced and modified from [343], based on data from Lewis and von Elbe 1951)

#### 7.10.4 Limits of Flammability of Hydrogen in Oxygen

The limits of flammability of hydrogen in undiluted oxygen are substantially wider than the limits of flammability of hydrogen in air. For upward flame propagation, the flammable range of hydrogen in oxygen extends from 4.1 to 94.0 vol.-% H<sub>2</sub>, and the limits for downward propagation are not much different.

Diluents like nitrogen, argon or helium will narrow the flammable range of hydrogen with oxygen, both at atmospheric pressures and above or below atmospheric pressures.

The parameters of spark ignition of hydrogen in oxygen/nitrogen mixtures affected by cryogenic temperatures are breakdown voltage, quenching distance, flammability limit, and spark ignition energy. Analytical methods for predicting values of most spark ignition parameters for engineering application are cumbersome and far-fetched. Very few data were available in the literature on ignition at cryogenic temperatures. The ignitability of gaseous  $O_2/H_2/N_2$  mixtures at 100 K was tested with a glow plug igniter in a closed bomb at 34.4, 101, and 274 kPa (0.34, 1.0, and 2.7 atm). Data were compared to results of tests conducted at standard conditions, 289 K and 101 kPa (520°R and 14.75 psia) [995].

Experimental studies were carried out to determine the quantities of helium or nitrogen needed for suppressing ignition of mixtures of oxygen with hydrogen under conditions of turbulent flow in a 15-cm (6-in.) diameter tube [996]. The results indicated that on a weight basis the order of effectiveness of the various agents was  $He \gg N_2$ . The quantities of inerting agents required were large enough to preclude widespread in-flight applications to inert leakage once it is detected. The principal utility of inerting processes is probably only in connection with fire prevention during static firing and prelaunch operations on the ground.

Flammability limits of hydrogen-oxygen-diluent mixtures were determined in a 5-cm diameter, 1.8-m long tube, for upward, downward and horizontal propagation of the flame [997]. It was found that for fuel-lean mixtures, upward propagation limits were nearly independent of the diluent type and concentration, but downward limits showed a slight dependence on diluent type and concentration. Limits for fuel-rich mixtures were independent of the direction of propagation of the flame. In all cases, to a good approximation, horizontal limits lay midway between the upward and downward limits. Limits for fuel-rich mixtures were very dependent on the oxygen volume fraction.

Flammability limits in oxygen/hydrogen/inert diluent (helium, argon, carbon dioxide, steam) mixtures at temperatures up to 523 K and pressures up to 2 MPa as well as of the burning velocities of  $O_2/H_2/N_2$  mixtures at 293 K and 4 MPa were measured in a vertical cylinder 50 L in volume (diameter 30 cm and height 80 cm) [998]. The mixture was ignited by fusion of a heated nichrome wire. An anomalous effect of helium on the lower flammability limit in an oxygen-hydrogen-helium mixture was noted. There was a synergistic effect for helium-carbon dioxide and helium-steam mixtures used as inert retardants. The data were interpreted theoretically on the assumption of the important role played by the selective diffusion of hydrogen and helium from the initial mixture into the flame. See also [999].

### 7.11 Radiation from Hydrogen Flames

The heat radiation of an air/hydrogen flame is only 1/10 of the radiation intensity of a hydrocarbon flame. Firefighting crews can operate closer to a hydrogen fire without getting scorched by heat radiation. A hydrogen fire does not expand as rapidly to adjacent combustible structures as a hydrocarbon fire. A pool of burning liquid hydrogen is consumed in 1/10 of the time of a pool of gasoline or kerosene of the same volume. The emission spectrum of hydrogen flames was already described in Section 3.2.4 “Radiation Emission Spectra of Oxygen/Hydrogen Flames.”

The emissivity of a hydrogen flame is only 0.09 compared to the emissivity of a black body radiator which is close to 1.0. Radiation measurements showed that persons could approach a large hydrogen fire for 30 s to as close as 54 m without suffering heat burns [497, 499]. Atmospheric moisture absorbs thermal energy radiated from a hydrogen fire and can reduce the radiation values recorded from laboratory experiments in dry air.

In a study of the structure and radiation properties of round turbulent hydrogen/air diffusion flames, measurements were made of mean and fluctuating stream-wise velocity, mean temperatures, species concentrations, spectral radiation intensities, and radiant heat fluxes [1000]. The measurements were used to evaluate predictions based on the laminar flamelet concept and narrow-band radiation models, both ignoring (using mean properties) and considering effects of turbulence/radiation interactions. Physical property state relationships found by correlating auxiliary measurements in laminar flames proved to be almost equivalent to conditions for local thermodynamic equilibrium. The agreement of structure and radiation predictions was reasonably good. Effects of turbulence/radiation interactions were significant for these flames, causing almost a 100% increase in spectral radiation intensities, in comparison to mean property predictions upstream of the flame tip.

Burning hydrogen emits heat radiation effected by broad water bands in NIR and IR spectral ranges. In the case of large cloud explosions, the risk of heat radiation is commonly underestimated due to the non-visible flame of hydrogen-air combustion. Organic vapor and particulate contaminants entrained into the flames will contribute to the intensity of heat radiation [1001]. Different hydrogen-air mixtures were ignited in a closed vessel and the combustion was observed with fast scanning spectrometers using a sampling rate up to 1000 spectra/s. In some experiments, to take into account the influence of organic contaminants, a spray of a liquid glycol-ester or milk powder was added to the mixture to enhance the radiation signature. During hydrogen combustion,  $\cdot\text{OH}$  free radicals emit an intense spectrum at 306 nm. This intermediary radical allows monitoring the reaction progress. Intense water band systems between 1.2 and 3  $\mu\text{m}$  emit remarkable amounts of heat radiation at a measured flame temperature of 2000 K. At this temperature broad optically thick water bands between 4.5 and 10  $\mu\text{m}$  contribute only scarcely to the total heat output.

Measurements were performed in large-scale vertical flames to characterize the dimensional and radiative properties of an ignited hydrogen jet [1002]. Visible and IR video and UV flame luminescence imaging were used to evaluate flame length, diameter, and structure. Radiometer measurements allowed determination of the radiant heat flux from the flame.

The radiative characteristics of large-scale (visible length 1.4–9.1 m) hydrogen jet flames that simulate an accidental leak from a high-pressure hydrogen container were compared with previous experimental and theoretical results for laboratory-scale non-sooting flames [1003]. The comparison showed that correlations of radiative heat fraction with global residence time need to account for the differences in thermal emittance of combustion gases for different fuels. This correction was found to be particularly important when hydrogen flames were compared to flames with  $\text{CO}_2$  as a radiation-emitting product species. The radiative fraction of large-scale jet flames was found to be smaller than that predicted by the correlation obtained for laboratory-scale flames. This was explained by an increase in optical thickness as the flame size increases.

Jet flames originating from high-pressure sources up to 413 bar (6000 psi) were studied to verify the application of correlations and scaling laws based on lower-pressure subsonic and choked-flow jet flames [1004]. These higher pressures were expected to be typical of the pressure ranges in future hydrogen storage vessels.

The dimensions of hydrogen jet diffusion flames in air formed by release of high-pressure hydrogen gas from circular nozzles with diameters ranging from 0.1 to 4 mm and release pressures from 0.01 to 40 MPa (gauge) were measured [1005]. The blow-off limits were determined as a function of nozzle diameter and feed pressure. The flame sizes were measured, and experimental equations were obtained for the length and width of the flames. The flame sizes depended not only on the nozzle diameter but also on the feed pressure. The heat radiation from the hydrogen flames could be predicted from the flow rate of the gas and the distance from the flame.

Open hydrogen flames were observed with feed pressures from 900 bar down to 1 bar (gauge) with orifices ranging from 1 to 3 mm. These data can be used to derive scaling laws about the main flame characteristics and about some thermodynamic aspects of hydrogen releases under high pressure [1006].

The temperature, velocity, turbulence and concentration distribution of hydrogen flames with different circular nozzle diameters and reservoir conditions of horizontal cryogenic hydrogen gas jets at temperatures of 35–65 K and pressures from 0.7 to 3.5 MPa were investigated [1007]. Combustion experiments of burning hydrogen jets included investigations on the stability of the flame and its propagation behavior as a function of the ignition position. Then combustion pressures and heat radiation from the sonic jet flame during the combustion process were measured. Safety distances were evaluated and an extrapolation model to other jet conditions was proposed to quantify the hazard potential arising from leaks and fires in liquid hydrogen reservoirs.

In the past, analytical methods used to establish thermal radiation hazard safety boundaries from ignited hydrogen plumes were based on models previously developed for hydrocarbon jet fires. Radiative heat flux measurements of small-scale and medium-scale hydrogen jet flames (i.e., visible flame lengths <10 m) compared favorably to theoretical calculations provided corrections were applied to correct for the product species thermal emittance and the optical flame thickness [1008]. Flame radiation measurements from two larger scale hydrogen jet flames were made to determine the applicability of current modeling approaches to these larger flames. The horizontally orientated releases were from 20.9 and 50.8 mm ID pipes with a nominal 60 bar gauge source pressure and respective mass flow rates of 1.0 and 7.4 kg/s. Care was taken to ensure no particles were entrained into the flame, either from the internal piping or from the ground below. Radiometers were used to measure radiative heat fluxes at discrete points along the jet flame radial axis. The estimated radiant fraction, defined as the radiative energy escaping relative to chemical energy released, exceeded correlation predictions for both flames.

The flame velocities of unconfined air/hydrogen gas explosions depend on the cloud size and the distance from the initiating source, related to turbulence generated by the propagating flame front. The molecular absorption bands in the flame front are exposed to continuously increasing radiation intensity of water emission bands from the interior of the reaction product fireball. The air/hydrogen flame propagation in 1-m diameter balloons was observed by high-speed video techniques including time resolved spectroscopy in the UV-Vis-NIR spectral range with a time resolution up to 3000 spectra/s [356, 1009]. Ignition, flame head velocity, flame contours, reacting species and temperatures were evaluated. Flame front velocities were found to be between 16 and 25 m/s. The flame front is not smooth, having cellular structures. The radiation of various bands from the fireball absorbed by the reacting species is estimated to have an influence on the flame velocity depending on the distance from initiation. Evaluation of OH-band and water band spectra might indicate higher temperatures of the flame front induced by radiation of the fireball [1010].

Deflagration phenomena in air/hydrogen mixtures initially filled in 1.4-m<sup>3</sup> spherical latex balloons were measured using a high-speed digital video camera and pressure transducers [1011]. A maximum flame propagation velocity of about 100 m/s was observed with a maximum overpressure of 15 kPa at 1 m from the ignition point. According to the detailed flame propagation velocity records, there were long deceleration durations. The observed maximum overpressure was smaller than the overpressure estimated on the basis of the observed maximum flame propagation velocity and the pressure wave theory of spherical flames.

High-speed cinematography in combination with image processing techniques, background-oriented schlieren technique and a difference method were used to visualize the shape of burning hydrogen jets [1012]. The combustion zone was recorded by a high-speed IR camera. The IR camera was synchronized with a rotating filter wheel to generate four different motion pictures at 100 Hz each on a defined spectral range.

The experiments provided detailed information that might be used for improving jet fire model predictions.

## 7.12 Explosion Hazards of Hydrogen

This section deals with explosions and detonations of hydrogen in air or in oxygen. There is primarily the concern about accidental explosions of hydrogen leaks in air, but there are also many practical applications of hydrogen detonations, such as drivers in shock tubes, in pulsed detonation engines, and rotating detonation engines.

A detonation explosion is capable of causing much greater physical damage to the environment due to the significantly higher shock pressure that is generated (a detonation creates as much as 20 times the initial stoichiometric pressure versus about 8 times the initial pressure for a deflagration).

### 7.12.1 Gaseous Air/Hydrogen Detonations

Spherical detonations in gas-filled balloons were initiated in a range of mixtures of hydrogen and air, at one atmosphere initial pressure, by tetryl charges with masses of 0.78–2.40 g [1013]. Due to the small size of the detonation vessel ( $= 1.5 \text{ m}^3$ ), they were limited to a maximum charge weight of only 2.4 g of tetryl and were able to initiate detonation in a stoichiometric air/ $\text{H}_2$  mixture (29.6 vol.-%  $\text{H}_2$ ) with a charge of 1.1 g of tetryl. By kinetic modeling, they estimated that a charge of 10 g of tetryl (heat of detonation  $= 4.27 \text{ kJ/g}$ ) would initiate mixtures in the concentration range from 22.7 to 49.1 vol.-%  $\text{H}_2$ , whereas for a 100 g charge, the corresponding range would be from 17.3 to 56.5 vol.-%  $\text{H}_2$ . The results were similar to those from earlier experiments by Cassutt [927], but contrary to predictions by Lee [1014, 1015]. A theoretical model embracing the full kinetic scheme for hydrogen oxidation was made to fit the experimental detonability data and can predict the variation of detonability with concentration over a much wider range. An important conclusion from the model study was that it predicts for the first time for spherical detonation the existence of concentration limits to detonability. A kinetic explanation is offered for these limits, which are approximately in the range of 13–70 vol.-% hydrogen in air.

The hazards due to deflagrative air/hydrogen blast waves were experimentally evaluated using three different sizes of latex balloons ranging from 5.4 to 1400 L [1016]. The rate of development of flame velocity and blast pressure were monitored simultaneously as a function of equivalence ratio ( $\phi = 0.5\text{--}4.0$ ), diameter of the balloon ( $d = 65$  or  $150 \text{ cm}$ ), ignition point, and ignition timing. In some tests the balloon was cut open just before the igniter was activated. In other tests ignition occurred in the center and the balloon burst as the result of overpressure from the inside.

The overpressure created by air/hydrogen explosions and detonations can be very destructive and depends on the composition and size of the air/hydrogen cloud, the degree of confinement and the mode of initiation [523]. See Section 7.12.8.1 “Overpressure from Unconfined Air/Hydrogen Explosions.”

The explosion characteristics of air/hydrogen mixtures including the maximum explosion pressure, deflagration index, the exponent parameter of the burning velocity and the burning parameter were measured in a 20-L sphere [1017]. Methods and equations are provided to estimate these parameters.

The experimental maximum explosion pressure agreed with the theoretical value estimated using a chemical equilibrium program if the concentration of hydrogen was from 10 to 75% in air, but not close to the flammable limits. The deflagration index for air/hydrogen mixtures, even if normalized by the cube root of the volume of explosion vessel, was found to be sensitive to the vessel volume. The maximum deflagration index in a 20-L explosion vessel was  $970 \text{ bar m s}^{-1}$  at 36 vol.-% of hydrogen in air. Other investigators have shown that it increases with the volume of the explosion vessel. The apparent burning velocity increased as the pressure increased during the explosion. The burn rate exponent was 0.45 for air/hydrogen mixtures. The maximum value of the burning rate occurred at about 40 vol.-% of hydrogen in air, which was above the stoichiometric concentration of 29.6 vol.-%  $\text{H}_2$ .

The critical energies of ignition of some gaseous fuels and oxygen mixtures at different initial pressure and equivalence ratios were measured [1018]. The determination of direct initiation of detonation was based on the overpressure signal from a pressure transducer. The effective energy responsible for the direct initiation was considered as the first quarter cycle of the current discharge. The effect of initial pressure and equivalence ratio on the critical energy of direct initiation was investigated in some typical gaseous oxygen and fuel (i.e.,  $\text{H}_2$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$ ) mixtures. It was shown that the relationship between critical energy and initial pressure is inversely exponential and it is U-shaped between critical energy and equivalence ratio.

### 7.12.2 Explosion Velocity and Overpressure of Unconfined Air/Hydrogen Mixtures

Unconfined air/hydrogen mixtures will deflagrate, but not detonate. The overpressure of such events is less than that experienced with detonations in confined spaces.

Large eddy simulation modelling of unconfined large-scale explosions were compared to results from a large air/hydrogen deflagration experiment in a 20-m diameter hemispherical polyethylene shell in the open [1019]. Two combustion sub-models, one developed on the basis of the renormalization group theory and another derived from the fractal theory, were applied. Both sub-models included a sub-grid scale model of the turbulence generated by flame front itself based on theory and observations by others on a critical distance for transition from laminar to detonative flame propagation regime. The best fit flame propagation dynamics were obtained for the fractal sub-model with a fractal dimension  $D = 2.22$ . The fractal sub-model reproduced the

experimentally observed flame acceleration during the whole duration of explosion, accurately simulating the negative phase of the pressure wave but overestimating by 50% the positive phase amplitude. The other sub-model was closer to the experiment in predicting the positive phase but under-predicted by 30% the negative phase amplitude. Both sub-models simulated experimental flame propagation up to 20 m and pressure dynamics up to 80 m with reasonable accuracy.

The blast wave in rich air/hydrogen mixtures dramatically accelerates in its later stage. The intensity of the blast wave is strongly affected by flame speed acceleration. The flame propagation behavior and the intensity of the blast wave by an accidental explosion of an air/hydrogen mixture in an open space were measured simultaneously using a soap bubble method [1020]. The blast wave in lean hydrogen mixtures grew rapidly with time because of the diffusional-thermal instability. The results showed that the flame in lean hydrogen-air mixtures was propagated by spontaneous flame instabilities. The flame in rich hydrogen-air mixtures propagated smoothly in the early stage and was intensively wrinkled and accelerated in the later stage by different types of instabilities. The flame wrinkling in the later stage of rich hydrogen flames was triggered when the flame approached the non-uniformity transition region of concentration distribution. The intensity of the blast wave of air/hydrogen mixtures was strongly affected by the acceleration of the flame propagation by these spontaneous flame disturbances.

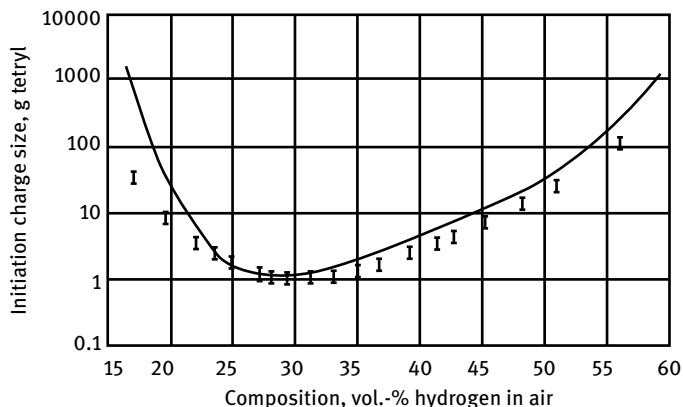
Air/hydrogen mixtures of various concentrations were filled in a plastic tent of thin vinyl sheet of  $1\text{ m}^3$  and ignited by an electric spark [1021]. Flame behavior and blast waves generated during unconfined hydrogen deflagrations were studied using IR photography. IR photography enabled expanding spherical flame behaviors to be measured and flame acceleration exponents to be evaluated. The onset of accelerative dynamics on the flame propagation was analyzed by the time histories of the flame radius and the stretched flame speed. The results demonstrated that the self-acceleration of the flame, which was caused by diffusional-thermal and hydrodynamic instabilities of the blast wave, was influenced by hydrogen deflagrations in unconfined areas and the overpressure rapidly increased with time. The burning velocity acceleration was greatly enhanced with spontaneously formed turbulence.

The existing methods for calculating overpressure resulting from a vapor cloud explosion (VCE) were tested for their ability to predict overpressures from unconfined hydrogen explosions [1022]. Examining data collected from five reported experimental investigations on open air/hydrogen explosions covering  $1.4\text{--}300\text{ m}^3$  volume of air/hydrogen mixtures and concentrations of 20–57 vol.-%  $\text{H}_2$  showed that the existing VCE models were grossly inadequate for predicting the overpressure generated by unconfined hydrogen explosions. A new method was developed for assessing overpressures from hydrogen explosions for a given concentration and volume of release which had a much better ability to fit the experimental data, hence much stronger ability to accurately forecast the severity and consequences of hydrogen-based VCEs.



### 7.12.3 Required Minimum Initiation Energy for Air/Hydrogen Detonations

If initiated by a source other than a transition from deflagration to detonation in confined spaces, the energy required to reproducibly initiate detonations in air/hydrogen mixtures is dependent on the air : hydrogen mixture ratio. Figure 79 shows the amount of tetryl booster charge required to initiate detonations in air/hydrogen mixtures as a function of the volume percent hydrogen in air [1023]. A similar correlation can be shown for the detonation cell size determined with a sooted foil in the detonation chamber.



**Figure 79:** Minimum initiation energy for direct detonation of air/hydrogen mixtures. (Reproduced and modified from [1023].)

Experimental measurements of cell size  $\lambda$  for air/hydrogen/carbon dioxide mixtures for hydrogen/air volume ratios between 0.16 and 1.5 and carbon dioxide mol fractions of 0, 0.05, 0.10, and 0.15 showed that the cell sizes are at a minimum for both diluted and undiluted air/hydrogen mixtures near stoichiometric composition (i.e., hydrogen/air = 0.4) [1023, 1024]. Minimum cell sizes for carbon dioxide mol fractions of 0, 0.05, 0.10, and 0.15 were 1.51, 2.05, 4.2, and 15.0 cm, respectively. Results of large-scale and small-scale critical tube diameter ( $d_c$ ) measurements were presented and showed good agreement with the empirical scaling law,  $d_c = 13\lambda$ . Mean detonation velocities and pressures were measured and compared to the theoretical Chapman-Jouguet (C-J) values.

The minimum required critical energy for direct initiation of spherical detonations in stoichiometric oxygen/hydrogen mixtures at elevated pressures up to an initial pressure of 20 atm in a spherical bomb was measured to look at the effect of explosion limits on the detonation sensitivity [1025]. Direct initiation was achieved via spark ignition from a high-voltage capacitor discharge. At elevated initial pressure, the second explosion limit effect plays a significant role leading to slow-branching

reactions and the detonation sensitivity of hydrogen mixtures is comparable to other common hydrocarbon mixtures under such conditions.

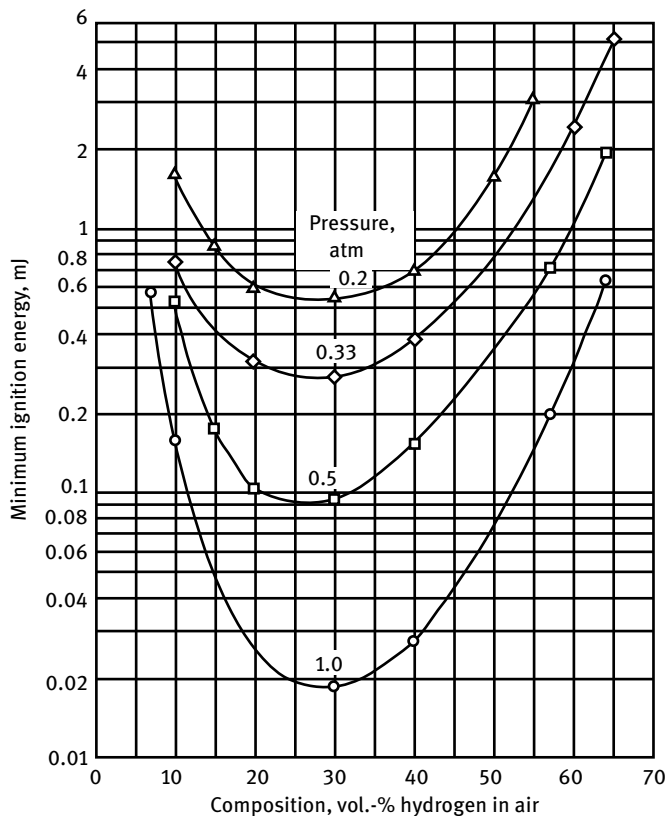
Critical conditions for the direct initiation of self-sustained detonation in cold gaseous oxygen/hydrogen mixtures were examined experimentally [1026]. These initial conditions were expected to depend mainly on four parameters: the equivalence ratio of the mixture, the amount of the initial energy deposition, the initial temperature and pressure of the mixture. These critical conditions were determined by fixing alternatively three of these parameters and varying the fourth one from subcritical to supercritical detonation conditions. Results were presented for initial pressures  $P_0$  and equivalence ratios  $\Phi$  ranging from 0.3 to 1 bar and from 1 to 2, respectively, for the two initial temperatures  $T_0$ , 123 and 293 K. Detonations were initiated via an exploding wire considered as a point source of energy. The results included: **(1)** the critical initial pressures and equivalence ratios for a given initiation energy, **(2)** direct measurements of the critical energy for given initial conditions, and **(3)** cell sizes measurements in both ambient and low temperature cases. In order to bracket the critical condition, when the critical condition needed for the initiation of a self-sustained detonation was reached, the procedure was carried out at least a second time. The results indicated that for the lowest values of the initial pressure, a decrease of initial temperature may favor the onset of detonation. For most of the initial conditions, the measured detonation pressures and velocities were in agreement with C-J values computed using the ideal-gas equation of state.

The common method for measuring spark ignition energy uses a measured amount of electrical energy in the form of a short-duration capacitance discharge spark which is introduced very rapidly into a mixture of given pressure, temperature and composition and with a given electrode separation. The smallest energy that will ignite the mixture is found, and the process is repeated for other electrode spacings to find the gap for which the energy is lowest. Figure 80 is a plot of ignition energy in millijoules against fuel concentration for mixtures at room temperature and several pressures [343, 1027]. The 1-atmosphere curve indicates a minimum energy of 0.019 mJ at about the stoichiometric mixture and rises steeply toward the lean and rich flammability limits.

#### 7.12.4 Critical Diameter for Propagation of Air/Hydrogen Detonations

Knowledge of the critical diameter for propagation of detonations is required for the design of flame arrestors and detonation arrestors. The critical diameter is the diameter of tubing or orifices below which detonation from a donor section cannot propagate into an acceptor section of detonable gas.

An experimental study to investigate the transmission of a planar detonation wave through an orifice into an unconfined medium used mixtures of  $O_2 + 2H_2 + \beta N_2$  for a range of nitrogen concentrations corresponding to  $1 \leq \beta \leq 3.76$  and at an initial pressure of 1 atm [1028]. It was found that the critical diameter for the transmission



**Figure 80:** Spark ignition energies for air/hydrogen mixtures at various pressures. (Reproduced and modified from [343].)

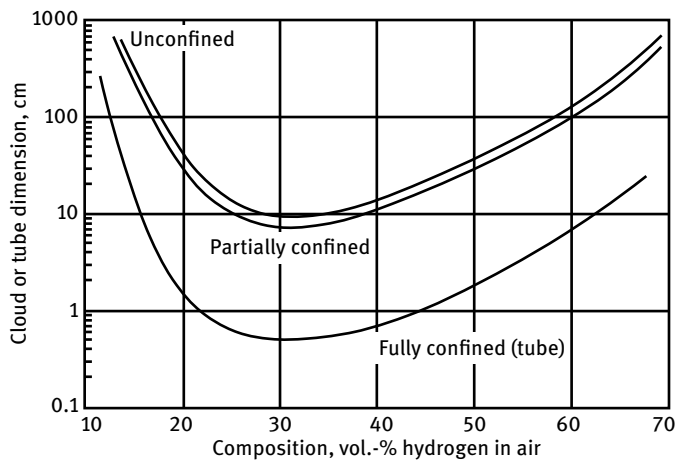
through an orifice was identical to that for a straight tube and both followed the empirical correlation of  $d_c \cong 13\lambda$ . The transmission through square, triangular, elliptical, and rectangular orifices has led to the development of a correlation based on the effective diameter similar to the case of circular geometry (i.e.,  $d_{\text{eff}} \cong 13\lambda$ ). The effective diameter was defined as the mean value of the longest and shortest dimensions of the orifice shape. The effective diameter correlation suggested that the criterion for transmission may be based on the mean curvature of the wave front, the implication being that it is not to exceed a certain critical value. The results suggested that local properties in the immediate vicinity of the wave front are the controlling parameters for reinitiation rather than the properties of the gas dynamic flow structure in the wake.

The critical diameter for propagation of air/hydrogen detonations is related to the detonation cell width that is often determined by placing a sooted metal foil along the wall of a detonation test chamber. The cell width  $\lambda$  is an intrinsic length scale that characterizes detonations. Highly detonable mixtures have small cell widths, while

increasingly less detonable mixtures have increasingly larger cell widths. An empirical correlation exists between the critical diameter of round tubing through which detonation can no longer propagate and the cell width measured on the sooted plates

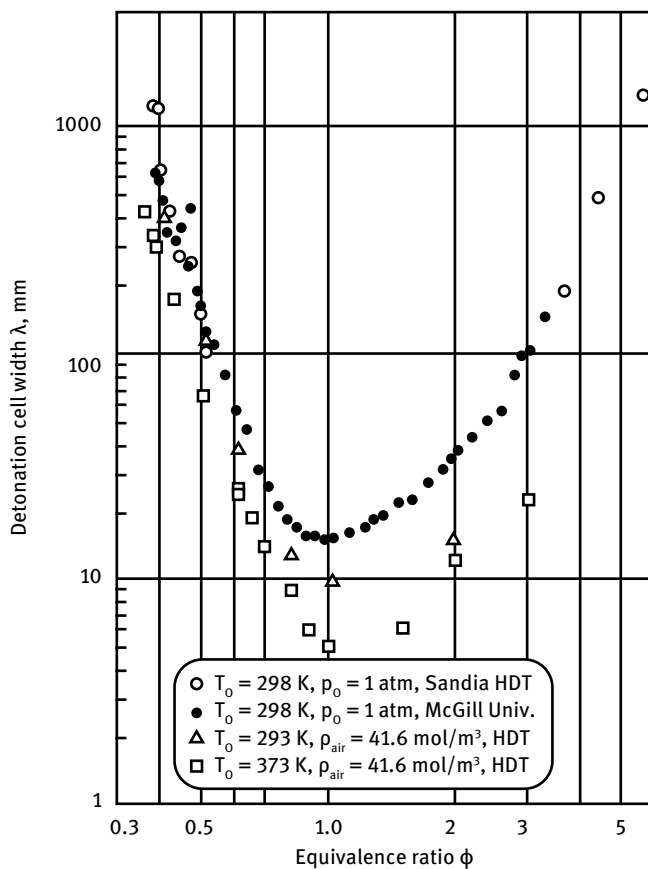
$$d_c = 13\lambda$$

The diamond-shaped pattern on the sooted foil is the result of a three-dimensional transverse wave structure which is the direct consequence of the non-linear coupling of the exothermic chemical reactions and the shock-induced hydrodynamic flow field. The critical diameter of air/hydrogen detonations is at a minimum for stoichiometric air : hydrogen ratios (Figure 81).



**Figure 81:** Minimum dimensions of air/GH<sub>2</sub> mixtures for detonation at 101.3 kPa and 298 K. (Reproduced and modified from [1023].)

A 43-cm (17-in) inside diameter, 13-m (43-ft) long heated tube was used to study detonations in air/H<sub>2</sub>/steam mixtures [1029]. Detonation cell width and velocity results were measured for air/H<sub>2</sub> mixtures, undiluted (Figure 82) and diluted with CO<sub>2</sub> or H<sub>2</sub>O for a range of H<sub>2</sub> concentrations, initial temperatures, and pressures. The results showed that the cell width is at a minimum for stoichiometric mixtures and that addition of either CO<sub>2</sub> or H<sub>2</sub>O significantly increased the detonation cell width and hence reduced the detonability of the mixture. The results also showed that the detonation cell width was reduced (detonability was increased) for increased initial temperature and/or pressure. Using a larger diameter tube, it was discovered that air/H<sub>2</sub> will detonate for a wider range of concentrations than previously believed because a mixture as lean as 13 vol.-% H<sub>2</sub> has detonated. The abbreviation HDT stands for Heated Detonation Tube, a 43-cm-diameter detonation tube at Sandia National Laboratory. The image based on data from Lee et al. [1023] is shown as Figure A2.8 on page A43 of Gregory, NASA Safety standard for hydrogen and hydrogen systems [305].



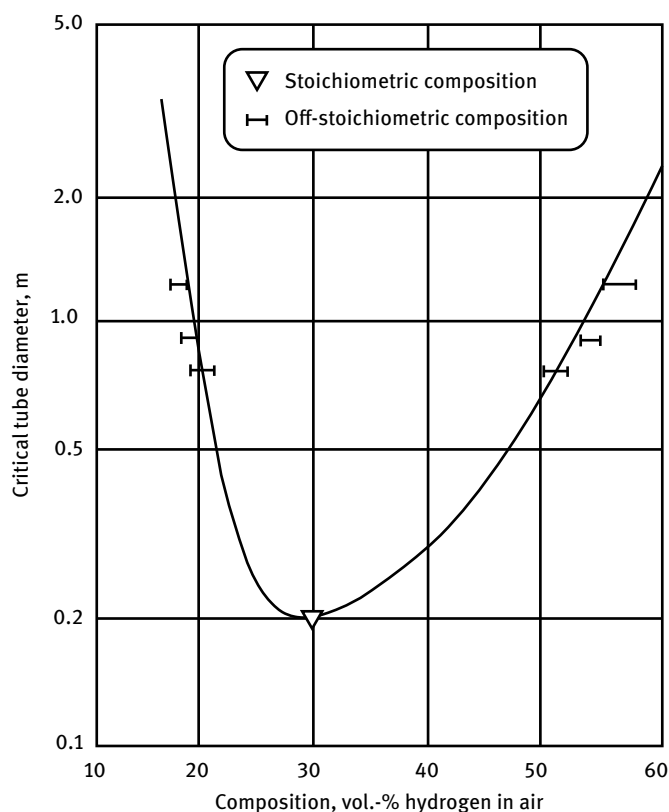
**Figure 82:** Detonation cell width of air/hydrogen detonations. (Reproduced and modified from [1024].)

For pure or diluted air/H<sub>2</sub> mixtures, the variation of cell size as a function of hydrogen concentration exhibited a characteristic U-shaped curve with a minimum around the stoichiometric composition (29.6 vol.-% H<sub>2</sub>). For air/H<sub>2</sub> mixtures at NTP initially, the cell size increased from  $\lambda = 1.5$  cm for the stoichiometric composition to  $\lambda = 1.03$  m for the leanest mixture tested (13.6 vol.-% H<sub>2</sub>) and  $\lambda = 1.35$  m for the richest mixture tested (70 vol.-% H<sub>2</sub>) [1024].

Gaseous detonation propagation phenomena are characterized by cellular structure and cell size, detonation initiation threshold, transmission, attenuation, and failure. Experimental measurements of cell size  $\lambda$  for air-hydrogen-carbon dioxide mixtures in the hydrogen/air volume ratios ranging between 0.16 and 1.5, showed that cell sizes were a minimum for both diluted and undiluted hydrogen-air mixtures near stoichiometric ratios (i.e., hydrogen/air = 0.4) [1023]. Results of large-scale and small-scale

critical tube diameter ( $d_c$ ) measurements showed good agreement with the empirical scaling law,  $d_c = 13\lambda$  for round tubing and  $d_c = 11\lambda$  for square tubes. Detonation velocities and pressures were measured and compared to the theoretical Chapman-Jouguet values. The critical tube diameter for air/ $H_2$  mixtures varies with fuel concentration as plotted in Figure 83, and exhibits the same U-shape dependence as the detonation cell size data from which it has been derived using the empirical correlation  $d_c = 13\lambda$ .

As shown in Figure 83, good agreement can be achieved between the direct measurements of  $d_c$  and the estimated values from the  $d_c = 13\lambda$  relationship. For stoichiometric composition, a critical tube diameter of the order of 20 cm was directly measured in small-scale tests in good agreement with the value  $d_c = 19.6$  cm estimated from the  $d_c = 13\lambda$  correlation using the value  $\lambda = 1.51$  cm directly measured from smoked foil records. For off-stoichiometric mixtures, direct measurements of  $d_c$  in large-scale experiments were carried out in tubes of diameters 76, 91, and 121 cm. The critical hydrogen concentrations were 21 and 51 vol.-%  $H_2$  for the 76-cm-diameter tube, 19.2 and 53.3 vol.-%  $H_2$  for the 91-cm diameter tube, 18.1 and 55.5 vol.-%  $H_2$  for the 121-cm diam-



**Figure 83:** Variation of critical tube diameter with fuel percentage in air/ $H_2$  mixtures at NTP. (Reproduced and modified from [1024].)

eter tube. As shown in Figure 83, these large-scale results fall into the range predicted by cell size data using the  $d_c = 13\lambda$  correlation.

Diluting air/H<sub>2</sub> mixtures with CO<sub>2</sub> at NTP decreased the detonation sensitivity. For example, the addition of 5, 10, and 15 vol.-% CO<sub>2</sub> to a stoichiometric air/H<sub>2</sub> mixture (29.6 vol.-% H<sub>2</sub>) increased the cell size by factors of 1.5, 2.8, and 12.8, respectively. Diluting with steam air/H<sub>2</sub> mixtures at 373 K (100 °C) and superatmospheric pressure initially caused a reduction in detonation sensitivity. For example, the addition of 10, 20, and 30 vol.-% steam to a stoichiometric air/H<sub>2</sub> mixture at 373 K (100 °C) initially increased the detonation cell size by factors of 6, 30, and 60, respectively.

In studying the influence of steam and carbon dioxide diluents on the detonability of air/hydrogen mixtures, data were obtained on the detonation cell width in a heated detonation tube that was 0.43 m in diameter and 13.1 m long [1030]. The detonation cell widths were correlated using a characteristic length calculated from a chemical kinetic model. The addition of either diluent to an air/hydrogen mixture increased the cell width for all equivalence ratios. For equal diluent concentrations, however, carbon dioxide not only yielded larger increases in the cell width than steam, but its efficacy relative to steam was predicted to increase with increasing concentration. The range of detonable hydrogen concentrations in an air/hydrogen mixture initially at 1 atm pressure was found to be between 11.6 and 74.9 vol.-% for mixtures at 293 K (20 °C) and between 9.4 and 76.9 vol.-% for mixtures at 373 K (100 °C). The detonation limit was between 38.8 and 40.5 vol.-% steam for a stoichiometric air/hydrogen/steam mixture initially at 373 K (100 °C) and 1 atm.

Detonation cell widths for stoichiometric oxygen-hydrogen-diluent mixtures in a 15-cm diameter, 7.5-m-long, steel pipe with helium, carbon dioxide, steam, and argon as diluents were measured for initial temperatures from 293 to 373 K (20–100 °C), initial pressures from 200 to 160 kPa, and hydrogen concentrations up to 60% by volume [1031]. Experiments conducted over a range of hydrogen concentrations indicated that detonation was possible down to flammability limits for certain mixtures. Over the range investigated, the initial temperature appeared to have no significant effect on the cell width. It was attempted to develop an empirical correlation to predict the cell width.

In order to design combustion chambers for detonating engines, specifically pulse detonation engines and rotating detonation engines, the cell size of detonation waves is needed. Higher than atmospheric mixture pressure detonation cell sizes are important for scaling the combustion chambers, and only few data existed for air/hydrogen detonation cell sizes at mixture pressures up to 1 MPa (10 atm). A new detonation cell size measurement technique was used to measure 15 cases for varying mixture pressures up to 1 MPa (10 atm) and different equivalence ratios [1032]. An increase in mixture pressure decreased detonation cell size and a decrease in equivalence ratio from stoichiometric composition increased detonation cell size. The experimental results were used to establish a correlation that estimated air/hydrogen detonation cell sizes given initial mixture pressures and equivalence ratios.

### 7.12.5 Detonability Range of Hydrogen Gas in Air

The detonability range of air/hydrogen gas mixtures depends on the air : hydrogen ratio, the mode of initiation, and the degree of confinement [1033]. In the wake of water-cooled nuclear reactor loss of coolant and melt-down incidents like Three Mile Island and Fukushima Daiichi, where zirconium cladding reacted with steam to create clouds of hydrogen gas inside the containment structure that later ignited and exploded, there have been many studies of air/hydrogen detonations in enclosed structures. The results of these studies in the nuclear industry would also help to examine the hazards of hydrogen explosions in rocket propellant test facilities.

Older data on detonation limits were obtained in small diameter tubes, usually 2.5 cm (1 in.) or less in diameter. One must remember that the old values represented the limit of propagation for that diameter tube. Larger tubes have produced wider limits. Several experimental studies that were completed following the Three Mile Island incident showed that the classical literature 18 and 59% detonation limits in dry air/H<sub>2</sub> mixtures in confined spaces are not correct.

A comparison of the critical tube diameter of stoichiometric air/hydrogen mixtures ( $d_c = 20$  cm) with that of stoichiometric air/acetylene mixtures ( $d_c = 12$  cm) indicated that hydrogen is slightly less sensitive than acetylene [1034]. The relatively slow increase in  $d_c$  for H<sub>2</sub>-rich mixtures (as compared to lean mixtures) indicated that fuel-rich mixtures are more hazardous from the detonation point of view than fuel-lean mixtures. Detonability limit criteria for different boundary conditions were based on the cell size of the mixture. For fully confined detonations in tubes, limits were set by the onset of single-headed spin.

The rich and lean detonation limits of air/hydrogen mixtures are dependent on critical dimensions of the detonation channel. Extrapolation of laboratory scale air/hydrogen detonations, verified by some large-scale detonations, increased confidence for further extrapolation to the very large dimensions associated with nuclear reactor containment buildings where hydrogen may accumulate during reactor meltdown. Laboratory-scale experiments were complemented with large-scale experiments [1035–1037]. Both rich and lean air/hydrogen mixtures were confined in thin-wall (100  $\mu$ m) transparent polyethylene envelopes to provide minimum lateral confinement. The diameter of the envelopes ranged from 0.75 m to about 2 m, depending upon the mixture under study. For the critical tube diameter experiments, the polyethylene tube was attached to a steel tube which was generally smaller than the polyethylene tube. High explosive was used to launch a detonation in the steel tube, the emergent detonation wave then propagated into a larger diameter plastic envelope.

Flame acceleration studies of deflagrating hydrogen/air mixtures were carried out in free and partially confined homogeneous clouds [1038]. The experiments in an unconfined hemispherical configuration showed a distinct dependence of the flame velocity on the cloud size which did not exceed, however, an upper limiting value. The experiments under partially confined conditions without additional turbulence indi-



cated that the flame velocity and consequently the pressure field was governed by the hemispherical flame front initially formed, i.e. the flame velocity was not affected by the partial confinement. To increase the turbulence effects, further experiments were carried out with a fan and with jet ignition. In the case of fan-induced turbulence the flame velocity was strongly influenced by the fan speed. At a certain fan capacity the transition of a deflagration into a detonation was observed. With jet ignition produced by venting an explosion chamber into the partially confined cloud the transition occurred even with hydrogen concentrations in air as low as 22 vol.-%. Turbulence models showed that high damaging overpressures or the transition from a deflagration into a detonation are only generated by strong turbulences as a consequence of flow and/or obstacles.

Large-scale experiments have indicated that scale and geometric effects can strongly influence both the ability of an air/hydrogen mixture to propagate or sustain a detonation, and the probability that a deflagration will undergo a transition to detonation [1039]. The data showed that many past concepts concerning detonations, which were derived from small-scale experiments, should be revised. In particular, the occurrence of detonations may not be as unlikely as previously considered, especially in large-scale industrial environments in which obstacles are present.

Partial confinement may aid in the transition of burning hydrogen from deflagration to detonation. A “lane” is a long partial confinement of air/hydrogen mixtures, confined at the bottom and on two sides, but open to the top [1040].

Several different large-scale deflagration and detonation experiments of hydrogen and air mixtures were performed measuring flame-front time of arrival using ionization probes, blast pressure, heat flux, high-speed video, standard video and infrared video [943]. The large-scale open-space tests used a hemispherical facility that confined the mixture within a thin plastic tent that was cut prior to initiation of a deflagration. Initial homogeneous hydrogen concentrations varied from 15 to 30%. All tests were ignited at the bottom center of the facility using either a spark or, in one case, a small quantity of high explosive to generate a detonation. Spark-initiated deflagration tests were performed in a 1/5-scale tunnel using homogeneous hydrogen mixtures to compare against similar tests performed in the open space. Several experiments performed in the 1/5-scale tunnel released 0.1 and 2.2 kg of hydrogen into the tunnel with and without ventilation to represent, respectively, a release from a fuel cell vehicle or the storage cylinder on a hydrogen transport. A test was performed to investigate any enhancement of the deflagration due to partial confinement produced by a narrow gap between aluminum plates.

## **7.12.6 Gaseous Oxygen/Hydrogen Detonations**

### **7.12.6.1 Undiluted Gaseous Oxygen/Hydrogen Detonations**

Within the flammable range, mixtures of gaseous hydrogen with undiluted oxygen instead of air will always detonate, regardless of the mode of initiation and the de-

gree of confinement. While the flammable range of hydrogen in dry air is “only” 4.1–74.8 vol.-%  $H_2$ , the flammable and detonable range of hydrogen in oxygen is much wider, 4.1–94.0 vol.-%  $H_2$  [1015, 1041].

Detonation velocities were measured in mixtures of oxygen and hydrogen containing 25–75 mol-% hydrogen at initial temperatures from 160 to 580 K and initial pressures from 50.5 to 202 kPa (0.5–2 atm) [1042]. The measurements were made in a number of tubes of different diameter to permit extrapolation to a tube of infinite diameter. Theoretical detonation characteristics were computed for the same range of conditions. The measured and computed velocities were in good agreement except in rich mixtures and at subatmospheric pressures. Schlieren photographs revealed that the detonation wave front is very thin for a stoichiometric mixture but degenerated to a complicated zone of interacting shock waves and turbulent combustion as the percentage of hydrogen was reduced. The detonation velocity depended only slightly on initial temperature and pressure. The computed pressures behind the detonation and reflected waves were roughly proportional to the initial pressure and to the reciprocal of the initial temperature.

Detonation velocities of oxygen/hydrogen mixtures were measured for initial pressures from 99 kPa to 6.89 MPa (14.4–1000 psia) and compositions from 40 to 80 mol-% dihydrogen [1043]. Detonation and impact characteristics were computed for essentially the same range of conditions by the use of the elementary theory of detonation. Equilibrium compositions of oxygen/hydrogen mixtures at pressures from 1 to 202 MPa (10–2000 atm) and temperatures from 3000 to 5000 K were included in the computations. The effect of non-ideal thermodynamic properties on the computed detonation velocities must be considered.

Composition, temperature, pressure and density behind a stable detonation wave and its propagation rate have been calculated for 7 oxygen/hydrogen mixtures at 1, 5, 25, and 100 atm initial pressure, and at an initial temperature of 313 or 473 K (40 or 200 °C) [1044–1046]. According to these calculations the detonation velocities of oxygen/hydrogen mixtures increase with increasing initial pressure but decrease slightly when the initial temperature is raised from 313 to 473 K (40 to 200 °C). The calculated detonation velocities agreed with values determined experimentally.

The transition from deflagration to detonation occurs when the pre-flame shock becomes strong enough to cause the mixture to explode. The limits of detonability can be predicted if one knows:

1. The chemical-kinetics condition for branched-chain explosion of hydrogen in terms of temperature, pressure and mixture composition.
2. Standard shock-wave equations for a given mixture, the temperature and pressure of the shocked gas in terms of shock strength.
3. The explosion condition in terms of shock strength and mixture composition.

It will be found on the basis of conservation of energy that some mixtures, on burning, can support a shock of the critical strength, whereas others cannot. That delineates the limits of detonability [1047].

The detonability of gaseous oxygen/hydrogen mixtures contained in 61-cm and 91-cm (2-ft and 3-ft) diameter cylindrical vessels, 6.08 and 12.16 m long (20 and 40 ft long), was investigated for initial pressures ranging from 101 kPa to 13.3 Pa (760–0.1 mm Hg) and initial temperatures of 155, 200, 294, and 366 K (–180, –100, +70, and +200 °F) [1048, 1049]. Both strong igniters, comprised of approximately 70 grains of PETN, and weak sources of ignition, such as spark discharge, were used. Tests with PETN, which produced a strong initiating wave, indicated that detonation cannot be supported below an initial pressure of 10 mm Hg. In general, measured steady wave velocities were lower and pressures higher, than the corresponding theoretical Chapman-Jouguet values, the differences becoming more pronounced at lower initial pressures and temperatures. The weak igniter tests provided information on the development of detonation. Observations of initial flame acceleration were explained on the basis of a theory in previous studies in small-scale equipment, demonstrating its validity regardless of the size of the apparatus.

A study was performed on the detonation properties of cryogenic mixtures of gaseous hydrogen and oxygen at 100 K initial temperature and various initial pressures and equivalence ratios [1050]. Measured detonation pressures and velocities agreed quite well with the computed C-J values based on the ideal gas equation of state. Numerical computations of idealized, steady-state, one-dimensional structures with detailed chemical reaction kinetics were used to evaluate the reaction zone thickness and to estimate cell size, critical tube diameter and critical initiation energy. Predictions of critical tube diameter using calculated reaction zone thickness agreed reasonably well with experimental data. The kinetic modeling indicated that the initial pressure had a much smaller effect on reaction zone length at low initial temperatures (50–100 K) than at room temperature (300 K). This was due to a shift in the reaction mechanism as initial density (and, therefore, final pressure) increased with decreasing initial temperature at a fixed initial pressure.

#### 7.12.6.2 Gaseous Oxygen/Hydrogen Detonations with Diluents

Numerous experiments have been conducted with detonations of oxygen/hydrogen mixtures with inert diluents other than nitrogen or with oxygen : nitrogen ratios in the oxidizer other than 21 : 79. The objective was to slow down the reaction so it could be safely studied without destroying the apparatus. Other studies compared the well-known nitrogen diluent in air to the effect of other inert diluent gases on detonation limits and detonation velocities.

A test apparatus was designed to simulate the space around the shaft that connects the turbine and the turbopumps in a liquid hydrogen rocket engine [1051]. Hydrogen leakage past the rotary seals in a hydrogen pump is difficult to avoid. This space is typically purged with helium to reduce the risk of fires or explosions. The flammabil-

ity limits for a gap size of 5.3 mm (0.21 in.) were 8.1 vol.-%  $H_2$  LFL and 90.6 vol.-%  $H_2$  for the UFL in oxygen. The flammability limits for the apparatus without an inner cylinder were 5.8 vol.-%  $H_2$  LFL and 91.2 vol.-%  $H_2$  UFL. Additional measurements were made with different gap widths of 2.5 and 0.6 mm (0.1 and 0.025 in.) [1052].

The limiting (minimum) concentrations of hydrogen in oxygen, in the presence of added helium, at elevated temperatures and pressures were determined in a 5-L explosion vessel [1053]. The limiting concentrations of hydrogen in oxygen and helium at different initial pressures and temperatures, and the influence of ignition energy and initial temperature on the limiting concentration of hydrogen in oxygen and helium were measured. The variation of ignition energy was found to have a significant effect on the limiting concentration of hydrogen in oxygen and helium at lower initial temperatures; however, when the ignition energy was above 32 mJ, the limiting hydrogen concentration remained almost unchanged as the initial temperature was increased from 294 to 363 K (21 to 90 °C). The limiting explosive concentration of oxygen/hydrogen/helium mixtures decreased as the ignition energy increased when the initial temperature was lower. When the initial temperature was higher, the ignition energy had little effect on the limiting hydrogen concentration of oxygen/hydrogen/helium mixtures. When the initial temperature was set at 363 K (90 °C), the limiting hydrogen concentration remained almost unchanged with an increase in ignition energy. The limiting explosive concentration of hydrogen in the mixtures, at the initial temperature of 294 K (21 °C) and an ignition energy of 0.5 mJ, was 8.5 vol.-% and that of oxygen was 11.25 vol.-%.

Detonation limits in two stoichiometric  $O_2/H_2/Ar$  mixtures ( $O_2 + 2H_2 + 3Ar$  and  $O_2 + 2H_2$ ) were tested in three different diameter round tubes ( $D = 1.8, 4.6,$  and  $10.9$  mm) [1054]. The choice of the two mixtures represented those considered as “stable” with a regular cellular pattern and “unstable” with an irregular cellular pattern. Detonation velocity was measured by ionization probes spaced at regular intervals along the small tubes. Consistent with previous findings, the results showed that while well within the limits the detonation wave in hydrogen mixtures propagated at a steady velocity close to the theoretical C-J value. With decreasing initial pressure, the velocity deficit increased. It was found that the detonation velocity decreased with decreasing tube diameter, which is a result of the wall boundary layer effect being more prominent for smaller tubes. At the limiting pressure, the steady velocity decrease for both tested mixtures in three different diameter tubes was about 15–18%. Velocity deficits were estimated theoretically using the Fay model. For the mixture of  $O_2 + 2H_2 + 3Ar$ , good agreement was found between the theoretical prediction and the experimental result of detonation velocity. For the mixture of  $O_2 + 2H_2$ , however, the theoretical prediction deviated from the experimental measurement. This observation suggested that, apart from losses due to the flow divergence caused by the boundary layer effect, instabilities are also significant for the detonation propagation and failure in an  $O_2 + 2H_2$  mixture. At the limits of propagation, the value of  $D/\lambda$  was found to agree with that for the onset of single-headed spin detonation.

It was concluded that the single-headed spin criterion can be used for defining the detonation limits for hydrogen mixtures. See also [1029, 1030].

### 7.12.6.3 Study of Gaseous Oxygen/Hydrogen Detonations in Shock Tubes

Oxygen/hydrogen gas mixtures are often used in the driver (donor) section of shock tubes to reproducibly produce shock waves of known strength and measure their effects on other gas mixtures [1055].

The shock strength required to ignite stoichiometric oxygen/hydrogen mixtures corresponds to an ignition temperature that is in agreement with explosion limit data measured in glass bulbs [1056]. This is surprising, because the existence of explosion limits implies a steady state involving diffusion of reacting species to and from, and reaction at the walls of the reaction vessel. Such a condition is not expected to exist in a shock tube experiment. Measurements on several hydrogen mixtures near the composition limits of detonation showed that the agreement is fortuitous and is not a general feature of shock wave ignition. They also showed that there is no apparent relation between ignition and detonation limits. There are chemical factors that determine the limits, and it was concluded that the chain branching reaction plays a controlling role.

Shock-induced ignition and combustion of hydrogen was examined by stabilizing a flame behind the normal shock wave of a Mach-reflected shock pattern generated in a high temperature airstream of Mach number 1.91 [1057]. The stagnation temperature was varied from 1000 to 1400K to identify its effects on the shock configurations and the flame induction length. It was found that the exothermic chemical reaction behind the normal shock wave caused it to increase in size and to move upstream. The flow expansion behind the normal shock wave had quenched the downstream portion of the induced flame but a quasi one-dimensional reactive flow calculation revealed that effect of the expansion on the induction length was not as important as that of chemical kinetics.

The detonation in  $O_2/H_2/He/Ar$  mixtures at elevated initial pressures was investigated in an initiation tube for a detonation driver with an exploding wire as the ignition source [1058]. In most experiments the detonation wave was formed by a DDT process in which a reactive shock wave accelerated behind the leading shock wave and eventually made a transition to the onset of detonation. The onset position was found to be at the leading shock wave or behind it. Only in very sensitive mixtures at high initial pressures was the direct initiation of detonation observed. The influence of ignition energy, initial pressure, and composition on the detonation induction distance was determined. The results showed that the detonation induction distance increased with the decrease of ignition energy and initial pressure and with the increase of the mol fraction of helium or argon. With the same mol fraction, argon increased the induction distance more than helium. The DDT upper and lower limits of hydrogen in  $O_2/H_2$  mixtures were in the ranges from 36 to 40% and from 78 to 82%, respectively, and the upper limits for helium and argon in stoichiometric  $O_2/H_2$  mixtures were 40

and 36%, respectively. High pressure peaks generated by the DDT process were measured, especially in mixtures near the DDT limits. Such peak pressures can be up to 6 times higher than the C-J pressures.

The ignition of oxygen/hydrogen mixtures by detonation waves at 0.1–0.5 MPa and mixture ratios of 1.6–9.4 at room temperature was measured in a shock tube [1059]. The results showed that pressures above 1 MPa and temperatures over 1573 K (1300 °C) could be produced from lower gas pressures by the detonation wave ignition technique, and the variation in ignition delay time from run to run was less than 0.3 ms.

The temporal variation of  $\bullet\text{OH}$  chemiluminescence in hydrogen oxidation chemistry has been studied in a shock tube behind reflected shock waves at temperatures of 1400–3300 K and at a pressure of 1 bar [1060]. The aim of that work was to obtain a validated reaction scheme to describe  $\bullet\text{OH}$  formation in the  $\text{O}_2/\text{H}_2$  system. Temporal  $\bullet\text{OH}$  emission profiles and ignition delay times for lean and stoichiometric  $\text{O}_2/\text{H}_2$  mixtures diluted in 97–98% argon were obtained from the shock tube experiments. The key reaction considered was



The temperature dependence of the measured peak  $\bullet\text{OH}$  emission from the shock tube and the peak  $\bullet\text{OH}$  concentration from a homogeneous closed reactor model were compared. Based on these results a reaction rate coefficient of

$$k_1 = (1.5 \pm 0.4) \times 10^{13} \exp(-25 \text{ kJ mol}^{-1}/RT) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

was found for the forward reaction (R1) which was slightly higher than the rate coefficient reported by others.

Ignition delay times of  $\text{O}_2/\text{H}_2$  mixtures highly diluted with Ar and doped with varying amounts of  $\text{N}_2\text{O}$  (100, 400, 1600, 3200 ppm) were measured in a shock tube behind reflected shock waves over a wide range of temperatures (940–1675 K) and pressures (1.6, 13, and 32 atm) [1061]. Ignition delay times were decreased when  $\text{N}_2\text{O}$  was added to the mixture only for the higher nitrous oxide concentrations and decreases were proportional to the amount of  $\text{N}_2\text{O}$  added. A chemical kinetics model was developed using kinetic mechanisms from the literature. This model predicted and matched the experimental data obtained during this study and from the literature. The chemical analysis using this model showed that the decrease in the ignition delay time was mainly due to the reaction  $\text{N}_2\text{O} + \text{M} \rightarrow \text{N}_2 + \text{O}\bullet + \text{M}$  which provides  $\bullet\text{O}$  atoms to strengthen the channel  $\text{O}\bullet + \text{H}_2 \rightarrow \bullet\text{OH} + \text{H}\bullet$ .

### 7.12.7 Deflagration-to-Detonation Transitions

Because very powerful ignition sources such as solid explosives are usually required to initiate unconfined air/hydrogen detonations, most accident scenarios assign a very low probability to the detonation mode (as opposed to deflagration mode) in accidental air/hydrogen explosions; however, detonations cannot be completely ruled out,

since depending on geometry, a flame can accelerate to a sufficiently high speed and transit to detonation. An explosive mixture at given initial and boundary conditions is expected to undergo transition from deflagration to detonation (DDT) if the following conditions are satisfied: **(1)** the mixture composition must be within the detonability limits, and **(2)** powerful acceleration mechanisms such as turbulence generated by obstacles and adequate boundary conditions (confinement) must be present. Therefore, the transition event involves detonability limits, flame acceleration mechanisms, and the mechanisms responsible for the onset of detonation itself.

Flame acceleration and DDT transitions can occur in straight tubes but are more likely to occur when the combustion front encounters obstacles in its travel which cause turbulence and hot spots. Whereas for confined mixtures, DDT may result from flame acceleration due to turbulence generated by obstacles, large-scale experiments without obstacles indicated that turbulent jet mixing is the mechanism responsible for DDT in unconfined mixtures.

Air/hydrogen combustion can start as a detonation, or it can start as a deflagration and then transition to a detonation after the flame has traveled for some distance [523]. The composition range in which a detonation can take place is narrower than that for deflagration. The commonly quoted range for detonation in an air/hydrogen mixture is from 18.3 to 59 vol.-% hydrogen; however, with higher energy ignition/initiation sources, the limits can be extended. The factors that influence whether air/hydrogen combustion will occur as a detonation rather than as a deflagration include the hydrogen percentage, the strength of the initiator, complete or partial confinement of the reaction, and the presence of structures that can induce turbulence in the flame front. An energetic source of initiation is required for combustion to start as a detonation. A mechanism to accelerate the flame velocity is necessary for a deflagration to transition to detonation. Factors that favor this transition include the composition being within the detonation range, a degree of confinement, and anything that can induce turbulence in the flame front as it travels through the combustible mixture. The latter tends to stretch out the flame front and increase its velocity [1062, 1063]. A special case occurs when a deflagration combusts and propagates into a “dead-headed” volume. This can lead to exceptionally high overpressures. Under such circumstances (also described as pressure-piling), the unburned gases in the worst case can pressurize to the dynamic pressure produced by the accelerated flame [1064]. Under these conditions, should DDT ensue, the worst-case result can be an overpressure that is characterized by the multiplicative factors of both deflagration and detonation, far beyond the initial pressure within the system.

Dynamic detonation and DDT parameters of air/hydrogen explosions were reviewed [1024]. These parameters included the characteristic chemical length scale, such as the detonation cell width, associated with the three-dimensional cellular structure of detonation waves, critical transmission conditions of confined detonations into unconfined environments, critical initiation energy for unconfined detonations, detonability limits, and critical conditions for DDT. The detonation

cell width, which depends on hydrogen and diluent concentrations, pressure and temperature, is an important parameter in the prediction of critical geometry-dependent conditions for the transmission of confined detonations into unconfined environments and the critical energies for the direct initiation of unconfined detonations. Detonability limits depend on both initial and boundary conditions. The criteria for DDT are different for smooth-walled tubes and tubes with trip ledges (obstacles). The report was intended to examine all aspects of detonative combustion that are commonly studied and are of practical interest. These included problems of initiation, transition, transmission, and detonability limits.

The equilibrium detonation parameters (i.e., detonation velocity, pressure, density and temperature ratios, and equilibrium composition of the reaction products) are adequately predicted by the classical C-J theory, which models gaseous detonation waves as one-dimensional, steady combustion waves; however, the C-J theory, which is essentially an equilibrium calculation, cannot predict the non-equilibrium or dynamic detonation parameters which are related to the chemical reaction rates, i.e., to the structure of the detonation wave.

Accidental ignition in flammable air/hydrogen/diluent mixtures will normally lead to a deflagration wave (slow flame). A freely propagating flame strongly influences the flow conditions ahead of it. Particular conditions can accelerate this flame and cause a transition from deflagration to a detonation wave (rapid flame), with its spatially non-uniform and very high blast pressures [1065]. The differences between deflagration and detonation of air/H<sub>2</sub> mixtures were outlined, and the various flame acceleration mechanisms were reviewed. The DDT was described as a two-step process, a local explosion followed by an amplification of the resulting blast wave into a detonation wave. This was based on the occurrence of a local explosion in hot spots generated by the focusing of shock waves existing ahead of a fast flame, or in high-reactivity centers generated by turbulence-induced rapid mixing of flame and unburnt gas, and the resulting local quenching of the flame. There are only few qualitative criteria available for assessing the likelihood of transition to detonation under a set of given starting conditions. A goal of the study was to develop a quantitative methodology for assessing this likelihood.

The emergency venting of a gaseous deflagration is widely used to prevent severe consequences of a confined explosion. Processes of vented deflagrations have been studied extensively and a substantial amount of experimental data has been analyzed. It has been found that venting, in some cases, can result in strong explosions [1066]. This may be caused by flame instabilities, which give rise to a flame area increase, and the generation of high peak overpressures. Onset of detonations has been observed in the course of hydrogen-air deflagration, due to sudden venting. Although the aim of the tests initially was not to investigate the effect of venting on gaseous explosions, this effect appeared to be defining the explosion mode, based on unconfined turbulent jet initiation experiments. Test variables were hydrogen concentration, jet orifice diameter, and size of the enclosure. Measurement equipment included pressure trans-



ducers, photodiodes, and two high-speed cameras (2500 frames/s). Contact gauges gave the times of jet membrane rupture and of panels destruction.

Large-scale experiments on turbulent flame propagation and transition to detonation in a confined volume of lean hydrogen-air mixtures were conducted in a strong concrete enclosure of  $480\text{ m}^3$ , and  $69.9\text{ m}$  length with a straight channel ( $34.6\text{ m}$  length,  $2.3\text{ m}$  height,  $2.5\text{ m}$  width) with or without obstacles, a canyon ( $10.55 \times 6.3 \times 2.5\text{ m}$ ), and a final channel to study the effect of hydrogen concentration (9.8–14 vol.-%) on turbulent flame propagation and transition to detonation [1067]. Ignition was with a weak electric spark at the beginning of the first channel. A minimum of 12.5 vol.-% of hydrogen was necessary for transition to detonation. This is a much less sensitive mixture than those in which the onset of spontaneous detonation has previously been observed (minimum of 15 vol.-% of hydrogen in air).

The High-Temperature Combustion Facility at Brookhaven Natl. Lab. was used to conduct DDT experiments [950, 951]. Periodic orifice plates were installed inside the entire length of the detonation tube in order to promote turbulence and flame acceleration. The orifice plates were  $27.3\text{ cm}$  outer diameter, which is equivalent to the inner diameter of the tube, and  $20.6\text{ cm}$  inner diameter. The detonation tube was  $21.3\text{ m}$  long, and the spacing of the orifice plates was one tube diameter. A standard automobile diesel engine glow plug was used to ignite the test mixture at one end of the tube. Hydrogen-air-steam mixtures were tested at a range of temperatures up to  $650\text{ K}$  and at an initial pressure of  $0.1\text{ MPa}$ . In most cases, the limiting hydrogen mol fraction which resulted in DDT corresponded to the mixture whose detonation cell size,  $\lambda$ , was equal to the inner diameter of the orifice plate,  $d$  (e.g.,  $d/\lambda = 1$ ). The only exception was in the dry hydrogen-air mixtures at  $650\text{ K}$  where the DDT limit was 11 vol.-% hydrogen, corresponding to a value of  $d/\lambda$  equal to 5.5. For a 10.5 vol.-% hydrogen mixture at  $650\text{ K}$ , the flame accelerated to a maximum velocity of about  $120\text{ m/s}$  and then decelerated to below  $2\text{ m/s}$ . It was observed that the distance required for the flame to accelerate to the point of detonation initiation, referred to as the run-up distance, was a function of both the hydrogen mol fraction and the gas mixture initial temperature. Decreasing the hydrogen mol fraction or increasing the initial mixture temperature resulted in longer run-up distances.

Critical conditions for onset of detonations were compared at **(1)** two significantly different scales, **(2)** for a range of air/ $\text{H}_2$  mixtures diluted with  $\text{CO}_2$  or  $\text{H}_2\text{O}$ , and **(3)** for two types of geometry: one a long, obstructed channel and the other a room with a relatively small aspect ratio [1068]. For the range of scales, mixtures and initial conditions tested, the detonation cell size  $\lambda$  was shown to be a reliable scaling parameter for characterization of detonation onset conditions. An experimental correlation was suggested for the critical detonation onset conditions. This correlation was based on a wide variety of available experimental data on DDT in mixtures of hydrogen and hydrocarbon fuels with air and on the use of detonation cell size  $\lambda$  as a scaling parameter characterizing the mixture.

Turbulent flame propagation in obstructed channels was measured over a wide range of air/H<sub>2</sub> and air/H<sub>2</sub>/steam. From lean to rich mixtures at normal and elevated initial temperatures. From 298 to 650 K and pressures. From 1 to 3 bar and stoichiometric O<sub>2</sub>/H<sub>2</sub> mixtures diluted with N<sub>2</sub>, Ar, He, and CO<sub>2</sub> at normal initial conditions [1069]. It was shown that basic flame parameters, such as mixture expansion ratio  $\sigma$ , Zeldovich number  $\beta$ , and Lewis number Le, can be used to estimate *a priori* a potential for effective flame acceleration for a given mixture. Critical conditions for effective flame acceleration were suggested in the form of correlations of critical expansion ratio  $\sigma^*$  versus dimensionless effective activation energy. On this basis, limits for effective flame acceleration for hydrogen combustibles can be estimated with only modes uncertainties in critical  $\sigma^*$  values.

Flame acceleration and DDT in obstructed channels was modeled using 2-D reactive Navier-Stokes numerical simulations [1070]. The energy release rate for stoichiometric hydrogen-air mixtures was modeled by one-step Arrhenius kinetics. Channels with symmetrical and staggered obstacle configurations showed two main effects of obstacle spacing (S). First, more obstacles per unit length created more perturbations that increased the flame surface area more quickly, and therefore the flame speed grew faster. Second, DDT occurred more easily when the obstacle spacing was large enough for Mach stems to form. These two effects were responsible for three different regimes of flame acceleration and DDT observed in these simulations: **(1)** detonation was ignited when a Mach stem by the diffracting shock reflecting from the bottom wall collided with an obstacle, **(2)** Mach stems did not form, and the detonation was not ignited, and **(3)** stems did not form, but the leading shock became strong enough to ignite a detonation by a direct collision with the top part of an obstacle. For staggered obstacle configurations, resonance phenomena significantly reduced the DDT time when  $S/2$  was comparable to the channel width in regime **(1)**. Simulations also showed that phenomena responsible for DDT are the same for obstructed channels and 2D arrays of obstacles, even though final detonation ignition may be different. A detailed overview of flame acceleration and transition to detonation in ducts is available in [951].

The hazardous potential of air/hydrogen mixtures has intensively been studied assuming a perfectly homogeneous mixture of oxidant and fuel; however, comprehensive risk assessment studies have shown that an inhomogeneous mixture with a vertical concentration gradient is much more likely to be generated in a real accident scenario. From a safety point of view, an open question was whether established criteria such as the  $7\lambda$  criterion for the determination of the DDT limits can be applied to inhomogeneous mixtures as well. For the experimental investigation of DDT in such mixtures an injection mechanism has been developed that produced vertical fuel concentration gradients inside a horizontal channel with large aspect ratio [1071]. The channel was equipped with obstacles to enhance flame acceleration. Photodiodes and pressure transducers measured flame and shock arrival times. Schlieren measurements were conducted to track gas mixing behind the obstacles and to track the for-

mation of the detonation wave front. In the experimental study, the fuel content, the strength of concentration gradient, the blockage ratio, and the spacing of the obstacles inside the channel were varied. The maximum flame velocity observed in each experiment was compared with the velocities obtained from one-dimensional theory. A DDT leads to a steep velocity rise from the sound speed of the combustion products to the Chapman-Jouguet velocity of the mixture and generated a considerable increase in peak pressure.

A numerical approach to simulate flame acceleration and DDT in air/hydrogen mixtures and two different approaches to detonation modelling provided predictions in identical scenarios which were then compared [1072]. The DDT model solved fully compressible, multi-dimensional, transient, reactive Navier-Stokes equations with a chemical reaction mechanism for different stages of flame propagation and acceleration from a laminar flame to a highly turbulent flame and subsequent transition from deflagration to detonation. The model has been used to simulate flame acceleration and DDT in a 2-D symmetrical rectangular channel with 0.04 m height and 1 m length which is filled with obstacles. Comparisons were made between the predictions using a 21-step detailed chemistry or a single-step reaction mechanism. The effect of initial temperature on the run-up distances to DDT has been investigated. Another detonation equation solver was developed based on the solution of reactive Euler equations while the other solver took a simpler approach based on C-J model and the programmed C-J burn method. Comparison has shown that the relatively simple C-J burn approach is unable to capture some very important features of detonation when there are obstacles present in the cloud.

A model for the CFD simulation of air/hydrogen explosions (including DDT) in large volumes was validated by means of the largest ever conducted indoor DDT experiments in the RUT facility operated by Kurchatov Institute in Russia [1073]. A combination of models was developed with a particular emphasis on the influence of flame instabilities, especially of a thermal-diffusive nature, which are crucial for combustion of very lean mixtures. Good agreement was achieved in terms of flame acceleration. The quality of DDT predictions itself depended on the underlying mechanism. Whereas DDT by shock-focusing was successfully simulated on under-resolved meshes, DDT by local explosions in the vicinity of the turbulent flame brush remained a challenge. Adaptive mesh refinement therefore emerged as a key technique to resolve more of the essential phenomena at reasonable computational costs. A generic example case demonstrated the influence of mixture inhomogeneity, which can promote flame acceleration and ultimately DDT.

Air/H<sub>2</sub> and O<sub>2</sub>/H<sub>2</sub> flame propagation across a single obstacle in a closed channel has been studied by means of simultaneous single image planar laser-induced fluorescence (PLIF) and high-speed schlieren visualization [1074]. The test mixtures were stoichiometric O<sub>2</sub>/H<sub>2</sub> at an initial pressure of 8 kPa and lean air/H<sub>2</sub> ( $\varphi = 0.5$ ) at an initial pressure of 100 kPa. The OH-PLIF technique overcomes the problem of line-of-sight integration associated with schlieren visualization and thus enables the investigation of

flame topology. For  $O_2/H_2$ , a smooth (laminar) flame front was observed upstream of the obstacle. Downstream, the flame interacted with vortices being shed off the obstacle corners and appeared wrinkled in the obstacle recirculation zones.

A CFD explosion modeling for lean air/hydrogen mixtures with 6–19 vol.-%  $H_2$  on under-resolved grids can now be validated with data obtained from an entirely enclosed laboratory scale explosion channel at  $p = 1 \text{ atm}$  and  $T = 293 \text{ K}$  [1075]. Two time-resolved optical measurement techniques were applied simultaneously: (1) 10 kHz shadowgraphy captured line-of-sight integrated macroscopic flame propagation and (2) 20 kHz OH-PLIF (planar laser-induced fluorescence of the OH radical) resolved microscopic flame topology without line-of-sight integration. A detailed time-resolved quantification of flame topology based on OH-PLIF images revealed the expected enlargement of flame surface area by instabilities on microscopic level and a strong dependence on mixture composition.

In the real world, combustible air/hydrogen mixtures causing catastrophic damage are usually inhomogeneous and subject to both vertical and horizontal concentration gradients. There was still very limited understanding of the explosion characteristics in such situations. A study aimed to investigate DDT in such inhomogeneous mixtures [1076]. Two sample cases in a horizontal obstructed channel with 30 and 60% blockage ratios filled with air/hydrogen mixtures with vertical concentration gradients were numerically modeled. These cases were experimentally investigated and hence some experimental measurements are available for model validation. The numerical results were in good agreement with the experiments. The predictions showed that the overpressure at the DDT transition stage is higher in the non-uniform mixtures than in homogeneous mixtures under similar conditions. It was also found that increasing the blockage ratio from 30 to 60% resulted in faster flame propagation and lower propensity to DDT.

The possibility of a laminar flame in a stoichiometric  $H_2/O_2$  mixture accelerating along a cylindrical tube, closed at one end, and transitioning from a deflagration to detonation was analyzed [1077]. It was predicted that the pressure and temperature ratios at the ensuing shock wave increase as do laminar burning velocities, while autoignition delay times decrease. Combined with appreciable elongation of the flame, these enhance the strength of the shock. The conditions necessary for delay times of 0.05, 0.1, 1.0, and 5.0 ms, at an unburned mixture critical Reynolds number of 2300, were computed for different tube diameters. Probable consequences of the different delay times and hot spot reactivity gradients, including detonation must be considered. The probability of a purely laminar propagation leading to a detonation is marginal. Only when the initial temperature is raised to 375 K, do purely laminar detonations become possible in tubes of between about 0.5 and 1.35 mm diameter.

#### 7.12.7.1 Detonation Induction Distance in Air/Hydrogen Mixtures

The detonation induction distance is the distance required for a DDT in a detonable fuel-air mixture. This distance is usually experimentally determined in a long cylin-

dricial tube with a spark or hot wire ignitor on one end of the tube. The tube is instrumented along its length to sense the velocity of the flame front as it propagates through the detonable mixture of gases. The distance from the ignitor to the axial position in the tube where the flame front first attains the detonation velocity is defined as the induction distance. This distance is dependent upon the combustible mixture constituents, the pressure, temperature, and concentration of the gaseous mixture, the enclosure geometry and strength of the ignition source. A deflagration is a low order explosion resulting from subsonic flame speed, relative to the unburned gas. It is conventionally defined as a propagating reaction in which the energy transfer from the reaction zone to the unreacted zone is achieved through ordinary rate-limiting transport processes such as radiation and convection heat transfer and mass transfer. A detonation is a high-order explosion resulting from supersonic flame speed, relative to the unburned gas. It may be defined as a propagating reaction in which energy is transferred from the reaction zone to the unreacted zone on a reactive shock wave [1033, 1078]. Detonations may propagate in flowing oxygen/hydrogen mixtures, but always faster than the unburnt gases can flow [1079].

In order to study the combustion of unconfined samples, combustion tests with air/gaseous hydrogen mixtures were conducted in balloons of 1.5 and 2.4 m diameter with contents of 2380 and 11320 L of mixed gas. Initiation was through detonators, flames, glowing wires or sparks [497]. The first tests showed that in a 1.5-m balloon with near-stoichiometric mixtures it will not come to a three-dimensional shock wave if the initiation does not have enough energy. In order to achieve detonations in 100% of the cases, a booster charge of 2 g PETN was required. A detonator that contains only 0.5 g primary explosive would cause a detonation in only 5% of the several tests conducted. Flames, hot wires, and sparks caused the mixtures to burn peacefully without measurable pressure spikes. Subsequent tests were all conducted with a 2-g booster and the effect of mixture ratio on detonable limits was bracketed. The highest detonation pressure spikes were obtained with mixtures containing 30–40 mol-% hydrogen. The explosive range in a 1.5-m balloon was from 20 to 50 mol-%  $H_2$ . This range is very similar to the range observed in confined samples in tubes (18–59 mol-%  $H_2$ ). The scale effect was studied by comparing results with larger 2.4-m balloons to those with the 1.5-m balloons. The question was if the longer pathway will facilitate a transition from combustion to detonation and to determine the critical diameter for unconfined explosions. Similar to earlier results with the 1.5 m balloon, detonations were only observed with the 2-g booster and occasionally with the detonator by itself. The ignition by spark caused only a smooth combustion without explosion. The tests showed that unconfined air/hydrogen mixtures can be made to detonate only by using a strong booster charge as the initiation source. Because it is unlikely that a detonator or a booster charge will detonate accidentally in the vicinity of hydrogen spills, the danger of air/hydrogen explosions as a result of hydrogen spills is relatively low.

### 7.12.7.2 Detonation Induction Distance in Air/Hydrogen and Oxygen/Hydrogen Mixtures

The detonation induction distances in oxygen/hydrogen mixtures depend on the mode of initiation and the extent of confinement [1080, 1081]. The detonation induction distance is also called the run-up distance.

While extensive studies have been conducted examining the formation of detonation waves in various combustible gaseous mixtures under static conditions, there was very little experimental work on propagation of detonations in simple flowing systems. Experiments on the DDT of a flowing air/hydrogen stream were carried out to see the effects of tube diameter, equivalence ratio and flow types on flame propagation in a pre-mixed and non-premixed flow [1082]. Tube diameters used were 25, 50, and 100 mm. The pre-mixed experiments showed that the larger tube diameter provided a wider range in run-up distance, reduction of  $L_{DDT}/D$  (ratio of the run-up distance,  $L_{DDT}$  to tube diameter  $D$ ), and expansion of the detonable concentration limit by spreading the cell width. The result of the non-premixed experiments showed that similar values of the run-up distance to the pre-mixed experiments were obtained at an equivalence ratio of about 1.0; however, fluctuations of DDT occur near the DDT concentration limit. Under laminar flow conditions at a Reynolds number of less than 2300, the difference between the two systems could not be observed; however, when the Reynolds number increased towards turbulent conditions, the DDT run-up distance decreased compared to that of static flow conditions.

It was observed that the distance required for the flame in air/hydrogen mixtures to accelerate to the point of detonation initiation, referred to as the run-up distance, was a function of both the hydrogen mol fraction and the gas mixture initial temperature. Decreasing the hydrogen mol fraction or increasing the initial mixture temperature resulted in longer run-up distances [950, 951].

## 7.12.8 Overpressure from Air/Hydrogen Explosions

### 7.12.8.1 Overpressure from Unconfined Air/Hydrogen Explosions

The ignition of air/GH<sub>2</sub> mixtures usually results in ordinary deflagration. In general, without initiation sources that produce strong shock waves (such as high explosives or powerful electric arcs), flammable unconfined hydrogen mixtures ignited in the open do not produce significant overpressure.

Field explosion tests have been performed to obtain fundamental data concerning the explosion strength generated by a stoichiometric mixture of hydrogen and air [1083]. Hydrogen-air mixtures filled in a tent covered with thin plastic sheets were ignited by an electric spark to explode. The generated blast wave pressure was measured with piezoelectric pressure sensors. Deflagration tests with volumes of 9.4, 75, and 200 m<sup>3</sup> were carried out to investigate the scale effect (i.e. volume dependency) of peak overpressure and blast wave impulse. The measured data showed that peak overpressure and impulse exhibited different volume dependencies. Similar field ex-

plosion tests of three air/hydrogen mixtures with hydrogen contents of 21.0, 28.7, and 52.9 vol.-% were carried out in a volume of 31 m<sup>3</sup> [1084]. Each mixture was ignited by a booster charge of 0.1 kg of Composition C-4 explosive and guided to detonation. Peak pressures of blast waves caused by detonation were measured by piezoelectric pressure sensors. The measured peak overpressures and impulses were comparable in intensity to those of the TNT equivalent in lower heating value. The results showed that the strength of a blast wave generated by detonation of air/hydrogen mixtures is approximately the same as that of a TNT explosive.

A simple method for approximate evaluation of blast effects and safety distances for unconfined hydrogen explosions included models for flame speeds, hydrogen dispersion, blast overpressure parameters and blast damage criteria [1085]. An example of the application of this methodology for accidental hydrogen release in three hypothetical obstructed areas with different levels of congestion was presented. The severity of the blast effect of unconfined hydrogen explosions was shown to depend strongly on the level of congestion (confinement) for relatively small releases. Extremely large releases of hydrogen were predicted to be less sensitive to the congestion level.

Development tests were conducted to characterize unconfined air/hydrogen and oxygen/hydrogen blast characteristics [1086]. Most of the existing experiments for these types of explosions address contained explosions, like in shock tubes. Therefore, a Hydrogen Unconfined Combustion Test Apparatus was developed as a gaseous combustion test device for determining the relationships between overpressure, impulse and flame speed at various mixture ratios for unconfined reactions of oxygen/hydrogen and air/hydrogen. The system consisted of a central platform plumbed to inject and mix component gasses into an attached translucent bag or balloon with 340 or 1850 L while monitoring hydrogen concentration. All tests were ignited with a spark. Surrounding the platform were 9 blast pressure “Pencil” probes. Two high-speed cameras were used to observe flame speed within the combustion zone. The entire system was raised approx. 1.5 m (6 ft) off the ground to remove any ground reflection from the measurements. Overpressure and impulse data obtained from these tests were used to calibrate engineering analysis tools, CFD models and in the development of blast and fragment acceleration models.

A computational fluid dynamics simulation software was used to determine the potential of unconfined hydrogen in air to explode [1087]. The study included the analysis of parameters that can promote hydrogen vapor cloud explosions, e.g., initial pressure, time to ignition and leak height position. The study concluded that leaking high-pressure hydrogen has the potential to build up a large vapor cloud and may explode even without confinement when the leak source is close to the ground. The highest overpressure produced in the simulation was 0.71 bar gauge, which resulted from igniting a hydrogen gas cloud from a 207 bar hydrogen source leaking at 1 m height. The high overpressure suggested that hazard studies for hydrogen leaks near the ground should not assume a free flow jet release.

### 7.12.8.2 Overpressure from Confined and Vented Air/Hydrogen Explosions

Vented explosion tests using lean air/hydrogen mixtures with concentrations from 12 to 19 vol.-%  $H_2$  in a  $63.7\text{ m}^3$  chamber with a vent size of either  $2.7$  or  $5.4\text{ m}^2$  were focused on the effect of hydrogen concentration, ignition location, vent size, and obstacles on the overpressure development of a propagating flame in a vented enclosure [1088]. Deriving an equation for the dependence of the maximum pressure generated on the experimental parameters confirmed that the pressure maxima were caused by pressure transients controlled by the interplay of the maximum flame area, the burning velocity and the overpressure generated outside of the chamber by an external explosion.

A series of medium-scale experiments on vented hydrogen deflagration was carried out in a chamber of  $1 \times 1 \times 1\text{ m}$  size with different vent areas [1089]. The experimental program was divided in three series: **(1)** uniform air/hydrogen mixtures, **(2)** stratified air/hydrogen mixtures within the enclosure and **(3)** a layer deflagration of uniform mixture. Different uniform air/hydrogen mixtures from 7 to 18% hydrogen were tested with variable vent areas of  $0.01$ – $1.0\text{ m}^2$ . One test was done for a rich mixture with 50%  $H_2$ . Experiments with stratified air/hydrogen mixtures had about 4%  $H_2$  at the bottom and 10–25%  $H_2$  at the top of the enclosure.

Validated computational fluid dynamics (CFD) based methodologies for predicting propellant detonations and blast environments relevant to rocket propulsion test and launch facilities were developed [1090]. Verification and validation studies were conducted for hydrogen-fueled detonation phenomena such as shock-induced combustion, confined detonation waves, vapor cloud explosions, and DDT processes. The DDT validation cases included predicting flame acceleration mechanisms associated with turbulent flame-jets and flow-obstacles. The CFD methodology was applied to model a detonation event that occurred during liquid oxygen/gaseous hydrogen rocket diffuser testing at NASA Stennis Space Center.

Two thermochemical models have been derived for predicting the post-ignition state of hydrogen explosions in the containment vessel of a melting water-cooled nuclear reactor [1091]. The first model was based on internal energy balance while the second model used the concept of element potentials to minimize the free energy of the system with internal energy imposed as a constraint. Predictions from both the models were compared against published data over a wide range of mixture compositions. There were noticeable differences between the regions close to the flammability limits and for stoichiometric mixtures. The equilibrium model has been validated for varied temperatures and pressures representative of initial conditions that may be present in a reactor containment shell during meltdown accidents.

Explosion venting of air/hydrogen mixtures with equivalence ratios ranging from 0.4 to 6.0 was investigated in a small vented cylindrical vessel and the experimental results showed that the maximum internal overpressure initially increased with an increase in hydrogen equivalence ratio up to approximately 1.6 and subsequently decreased [1092]. The discrepancy between the maximum internal overpressure and the



vent burst pressure was high for equivalence ratios ranging from 1.0 to 2.0 but low for very lean or very rich mixtures. Buoyancy had a significant effect on the evolution of the internal flame bubble for very lean air/hydrogen mixtures only.

### 7.12.9 Liquid Oxygen/Liquid Hydrogen Mixture Detonability

In this encyclopedia, detonability of non-hypergolic mixtures of oxidizers with fuels can be discussed either under the heading of the oxidizer in *Encyclopedia of Oxidizers*, or the fuel in (this) *Encyclopedia of Liquid Fuels*, or in a future set along with non-hypergolic combinations of such oxidizers and fuels. There may be some overlap between these parts of the book. Many of the studies of the detonability of LOX/LH<sub>2</sub> also included experiments with LOX/RP-1 and comparisons of these two most widely used liquid propellant combinations.

The explosive hazard of mixtures of liquid hydrogen and solid air is less than what was initially feared. In small-scale experiments where liquid air was poured into liquid hydrogen and then ignited, in one case pouring 300 g of liquid air into 4.7 L liquid hydrogen, the mixture when ignited with a glowing wire would not detonate. It would detonate only if the liquid air had been standing in a Dewar flask for a while and had enriched itself with the lower boiling oxygen [500]. Air condensing into a reservoir of liquid hydrogen may be enriched in the lower boiling and more readily condensing oxygen.

Liquid hydrogen filled chambers are sometimes used adjacent to nuclear research reactors to moderate the flux of neutrons and create a collimated beam of low-energy neutrons. Negligent operation could allow air to leak into these chambers. Solid air/liquid hydrogen explosions have been carried out in a closed volume to assess the possible hazards of an explosion in such nuclear reactor experiment [1093]. Mixtures of solid air and liquid hydrogen are not shock sensitive, because they could not be made to detonate when hit by a falling hammer in a drop weight tester, not even at the highest drop height the apparatus was capable; however, mixtures of solid oxygen and liquid hydrogen are shock sensitive and detonated under the same conditions of mechanical impact [500, 1094, 1095]. Mixtures of solid air in liquid hydrogen were reported to be detonable for concentrations of less than 40% oxygen [1096].

The development of large launch vehicles has created safety concerns in the siting of test stands and launch pads. Thus, LOX/RP-1 launch vehicles are sited by using a TNT equivalent of 20% for quantities up to 226 000 kg (500 000 lb) and an equivalent of 10% for any excess over that amount; however, LOX/LH<sub>2</sub> launch vehicles were at one time sited using a TNT equivalent of 60% [1097]. Tests using 90.6 kg (200 lb) of LOX/RP-1 and LOX/LH<sub>2</sub> were made with spill test and simulated tankage configurations. The results indicated that the spill test method of investigation on which the TNT equivalent for LOX/LH<sub>2</sub> vehicles was based probably gave excessive yields and, therefore, may not be valid for this propellant combination. The tandem tank tests were made to provide information about the explosive yields occurring under condi-

tions more closely simulating various types of vehicle failures on the launch pad. The average yields for simulated destruct tests ranged from 0.6 to 1.6%, and those for the tests using a bulkhead failure mode ranged from 0.4 to 1.4%.

One series of tests with LOX and LH<sub>2</sub> was performed to simulate the conditions which might exist in the common bulkhead separating the two tanks in upper stages if the bulkhead would spring a leak [1098]. In a sealed bomb solid oxygen was pressurized with cold hydrogen at a little above 20 K and ignited with a glow plug. The cold mixture ignited only in 80% of the tests and required a substantial heat input of the order of 3–4 J. When the initial pressure was 12.16 kPa (0.12 atm), the pressure at the end of the reaction had risen 80-fold. Higher pressure rise was encountered if both reactants were gaseous at 83 K (–190 °C) to start with. The space between the two propellant tanks is not empty but filled with insulating material and the dimensions in the insulating layer are below the critical diameter for explosion propagation in O<sub>2</sub>/H<sub>2</sub>.

In the case of launch pad accidents, LOX and LH<sub>2</sub> or RP-1 may have an opportunity to pre-mix before they are ignited by an external source of ignition. The worst-case explosive yield of such explosions has been predicted by model experiments and by calculations [1095, 1097, 1099–1100]. The worst-case maximum explosive yield is predicted with delayed ignition about half-way through the propellant spill event, giving the propellants enough time to mix before they are ignited.

The explosive yield is proportional to the contact area between oxidizer and fuel as they begin to mix and before they are ignited. The primary purpose of the second phase of a test series was to compare the explosive yield of LOX/LH<sub>2</sub> explosions to those of LOX/RP-1 and N<sub>2</sub>O<sub>4</sub>/Ae-50 [1101]. The second series of 10 tests included two LOX/LH<sub>2</sub> tests at a contact area  $A_c = 2.33 \text{ m}^2$  (25.1 ft<sup>2</sup>), two tests were performed at  $A_c = 3.42 \text{ m}^2$  (36.8 ft<sup>2</sup>), and two tests were performed at  $A_c = 5.22 \text{ m}^2$  (56.2 ft<sup>2</sup>). Two LOX/RP-1 tests and two N<sub>2</sub>O<sub>4</sub>/Ae-50 tests were performed at the intermediate contact area  $A_c$  of 3.42 m<sup>2</sup> (36.8 ft<sup>2</sup>). As a reference for the tests and for calibration of the instruments, a series of unconfined 10, 25, 50, and 100 lb<sub>m</sub> trinitrotoluene (TNT) charges were detonated.

The yield produced by explosions of the LOX/LH<sub>2</sub> propellant system (after short ignition delay times) is similar to the yields produced by the N<sub>2</sub>O<sub>4</sub>/Ae-50 and the LOX/RP-1 propellant systems (all at the same contact area). The past practice of using much larger yield criteria for LOX/LH<sub>2</sub> than for LOX/RP-1 probably overrated the hazard of LOX/LH<sub>2</sub> relative to LOX/RP-1 for reasonable modes of launch-vehicle failure.

#### 7.12.10 Explosion Blast Overpressure from LOX/LH<sub>2</sub> Launch Mishaps

Spill and explosion tests using 200 lb of LOX/LH<sub>2</sub> were made with simulated tankage configurations. The results indicated that the spill test method of investigation on which the pre-1965 TNT equivalent for LOX/LH<sub>2</sub> vehicles was based probably gave excessive yields and, therefore, may not be valid for this propellant combination. It was

suggested that future investigations of liquid propellant blast hazards must simulate vehicle configurations and failure modes and that the pre-1965 LOX/LH<sub>2</sub> TNT equivalent used for siting should be re-examined [1097, 1102].

Project Pyro was an experimental program designed to obtain data useful for assessing the hazards from liquid propellant rocket explosions. The program was conducted at the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base. The URS Corp., Burlingame, CA, established the overall design of the program, designed and constructed the test articles, and analyzed the data. The tests were conducted primarily with small propellant weights (200 and 1000 lb) under a variety of failure modes and geometry configurations. It was intended that this data, supplemented by a limited number of 25000 lb tests and two full-scale 94000 lb tests would then provide a basis from which explosive effects from operational vehicles might be predicted. The results from these tests were later analyzed statistically [1103]. See also [1095, 1104].

A generalized method was developed for predicting the blast and thermal environment resulting from explosions of the three most common liquid propellant combinations: LOX/RP-1, LOX/LH<sub>2</sub>, and NTO/Ae-50 [1105]. The blast prediction method took into account the fact that the explosive potential of a given liquid propellant combination in accidental failures is not a unique value but depends on the manner in which the propellants are brought together during the failure process and on the time of ignition after the start of mixing. The method provided a means for predicting the blast environment as a function of the following system characteristics: tank configuration, propellant type, propellant weight, nature of failure mode and ignition time.

Three independent methods which have been worked out theoretically and verified through experimental procedures were used to predict explosive yield values for liquid rocket propellants. All three gave the same end result even though they utilized different parameters and procedures. The three methods were: **(1)** mathematical model, **(2)** seven chart approach and **(3)** critical mass method [1099, 1106, 1107]. The methods were used and their value demonstrated in analyzing real problems, among them the destruct system of SATURN 5, and early configurations of the Space Shuttle.

The TNT equivalency criterion for LOX/LH<sub>2</sub> explosions in effect prior to 1971 was re-evaluated [1108]. The study addressed the static, on-pad phase of the space shuttle launch operations and was performed to determine whether the use of a TNT equivalency criterion lower than that used as of 1971 (60%) could be substantiated. The large quantity of propellant on-board the space shuttle,  $4 \times 10^6$  lb, was considered of prime importance to the study. A qualitative failure analysis of the space shuttle on the launch pad was made because it was concluded that available test data on the explosive yield of LOX/LH<sub>2</sub> propellant was insufficient to support a reduction in the present TNT equivalency value, considering the large quantity of propellant used in the Space Shuttle. The failure analysis had two objectives: The first was to determine whether a failure resulting in the total release of propellant could occur. The second was to determine whether, if such a failure did occur, ignition could be delayed long enough to allow the degree of propellant mixing required to produce an explosion of

60% TNT equivalency since the explosive yield of this propellant is directly related to the quantities of LOX and LH2 mixed at the time of the explosion. The analysis indicated that the occurrence of such a failure is unlikely and that a TNT equivalency of 20% would be a more realistic value for the static, on-pad phase of the Space Shuttle launch operations [1102].

Explosions were examined which may result from the mixing of liquid oxygen and liquid hydrogen (LOX/LH2) such that the reactants are confined by a rocket body shell such as the CENTAUR upper stage [1109]. Explosions which were confined by the ground surface were also studied, with results reported elsewhere. Initial attempts to predict the reported Pyro experimental results were unsuccessful. A new reaction energy addition hypothesis was then developed and tested. The results provided reasonable agreement with the experiments both in the near and far field.

An engineering risk assessment of the conditions for massive explosions of cryogenic LOX/LH2 rockets during launch accidents was based on the analysis of experimental data from purposeful rupture experiments with liquid oxygen and hydrogen tanks and on an interpretation of these data via analytical semi-quantitative estimates and numerical simulations of simplified models for the whole range of the physical phenomena governing the outcome of a propellant-tank breach [1110]. The following sequence of events was reconstructed in a computer model: rupture of fuel tanks, escape of the fluids from the ruptured tanks, liquid film boiling, fragmentation of liquid flow, formation of aerosol oxygen and hydrogen clouds, mixing of the clouds, droplet evaporation, self-ignition of the aerosol clouds and aerosol combustion. The power of the explosion was determined by a small fraction of the escaped cryogenes that became well mixed within the aerosol cloud during the delay time between rupture and ignition. Several scenarios of cavitation-induced self-ignition of the cryogenic hydrogen/oxygen mixture were discussed. The explosion parameters in a particular accident are expected to be highly varied and unpredictable due to randomness of the processes of formation, mixing, and ignition of oxygen and hydrogen clouds. Under certain conditions rocket accidents may result in very strong explosions with blast pressures from a few atm up to 100 atm.

A Liquid Propellant Fragment Overpressure Acceleration Model that produced a representative debris cloud from an exploding liquid-propellant launch vehicle was applied to the Core Stage of the NASA Space Launch System (SLS) launch vehicle [1111]. A combination of probability density functions based on empirical data from rocket accidents and applicable tests, as well as SLS specific geometry were combined in a MATLAB script to create unique fragment catalogues. By accelerating the debris catalogue with the blast model for LOX/LH2 explosions, the result was a fully integrated code that modeled the destruction of the core stage at a given point in its trajectory and generated hundreds of individual fragments with initial imparted velocities. The blast model provided the blast size (radius) and strength (blast wave overpressure) as probabilities based on empirical data and anchored with analytical work. The objective was to quantify the risk for a multitude of potential core stage destruct scenarios.

Examples included the effect of warning time on the survivability of an escaping crew capsule or the maximum fragment velocities generated by the ignition of leaking propellants in internal cavities.

#### 7.12.11 Pre-Mixed Solid Oxygen/Liquid Hydrogen Detonations

Most of the published information on explosive yield estimation was dealing with either LOX/RP-1 or LOX/LH<sub>2</sub>. The main concern is about the failure of the dome separating the LOX and LH<sub>2</sub> tanks in launch vehicles. Initially the concern was limited to simulating failures in the CENTAUR upper stage, but then the concern expanded to include the Space Shuttle STS external tank and more recently, the DELTA, H-II, ARIANE-5, and SLS launch vehicles [943].

The concern about the handling hazard associated with the potential explosibility of mixtures of solid oxygen with high-pressure gaseous hydrogen provided the incentive for a phase equilibria and thermodynamic study [57]. The specific concern was (is) with the behavior of oxygen which is present as a trace impurity (concentration of a few parts per million) in a high-pressure hydrogen stream which is being cooled. Oxygen crystallizes during the cooling process when the saturation concentration of oxygen is reached. The exact temperature depends upon the total pressure and the oxygen concentration. For low concentrations, the temperature is below the triple-point temperature of 54.37 K (−361.8°F). The possibility always exists that solid oxygen may concentrate in heat exchangers and other process components which are at temperatures lower than the triple point. Even at very low concentrations, the oxygen may accumulate and cause hazardous conditions. The data on the solid-vapor equilibria of the oxygen/hydrogen system are, therefore, of considerable interest for the safe design and operation of hydrogen liquefaction equipment. While accidental detonations of LOX/LH<sub>2</sub> can have disastrous consequences, controlled detonation of O<sub>2</sub>/H<sub>2</sub> in pulsed or spinning detonation engines is actively investigated in an effort to achieve higher specific impulse.

Direct initiation and propagation of detonation through a cryogenic two-phase flow of liquid oxygen droplets in cold gaseous hydrogen at 100 K were experimentally investigated [1112]. The influence of droplet size distribution was characterized in a cryogenic gaseous hydrogen and liquid oxygen two-phase flow. Droplet sizing and detonation experiments were conducted by varying different parameters: distance from the injector, helium and hydrogen mass flow rates, global equivalence ratio, and addition of gaseous nitrogen. Droplet size distributions revealed quick vaporization of the smallest droplets of the cryogenic jet. Results in terms of wave velocity, pressure, and detonation cells showed that a detonation wave can be directly initiated, with a propagation wave velocity of 20% higher than the predicted C-J value. Cell size measurements showed that the mixture sensitivity was not affected by the presence of droplets. Addition of gaseous nitrogen reduced the peak pressure only slightly but the detonation velocity was reduced by about 30%.

## 8 Toxic Properties of Hydrogen

Hydrogen is not toxic; however, because it does not sustain breathing, inhalation of hydrogen will lead to a lack of oxygen and suffocation. Because warm hydrogen is much lighter than air it is unlikely that oxygen-depleted spaces at ground level are formed as the result of venting hydrogen. This is unlike the asphyxiation hazard from venting of nitrogen in enclosed spaces.

The main hazard to the operators during handling of liquid hydrogen is frostbite due to freezing of tissue if liquid hydrogen is accidentally spilled on the skin or if an operator accidentally comes into contact with a cold line with bare skin. Moist skin, like fingers on a bare hand touching a cold surface will instantly freeze onto the surface and is only difficult to remove by pouring on copious amounts of lukewarm water. Frostbite caused by liquid hydrogen is similar to frostbite caused by liquid oxygen or liquid nitrogen.

## 9 Accident History of Hydrogen

Section “Liquid Hydrogen Transportation Accident History” dealt with transportation accidents during the transportation of liquid hydrogen in tank cars, rail cars, and barges. These accidents may or may not have resulted in ignition of the spilled liquid or released gas. Accidents with LOX and liquid hydrogen were included in a summary of launch vehicle accidents, including launch failures and launch aborts [1113].

In the accident history with LOX and LH2 there are at least three incidents with liquid propulsion systems containing a combination of LOX and LH2. Two propellant tank confinement by outer shell (interior tank bulkhead rupture) failure accidents occurred during preparations for static tests of SATURN-V vehicle propulsion stages in 1964 and 1967. In addition, a full-scale SATURN stage was also tested to similar confinement-by-missile failure during Project Pyro. The first LOX/LH2 static test accident involved a fully loaded S-IV third stage of a SATURN V launch vehicle [1114]. The stage contained approximately 84000 lb of LOX and 17000 lb of LH2. An explosion occurred 5 s before ignition of the engine. The immediate cause of the failure was determined to be overpressurization of the liquid oxygen tank, which resulted in either rupture of the common bulkhead between the LOX and LH2 or nearly simultaneous external rupture of both propellant tanks with subsequent mixing. In either case, the failure simulated a confinement-by-missile failure mode as defined in Project Pyro. All available evidence indicated that ignition occurred almost immediately upon contact of the two propellants, with very limited mixing of the hydrogen and oxygen. Spontaneous ignition has also been observed in many large-scale controlled LOX-LH2 tests during Project Pyro and other test programs. TNT equivalence of the LOX-LH2 explosion was estimated during the post-accident investigation by considering damage to specific structures [1102]. One estimate was obtained based on damage to a lightweight

sheet metal building located 63.8 m (210 ft) from the test stand. Damage consisted of wrinkling/slight crushing of the metal wall and roof panels, buckling/deflecting of structural members in the roof to about 5 cm (2 in.), and breaking of several windows on the wall facing the explosion and one window on the opposite wall. Overpressure required to produce this magnitude of damage was estimated to be about 34 kPa (5 psi) (reflected) and 17 kPa (2.5 psi) (side-on) yielding a TNT equivalent weight for the explosion of approximately 344 kg (760 lb<sub>m</sub>). Another estimate was based on the 30-cm (12 in.) permanent deflection observed in a structural steel I-beam of the test stand located approximately 3.9 m (13 ft) from the center of explosion. The estimated TNT equivalent weight based on overpressure impulse for this type of damage was about 453 kg (1000 lb<sub>m</sub>). TNT equivalence was also estimated from glass breakage which occurred at distances up to approximately 334 m (1100 ft). The agreement between estimates derived independently from different effects was very good and all of the analyses converged to an average equivalent weight value of 494 kg (1090 lb<sub>m</sub>) TNT. Based on the total LOX-LH2 propellant load, the average TNT equivalence for the event was estimated to be about 1.1%, with a maximum of about 1.4%. Fragments from the event were thrown to a maximum distance of 334 m (1100 ft).

The other LH2-LOX static test explosion occurred with a SATURN-V S-IVB third stage. The total propellant load involved in this incident was about 104643 kg (231000 lb<sub>m</sub>) (5:1 mass ratio of oxidizer to fuel). The failure also simulated a confinement-by-missile mixing mode. Again, TNT equivalence was estimated based on damage observed from the explosion. The estimated equivalent weight was between 906 and 1132 kg (2000 and 2500 lb<sub>m</sub>) yielding a calculated TNT equivalence again of approximately 1%. Fragments from this event were thrown to a maximum distance of 300 m (984 ft). These data are also consistent with estimates of TNT equivalence for LH2-LOX explosions observed in other large scale test programs.

A full-scale SATURN upper stage containing 34428 kg LOX and 6886 kg LH2 (76000 lb<sub>m</sub> LOX and 15200 lb<sub>m</sub> LH2) was tested to common bulkhead rupture in Project Pyro. Bulkhead rupture was accomplished using a 46 cm (18 in.) diameter explosively driven ram cutter assembly. Ignition of the propellants occurred spontaneously at about 183 ms after rupture of the bulkhead. Air blast data recorded in the test indicated a maximum TNT equivalence of 3.5% based on overpressure and 6.8% based on overpressure impulse. Fragment dispersion ranged to a maximum of 300 m (984 ft).

This section deals with all other types of accidental releases of liquid or gaseous hydrogen, some of which lead to autoignition by buildup of electrostatic charge in the flowing gas [1115].

### 9.1 Liquid Hydrogen Leaks without Ignition

A US Department of Energy-sponsored web site maintains a list of hydrogen incidents and as an educational tool, informs about lessons learned in trying to prevent recurrence of such disasters [1116]. Several incident examples from the web site are quoted here

While disconnecting a liquid  $H_2$  fill line from a liquid  $H_2$  trailer, liquid  $H_2$  escaped, frost-burning a second man who was holding the hose. The man was burned on his hands and on his stomach. The cause of the accident was that the liquid  $H_2$  shut off valve was partially open, but both men assumed it was closed. Prescribed clothing was being worn.

### 9.2 Liquid Hydrogen Tank Accidental Venting without Ignition

A ruptured disk on a liquid hydrogen tank failed prematurely, which caused the tank to vent its entire gas contents through the tank's vent stack while the pilot flame was not lit [1117]. Venting was very loud and formed a condensed moisture cloud visible from the top of the stack. Liquid air was also visible coming off the stack. Venting ceased after approximately 5 minutes. Important to note that the safety system functioned as intended. Most prevalent learning is that liquid air will form and fall off the vent stack due to very high flow of very cold gas when the relief systems are flowing at capacity. Liquid air may also splash off flanges or other pieces and will cause a small vapor cloud as it falls from the stack. Falling raining liquid air was mistaken for liquid hydrogen during the event.

### 9.3 Liquid Hydrogen Fires

In this case, a liquid hydrogen tank incident caused a second incident. While attempting to replace a rupture disk in an  $LH_2$  vessel,  $GH_2$  gas was released and ignited. In fighting the fire, liquid  $N_2$  was sprayed by the incident response team onto a second  $LH_2$  vessel located nearby. This resulted in cracking of the outer mild steel vacuum jacket. The loss of the vacuum caused a rapid increase in pressure and rupture of the burst disk of the second vessel.  $H_2$  boiled off and was burned in the fire. The cause of the problem was that the rupture disk was being replaced with a load of liquid  $LH_2$  in the vessel and no separating inerting gas. The  $H_2$ -air mixture was probably ignited by static discharges. Rupture of the second vessel burst disk was caused by the low-temperature exposure embrittlement of the mild steel vacuum jacket.

In another incident, a rupture disc blew on a  $75\text{-m}^3$  (20000 gallon) liquid hydrogen tank, causing the vent stack to exhaust cold gaseous hydrogen [1118]. Emergency responders were called to the scene. To stabilize the tank, the remaining hydrogen was



removed from the tank except for a small volume in the heel of the tank that could not be removed manually. The tank vacuum was lost. Firemen sprayed the tank with water and directed a stream onto the fire exiting the vent stack. The water was channeled directly into the open vent stack, and the exiting residual hydrogen gas (between 20 and 32 K = −423 and −402 °F) caused the water in the vent stack to freeze. The water freezing caused the vent stack to be clogged, disabling the only exit for the cold hydrogen gas. After a time, the residual hydrogen gas in the tank warmed up, causing the tank to overpressurize and rupture with an explosion known as a BLEVE (boiling liquid expanding vapor explosion) and ignite.

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# Hydronitrogen Compounds

## Hydronitrogen Compounds

*Encyclopedia of Liquid Fuels* contains six chapters dealing with hydronitrogen compounds and four chapters dealing with hydrazines: “Ammonia” is the simplest hydronitrogen, the chapter “Hydrazine” deals with the parent inorganic compound hydrazine, while “Alkylhydrazines” deals with alkylhydrazines other than methylhydrazine and dimethylhydrazines, which are covered in the chapters “Methylhydrazine” and “Dimethylhydrazines,” respectively. The latter two chapters are about alkyl-substituted hydronitrogen compounds. Amines, amides, and imides are not counted as hydronitrogen compounds, although many of them contain N–H bonds.

Besides ammonia  $\text{NH}_3$ , hydrazine  $\text{H}_2\text{NNH}_2$ , hydrazoic acid  $\text{HN}_3$ , and their salts, there are several other hydronitrogen compounds under consideration as rocket propellants, but they are all very unstable and occur only very briefly as transients and intermediates in the decomposition of any of the aforementioned more stable hydronitrogens. It is unlikely that any of the other hydronitrogen compounds could ever be used as rocket propellants, but we include them in our discussion of rocket propellants because of their close relationship to ammonia and hydrazine. Some of these unusual hydronitrogen compounds may form in the interiors of gaseous planets at very high pressures and eventually diffuse to the surface, contributing to the hydronitrogens we can observe in the outer atmospheres of some of the giant gaseous planets. Much of the research into higher ( $\text{N} > 2$ ) polynitrogen and hydronitrogen compounds was motivated by the search for more energetic rocket propellants. If higher hydronitrogen compounds could be synthesized, they could be stored and stabilized in ammonia solution or hydrazine solution.

The introduction to the second edition (published in 2001) of Schmidt’s hydrazine book [1] contains a section on other hydronitrogen compounds, also called nitrohydrogen compounds. That section can suffice as a starting point for information on this subject; we try to expand upon it and update it here.

In this *Encyclopedia of Rocket Propellants*, a future set on solid propellants will contain a chapter on high-nitrogen compounds, most of which are organic compounds that contain at least one carbon in addition to nitrogen, and most of those are solids. The search is on for all-nitrogen compounds other than dinitrogen, but so far, all synthesis efforts have resulted in premature decomposition of the desired compounds. Theoretical computations to predict the existence and stability of all-nitrogen compounds will be described in the chapter on high-nitrogen compounds. Similar computations have been done for higher hydronitrogen compounds. The search for new all-nitrogen compounds and the search for new hydronitrogen compounds are related and go on in parallel.

The current chapter on hydronitrogen compounds was at one time part of the hydrazine chapter, but it had to be split off because the hydrazine chapter needed to be shortened. The chemistry of hydrazine is closely related to the search for other hydronitrogens with more than two nitrogens linked together. The analogy of hydronitrogens with hydrocarbons, which can form long C—C chains, is deceiving. When comparing ammonia with methane and then comparing hydrazine with ethane, the analogy ends just about right there at hydrazine, with two atoms in the N—N chain. In contrast to carbon, nitrogen does not have the capability to form stable long-chained (*catenated*) and branched or closed-ring compounds without the participation of carbon or other heteroelements. The only known stable hydronitrogens are ammonia, hydrazine, hydrogen azide (hydrazoic acid), and their salts. One would hesitate to refer to hydrogen azide as a “stable” compound because it is metastable in its pure form and is known to explode most violently. However, it is at least stable enough to be characterized as a compound by itself. Another hydronitrogen compound of interest is hydroxylamine  $\text{NH}_2\text{OH}$ , but this contains one other hetero element, oxygen. Hydroxylamine, the free base, deserves another monograph on its own, and is included in the chapter “Hydroxylammonium Salts” in of the *Encyclopedia of Oxidizers* as the parent of a series of energetic salts that are of interest as rocket propellants.

Inorganic hydronitrogen compounds that are anticipated to exist include triazane  $\text{H}_2\text{N—NH—NH}_2$ , CAS RN [14451-01-5], and tetrazane  $\text{H}_2\text{N—NH—NH—NH}_2$ , CAS RN [6054-69-9]. Many organic triazenes, tetrazanes, and tetrazenes where the hydrogen is replaced by alkyl or aryl groups are known. These are polynitrogen open-chain molecules where one or more of the hydrogens have been replaced by organic groups. Aromatic triazenes and tetrazenes are stabilized by the resonance of the azo groups with the electron system of the benzene ring. However, the inorganic unsubstituted or unprotonated parent compounds are unstable, and all attempts at their preparation have failed so far. In analogy to the hydrocarbon series of alkanes and alkenes, a saturated and an unsaturated series of compounds can be defined, the azanes and azenes. The latter group has one or more  $\text{—N=N—}$  nitrogen–nitrogen double bonds in the molecule.

## 1 High-Pressure Behavior of Hydronitrogen Compounds

Starting with gaseous elemental dinitrogen and dihydrogen, if these two gases are subjected to higher and higher pressures, which hydronitrogens will form, and which will persist even after the pressure is relieved? The Haber–Bosch synthesis of ammonia from its elements is a chemical process of vital importance for agriculture and the chemical industry. Twenty percent of the world’s population could not survive without fertilizer-supported agriculture, a process that starts with nitrogen and hydrogen under pressure. The formation of ammonia depends on the presence of catalysts and

has been thoroughly investigated. What if the two gases are compressed in the absence of catalysts to beyond their points of liquefaction and solidification? Ammonia and/or hydrazine and/or yet unknown hydronitrogens are likely to form under these extreme conditions. These questions are of interest in the study of planetary cores and atmospheres, especially those of Jupiter, and have been studied both experimentally and theoretically [2, 3]. Even if such previously unknown hydronitrogen compounds do form at very high pressure, the question of whether they survive after the pressure is relieved remains. If they can be stabilized, such as in a matrix of frozen nitrogen, they would be even more energetic than hydrazine.

Binary nitrogen/hydrogen mixtures subjected to very high pressures were analyzed using Raman spectroscopy, synchrotron XRD, synchrotron IR microspectroscopy, and visual observation [4]. A eutectic-type binary phase diagram with two stable high-pressure van der Waals compounds, identified as  $(\text{N}_2)_6(\text{H}_2)_7$  and  $\text{N}_2(\text{H}_2)_2$ , was found. The former represents a new type of van der Waals host–guest compound in which hydrogen molecules are contained within channels in a nitrogen lattice. This compound showed evidence of a gradual pressure-induced change in bonding from van der Waals to ionic interactions near 50 GPa, forming an amorphous dinitrogen network containing ionized ammonia in a room-temperature analogue of the Haber–Bosch process. Hydrazine was recovered on decompression.

Phase changes that occur in hydrazine under very high pressures are discussed in the chapter “Hydrazine” in the present *Encyclopedia of Liquid Fuels*.

The formation of nitrohydrogen compounds at pressures up to 50 GPa and their structural transformations upon applying and releasing pressure were predicted using density functional theory and evolutionary algorithms [5]. Nitrogen–hydrogen structures with N:H ratios of 3:1, 4:1, and 9:1 were simulated at high pressures (10–50 GPa). Stable crystalline structures with high symmetry and covalent bonds were predicted that had infinitely long chains or two-dimensional nitrogen–hydrogen sheets. The structure with an N:H ratio of 4:1 was found to be metallic at 50 GPa. Some crystalline phases stabilized by high pressure may exist as metastable structures of high symmetry and high mass density after lowering the pressure from 50 GPa down to 10 GPa.

Theory predicts a very diverse high-pressure chemistry of hydronitrogens, with the existence of many  $\text{N}_x\text{H}_y$  compounds [6]. The stability of these phases under pressure was investigated by the compression of  $\text{N}_2/\text{H}_2$  mixtures of various compositions. A eutectic-type  $\text{N}_2/\text{H}_2$  phase diagram with two stoichiometric van der Waals compounds,  $(\text{N}_2)_6(\text{H}_2)_7$  and  $\text{N}_2(\text{H}_2)_2$ , was discovered. The structure of the  $\text{N}_2(\text{H}_2)_2$  compound and chemical changes under a pressure cycle up to 60 GPa and back to ambient conditions were characterized using Raman spectroscopy. An  $\text{N}_2(\text{H}_2)_2$  single crystal was grown from a 1:2  $\text{N}_2/\text{H}_2$  mixture and its crystalline structure was determined using synchrotron X-ray diffraction. Like the solid  $(\text{N}_2)_6(\text{H}_2)_7$ ,  $\text{N}_2(\text{H}_2)_2$  has a remarkable host/guest structure containing orientationally disordered  $\text{N}_2$  molecules with spherical, ellipsoidal, and planar shapes. Above 50 GPa,  $\text{N}_2(\text{H}_2)_2$  was



found to undergo a chemical reaction. The reaction products were determined to be from the azane family, with  $\text{NH}_3$  as the main constituent, along with molecular nitrogen. Upon decreasing the pressure, the reaction products were found to react in such a way that below 10 GPa, hydrazine was the sole azane detected. Observed down to the opening of the diamond anvil cell, the formation of metastable hydrazine instead of the more energetically favorable ammonia was surprising and could change the current view of Jovian planetary atmospheres, in which ammonia was previously assumed to be the only stable hydronitrogen molecule.

Compressing lithium metal embedded in a matrix of solid  $\text{N}_2$  to very high pressures (45 GPa) resulted in lithium pentazolate  $\text{LiN}_5$  formation [7]. The observation by Raman spectroscopy of vibrational modes unique to the cyclo- $\text{N}_5^-$  anion was the signature of the formation of  $\text{LiN}_5$ . Mass spectroscopy experiments confirmed the presence of the pentazolate anion in the recovered compound. A monoclinic lattice was obtained from XRD measurements, and the unit cell volume of the  $\text{LiN}_5$  compound under pressure was in good agreement with theoretical calculations.

## 2 Homocyclic Hydronitrogen Compounds

Homocyclical-nitrogen ring compounds (as opposed to the heterocyclic compounds discussed in the chapter “Heterocyclic and Heterocycloaliphatic Amines” in this volume) are unstable and difficult to obtain. They can be stabilized by adjacent fused aromatic rings.

### 2.1 Three-Membered Ring Homocyclic Hydronitrogen Compounds

It is difficult enough to obtain carbon-based three-membered ring compounds, and some of those, e.g., ethylene oxide, have been tested as monopropellants. Ethyleneimine ( $\text{C}_2\text{H}_5\text{N}$ , aziridine) would be a good fuel. Diazomethane ( $\text{CH}_2\text{N}_2$ , diazirine) is unstable and handled only in solution. Triaziridine ( $\text{N}_3\text{H}_3$ ) can be stabilized by adsorption on silver zeolites, and organic triaziridines with various substituents have been made. It is unclear if stable isomers of triaziridine exist [8].

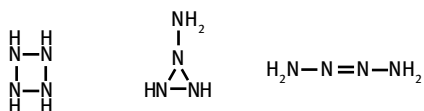
Portions of the  $\text{N}_3\text{H}_3$  singlet potential energy surfaces corresponding to triaziridines, azimines, and triazenes have been calculated by *ab initio* methods [9]. Minima and transition states were located by force gradient geometry optimization. The configuration at the three N atoms in triaziridines is pyramidal. The N–N bonds in triaziridine are longer and weaker than those in hydrazine. *trans*-Triaziridine has better stability than *cis*-triaziridine. In azimine, all six atoms are in the same plane. There are three stereoisomers. In triazene, all six atoms are in the same plane. There are two stereoisomers.

Of all the  $(\text{NH})_n$  ring-shaped hydronitrogens, triaziridine, with  $n = 3$ , if it existed, would have the highest strained ring energy [10]. Thermochemical properties of two molecules containing three nitrogen atoms in a ring, triaziridine and triazirine, were calculated [11]. Predicted enthalpies of formation of *trans*-triaziridine ranged from +405.0 to +418 kJ/mol.

Nitrotriaziridines would be nitramines without a carbon skeleton, like RDX with the  $-\text{CH}_2-$  linkages removed. It was hoped that the electron-drawing ability of the  $-\text{NO}_2$  groups would stabilize the three-membered ring, but, at the same time, steric hindrance from the presence of more than one bulky  $-\text{NO}_2$  group in a crowded space near the small ring makes these compounds less stable. Predicted enthalpies of formation of nitrotriaziridine, dinitrotriaziridine, and trinitrotriaziridine are +486.79, +606.64, and +706.38 kJ/mol, so they truly are highly energetic compounds, but these high numbers also indicate that these compounds would be unstable [12]. These compounds were not included in the chapter on nitramines because they do not exist.

## 2.2 Four-Membered Ring Homocyclic Hydronitrogen Compounds

Tetrazetidine,  $\text{N}_4\text{H}_4$ , CAS RN [58674-00-3], which consists of four NH groups linked in a square four-membered ring, is an isomer of ammonium azide  $\text{NH}_4\text{N}_3$ , an isomer of aminoaziridine, CAS RN [176109-57-2], a three-membered ring with an amino group attached, and an isomer of tetrazene-2,3, CAS [RN 54410-57-0], which has an azo group with two amino groups  $\text{H}_2\text{N}-\text{N}=\text{N}-\text{NH}_2$ .



Tetrazetidine    Aminoaziridine    Tetrazene-2,3

There have been many attempts to convert ammonium azide to some of its isomers by subjecting it to very high pressures. Ammonium azide was the preferred starting reactant for such investigations. It does not appear that any of these isomers are more stable or more suitable as rocket propellants than ammonium azide itself. Similarly, hydrazinium azide has been subjected to very high pressures in the search for other hydronitrogens.

First-principles and *ab initio* calculations were made to investigate the structural, elastic, and electronic properties of  $\text{N}_4\text{H}_4$  compounds, with the ring compound compared to its straight-chain analogs [13–16]. The calculated structural parameters of three structures were in agreement with the available theoretical and experimental data. The most stable  $\text{N}_4\text{H}_4$  isomer is the straight-chain tetrazene-2,3,  $\text{H}_2\text{N}-\text{N}=\text{N}-$

NH<sub>2</sub>. The independent elastic constants, bulk moduli, shear moduli, Young's moduli, and Poisson ratios of the three structures were calculated and agreed with predicted elastic and mechanical properties. The electronic band structures, densities of states, and charge density distributions of the three structures indicated that there are covalent N—N and N—H bonds. In a computational study of the pressure-induced phase transition in the hydronitrogen compound N<sub>4</sub>H<sub>4</sub>, a tetragonal structure with a space group of *P4<sub>2</sub>/n* was mechanically stable and ductile [17]. With increasing pressure, the phase transition pressures were 5.6, 15.0, 30.0, and 69.2 GPa.

### 3 Hydronitrogens Derived from Compressed Ammonium Azide

Ammonium azide, NH<sub>4</sub>N<sub>3</sub>, is a hydronitrogen that is relatively stable at room temperature and makes a good starting point in the attempted synthesis of higher hydronitrogens. The preparation and properties of ammonium azide are summarized in the chapter "Azides and Azido Compounds" in this publication, the *Encyclopedia of Liquid Fuels*.

A combined theoretical and experimental study of the high-pressure behavior of ammonium azide using density functional theory considered the relative thermodynamic stability of the material with respect to two other crystal phases, (NH)<sub>4</sub> and *trans*-tetrazene [18, 19]. Raman spectra of NH<sub>4</sub>N<sub>3</sub> were measured at pressures up to 71 GPa at room temperature. There was no evidence of a phase transition to either tetrazene or tetrazetidine (NH)<sub>4</sub>.

The transformation of hydrazinium azide into molecular N<sub>8</sub> has been investigated at high pressures (up to 68 GPa) using confocal micro-Raman spectroscopy and synchrotron powder XRD [20]. The results showed that HA undergoes a structural phase transition from solid HA-I to HA-II at 13 GPa that is associated with the strengthening of hydrogen bonding, and then to N<sub>8</sub> at 40 GPa. When working with ammonium azide, one must remember that it is detonable and toxic [21].

#### 3.1 Five-Membered Ring Homocyclic Hydronitrogen Compounds

It appears that the electronic structures of certain five-membered nitrogen rings could be isoelectronic with that of benzene and thus possess aromaticity-supported stability. The stability of pentazole rings would be improved by the presence of adjacent aromatic rings to share the electron cloud with.

The short-lived existence of tetrazolylpentazole has been shown using low-temperature <sup>15</sup>N/<sup>1</sup>H NMR spectroscopy [22]. Tetrazolylpentazole was identified as an intermediate in the reaction of tetrazolediazonium chloride with lithium azide by low-temperature <sup>15</sup>N NMR spectroscopy. The decomposition of <sup>15</sup>N-labeled

tetrazolylpentazole to form  $^{15}\text{N}$ -labeled tetrazole azides and dinitrogen was followed by low-temperature  $^{15}\text{N}$  NMR spectroscopy.

The possibility of the existence of cyclopentazane, which is a polynitrogen compound with a formula of  $\text{N}_5\text{H}_5$ , has been examined, and it has been compared to the pentazolate anion, which is an all-nitrogen aromatic compound with a formula of  $\text{N}_5^-$  [23]. The syntheses of various arylpentazoles were followed by oxidative or reductive paths to the pentazolate anion. Polynitrogen-based compounds – triazanes and azimines – were then used in attempts at cycloaddition, which were hoped would lead to the cyclopentazane. Complexing polynitrogen compounds with various metal cations may result in more stable compounds.

### 3.2 Pentazolate Salts

The cyclo- $\text{N}_5$  molecule was synthesized for the first time by the reaction of benzenediazonium chloride with lithium azide in methanol at 233 K ( $-40^\circ\text{C}$ ), giving a phenylpentazole. In this compound, the  $\text{N}_5$  ring was covalently bonded to a larger aromatic ring molecule. XRD measurements showed that cyclo- $\text{N}_5^-$ , an analog of the cyclopentadienyl anion  $\text{C}_5\text{H}_5^-$ , is aromatic, with N–N bond lengths of 1.3–1.35 Å, intermediate between those of single (hydrazine, 1.45 Å) and double (*trans*-diazene, 1.25 Å) nitrogen bonds [24].

The existence of the cyclo- $\text{N}_5^-$  anion was proven in 2002 by electrospray ionization mass spectroscopy [25]. This anion is isoelectronic with the cyclopentadienide anion, and one could envision a wide array of inorganic ferrocene-type chemistry using cyclo- $\text{N}_5^-$ . The pentazolate anion has been generated from *p*-hydroxyphenylpentazole and identified by electrospray ionization mass spectrometry [26]. Whereas at low collision voltages the *para*-phenoxyphenylpentazole anion undergoes stepwise  $\text{N}_2$  elimination, generating the corresponding azide and nitrene, at high collision voltages the  $\text{N}_5^-$  anion is formed. Fragmentation of the pentazolate anion produces the  $\text{N}_3^-$  anion as the principal negative ion. It was demonstrated that under suitable reaction conditions, the C–N bond in a phenylpentazole can be selectively broken while conserving the pentazole ring, thus providing a potential synthetic route to the pentazole anion. Once the existence of the pentazolate anion in the gas phase was proven, the next target was to obtain and stabilize it in bulk in solution. Reports [27] of a bulk synthesis of  $\text{N}_5^-$  were later shown to be in error [28, 29].

Theoretical calculations showed that  $\text{N}_5^-$  favors the formation of  $\sigma$ -complexes over  $\pi$ -complexes, resulting in a loss of aromaticity for  $\text{N}_5^-$  and facilitating  $\text{N}_2$  elimination. To circumvent this problem, the plan was to complex the cations with crown ethers. The resulting flat, bulky cations were expected to favor sandwich structures and  $\pi$ -bonding.

Isolating the  $N_5^-$  anion proved to be difficult, and it was not until 2002 that  $N_5^-$  was obtained in the gas phase for the first time by cleaving the C–N bonds in substituted phenylpentazoles [25, 26]. However, the free acid pentazole  $HN_5$  has not yet been successfully isolated. In 2017, a breakthrough was made in polynitrogen chemistry with the synthesis of  $N_5^-$  in the condensed phase at ambient pressure as part of a metal–organic framework. The pentazole was prepared in a THF solution with sodium and was reported to be stable below 233 K ( $-40^\circ\text{C}$ ) [30, 31]. The main method for producing standalone  $N_5^-$  was through the cleavage of the C–N bond in arylpentazoles [32] and then by stabilizing the anion with various other cations such as hydronium, ammonium, or water as well as metal cations such as sodium, cobalt, iron, or manganese. Several solid saline compounds such as  $(N_5)_6(H_3O)_3(NH_4)_4Cl$  (stable below 390 K =  $117^\circ\text{C}$ ),  $Co(N_5)_2(H_2O)_4 \cdot 4H_2O$  [31, 32] (stable at room temperature), and the hydrate  $[Na(H_2O)(N_5)]_2H_2O$ ,  $[M(H_2O)_4(N_5)_2]_4H_2O$  ( $M = Mn, Fe, \text{ and } Co$ ) (stable near to 373 K =  $100^\circ\text{C}$ ) were also synthesized [33]. Although it is not clear what the energy densities of these materials are, the results demonstrated that the  $N_5^-$  anion is stable enough to exist near ambient conditions in the solid state.

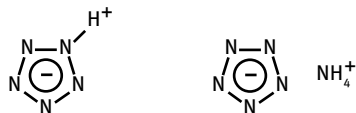
Planar  $N_x$  systems such as cyclo- $N_5^-$  and  $N_5^+$  tend to be more stable than nonplanar systems such as the neutral cyclo- $N_6$ . It was proposed that the key to stabilization is the separation of the  $\sigma$ - and  $\pi$ -electron systems [34]. In both cyclo- $N_5^-$  and  $N_5^+$ , a six- $\pi$ -electron system is created upon either adding an electron to or removing an electron from the cyclo- $N_5$  radical. Judicious addition of oxygen atoms to polynitrogen ring compounds such as cyclo- $N_4$  and cyclo- $N_6$  can increase their thermodynamic and kinetic stabilities, which is accompanied by only a small reduction in their efficiency as high-energy-density materials.

It was hoped that derivatives of pentazole could lead to new high-energy-density materials to be used as rocket propellants or explosives. However, these molecules are potentially hazardous because of their high formation enthalpies and weak N–N bonds. Possible routes for the synthesis of nitro and azido derivatives of pentazole and their mono- and dioxides have been explored using quantum chemical methods [35]. Reaction pathways have been investigated in detail, with emphasis on locating transition states and obtaining a reliable treatment of solvent effects.

A thorough survey of energetic polynitrogen compounds at high pressure was provided in [36, 37]. XRD patterns and corresponding Raman spectra were calculated for several candidate structures. Cesium pentazolate was synthesized by compressing and heating cesium azide  $CsN_3$  and  $N_2$  precursors in a diamond anvil cell.

### 3.2.1 Ammonium Pentazolate

After the discovery of lithium pentazolate  $LiN_5$ , the search started for other pentazolate salts. The formation of ammonium pentazolate  $NH_4N_5$  is predicted by computational methods, but the compound has not yet been isolated.



The existence of pentazole ( $\text{N}_5\text{H}$ ) and ammonium pentazolate ( $(\text{NH}_4)(\text{N}_5)$ ) was predicted using a first-principles evolutionary search of the nitrogen-rich portion of the hydronitrogen binary phase diagram ( $\text{N}_x\text{H}_y$ ,  $x = y$ ) at high pressures [38]. Both crystals would consist of pentazolate ( $\text{N}_5^-$ ) anions and ammonium ( $\text{NH}_4^+$ ) or hydrogen ( $\text{H}^+$ ) cations. These two crystals are predicted to be thermodynamically stable at pressures above 30 GPa for  $(\text{NH}_4)(\text{N}_5)$  and 50 GPa for pentazole  $\text{N}_5\text{H}$ . The chemical transformation of ammonium azide  $\text{NH}_4\text{N}_3$  mixed with dinitrogen ( $\text{N}_2$ ) to ammonium pentazolate ( $(\text{NH}_4)(\text{N}_5)$ ) was predicted to become energetically favorable above 12.5 GPa. To assist in the identification of newly synthesized compounds in future experiments, the Raman spectra of both crystals were calculated, and mode assignments were made as a function of pressure for pressures up to 75 GPa.

After the synthesis of  $(\text{N}_5)_6(\text{H}_3\text{O})_3(\text{NH}_4)_4\text{Cl}$ , in which the cyclo-pentazolate anions were stabilized extensively by hydrogen bridges with  $\text{NH}_4^+$  and  $\text{OH}_3^+$  cations, significant efforts were made to replace these non-energetic cations and the  $\text{Cl}^-$  anion by more energetic cations [39]. The salts made by metathetical syntheses of cyclo-pentazolate salts containing the simple nitrogen-rich cations  $\text{NH}_4^+$ ,  $\text{NH}_3\text{OH}^+$ ,  $\text{N}_2\text{H}_5^+$ ,  $\text{C}(\text{NH}_2)_3^+$ , and  $\text{N}(\text{CH}_3)_4^+$  were characterized by their crystal structures, their vibrational, mass, and multi-nuclear NMR spectra, thermal stability measurements, sensitivity data, and performance calculations. It was shown that the cyclo-pentazolates are more energetic than the corresponding azides but are less thermally stable, decomposing in the range of 333–378 K (80–105 °C). As rocket propellant ingredients, the hydrazinium and hydroxyl ammonium salts were predicted to exceed the performances of RDX and HMX. The crystal structures showed that the cyclo-pentazolate anions were generally stabilized by hydrogen bonds to the cations, except for the  $\text{N}(\text{CH}_3)_4^+$  salt, which also exhibited strong cation– $\pi$  interactions. This difference in anion stabilization was also detectable in the vibrational spectra, which showed for the  $\text{N}(\text{CH}_3)_4^+$  salt a decrease in cyclo- $\text{N}_5^-$  stretching vibrations of about  $20\text{ cm}^{-1}$ .

A debate arose on the possible existence of a neutral  $\text{HN}_5$  species in the pentazolate salt. It was suggested that a few neutral  $\text{HN}_5$  species co-exist in the pentazolate salt, which is consistent with some single-crystal XRD measurements [40].

High yields (>90%) of potassium, ammonium, hydroxylammonium, hydrazinium, aminoguanidinium, diaminoguanidinium, biguanidinium, 3,4-diamino-1,2,4-triazolium, and 3,6,7-triamino-7*H*-[1,2,4]triazolo[3,4-*b*][1,2,4]triazol-2-ium pentazolates were obtained by metathesis reactions of  $\text{AgN}_5$  and the respective chloride salts driven by the precipitation of  $\text{AgCl}$  [41]. All compounds were thoroughly characterized via IR and multi-nuclear NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectroscopy and elemental analysis. The solid-state structural features of the synthesized compounds were also

investigated via single-crystal XRD. The thermal stabilities were investigated by TGA and DSC, and heats of formation and detonation performance were calculated using the Born–Haber energy cycle and the EXPLO5 v6.01 program, respectively. Based on the experimental and theoretical data, biguanidinium pentazolate ( $N = 81.36\%$ ,  $T_d = 397.9\text{ K} = 124.8^\circ\text{C}$ ,  $\Delta H_f = 1362.0\text{ kJ/mol}$ ,  $v_D = 9.257\text{ km/s}$ ,  $P_D = 33.0\text{ GPa}$ ) showed potential as a high-performance energetic material.

The enthalpies of formation of the cyclo-pentazoles and azides of  $\text{NH}_4^+$ ,  $\text{NH}_3\text{OH}^+$ ,  $\text{N}_2\text{H}_5^+$ ,  $\text{C}(\text{NH}_2)_3^+$ , and  $\text{N}(\text{CH}_3)_4^+$  were calculated and, together with experimental densities, used to predict the performances of these salts as explosives and propellants [42]. As explosives, the cyclo- $\text{N}_5^-$  salts outperform the corresponding azides by a significant amount, but as rocket propellants, their performance is slightly inferior. Although the cyclo- $\text{N}_5^-$  salts are building blocks for future energetic materials, their predicted performances are not revolutionary, falling within the range of known CHNO compounds, and they do not approach those expected for polynitrogen cations or neutral polynitrogens. Lattice energy calculations also indicated that the previously reported experimental value of  $114.28 \pm 0.84\text{ kJ/mol}$  for the enthalpy of formation of solid  $\text{NH}_4\text{N}_3$  may need revision.

### 3.3 Six-Membered Ring Homocyclic Hydronitrogen Compounds

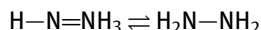
The all-nitrogen analogue of cyclohexane,  $\text{N}_6\text{H}_6$ , could be called hexazine or hexaaza-cyclohexane. Forty-eight possible isomers of  $\text{N}_6\text{H}_6$  have been investigated by computational quantum-mechanical modeling [43]. The results showed that the heats of formation of all isomers were positive. The energies and the heats of formation of the ring-shaped isomers were higher than those of the open-chain isomers. Among the ring-shaped isomers, the four-membered ring isomers had the highest heats of formation and the five-membered ring isomers had the lowest. For six-membered ring isomers, only the chair-shaped isomers were predicted to be stable.

## 4 Nitrogen Pentahydride

One has become accustomed to thinking of nitrogen as a trivalent atom when discussing nitrogen hydrides. It would be nice to have a hydronitrogen such as  $\text{NH}_5$  and use it as a rocket propellant, which is not totally improbable since nitrogen is pentavalent in other compounds. Nitrogen pentahydride  $\text{NH}_5$  has been postulated as an intermediate in the reaction of ammonium salts with lithium hydride. Taking speculation about pentavalent nitrogen hydrides one step further,  $\text{H}_2\text{N}-\text{NH}_4$  or even  $\text{H}_4\text{N}-\text{NH}_4$  could be postulated as intermediates in the reaction of hydrazinium(1+) and (2+) salts with lithium hydride.

## 5 Open-Chain Hydronitrogens

The gross formulas of the series of open-chain saturated hydronitrogens follow the general formula  $N_nH_{n+2}$ , where  $n = 1$  gives ammonia and  $n = 2$  gives hydrazine. Hydrazine may also exist (at least temporarily) in the form of isohydrazine  $H-N=NH_3$ . Isohydrazine, predicted by *ab initio* calculations [44], is unlikely to be isolated in measurable amounts because of rapid bimolecular tautomerization:



### 5.1 Diazene

In the singly unsaturated series of hydronitrogens, the gross formula can be represented by the general formula  $N_nH_n$ , including diazene  $N_2H_2$  (also called *diimine* or *diimide*), triazene  $N_3H_3$ , and tetrazene  $N_4H_4$ . Theoretically, the imidogen (imine) radical  $NH$  could also be included in this group, but it is a very unstable compound, though its brief existence in glow discharges has been proved by its emission spectrum. None of these compounds are suitable as rocket propellants, but they may be encountered as intermediates in the decomposition of other hydronitrogens.

Diazene,  $HN=NH$ ,  $N_2H_2$ , CAS RN [3618-05-1], is sometimes also called *diimide* or *diimine*, but the name *diazene* is preferred here. Diazene is a very short-lived species. It has been identified as an intermediate in the decomposition and oxidation of hydrazine. Diazene exists in *cis* [15626-42-3] and *trans* [15626-43-4] forms. It can be stabilized by freezing in a matrix of solid argon or by complexing with transition metal ions. Stable complexes with diazene as a ligand have been described [45, 46]. Such diazene complexes may be intermediates in biological nitrogen fixation. The decomposition of hydrazine in a microwave-induced glow discharge produced a mixture of diazene and ammonia [47]. However, relatively pure diazene can be obtained by pyrolysis of alkali metal tosyl hydrazides [48–50]. The enthalpy of formation of diazene in the gas state is  $+150 \pm 8$  kJ/mol ( $+36 \pm 2$  kcal/mol) [51].

### 5.2 Triazane and Triazene

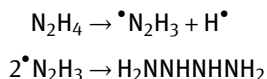
Triazane,  $H_2N-NH-NH_2$ ,  $N_3H_5$ , CAS RN [14451-01-5], and triazene,  $H_2N-N=NH$ ,  $N_3H_3$ , are not known as stable compounds and may only exist for a short time during the decomposition of other hydronitrogen compounds. Triazane and triazene exist only on paper or in the memories of computers [52, 53]. Predictions were that the *cis* form of triazene would have a specific enthalpy of combustion of 15.2 kJ/g and the *trans* form would have a specific enthalpy of combustion of 14.7 kJ/g. Triazane, if it existed, would have a specific enthalpy of combustion of about 20 kJ/g.



### 5.3 Tetrazane

Tetrazane,  $\text{H}_2\text{N}-\text{NH}-\text{NH}-\text{NH}_2$ ,  $\text{N}_4\text{H}_6$ , CAS RN [6054-69-9], is not known as a stable substance. The properties of tetrazane,  $\text{H}_2\text{N}-\text{NH}-\text{NH}-\text{NH}_2$ , have been predicted from quantum-mechanical calculations [54]. Optimized geometries, vibrational frequencies, conformation energies, heats of formation, and proton affinities for tetrazane were determined using various-level *ab initio* methods.

During the decomposition of hydrazine, it would be easy for two hydrazyl free radicals to combine to form tetrazane:



However, there is no evidence that this actually takes place [55]. Stabilized tetrazane (*n*- $\text{N}_4\text{H}_6$ ) formation from  $\cdot\text{N}_2\text{H}_3 + \cdot\text{N}_2\text{H}_3$  becomes significant only at relatively high pressures and low temperatures because the reverse dissociation back into  $\cdot\text{N}_2\text{H}_3 + \cdot\text{N}_2\text{H}_3$  is the preferred direction.

### 5.4 Pentazenium Salts as $\text{N}_5^+$ Chain Compounds

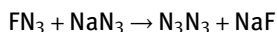
One of the first  $\text{N}_5^+$  pentazenium salts was  $\text{N}_5^+\text{AsF}_6^-$ , synthesized in 1999 [56, 57]. The assignment of the  $\text{C}_{2v}$ -symmetric structure predicted by calculations was supported by IR and Raman as well as  $^{14}\text{N}$  and  $^{15}\text{N}$  NMR spectroscopic studies of the isotopically labeled product. In inorganic chemistry, a homoleptic chemical compound is a compound in which all bonds and ligands are identical. The five nitrogen atoms are in a linear, V-shaped arrangement, not in a pentazole ring. Similar salts with hexafluoroantimonate [58] or hexafluorostannate [59] as the anion showed surprisingly good thermal stability. One of the  $\text{N}_5^+$  structures was illustrated by a structural model of  $\text{N}_5[\text{Sb}_2\text{F}_{11}]$  that was not only a stick model but also showed the sizes of the atomic (ionic) radii and potential overlaps of the electron clouds [58]. Studying the stability of  $\text{N}_5^+\text{SbF}_6^-$  at higher pressures may aid the discovery of other polynitrogen species. It was found that  $\text{N}_5^+\text{SbF}_6^-$ , when pressurized to 4.5 GPa and heated, was stable to 478 K (205 °C) [60]. The thermal stability of the  $\text{N}_5^+$  cation can be enhanced by pressure.

Now, if one could synthesize  $\text{N}_5^+$  salts with an all-nitrogen anion such as azide  $\text{N}_3^-$  or  $\text{N}_5^-$ , they would make a good source of nitrogen for an airbag inflator and other applications. When investigating the stability of  $\text{N}_5^+\text{N}_5^-$  as an isolated species and in a potential crystal structure, it was predicted that its barriers to loss of  $\text{N}_3^-$  from the  $\text{N}_5^+$  ion and to addition to form  $\text{N}_{10}$  are 105 and 63 kJ/mol (25 and 15 kcal/mol), respectively, and that the barrier to loss of  $\text{N}_2$  from the  $\text{N}_5^-$  ion is 63 kJ/mol (15 kcal/mol) [61].

Attempts to synthesize the all-nitrogen compound  $[\text{N}_5^+][\text{N}_5^-]$  have so far been unsuccessful. It was predicted that neither the  $\text{N}_5^+\text{N}_5^-$  nor the  $\text{N}_5^+\text{N}_3^-$  ion pair are stable

[62]. Both were predicted to spontaneously decompose into  $N_3$  radicals and  $N_2$ . On closer examination, it became increasingly clear that the synthesis of an ionic polynitrogen compound such as  $N_5^+N_5^-$  or  $N_5^+N_3^-$ , consisting of a polynitrogen cation and a polynitrogen anion, is not feasible. This is due to the fact that the first ionization potential of a neutral species is always much higher than its electron affinity. The difference between the two would have to be made up by the lattice energy of the ionic solid.

Unlike  $N_5^+N_5^-$ , for which marginal stability was predicted, the  $N_5^+N_3^-$  ion pair can spontaneously isomerize to azidopentazole, an intermediate with a lower level of energy, which in turn will decompose to molecular dinitrogen [63, 64]. Mixing  $N_5^+SbF_6^-$  and sodium azide  $NaN_3$  did not result in the desired product. Isolation of covalently bonded  $N_8$  from  $N_5^+$  and  $N_3^-$  will be difficult because the most likely product has a decomposition barrier of only 75 kJ/mol (18 kcal/mol). It may not be formed at all, because one of the approach pathways has great potential for mutual neutralization and subsequent fragmentation. Using similar computational techniques, the feasibility of a  $N_3^+N_3^-$  salt has been investigated. It appeared to have sufficient stability to warrant further investigations, but the reaction



did not give the desired product. Attempts were also made [65, 66] to combine the  $N_5^+$  cation with energetic counter-ions such as  $NO_3^-$ ,  $ClO_4^-$ ,  $B(N_3)_4^-$ , and  $P(N_3)_6^-$ .

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# Hydrazine

## Hydrazine

Hydrazine, also known as diamide, dinitrogen tetrahydride,  $\text{N}_2\text{H}_4$ ,  $\text{H}_2\text{NNH}_2$ , CAS RN [302-01-2], is the most versatile rocket propellant in that it can be used as a bipropellant fuel, monopropellant, working fluid for electrothermal and arc-jet-augmented thrusters, and as a gas generant. Hydrazine blends with other fuels or water expand the operating temperature range of anhydrous hydrazine under a wide variety of environmental conditions. Hydrazine solutions with dissolved solid oxidizers provide a higher specific impulse than hydrazine by itself. This chapter deals only with hydrazine,  $\text{N}_2\text{H}_4$ , by itself and with hydrazine hydrate,  $\text{N}_2\text{H}_5\text{OH}$ . Hydrazine derivatives like alkylhydrazines will be described in *Encyclopedia of Liquid Fuels*, in three additional chapters: “Alkylhydrazines,” “Dimethylhydrazines,” and “Methylhydrazine.” Hydrazinium salts as solid propellant ingredients were already discussed in *Encyclopedia of Oxidizers*, in the chapter “Hydrazinium Salt Oxidizers.” Solid organic hydrazides, useful as coolants and high-nitrogen compounds for gas generators, will be listed in *Encyclopedia of Liquid Fuels*, in the chapter “Amides and Imides.” The current chapter on hydrazine is larger than most other chapters in this book because in many instances, information is provided not only on hydrazine,  $\text{N}_2\text{H}_4$ , itself but also on hydrazine in comparison to its methyl derivatives monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH).

One of the first suggestions for the use of hydrazine as a rocket fuel was in Wernher von Braun’s 1932 book *The Mars Project* (*Das Mars Projekt*, in German) [1]. The launch vehicle would have used white fuming nitric acid (WFNA) and anhydrous hydrazine, certainly a very energetic and storable propellant combination. The first stage of the four-stage launch vehicle would have used 4800 tons of propellants including 1820 tons of hydrazine, the second stage would have used 700 tons of propellants including 266 tons of hydrazine. There was no industrial hydrazine or hydrazine hydrate production in the entire world at the time when that book was written.

It was not anhydrous hydrazine but hydrazine hydrate in a mixture with methanol that was used as the fuel for the world’s first rocket plane, the Me-163B, in combination with hydrogen peroxide as the oxidizer. That was the first time hydrazine (hydrate) got to fly. The fuel requirements for this military war project stimulated hydrazine hydrate production in at least two industrial locations in Germany during World War II (WWII) [2, 3]. Knowledge on how to produce hydrazine hydrate gained during those years served as the starting point and catalyst for the development of a broader-based hydrazine hydrate industry in other countries after WWII, partially helped by hydrazine hydrate production facilities that had been confiscated and dismantled in Germany, shipped out and reassembled by the victorious allied forces in their own countries. Once hydrazine hydrate became available, its usefulness as boiler



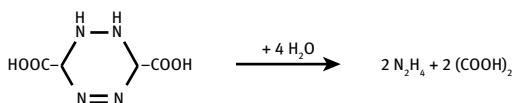
feedwater deoxygenating reagent was recognized and led to further expansion of production facilities.

In the post-WWII years, hydrazine, along with hydrazine hydrate and ammonia, was first evaluated as a fuel for hypergolic combinations with chlorine trifluoride or WFNA as oxidizers [4], but it took several years before enough anhydrous hydrazine became available for rocket and liquid gun testing. It took a long time before its true value as a hypergolic storable bipropellant fuel (component) and as a monopropellant was recognized. Early investigators predicted correctly that sustained and technically sound research and development efforts would inevitably lead to the use of hydrazine as an operationally safe and reliable rocket fuel.

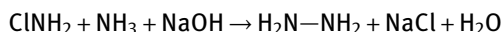
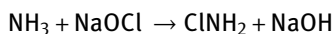
## 1 Production of Hydrazine Hydrate and Hydrazine

The first part of this chapter deals just with the production of hydrazine hydrate, often initially in dilute solutions, that cannot be concentrated beyond 64%  $\text{N}_2\text{H}_4$  by simple distillation. Many investigators ignored the fact that a 64%  $\text{N}_2\text{H}_4$  solution is actually a different chemical compound, hydrazine hydrate,  $\text{N}_2\text{H}_5\text{OH}$ , with its own Chemical Abstracts Registry Number CAS RN [7803-57-8], and not concentrated enough to be used as a rocket propellant (unless you dissolve it in another fuel like UDMH or methanol, which has been done). Methods for converting hydrazine hydrate to anhydrous hydrazine will be described at the end of this section.

This chapter provides an update to a summary of methods for the industrial production of hydrazine. Hydrazine (hydrate) is manufactured in large quantities today by reactions that differ markedly from the reaction by which it was first discovered. Curtius discovered hydrazine (hydrazine hydrate, to be precise) in 1887 when he hydrolyzed and simultaneously dimerized diazoacetic acid ethyl ester with a warm, concentrated solution of potassium hydroxide to obtain the dimeric potassium bisdiazooacetate, which is a symmetrical tetrazine derivative [5]. He initially (erroneously) assumed that the acid was a tris-diazoacetic acid. Later investigations showed that both the *3H,6H*-1,2,4,5-tetrazine-3,6-dicarboxylic acid and the more stable *1H,2H*-1,2,4,5-tetrazine-3,6-dicarboxylic acid (with conjugated double bonds) could be formed. When the potassium salt of the dimeric acid was acidified, it yielded an acid that crystallized into yellow plate-shaped crystals. This was distinctly different from the monomeric diazoacetic acid, which would have decomposed in the evolution of nitrogen immediately after liberation. When treating an aqueous solution of the yellow dimeric acid with excess dilute sulfuric acid, the solution became colorless, and the tetrazine derivative was hydrolyzed to hydrazinium(2+) sulfate and oxalic acid



Hydrazinium(2+) sulfate is sparsely soluble in water and precipitated. Additional support for the formation of the dinitrogen base (“diamid”) was proposed by preparing hydrazinium(1+) chloride by the reaction of the newly discovered hydrazinium(2+) sulfate with barium chloride. The reaction based on the hydrolysis of bis-diazoacetic acid could not be scaled up for the industrial production of hydrazinium salts. The industrial production of hydrazine had to wait for Raschig to discover a simpler reaction in 1907, which eventually was named after him:



There are numerous variations of this basic process to protect the formed hydrazine and hydrazine hydrate from further oxidation, but until 50 years ago all industrial processes involved at least partial use of one of these equations (with or without the formation of a ketazine as intermediate). In the meantime, a different process based on ammonia and hydrogen peroxide has gained a larger and still increasing share of the total world production of hydrazine hydrate.

These industrial processes yield not anhydrous hydrazine but a dilute aqueous solution of hydrazine hydrate as the primary product. Most of the hydrazine is used as the hydrate, but several applications, in particular involving its use as a rocket propellant or as an explosive, require anhydrous hydrazine. The various methods for dehydration are discussed in later sections of this chapter. The first chemist to prepare anhydrous hydrazine as a water-free (not quite anhydrous) compound was de Bruyn in 1893.

Numerous alternative methods for the production of hydrazine hydrate have been studied, but so far only one of these methods (the hydrogen peroxide-based process developed by Produits Chimiques Ugine Kuhlmann, or PCUK) is now used on an industrial scale and has overtaken the chlorine-based Raschig and ketazine processes. A shift in the availability of raw materials and energy has made several of these alternate routes for hydrazine hydrate synthesis economically competitive with the Raschig and ketazine processes. More recently, environmental restrictions on the disposal of waste effluents (brine) from hydrazine hydrate manufacturing operations have made the processes with the least waste products more attractive.

Alternate routes to hydrazine include electrolysis, photolysis, radiolysis, and glow discharge ionization of ammonia. A fascinating new synthesis of hydrazine from nitrogen and water was discovered during studies on biotic or abiotic nitrogen fixation with ammonia as the initial target. Hydrazine may be an intermediate of natural nitrogen fixation by bacteria in the root knolls of *Leguminosae* plants. Doing this synthesis *in vitro* would be particularly appealing because nitrogen and water would constitute cheap raw materials on which to base future hydrazine production.

A large portion of information on hydrazine manufacture originates in the patent literature. Although perhaps not all the claims will prove true, patents are included in

this review to show the wide variety of possibilities. A summary of hydrazine manufacturing patents and related literature has been published [6]. Older summaries on hydrazine, landmarks in their own right among the group of hydrazine publications, have been published in book format [7–11], as chapters in conference proceedings [3, 12], or chapters in encyclopedias and monographs [13–21]. None of these sources is nearly as comprehensive as the 2001 second edition of the hydrazine book [22]. A more complete summary of all methods of hydrazine production is presented in that book and need not be repeated here. Here we discuss only a few typical hydrazine-producing reactions that are of interest for hydrazine as a rocket propellant.

The methods for the formation and synthesis of hydrazine can be grouped in the following manner:

- Reduction of compounds containing a nitrogen-to-nitrogen linkage
- Decomposition of ammonia
- Oxidation of ammonia by methods other than those involving the use of hypochlorite
- The Raschig synthesis and related methods.

A rocket engineer would not need to know how to make hydrazine hydrate, except that some of the hydrazine hydrate manufacturing processes introduce unwanted contaminants that are difficult to remove in the dehydration step and are carried over into the anhydrous hydrazine product later used as rocket propellant. These organic contaminants may poison the catalyst in monopropellant thrusters and cause carbide precipitation in refractory alloys at the high operating temperatures of gas generators and electrically augmented monopropellant thrusters.

## 1.1 Natural Occurrence of Hydrazines

Hydrazine may be an intermediate of natural nitrogen fixation by bacteria in the root knolls of *Leguminosae* plants. Methylhydrazine and phenylhydrazine derivatives are found in poisonous and edible mushrooms. The amount of phenylhydrazine eaten by the US population in brown cap mushrooms may equal the amount of hydrazines used as rocket propellants. Many other natural products carry N–N linkages, and their biosynthesis may involve hydrazine intermediates [23].

Anammox bacteria are able to synthesize hydrazine from ammonia and hydroxylamine or ammonia and nitrite in millimolar quantities and play an important role in the nitrogen cycle between oceans, soils, and atmosphere on Earth [24]. Anaerobic ammonium oxidation (anammox) plays a major role in Earth's nitrogen cycle and is used in wastewater treatment. This bacterial process combines nitrite and ammonium to form dinitrogen ( $N_2$ ) gas and has been estimated to synthesize up to 50% of the dinitrogen gas emitted into our atmosphere from the oceans. An optimum ratio of ammonia and nitrite in an anammox bioreactor feed will result in a distinct yield of hydrazine

when samples are taken at different times [25]. The optimal ratio of ammonium and nitrite is essential for the successful operation of the subsequent anammox process. A partial nitrification experiment using an upflow air-lift reactor was carried out to determine operational parameters for achieving the optimal ratio of ammonium to nitrite by feeding supernatant of anaerobic digester effluent, high-nitrogen-containing rejection water to the reactor. Hydrazine concentration increased during partial nitrification by 60–130%. Surprisingly, the anammox process relies on the highly unusual, extremely reactive intermediate hydrazine. So far, the exact enzymatic mechanism by which hydrazine is synthesized is unknown [26], but investigators have begun to shed light on this multi-step biological process [27]. Hydrazine synthase, a gene in anammox bacteria, is the enzyme that achieves this reaction. One day in the distant future it will be possible to synthesize hydrazine in quantity by a bacterial process similar to the fermentation of sugar to make ethanol.

Hydrazine synthase, encoded by the *hzsABC* gene cluster, is a unique and irreplaceable enzyme for the anammox reaction in many bacteria. This gene is widely used as a functional gene biomarker to retrieve the diversity, abundance, and activity of anammox bacteria in different ecological niches. The genome of anammox bacteria contains two identical copies of the *hzsABC* gene cluster [28].

Bacteria can digest isotope-labeled lysine and glycine and form a compound in which the two amino acids are linked by a hydrazine bridge [29]. L-lysine and glycine units were connected via a hydrazine linkage. Acid hydrolysis of the dipeptide gave hydrazinium salts and hydrazinoacetic acid. It may be possible to manipulate genes in bacteria such that hydrazine becomes a major product of bacteria metabolism. Thus, some bacteria can thrive on hydrazine as a nutrient, and other bacteria incorporate —NH—NH— compounds in their digestive output.

There is a potential in the future for producing hydrazine via microbial conversion of NO and ammonium in an industrial process [30], much like ethanol is made by the fermentation of sugars.

The clouds on Jupiter consist of ammonia, and some hydrazine may form in these clouds and rain or snow from ammonia clouds under the sunlight UV and cosmic radiation conditions of Jupiter [31–36]. The discrepancy between the Jovian albedo in the IR and UV may still be an open question. However, if condensation nuclei were present to such an extent that  $N_2H_4$  condensed before it reacted or photodissociated, then an explanation of the discrepancy might be possible [37]. There would be a stationary hydrazine concentration because hydrazine decomposes just as fast as it forms under the conditions of the upper Jovian atmosphere (except when it condenses and rains down into the lower atmosphere, where it is protected from radiation). Even under the most conservative estimates, the amount of hydrazine present in the Jovian atmosphere at any one time could equal the mass of Earth's oceans. In the presence of both ammonia and methane, methylamines and other organics might form as well. Ammonia, amines, and hydrazine might form hydrosulfides in the presence of hydrogen sulfide. The hydrosulfide salts might condense and precipitate, but they also easily dissociate

and sublime once they enter warmer regions in the atmosphere. The maximum hydrazine ice production rate was estimated to be about  $6.9 \times 10^{10}$  molecules  $\text{cm}^{-2} \text{s}^{-1} = 1.3 \text{ mg m}^{-2}$  Jovian day<sup>-1</sup> [38].

From an analysis of the GALILEO and CASSINI Infrared Imaging Spectrometer data, it was reported that spectrally identifiable ammonia clouds cover less than 1% of Jupiter. Yet ground-based, satellite, and spacecraft observations show that clouds exist everywhere on Jupiter. Thermochemical models also predict that Jupiter must be covered with clouds, with the top layer made up of ammonia and/or hydrazine ice [39]. A substantial amount of haze material can deposit on the upper cloud layer of Jupiter, possibly enough to mask (disperse) its spectral signature.

Observations by VOYAGER, CASSINI, and NEW HORIZONS fly-bys and GALILEO and JUNO planetary probes in orbits around Jupiter have confirmed the presence of white clouds, which could be a hydrazine haze [40]. Ammonia is by far the dominant cause of microwave opacity in Jupiter's molecular atmosphere, surpassing water vapor by more than an order of magnitude. Ammonia and hydrazine IR spectra overlap in the N—H region. If there are aqueous ammonia clouds on Jupiter, then aqueous hydrazine (i.e., hydrazine hydrate) clouds are likely to condense before ammonia-water clouds do.

The hydrazine stratospheric haze would be expected between 40 and 20 mbar centered at 30 mbar with a particle volume density of about 4 particle/ $\text{cm}^3$ . Graphs derived from JUNO 2016 based on an analysis of the spectral range between 2.4 and 3  $\mu\text{m}$  showed maps of the hydrazine column particle density and peak altitude in areas of oval white spots in the southern hemisphere [41].

Hydrazine is a known byproduct of chloramination in the disinfection of drinking water. Trace amounts of hydrazine have been reported in chloraminated drinking water samples.

## 1.2 Production of Hydrazine from Nitrogen and Hydrogen

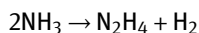
The direct synthesis of hydrazine from the elements has been attempted by numerous investigators using a variety of methods. They attempted to stimulate the otherwise inert nitrogen to enter into bonding with hydrogen. At best, however, the result was ammonia. Traces of hydrazine were detected in some cases, but the yield was in the fractional percents and did not warrant commercial exploitation of the new synthesis. The nitrogen/hydrogen mixture has been stimulated by high pressure, glow discharge, RF plasma discharge,  $\beta$  radiation, or  $\gamma$  radiation in unsuccessful attempts to produce hydrazine more economically than with the current aqueous processes followed by the dehydration of hydrazine hydrate. It was suspected that under the conditions of industrial ammonia synthesis from the elements, a small fraction of hydrazine might form under non-equilibrium conditions but would most likely decompose during cooling of the reaction mixture. Nitrogen/hydrogen mixtures were flowed over ammonia

catalysts at high space velocities and short contact time. The condensate contained a trace of a reducing compound (hydrazine??) besides ammonia; however, hydrazine was not positively identified. Thus, if hydrazine could be obtained economically as a byproduct of ammonia synthesis, even a hydrazine yield of a fraction of a percent of all ammonia formed in the same process would be enough to meet current world demand for hydrazine.  $\text{Co}_3\text{Mo}_3\text{N}$  is one of the most active catalysts for ammonia synthesis; however, little is known about the atomistic details of  $\text{N}_2$  adsorption and activation. Density functional theory (DFT) calculations have been applied to elucidate the associative mechanism for hydrazine and ammonia synthesis in the gas phase and hydrazine formation on  $\text{Co}_3\text{Mo}_3\text{N}$  [42].

Compressing mixtures of nitrogen and hydrogen at very high pressures (as they might exist in the interior of gaseous giant planets) is predicted to form ammonia and hydrazine and some hitherto unknown compounds, such as pentazole or ammonium pentazolate. Some of these hypothetical hydronitrogens are discussed in *Encyclopedia of Liquid Fuels*, in the chapter “Hydronitrogen Compounds.”

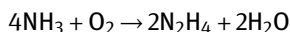
### 1.3 Production of Hydrazine from Ammonia

The difficult task of arranging two nitrogen and four hydrogen atoms in proper order to form hydrazine gets a head start if ammonia (instead of a random mixture of nitrogen and hydrogen as in the preceding section) is used initially. There are essentially two different ways to knock off one hydrogen from ammonia and have the remainder combine to form hydrazine: by ammonia decomposition or by chemical oxidation. Ammonia decomposition according to



tends not to be very selective and frequently proceeds all the way to nitrogen and hydrogen without intermediate formation of hydrazine. One must quench the reaction mixture at the right moment. Methods of ammonia decomposition include pyrolysis, photolysis,  $\alpha$ -radiolysis,  $\gamma$ -radiolysis, glow discharge, electric arc plasma, and utilization of radioactive decay recoil energy. Numerous publications deal with the UV photolysis of ammonia that results in hydrazine formation. Not all of those need to be referenced here. These reactions are summarized in detail in [43]. The discussion of hydrazine made by the photolysis or radiolysis of ammonia would constitute a major chapter by itself. The clouds on Jupiter consist of ammonia, and it is possible that some hydrazine can form in ammonia clouds under the conditions of Jupiter with cosmic radiation or UV light from the Sun. More energetic radiation, like  $\gamma$  radiation from a  $^{60}\text{Co}$  source, will convert ammonia to hydrazine or hydrogen azide. Glow discharges can work with electrodes immersed in plasma or with electrodeless discharges in an intense RF field. The cost of electricity are very high and the yields of hydrazine very low.

Chemical oxidation, on the other hand, can be better controlled and under suitable conditions will lead to better conversion of ammonia to hydrazine. In many cases, ammonia derivatives (e.g., urea) are used in place of ammonia, or the hydrazine is protected from further interaction with the oxidizer by forming an azine (Bayer process). Under current market and raw material conditions, the chemical oxidation of ammonia, as opposed to the pyrolysis or photolysis of ammonia, is the most economical method for manufacturing hydrazine on a large industrial scale. The oxidant can be chlorine (hypochlorite) or hydrogen peroxide. Why not use air? It would be tempting to write an equation for the formation of hydrazine from ammonia by oxidation with air,



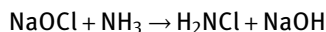
but under real-life conditions the hydrazine formed would be quickly destroyed by oxidation before any more ammonia could be reacted.

### 1.3.1 Production of Hydrazine by Chemical Oxidation of Ammonia

All hydrazine syntheses discussed in the previous section on ammonia decomposition had one scheme in common, the generation and recombination of amidogen  $\cdot\text{NH}_2$  free radicals. In the case of ammonia electrolysis, one may speak of an anodic oxidation. The technically more important processes for the production of hydrazine from ammonia involve a chemical oxidation, usually in aqueous solution and only yielding hydrazine hydrate instead of hydrazine. Throughout the following discussions, when the word *hydrazine* is used in reference to aqueous solutions, it should be understood that the real species in aqueous solution is hydrazine hydrate,  $\text{N}_2\text{H}_5\text{OH}$ , and *not* free hydrazine,  $\text{N}_2\text{H}_4$ . The oxidizing agent in most cases is chlorine or hypochlorite. The oxidation may proceed through a well-defined intermediate, such as chloramine, and would be conducted stepwise.

#### 1.3.1.1 Production of Hydrazine by Raschig Process

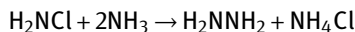
The most important method for hydrazine preparation was for a long time the Raschig process. The explanation of how the Raschig process works usually goes as follows. The initial reaction of sodium hypochlorite with one molecule ammonia forms chloramine:



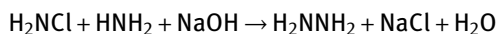
This reaction takes place very rapidly. Chloramine  $\text{ClNH}_2$  is sometimes also called monochloramine in order to differentiate it from dichloramine  $\text{Cl}_2\text{NH}$  (dichloroamine).

Chloramine in alkaline solution is not infinitely stable at temperatures above 268 K ( $-5^\circ\text{C}$ ). If it did not react with another molecule of ammonia in time, it

might hydrolyze and decompose to nitrogen, hydrogen chloride, and water. The pH for chloramine synthesis and subsequent hydrazine synthesis must be kept in a certain range for optimum yields. At values below 8.5, the unstable more highly chlorinated byproducts dichloramine and nitrogen trichloride may lead to accidental explosions. If the pH increases above 11, the preceding equation reverses itself, and the chloramine hydrolyzes. The best chloramine yields are obtained in the presence of an excess of ammonia, but the higher pH limits the life of the resulting solutions, and the half-life at 273 K is on the order of 10–15 h. The reaction of chloramine with ammonia forms hydrazine:



Or, in the presence of an excess of ammonia and alkali [44],



It has been found advantageous to separate hydrazine production into two steps: reaction of hypochlorite with a moderate excess of ammonia at low temperatures (forming chloramine as main product) followed by sudden reaction with a larger excess of ammonia at 400 K. This two-step reaction is reflected in the flow diagram of an industrial process (Figure 1).

In aqueous solutions this reaction produces a dilute solution of hydrazine hydrate (not hydrazine). Chloramine solutions find use in the synthesis of other hydrazines (MMH, UDMH) reacting chloramine with alkylamines instead of ammonia.

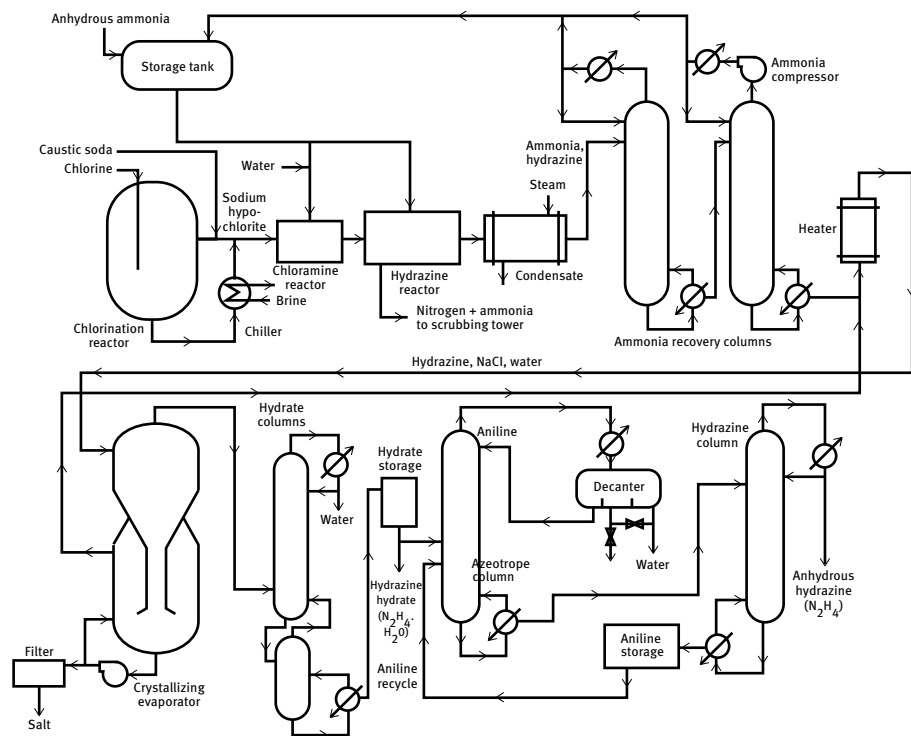
Chloramine is also used in the disinfection of drinking water. Active chlorine in the form of chloramine tends to last longer and will not evaporate as quickly as free dichlorine. The use of chloramine instead of free chlorine for drinking water treatment reduces the formation of toxic trihaloalkanes (chloroform) but may lead to traces of hydrazine among other byproducts of drinking water disinfection [45–47].

### 1.3.1.2 Separation of Hydrazine Hydrate and Water

One of the main disadvantages of the Raschig and other hydrazine processes is the low concentration of hydrazine, requiring repeated distillation or intermediate precipitation as hydrazinium sulfate to obtain a product with an acceptable hydrazine concentration. Numerous methods have thus been developed and patented to recover the hydrazine from reaction liquor. The economy of hydrazine production depends heavily on the method of hydrazine recovery. Solutions of hydrazine in water with less than 64%  $\text{N}_2\text{H}_4$  are actually solutions of hydrazine hydrate in water.

Most hydrazine hydrate synthesis processes produce dilute solutions containing less than 10%  $\text{N}_2\text{H}_4$ . The solutions must be concentrated by distillation or other separation process to achieve 64% in the first step and eventually 99–100%  $\text{N}_2\text{H}_4$  before it can be used as a rocket propellant.





**Figure 1:** Raschig process and dehydration plant design. (Reproduced from [22]. Courtesy of Wiley-Interscience.)

### 1.3.1.3 Separation of Hydrazine Hydrate and Water by Pervaporation

Pervaporation can separate liquids of different polarity and molecular structure due to different levels of permeability. The permeate, once it has traveled through the membrane, is removed by evaporation instead of being accepted into another liquid phase, as in osmosis.

Ethylcellulose membranes have been selected for the separation of hydrazine and MMH solutions by pervaporation based on an extensive study of the overall mass transfer resistance experienced by permeants [48]. Resistance values were quantitatively estimated by changing the membrane thickness and calculating the corresponding flux. Because of its lower sorption and fewer interactions, the membrane showed the least amount of desorption resistance toward water, and so it is permselective with respect to water. The results of pervaporation selectivity obtained in the separation of water/hydrazine and water/MMH mixtures at azeotropic compositions have been correlated. Higher sorption of MMH and hydrazine did not result in preferential separation despite lower membrane resistance. Experimental results clearly showed that desorption resistance and diffusivity predominated over the corresponding solubilities. To confirm the reasons for these phenomena,

Fourier transform infrared (FTIR) spectra and differential scanning calorimetry (DSC) thermograms of membranes soaked in pure hydrazine, MMH, water, or hydrazine hydrate were compared.

### 1.3.2 Production of Hydrazine by Sisler Process

Although the Sisler process has never advanced to the level of industrial usage, the concept is mentioned here because it skips the stage of hydrazine hydrate and leads directly to anhydrous hydrazine.

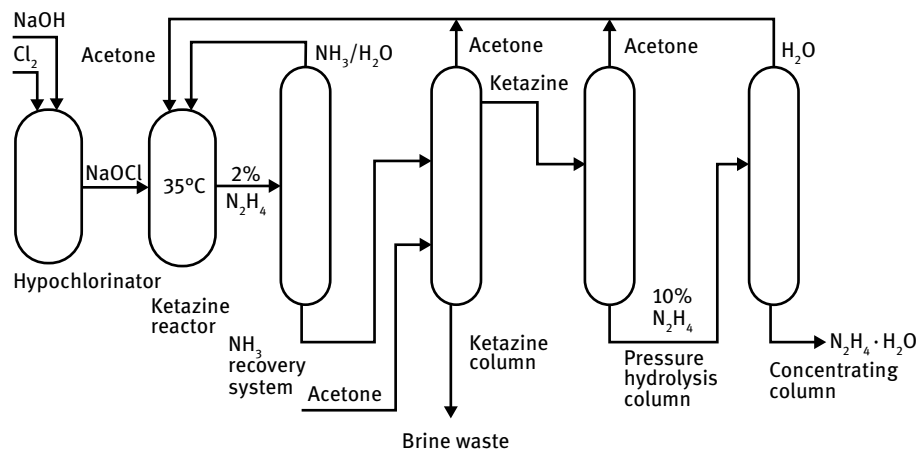
### 1.3.3 Production of Hydrazine by Ketazine Process

The yield of hydrazine in the Raschig processes is limited by the undesirable reaction of hydrazine with chloramine. The required large ammonia excess leads to bulky equipment and low hydrazine concentrations in the aqueous product solution. The removal of water and the concentration of the dilute hydrazine solution require substantial amounts of energy. Some of the disadvantages of the Raschig process are overcome by the ketazine process, in which hydrazine is reacted with carbonyl compounds immediately after its formation and so is protected from further reaction. Other disadvantages of either of the two aforementioned processes are avoided by the PCUK process discussed subsequently. The most commonly used carbonyl compound is acetone, which forms a ketazine, acetone azine  $(\text{CH}_3)_2\text{C}=\text{N}=\text{N}=\text{C}(\text{CH}_3)_2$ , or a hydrazone, acetone hydrazone  $(\text{CH}_3)_2\text{C}=\text{N}-\text{NH}_2$ . Typically, a molar ratio of ketone : hydrazine above 2 is used to obtain the ketazine. The reaction can be carried out at ambient pressure and does not require heating of the reaction mixture.

The main advantage of the ketazine process is that the diaziridine or ketazine is not susceptible to further oxidation by chloramine unlike hydrazine. The energy required for distillation is significantly less than in the Raschig process. Less ammonia excess is used, and ammonia is not as soluble in the ketone/water mixture as in water. A process flow schematic of the ketazine process is shown in Figure 2.

The high organic content of the ketazine process product has restricted the use of ketazine-produced hydrazine hydrate for applications where high-purity hydrazine is required, as in monopropellant rocket engines. Vacuum distillation was attempted for the removal of organics.

The hydrazine hydrate resulting from ketazine hydrolysis contains large amounts of organic contaminants [corresponding to 500 to 1500 ppm total organic carbon (TOC)]. The list of contaminants found in ketazine product and ketazine wastewater is several pages long. Compounds found include various alcohols, ketones, amines, amides, oximes, pyrazines, pyrazoles, pyrazolines, pyrrols, pyridines, pyridazines, triazoles, and even imidazole. Of these, the amides are the least volatile and may require a separate removal step. Distillation of a ketazine-process product in a 40-tray column that had a stream of hydrazinium salt or other salt solution fed to the tenth tray from the top and feed (100% hydrazine hydrate) fed to the tenth tray from the

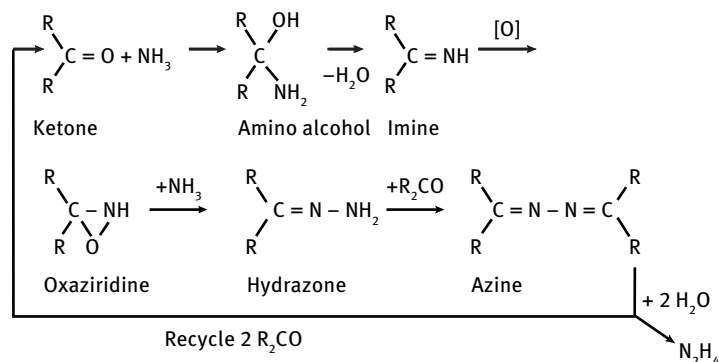


**Figure 2:** Bayer ketazine process flow chart. (Reproduced from [22]. Courtesy of Wiley-Interscience.)

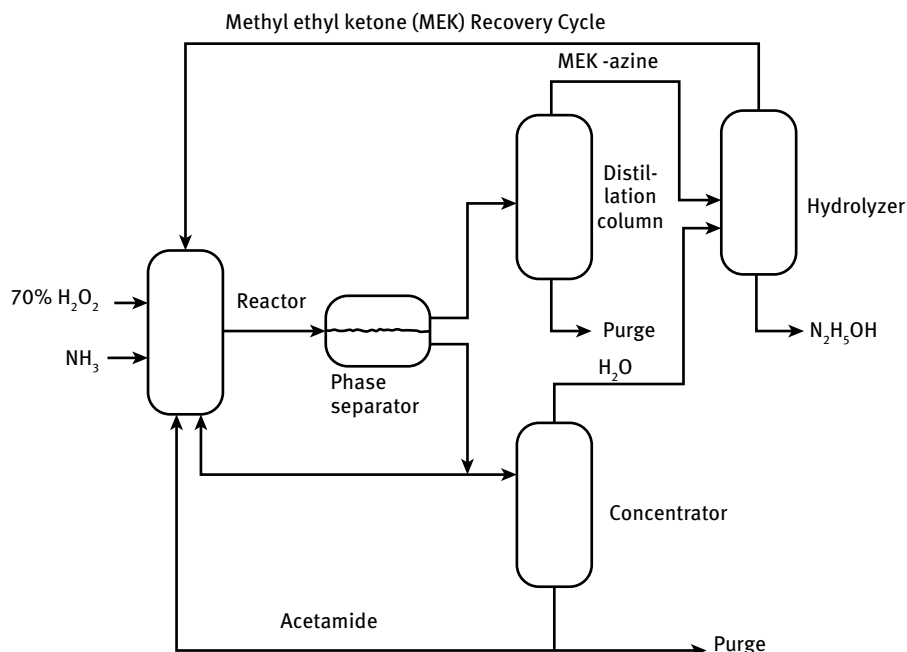
bottom was shown to reduce the TOC from 720 to 90 ppm following a second, simple hydrazine hydrate distillation process at a reduced pressure of 9.3 kPa (70 mm Hg) [49].

### 1.3.4 Production of Hydrazine Hydrate by PCUK Process

The French process using acyl peroxides for oxidizing ammonia in the presence of a ketone to synthesize hydrazine hydrate deserves special mention because it may be conducted as a cyclic process where one of the raw materials can be recovered. Ammonia and hydrogen peroxide are consumed in the process. The synthesis cycle is shown here, and a process flow schematic is shown in Figure 3.



The process was announced in initial press releases by Produits Chimiques Ugine Kuhlmann (PCUK, later Atofina S.A., now Arkema) and has found widespread application. Most new plant constructions during the past two decades were based on



**Figure 3:** PCUK/Atofina/Arkema peroxide process flow chart. (Reproduced from [22]. Courtesy of Wiley-Interscience.)

the PCUK/Atofina/Arkema process. The PCUK/Atofina plant at Lannemezan in France was the first of its kind. It began operation in October 1981. The process works with either methylethylketone or acetone. The hydrazine hydrate product contains varying amounts of ketone-derived organics as contaminants, many of a heterocyclic nature with boiling points like that of hydrazine hydrate, such that they cannot be removed by simple distillation. While these organics may not interfere with other industrial uses of hydrazine hydrate, they would cause problems if ketazine-derived hydrazine hydrate were dehydrated to make anhydrous hydrazine, and the contaminants would carry over into the anhydrous hydrazine, which then could not be used as a monopropellant.

#### 1.4 Preparation of Hydrazine Free Base from Salts

The first method for the industrial production of hydrazine hydrate, before the distillation methods were perfected, used the reaction of the relatively insoluble, easily crystallized hydrazinium(2+) sulfate with aqueous alkali to liberate the free base and distill it once [50].

Anhydrous hydrazine can be obtained by a dry-state reaction between hydrazinium(2+) chloride and sodium hydroxide in the absence of water. The reaction between the two salts starts by slowly heating the mixture under vacuum in a flask connected to a cold trap and immediately removing the heat source as soon as the reaction starts [51]. This method can also be used for the preparation of deuterated hydrazine,  $N_2D_4$ .

### 1.5 Dehydration of Hydrazine Hydrate

A significant fraction of hydrazine is used as hydrazine hydrate, but its application as rocket propellant requires anhydrous hydrazine. In an attempt to obtain hydrazine with more than 64%  $N_2H_4$ , the last water is not easily removed from the hydrazine hydrate commonly used as a starting material. Hydrazine hydrate cannot be dehydrated by simple distillation. The water can be removed by chemical reaction followed by distillation or by azeotropic distillation with an auxiliary fluid. The best method of separation is by distillation, which is a continuous, not batch, process, but special precautions are required to prevent explosive decomposition of hydrazine vapors in the still.

Historically, anhydrous hydrazine in the US has always been made from Raschig-process hydrazine hydrate. Nowadays it is much cheaper to make hydrazine hydrate by the Bayer ketazine or Arkema peroxide process. Anhydrous hydrazine made by the aniline dehydration process was discontinued in 2004. A different process was used until 2013 at Lonza-Arch to make ultrapure hydrazine from hydrazine hydrate. The hydrazine hydrate for it was initially made by the traditional Raschig process, which is no longer in operation. At one time, managers decided it would be cheaper to use hydrazine hydrate that came from a ketazine or peroxide process, not realizing that the resulting anhydrous hydrazine would not be acceptable for long-duration, high investment space missions requiring ultrapure hydrazine in monopropellant and electrically augmented thrusters. Anhydrous hydrazine made from ketazine HH100 is not acceptable for electrothermal thrusters owing to its high content of organic contaminants. The reason for this is the carryover of organic contaminants with similar boiling points from the ketazine process into the product hydrazine. What is still missing is a good and thorough study of typical organic contaminants in ketazine-process hydrazine hydrate. Unpublished information indicates that there are several dozen organic contaminants in ketazine hydrazine hydrate, many of which are heterocyclic compounds with boiling points similar to those of hydrazine hydrate and hydrazine. There may be methods to purify ketazine hydrazine hydrate (100%  $N_2H_5OH = HH100$ ) and remove all organics before it is processed into anhydrous hydrazine. A two-step fractionated distillation, the second step performed under reduced pressure, with a nitrogen purge, can produce anhydrous hydrazine without the aid of an auxiliary fluid [52, 53].



tion **D** (5.7%  $\text{N}_2\text{H}_4$ , 24.3%  $\text{H}_2\text{O}$ , 70%  $\text{NaOH}$ ) and 17.6 parts of an upper, hydrazine-rich layer of the composition **E** (92.7%  $\text{N}_2\text{H}_4$ , 4.4%  $\text{H}_2\text{O}$ , 2.9%  $\text{NaOH}$ ). A similar composition is obtained by mixing equal amounts of sodium hydroxide and 100% hydrazine hydrate (point **C'**). The upper layer contains 78% of the hydrazine in the total system. The two layers are usually separated while still hot, and various methods for the purification and further concentration of the upper layer have been proposed. These involve reaction with barium oxide or distillation. The use of sodium hydroxide in excess of concentration at point **C** or **C'** is not recommended, because this will result in a third phase, solid sodium hydroxide, occurring in region **III**. The example cited in [56] used 500 parts of a 54.5% aqueous solution of hydrazine, 523 parts of sodium hydroxide, and 200 parts of an inert paraffinic hydrocarbon boiling between 394 and 416 K (121 and 143 °C) as a blanketing fluid. *n*-Heptane has been used for this purpose. The hydrocarbon is not miscible with hydrazine and can easily be separated from the distillate by decantation. The purpose of adding the hydrocarbon is to dilute the hydrazine vapor below the detonable concentration.

The early Brauer *Handbook of Preparative Inorganic Chemistry* (in German) method should no longer be used and should NOT be scaled up to the 1-kg level because of the risk of explosion [57]. This hazardous procedure was removed from later editions of the book. Another investigation of different  $\text{NaOH}$  dehydration methods is described in [58].

The water-rich  $\text{NaOH}/\text{H}_2\text{O}$  phase that is obtained when adding at least one mol of  $\text{NaOH}$  for each mol of  $\text{H}_2\text{O}$  to be removed can later be used to make sodium hypochlorite for making more hydrazine by the Raschig process [59]. Besides solid sodium hydroxide in a batch process, concentrated aqueous sodium hydroxide solution can be used as a desiccant when exposed to a countercurrent stream of hydrazine hydrate vapor in a continuous process [60, 61]. The caustic solution must be very, very concentrated, approximately >50 mol-%  $\text{NaOH}$ . Downstream, the water is driven off from the exhausted desiccant by heating, thereby concentrating the solution and making it ready for recycling.

Distillation of hydrazine in the presence of alkali can be avoided by extracting the hydrazine in the upper phase of the  $\text{NaOH}/\text{N}_2\text{H}_4/\text{H}_2\text{O}$  system with aniline, drying with solid  $\text{NaOH}$ , and distilling the 7% hydrazine/93% aniline extract under anhydrous low-pressure conditions [62, 63]. This method will give a product with 97.1%  $\text{N}_2\text{H}_4$ .

A detailed description of the operational details of the sodium hydroxide/hydrazine/water phase separation process is given in a French patent [64]. The upper phase can be purified either by distillation, as described in several references, or by a combination of ion exchange and zone refining.

The need to reflux the mixture prior to phase separation has been questioned. Some authors distilled the entire mixture without prior phase separation. In one test series, 25.3 g hydrazine hydrate (64%  $\text{N}_2\text{H}_4$ ) and 24.7 g reagent-grade  $\text{NaOH}$  were heated in an oil bath to 351–368 K (78–95 °C) and distilled at 21 kPa (160 mm Hg)

through a glass distillation column [column head temperature 342–349 K (69–76 °C)] with a slow purge of nitrogen [65]. The hydrazine assay was 98.6 to 99.5%  $\text{N}_2\text{H}_4$ , and the yield was 82 to 91%.

More detailed data on the phase boundaries in the ternary  $\text{NaOH}/\text{NH}_3/\text{H}_2\text{O}$  system and the quaternary system  $\text{NaOH}/\text{N}_2\text{H}_4/\text{NH}_3/\text{H}_2\text{O}$ , which are useful for optimizing semi-industrial batch processes for making anhydrous hydrazine, have become available [66–68]. The sodium hydroxide and water content in the upper phase can be reduced by adding an excess of ammonia under pressure. The  $\text{NaOH}/\text{NH}_3/\text{H}_2\text{O}$  system has immiscible phase boundaries like the  $\text{NaOH}/\text{N}_2\text{H}_4/\text{H}_2\text{O}$  system, but with less  $\text{NaOH}$  in the upper phase. The quaternary system  $\text{NaOH}/\text{N}_2\text{H}_4/\text{NH}_3/\text{H}_2\text{O}$  was studied to obtain the optimum demixing temperature and minimize the  $\text{NaOH}$  content of the upper phase. The process is based on the presence of a miscibility gap under pressure in the solid/liquid/liquid  $\text{NaOH}/\text{NH}_3/\text{H}_2\text{O}$  ternary system. In the new process, ammonia was no longer evacuated by stripping (as in the traditional process) but retained in the demixing step, in order to apply its solvent effect to the  $\text{N}_2\text{H}_4$  extraction. After separating the two phases, it is then easy to drive off the excess ammonia and recycle it. The upper phase can be purified by fractionated crystallization instead of distillation, thereby avoiding the most dangerous step of the older methods.

In the early 1990s, Japan developed the capability to produce 400 kg anhydrous hydrazine/month through a sodium hydroxide process starting with commercial-grade hydrazine hydrate and using toluene as a blanketing fluid during distillation [69]. This hydrazine was used for the H-II second-stage roll control system. This was a two-step distillation that produced 94%  $\text{N}_2\text{H}_4$  as an intermediate product. The domestic Japanese specification allowed 0.5% toluene and 0.1% sodium to remain in the product (comparable to the 0.5% aniline in US MIL-SPEC monopropellant-grade hydrazine), but advertised product contained only 0.002% toluene and 0.001% sodium.

The process once used by Lonza-Arch (former Olin Chemicals, now Arxada) in the United States for making a product called *Ultrapure*® Hydrazine is assumed to be a distillation process similar to that described in a series of Olin patents [70, 71]. Those patents describe the preparation of high-purity hydrazine from hydrazine hydrate and sodium hydroxide in a batch process where the product is distilled at reduced pressure ( $<8 \text{ kPa} = <60 \text{ mm Hg}$ ) in a fractionation column directly from a sump containing the mixture of hydrazine hydrate and sodium hydroxide. The patents do not indicate whether or not the two liquid phases are separated prior to distillation. In one of the variants, less than 0.5 mol sodium hydroxide per mol of water are used, which may be insufficient to achieve phase separation. The UltraPure® hydrazine was produced in commercial quantities and supplied to the US Air Force (USAF) and the aerospace industry for use in satellites, space probes, and launch vehicles for several decades until the supply of Raschig HH100 was exhausted and an inferior-quality AH was made from a ketazine HH100.



Removing water by adding sodium hydroxide is not truly a chemical reaction. Some of the dehydrating reactions use chemical water scavengers, where the water is consumed in irreversible reactions. Sodium amide, calcium hydride, calcium carbide, calcium oxide, or barium oxide were also used to remove water from hydrazine hydrate or to remove the last traces of water from hydrazine that had been mostly, but not completely, dehydrated by other methods.

### 1.5.2 Dehydration by Distillation with Azeotrope-Forming Auxiliary Fluids

The water that is firmly bound as hydrazine hydrate in  $\text{N}_2\text{H}_5\text{OH}$  can be removed by distillation with azeotrope-forming auxiliary (entrainer) fluids. The fluid most frequently used for this purpose was aniline. Aniline was ideally suited for this purpose, and its use is described in several patents and publications [72–76]. Other fluids evaluated for this purpose, but found to be less suitable, included lower alkyl monoethers of diethylene glycol [77], *n*-propanol or 2-propanol, phenol, cresol, 1,2,6-hexanetriol, glycol, pyridine, *n*-hexylamine, *n*-hexanol, phenol, xylidine, and aromatic hydrocarbons like benzene, toluene, or xylene. Any distillation process involving anhydrous hydrazine, be it with an entrainer fluid or not, is potentially hazardous since hydrazine vapor can explode over a wide range of partial pressures. When operating a continuous distillation process, the aniline reflux ratio can be adjusted to achieve an optimum dehydration and to minimize the overall energy consumption. Depending on the reflux ratio, up to 0.5% aniline may remain in the hydrazine product, which is not very desirable. Usually, this small amount of aniline does not interfere with some of the intended uses of anhydrous hydrazine, such as in bipropellant applications, where it is mostly mixed with UDMH anyway. However, for monopropellant applications, even ppm quantities of aniline have been shown to have adverse effects on ignition delay with catalysts. One way to lower the aniline content is to extract it with a low-boiling-point hydrocarbon, such as benzene or butane. The other method for aniline removal is fractionated freezing (Section 1.6.1).

The hydrazine book [22] contains more details on the use of aniline for the dehydration of hydrazine hydrate, but because this process has now been abandoned and is only of historical interest, this information is not repeated here.

### 1.5.3 Removal of Water by Two-Phase Liquid-Liquid Extraction

Attempts have been made to split hydrazine hydrate into water and hydrazine by two-phase liquid-liquid extraction, but these processes have never been used on an industrial scale. Starting with the very dilute solution of hydrazine hydrate in water as it emerges from the Raschig process, it is possible to end up with pure anhydrous hydrazine by a combination of distillation, two-phase extraction, and fractionated crystallization processes [78].

#### 1.5.4 Removal of Water by Membrane Separation

It would be quite desirable to find a process by which water can be removed from dilute solutions of hydrazine (or even from hydrazine hydrate) by selective permeation through semi-permeable membranes. The other side of the membrane could be wet and flushed by a liquid that is easily separated from anhydrous hydrazine by simple distillation, or the other side could be dry with a purge gas, in which case this process is called pervaporation [79–84]. Pervaporation for concentrating process liquors has been tested for hydrazine as well as MMH and UDMH. A variety of membrane materials have been tested for this purpose, including ethyl cellulose [85–87]. It is not known whether pervaporation is already used in any of the industrial production plants for these three rocket fuels.

The pervaporation of hydrazine can also be accomplished in high-surface-area hollow fiber modules like those used for desalination [88]. Chitosan, ceramic, and zeolite membranes can be used for the dehydration of hydrazine fuels by pervaporation [89]. Molecular sieve membranes have selective permeability for molecules of a certain size and polarity [90].

Because the pore openings in molecular sieves allow only the passage of small molecules, this method can be used for the purification of hydrazine in aqueous solutions. It is not known whether the membrane would also work for the purification of anhydrous hydrazine.

Membrane distillation is an alternative but safe process for the dehydration of hydrazine hydrate since water can be vaporized thermally through a porous hydrophobic membrane. The proper selection of membrane polymer is an important pre-condition due to the high corrosivity of hydrazine. A solvent-resistant, hydrophobic, and mechanically robust microporous polystyrene membrane was prepared on a macroporous polyester fabric support using a phase inversion technique and crosslinked with tetraethyl orthosilicate for membrane distillation dehydration of hydrazine hydrate [91]. SEM and FTIR studies were performed to study membrane morphology and intermolecular interactions. Microporous polystyrene membranes were able to separate feed mixture containing 50 mass-% hydrazine by exhibiting a reasonable water flux of  $5.03 \text{ kg m}^{-2} \text{ h}^{-1}$ , with water concentration in permeate being 97.18% at 75 mm Hg downstream vacuum. Similar membranes were also used for the distillation of MMH or UDMH.

### 1.6 Purification of Anhydrous Hydrazine

Contaminants can be removed from anhydrous hydrazine by various methods. Hydrazine contaminated by UDMH had to be sparged with pure nitrogen gas for several days in an effort to remove the more volatile contaminant. Contaminants with boiling points like that of hydrazine are more difficult to remove.

### 1.6.1 Purification of Anhydrous Hydrazine by Freeze-Thaw Process

An efficient method for aniline and water removal had been developed by Martin Marietta Aerospace Corporation, Denver Division [92]. The requirement for high-purity, aniline-free hydrazine came about as a result of the Viking spacecraft mission to Mars in the 1970s. This spacecraft required a propellant free from organic contaminants for its landing rocket engines using hydrazine monopropellant. Organic contaminants, in particular hydrogen cyanide, would have interfered with the biology/life-detection experiments. As a result of this space program, hydrazine purification technology received a new impetus, and many other programs have benefited from the availability of what was initially called Viking Grade hydrazine.

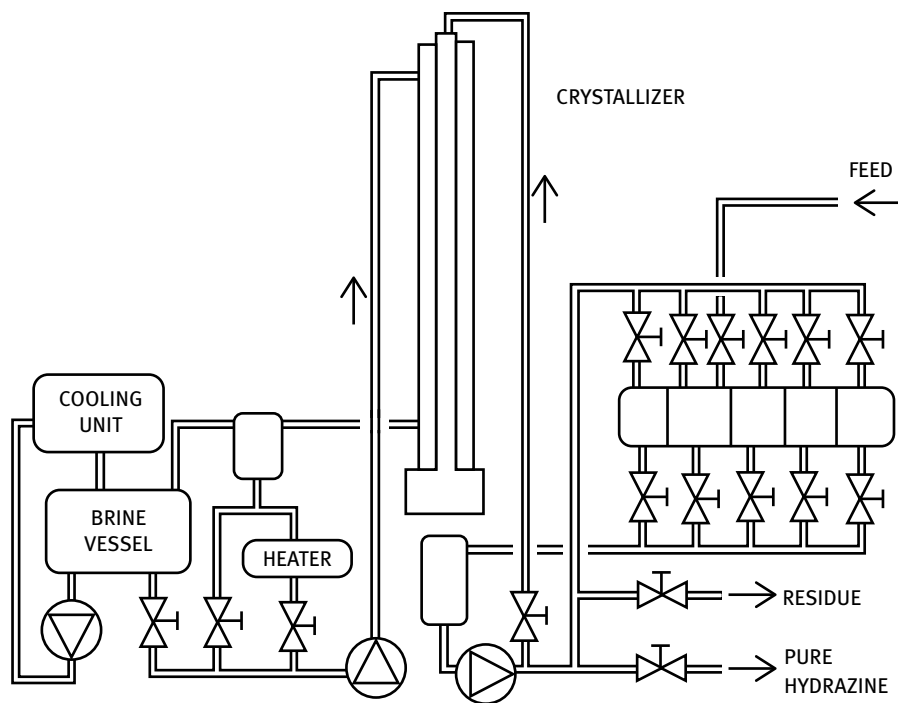
The process used by Martin Marietta for several decades consisted of two large trays, which could be operated independently of each other and together held 272 kg (600 lb) of hydrazine. Refrigerant was fed to the purification tray heat exchanger coil at a temperature of  $262.6 \pm 1$  K ( $13 \pm 2$  °F). The refrigerant flow rate was adjusted such that the outlet-inlet temperature difference was only 2 °C. The objective was to freeze the contents of the tray slowly with gentle rocking, allowing the pure crystals to settle and the contaminants to accumulate in the supernatant fluid, which was later decanted. The supernatant fluid of the first cycle was usually discarded, but low-melting fractions from subsequent cycles could be collected and worked up to give an additional crop of hydrazine that could be recycled. After three to four freeze-thaw cycles, the aniline content was lowered to less than 5% of the aniline content in the starting process feed. The carbon content was lowered from approximately 7000 ppm to less than 20 ppm. Special precautions were necessary to prevent atmospheric carbon dioxide contamination of the purified product during transfer, sampling, and preparation for shipment.

A few years after Martin Marietta closed the freeze-thaw purification plant in Denver, Entwicklungsring Nord, Bremen, Germany, later a division of Messerschmitt-Bölkow-Blohm (MBB-ERNO, later a division of Astrium, now part of Ariane Group) installed a more sophisticated freeze-thaw purification plant under contract from the European Space Agency (ESA) in Trauen, Germany [93]. This plant utilized a modification of a commercially available crystallization apparatus that was previously used for other (pharmaceutical, organic fine chemical, natural product purification) applications. The plant was designed to be able to operate on three different types of feedstock:

1. Standard-grade hydrazine
2. Monopropellant-grade hydrazine
3. A 92%  $\text{N}_2\text{H}_4$  sodium-rich concentrate that is typically obtained from hydrazine hydrate by addition of sodium hydroxide and phase separation.

The plant was expected to mostly operate on monopropellant-grade hydrazine feedstock. It differed from the Martin Marietta batch-mode rocking-tray-decantation pro-

cess in that it was a progressive freezing process, not a suspension crystallization process. In progressive freezing, pure hydrazine crystallizes on a surface cooled in a heat exchanger while the solution to be purified flows over the crystals and the cold surface and recirculated (vertical falling film) until the desired fraction of liquid has been immobilized and the impurities accumulate in the sump of the crystallizer. The purified hydrazine crystals build up on the cooled surface in layers like stalactites in a limestone cave. However, a single freeze-thaw (crystallization-sweating) sequence does not provide sufficient purification, and the process is conducted as a multi-stage separation, where the purified product of the first stage is separated from the mother liquor and subjected to a second stage and so on for a total of five to six stages, depending on the purity of the feedstock. A flow schematic of the apparatus is shown in Figure 5.



**Figure 5:** Hydrazine purification plant flow sheet. (Courtesy of Astrium-Space Infrastructure, Germany.)

Starting with monopropellant-grade hydrazine (which is no longer made), five stages were sufficient to achieve a high-purity-grade product that met the high-purity-grade requirements of MIL-P-26536D. For the sodium hydroxide upper phase, at least six

steps were required. The impure liquids gathered from each stage can be combined and reworked to obtain an intermediate-grade hydrazine that can be recycled in a separate purification campaign and improve overall product yield and reduce the costs associated with disposing of hazardous waste. The hydrazine purification plant at Trauen was designed to produce 10 to 30 kg of high-purity-grade hydrazine per day and the operation was highly automated and computer controlled with a minimum of hands-on transfer operations required.

On a smaller scale, very pure hydrazine can be prepared by directional crystallization in the laboratory. This can be done by slow passage of the crystallization zone through a stirred sample in a large test tube, which is slowly (20 mm/h) lowered into a cold bath at 223 K [94]. See also [95].

### 1.6.2 Purification by Adsorption

Passing MIL-SPEC-grade hydrazine through a column filled with activated alumina will decrease the water content from 0.92 to 0.07% H<sub>2</sub>O [96]. The alumina column will become exhausted after several times its bulk volume in hydrazine has passed through the trickle column. The wet alumina can be regenerated and recycled by heating it slowly in a stream of nitrogen to 810 K. Aniline, once a frequent contaminant of hydrazine, can be selectively adsorbed on alumina. Attempts to achieve the same purification of aniline-containing anhydrous hydrazine with activated charcoal resulted in the ignition of the wet activated charcoal as soon as air was accidentally admitted to the hydrazine-wet charcoal at the end of the test. Without any precautionary warning, activated carbon was listed along with alumina and other desiccants in a competing patent [97].

Organics in hydrazine hydrate from a ketazine or peroxide process can be removed by adsorption on microporous organic polymer beads [98]. Traces of water can be removed from hydrazine by treatment with calcium hydride then passing the vapor through a molecular sieve Linde 3A column [99].

## 2 Physical Properties of Hydrazine Hydrate and Hydrazine

The physical properties of hydrazine and hydrazine hydrate are summarized in Table 1. Several other authors have published summaries of the physical properties of hydrazines [17–21, 100–102], but of course none of these summaries comes anywhere near the second edition of the hydrazine book [22] in terms of completeness of data to date. The thermodynamic properties of hydrazine were summarized on several occasions in other publications [103–106] (Section 2.2).

**Table 1:** Physical properties of anhydrous hydrazine and hydrazine hydrate.

| Property                                  | Unit                                                 | N <sub>2</sub> H <sub>4</sub> | N <sub>2</sub> H <sub>5</sub> OH |
|-------------------------------------------|------------------------------------------------------|-------------------------------|----------------------------------|
| Molecular mass (weight)                   | g/mol                                                | 32.0452                       | 50.0607                          |
| Melting point                             | K                                                    | 275.16                        | 221.5                            |
|                                           | °C                                                   | 2.01                          | −51.6                            |
|                                           | °F                                                   | 35.6                          | −61.0                            |
| Boiling point at 101 kPa (760 mm Hg)      | K                                                    | 386.6                         | 389.55                           |
|                                           | °C                                                   | 113.5                         | 116.4                            |
|                                           | °F                                                   | 236.3                         | 241.5                            |
| Vapor pressure                            | kPa                                                  | 1.89                          | 1.19                             |
|                                           | mm Hg                                                | 14.19                         | 8.97                             |
|                                           | psia                                                 | 0.274                         | 0.173                            |
| Density, liquid                           | g/cm <sup>3</sup>                                    | 1.0037                        | 1.032                            |
|                                           | (lb/ft <sup>3</sup> )                                | (62.659)                      | (64.426)                         |
| Viscosity, liquid                         | cPs                                                  | 0.913                         | 1.50                             |
| Surface tension                           | mN/cm = dyn/cm × 10 <sup>2</sup>                     | 0.6645                        | 0.743                            |
| Thermal conductivity, liquid              | cal cm <sup>−1</sup> K <sup>−1</sup> s <sup>−1</sup> | 1.17 × 10 <sup>−3</sup>       | 8.69 × 10 <sup>−4</sup>          |
| Heat capacity, liquid                     | J g <sup>−1</sup> K <sup>−1</sup>                    | 3.0778                        | 3.360                            |
|                                           | (cal g <sup>−1</sup> °C <sup>−1</sup> )              | (0.7356)                      | (0.803)                          |
| Heat of formation, liquid                 | kJ/mol                                               | +50.434                       | −209.27                          |
|                                           | (kcal/mol)                                           | (+12.054)                     | (−58.018)                        |
| Heat of fusion, solid*                    | kJ/mol (kcal/mol)                                    | 12.657 (3.025)                | —                                |
| Heat of vaporization, at normal bp*       | kJ/mol (kcal/mol)                                    | 39.079 (9.34)                 | 47.7 (11.4)                      |
| Standard entropy, liquid                  | J mol <sup>−1</sup> K <sup>−1</sup>                  | 121.21                        | —                                |
|                                           | (cal mol <sup>−1</sup> °C <sup>−1</sup> )            | (28.97)                       |                                  |
| Standard entropy, vapor                   | J mol <sup>−1</sup> K <sup>−1</sup>                  | 238.4                         | 265.3                            |
|                                           | (cal mol <sup>−1</sup> °C <sup>−1</sup> )            | (56.97)                       | (63.4)                           |
| Dielectric constant, liquid               |                                                      | 51.7                          | 61.2                             |
| Dipole moment, liquid                     | Debye units                                          | 1.84                          | —                                |
| Index of refraction <i>n</i> <sub>D</sub> |                                                      | 1.4683                        | 1.4644                           |

Properties at 298 K, except those marked with an asterisk.

Data source: [22].

## 2.1 Mechanical Physical Properties of Hydrazine Hydrate and Hydrazine

### 2.1.1 Freezing and Melting Points of Hydrazine, Hydrazine Mixtures, and Hydrazine Compounds

The relatively high freezing point of hydrazine is a disadvantage when hydrazine is sent out into the vastness of outer space to provide propulsion on satellites, space probes, and piloted spacecraft. Special design complications (temperature probes, heaters, thermostats, albedo control, radiation shields) must be installed to prevent hydrazine from freezing. Despite all precautions, there are several instances where hydrazine in a satellite has frozen accidentally and jeopardized the mission.

Melting points of pure compounds frequently serve as a quick means for checking the purity of a sample. In many cases the melting point of hydrazine reported in the literature is inaccurate because the sample contained impurities. For the determination of freezing points, hydrazine and many hydrazine mixtures have a tendency to supercool, so freezing-point determination is not very accurate.

The melting and freezing points of hydrazine depend strongly on the purity of the sample used in the determination. Water has a very pronounced effect on the melting point of hydrazine (Figure 8), and many reported melting points disagree among each other as a result of the different purity of the sample used. A melting point of 274.69 K for pure hydrazine was extrapolated from a sample with a melting point of 274.56 K that analyzed as 99.75%  $\text{N}_2\text{H}_4$  [107].

Extrapolation of the melting point of hydrazine/water mixtures to 100%  $\text{N}_2\text{H}_4$  gave a calculated melting point of 275.16 K (35.6 °F) [108]. Ultrapure hydrazine purified by repeated recrystallization had a melting point of 275.35 K (2.2 °C), slightly higher than commonly reported literature data [109]. Purified hydrazine with 0.01% water and less than 1 ppm of other impurities was found to have a freezing point of  $274.655 \pm 0.002$  K ( $1.495 \pm 0.002$  °C) [110].

#### 2.1.1.1 Triple Point of Hydrazine

A true measured triple point of hydrazine has not yet been reported. In analogy to that of water, it is assumed to be close to the freezing point of hydrazine at ambient pressure, which is 274.82 K (1.67 °C). Hydrazine leaking into vacuum will quickly freeze and assume triple-point conditions. The rate of hydrazine sublimation may be very low, depending on available sources of heat. Hydrazine spilled on a space suit during extra vehicular activities (EVA) may not evaporate quickly enough and could be dragged into the space station after the astronauts enter the air lock [111]. Like ice nuclei of comets, chunks of frozen hydrazine in outer space mixed with frozen ammonia are suspected of occurring on some outer planets and moons and may survive for very long periods of time.

### 2.1.1.2 Pressure Dependence of Freezing Point

The freezing point of hydrazine is dependent on pressure. Unlike water ice, the freezing point of hydrazine shifts to higher temperatures with increasing pressure. Researchers became painfully aware of this phenomenon when a hydrazine-powered buoyancy inflation system failed to operate at low temperatures at the bottom of the ocean, surrounded by very high pressure. The hydrazine in the pressure-equilibrated propellant supply tank had frozen.

For high-pressure applications of hydrazine, it may be occasionally overlooked that the freezing point of hydrazine is a function of pressure. During a deep-sea experiment for buoyancy generation with hydrazine, the propellant was found to freeze at depths below 2880 m (9500 ft) and an ocean water temperature of 274.7 K (1.55 °C = 34.8 °F), which came as a surprise to many observers. Subsequent investigation showed that theoretically the freezing point increases from 275 K at ambient pressure to 279 K at 60 MPa [112]. The pressure dependence of the freezing point can be expressed by the Clausius-Clapeyron equation

$$\frac{dp}{dt} = \frac{\Delta H_{\text{melting}}}{T(V_{\text{liquid}} - V_{\text{solid}})}$$

where  $\Delta H$  is the heat of fusion and  $V$  the specific volume of the liquid and solid, respectively. With numerical data inserted, this equation becomes

$$T_f = T_{fa} e^{\frac{p-1}{38000}}$$

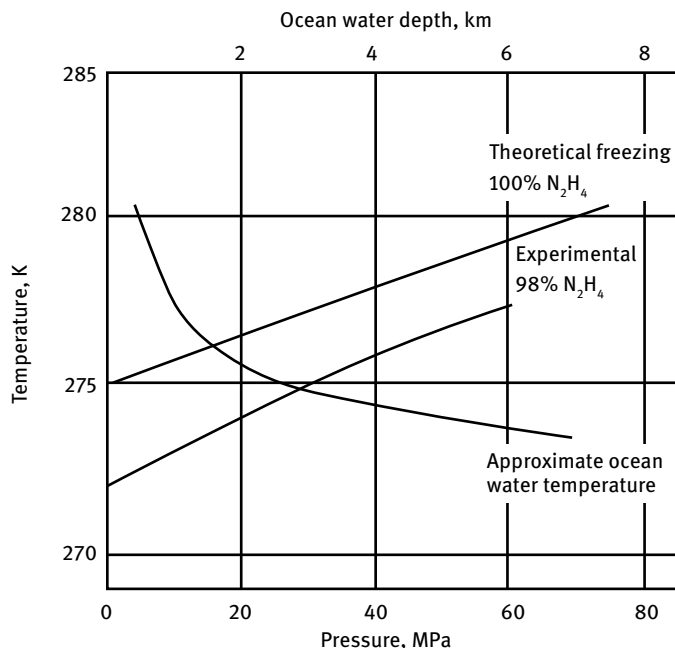
where  $T_{fa}$  is the freezing point at ambient pressure and  $p$  is the pressure in bar (1 bar =  $10^5$  Pa). For example, the increase in the freezing point is 0.39 °C (0.70 °F) for an increase of 4.1 MPa (600 psig) in pressure [113]. If the pressurant gas is nitrogen and the frozen hydrazine is saturated with nitrogen, the freezing point will be lowered by the presence of dissolved nitrogen. The depression of the freezing point,  $\Delta T_{fr}$ , for dissolved nitrogen can be calculated from

$$\chi_2 = 0.02011 \Delta T_{fr}$$

where  $\chi_2$  is the mol fraction dinitrogen. The result from this equation is  $\Delta T_{fr} = -0.011$  °C.

Figure 6 shows the dependence of the freezing point of hydrazine on ambient pressures, up to very high pressures, which may be encountered by deep-sea underwater vehicles at the bottom of oceans. For those deep-sea applications, the dependence of the freezing point on pressure becomes a very important design consideration (see *Encyclopedia of Monopropellants*, chapter “Hydrazine Monopropellants”). It may have been for this reason that hydrazine monopropellant gas generant for a submarine emergency deballasting system was amended with some ammonia to lower its freezing point. The other research area where hydrazine is taken to very high pressures, usually in a diamond anvil cell, is in the search for other hydronitrogen compounds.





**Figure 6:** Freezing point of hydrazine as a function of pressure. (Reproduced and modified from [22].)

### 2.1.1.3 Supercooling of Freezing Hydrazine

When studying the supercooling of hydrazine, it has been found that hydrazine could be supercooled by 70 K in capillaries, whereas under the same conditions water could be supercooled by only 35.5 K and benzene by only 54.5 K [114]. Hydrazine used for these tests had to be specially purified and freed from condensation nuclei. When liquid hydrazine is flash-evaporated into vacuum, some of it evaporates and some of it freezes to hydrazine “snow” at the triple point. Liquid hydrazine has been observed to supercool when first exposed to vacuum.

The high degree of supercooling that can be observed with small droplets of hydrazine cannot be achieved with bulk quantities of hydrazine in the tank of a satellite. For all practical purposes, one must assume that pure hydrazine will freeze at 274.6 K, although in a few instances it will supercool and refuse to freeze. For some applications of hydrazine, the relatively high freezing point of hydrazine is a serious shortcoming. One cannot rely on supercooling of hydrazine or hydrazine blends as a method to extend the liquid range. It may or may not freeze soon after the temperature drops below the literature freezing point.

#### 2.1.1.4 Melting and Freezing Points of Hydrazine Hydrate

The melting point of hydrazine hydrate (64%  $\text{N}_2\text{H}_4$  in  $\text{H}_2\text{O}$ ) as read from the freezing-point diagram of the hydrazine/water system (Figure 8) is 221.48 K ( $-51.67^\circ\text{C} = -61^\circ\text{F}$ ) [108]. Like other hydrazine blends, hydrazine hydrate also has a tendency to supercool, and experimental freezing-point determinations are not very accurate. Accurate freezing points for supercooling liquids are usually extrapolated from phase diagrams.

#### 2.1.1.5 Problems with Freezing Hydrazine

Unlike water, hydrazine does not expand on approaching the freezing point and freezing. Unwanted freezing of hydrazine in spacecraft in the shadow of the Earth or at great distances from the Sun is a design problem that has occupied many thermal analysts and component engineers. In many cases, electrical heaters are wrapped around the tanks and propellant lines to keep them warm and prevent the hydrazine from freezing. This is one of the few complications caused by the high freezing point of hydrazine. It is obvious that the freezing of hydrazine will block flow. Partial freezing may cause liquid flow restrictions. In addition to flow restrictions that are reversible after the spacecraft returns to warmer regions or after the line heater power is increased, there is concern about lines rupturing as a result of freeze-thaw cycles, resulting in catastrophic failure of a satellite propulsion subsystem. In most instances freezing is undesirable, but in an isolated case, such as in some TIROS/DMSP spacecraft, it was desirable, and the propellant was allowed to freeze on purpose to prevent it from sloshing around. For this satellite, the hydrazine was used only for orbit insertion and initial orbit adjustment. After the satellite achieved the desired orbit, the propellant was allowed to freeze on purpose to minimize slosh disturbance of the gravity-stabilized satellite with a cold gas attitude control system (ACS). If such a spacecraft experiences freeze-thaw cycles, or the albedo of reflecting surfaces changes after years in space, propellant lines may rupture when warming from the wrong end [115]. Since hydrazine, unlike water, does not expand on freezing, the freezing alone does not cause a problem for the spacecraft. It is only where thawing may start from the same end from where freezing started a few orbital revolutions or a few days earlier that line rupture may result. Gaps formed between tubing wall and the slug of hydrazine during previous freezing events will fill in with liquid and freeze on the next partial freeze-thaw cycle. It is only in the case of repeated freeze-thaw cycles, only if thawing starts from the same end as the freezing, where very high pressures can occur because a slug of frozen hydrazine will still prevent the escape of the expanding melt. It is suspected that at least one spacecraft was lost due to the rupture of hydrazine lines during freeze-thaw cycles.

### 2.1.2 Freezing Points of Hydrazine Mixtures

Various additives have been tested as freezing-point depressants for hydrazine. The types of additives that meet certain criteria depend on the planned use of hydrazine, which could be either as a fuel in a bipropellant engine or as a monopropellant in a monopropellant engine. A low-freezing blend intended as a bipropellant fuel is allowed to contain organics like MMH, UDMH, or methanol. A low-freezing monopropellant may not contain any organics, or the carbon would poison the catalyst. Low-freezing monopropellant blends of hydrazine with MMH or other organics can be used in thermal bed (as opposed to catalytic) gas generators that are insensitive to carbon poisoning. Most freezing-point-depressing additives to hydrazine result in a decrease of rocket performance. An exception is hydrazinium nitrate (HN), which lowers the freezing point and increases the performance as a monopropellant at the same time.

One of the main disadvantages of hydrazine in view of its various uses for space propulsion and other applications is its high freezing point. Accordingly, numerous attempts have been made to lower its freezing point by freezing-point-depressing additives. The selection of additives is frequently limited by other considerations, such as loss of performance, increased corrosion, initial instability, or catalyst poisoning. The most thoroughly studied freezing-point-decreasing additives include water, MMH, UDMH, ammonia, and HN. For the use of hydrazine as a rocket propellant under low-temperature battlefield or outer space conditions, additives were sought that would at the same time increase its performance as a monopropellant or as a bipropellant fuel. Additives that meet these objectives are oxidizers for monopropellants or compounds with high heats of combustion as bipropellant additives.

Theoretical freezing-point depression can be calculated from the equation

$$\lambda = \frac{MRT_f^2}{1000\Delta H_f}$$

where  $M$  is the molecular weight of the solvent,  $R$  is the universal gas constant in calories per mol per degree,  $T_f$  is the freezing point in K, and  $\Delta H_f$  is the molar heat of fusion. The molal freezing-point depression constant  $\lambda$  of hydrazine was calculated from the preceding formula to be 1.5916 based on a heat of fusion of 12.63 kJ/mol at 274.7 K (3.020 kcal/mol at 1.6 °C) [116]. This equation is only valid for nondissociating freezing-point depressants. Salts will typically dissociate into ions and thus increase their effectiveness as freezing-point depressants. Depending on the number of ions formed and the degree of dissociation, degree of dimerization, and ratio of solvation, the effective freezing-point depression may differ substantially from that predicted by the foregoing equation. This relationship is illustrated in Figure 7, where curve 1 represents an ideal solution, curve 2 assumes solvation of one molecule of solvent with one molecule of solute, curve 3 assumes solvation of two molecules of solvent with one molecule of solute, curve 4 assumes complete dissociation into two different ions, and curve 5 assumes the solute remains associated to dimers in hydrazine (which reduces its effectiveness as a freezing-point depressant).

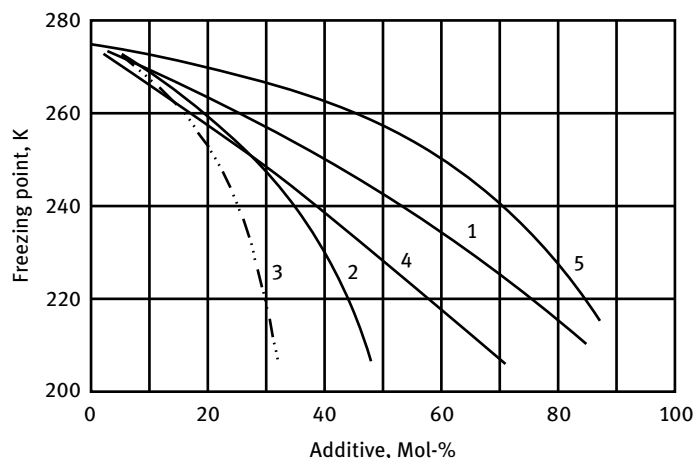


Figure 7: Theoretical freezing-point depression of hydrazine. (Reproduced and modified from [22].)

### 2.1.2.1 The Hydrazine/Water System

Propellant mixtures of hydrazine and water are important for several reasons. First, all hydrazine that is currently made starts out as a hydrazine/water solution. Second, hydrazine hydrate is used as a fuel ingredient in UH25, a hypergolic fuel blend with UDMH. Third, the H-70 used as a gas generant in the F-16 Emergency Power Unit (EPU) is a hydrazine/water blend with a low freezing point.

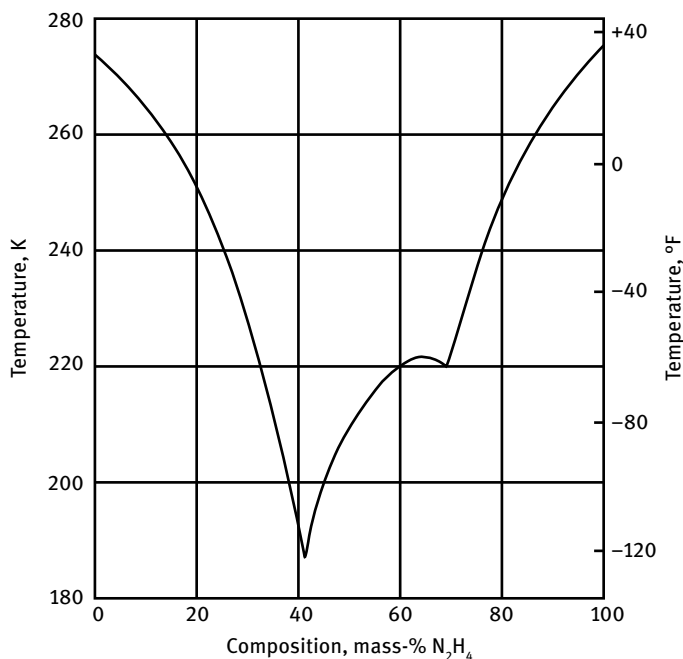
As simple as it may seem at first glance, the binary system hydrazine/water is in reality very complex. It has been investigated several times over the centuries since it was first discovered, and each time the investigators found something new. The investigation of the phase diagram of the hydrazine/water system often had a practical purpose: It was hoped that by simple freezing or even multiple freezing cycles it would be possible to enrich hydrazine in solution, thereby avoiding the sometimes hazardous distillations. Purification of hydrazine by freeze-thaw cycles was already discussed in Section 1.6. The formation of hydrazine hydrate as a well-defined compound is clearly expressed as a peritectic in the melting-point diagram of the hydrazine/water system. The melting-point diagram in Figure 8 shows two eutectic compositions, one at 69 mass-% (219 K) and one at approximately 41 mass-% with a freezing point below 190 K [108].

The conversion of mass percentage to mol percentage in aqueous solutions is achieved by

$$\text{mol-\% N}_2\text{H}_4 = \frac{100}{1 + \left( \frac{100 - \text{mass-\%}}{\text{mass-\%}} \right) \left( \frac{32.045}{18.015} \right)}$$

The conversion in the opposite direction is accomplished using

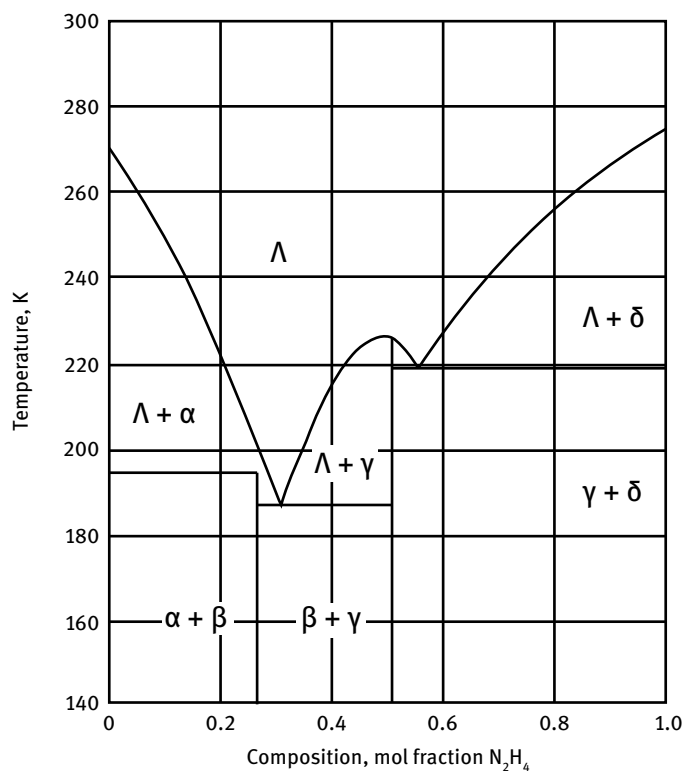
$$\text{mass-\% N}_2\text{H}_4 = \frac{100}{1 + \left( \frac{100 - \text{mol-\%}}{\text{mol-\%}} \right) \left( \frac{18.015}{32.045} \right)}$$



**Figure 8:** Freezing point of hydrazine/water mixtures. (Reprinted and modified from [108], with permission of ©American Chemical Society; permission conveyed through RightsLink.)

Hydrazine or water by themselves do not supercool to a large extent, but their mixtures do so noticeably. Many hydrazine/water mixtures do not show a distinct freezing point but rather solidify gradually to a highly viscous, glassy material. During the transition period as the temperature of the mixture approaches the freezing point (if it ever freezes), the material has a very high viscosity. Early freezing-point investigations published in 1949 did not cover the complete range of compositions because of difficulties encountered at lower temperatures. Subsequent reexamination in 1951 showed water-hydrazine mixtures freezing at record low temperatures, down to 183 K for a eutectic 40.5% hydrazine/59.5% water mixture [117]. The higher freezing eutectic was recorded at 69.3 mass-%  $N_2H_4$ , melting at 219.6 K. Later investigations assigned a univariant equilibrium at 28 mol-% to the same eutectic as that observed by Hill and Sumner [118]. The melting point and composition of the water-rich eutectic of hydrazine and water were determined by differential thermal analysis as  $193 \pm 0.5$  K and  $27 \pm 1$  mol-% hydrazine, respectively [119]. Some of the mixtures turned into a rigid glassy state without ever crystallizing. Some crystallized belatedly on warming from the glassy state. Some crystallized only after being cycled around the freezing/melting point several times at very slow heating/cooling rates of  $1^\circ/\text{min.}$  or less. Some release the heat of crystallization suddenly, causing a distinct exotherm.

Glass transformation temperatures can be measured repeatedly at the same point. A time/activation energy relationship can be established if plotting the warmup-crystallization temperature as a function of the warmup rate and the sample's thermal history [120]. Since some of these non-equilibrium phase transitions are not visible to the naked eye of an observer, they can only be identified by heat capacity measurements or differential thermal analysis or differential scanning calorimetry. There are indications of the existence of a tetrahydrate  $\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}$  at 20 mol-% that forms a eutectic (containing 28 mol-%  $\text{N}_2\text{H}_4$ ) with the monohydrate. However, the behavior in this region of the phase diagram is not very reproducible, discouraging investigators from additional experimentation. The tetrahydrate melts incongruently at 193 K. Consequently, there are four univariant equilibria in the  $\text{N}_2\text{H}_4/\text{H}_2\text{O}$  solid system shown in the phase diagram in Figure 9.



**Figure 9:** Phase diagram of hydrazine/water system. (Republished and modified from [119], with permission of ©1965 AIP Publishing; permission conveyed through RightsLink)  
 Legend:  $\Lambda$  = Liquid phase;  $\alpha$  =  $\text{H}_2\text{O}(\text{S})$  = water ice;  $\beta$  =  $\text{N}_2\text{H}_4 \cdot 4\text{H}_2\text{O}(\text{S})$ ;  $\gamma$  =  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}(\text{S})$ ;  $\delta$  =  $\text{N}_2\text{H}_4(\text{S})$ .

The thermodynamics and kinetics of crystallization during warmup of hydrazine hydrate from a supercooled solution are very complex. There are several unknowns in trying to express this process mathematically. It appears that liquid layers close to the growing crystal are already in a partially ordered state [121].

The peritectic at 50 mol-%  $\text{N}_2\text{H}_4$  + 50 mol-%  $\text{H}_2\text{O}$  is due to a distinct compound, hydrazine hydrate,  $\text{N}_2\text{H}_5\text{OH}$ , not just a simple hydrate  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ . The existence of this discrete compound is also supported by vapor density and viscosity measurements. This compound has thus been assigned its own CAS registry number, different from that of hydrazine. Hydrazine solutions in more than 36% water should be called hydrazine hydrate solutions. Chemical manufacturers often use the wrong CAS number on the labels of hydrazine hydrate and hydrazine hydrate solution drums and Material Safety Data Sheets (MSDSs). They often use the CAS number for anhydrous hydrazine when they should be using the CAS number for hydrazine hydrate.

DSC measurements of hydrazine/water mixtures with a hydrazine mol fraction of 0.4 showed three distinct endotherms between 220 and 130 K [122, 123]. Phase transformations in the solid state document themselves by changes in the Raman spectra of the solids, in particular in the regime of  $2900\text{ cm}^{-1}$ , where OH and NH vibrations are seen, and also at  $3340\text{ cm}^{-1}$ .

### 2.1.2.2 The Hydrazine/Ammonia System

Hydrazine and ammonia are both hydronitrogens. Both are being or have been used as rocket fuels. As close relatives of the same family of chemical compounds, they are totally miscible with each other over the entire range of compositions. Ammonia is one of the products of slow decomposition of hydrazine during storage, so aged hydrazine always has a little ammonia dissolved in it. Ammonia can be added to hydrazine to lower its freezing point and flame temperature. However, adding ammonia to hydrazine will lengthen the ignition delay and shorten the catalyst life when many start-ups are needed. Hydrazine can be added to ammonia to improve its hypergolic ignition with nitric acid or dinitrogen tetroxide (NTO) as the oxidizer.

### 2.1.2.3 Hydrazine/Alcohol Systems

Both hydrazine and ethanol are used as rocket fuels. Mixtures of hydrazine and alcohols were once studied as bipropellant fuels. These mixtures can combine the hypergolicity of hydrazine with the low freezing points of alcohols. The melting-point diagram of hydrazine and methanol mixtures showed three addition compounds,  $\text{N}_2\text{H}_4 \cdot \text{CH}_3\text{OH}$ ,  $\text{N}_2\text{H}_4 \cdot 2\text{CH}_3\text{OH}$ , and  $\text{N}_2\text{H}_4 \cdot 4\text{CH}_3\text{OH}$ , which melted at 225.7, 215.3, and 203.6 K ( $-47.3$ ,  $-57.8$ , and  $-69.5^\circ\text{C}$ ), respectively [124, 125]. Eutectics were found that melt at 213 and 173 K but did not exhibit distinct freezing-point minima. In contrast, the hydrazine/ethanol system showed the existence of only one addition compound,  $\text{N}_2\text{H}_4 \cdot 2\text{C}_2\text{H}_5\text{OH}$ , which melted at 241.9 K ( $-31.2^\circ\text{C}$ ). The eutectic between hydrazine and the addition compound contained 45 mol-% hydrazine and melted at 239.4 K ( $-33.7^\circ\text{C}$ ).

In a continuation of these studies with methanol and ethanol, higher  $C_{\geq 2}$  alcohols were investigated as freezing-point depressants and fuel additives [126, 127]. The hydrazine/*n*-propanol system resembled the hydrazine/ethanol system in exhibiting one weak addition compound,  $N_2H_4 \cdot 2C_3H_7OH$ , melting point 231.8 K ( $-41.3^\circ C$ ). A eutectic at 65 mol-% propanol melted at 230.7 K ( $-42.4^\circ C$ ). The hydrazine/isopropanol system was more complex and showed several deflections before reaching a eutectic at 96 mol-% *iso*- $C_3H_7OH$ , melting point 183 K ( $-90^\circ C$ ). The two inflections were attributed to the polymorphism of hydrazine. Mixtures with allyl alcohol showed the formation of a 1:2 compound that melted at 205 K ( $-68^\circ C$ ). A eutectic of this compound and hydrazine contained 62 mol-% allyl alcohol and solidified at 204 K ( $-69^\circ C$ ). Thus, none of the higher alcohols is as effective as freezing-point depressant as methanol or water. The hydrazine/propargyl alcohol system has also been investigated [128]. Propargyl alcohol would be a good fuel because it has a high heat of combustion since it contains a  $C \equiv C$  triple bond. Of all the alcohols tested as freezing-point depressants, propargyl alcohol was the most active freezing-point depressant.

Glycerol and other hydroxyl compounds have been evaluated as freezing-point depressants for hydrazine [129]. Addition of 20% glycerol lowered the freezing point of hydrazine to 258.1 K.

#### 2.1.2.4 The Hydrazine/MMH System

The most frequently used hydrazine/MMH mixture is the 14 mass-% hydrazine/86% MMH mixture ("M-86," "MHF-3") with a freezing point of 219 K ( $-65^\circ F$ ). Another hydrazine/MMH mixture of practical interest is Ae-76, a blend of 76% MMH and 24% hydrazine formulated by Aerojet to contain the same amount of carbon as Aerozine-50 and at one time intended as a replacement for Ae-50. It freezes at  $\sim 237$  K ( $-33^\circ F$ ). A third blend of interest is M-20, containing 20% MMH in hydrazine, freezing at  $\sim 269$  K ( $25^\circ F$ ), and proposed as a replacement for hydrazine in bipropellant rocket engines. Hydrazine/MMH fuel blends will be described in this set's chapter "Methylhydrazine."

#### 2.1.2.5 The Hydrazine/UDMH System

Both hydrazine and UDMH are excellent rocket fuels, as evidenced by their widespread use as hypergolic fuels with NTO. The mixture of hydrazine and UDMH, also called Aerozine-50, Ae-50, A 50, a 50:50 (by weight) mixture of hydrazine and UDMH, was formulated to be suitable as a regenerative coolant in bipropellant rocket engines. The lower melting point was only a secondary benefit of adding UDMH to hydrazine without losing performance as a rocket fuel. Aerozine-50 freezes/melts at 265–267 K ( $17.6$ – $21.2^\circ F$ ). There is a eutectic point at 214 K ( $-74.5^\circ F$ ) close to the UDMH end of the system at 96.7 mass-% UDMH [130]. The freezing point of the system  $N_2H_4$ /UDMH is illustrated in the chapter on dimethylhydrazines (Figure 31). Ae-50 that leaks past a valve and is suddenly exposed to vacuum will cool (mainly by evaporation of UDMH), and the remaining hydrazine-rich fuel will freeze at the triple point, clogging the injector tubes [131]. Evaporation of Ae-50 in



propellant valve seats or narrow passages under space vacuum conditions may clog the tubes and prevent fuel flow [132, 133]. The freezing points of hydrazine/UDMH mixtures under those shifting conditions with diminishing UDMH content must be known to better understand this potential failure mode. Hydrazine/UDMH fuel blends will be described in more detail in the present publication in the chapter on dimethylhydrazines.

#### 2.1.2.6 The Hydrazine/EDH System

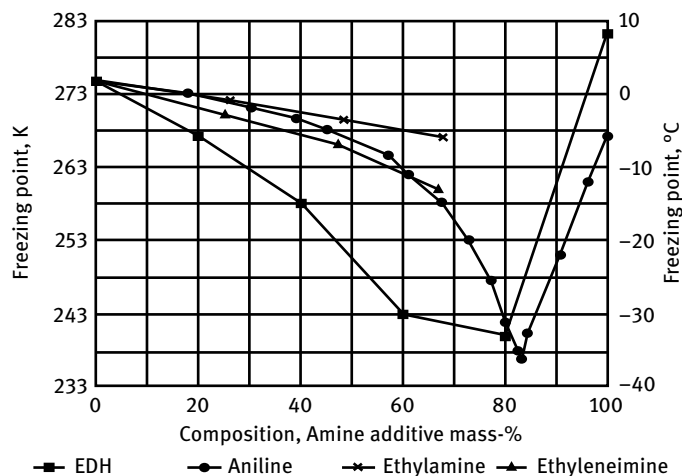
One way to reduce the undesirably high vapor pressure and associated toxicity hazard of hydrazine/UDMH mixtures is to substitute a low-volatility hydrazine for UDMH. One such low-volatility hydrazine is ethylenedihydrazine (EDH) (1,2-dihydrazinoethane or 1,2,5,6-tetraazahehexane). The physical properties of hydrazine/EDH mixtures are presented in *Encyclopedia of Liquid Fuels*, chapter “Alkylhydrazines.” The freezing point of the binary system shows a minimum near 80% EDH. One disadvantage of EDH is that it is very viscous. Hydrazine addition would lower the viscosity.

#### 2.1.2.7 Hydrazine/Amine Systems

Freezing-point depressants that are chemically similar to hydrazine or alkylhydrazines, such as alkyl or aryl amines, are expected to have the necessary solubility in hydrazine and contribute to the fuel value to result in practical propellant blends. Methylamines (mono- and dimethylamine) have been considered as freezing-point-depressing additives to hydrazine. Surprisingly, trimethylamine is not miscible with hydrazine. Freezing-point curves of ethylamine mixtures with hydrazine (95.5% hydrazine, some water contamination) are shown in Figure 10.

Ethylamine is not effective as a freezing-point depressant, the eutectic mixture freezing at only 271 K ( $-2^{\circ}\text{C}$ ) in dry hydrazine. Ethylenediamine is slightly more effective (261 K =  $-12^{\circ}\text{C}$ ) but still a long shot from reaching a typical goal of a 219 K =  $-65^{\circ}\text{F}$  =  $-54^{\circ}\text{C}$  freezing point. Diethylenetriamine and hydrazine form a eutectic at 97% diethylenetriamine, which freezes near 232 K ( $-41^{\circ}\text{C}$ ) and has a tendency to supercool [135]. A comparison of ethylamine, ethyleneimine, and aniline is given in Figure 10. Note that in this example, which used hydrazine with several percent water, ethylamine achieved low-freezing mixtures down to only 267 K ( $-6^{\circ}\text{C}$ ). Ethyleneimine is not an acceptable additive because of its high toxicity. The gross composition of many alkylamine/hydrazine blends as fuels in bipropellant rockets would be similar to Aerozine-50, but the vapor pressure would be much higher. Hydroxylamine, cyanamide, and methoxyamine (*O*-methylhydroxylamine) react with hydrazine and were found to be unfit as freezing-point depressants [136]. Twenty percent diethylenetriamine in hydrazine will lower the freezing point to 262 K [129].

Aniline mixtures have been used as rocket fuels. Aniline flew in sounding rockets before anhydrous hydrazine did. The eutectic mixture of hydrazine and aniline contains 18% hydrazine and melts at 234 K ( $-39^{\circ}\text{C}$ ) [137, 138] (Figure 10). Addition of only 20% hydrazine to aniline lowered the ignition delay with NTO by several orders



**Figure 10:** Comparison of three amines and ethylenedihydrazine as freezing-point depressants in hydrazine. (Image created by Schmidt 2020, based on data from [134].)

Note: The hydrazine contained several percent water.

of magnitude. Diphenylamine is used as a stabilizer in double-base propellants. In one study, 26 mol-% diphenylamine lowered the freezing point of hydrazine to 236 K ( $-37^{\circ}\text{C}$ ). Data were also available for the range from 48 to 100 mol-% diphenylamine where the melting point continually increased from 314 K ( $41^{\circ}\text{C}$ ) to 327 K ( $54^{\circ}\text{C}$ ).

#### 2.1.2.8 Hydrazine/Amide Systems

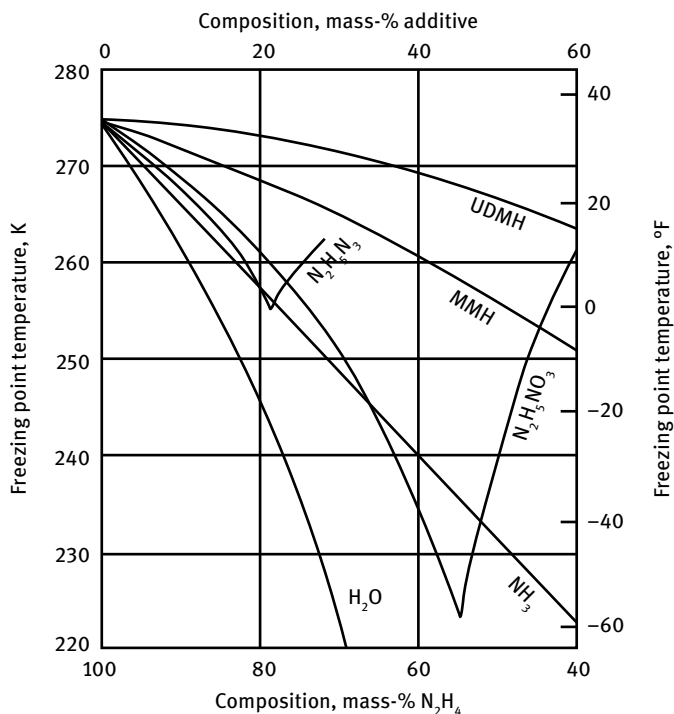
It is uncertain to what extent mixtures of hydrazine and amides can be investigated without substitution of the  $-\text{CO}-\text{NH}_2$  amido group and formation of hydrazides  $-\text{CO}-\text{NH}-\text{NH}_2$ . Acetamide in hydrazine shows one freezing-point minimum at 22.5 mol-% acetamide, melting point 259.5 K ( $-13.6^{\circ}\text{C}$ ). Similarly, the hydrazine-urea system exhibits a minimum freezing point of 243.7 K ( $-29.4^{\circ}\text{C}$ ) near 31.4 mol-% urea. It is likely that compound (hydrazide) formation has been overlooked during all these freezing-point determinations. Some freezing-point determinations were made immediately after dissolving the amide and again several days later, showing significant differences in freezing points. Guanidinium nitrate in anhydrous hydrazine would convert to triaminoguanidinium nitrate. Triaminoguanidine and its salts are considered to be freezing-point depressants, but they are not very soluble. Triaminoguanidinium nitrate was not found to be suitable for this application as a freezing-point depressant [139].

#### 2.1.3 Freezing Points of Solutions of Solids in Hydrazine

Because hydrazine freezes at a comparatively high temperature, its useful range can be extended by suitable freezing-point-depressing additives. The additives can be neu-

tral molecules, as shown in the previous section, or they can be saline compounds. Selection criteria limit the number of practical freezing-point-depressing additives to only a few candidates, which must have compatibility with hydrazine, stability in hydrazine solution, sufficient solubility in hydrazine, a positive effect on rocket propellant performance of hydrazine, and minimal corrosion.

Many of the ionized compounds, such as hydrazinium(1+) nitrate, when dissolving in hydrazine will cause a freezing-point depression beyond that expected from their molecular weight. This is caused by the dissociation of neutral molecules into ions under the effect of hydrazine as a solvent. Solutions of freezing-point-depressing salts in hydrazine can be based on hydrazine by itself as the solvent (resulting in binary systems) or on hydrazine mixtures as solvents, resulting in ternary systems. The relative efficiency of additives in lowering the freezing point of hydrazine is illustrated in Figure 11. Water and ammonia lower the freezing point more efficiently than do hydrazinium salts ( $\text{HN}$  or hydrazinium azide,  $\text{N}_5\text{H}_5$ ,  $\text{HA}$ ), but these additives decrease the performance of these mixtures as monopropellants.



**Figure 11:** Comparison of freezing-point-depressing additives to hydrazine. (Reproduced and modified from RRC Hydrazine Handbook.)

### 2.1.3.1 Binary Systems Hydrazine/Hydrazinium Salts

Binary systems of hydrazine with hydrazinium salts have been most extensively investigated (Table 2).

**Table 2:** Minimum freezing points of solutions of hydrazinium salts in hydrazine.

| Compound                    | Composition, salt mass-% | Freezing point |       | References |
|-----------------------------|--------------------------|----------------|-------|------------|
|                             |                          | K              | °F    |            |
| Hydrazinium azide           | 23.7                     | 257            | 3     | [140]      |
| Hydrazinium azide           | 20 E                     | 255.3          | 0     | [129]      |
| Hydrazinium azide           | 23.8                     | 258            | 5     | [141, 142] |
| Hydrazinium sulfide         | 18% H <sub>2</sub> S     | 243            | −23   | [143]      |
| Hydrazinium(1+) nitrate     | 45 E                     | 223.3          | −57.6 | [144]      |
| Hydrazinium(1+) perchlorate | 50 E                     | 205            | −90.4 |            |

E = eutectic composition

In a few cases, the mixtures can be prepared by **very slow** direct addition of the salt-forming acid to pure, anhydrous hydrazine. In most cases, this is not possible because of the strong exothermicity of the salt-forming reaction that may cause explosive decomposition of hydrazine. It is safer and more accurate to prepare the solution by another method: Weigh the previously prepared and dried salt first, and then dissolve it in hydrazine. Another method that makes use of metathetical reactions is to dissolve the corresponding ammonium salt in an excess of hydrazine and then remove the ammonia by sparging with an inert gas.

Hydrazinium nitrate is here often abbreviated as HN. This abbreviation is not to be confused with the diatomic imidogen radical NH. The binary system hydrazine/hydrazinium nitrate has been thoroughly investigated ([144], see Figure 1 in *Encyclopedia of Oxidizers*, in the chapter “Hydrazinium Salt Oxidizers” and [145] and [146]). The phase diagram indicated the formation of a hydrazinium nitrate hydrazinate  $\text{N}_2\text{H}_5\text{NO}_3 \cdot \text{N}_2\text{H}_4$  with a melting point of 274.8 K (+1.7 °C). There are two eutectics, one each located on either side of the 1:1 compound, the lower-melting eutectic containing 45% HN and melting at 223.3 K (−49.8 °C = −57.6 °F). Hydrazine/hydrazinium nitrate solutions have been tested as monopropellants (see *Encyclopedia of Monopropellants*, in the chapter “Hydrazine Monopropellants”) [147, 148].

The binary system hydrazine/hydrazinium azide has been investigated repeatedly, with a eutectic mixture reportedly melting at 255.6 K (−17.5 °C) and containing 77%  $\text{N}_2\text{H}_4$  [149] (Figure 44 in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salt Oxidizers”). Other investigators found a minimum melting composition at 258 K (−15 °C) that contained 76.2%  $\text{N}_2\text{H}_4$  [142, 150]. Finally, a third party arrived at a melting point of 257 K with a mixture containing 76.3% hydrazine [140]. These variations in melting

point were most likely caused by unrecognized traces of water in the mixtures. The ternary system  $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{N}_3/\text{H}_2\text{O}$  has been investigated for four hydrazine-water solvents initially containing 85.2, 90.5, 95.9, and 98.8%  $\text{N}_2\text{H}_4$  (Figure 45 in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salt Oxidizers”). Hydrazine/hydrazinium azide solutions have been tested as monopropellants [151].

Hydrocyanic acid has been considered as a freezing-point depressant for hydrazine propellant [152, 153], but safety concerns have prevented the use of this fuel because the dissociation constant of hydrazinium cyanide is high, and free HCN exists in the vapor phase above the liquid. Later investigations noted that hydrazinium cyanide solutions decomposed with gas evolution at 344 K. Another of the pseudohalogenide salt additives studied as a freezing-point depressant for hydrazine is ammonium thiocyanate [154]. Hydrazine-ammonium thiocyanate mixtures can be analyzed by redox titration with potassium iodate and ammonia removal by Kjeldahl distillation, followed by acidimetric titration [155, 156]. The ability of ammonium thiocyanate to form low-freezing, low-vapor-pressure solutions in hydrazine is like the formation of Divers’ solution of ammonium thiocyanate in ammonia, which is a low-vapor-pressure (compared to liquid ammonia) liquid that can be stored at room temperature.

Eutectic mixtures of hydrazine and hydrazinium sulfide containing 82 mass-% hydrazine and 18% hydrogen sulfide freeze at 243 K ( $-30^\circ\text{C} = -23^\circ\text{F}$ ) and were proposed as fuels for bipropellant engines [143]. The freezing point can be lowered further by making ternary mixtures with a little water, which lowers the freezing point to 233 K ( $-40^\circ\text{C} = -40^\circ\text{F}$ ). This fuel is not environmentally friendly.

### 2.1.3.2 Binary Systems of Hydrazine with Other Salts

If one is looking for salts to lower the freezing point of hydrazine, the first choice would be hydrazinium salts. Other salts have been tested for this purpose. In the case of ammonium salts, the freezing point would depend on retaining the volatile free ammonia that is formed as a result of the metathetical reaction between the ammonium salt and hydrazine. Table 3 lists the freezing points of salt solutions other than hydrazinium salts, although only a few of these may be useful as propellants.

### 2.1.3.3 Binary Systems of Solutions of Other Nonionized Compounds in Hydrazine

Besides salts that typically dissociate in hydrazine as a polar solvent (thereby increasing their effectiveness as freezing-point depressants), numerous other nonionizing compounds (mostly organics) have been tested as freezing-point depressants for hydrazine. First among these are hydrazine derivatives such as carbonohydrazide, because it was thought that, owing to their structural similarity, they should have good solubilities in hydrazine. Other compounds proposed included 5-aminotetrazole and nitroguanidine [161]. Freezing-point data for non-ionized compounds dissolved in hydrazine are summarized in Table 4.

**Table 3:** Hydrazine solutions of freezing-point-depressant salts.

| Salt compound                                | Additive concentration | Freezing point |            | References |
|----------------------------------------------|------------------------|----------------|------------|------------|
|                                              | Mass-%                 | °C             | K          |            |
| Ammonium perchlorate                         | 5.68                   | −3             | 270.1      | [157]      |
| Ammonium perchlorate                         | 9.99                   | −6             | 267.1      |            |
| Ammonium perchlorate                         | 14.71                  | −10.2          | 262.9      |            |
| Ammonium perchlorate                         | 20.20                  | −14.4          | 258.7      |            |
| Ammonium perchlorate                         | 25.15                  | −21.3          | 251.8      |            |
| Ammonium perchlorate                         | 31.15                  | −25.61         | 247.54     |            |
| Ammonium tetrafluoroborate                   | 20                     | −12.2          | 260.9      | [129]      |
| Ammonium thiocyanate                         | 32                     | −53.9          | 219.2      |            |
| Hydroxylammonium chloride                    | 20 (E)                 | −11            | 262        | [158]      |
| Lithium borohydride                          | 15                     | −46            | 227        |            |
| Sodium borohydride                           | 15                     | −25            | 248        |            |
| <i>N</i> -Methylhydroxylammonium chloride    | 30 (E)                 | −47.6          | 225.3      |            |
| <i>O</i> -Methylhydroxylammonium chloride    | 30 to 35               | −40 to −60     | 233 to 213 |            |
| <i>O</i> -Methylhydroxylammonium perchlorate | 42                     | −54            | 219        | [159, 160] |
| Guanidinium nitrate                          | 27.5                   | −32            | 241        | [139]      |

**Table 4:** Freezing point of solutions of nondissociating liquids and solids in hydrazine.

| Compound                      | Additive concentration | Freezing point |       | References |
|-------------------------------|------------------------|----------------|-------|------------|
|                               | Mass-%                 | °C             | K     |            |
| 5-Amino-1,3,4-triazole        | 32 E                   | −19            | 254   | [135]      |
| 5-Aminotetrazole              | 34 E                   | −36            | 237   |            |
| 5-Aminotetrazole hydrate      | 35                     | −53            | 220   |            |
| 5-Aminotetrazole nitrate      | 35                     | −57            | 216   |            |
| Acetamide <sup>a</sup>        | 30                     | −21            | 252   |            |
| Diethylenetriamine            | 97 E                   | −41            | 232   |            |
| Triethylenetetramine          | 85 E                   | −23            | 250   | [129]      |
| Ethanolamine                  | 55 E                   | −21            | 252   |            |
| Formamide <sup>a</sup>        | 35                     | −31            | 242   |            |
| Furfural (aldehyde)           | 50                     | −53            | 220   |            |
| Furfurylamine                 | 91 E                   | −49            | 224   |            |
| <i>N</i> -Methylhydroxylamine | 53                     | −38.2          | 234.9 |            |
| Diethylenetriamine            | 20                     | −23            | 250   | [161]      |
| 5-Aminotetrazole hydrate      | 37.3                   | −79            | 194   |            |
| Carbohydrazide                | 22.86                  | −5.8           | 215.3 |            |

### 2.1.4 Freezing and Melting Points of Ternary Hydrazine Solutions

As opposed to a previous section that discussed all-liquid binary mixtures, this section summarizes information about ternary mixtures involving free hydrazine, one other liquid component, and one solid, dissolved salt. One of the most thoroughly investigated ternary systems involving free hydrazine (or hydrazine hydrate), one other liquid component, and one salt is the hydrazine/water/hydrazinium nitrate system. Hydrazinium nitrate is here often abbreviated as HN. This abbreviation is not to be confused with the diatomic imidogen radical NH. The  $\text{N}_2\text{H}_4/\text{H}_2\text{O}/\text{N}_2\text{H}_5\text{NO}_3$  system is separated into two regions by the boundary of detonability as described in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salt Oxidizers.” Accordingly, it offers a wide range of propellants and explosives, depending on the choice of composition and the intended application. Next to performance as a propellant or explosive, melting point is the most important selection criterion. A detailed knowledge of the melting points, eutectic points, and eutectic valleys in the ternary system  $\text{N}_2\text{H}_4/\text{H}_2\text{O}/\text{N}_2\text{H}_5\text{NO}_3$  enables one to select propellants for maximum  $I_{\text{sp}}$  or lowest exhaust gas temperature within certain freezing-point boundaries. Military and deep-space applications frequently require freezing points below that of pure hydrazine. The physical, chemical, and safety properties of ternary  $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$  mixtures were described in detail in *Encyclopedia of Oxidizers* in the chapter on hydrazinium salts.

Other ternary hydrazine mixtures consist of hydrazine, MMH, and HN. Freezing points of mixtures of hydrazine/MMH/HN and hydrazine/UDMH/HN have been thoroughly investigated (*Encyclopedia of Liquid Fuels*, chapter “Methylhydrazine”). A mixture with a nominal composition of 23.3% hydrazine, 45.3% MMH, and 31.4% HN freezes at 219 K (−65 °F) and has been named Mixed Hydrazine Fuel-1 (MHF-1).

The physical, chemical, and safety properties of ternary  $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{N}_3/\text{H}_2\text{O}$  mixtures were described in detail in *Encyclopedia of Oxidizers* in chapter “Hydrazinium Salt Oxidizers.” The melting points and other physical properties of ternary hydrazine/ammonia/water mixtures were already described in *Encyclopedia of Liquid Fuels*, chapter “Ammonia.”

#### 2.1.4.1 Melting-Point Diagrams of Systems Including Hydrazinium Salts

Hydrazinium salts in mixture with other salts (mostly alkali metal salts) give low-melting eutectics with interesting properties.

#### 2.1.4.2 Phase Diagrams of Mixtures of Hydrazinium Salts with Other Salts

The first product of the Sisler process in anhydrous ammonia is a mixture of ammonium chloride and hydrazinium(1+) chloride. The binary system hydrazinium(1+) chloride/ammonium chloride in the range 0–23 mol-% ammonium chloride has been investigated as part of a study on the conversion of chloramine-ammonia reaction products from the Sisler process to free hydrazine by reaction with caustic or sodium amide in ammonia [162].

The hydrazinium salt with the highest level of interest as a rocket propellant is hydrazinium nitrate. It is too sensitive to be used in the dry state, but it has been used in a variety of solutions in hydrazine or MMH. The properties of hydrazinium nitrate (HN) are described in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salt Oxidizers.” We must therefore look at the melting of hydrazinium nitrate and its mixtures with other nitrate salts. The eutectic compositions and melting points of mixtures of five alkali metal nitrates or ammonium nitrate with hydrazinium nitrate are listed in *Encyclopedia of Oxidizers* in the chapter “Hydrazinium Salt Oxidizers,” Table 3, based on data from [163]. No well-defined compounds or double salts could be identified in these binary systems.

It was possible to draw phase diagrams and triangular charts of ternary systems involving ammonium nitrate, hydrazinium(1+) nitrate, and any one of the following five nitrates using theoretical equations: lithium nitrate, sodium nitrate, potassium nitrate, hydroxylammonium nitrate, and hydrazinium(2+) dinitrate [164]. The data are summarized in *Encyclopedia of Oxidizers* in the chapter “Hydrazinium Salt Oxidizers,” Table 4. The lowest-melting eutectic in the latter system melted at only 300 K (27 °C). Even lower-melting systems are formed with small amounts of water contamination. Many of these low-melting eutectics are of practical interest in emulsion explosives or emulsion propellants. This is an interesting mathematical analytical technique for obtaining phase diagrams when experimental measurements are not yet available.

#### 2.1.4.3 Solutions of Hydrazinium Salts in Other Solvents

The most common other solvent for hydrazinium salts besides hydrazine is water. Solubility data for such systems frequently provide melting points along with solubility at the saturation point. The solubility of hydrazinium(1+) nitrate in water is summarized in *Encyclopedia of Oxidizers* in the chapter “Hydrazinium Salt Oxidizers,” Table 5. The solubility of hydrazinium(1+) perchlorate in water is summarized in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salt Oxidizers,” Table 23. The solubility of hydrazinium nitroformate,  $\text{N}_2\text{H}_5\text{C}(\text{NO}_2)_3$ , HNF, in water at 293 K (20 °C) is 52.88 mass-% HNF [165]. The solubility of HNF in water is approximately 50 mass-% at 293 K (20 °C) and 80% at 328 K (55 °C). The melting point of the hydrazinium nitrate/water system has been investigated repeatedly over the years. The graph in *Encyclopedia of Oxidizers*, in the chapter on hydrazinium salts, Figure 2, is a combination of earlier and later data. The system has a simple eutectic containing 37.5 mass-% HN and melting at 263.9 K (−9.2 °C).

#### 2.1.5 Boiling Point of Hydrazine

If hydrazine did not have strong hydrogen bonding between molecules, its boiling point would be closer to that of ethane. A collection of boiling points from eleven different sources in the literature showed surprisingly close agreement among the data, and the spread was less than 1 °C [105]. Most boiling-point data were in the vicinity of



113.5°C (386.6 K). The average of eleven data points was 113.4°C (386.7 K). The boiling point of hydrazine is closely tied to the vapor pressure, which will be discussed in Section 2.1.9 below. In describing the physical properties of hydrazine and hydrazinium salts, precautionary remarks are highly appropriate regarding the explosive hazards of melting hydrazinium(1+) nitrate in bulk quantities or the boiling and possibly distilling of hydrazine and hydrazine derivatives at ambient pressure. Many hydrazine derivatives are simply too unstable to be boiled. Consequently, few boiling points of hydrazine derivatives are reported in the literature. Those that were found were mostly at reduced pressure. Additional boiling-point data can be derived from the vapor pressure curves of Section 2.1.9 below.

## 2.1.6 Density of Hydrazine

### 2.1.6.1 Density of Liquid Hydrazine

The density of hydrazine is sometimes difficult to determine, especially at higher temperatures when tiny bubbles of gases caused by incipient decomposition attach themselves to a float of a hydrometer or to the inside of a pycnometer, thus feigning high or low density. Therefore, care must be taken to carefully degas a sample prior to measurements and complete the test before any significant amount of gas has formed again.

Many sources exist for the density of pure hydrazine (Table 5). The most comprehensive set of data available was obtained with a double-distilled sample [166]. The temperature dependence of the density of hydrazine is best described by

$$\rho = 1.23078 - 6.2668 \times 10^{-4} T - 4.5284 \times 10^{-7} T^2$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. This equation is a composite of the density data obtained by five different authors. The line in Figure 12 was drawn using this equation.

A slightly different equation was obtained using a combination of their own data and those of four previous authors [166]:

$$\rho = 1.2471 - 7.226 \times 10^{-4} T - 3.191 \times 10^{-7} T^2$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. This equation represents all experimental data with a standard deviation of  $\pm 6 \times 10^{-4} \text{ g/cm}^3$ . Other authors obtained the following relationship, giving slightly higher densities [170]:

$$\rho = 1.1310 + 3.0983 \times 10^{-5} T - 1.410 \times 10^{-6} T^2$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin.

The liquid density data listed in [7] can also be represented by the following equation [172]:

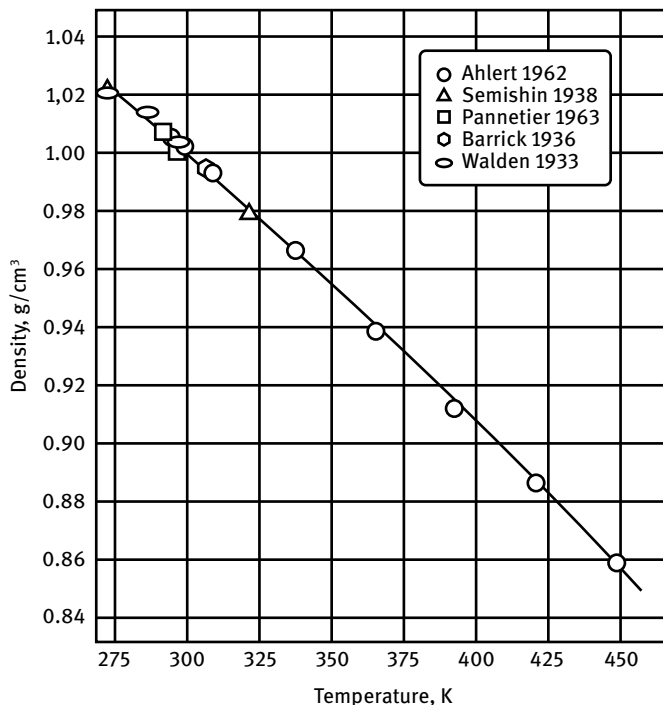
$$\rho = \rho_c + a(1 - \tau) + b(1 - \tau)^{1/2} + c(1 - \tau)^{1/3} + d(1 - \tau)^2$$

**Table 5:** Density of anhydrous hydrazine.

| Temperature |        | Density           | References |
|-------------|--------|-------------------|------------|
| K           | °C     | g/cm <sup>3</sup> |            |
| 296.24      | 23.09  | 1.0059            | [166]      |
| 299.75      | 26.6   | 1.0026            |            |
| 310.26      | 37.11  | 0.9942            |            |
| 310.26      | 37.11  | 0.9946            |            |
| 310.26      | 37.11  | 0.993             |            |
| 310.26      | 37.11  | 0.9931            |            |
| 338.73      | 65.58  | 0.9672            |            |
| 338.73      | 65.58  | 0.9671            |            |
| 366.49      | 93.34  | 0.9388            |            |
| 366.49      | 93.34  | 0.9398            |            |
| 366.49      | 93.34  | 0.9391            |            |
| 394.27      | 121.12 | 0.9124            |            |
| 394.27      | 121.12 | 0.9124            |            |
| 422.05      | 148.9  | 0.8862            |            |
| 422.04      | 148.89 | 0.8863            |            |
| 449.83      | 176.68 | 0.8573            | [167]      |
| 449.83      | 176.68 | 0.8577            |            |
| 273.2       | 0      | 1.0258            |            |
| 293.2       | 20     | 1.0085            |            |
| 295.5       | 22.35  | 1.0065            |            |
| 308.2       | 35.05  | 0.9955            |            |
| 273.2       | 0      | 1.0253            | [168]      |
| 298.2       | 25     | 1.0045            |            |
| 298.2       | 25     | 1.0036            |            |
| 288.2       | 15     | 1.0131            | [169]      |
| 278         | 5      | 1.0305            | [170]      |
| 293         | 20     | 1.0140            |            |

where  $\rho_c$  = critical density,  $\tau$  is the reduced temperature  $T/T_c$ ,  $T_c$  is the critical temperature ( $653\text{ K} = 380^\circ\text{C} = 716^\circ\text{F}$ ), and the following constants listed in Table 6 apply for English and SI units, respectively.

This equation fits the data up to  $640\text{ K}$  ( $367^\circ\text{C} = 692.6^\circ\text{F}$ ) within their probable experimental precision. Haws and Harden [172] incorrectly assumed that the data attributed to Audrieth and Ackerson-Ogg [7] were **saturated** liquid density data when actually they were not. The claim of saturation conditions of the experimental data they referenced and reported turned out to be unfounded. It can, thus, be maintained that no direct experimental determination of the **saturated** liquid density (liquid under its own vapor pressure) has ever been attempted. There is concern for the accuracy of liquid phase density data because the weak dependence of specific volume on



**Figure 12:** Density of liquid hydrazine. (Reproduced and modified from [171].)

**Table 6:** Coefficients for high-temperature density of hydrazine.

| Coefficients | English units<br>lb/ft <sup>3</sup> | SI Units<br>g/cm <sup>3</sup> |
|--------------|-------------------------------------|-------------------------------|
| $\rho_c$     | 14.4                                | 0.2307                        |
| a            | 86.820                              | 1.3907                        |
| b            | 6.343                               | 0.1016                        |
| c            | 17.716                              | 0.2838                        |
| d            | -60.654                             | -0.9715                       |

Data source: [172]

pressure. The source of other data used by Haws and Harden 1965 remains unclear, therefore suspicious. Other investigators [173] repeated this misinterpretation.

### 2.1.6.2 Density of Hydrazine Vapor

Vapor density measurements were made to determine the degree of association of hydrazine molecules to clusters in the vapor space. The pressure-volume-temperature (PVT) measurements carried out by Giguere and Rundle constitute basically the only

available data in the literature for the density of  $\text{N}_2\text{H}_4$  in the vapor phase. Their experimental data, tabulated in Table 7, are based on two samples of  $\text{N}_2\text{H}_4$  with different mass. Thus, the experimental points from 90 to 120 °C (363 to 393 K) belong all to the isochor  $\rho = 0.3653 \text{ kg/m}^3$  while the single test at 131 °C (404 K) corresponds to  $\rho = 0.95 \text{ kg/m}^3$ .

**Table 7:** Experimental  $P$ - $V$ - $T$  data for hydrazine vapor.

| Original units |              |                        |          | SI units |                          |                                   |                       |
|----------------|--------------|------------------------|----------|----------|--------------------------|-----------------------------------|-----------------------|
| $t$<br>°C      | $P$<br>mm Hg | $V$<br>cm <sup>3</sup> | $m$<br>g | $T$<br>K | $p \times 10^{-4}$<br>Pa | $V \times 10^6$<br>m <sup>3</sup> | $m$<br>kg             |
| 90             | 265          | 213                    | 0.0778   | 363.15   | 3.533                    | 213                               | $7.78 \times 10^{-5}$ |
| 95             | 273          | 213                    | 0.0778   | 368.15   | 3.640                    | 213                               | $7.78 \times 10^{-5}$ |
| 100            | 277          | 213                    | 0.0778   | 373.15   | 3.693                    | 213                               | $7.78 \times 10^{-5}$ |
| 110            | 287          | 213                    | 0.0778   | 383.15   | 3.826                    | 213                               | $7.78 \times 10^{-5}$ |
| 120            | 294          | 213                    | 0.0778   | 393.15   | 3.920                    | 213                               | $7.78 \times 10^{-5}$ |
| 131            | 747          | 220                    | 0.2090   | 404.15   | 9.959                    | 220                               | $2.09 \times 10^{-4}$ |

Data source: [174]

The PVT experimental data of Giguere and Rundle relative to nonsaturated vapor are also superimposed (as circular symbols  $\otimes$  at  $\rho/\rho_c = 1.583 \times 10^{-3}$  and  $\rho/\rho_c = 4.120 \times 10^{-3}$ ) on the vapor pressure data shown in Figure 20.

When examining literature data for vapor density of hydrazine, it was noted that Kit and Evered 1960 [175] on page 102 of that book have incorrectly labelled as **saturated** the vapor whose density was calculated by them from the experimentally determined PVT data of Giguere and Rundle. Kit and Evered [175] and also Das and Kuloor [173] erroneously assumed the PVT data as corresponding to saturated vapor conditions.

### 2.1.6.3 Density of Solid Hydrazine

The density of solid hydrazine can be expressed by the equation

$$\rho_s = 1.1869 - 0.000675t$$

with a maximum deviation of  $\pm 0.17\%$ , where  $\rho_s$  is the density of the solid in  $\text{g/cm}^3$  and  $t$  is the temperature in °C [113]. Unlike water, solid hydrazine does not expand as it freezes and cools off. This curve is consistent with the equation

$$\rho_L = 1.02492 - 0.000865t$$

for the density of the liquid where it overlaps, where  $\rho_L$  is the density of the liquid in  $\text{g/cm}^3$  and  $t$  is the temperature in °C.

### 2.1.6.4 Densities of Hydrazine Mixtures

#### Density of Hydrazine/Water Mixtures

The densities of hydrazine-water mixtures, or, to be accurate, hydrazine hydrate-water and hydrazine hydrate-hydrazine mixtures are of technical significance in the production of hydrazine hydrate and hydrazine and also for some applications of such mixtures as rocket propellants and gas generants. We need functions that present the density of hydrazine-water mixtures as a function of composition, temperature and maybe even pressure.

Some hydrazine/water mixture density data at 273 and 323 K and reported in the older literature [176] disagreed with later measurements and are not considered reliable data. The density of 51% and 70%  $\text{N}_2\text{H}_4$  as a function of temperature can be expressed by

$$\rho = A + BT + CT^2 + DT^3$$

where  $\rho$  is the density of the liquid in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin. The coefficients for this equation are listed in Table 8.

**Table 8:** Curve fit coefficients for hydrazine/water density equations.

| Mass-% $\text{N}_2\text{H}_4$ | A      | B                        | C                         | D                        |
|-------------------------------|--------|--------------------------|---------------------------|--------------------------|
| 51                            | 1.0222 | $1.43321 \times 10^{-3}$ | $-7.38283 \times 10^{-6}$ | $8.70554 \times 10^{-9}$ |
| 70                            | 0.9195 | $2.67513 \times 10^{-3}$ | $-1.18067 \times 10^{-5}$ | $1.35250 \times 10^{-8}$ |

Data source: Rocket Research Co. as referenced in [22]

Vapor pressure, density, and viscosity data applied to a chemical association model indicated that the hydrazine/water solutions contain a hydrazine monohydrate, a tetrahydrate, and a hydrazine dimer [170, 177]. Density data for hydrazine/water mixtures are summarized in Table 9. As illustrated in Figure 13, the density of hydrazine/water mixtures does not appear to peak exactly at a molar ratio of  $\text{H}_2\text{O}:\text{N}_2\text{H}_4 = 1:1$ , but at slightly hydrazine-rich mixtures.

Hydrazine/water mixtures are notorious for their tendency to supercool, and it is sometimes difficult to obtain exact melting points and density data near the phase-change boundary. On the other hand, density measurements of the supercooled solution provide insight into the structure of supercooled liquids [178].

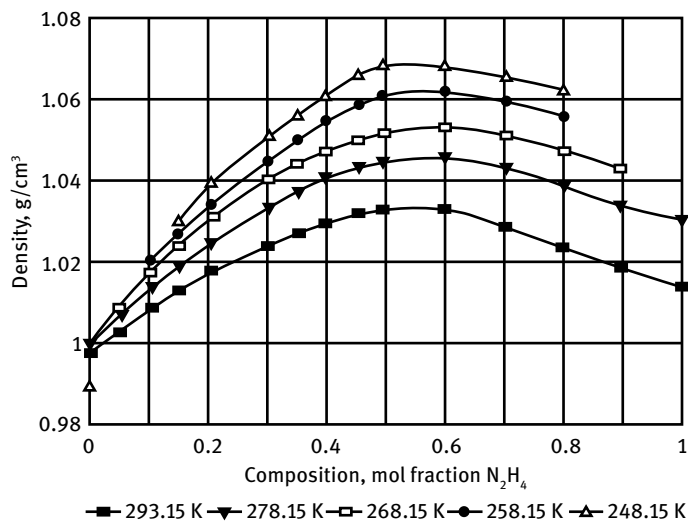
In the early days of hydrazine chemistry, 82 to 98%  $\text{N}_2\text{H}_4$  was often all that was available. Using a sealed glass dilatometer, the coefficient of thermal expansion

$$\beta = \frac{1}{V_0} \frac{dV}{dt}$$

**Table 9:** Density of hydrazine/water mixtures.

| Temperature, K        | 293.15            | 278.15 | 268.15 | 258.15 | 248.15 |
|-----------------------|-------------------|--------|--------|--------|--------|
| Mol fraction $N_2H_4$ | Density, $g/cm^3$ |        |        |        |        |
| 0.0000                | 0.9982            | 0.9999 | 0.9993 | 0.9963 | 0.9896 |
| 0.0526                | 1.0030            | 1.0075 | 1.0084 | —      | —      |
| 0.1045                | 1.0090            | 1.0140 | 1.0175 | 1.0202 | —      |
| 0.1502                | 1.0130            | 1.0188 | 1.0240 | 1.0267 | 1.03   |
| 0.2047                | 1.0181            | 1.0245 | 1.0312 | 1.0345 | 1.0398 |
| 0.3013                | 1.0238            | 1.0340 | 1.0405 | 1.0450 | 1.051  |
| 0.3512                | 1.0274            | 1.0372 | 1.0440 | 1.0502 | 1.0562 |
| 0.3967                | 1.0295            | 1.0408 | 1.0472 | 1.0550 | 1.0607 |
| 0.4526                | 1.0320            | 1.0434 | 1.0500 | 1.0588 | 1.066  |
| 0.4938                | 1.0328            | 1.0450 | 1.0520 | 1.0610 | 1.068  |
| 0.5997                | 1.0331            | 1.0460 | 1.0538 | 1.0620 | 1.0688 |
| 0.7032                | 1.0290            | 1.0432 | 1.0516 | 1.0598 | 1.066  |
| 0.8022                | 1.0240            | 1.0390 | 1.0473 | 1.0560 | 1.062  |
| 0.8961                | 1.0190            | 1.0340 | 1.0430 | —      | —      |
| 1.0000                | 1.0140            | 1.0305 | —      | —      | —      |

Data source: [170]

**Figure 13:** Density of hydrazine/water mixtures. (Image created by Schmidt 2020, based on data from [170].)

of three hydrazine/water mixtures was measured between 273 and 348 K (0 and 75 °C) and  $V_t$  expressed as a polynomial function

$$V_t = V_0(1 + at + bt^2 + ct^3)$$

where  $V_t$  is the volume at temperature  $t$ ,  $V_0$  is the volume of a propellant sample at 0 °C,  $t$  is the temperature in °C, and the coefficients  $a$ ,  $b$ , and  $c$  are summarized in Table 10.

**Table 10:** Cubical thermal expansion coefficients of three hydrazine/water mixtures.

| Concentration,<br>mass-% $\text{N}_2\text{H}_4$ | Temperature coefficient<br>of expansion, at 25 °C | Polynomial coefficients |                 |                 |
|-------------------------------------------------|---------------------------------------------------|-------------------------|-----------------|-----------------|
|                                                 | $\beta \times 10^3$                               | $a \times 10^3$         | $b \times 10^6$ | $c \times 10^8$ |
| 82.9                                            | 0.4871                                            | 0.42033                 | 0.72579         | 0.40714         |
| 93.9                                            | 0.9391                                            | 0.86661                 | 0.55358         | 0.55769         |
| 98.5                                            | 0.9538                                            | 0.85706                 | 0.64608         | 0.85869         |

Data source: [179]

The density of hydrazine/water mixtures was measured in a range of 10 to 90 mol-%  $\text{N}_2\text{H}_4$ , at temperatures from 293 to 558 K, and at pressures from 0.1 to 58 MPa [180–184].

### Density of Hydrazine/Ammonia Mixtures

The density of hydrazine/ammonia and hydrazine/ammonia/water mixtures was already described in *Encyclopedia of Liquid Fuels* in the chapter “Ammonia.”

### Density of Hydrazine/Alkanol Mixtures

Both hydrazine(s) and alcohols are useful rocket fuels. Mixtures of hydrazine and lower alkyl alcohols have been characterized. The density of hydrazine/methanol mixtures was not truly a linear function of composition but showed a deviation in the direction toward higher than theoretical densities [185, 186]. Apparently no compound formation takes place in ethanol. This is different from the hydrazine/water system, where compound formation is documented by the nonadditive behavior of partial molar volumina and parachors. The formation of association compounds of mixtures of hydrazine with other liquids and the solution of solids in hydrazine are usually accompanied by a contraction of the volume. The maximum density occurs at a composition of a mixture that is indicative of the composition of the association compound formed in solution. The maximum volume contraction in the hydrazine-methanol system is observed at 33 mol-% hydrazine, indicative of a compound  $\text{N}_2\text{H}_4 \cdot 2\text{CH}_3\text{OH}$ . The deviation from a straight-line interpolation of densities is at a maximum at this composition.

The volume of this mixture is only 96% of that calculated from its constituents, assuming an ideal mixture. The density of hydrazine/alkanol mixtures can be expressed by

$$\rho = A + BX + CX^2 + DX^3$$

where  $\rho$  is the density (in  $\text{g/cm}^3$ ) and  $X$  is the hydrazine concentration in mass-%, and  $A$ ,  $B$ ,  $C$ , and  $D$  are constants (Table 11).

**Table 11:** Coefficients for density of hydrazine/alkanol mixtures.

| Alkanol           | A       | B                       | C                        | D                     |
|-------------------|---------|-------------------------|--------------------------|-----------------------|
| Ethanol at 298 K  | 0.78529 | $2.8642 \times 10^{-3}$ | $-6.2387 \times 10^{-6}$ | $-5.9 \times 10^{-9}$ |
| Ethanol at 313 K  | 0.77314 | $2.9479 \times 10^{-3}$ | $-6.9823 \times 10^{-6}$ | $-2.8 \times 10^{-9}$ |
| Methanol at 298 K | 0.79391 | $3.2807 \times 10^{-3}$ | $-1.9856 \times 10^{-5}$ | $8.47 \times 10^{-8}$ |

Data source: [185, 187]

### Density of Solutions in Hydrazine

The density and performance of hydrazine can be increased by dissolving energetic salts like hydrazinium nitrate in hydrazine [147, 148, 188, 189]. The properties of hydrazinium nitrate solutions in hydrazine and hydrazine/water mixtures were already summarized in *Encyclopedia of Oxidizers* in the chapter “Hydrazinium Salt Oxidizers.”

#### 2.1.7 Compressibility of Hydrazine

Rocket propellants go through changes in pressure as they pass from the propellant tank through the pumps or valves into the combustion chamber. To accurately model instability and pogo phenomena in propellant feed systems, the compressibility of the liquid fluids must be known.

The bulk modulus is the reciprocal of the coefficient of compressibility. Two types of compressibility are generally measured and reported in the literature, the isothermal and the adiabatic compressibility. The isothermal compressibility of anhydrous hydrazine and several other rocket propellants was determined by a so-called Cartesian diver method [190]. Compressibilities can also be derived from the velocity of sound [191]. Two different samples measured at 298 K had compressibilities of  $24.83 \times 10^{-6}$  and  $24.38 \times 10^{-6} \text{ cm}^2/\text{kg}_f = 2.53 \times 10^{-6}$  and  $2.48 \times 10^{-6} \text{ cm}^2/\text{N}$ . The coefficients  $10^{-6}$  were accidentally omitted in the first edition of the hydrazine book, but this mistake was corrected in the second edition.

The coefficients of thermal expansion  $\alpha$  and compressibility  $\beta$  can be calculated from partition functions based on statistical thermodynamics, which also lead to values for heat capacities at constant volume or constant pressure. Calculated results are summarized in Table 12.



**Table 12:** Compressibility of liquid hydrazine calculated from partition functions.

| Temperature, K | $\alpha \times 10^3, \text{K}^{-1}$ | $\beta \times 10^5, \text{atm}^{-1}$ | $C_v, \text{cal mol}^{-1} \text{K}^{-1}$ | $C_p, \text{cal mol}^{-1} \text{K}^{-1}$ |
|----------------|-------------------------------------|--------------------------------------|------------------------------------------|------------------------------------------|
| 274.69 (m.p.)  | 0.6232                              | 0.1225                               | 14.23                                    | 20.84                                    |
| 288.15         | 0.6083                              | 0.1287                               | 14.53                                    | 20.87                                    |
| 308.15         | 0.6569                              | 0.1541                               | 14.97                                    | 21.66                                    |
| 328.15         | 0.7135                              | 0.1853                               | 15.41                                    | 22.49                                    |
| 358.15         | 0.8090                              | 0.2441                               | 16.04                                    | 23.77                                    |
| 387.3 (b.p.)   | 0.9180                              | 0.3202                               | 16.62                                    | 25.03                                    |

Data source: [192]

The compressibility of solid hydrazine is approximately  $10^{-9} \text{ m}^2/\text{N}$  ( $10^{-4} \text{ atm}^{-1}$ ) [113]. Less reliable sources report a compressibility of  $2.58 \times 10^{-10} \text{ m}^2/\text{N}$  ( $2.54 \times 10^{-5} \text{ atm}^{-1}$ ) for liquid hydrazine.

### 2.1.7.1 Adiabatic Compressibility of Hydrazine

Adiabatic compressibilities in liquids and gases can be calculated from sonic velocity data with the aid of the following equation:

$$\beta_a = \frac{1}{\rho c^2}$$

where  $\beta_a$  is the adiabatic compressibility in  $\text{m}^2/\text{N}$ ,  $\rho$  is the density in  $\text{g}/\text{m}^3$ , and  $c$  is the velocity of sound in  $\text{m}/\text{s}$ . Using this equation to convert velocity measurements, velocity of sound measurements of anhydrous hydrazine gave an adiabatic compressibility of  $2.35 \times 10^{-5} \text{ cm}^2/\text{kg}_f = 2.39 \times 10^{-10} \text{ m}^2/\text{N}$  at 298 K (but the accuracy of this number was questioned in later publications in 2001). Data compiled by Rocketdyne over a wider temperature range (280–360 K), illustrated in Figure 14, gave the following equations for the temperature dependence of the adiabatic compressibility [193]:

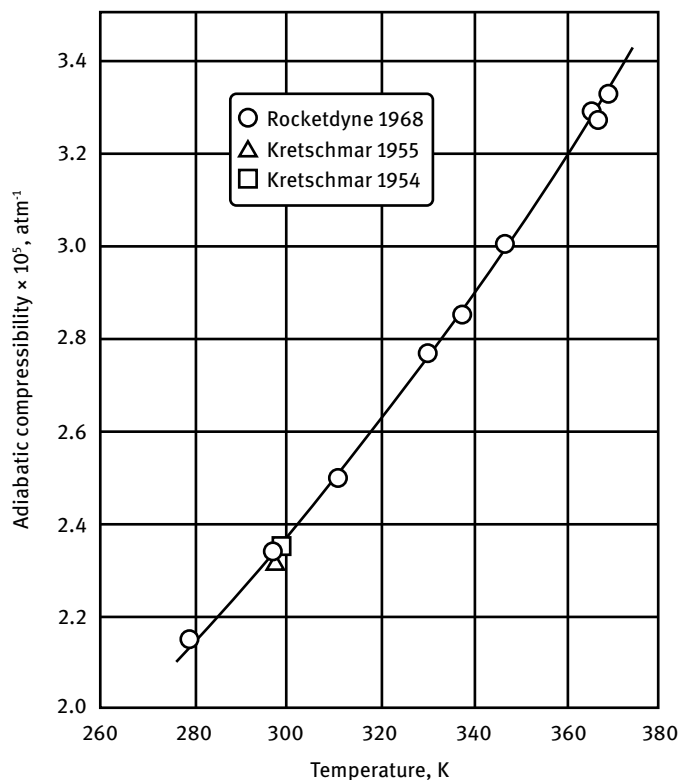
$$\beta_a = 1.2742 \times 10^{-5} - 4.5295 \times 10^{-8} T + 2.7274 \times 10^{-10} T^2$$

where  $\beta_a$  is the adiabatic compressibility in  $\text{cm}^2/\text{kg}_f = \text{atm}^{-1}$  and  $T$  is the temperature in kelvin, or in SI units:

$$\beta_a = 1.2989 \times 10^{-10} - 4.6172 \times 10^{-13} T + 2.7802 \times 10^{-15} T^2$$

where  $\beta_a$  is the adiabatic compressibility in  $\text{m}^2/\text{N}$  and  $T$  is the temperature in kelvin. The data in Figure 14 were calculated from sonic velocity measurements.

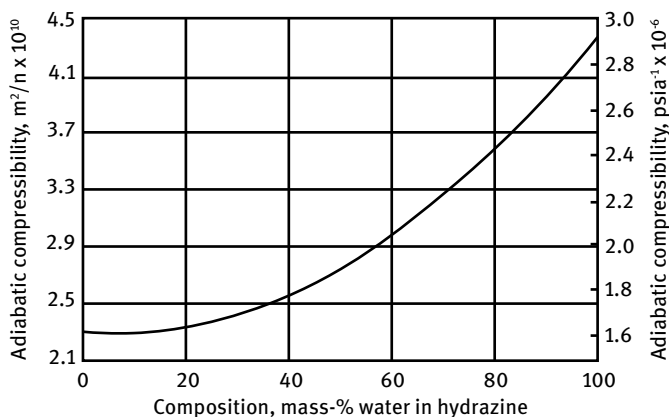
The compressibility of hydrazine is an important physical property when it comes to calculating water hammer and surge flow pressure spikes in propellant feed systems (Section 8.8). If liquid propellant becomes trapped between two valves and experiences an increase in temperature and there are no gas bubbles in the system, then thermal expansion upon heating can cause a devastating increase in pressure. The pressure rise will be greater if the coefficient of thermal expansion is greater and the



**Figure 14:** Adiabatic compressibility of anhydrous hydrazine. (Reproduced and modified from [171].)

compressibility is smaller. Calculations of the pressure-temperature slope for liquid-locked hydrazine (held at constant volume) have been carried out on the basis of existing experimental data for isothermal and adiabatic compressibility in conjunction with thermodynamic relations [194]. The pressure-temperature slope was evaluated as the ratio of the volumetric coefficient of thermal expansion to the compressibility. The volumetric coefficient of expansion is in turn determined from the difference between the isothermal compressibility and adiabatic compressibility by a well-known thermodynamic relation. Based on these considerations, the pressure-temperature slopes were estimated for liquid-locked hydrazine components over a range of temperatures (283–323 K = 10–50 °C) of interest for propulsion applications. It was shown that the pressure-temperature slope decreases with an increase in temperature, which is contrary to the trend for water. The results indicate that the pressure rise in liquid-locked hydrazine systems is considerably higher than for water in the range of temperatures considered.

The corresponding compressibilities of hydrazine/water mixtures are presented in Figure 15. The compressibility or the velocity of sound as a function of hydrazine



**Figure 15:** Adiabatic compressibility of hydrazine/water mixtures at 298 K. (Reprinted and modified from [195], with permission of ©1955 AIP Publishing; permission conveyed through RightsLink.)

concentration shows no discontinuities like the melting-point diagram or maxima like the density and viscosity diagrams [195].

Some liquids solidify under very high pressure, and some solids undergo phase changes at very high pressure, but hydrazine monohydrate has been shown to be free of high-pressure enantiotropy and instead showed true ( $p$ ,  $T$ ) monotropy [196]. The monotropic behavior of hydrazine hydrate is well understood and extends to pressures higher than atmospheric pressure. The decomposition of hydrazine hydrate has been used as a heat source for deep-ocean power supplies, so its high-pressure behavior must be accounted for.

#### 2.1.7.2 Phase Transitions at Very High Pressures

Subjecting hydrazine in a diamond anvil to very high pressures causes new peaks to appear in its Raman spectrum. A new peak near  $3000 \text{ cm}^{-1}$  emerged above 8 GPa, indicating a new phase of hydrazine at high pressure. There were two new phase transitions near 5.5 and 8 GPa [197]. The pressure-induced changes appeared to be reversible as pressure was cycled down to 3.5 GPa.

The high-pressure behavior of hydrazine has been investigated by *in situ* Raman spectroscopy and synchrotron X-ray diffraction (XRD) experiments under pressure up to 46.5 and 33.0 GPa [198]. It was found that the liquid hydrazine solidified into phase I at about 1.2 GPa. The symmetry of phase I was confirmed to be space group  $P2_1$  by the peak assignment, group theory analysis, and Rietveld refinement of XRD patterns. A solid-solid transition from phase I to phase II was observed in both Raman spectroscopy and XRD experiments at about 2.4 GPa, which was ascribed to the formation of new hydrogen bonds between hydrazine molecules. At 18.4 GPa, an isostructural transition from phase II to the final phase III was observed.

Pressure-induced changes to the structure and bonding in hydrazine have been investigated at pressures up to 20 GPa using a diamond anvil cell with *in situ* Raman spectroscopy [199]. Liquid hydrazine solidified at 0.3 GPa into a crystalline phase, and its structure was established using synchrotron XRD measurements. The high-pressure phase is monoclinic (space group  $P2_1$ ). With increasing pressure, the modifications to N—H···N hydrogen bonding spectra were observed with the emergence of new peaks beyond 5 GPa as well as the appearance of new lattice modes. Based on these observations, it was concluded that a sluggish phase transition in the 5–7 GPa range was accompanied by selective strengthening and restructuring of the hydrogen bonding network. Inelastic neutron scattering measurements performed in the 10–250 K range indicated that the order-disorder phase transition (observed in thin films at 175–180 K) driven by conformational changes was not observed in a bulk sample. It is possible that pressure-solidified hydrazine exists along with solid ammonia at a certain depth at the bottom of the atmosphere of Jupiter.

Compressing hydrazine to very high pressures does not appear to result in the formation of new hydronitrogen compounds, such as those discussed in chapter “Hydronitrogens” in *Encyclopedia of Liquid Fuels*.

### 2.1.8 Velocity of Sound in Hydrazine

The knowledge of the velocity of sound in hydrazines is of interest in the design of rocket engine feed systems, where destructive pressure oscillations can develop and propagate upstream. Resonance phenomena must be avoided to obtain stable combustion. The velocity of sound is also useful in calculating the compressibility of hydrazine. Compressibility, in turn, is of interest in predicting the behavior of hydrazine under extremely high pressures, such as those encountered in underwater applications of hydrazine or at the bottom of ammonia-loaded planetary atmospheres.

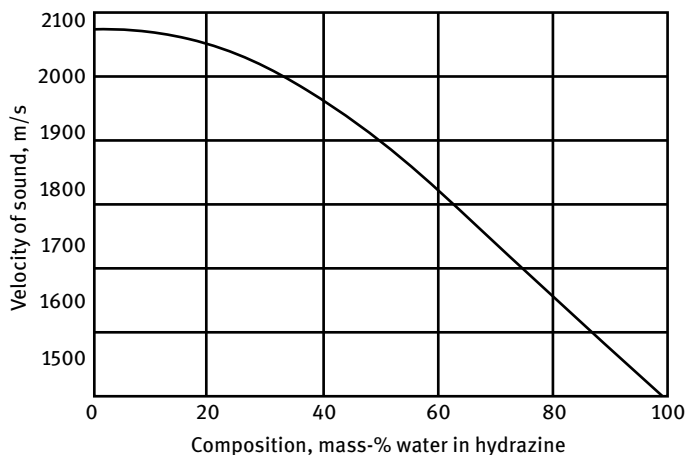
#### 2.1.8.1 Velocity of Sound in Liquid Hydrazine

Several measurements of the velocity of sound of hydrazine have been used to calculate the adiabatic compressibilities mentioned earlier. The data varied slightly depending on the purity of the sample used; in one case, a velocity of  $2059 \pm 6$  m/s at 298 K was reported for 96%  $N_2H_4$  [191], and in another case two different samples of hydrazine gave identical sound velocities of 2090 m/s at 298 K. The dependence of the velocity of sound in anhydrous hydrazine on sample temperature can be expressed by

$$c = 3224.9 - 3.8611T$$

where  $c$  is the velocity of sound in m/s and  $T$  is the temperature in kelvin.

Sound velocities in hydrazine/water mixtures were measured as a function of composition for a large number of different concentrations of hydrazine in water from 8 to 99 mass-% of hydrazine at 298 K by means of the Debye-Sears ultrasonic light diffraction method (Figure 16) [195, 200].



**Figure 16:** Velocity of sound in hydrazine/water mixtures at 298 K. (Reprinted and modified from [195], with permission of ©1955 AIP Publishing; permission conveyed through RightsLink.)

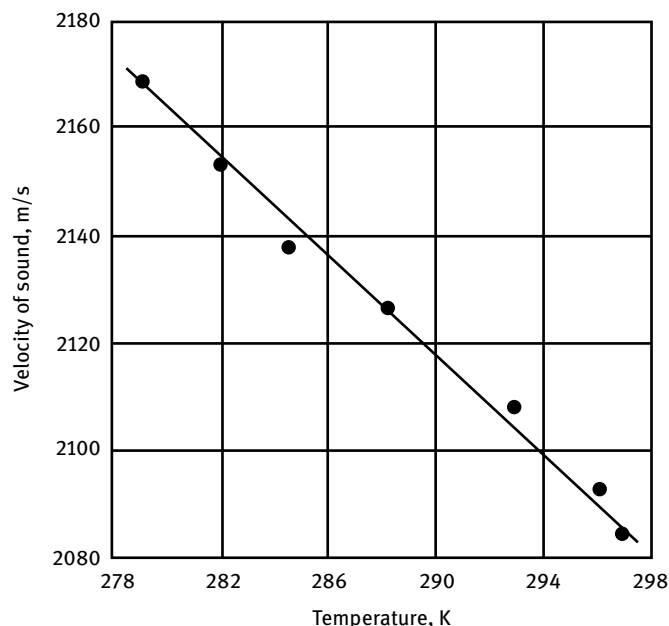
The method used for measuring the velocity of sound is essentially like the diffraction of light by a ruled grating, except in this case the standing wave pattern of the ultrasonic waves through the liquid acts as the grating. From the known wavelength of the light source, the frequency of the quartz crystal tuned to create standing waves, and the angle of diffracted light, the distance of the standing wave nodes can be measured. The data can be represented by the equation

$$c = 1497.40 + 745.460X_H + 382.353X_H^2 - 556.3361X_H^3$$

where  $c$  is the velocity of sound in m/s and  $X_H$  is the mass fraction hydrazine in the binary mixture. For pure hydrazine ( $X = 1.00$ ), a sonic velocity of 2069 m/s was obtained by extrapolation from this equation. The velocity of sound in hydrazine is the highest of any liquid for which data are found in the literature. Likewise, this would translate into hydrazine being one of the least compressible fluids with a very high susceptibility to hydraulic shocks and pressure spikes when flowing hydrazine is abruptly stopped by the sudden closing of a valve (“water hammer”).

The velocity of ultrasound (or any sound or compression wave) in hydrazine decreases with increasing temperature (Figure 17) and increases linearly with increasing hydrazine content (tested up to 64%) [201]. The velocity of sound in liquid hydrazine at 293.15 K was measured to be  $2092 \pm 12$  m/s [202, 203], in agreement with previous measurements reported in the literature.

It is planned to determine the density of hydrazine by the buoyancy of a floater and to determine the velocity of sound in hydrazine along the saturation curve at temperatures up to the critical point and pressures up to 200 bar by measuring the resonant frequency in a high-pressure bomb made of titanium with sapphire windows [204].



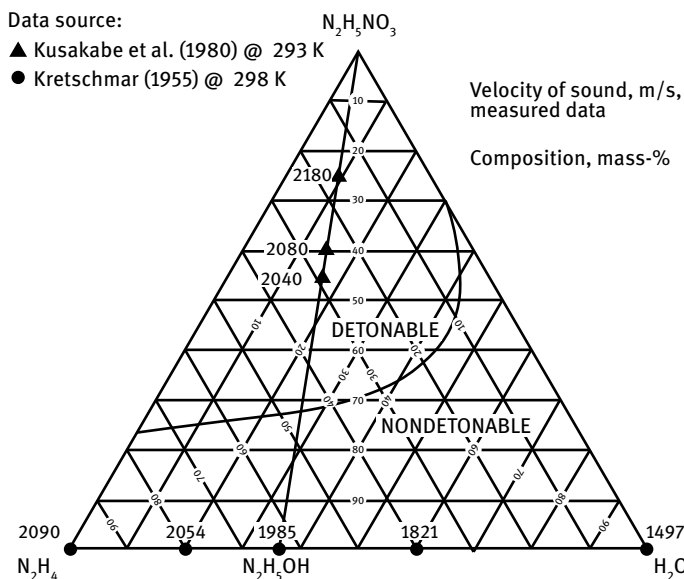
**Figure 17:** Velocity of sound in anhydrous hydrazine as a function of temperature. (Reprinted and modified from [201].)

### 2.1.8.2 Velocity of Sound in Solutions of Salts in Hydrazine

Solutions of hydrazinium nitrate in hydrazine and hydrazine/water mixtures have been tested as rocket propellants and, consequently, the velocity of sound in several of such solutions has been measured. Physical property data for hydrazinium nitrate solutions in hydrazine were already described in *Encyclopedia of Oxidizers*, in the chapter “Hydrazinium Salt Oxidizers.” The velocity of sound is closely related to the detonation velocities of liquid explosives. Therefore, the velocity of sound in hydrazine/hydrazinium nitrate/water ternary mixtures was measured and compared to detonation velocity data (Figure 18) [205]. See also [201].

### 2.1.9 Vapor Pressure of Hydrazine and Vapor-Phase Composition

Vapor pressure data of hydrazine and hydrazine compounds are important for the calculation of heats of vaporization and vaporization losses, the assessment of toxicity and flammability hazards, and the solution of many other technical problems. Numerous vapor pressure measurements exist, but many measurements were plagued with incipient hydrazine decomposition during measurements, feigning higher than real vapor pressures. At other times, at very low pressures, hydrazine adsorption on glass surfaces may result in erroneously low pressure readings.



**Figure 18:** Velocity of sound in ternary hydrazine/hydrazinium nitrate/water mixtures. (Reprinted and modified from [205])

### 2.1.9.1 Vapor Pressure of Pure Hydrazine

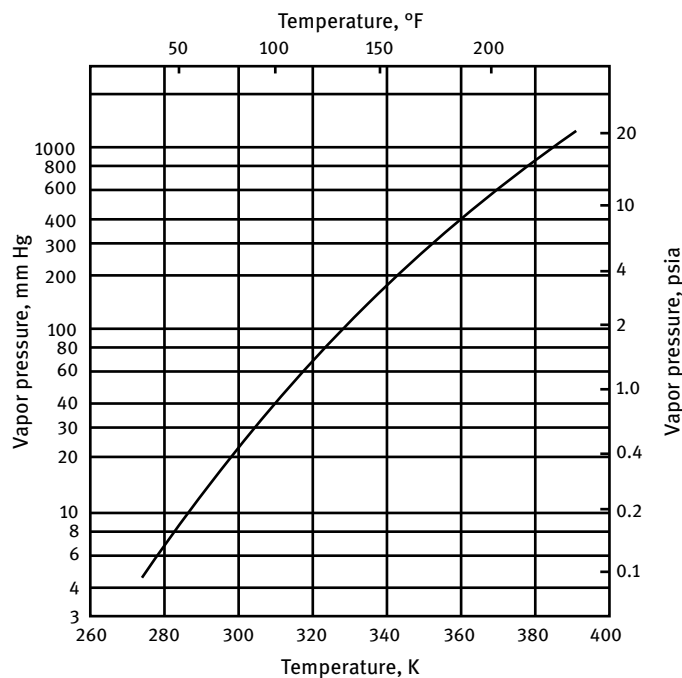
Vapor pressure measurements of hydrazine are not always accurate. In addition to differences encountered due to incipient decomposition, some early investigators had only hydrazine of insufficient purity available for their work. Some reports on vapor pressure measurements of hydrazine may have to be disregarded for this reason if the discrepancy is too large. One set of vapor pressure data of pure hydrazine could best be represented by [107]

$$\log P = 7.80687 - \frac{1680.745}{t + 227.74}$$

where  $P$  is the vapor pressure in mm Hg and  $t$  is the temperature in °C. The data of Scott 1949 are consistently higher than those previously reported [206], a fact suggesting that the earlier investigators used a sample of lesser purity. The most likely contaminant was water, which would lower the vapor pressure below that of pure hydrazine because hydrazine and water form an azeotrope. Additional vapor pressure data (over a narrower range of temperatures) agree well with those obtained by previous authors [207]. Combining three sets of data and curve-fitting by the least-squares method resulted in the following equation [171]

$$\log P = -6.50603 - \frac{653.880}{T} + 0.047914T - 4.9886 \times 10^{-5}T^2$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The normal boiling point obtained by extrapolation to 760 mm Hg from this equation is 387.37 K (114.2°C = 237.6°F). The curve shown in Figure 19 is based on this equation.



**Figure 19:** Vapor pressure of liquid anhydrous hydrazine. (Reproduced and modified from [22].)

Another vapor pressure correlation for hydrazine suggested the following equation [208]:

$$\log P = 60.003 - \frac{3880.3}{T} - 20.575 \log T + 1.5585 \times 10^{-2} T + 5.0525 \times 10^{-6} T^2$$

where  $P$  is the pressure in kPa and  $T$  is the temperature in kelvin. All previous vapor pressure determinations cover only the range below atmospheric pressure. The only vapor pressure determination above atmospheric pressure dates back two centuries and was performed by Lobry de Bruyn in 1895 [169]. It appears that during the entire 120 intervening years, nobody was daring enough to repeat these measurements at higher temperatures. These “archaic” data can be represented by

$$\log P = 4.73294 - \frac{1457.79}{T} - \frac{145452.1}{T^2}$$

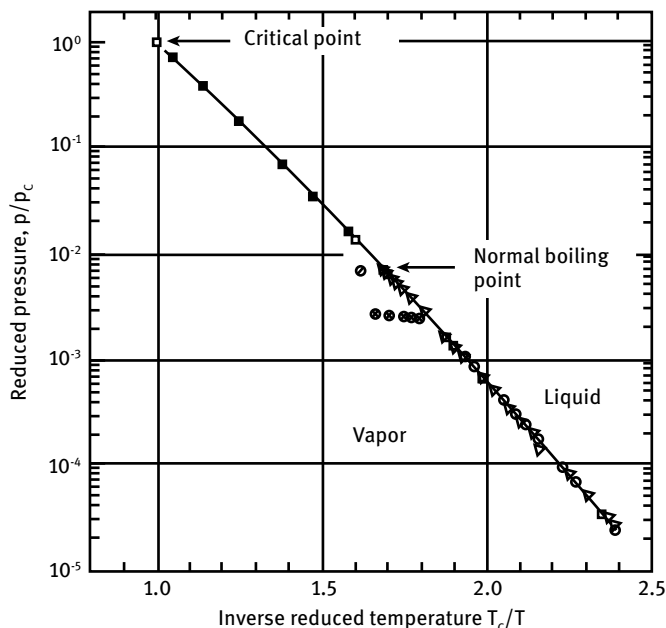


where  $P$  is the pressure in atm and  $T$  is the temperature in kelvin. It is very difficult to obtain vapor pressure data above the normal boiling point and above atmospheric pressure because of incipient decomposition and the explosion hazard. It would be very desirable to repeat and verify de Bruyn's measurements with modern techniques. These data are of interest for calculating boiling phenomena in injector portions of rocket engine systems using hydrazine at high pressure. Of course, anhydrous hydrazine is no longer used in regeneratively cooled engines, but that is an area where vapor pressure at higher pressures must be known to design a system. The XLR117-NA-1 rocket engine intended for use on the NOMAD upper stage apparently was regeneratively cooled with hydrazine. It is assumed that the fuel passages were purged with inert gas after engine shutdown.

A comparison of vapor pressure data from numerous sources and presented in logarithm of reduced pressure ( $p/p_c$ ) versus inversed reduced temperature ( $T_c/T$ ) coordinates showed that most of the data fall on a straight line, many data points superimposed, with only a few outliers [105] (Figure 20).

The vapor pressure equation proposed by [173]

$$\ln P = 58.7582 - \frac{0.707 \times 10^4}{T} - 7.088 \ln T + 0.457 \times 10^{-2} T$$



**Figure 20:** Comparison of vapor pressure of hydrazine data from several sources. (Reprinted and adapted from [105], with permission from ©2001 American Chemical Society; permission conveyed through RightsLink.)

where  $P$  is the vapor pressure in atm and  $T$  is the temperature in kelvin, appeared to be the most remarkable one because it accurately reproduced (dashed line in Figure 20) the experimental data from 273 to 653 K (0 to 380 °C), that is, up to the critical point. Das and Kuloor made no measurements themselves. Their vapor pressure equation was based on data previously published in Audrieth and Ackerson-Ogg 1951 [7].

Readers are warned that the interpolating function published by Haws and Harden 1965 [172] and unfortunately repeated also on page 142 of Schmidt 1984 (first edition [11]) failed completely in reproducing the experimental data. For this reason, it was deleted from the second edition of the hydrazine book. It was also pointed out that the interpolating equation given as Equation B on page 58 of Audrieth and Ackerson-Ogg 1951 [7] suffered excessive deviations when  $T$  approached 273 K.

Unfortunately, the vapor pressure data provided by the International Critical Tables appear to be incorrect, and the source of their data could not be verified. A repeated and careful inspection of all de Bruyn's publications on hydrazine, performed in 1998, revealed no trace of such data in any of de Bruyn's publications. One must conclude, therefore, that, although the data (solid squares in Figure 20) seem to fit consistently with those of others, their origin is unknown and their experimental nature is open to doubt.

An evaluation of equation of state (EOS) and vapor pressure data led to the following equation for the vapor pressure of hydrazine [209]:

$$\log_{10} P = 60.003 - 3880.3/T - 20.575 \log_{10} T + 1.5585 \times 10^{-2} T - 5.0525 \times 10^{-6} T^2$$

where  $P$  is the vapor pressure in kPa and  $T$  is the temperature in kelvin.

At the opposite end of the temperature spectrum, there exist no good measured data on the sublimation pressure of frozen hydrazine at subfreezing temperatures, yet there may be tons of frozen hydrazine crystals in the white clouds above the ammonia clouds on Jupiter. Troublesome leaks of propellant lines in spacecraft have occasionally resulted in the formation of hydrazine icicles at the triple point when liquid hydrazine leaked into vacuum. Insufficient vapor pressure data exist to calculate the rate of hydrazine sublimation if, as the first step of problem mitigation, that part of the spacecraft was deliberately turned toward the direct sunlight to make the "hydrazinicles" disappear [111]. Another need for hydrazine evaporation data arose from the new regulations requiring that propellant tanks in idle, end-of-mission satellites, and upper stages be inerted ("passivated") to prevent tank explosions and fragmentation that would add to orbital debris (Section 7.14).

### 2.1.9.2 Equation of State of Hydrazine

The simplest equation of state (EOS) is the van der Waals equation. The van der Waals coefficients for liquid hydrazine were given as  $a = 0.846 \text{ Pa m}^6 \text{ mol}^{-2}$  and  $b = 0.0462 \times 10^{-3} \text{ m}^3/\text{mol}$ . The EOS of hydrazine was known only for near-ambient temperatures and pressures until the design of rocket cooling systems necessitated pressure-volume-temperature (PVT) data over a wide range of temperatures and pressures up to and beyond the critical point. Besides some ancient, relatively inaccessible data from 0.1 to 14.7 MPa (1.5 to 2131 psia) and 386 to 1000 K [210], no data were published for a long time until 1965. Then, using the old (very old!) vapor pressure data of de Bruyn, a Mollier diagram was calculated for hydrazine, using liquid density, heat capacity, and PVT data already available from the literature [172]. The vapor pressure equation used in this study was

$$\ln p = 24.24 - \frac{18184.9}{T} + 0.47629 \ln T - 0.003836T + \left[ \frac{1115.43(1190.08 - T)}{1190.088} \right] \ln(1190.08 - T)$$

where  $p$  is the pressure in psia and  $T$  is the temperature in °R. Comparison of this equation with experimental results revealed that the deviations never exceeded 3% and did not follow a steady pattern. The following EOS was developed for hydrazine [172] (we apologize for the use of non-SI units):

$$p = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2e^{-xT/T_c}}{(V-b)^2} + \frac{A_3 + B_3T + C_3e^{-xT/T_c}}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{B_5T}{(V-b)^5}$$

with  $p$  in psia,  $R$  the universal gas constant = 10.7315/mol. wt.,  $T$  in °R,  $b = 0.0299451 \text{ ft}^3/\text{lb}_m$ ,  $x = 8.0000$ ,  $T_c$  the critical temperature = 1175.69°R,  $A_2 = -32.21898$ ,  $A_3 = 0.869588$ ,  $A_4 = -0.202100 \times 10^{-1}$ ,  $B_2 = 0.00294549$ ,  $B_3 = 0.16838487 \times 10^{-3}$ ,  $B_5 = 0.12899897 \times 10^{-6}$ ,  $C_2 = -1171.2876$ , and  $C_3 = 46.250721$ . The Haws and Harden 1965 paper [172] contains severe errors for heat capacity, so all other equations from that paper will need to be critically examined for accuracy.

Mitchell [211] reexamined the Martin EOS

$$p = \frac{RT}{\underline{V}-b} + \frac{A_2 + B_2T + C_2e^{-xT/T_c}}{(\underline{V}-b)^2} + \frac{A_3 + B_3T + C_3e^{-xT/T_c}}{(\underline{V}-b)^3} + \frac{A_4}{(\underline{V}-b)^4} + \frac{B_5T}{(\underline{V}-b)^5}$$

and assigned the following constants, converted to SI units:

$$A_2 = -889.02$$

$$B_2 = 0.14629$$

$$C_2 = -32319$$

$$A_3 = 48.001$$

$$B_3 = 0.016731$$

$$C_3 = 2553.0$$

$$A_4 = -2.2317$$

$$B_5 = 5.1295 \times 10^{-5}$$

$$x = 8.0000$$

$$b = 0.059905$$

The vapor pressure equation that Mitchell erroneously credited to Giordano 2002 is actually the one published earlier by Das and Kuloor 1968 [173].

A Russian publication on the thermodynamic properties of hydrazine extended the data to the range of nonideal behavior of hydrazine vapor at high temperatures and pressures [212]. The second virial coefficient  $B$  in the EOS

$$V = \frac{RT}{p} + B$$

can be expressed by

$$B = -9.0104668 + 0.2649938 \frac{1000}{T} - 0.8832357 \frac{1000}{T^2} + 0.6849432 \frac{1000}{T^3} - 0.2101736 \frac{1000}{T^4}$$

where  $B$  is in  $\text{cm}^3/\text{mol}$  and  $T$  is the temperature in kelvin. With this equation, hydrazine vapor data can be calculated in the temperature range 300–1000 K and at pressures of up to 10 MPa. These conditions may be encountered in the injector passages of hydrazine decomposition reactors or in the periphery of burning droplets, but hydrazine will not survive very long under these conditions.

EOSs consistent with published vapor pressure data for hydrazine and MMH have been derived [208, 209, 213]. Unfortunately sets of vapor pressure and vapor and liquid heat capacity data that were available at that time from various sources were inconsistent, and it was difficult to select the most reliable set of data without repeating some of the measurements. Some of the data may have been obtained several decades ago with hydrazine of inferior purity. The Peng-Robinson and Soave-Redlich-Kwong EOSs were each validated for hydrazine and MMH using fugacity coefficient comparisons at phase equilibrium. The Peng-Robinson equation best represented hydrazine states,

and the Soave-Redlich-Kwong EOS best represented MMH states. Partial Mollier diagrams were drawn for hydrazine and MMH. These data are useful for calculating the real-gas isentropic compression temperatures in suddenly compressed vapor pockets in propulsion systems. Sudden compression of bubbles (foam) may lead to explosions.

A review of the literature as of 2005 yielded three published EOSs for hydrazine: **(1)** Martin's EOS used by Haws and Harden 1965 [172], **(2)** a modified Clausius EOS also used by Giordano and de Serio 2002 [106], and **(3)** the Peng-Robinson EOS developed by Barragan et al. 2002 [209]. The three cited works concluded that each EOS was suitable for the authors' own purposes. However, no evaluation of the three equations has been conducted for the full range of engineering design and safety analysis problems that might be encountered when using hydrazine as a rocket propellant. Therefore, an evaluation of the applicability and thermodynamic consistency of these equations for hydrazine was needed [211]. The equations were applied to the vapor-liquid phase transition using a thermodynamic consistency test comparing liquid and vapor fugacity coefficients and liquid volumes and were subjected to a test of mechanical stability. The three EOSs were all reparameterized for a consistent set of units. The vapor pressure equation from Haws and Harden 1965 was not used since it is flawed. Only the Barragan 2002 and Das-Kapoor-Giordano 2002 vapor pressure equations were used. In all cases the following parameters for hydrazine were used:  $T_c = 653$  K,  $p_c = 14700$  kPa,  $MW = 32.045$  g/mol. To calculate vapor-liquid coexistence, first a temperature  $T$  in the two-phase region was chosen. Then the corresponding vapor pressure  $p$  was calculated. With this pressure and temperature combination, the EOS was solved for the specific volume  $V$  of both the liquid and vapor, and compressibility factors  $Z$  for both phases were calculated. Equation (1) was then used to calculate the fugacity coefficient for each phase:

$$\ln \phi = \frac{1}{RT} \int_0^V \left[ p - \frac{RT}{V} \right] dV + (Z^j - 1) - \ln Z^j \quad (1)$$

When plotting the fugacity coefficients of liquid vs. fugacity coefficients of vapor for the three EOSs, where one would expect a straight line with a slope of  $45^\circ$ , only the results of the Peng-Robinson EOS calculations showed that the predicted vapor-liquid coexistence values were thermodynamically consistent, i.e., they fell on a straight line together. Neither the Martin nor the Clausius EOS produced liquid and vapor fugacities of near equivalence. This indicated some degree of thermodynamic inconsistency in these equations. While neither of these three EOSs predicted equal liquid- and vapor-phase fugacity coefficients for the entire temperature range evaluated, the Peng-Robinson EOS followed the  $45^\circ$  line more closely than the Martin EOS. From this analysis, the Peng-Robinson EOS appeared to be a superior model for predicting a wide range of thermodynamic properties of hydrazine.

In another example, the Peng-Robinson EOS was used to calculate real fluid isentropic (near adiabatic) compression temperature for hydrazine vapor/ullage gas mix-

tures [209]. The isentropic final temperature  $T_2$  after compressing an ideal gas sample from  $P_1$  to  $P_2$  is

$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

where  $\gamma = C_p/C_v$ . For real gases and hydrazine vapors,  $C_p$  and  $\gamma$  vary with temperature. The EOS was inserted to calculate compression temperature as a function of compression ratio. Starting with hydrazine vapor at its room temperature vapor pressure, compression ratios beyond 200 would be required to heat the vapor to the autodecomposition temperature of hydrazine in nitrogen (about 800 K). But in air, the autoignition temperature of hydrazine would be reached with compression ratios of only 10 to 20. Similar calculations were made for helium, nitrogen, and mixtures of carbon monoxide, carbon dioxide, and water vapor in contact with hydrazine. It is assumed that the mixture of carbon monoxide, carbon dioxide, and water vapor was supposed to simulate the exhaust gas of a pyrotechnic charge in a pyro valve blow-by situation.

Most EOS computational analyses deal only with pure hydrazine. Real-life hydrazine, still in compliance with MIL-PRF specifications, may contain up to 1% water. EOS computations were performed for MIL-PRF-grade hydrazine and accounting for the contribution of a little water to the thermodynamics of the system [214]. The presence of water and other materials in MIL-SPEC hydrazine requires that thermodynamic analysis appropriate for mixtures be considered. The development of an appropriate thermodynamic description took three different approaches:

1. Using simple phase equilibrium models;
2. Using group contributions; and
3. Using new mixing rules.

Using various correlations and mixing rules, real fluid properties for hydrazine/water mixtures, as well as those containing more than 1% water, were derived and plotted. It was concluded that all three approaches chosen in this study for modeling hydrazine/water mixtures (except Raoult's law) accurately predicted vapor-liquid equilibrium at low pressures. The lessons to be drawn from this study were as follows: **(1)** an activity coefficient model will dramatically enhance a simple mixture model; **(2)** the UNIFAC model is a good predictor of hydrazine/water activity coefficients despite its intended design as a model for organic molecules; **(3)** the Peng-Robinson-Stryjek-Vera EOS is a better choice for mixtures involving water since it can predict pure water vapor pressure more accurately than the standard Peng-Robinson EOS.

### 2.1.9.3 Association in Vapor Phase

Many of the physical properties of hydrazine are due to hydrogen bonding and cluster formation in both the vapor and liquid states. The relatively high dipole moment and strong hydrogen bonding seen in IR spectra made it likely that hydrazine would be associated in the vapor phase. The association of hydrazine in the vapor phase was

already discussed in Section 2.1.6.2 on the vapor density of hydrazine vapor. There was at one point some spectroscopic evidence of hydrogen bonds in hydrazine [215]. However, early claims about dimerization of hydrazine in the vapor phase [174, 216] were proved wrong by data obtained by later investigators. Association in the vapor phase should be recognizable in the IR spectra [217]. Neither hydrazine nor 1,2-dimethylhydrazine (SDMH) or UDMH showed vapor-phase association in the range from 300 to 330 K. It was noted that hydrazine was strongly adsorbed by glass surfaces, which may account for low pressures observed by previous investigators.

Two methods exist for extrapolating unknown physical properties of chemical compounds from other known properties. One method is the so-called theorem of corresponding states, which normalizes properties by their respective critical property. The other method is the significant structure theory of liquids. The significant structure theory assumes that liquid molecules can have properties of a vapor molecule one moment and properties of a solid crystal the next. Starting with the vibrational energies of typical IR and microwave absorption bands, the rotational moments of inertia, Einstein characteristic temperature, the heat of sublimation, and the molar volume of a solid upon melting, several physical properties of liquid hydrazine, including vapor pressure between melting point and boiling point, were correctly predicted by computational methods [192]. Isotopic vapor pressure differences between  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{D}_4$  have also been explained in terms of the significant structure theory of liquids [218]. Vapor pressure differences are mainly affected by the heat of sublimation. To a lesser extent, molecular structure parameters, such as the molecular moment of inertia and the mass of isotopic molecules, also enter into the vapor pressure equation. In addition to vapor pressure, isotopic differences in molar volume, entropy, critical constants, heat capacity at constant pressure or volume, thermal coefficient of expansion, and compressibility were calculated and compared to experimental data [218].

Hydrazine in the vapor phase may form ion clusters  $(\text{N}_2\text{H}_4)_n^+$ , with  $n$  up to  $n = 5$  [219]. The structures of small hydrazine clusters from the dimer to the hexamer were calculated using a standard site-site intermolecular potential [220]. Based on these potentials, the vibrational spectra of the N—N stretching and the asymmetric  $\text{NH}_2$  wagging mode were calculated. Vibrational predissociation spectra of hydrazine  $(\text{N}_2\text{H}_4)_n$  clusters were measured from the dimer to the tetramer using a line-tunable, isotopically substituted  $\text{CO}_2$  laser [221]. The clusters were size-selected in a scattering experiment with helium atoms. These clusters can be fragmented by electron impact ionization in molecular beams [222].

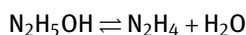
Terahertz vibration-rotation-tunneling spectroscopy of the ammonia dimer has led to a debate about the structure of ammonia dimers [223]. Measurements indicated that two ammonia molecules can form a “cyclic” dimer structure instead of the traditionally assumed  $\text{N}\cdots\text{H}$  linear hydrogen bond. This new instrumental technique has not yet been applied to hydrazine vapor to determine whether dimers form there as well and what structure they might have.

*Ab initio* calculations applied to hydrazine and its dimers found five optimized stable dimers on the potential energy surface [224]. The binding energy for the most stable dimer was predicted to be  $-18$  kJ/mol. The molecular interaction slightly hinders the internal rotation. The frequencies of both the  $\text{NH}_2$  wagging mode and their blue shifts relative to those of monomer were in good agreement with experiments.

Clusters of amines, hydrazine, MMH, and UDMH may contribute to the growth of nucleation clusters in the atmosphere. Structures of the hydrazine and amine clusters containing one or two common nucleation molecules along with other pollutants have been optimized using DFT calculation methods [225]. The clusters' growth mechanism has been explored based on the thermochemistry by calculating the Gibbs free energies of adding successively an ammonia, water, methanol, or sulfuric acid molecule step by step at room temperature. The results showed that hydrazine and its derivatives could enhance heteromolecular homogeneous nucleation in Earth's or Jupiter's atmosphere. The interaction between hydrazines and ammonia is slightly stronger than that between amines and ammonia.

#### 2.1.9.4 Vapor Pressure and Vapor-Phase Composition of Hydrazine Hydrate

The vapor pressure of hydrazine hydrate and hydrazine/water mixtures is an important property for the design of hydrazine hydrate concentration/distillation facilities. The vapor pressure must be known in order to be able to evaluate the hazard from propellant spills like those of H-70 that is used as gas generant in F-16 fighter jet emergency power units (EPUs). Hydrazine hydrate behaves differently from pure liquids, as evidenced by its vapor pressure at higher temperatures. The vapor pressure in a constant-volume apparatus is higher than what would be expected without dissociation of hydrazine hydrate into hydrazine and water:



The equilibrium constant of the vapor-phase equilibrium between hydrazine and water

$$K = \frac{P_{\text{H}_2\text{O}} P_{\text{N}_2\text{H}_4}}{P_{\text{N}_2\text{H}_5\text{OH}}}$$

can be expressed by the equation

$$\log K = 8.55 - \frac{3054}{T}$$

where  $K$  is in atm and  $T$  is in K [226]. From the slope of this curve, a heat of dissociation of the vapor may be derived:  $\Delta H = 58.45 \pm 0.48$  kJ/mol ( $13.97 \pm 0.10$  kcal/mol). The entropy of dissociation in the vapor phase is  $163.6 \pm 1.6$  J mol $^{-1}$  K $^{-1}$  =  $39.1 \pm 0.4$  cal mol $^{-1}$  K $^{-1}$ .



A determination of the vapor pressure of hydrazine hydrate between 294 and 351 K gave a vapor pressure function of

$$\log p = 9.17 - \frac{2450}{T}$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in K [227]. From this equation a heat of vaporization of 47.7 kJ/mol (11.4 kcal/mol) was calculated. That earlier study neglected the dissociation of hydrazine hydrate at temperatures near the boiling point. Earlier measurements had shown that hydrazine hydrate vapor at 373 K and reduced pressure is 58% dissociated [228]. At 443 K (170 °C) and atmospheric pressure, the dissociation is complete. Measurements above 456 K were hampered by incipient decomposition. Vapor pressure measurements between 300 and 393 K (27.6 and 120 °C) were curve-fitted and could be represented by the following equation [229]:

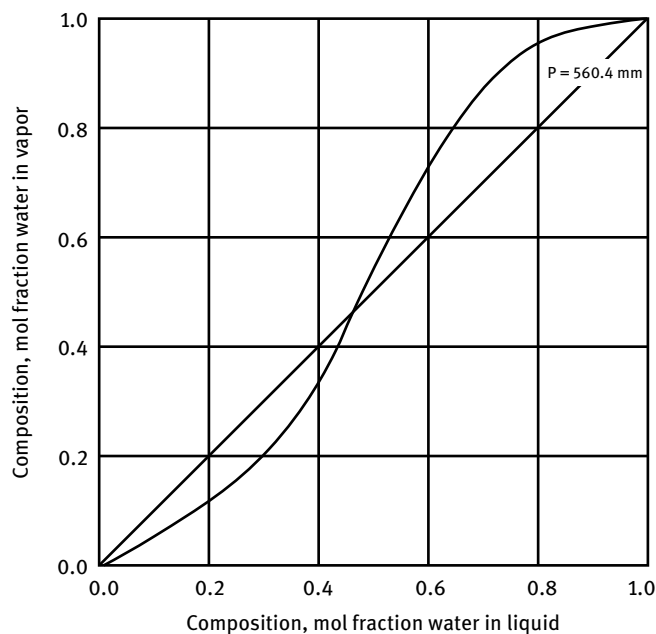
$$\log p = 0.3389 - \frac{752.5}{T} + 0.011338T$$

where  $p$  is the pressure in mm Hg and  $T$  is the temperature in K. Based on vapor density measurements in a constant-volume apparatus over the range from 343 to 423 K (70 to 150 °C), it was concluded that hydrazine hydrate vapor is completely dissociated above 343 K (70 °C). These vapor density measurements at pressures up to 67 kPa (500 mm Hg) were made in a constant-volume apparatus that was later also used for autoxidation kinetics studies.

The knowledge of the liquid-vapor phase equilibrium in the hydrazine-water system is required for the optimum design of fractionating and concentrating towers for hydrazine hydrate, a process of tremendous industrial importance. The liquid-vapor phase diagram of the hydrazine-water system was measured at five subatmospheric pressures over the entire range of compositions [230]. There are two different ways to illustrate the results. In Figure 21, the mol fraction water in the vapor is shown as a function of the mol fraction water in the liquid for one specific pressure.

For an ideal mixture of liquids, the function would be a straight line (also shown). However, as a result of the strong interaction of the two molecules with hydration, ionization, and hydrogen bonding, a significant deviation from the behavior of ideal liquids is observed. Only at one specific mixture composition, the azeotropic composition, do the two curves intersect the way they would for an ideal mixture.

From Figure 21 it can be observed that below 55 mol-% hydrazine, water will accumulate in a distillate, but its concentration in the distillate will never be less than 45 mol-%. It is noteworthy that for all pressures investigated, the azeotropic composition does not coincide with the theoretical composition of hydrazine hydrate (50 mol-%). Instead, the azeotrope always occurs on the hydrazine-rich side of the stoichiometric composition. The dependence of the azeotropic composition on pressure is sum-



**Figure 21:** Vapor-liquid equilibrium data for hydrazine-water system. (Reprinted and modified from [230], with permission from ©1952 American Chemical Society; permission conveyed through RightsLink.)

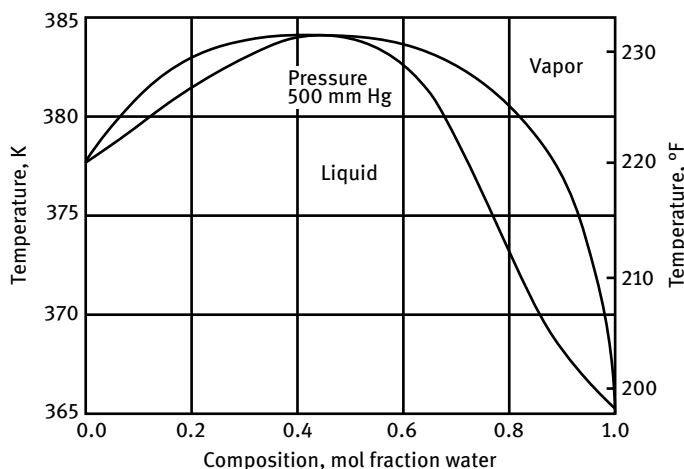
**Table 13:** Effect of pressure on azeotropic composition of hydrazine/water mixtures.

| Pressure |       | Composition                  |                               |
|----------|-------|------------------------------|-------------------------------|
| mm Hg    | kPa   | mol-% $\text{N}_2\text{H}_4$ | mass-% $\text{N}_2\text{H}_4$ |
| 124.8    | 16.60 | 53                           | 66.7                          |
| 281.8    | 37.57 | 54                           | 67.6                          |
| 411.2    | 54.81 | 55.5                         | 69.0                          |
| 560.4    | 74.70 | 55                           | 68.5                          |
| 700.6    | 93.38 | 54                           | 67.6                          |

Data source: [230]

marized in Table 13. Based on these data, it is impossible to concentrate hydrazine to more than 55.5 mol-% (69 mass-%)  $\text{N}_2\text{H}_4$  by simple single-stage distillation.

Figure 22 illustrates the same data as shown in Figure 21 in slightly different form. From this diagram one can read the composition of the liquid and vapor phase formed if a given vapor sample is allowed to cool off and condense progressively.



**Figure 22:** Boiling point as a function of composition for hydrazine-water system. (Reprinted and modified from [230], with permission from ©1952 American Chemical Society; permission conveyed through RightsLink.)

Extrapolation of data indicates a boiling point of 386.9 K (113.8°C) for pure hydrazine at 101 kPa (760 mm Hg). The boiling point of the azeotrope at the same pressure is approximately 393 K (120°C).

A similar, but more detailed, investigation of the vapor-liquid equilibrium in the hydrazine-water system was based on more data points (25 points) than the previous set, and the data were taken at exactly atmospheric pressure (760 mm Hg) [231]. The maximum boiling azeotrope boiled at 393.2 K (120.1°C = 248.2°F) and had a composition of 58.5 mol-% hydrazine. It was confirmed that it is not possible to completely dehydrate hydrazine by a straight distillation process. It is possible, however, to concentrate hydrazine solutions to approximately 69 mass-% hydrazine by distillation at atmospheric pressure. Concentrations beyond 70% can be achieved only by azeotropic distillation with an auxiliary fluid.

The azeotrope found by other authors was at 52.7 mol-% (66.6 mass-%) hydrazine, and its boiling point was at 760 mm Hg of 393.3 K (120.2°C) [232]. Extrapolating to 100% hydrazine, these authors cited a boiling point of 387.6 K (114.5°C) for pure hydrazine.

Another study measured the equilibrium compositions of the liquid and vapor phases at reduced pressures from 2.67 to 101 kPa (20 to 760 mm Hg) [233]. A change in pressure had only a very slight effect on the vapor-liquid equilibrium. The activity coefficients of the components were determined experimentally and compared to theoretical results derived from the Van Laar equation. Equilibrium data of the liquid-vapor system can also be used to calculate the heat of mixing of hydrazine and water in the liquid phase [234].

The equilibrium vapor pressure of hydrazine, MMH, or UDMH above dilute aqueous solutions is important in predicting the efficiency of packed-bed wet scrubbers for the removal of hydrazines from pressurization gases vented from propellant tanks to the atmosphere [235]. The activity coefficient of hydrazine  $\gamma_a$  in water can be calculated from

$$\log \gamma_a = \frac{-1.0680}{\left[1 + \frac{1.0680X_a}{0.5410(1-X_a)}\right]^2}$$

where  $X_a$  is the hydrazine mol fraction in the liquid phase. Initially,  $\text{N}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$  vapor-phase composition data were available only for the temperature range 329–385 K. Measurements of the  $\text{N}_2\text{H}_4$  partial pressure in the vapor phase above 35, 54.4, and 64% solutions of  $\text{N}_2\text{H}_4$  in  $\text{H}_2\text{O}$  expanded the range of measured data and agreed well with extrapolated data [236]. See also [237].

The vapor-phase composition measurements by Wilson, Munger, and Clegg [231] were reevaluated by Ferriol 1993 and illustrated in Figure 3 on page 293 of that publication [238]. Predictions for hydrazine-water isobaric vapor-liquid equilibria and vapor-phase compositions from quantum-mechanical and grand equilibrium and force field model computational methods were compared to measured data from Uchida or de Bruyn and were in moderately accurate agreement [239, 240].

Anhydrous hydrazine has a high affinity to moisture from the atmosphere, forming hydrazine hydrate. The hygroscopicity of hydrazine and the rate of water absorption were illustrated by spreading 25 mL anhydrous hydrazine in a Petri dish with a surface area of  $16.3\text{ cm}^2$ . The water content increased to 50% within 4 d [241]. The initial rate of water absorption was 90 ppm  $\text{H}_2\text{O}/\text{min}$  at 30% relative humidity (RH), 295 K, and 829 mbar (Denver). At the same time, substantial amounts of carbon dioxide were absorbed from atmospheric air.

#### 2.1.9.5 Vapor Pressure of Hydrazine Mixtures

The vapor pressures of hydrazine mixtures with ammonia were already described in the chapter on ammonia, including ternary mixtures containing hydrazine, ammonia, and water. Vapor pressures of mixtures of hydrazine with MMH or UDMH will be described in the chapters “Methylhydrazine” and “Dimethylhydrazines.”

#### 2.1.9.6 Vapor Pressure of Salt Solutions in Hydrazine

The one salt solution in hydrazine that is of particular interest as a rocket propellant is the solution of hydrazinium nitrate in hydrazine. Vapor pressures of ternary  $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$  mixtures, candidate liquid gun propellants, were first determined by heating the solutions to boiling temperature in a boiling refluxing dynamic system where a certain amount of decomposition was inevitable [242]. This slight decomposition had the effect of raising the pressure above the liquid, such that

temperature-pressure data pairs had to be read rapidly without too much time passing. The vapor pressure can be calculated from

$$\log p = A - \frac{B}{T}$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in K. The coefficients  $A$  and  $B$  were obtained by curve-fitting numerical data from various sources and are compiled in Table 14.

**Table 14:** Vapor-pressure equation coefficients for hydrazine/hydrazinium nitrate/water solutions.

| Composition (mass-%) <sup>a</sup> |                                               |                  | Range, K | Coefficients |         | References |
|-----------------------------------|-----------------------------------------------|------------------|----------|--------------|---------|------------|
| N <sub>2</sub> H <sub>4</sub>     | N <sub>2</sub> H <sub>5</sub> NO <sub>3</sub> | H <sub>2</sub> O |          | A            | B       |            |
| 82.04                             | 17.62                                         | —                | 273–333  | 8.6774       | 2259.76 | [188]      |
| 69.74                             | 29.97                                         | —                | 273–333  | 8.5181       | 2232.46 |            |
| 74.49                             | 24.19                                         | 0.99             | 272–332  | 8.8184       | 2312.03 | [189]      |
| 69                                | 20                                            | 11               | 273–348  | 9.6418       | 2583.74 | [243]      |
| 84.52                             | 4.81                                          | 10.53            | 312–345  | 6.4833       | 1516.73 | [242]      |
| 83.6                              | 4.72                                          | 11.4             | 328–364  | 6.1280       | 1340.04 |            |
| 77.0                              | 6.20                                          | 16.4             | 321–369  | 6.0213       | 1311.01 |            |
| 64.5                              | 4.76                                          | 30.4             | 338–365  | 6.3761       | 1448.11 |            |
| 79.0                              | 9.91                                          | 10.8             | 323–359  | 5.8435       | 1233.18 |            |
| 69.3                              | 9.2                                           | 21.2             | 317–358  | 5.7100       | 1201.56 |            |
| 59.4                              | 9.74                                          | 30.5             | 318–359  | 6.0512       | 1339.36 |            |
| 56.1                              | 13.2                                          | 30.5             | 323–362  | 6.0174       | 1326.91 |            |

<sup>a</sup> Numbers do not add up to 100%. Balance is assumed to be aniline and/or ammonia.

The vapor pressure of a 24% hydrazinium nitrate solution in hydrazine between 334.6 K/10 kPa and 452.6 K/752 kPa can be expressed by the following curve-fitting equation [244]:

$$\log p = 9.097817 - \frac{2446.4543}{T}$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in K. Vapor pressure data of hydrazinium azide solutions in hydrazine, hydrazine/ammonia, and hydrazine/water solvents were reported in [150] and [151].

### 2.1.10 Viscosity of Hydrazine

There are two common definitions of viscosity in use. The absolute (dynamic) viscosity  $\mu$  is defined as the force per unit area necessary to maintain a unit velocity gradient

at right angles to the direction of flow between two plates a unit distance apart; the SI unit for absolute viscosity is Pa s or N s m<sup>-2</sup>. The kinematic viscosity  $\sigma$  is defined by

$$\sigma = \frac{\mu}{\rho}$$

where  $\rho$  is the density of the incompressible fluid. The common unit for dynamic viscosity is centipoise (cP or cPs), 1 cPs = 10<sup>-3</sup> N s/m<sup>2</sup>. The common unit for kinematic viscosity is centistokes (cSt), 1 cSt = 10<sup>-6</sup> m<sup>2</sup>/s. Kinematic viscosity data can be converted back to dynamic viscosity by multiplying by the density:  $\mu = \sigma \times \rho$ .

### 2.1.10.1 Viscosity of Pure Hydrazine

The viscosity of liquid hydrazine and the methylhydrazines has been measured by numerous investigators as a function of temperature (Table 15).

**Table 15:** Viscosity of anhydrous hydrazine at 101 kPa.

| Temperature |       | Absolute viscosity | Kinematic viscosity | References |
|-------------|-------|--------------------|---------------------|------------|
| K           | °C    | cPs                | cSt                 |            |
| 288.16      | 15.0  | 1.0159             | 1.0225              | [166]      |
| 310.94      | 37.8  | 0.7316             | 0.7268              |            |
| 338.72      | 65.6  | 0.5399             | 0.5363              |            |
| 366.49      | 93.3  | 0.4286             | 0.4028              |            |
| 394.27      | 121.1 | 0.3578             | 0.3266              |            |
| 422.05      | 148.9 | 0.3081             | 0.2728              |            |
| 449.83      | 176.7 | 0.2733             | 0.2344              |            |
| 274.2       | 1.1   | 1.293              | —                   | [168]      |
| 275.2       | 2.1   | 1.272              | —                   |            |
| 276.2       | 3.1   | 1.251              | —                   |            |
| 278.2       | 5.1   | 1.207              | —                   |            |
| 283.2       | 10.1  | 1.118              | —                   |            |
| 288.2       | 15.1  | 1.044              | —                   |            |
| 293.2       | 20.1  | 0.9736             | —                   |            |
| 298.2       | 25.1  | 0.9049             | —                   |            |
| 298.2       | 25.1  | 0.9031             | —                   | [245]      |
| 323.2       | 50.1  | 0.6731             | —                   |            |
| 298.1       | 25    | 0.894              | —                   | [187]      |
| 313.1       | 40    | 0.727              | —                   |            |

The viscosity of hydrazine itself has even been measured as a function of pressure at pressures up to 25.25 MPa (250 atm) (Table 16). There are few viscosity data at temperatures above 360 K, where hydrazine begins to decompose.

**Table 16:** Absolute viscosity of hydrazine at elevated pressure.

| Temperature, K | Viscosity, cPs   |               |       |       |       |       |
|----------------|------------------|---------------|-------|-------|-------|-------|
|                | At boiling point | Pressure, MPa |       |       |       |       |
|                |                  | 5.05          | 10.1  | 15.15 | 20.2  | 25.25 |
| 283            | 1.240            | 1.246         | 1.258 | 1.265 | 1.273 | 1.278 |
| 293            | 1.048            | 1.058         | 1.064 | 1.075 | 1.090 | 1.098 |
| 303            | 0.888            | 0.897         | 0.906 | 0.917 | 0.930 | 0.937 |
| 313            | 0.765            | 0.775         | 0.783 | 0.792 | 0.800 | 0.808 |
| 323            | 0.665            | 0.676         | 0.682 | 0.688 | 0.696 | 0.702 |
| 333            | 0.582            | 0.591         | 0.598 | 0.602 | 0.611 | 0.617 |
| 343            | 0.508            | 0.518         | 0.524 | 0.530 | 0.538 | 0.546 |
| 353            | 0.438            | 0.448         | 0.456 | 0.464 | 0.472 | 0.482 |

Data source: [246]

The viscosity data by several authors can be represented by the following least-squares-fit equation:

$$\log \mu = 3.1788 - 0.015384T + 1.5395 \times 10^{-5} T^2$$

where  $\mu$  is the viscosity in cPs and  $T$  is the temperature in kelvin. A smoothed curve calculated with this equation is shown in Figure 23.

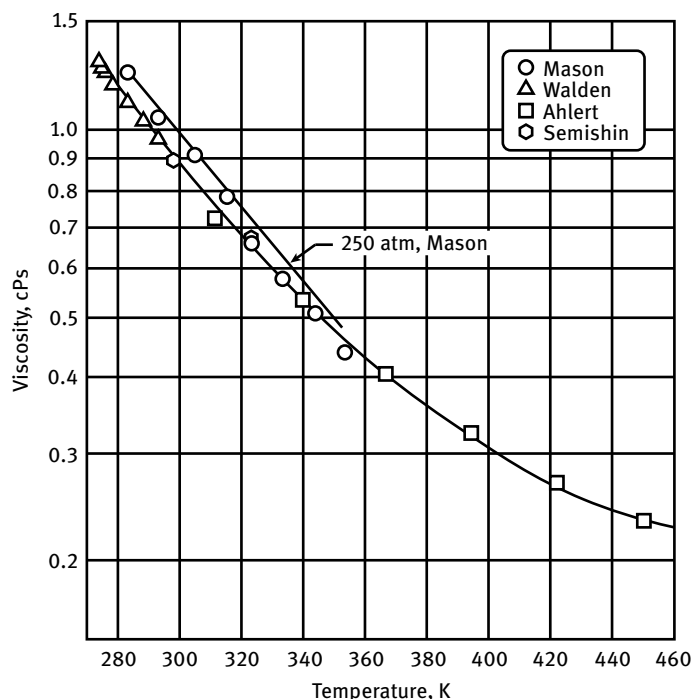
Taking the data by Ahlert, Bauerle, and Lecce [166] only, a more accurate correlation by least-squares fit is represented by the equation

$$\ln \sigma = -2.4830 + \frac{404.28}{T} + \frac{2.6197 \times 10^6}{T^3}$$

where  $\sigma = \mu/\rho$  is the kinematic viscosity in centistokes. Earlier, Walden and Hilgert [168] had expressed their dynamic viscosity data by means of the slightly simpler equation

$$\log \mu = \frac{536}{T} - 3.844$$

where  $\mu$  is the dynamic viscosity in  $\text{dyn scm}^{-2}$ , and  $T$  is the temperature in kelvin. Hydrazine is one of the few fluids for which viscosity is known as a function of not only temperature, but also pressure. The pressure dependence of hydrazine viscosity has been determined at pressures up to 25.25 MPa (250 atm) [246]. The data are tabulated in Table 16, and the highest pressure data are superimposed on the curve shown in Figure 23. The viscosity increases with increased pressure because the molecules are forced in a more regular arrangement where intermolecular forces (hydrogen bonding and van der Waals forces) become more effective. The increase is more pronounced at higher temperatures than at lower temperatures. Thus, at 353 K, the increase is almost



**Figure 23:** Absolute viscosity as a function of temperature for liquid anhydrous hydrazine. (Reproduced and modified from [171].)

10% when the pressure is increased from 0.1 to 25 MPa. At ambient temperature, the increase is only 3%. For most ordinary applications, the variation of viscosity with pressure may be neglected. When designing a feed system for deep-sea application of hydrazine, however, the pressure variation may have to be considered.

There are no measured data for the viscosity of hydrazine vapor, but extrapolated, theoretical data show hydrazine vapor viscosity increasing linearly from 80 micropoise at 273 K to 130 micropoise at 448 K [101]. Data beyond 500 K are meaningless because hydrazine vapor would not be stable under those conditions.

#### 2.1.10.2 Viscosity of Hydrazine/Water Mixtures

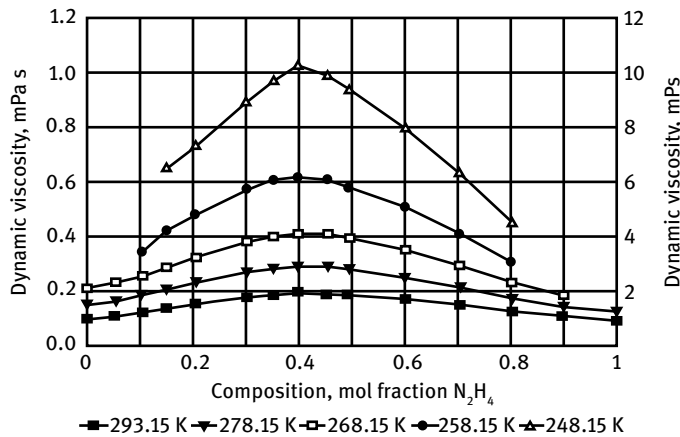
The viscosity of hydrazine/water mixtures indicates compound and hydrate formation at specific molecular ratios. Vapor pressure, density, and viscosity data applied to a chemical association model in the hydrazine-water system indicated that the solutions contain a hydrazine monohydrate, a tetrahydrate, and a hydrazine dimer [170, 177]. Viscosity data for hydrazine/water mixtures are summarized in Table 17. As illustrated in Figure 24, the viscosity of hydrazine-water mixtures does not appear to peak exactly at a molar ratio of  $\text{H}_2\text{O} : \text{N}_2\text{H}_4 = 1 : 1$ , but in slightly hydrazine-lean mixtures.



**Table 17:** Dynamic viscosity of hydrazine/water mixtures.

| Temperature, K                             | 293.15         | 278.15 | 268.15 | 258.15 | 248.15 |
|--------------------------------------------|----------------|--------|--------|--------|--------|
| Mol fraction N <sub>2</sub> H <sub>4</sub> | Viscosity, mPs |        |        |        |        |
| 0.0000                                     | 0.99           | 1.53   | 2.16   | —      | —      |
| 0.0526                                     | 1.11           | 1.66   | 2.33   | —      | —      |
| 0.1045                                     | 1.26           | 1.89   | 2.60   | 3.46   | —      |
| 0.1502                                     | 1.40           | 2.10   | 2.89   | 4.22   | 6.49   |
| 0.2047                                     | 1.57           | 2.36   | 3.27   | 4.82   | 7.33   |
| 0.3013                                     | 1.80           | 2.73   | 3.84   | 5.71   | 8.93   |
| 0.3512                                     | 1.88           | 2.88   | 4.04   | 6.11   | 9.69   |
| 0.3967                                     | 1.96           | 2.92   | 4.13   | 6.17   | 10.3   |
| 0.4526                                     | 1.92           | 2.92   | 4.14   | 6.08   | 9.91   |
| 0.4938                                     | 1.89           | 2.83   | 3.97   | 5.80   | 9.38   |
| 0.5997                                     | 1.71           | 2.52   | 3.55   | 5.09   | 7.98   |
| 0.7032                                     | 1.51           | 2.18   | 2.95   | 4.12   | 6.32   |
| 0.8022                                     | 1.28           | 1.75   | 2.33   | 3.08   | 4.53   |
| 0.8961                                     | 1.11           | 1.46   | 1.89   | —      | —      |
| 1.0000                                     | 0.94           | 1.27   | —      | —      | —      |

Data source: [170]



**Figure 24:** Dynamic viscosity of hydrazine/water mixtures. (Image created by Schmidt 2020 based on data from [170])

The kinematic viscosity of hydrazine/water mixtures as a function of temperature can be expressed by a polynomial equation:

$$\log \sigma = A + BT + CT^2 + DT^3$$

where  $\sigma$  is the kinematic viscosity in cSt and  $T$  is the temperature in kelvin and the coefficients A, B, C, and D are given in the following Table 18 for two different hydrazine concentrations:

**Table 18:** Coefficients for viscosity equation of hydrazine/water blends.

| Mass-% $\text{N}_2\text{H}_4$ | A       | B        | C                        | D                         |
|-------------------------------|---------|----------|--------------------------|---------------------------|
| 51                            | 40.6521 | -0.38006 | $1.21463 \times 10^{-3}$ | $-1.32110 \times 10^{-6}$ |
| 70                            | 33.8633 | -0.30279 | $9.19117 \times 10^{-4}$ | $-9.45536 \times 10^{-7}$ |

Data source: Rocket Research Co. as referenced in [22]

The density and dynamic viscosity of hydrazine/water mixtures in a range from 10 to 90 mol-%  $\text{N}_2\text{H}_4$ , at temperatures from 293 to 558 K, and at pressures from 0.1 to 58 MPa were measured [180–183, 247]. See also [248].

### 2.1.10.3 Viscosity of Hydrazine/Ammonia Mixtures

The viscosity of hydrazine-ammonia and hydrazine/ammonia-water mixtures was already described in the chapter “Ammonia.”

### 2.1.10.4 Viscosity of Hydrazine/Alcohol Mixtures

The kinematic viscosity of hydrazine/methanol mixtures listed in Table 19 shows a maximum at 40% hydrazine, close to the composition of a molar ratio hydrazine: methanol = 2 adduct for which other extremes of physical properties had been observed [185, 186].

The kinematic viscosity of hydrazine/methanol mixtures as a function of hydrazine concentration can be expressed by

$$\sigma = 0.7541 + 0.02742X - 4.4918 \times 10^{-4}X^2 + 1.9658 \times 10^{-6}X^3$$

where  $X$  = mass-%  $\text{N}_2\text{H}_4$  and  $\sigma$  = kinematic viscosity (cSt). The viscosity of hydrazine/ethanol mixtures also passes through a maximum at 60 mol-% (68.3 mass-%) hydrazine [187]. This corresponds to a  $\text{N}_2\text{H}_4:\text{C}_2\text{H}_5\text{OH}$  molar ratio of 1.5:1. Whereas density data did not indicate any compound formation between hydrazine and ethanol, there appears to be strong hydrogen bonding in  $\text{N}_2\text{H}_4/\text{C}_2\text{H}_5\text{OH}$  mixtures. Hydrazine/water and hydrazine/ethanol mixtures are notorious for their tendency to supercool, and it is sometimes difficult to obtain exact melting points and density data near the phase-change boundary. On the other hand, viscosity measurements of supercooled solutions provide insight into the structure of supercooled liquids [249]. The addition of hydrazine tends to diminish any anomalous increase in the viscosity of supercooled water, an effect like that seen in other types of measurements. Addition to ethanol, on the other hand, enhanced viscosity.

**Table 19:** Viscosity of hydrazine/alcohol mixtures.

| Alcohol  | Hydrazine,<br>mass-% | Kinematic viscosity <sup>a</sup> , cSt |          | References |
|----------|----------------------|----------------------------------------|----------|------------|
| Methanol | 0                    | 0.76 <sup>b</sup>                      |          | [185]      |
| Methanol | 20                   | 1.13 <sup>b</sup>                      |          |            |
| Methanol | 40                   | 1.28 <sup>b</sup>                      |          |            |
| Methanol | 60                   | 1.20 <sup>b</sup>                      |          |            |
| Methanol | 80                   | 1.08 <sup>b</sup>                      |          |            |
| Methanol | 100                  | 0.97 <sup>b</sup>                      |          |            |
| Alcohol  | Hydrazine,<br>mass-% | Dynamic viscosity, cPs                 |          | References |
|          |                      | at 293 K                               | at 313 K |            |
| Ethanol  | 0.0                  | 1.159                                  | 0.811    | [187]      |
| Ethanol  | 29.6                 | 1.553                                  | 1.028    |            |
| Ethanol  | 46.0                 | 1.648                                  | 1.099    |            |
| Ethanol  | 51.9                 | 1.665                                  | 1.136    |            |
| Ethanol  | 61.4                 | 1.564                                  | 1.192    |            |
| Ethanol  | 70.2                 | 1.197                                  | 0.924    |            |
| Ethanol  | 79.2                 | 1.102                                  | 0.898    |            |
| Ethanol  | 87.7                 | 1.006                                  | 0.819    |            |
| Ethanol  | 92.2                 | 1.001                                  | 0.812    |            |
| Ethanol  | 100.0                | 0.894                                  | 0.727    |            |

<sup>a</sup> Temperature not stated; presumably 298 K.<sup>b</sup> Numerical values interpolated from graph in [185].

### 2.1.10.5 Viscosity of Hydrazine/MMH and Hydrazine/UDMH Mixtures

The viscosities of hydrazine/MMH and hydrazine/UDMH mixtures will be described in *Encyclopedia of Liquid Fuels* chapters “Methylhydrazine” and “Dimethylhydrazines.”

### 2.1.10.6 Viscosity of Salt Solutions in Hydrazine

The viscosities of solutions of hydrazinium nitrate in hydrazine and hydrazine/water mixtures were already described in *Encyclopedia of Oxidizers* in the chapter on hydrazinium salts. Similar data are available for solutions of hydrazinium azide in hydrazine.

### 2.1.11 Surface Tension of Hydrazine

Knowledge of the surface tension of hydrazine and its derivatives is of both theoretical and practical interest because (1) the surface tension can be used to derive parachor data and obtain information on the molecular structure and association of molecules of these compounds and (2) the design of fuel tanks for retaining fluids by capillary forces in the weightlessness of outer space requires knowledge of the surface tension and wetting angles.

The surface tension of hydrazine as a function of temperature in a range of 294 to 313 K has been measured using the bubble method, also in comparison to that of water [250–253]. In addition to multi-point determinations, single-point surface tension determinations have been reported by other authors, as summarized in Table 20.

**Table 20:** Surface tension of hydrazine.

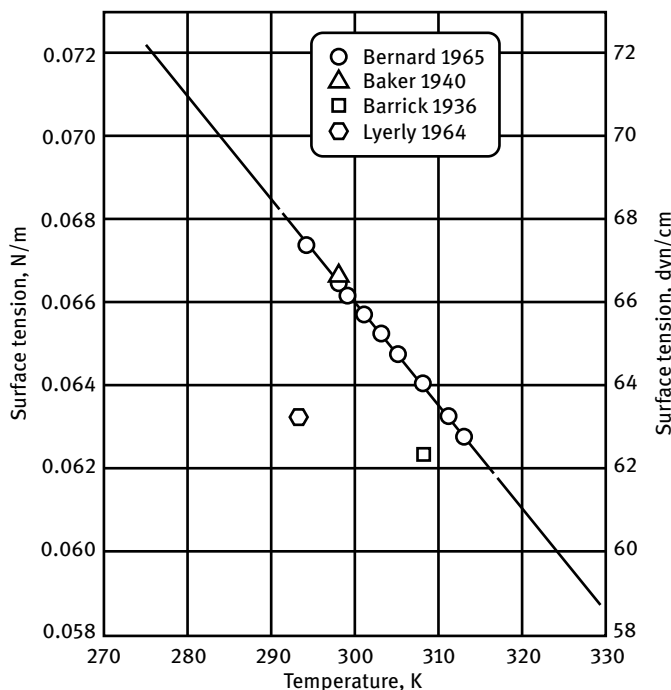
| Temperature |       | Surface tension, dyn/cm <sup>a</sup> |                  |          | References |
|-------------|-------|--------------------------------------|------------------|----------|------------|
| °C          | K     | Unspecified                          | Propellant grade | Purified |            |
| 21          | 294   | 67.35                                | —                | —        | [252]      |
| 25          | 298   | 66.45                                | —                | —        |            |
| 26          | 299   | 66.15                                | —                | —        |            |
| 28          | 301   | 65.65                                | —                | —        |            |
| 30          | 303   | 65.2                                 | —                | —        |            |
| 32          | 305   | 64.7                                 | —                | —        |            |
| 35          | 308   | 64.0                                 | —                | —        |            |
| 38          | 311   | 63.25                                | —                | —        |            |
| 40          | 313   | 62.75                                | —                | —        |            |
| 2.3         | 275.4 | —                                    | 71.8             | 72.8     | [254, 255] |
| 10          | 283.2 | —                                    | 70.3             | 71.2     |            |
| 20          | 293.2 | —                                    | 68.5             | 69.2     |            |
| 30          | 303.2 | —                                    | 66.5             | 67.2     |            |
| 40          | 313.2 | —                                    | 64.6             | 65.1     |            |
| 50          | 323.2 | —                                    | 62.7             | 63.0     |            |
| 60          | 333.2 | —                                    | 60.7             | 61.0     |            |
| 70          | 343.2 | —                                    | 58.7             | 58.9     |            |
| 80          | 353.2 | —                                    | 56.7             | 57.0     |            |
| 25          | 298   | 65.954                               | —                | —        | [187]      |
| 40          | 313   | 53.165                               | —                | —        |            |
| 25          | 298   | 66.67                                | —                | —        | [167]      |
| 35          | 308   | 62.32                                | —                | —        | [256]      |

<sup>a</sup> 1 dyn/cm equals  $10^{-3}$  N/m

Of these, only Baker's data [256] agree with Bernard's [252] curve. Using only these two sets of data points, the surface tension of hydrazine as a function of temperature can be described by a linear equation, also illustrated in Figure 25:

$$\gamma = 0.139903 - 0.24637 \times 10^{-3} T$$

where  $\gamma$  is the surface tension in N/m and  $T$  is the temperature in kelvin. The surface tension at 298 K is 0.06645 N/m.



**Figure 25:** Surface tension of anhydrous hydrazine. (Reproduced and modified from [171].)

The parachor, a dimensionless number, is an atomic characteristic that enables one to calculate the surface tension of liquids if the molecular mass (weight), the liquid density, and the vapor density are known. The parachors contributed by individual atoms are additive. Adding up atomic parachors of  $2 \times 12.5$  for nitrogen and  $4 \times 17.1$  for hydrogen reported in the literature [257], one obtains a parachor sum of 93.4, whereas above surface tension gives 91.2, in close agreement when entered into the following equation:

$$P = \frac{M\gamma^{\frac{1}{4}}}{\rho_1 - \rho_v}$$

where  $M$  is the molecular mass,  $\rho_1$  is the liquid density, and  $\rho_v$  is vapor density. The surface tension of liquids decreases with increasing temperature, and it should be equal to zero at the critical temperature. Extrapolation of the Razouk data represented by the equation

$$\gamma = 1.291 \times 10^5 \left(1 - \frac{T}{632}\right) \quad (\gamma = \text{N/m}; T = \text{K})$$

to  $\gamma = 0$  would give a critical temperature of 632 K. This is in fair agreement with the critical temperature determined by other methods (653 K). See also [258].

### 2.1.11.1 Wetting Angle of Hydrazine on Metal Surfaces

Whereas there are numerous data on hydrazine viscosity and surface tension, only very little data can be found on the angle of wetting of hydrazine in contact with various surfaces. Such wetting angle data are needed for the design of surface tension retention propellant management devices in hydrazine tanks for space use in zero-gravity environments (Section 6.8). The wetting angle is largely dependent not only on the chemical composition of the metal but also on the method of surface treatment prior to testing and on surface changes that may occur with prolonged wetting by hydrazine or exposure to hydrazine vapor. Measurements at Société d'Etude de Propulsion (SEP) in France [259] showed a wetting angle of 25–45° (mostly 40–45°) for hydrazine on titanium with a hysteresis of approximately 5°, whereas previous investigators had reported wetting angles of 0–2° for most materials studied (Harris Research Laboratory, no further information given).

### 2.1.11.2 Surface Tension of Hydrazine/Water Mixtures

The surface tension of hydrazine hydrate and numerous hydrazine/water mixtures has been measured, and the results summarized in Table 21 show a maximum at 30–33 mol-%  $\text{N}_2\text{H}_4$ . This is quite unusual, since other physical properties of the hydrazine-water system, such as density, viscosity, or melting point, show extreme values at 50 mol-%  $\text{N}_2\text{H}_4$ , corresponding to  $\text{N}_2\text{H}_5\text{OH}$ .

**Table 21:** Surface tension of hydrazine/water mixtures at 298 K.

| Hydrazine concentration |        | Surface tension     |
|-------------------------|--------|---------------------|
| Mol-%                   | Mass-% | dyn/cm <sup>a</sup> |
| 0.0                     | 0.0    | 71.96               |
| 6.7                     | 11.3   | 73.11               |
| 10.5                    | 17.3   | 73.68               |
| 20.5                    | 31.4   | 75.10               |
| 26.5                    | 39.1   | 75.41               |
| 28.7                    | 41.7   | 75.47               |
| 33.9                    | 47.7   | 75.47               |
| 40.1                    | 54.4   | 75.28               |
| 48.8                    | 62.9   | 74.18               |
| 49.1                    | 63.2   | 74.24               |
| 63.6                    | 75.2   | 72.38               |
| 69.7                    | 80.4   | 71.88               |
| 83.1                    | 89.7   | 69.97               |
| 84.9                    | 90.9   | 69.81               |
| 96.9                    | 98.2   | 67.57               |
| 100.0                   | 100.0  | 66.67               |

<sup>a</sup> 1 dyn/cm =  $10^{-3}$  N/m

Data source: [256]

Hydrazine, like water, forms hydrogen-bonded clusters in the liquid phase. The surface tension of hydrazine and water mixed together, forming hydrazine hydrate and new types of clusters, shows a highly unusual behavior not seen with other liquids [260].

### 2.1.11.3 Surface Tension of Hydrazine/Ethanol Mixtures

The addition of alcohols instead of water to hydrazine partially breaks up the hydrogen-bonded associated clusters and lowers the viscosity [261]. The surface tension of hydrazine/ethanol mixtures increases with hydrazine content (Table 22), but there is an abrupt increase in surface tension as the hydrazine concentration approaches 100%.

**Table 22:** Surface tension of hydrazine/ethanol mixtures.

| Composition, Hydrazine |       | Surface tension, dyn/cm at |         |
|------------------------|-------|----------------------------|---------|
| Mass-%                 | Mol-% | 298.1 K                    | 313.2 K |
| 0.0                    | 0.0   | 21.820                     | 20.658  |
| 29.6                   | 38.0  | 24.796                     | 24.078  |
| 46.0                   | 55.0  | 26.999                     | 25.416  |
| 51.9                   | 60.8  | 28.082                     | 27.146  |
| 61.4                   | 69.5  | 29.913                     | 29.299  |
| 70.2                   | 77.2  | 32.272                     | 31.251  |
| 79.2                   | 84.6  | 34.955                     | 34.191  |
| 87.7                   | 91.1  | 38.628                     | 40.184  |
| 92.2                   | 94.5  | 43.450                     | 43.669  |
| 100.0                  | 100.0 | 65.945                     | 53.165  |

1 dyn/cm =  $10^{-3}$  N/m

Data source: [187]

### 2.1.11.4 Surface Tension of Solutions of Hydrazinium Salts in Hydrazine

The surface tension of solutions of hydrazinium nitrate in hydrazine was already described in *Encyclopedia of Oxidizers*, in the chapter “Hydrazinium Salt Oxidizers.”

### 2.1.12 Pressurant Gas Solubility in Hydrazine

The solubility of gases in hydrazine(s) is of special interest in the application of hydrazine(s) as rocket propellants. In many cases the propellants are fed into the decomposition or combustion chamber by a pressurant gas, usually nitrogen or helium [262]. Unless a gastight, impermeable diaphragm is used, the fuels become saturated with the pressurant gas. The heat-transfer characteristics of gas-saturated liquids are significantly different from those of pure liquid because dissolved gas bubbles are released prematurely, blocking effective heat transfer and sometimes

causing the rocket chamber wall to burn out. Release of dissolved gases and loss of thermal margin causes two-phase flow. Two-phase flow has a higher pressure drop than clean single-phase flow. In other cases, the release of gas bubbles may cause thrust anomalies of rocket engines fed with two-phase propellant. An arcjet may extinguish if gas bubbles pass through the gas generator. Multitudes of gas bubbles (foam) make hydrazine more sensitive to explosion by adiabatic compression. Solubility-pressure relationships are governed by Henry's law

$$\chi = KP$$

where  $\chi$  is the mol fraction of dissolved gas,  $P$  is the partial pressure of the gas, and  $K$  is the solubility constant, or, rather, coefficient. If the pressure is entered in units of atmospheres, then the unit of  $K$  is  $\text{atm}^{-1}$ .

Henry's law describes the maximum amount of pressurant gas that can dissolve in a liquid under equilibrium conditions. The law states that at a constant temperature the concentration of a gas in the liquid phase is proportional to the partial pressure of the dissolving gas in the gas phase:

$$P_g = \chi_g \times k_{H,p,c} = N_{\text{gas}}/N_{\text{solvent}} \times k_{H,p,c}$$

where  $P_g$  is the partial pressure of the dissolving gas in the gas phase,  $\chi_g$  is the mol fraction of dissolved gas,  $k_{H,p,c}$  is Henry's constant (coefficient) in the dimension of  $\text{atm L/mol}$ , and  $N_{\text{gas}}$  and  $N_{\text{solvent}}$  are the number of mols in the saturated solution.

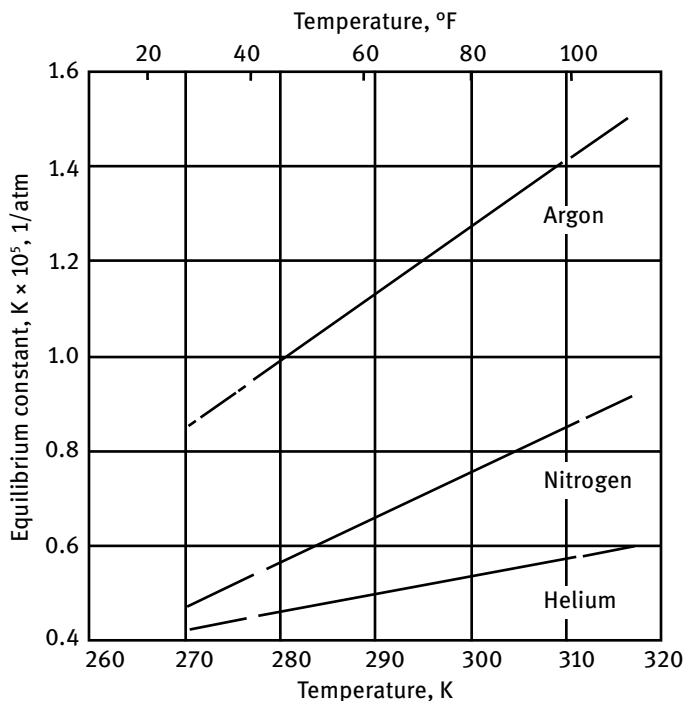
In reality, the variation of the partial pressure of a gas is never completely linear with the variation of the mol fraction  $\chi_g$  of gas in the liquid phase, especially when it is considered over the entire concentration range from  $\chi_g = 0$  to  $\chi_g = 1$ . Nevertheless, for low concentrations of gas in the liquid phase, when  $\chi_g < 0.01$ , the variation of mol fractions usually fit a linear relation within experimental error.

Because several forms of equations are used to express Henry's law, and all  $k_H$  may be referred to as Henry's law constants, readers of the technical literature must be quite careful to verify which version of the equation is being used because the constant will have different numbers and different units.

Henry's constant varies with temperature, which is why it would be better to call it Henry's *coefficient* instead of Henry's *constant*. Depending on the gas and the solvent, solubility can increase or decrease with increasing temperature. In a closed vessel with liquid at the bottom and gas in the ullage, when the temperature increases, **(1)** the density of the liquid propellant decreases, which leads to a smaller ullage volume and compression of the ullage volume gases. In addition, **(2)** the vapor pressure of the propellant increases, and in some cases, **(3)** the gas solubility increases. In tanks with a small ullage volume fraction the effects of **(1)** and **(3)** are accentuated.

The solubility of common pressurant gases (nitrogen, argon, helium) in hydrazine in the form of  $K$  as a function of temperature can be read from Figure 26, but these data were obtained only at very low pressure and were later shown to be inconsistent with





**Figure 26:** Gas solubility in liquid  $\text{N}_2\text{H}_4$  as a function of temperature at low pressure. (Chart created by Schmidt 2000, based on data from [263])

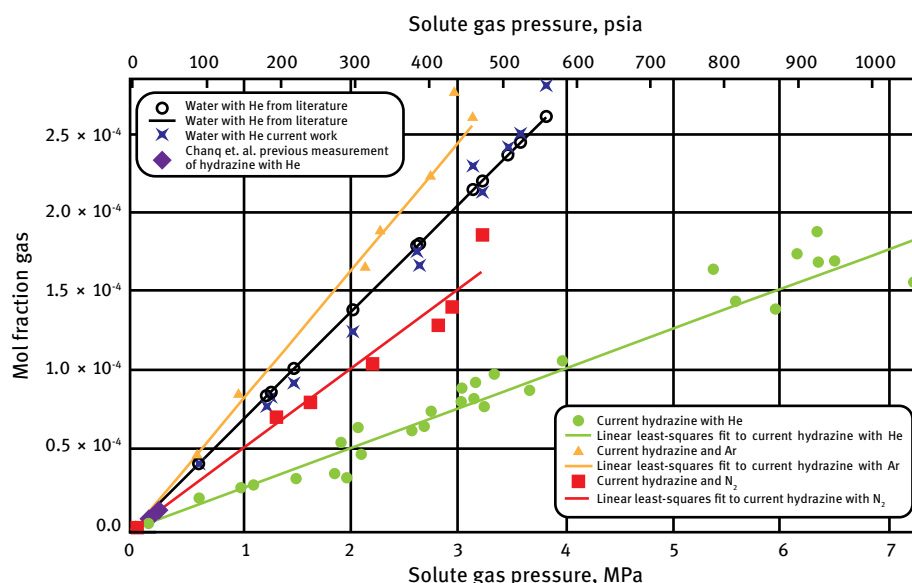
high pressure data. The newer data exhibited solubilities about half of what is shown in Figure 26.

The unit of  $K$  in this image is  $\text{atm}^{-1}$ . Most of the pressurant gas solubility data are from [263–265]. Similar data are available for methylhydrazines. For several decades, these were the only gas solubility data available in the open literature. These experiments were conducted in glass bulbs over a pressure range of 110 to 234 kPa (16 to 34 psia). The previous testing was limited due to the difficulties in conducting high-pressure experiments in glass bulb test apparatus. Although this pressure range is close to the pressure used during propellant filling on the ground, it is much lower than typical operating pressures of 1.38 to 2.8 MPa (200 to 400 psia) in satellites. Henry's law is obeyed for dilute solutions; thus, these older data should theoretically scale with pressure. However, there is considerable uncertainty involved in extrapolating data with 25% uncertainty an order of magnitude above its measured pressure range. The measured values for the mol fraction of helium at 293.16 K were  $0.52 \times 10^{-5}$  at 110 kPa and  $1.10 \times 10^{-5}$  at 234 kPa.

Attempts have been made to derive gas solubility for binary mixtures of hydrazine and UDMH from statistical thermodynamic considerations [266]. Henry's law constant

for the solubility of different gases in liquid hydrazine, MMH, and UDMH was computed from force field models [240].

Extending gas solubility measurements to higher pressures, the solubility of helium in hydrazine starting at 3.4 and 6.9 MPa (500 and 1000 psia) was measured by connecting thermostatted Teflon-lined stainless-steel cylinders of known volumes and observing the decay of pressure as the gas dissolved in the liquid, with different amounts of hydrazine loaded to vary the ullage, and with and without agitation of the liquid [267]. The accuracy of the apparatus and method was confirmed by measuring the solubility of helium in water and comparing the results to well-known literature data for water, also included in Figure 27 for comparison. Argon is more soluble in hydrazine than nitrogen and nitrogen is more soluble than helium.



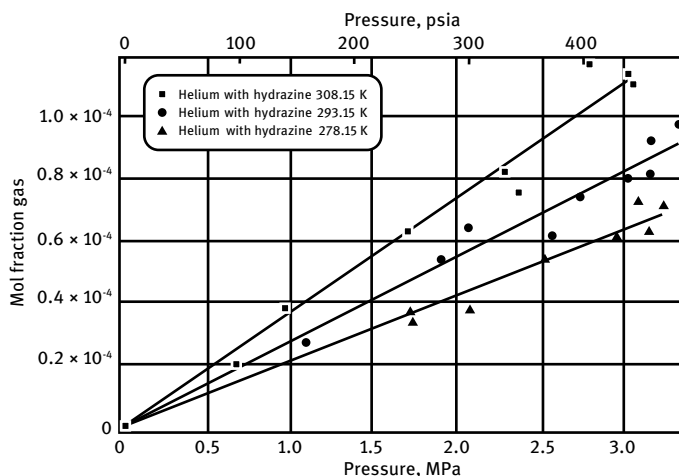
**Figure 27:** Measured mol fractions of gases in hydrazine as a function of gas pressure at high pressure at 293 K. (Reproduced and modified from [267]. Courtesy of and reprinted by permission of The Aerospace Corporation, granted 11 May 2021.)

The observed difference between the recent results and previous experiments can be discussed in terms of the equilibrium constant. The previous equilibrium constant [263–265] for helium dissolved in hydrazine was reported to be  $k_{\text{He}} = 5.0 \pm 1.0 \times 10^{-6} \text{ atm}^{-1}$ . The more recent determination was  $k_{\text{He}} = 2.60 \pm 0.35 \times 10^{-6} \text{ atm}^{-1}$  at 293.15 K. This value is about half (0.52) the previously measured value.

A small amount (5%) of water was added to hydrazine in recent experiments to test the effects of water content on helium solubility in an effort to explain the difference between the 1968 and 2015 data. Figure 6 of [267] shows the effect on the mol fraction of

helium as a result of increasing the water content of the hydrazine. The small change in water content did not greatly affect the measured mol fraction beyond the current scatter in the data. The purity of the hydrazine is not a likely source of the discrepancy between the 1968 and 2015 data.

It is interesting to note that in the case of hydrazine, the solubility of all three gases, helium, argon, and nitrogen, increases with temperature (Figure 28). This is different from the solubility behavior of other gases in other liquids.



**Figure 28:** Pressure dependence of the mol fraction for helium in hydrazine at three different temperatures. (Reproduced and modified from [267]. Courtesy of and reprinted by permission of The Aerospace Corporation, granted 11-May-2021.)

The equilibrium constants for argon and nitrogen in hydrazine were also found to be outside two standard deviations of the reference [263–265] results ( $k_{\text{Ar}} = 10.4 \pm 0.9 \times 10^{-6} \text{ atm}^{-1}$  at 293.15 K compared to the old value of  $k_{\text{Ar}} = 11.6 \pm 0.8 \times 10^{-6} \text{ atm}^{-1}$ ; and  $k_{\text{N}_2} = 5.13 \pm 0.78 \times 10^{-6} \text{ atm}^{-1}$  at 293.15 K compared to the old value of  $k_{\text{N}_2} = 6.9 \pm 0.4 \times 10^{-6} \text{ atm}^{-1}$  [267]).

It would be desirable to have a portable analytical instrument that could determine the propellant gas saturation level (like oxygen saturation in human blood) at launch sites where satellites are fueled. The method should also be capable of telling the difference between helium and other dissolved gases. There is always a small amount of nitrogen dissolved in hydrazine as a result of its slow decomposition during storage. Helium solubility in hydrazine at 295 K and 1786 kPa (245 psig) measured by a gas chromatographic technique was approximately 45% lower than previously published values [268]. There was significant scatter in five identical samples analyzed consecutively. The average of five measured values was 6.1 ppm (where ppm is the mass of helium/mass of propellant), whereas most other

publications reported 11.3 ppm. The scatter may be due to problems with reproducibly sampling saturated liquids under pressure. Hydrazine was saturated by sparging for 3 h at 295 K and 1786 kPa and allowing it to stand for 12 h to equilibrate. Samples taken after longer sparging times showed no further increase in saturation.

A gas chromatographic method was used to analyze dissolved helium in hydrazine and determine the time required to achieve saturation in stagnant (non-stirred) tanks loaded with hydrazine [269]. The time to achieve saturation at 482 kPa (70 psia) was 5 h.

Another purely mechanical method for determining the degree of helium saturation in hydrazine is to take a sample into an evacuated cylinder of known volume, seal it off, then connect its vapor space to another evacuated cylinder with a known volume, and measure the pressure after the two cylinders have equilibrated [270].

After a series of upper-stage explosions that scattered orbital debris, it has become a requirement to dump all residual propellant at the end of a mission and inert (passivate) the tanks by exposing them to the vacuum of space. The rate at which liquid hydrazine will escape once the drain valve is opened will depend on the degree of pressurant gas saturation [271]. Suddenly opening the drain valve is like opening a champagne bottle with too much fizz that has not been precooled. Some, but not all, of the liquid will be ejected along with the released gas.

Another important parameter involved in the mechanism of helium dissolving into hydrazine is the diffusion coefficient of the gas into the hydrazine liquid. This number has not previously been measured in the open literature. New experiments have attempted to measure this number for the first time [267]. The solubility was measured by determining the pressure drop in a closed stainless-steel bulb using pressure capacitance manometers. The pressure drop in a stirred bulb was used to determine the solubility, whereas the pressure drop in an unstirred bulb was used to determine the diffusion coefficient.

### 2.1.13 Thermal Conductivity of Hydrazine

#### 2.1.13.1 Thermal Conductivity of Solid Hydrazine

The thermal conductivity of solid hydrazine as expressed by the equation

$$\frac{dQ}{dt} = -Ak_s \frac{\delta T}{\delta x}$$

was measured as the temperature differential on a slab of frozen hydrazine with a surface area of  $A = 62.07 \text{ cm}^2$  and a thickness of 1.27 cm and calculated as  $k_s = 1.569 \times 10^{-1} \text{ W m}^{-1} \text{ K}^{-1} = 3.750 \times 10^{-3} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1} = 2.520 \times 10^{-4} \text{ BTU s}^{-1} \text{ ft}^{-1} \text{ }^\circ\text{F}^{-1}$  [272].

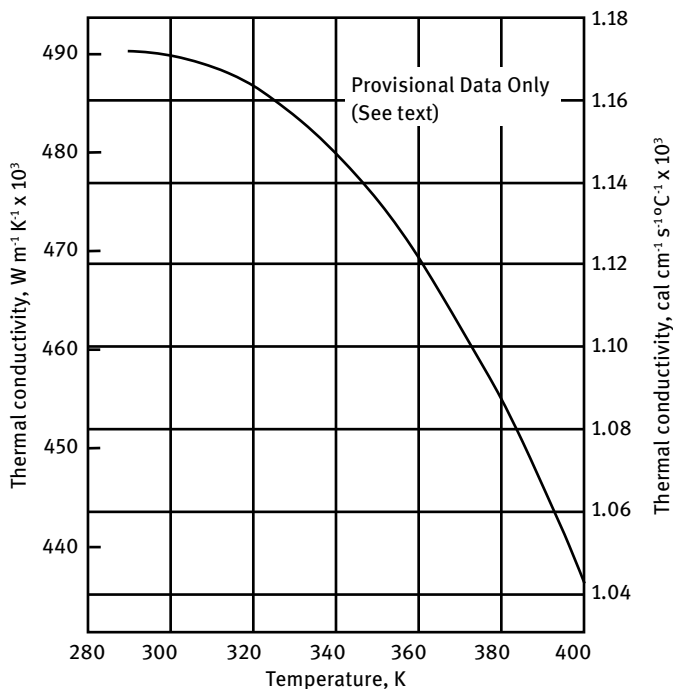
#### 2.1.13.2 Thermal Conductivity of Liquid Hydrazine

No experimental data have been published so far on the thermal conductivity of liquid hydrazine for a wide range of temperatures. A polynomial equation for calculating

thermal conductivity was found in a second-hand source, but no details were given as to how this equation was obtained [273]:

$$\lambda = 2.1067 \times 10^{-4} + 6.5541 \times 10^{-6}T - 1.1179 \times 10^{-8}T^2$$

where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. The curve illustrated in Figure 29 is only based on approximate data and not very accurate. We hesitated to include such preliminary data in this book, but more accurate data could not be found.



**Figure 29:** Thermal conductivity of liquid hydrazine. (Reproduced and modified from [171].)

Liquid thermal conductivity for hydrazine was estimated by means of a modified Schaeffer and Thodos correlation

$$k_L = k_c q(\text{Tr}, \text{Pr})$$

where  $k_c$  represents critical thermal conductivity and  $q(\text{Tr}, \text{Pr})$  is a functional relationship available from tables [102]. According to these data, the liquid thermal conductivity of hydrazine drops nearly linearly from  $2.2 \times 10^{-3} \text{ cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$  at 273 K to  $9 \times 10^{-4} \text{ cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$  at 520 K.

A single data point of  $0.50 \text{ W m}^{-1} \text{ K}^{-1}$  ( $0.29 \text{ BTU h}^{-1} \text{ ft}^{-1} \text{ }^{\circ}\text{F}^{-1}$ ) at  $293 \text{ K}$  referenced from another second-hand source was found in an old Jet Propulsion Laboratory (JPL) report [274]. The thermal conductivity of liquid hydrazine/methanol mixtures has also been measured [185, 186]. A thermal conductivity of  $5.4 \times 10^{-1} \text{ W m}^{-1} \text{ K}^{-1}$  ( $1.3 \times 10^{-3} \text{ cal }^{\circ}\text{C}^{-1} \text{ cm}^{-1}$ ) was measured for pure hydrazine in this series. This number is much higher than data reported by other sources.

The thermal conductivity of liquid hydrazine was measured by a steady-state hot-wire method at  $293.15 \text{ K}$  and  $0.101 \text{ MPa}$  [202, 203]. Eight pure organic liquids were used as reference liquids to calibrate the apparatus. The thermal conductivity was determined to be  $\lambda = 0.32 \pm 0.03 \text{ W m}^{-1} \text{ K}^{-1}$  at  $293.5 \text{ K}$  and  $0.101 \text{ MPa}$ , in agreement with the previous measurements of Safarov and Zaripova [275]. The thermal conductivity was determined to change very little over the pressure range of  $0.101$ – $2.068 \text{ MPa}$ . The pressure dependence of the thermal conductivity was found to not vary within error of the experiment in a pressure range of  $0.101$  to  $2.068 \text{ MPa}$ . The measurement of the thermal conductivity of hydrazine as a function pressure by the transient hot-wire method demonstrated that pressures typical for on-orbit storage of hydrazine do not change the thermal conductivity much. Large inaccuracies were obtained when estimating the thermal conductivity of hydrazine using standard estimation methods that utilize velocity of sound data.

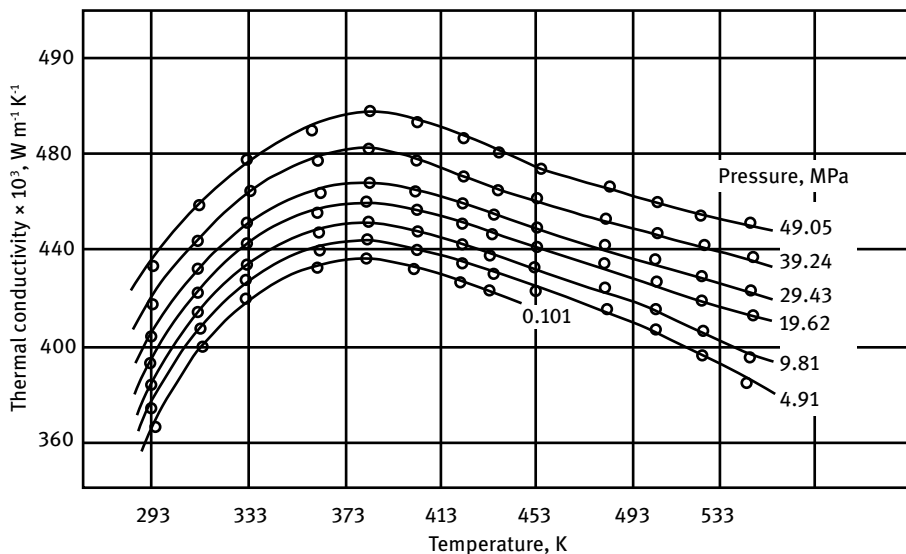
#### 2.1.13.3 Thermal Conductivity of Hydrazine Vapor

It is very difficult to measure the thermal conductivity of hydrazine vapor due to incipient decomposition. The thermal conductivity of hydrazine vapor was measured at  $800 \text{ Pa}$  ( $6 \text{ mm Hg}$ ) and  $298 \text{ K}$  and found to be  $3.49 \pm 0.04 \times 10^{-5} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^{\circ}\text{C}^{-1} = 1.4602 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$  [276]. Previously it had been assumed that the thermal conductivity of hydrazine was similar to that of ethylene ( $\text{N}_2\text{H}_4 = \text{C}_2\text{H}_4$ ), when in fact it is not. The thermal conductivity of hydrazine is closer to that of methanol, which is also a polar molecule and has an identical molecular weight. Using the same temperature dependence as methanol, the thermal conductivity at  $6 \text{ mm Hg}$  and higher temperatures was extrapolated to be  $6.5$ ,  $7.5$ ,  $15$ , and  $30 \times 10^{-5} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ }^{\circ}\text{C}^{-1}$  at  $373$ ,  $473$ ,  $773$ , and  $1273 \text{ K}$ , respectively. In another attempt, the thermal conductivity of hydrazine vapor was calculated using Bromley's correlation, with negligible contribution by internal rotation [102]. According to this correlation, thermal conductivity increases from  $10^{-5} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  at  $273 \text{ K}$  to  $2 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$  at  $873 \text{ K}$  (assuming that hydrazine vapor is stable enough to survive this temperature).

#### 2.1.13.4 Thermal Conductivity of Hydrazine/Water Mixtures

It is not quite clear why the thermal conductivity of hydrazine hydrate solutions was measured up to very high pressures and very high temperatures and at concentrations substantially above those encountered where hydrazine hydrate is used to deoxygenate boiler feedwater. There may be other applications we do not know about yet. The thermal conductivity of hydrazine hydrate was measured from atmospheric

pressure to 49.05 MPa and from 293 to 553 K [180, 277]. The results (Figure 30) showed that the thermal conductivity increased with pressure and went through a maximum near 380 K. Further study showed that thermal conductivity correlated quite well with density, which also went through a maximum when plotted in relative units [275, 278].



**Figure 30:** Thermal conductivity of hydrazine hydrate at high pressures and temperatures. (Republished and modified from [277], with permission of ©1993 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

#### 2.1.14 Heat-Transfer Coefficient of Hydrazine

Knowledge of the heat-transfer characteristics of hydrazine is important in the design of injectors for rocket engines and gas generators using this propellant. Although at one time the XLR117-NA-1 rocket engine intended for use on the NOMAD upper stage apparently was regeneratively cooled with hydrazine and probably had to be purged with inert gas after each engine shutdown, by now most rocket engine designers have begun to realize that hydrazine cannot be used as a coolant in regeneratively cooled rocket engines. Not that it is a poor coolant; on the contrary, it is a good coolant, almost as good as water; it is just that during the heat soakback after shutting down the engine, the residual hydrazine in the cooling jacket and injector passages may explode. An excellent summary of the heat flux limits of several storable rocket propellants, including hydrazine, MMH, UDMH, and their mixtures, is provided in [279]. After previous futile – and, in part, disastrous – attempts to use anhydrous hydrazine as a cooling medium in regeneratively cooled rocket engines [280], nobody now seriously considers anhydrous hydrazine as suitable fuel in regeneratively fuel-cooled engines.

However, hydrazine can be used in film-cooled rocket engines. It was thus a significant improvement when the 50:50 mixture of hydrazine with UDMH (called Aerozine-50) was developed in the 1950s and proved to be a suitable regenerative coolant.

The heat-transfer characteristics of hydrazine flowing in electrically heated round tubes were studied at Rocketdyne [281–283]. Burnout heat flux and the effect of additives on explosive burnout were investigated. A total of 143 determinations of non-boiling convective heat transfer were made with hydrazine over the following range of conditions: liquid velocity 7–37 m/s (23–123 ft/s), bulk temperature 293–343 K (68–158 °F),  $\Delta T = T_{\text{wall}} - T_{\text{sat}} = 30 - 250$  K (55–450 °F), and pressures of 13.8–69 bar (200–1000 psia). Forced-convection results were correlated using dimensionless parameters by the equations due to McAdams or Sieder and Tate and by a statistical fitting of data to the general dimensionless equation

$$\nu = a \text{Re}^b \text{Pr}^c \left( \frac{T_W}{T_B} \right)^d$$

where  $\nu$  is the Nusselt number, Re the Reynolds number, Pr the Prandtl number,  $a$ ,  $b$ ,  $c$ ,  $d$  coefficients characteristic for each fluid, and  $T_W/T_B$  the wall:bulk temperature ratio. The temperature rather than the viscosity ratio was used because insufficient data on the viscosity of hydrazine at higher temperature were available at that time. A curve-fitting exercise gave the best fit of data when the following coefficients and exponents were used:

$$\nu = 0.00161 \text{Re}^{0.98} \text{Pr}^{0.86} \left( \frac{T_W}{T_B} \right)^{0.24}$$

The results of more than 80 tests in the nucleate boiling regime at pressures from 1.376 to 6.88 MPa (200 to 1000 psia), liquid velocities from 7.3 to 25.2 m/s (24–83 ft/s), and bulk temperatures from 313 to 400 K (104–259 °F) were scattered over a wide range, and no numerical relationship could be derived. The maximum superheat measured was  $\Delta T = 42$  K (76 °F). In determining the peak boiling heat flux, the wall temperatures were increased until burnout occurred.

Many of these tests were accompanied by explosions. As would be expected for any liquid, the peak flux was found to increase with decreasing feed temperature and increasing velocity. Whereas Bartz [284, 285] found little pressure effect over the range 2.06–8.26 MPa (300–1200 psia), the Rocketdyne tests showed a distinct pressure dependence between 4.82 and 6.88 MPa (700–1000 psia). The data for the maximum heat flux at burnout can be represented by the following two equations:

1. In BTUs:  $Q/A$  in  $\text{BTU in.}^{-2} \text{s}^{-1}$ ,  $h$  in  $\text{BTU in.}^{-2} \text{s}^{-1} \text{°F}^{-1}$ ,  $T$  in °F:

$$\frac{Q}{A} = -0.21 + 0.013(T_S - T_B) + h(T_W - T_B) \quad \text{at } p = 700 \text{ psia}$$

$$\frac{Q}{A} = -0.28 + 0.052(T_S - T_B) + h(T_W - T_B) \quad \text{at } p = 1000 \text{ psia}$$



2. In SI units:  $Q/A$  in  $\text{W/m}^2$ ,  $h$  in  $\text{W m}^{-2} \text{K}^{-1}$ ,  $T$  in K:

$$\frac{Q}{A} = -3.43 \times 10^5 + 3.82 \times 10^4 (T_S - T_B) + h(T_W - T_B) \quad \text{at } p = 4.82 \text{ MPa}$$

$$\frac{Q}{A} = -4.57 \times 10^5 + 1.53 \times 10^5 (T_S - T_B) + h(T_W - T_B) \quad \text{at } p = 6.88 \text{ MPa}$$

where  $h$ , the convective liquid film coefficient, must be calculated from the Nusselt number equation shown earlier and  $T_S$  is the saturation temperature.

Burnout with mixtures of hydrazine with ethanol, ethylene diamine, or UDMH occurred only at higher heat fluxes. These additives appeared to have a stabilizing effect on hydrazine.

Some typical experimental values of  $(q/A)_{\text{ul}}$  are listed in Table 23. As can be seen from the numbers for hydrazine, maximum heat-transfer rates are less than double when the linear flow speed is tripled.

**Table 23:** Heat flux for surface nucleate boiling of hydrazine at upper limit.

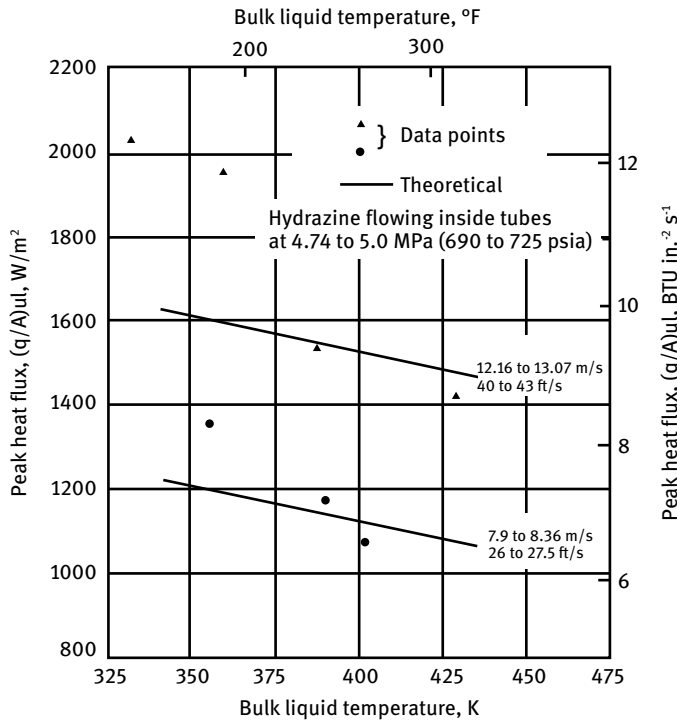
| Propellant                    | Pressure |      | Bulk temperature |     | Velocity |      | $(q/A)_{\text{ul}}$                   |                   |
|-------------------------------|----------|------|------------------|-----|----------|------|---------------------------------------|-------------------|
|                               | MPa      | psia | K                | °F  | m/s      | ft/s | BTU in. <sup>-2</sup> s <sup>-1</sup> | W/cm <sup>2</sup> |
| N <sub>2</sub> H <sub>4</sub> | 4.128    | 600  | 339              | 150 | 9.12     | 30   | 12.2                                  | 1994              |
| N <sub>2</sub> H <sub>4</sub> | 4.128    | 600  | 339              | 150 | 18.24    | 60   | 16                                    | 2165              |
| N <sub>2</sub> H <sub>4</sub> | 4.128    | 600  | 339              | 150 | 27.36    | 90   | 22                                    | 3595              |
| For comparison:               |          |      |                  |     |          |      |                                       |                   |
| Ae-50                         | 4.128    | 600  | 339              | 150 | 9.12     | 30   | 7.8                                   | 1275              |
| Ae-50                         | 4.128    | 600  | 339              | 150 | 27.36    | 90   | 15.9                                  | 2598              |
| NH <sub>3</sub>               | 3.440    | 500  | 333              | 140 | 9.12     | 30   | 5.3                                   | 866               |
| NH <sub>3</sub>               | 3.440    | 500  | 333              | 140 | 18.24    | 60   | 7.9                                   | 1291              |

Data sources: [282, 286]

Experimental data for hydrazine in Figure 31 are compared with predictions from the theoretical equation

$$(q/A)_{\text{ul}} = K\lambda\rho_v \left[ \frac{\sigma g_c g(\rho_L - \rho_v)}{\rho_v^2} \right]^{1/4} \left[ 1 + \left( \frac{\rho_L}{\rho_v} \right)^{0.923} \frac{C_L(T_S - T_L)}{25\lambda} \right] \\ + \left[ K' \frac{k}{D} \text{Re}^m \text{Pr}^n (T_W - T_L)_{\text{ul}} \right]$$

where  $K = \pi/24$ ,  $K' = 0.023$ ,  $m = 0.28$ ,  $n = 0.4$ ,  $\lambda$  is the latent heat of vaporization,  $\rho$  the density,  $\sigma$  the surface tension,  $g_c$  the universal constant ( $32.17 \text{ lb}_m \text{ ft lb}_f^{-1} \text{ s}^{-2}$ ),  $g$  the acceleration due to gravity,  $T_S$  the saturation temperature,  $T_W$  the wall temperature,  $T_L$  the fluid bulk temperature, and the subscript L is for liquid, V is for vapor, and ul is for the upper limit.



**Figure 31:** Peak heat flux for hydrazine flowing inside tubes. (Reproduced and modified from [286])

Considering the difficulty of measurements with near-boiling hydrazine, the agreement between experimental and theoretical data is reasonably good.

The upper limit of nucleate boiling ( $q_{ul}$ ) for hydrazine was measured for commercial-grade hydrazine in a range of 0.68 to 8.26 MPa (100 and 1200 psia), bulk temperatures from 292.5 to 445.9 K (67–343 °F), and velocities of 0.3–28.4 m/s (1–93 ft/s). Values of  $q$  ranged from  $1.09 \times 10^6$  to  $4.46 \times 10^7\ W/m^2$  (0.67 to 27.27  $BTU\ in^{-2}\ s^{-1}$ ) and can be represented by the following equation [274]:

$$q_{ul} = \left[ 1 - 0.236 \left( \frac{p - 675}{675} \right) \right]^2 \left[ 6.9 - 0.246v - T_b(0.015 + 2.7 \times 10^{-4} \times v) \right]$$

where  $p$  is the pressure in psia,  $v$  the velocity in ft/s,  $T_b$  the bulk temperature in °F, and  $q$  the heat flux in  $BTU\ in^{-2}\ s^{-1}$ . A less complicated equation is available that represents  $q_{ul}$  at 1.03–2.10 MPa (150–305 psia) and 0.6–9.4 m/s (2–31 ft/s), where it predicts  $q_{ul}$  more accurately than does the equation shown earlier:

$$q_{ul} = 5.98 + 0.304v - T_b(0.01175 + 5.47 \times 10^{-4}v)$$

The cooling capability of hydrazine was found to be far superior to that of any other storable rocket fuel tested at JPL up to that time, as long as the liquid was kept flowing and stagnant areas were avoided. A hydrazine mixture containing 10% ethylenediamine had slightly lower burnout limits than did pure hydrazine. Numerous attempts have been made to use hydrazine as a fuel in regeneratively cooled rocket engines, but many of these ended in disaster. There are several reports in the literature on previous efforts of this kind, but the reports are quite ancient and not easily accessible [280, 284, 287].

Burnouts due to exothermic reactions are characterized by an abrupt termination of the normal forced convection heat transfer. Generally, there is no warning of incipient burnout. There is no transition regime as with thermally stable fuels. There are significant contributions by sudden exothermic reactions in the boundary layer. Since these are associated with gas evolution, the quality of the liquid stream suffers at the same time. Catalytic contributions by the tube wall cannot be excluded. The  $q_{ul}$  in AMS 4130 steel tubes was as much as 75% lower than that in corrosion resistant eutectic steel (CRES) CRES-347 tubes; Al-52-SO, steel 17-7PH, Hastelloy-C, nickel braze, and even copper tubes behaved like CRES in these tests [274].

Scattered ultimate heat-flux data are available for hydrazine mixtures containing 5, 10, or 12% ethanol or 5% ammonia [279]. None of these additives improved the burnout limitations of hydrazine.

The heat flux at the upper limit of nucleate boiling was determined for two hydrazine-UDMH mixtures containing 50 and 77% hydrazine [288]. Nominal test conditions for the 50:50 mix ranged from 3.78 to 7.57 MPa fluid static pressure, 9.1–27 m/s fluid velocity, and 311–366 K liquid bulk temperature. The other mix was investigated only over a narrower range from 3.78 to 6.19 MPa and at two bulk temperatures, 333 and 366 K. Testing was done in an electrically heated CRES-347 tube with 6.3-mm outer diameter (O.D.) and 0.22-mm walls. The heated section was 75 mm long. The transition from nucleate to film boiling manifested itself experimentally by a sudden large increase in the tube-wall temperature. In most cases, the temperature rise resulted in a loss of tube-wall strength, and the test section would rupture before the heater power could be turned off. The  $q_{ul}$  of the 50:50 mix was typically 65% of that previously determined for pure hydrazine under similar conditions. The  $q_{ul}$  ranged from 229 to 638 cal cm<sup>-2</sup> s<sup>-1</sup> (5.85 to 16.33 BTU in.<sup>-2</sup> s<sup>-1</sup>). The numerical data can be approximated by the equation

$$q_{ul} = 7.86 - 4.93 \times 10^{-3}(p - 1100) + 0.1343(V - 50) - 1.20 \times 10^{-2}(T_L - 160)$$

where  $q_{ul}$  is the upper limit of nucleate boiling in BTU in.<sup>-2</sup> s<sup>-1</sup>,  $p$  the static fluid pressure in psia,  $V$  the fluid velocity in ft/s, and  $T_L$  the bulk temperature in °F. Ninety-five percent of the test data were within  $\pm 15\%$  of the  $q_{ul}$  dependence calculated using this equation. The mixture containing 77% hydrazine and 23% UDMH had upper limits at 77% of those of hydrazine. Demonstrated upper-limit heat fluxes ranged from  $1.31 \times 10^7$  to  $3.06 \times 10^7$  W/m<sup>2</sup> ( $312$ – $732$  cal cm<sup>-2</sup> s<sup>-1</sup> = 8 to 18.7 BTU in.<sup>-2</sup> s<sup>-1</sup>). Some of the older

reports on the heat-transfer properties of liquid hydrazine are more difficult to obtain [289].

### 2.1.15 Critical Point Constants of Hydrazine

For thermally stable fluids, it is often possible to determine the critical constants experimentally. This is not possible for hydrazine because it begins to decompose already at temperatures substantially below the critical temperature. Critical point parameters can be extrapolated from other physical and thermodynamic properties.

In some extreme cases of heat transfer to hydrazines at very high pressures and very high temperatures, the conditions may momentarily approach the critical point and reach supercritical conditions where totally different physical laws govern heat transfer. While this regime is well explored for water, liquid hydrogen, and other thermally stable fluids, very little information is available on hydrazines under supercritical conditions. The critical constants of hydrazine(s) are very difficult to determine because the liquid usually undergoes decomposition before the critical point is reached. Audrieth [7] on page 57 reported a critical temperature of 653 K (380 °C) for hydrazine based on the archaic work by [169]. The corresponding critical pressure given was 1.469 MPa = 145 atm = 2131 psia. Both sets of data are probably not very accurate. In the words of Audrieth: “*There is some question about the accuracy of the critical constants in view of the known tendency of hydrazine to undergo decomposition at higher temperatures.*” The data do not get more reliable each time they are quoted and passed on to the next generation of chemists. Most critical point data for hydrazine(s) are calculated from other physical and thermodynamic properties measured under noncritical conditions.

A critical review of critical point data [105] was unable to locate any more recent or more reliable data other than the ancient data traced back to Audrieth and de Bruyn. The set of critical point data chosen by Giordano for further calculations was  $T_c = 653.15$  K,  $p_c = 14.69$  MPa, and  $V_c = 4.335 \times 10^{-3}$  m<sup>3</sup>/kg. This is similar to critical point data derived by Das and Ausloos in 1968:  $T_c = 653.16$  K,  $p_c = 14.69$  MPa = 145 atm,  $\rho_c = 0.1389$  L/mol = 7.199 mol/L = 230.7 g/L = 0.2307 g/cm<sup>3</sup> = 4.335 cm<sup>3</sup>/g.

## 2.2 Thermodynamic Properties of Hydrazine

Hydrazine might still be an obscure chemical with few applications were it not for its unique enthalpy of formation, which is positive, such that on decomposition of hydrazine to its elements and a little ammonia, a good amount of useful energy is released. Thermochemical properties such as heat capacity, heat of formation, heat of combustion, heat of vaporization, and other thermal characteristics are needed to calculate the useful energy derived from hydrazine in several industrial applications, including rockets.

There are several summary publications with thermodynamic property data for hydrazine. The most thorough review was performed by Giordano [105]. The summary by Das and Kuloor in 1968 [173] contained eight pages of tabulated data for the specific volume, enthalpy, and entropy of hydrazine liquid and vapor and presented a full-page temperature-entropy diagram, the only one in the entire literature. The thermodynamic data used most often for rocket performance calculations are the JANNAF tables [290]. The JANNAF tables usually contain one page discussing the source of data, but it is incomplete. The curators of the NIST Chemistry WebBook web site [291] have done an incomplete job in summarizing and evaluating existing thermodynamic data. Nevertheless, the NIST Chemistry WebBook data are referenced here in our summary. See also [292].

### 2.2.1 Heat Capacity of Hydrazine

#### 2.2.1.1 Heat Capacity of Liquid Hydrazine

Whereas heat capacity data for ideal vapors can be calculated from IR or microwave spectroscopic data, heat capacity determination of liquids and solids depends on calorimetric measurements, which are usually less accurate. Heat capacities are important for the calculation of temperature changes in hydrazines during industrial processes. The heat capacity data are also required for the conversion of standard enthalpies and entropies of formation to other temperatures (other than 298 K).

Multiple determinations of the heat capacity of hydrazine have been made over the past century, but not all have yielded reliable data. It is difficult to decide in retrospect which data are the most reliable to use for future work. The most thorough critical examination of heat capacity data was done by Giordano in 2001.

In reviewing heat capacity data for hydrazine, we have attempted to arrange them in chronological order. That is not necessarily the same sequence they would be in if ranked by degree of reliability.

Data on the heat capacity of liquid hydrazine are available from at least three sources. Some data are for anhydrous (laboratory-prepared) hydrazine, [107, 176], whereas other data are for propellant-grade hydrazine [293]. Because propellant-grade hydrazine contains some impurities, the results differ slightly.

The heat capacity of a hydrazine sample presumed to be at least 99.75% by weight was measured at 12–340 K [107] (Table 24). The phase change at 274.69 K was associated with a melting enthalpy of 12.657 kJ/mol (3.025 kcal/mol = 94.4 cal/g).

The heat capacity is a function of the pressure, and results would be different if measurements were conducted at saturation pressure or under truly isobaric conditions. The heat capacity data by Hough, Mason, and Sage [176] for liquid hydrazine were lower than those reported by Scott et al. [107] over the entire range of data, with the maximum deviation (–1.0%) occurring at 313 K. If one combines the two sets of data and applies a curve-fitting method, the following equation will represent the best

combination of heat capacity data for liquid hydrazine [171]:

$$c_p = 0.88415 - 1.3949 \times 10^{-3}T + 3.0074 \times 10^{-6}T^2$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin, or

$$c_p = 3.6993 - 5.8363 \times 10^{-3}T + 1.2583 \times 10^{-5}T^2$$

where  $c_p$  is the heat capacity in  $\text{J g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin.

The sample used by Ahlert and Younts [293] for measurements in a range of 331 to 464 K was a propellant-grade hydrazine containing 2.5%  $\text{H}_2\text{O}$ , 0.5%  $\text{NH}_3$ , and traces of aniline and heptane. The heat capacity measurements were made in a counterflow heat exchanger under dynamic conditions. At the highest temperature, hydrazine decomposition became noticeable. Therefore, a correction for heat released by decomposition was applied. The heat capacity of this fuel was up to 1.3% higher than that of pure hydrazine, and the slope of the straight-line function was 1.5% less steep in the overlapping temperature range. A linear least-squares fit of the Ahlert and Younts data gave an equation valid for the range from 331 to 464 K

$$c_p = 0.734 + 5.33 \times 10^{-4}t$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{K}^{-1}$  and  $t$  is the temperature in  $^{\circ}\text{C}$ . Other sources ([171], see Equation 2.3-16) represent the same Ahlert and Younts [293] data for a propellant-grade hydrazine by a more sophisticated equation (a higher-order polynomial fit):

$$c_p = 0.29512 + 2.0193 \times 10^{-3}T - 1.8559 \times 10^{-6}T^2$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin, which corresponds to

$$c_p = 1.2348 + 8.4487 \times 10^{-3}T - 7.7651 \times 10^{-6}T^2$$

in SI units, where  $c_p$  is the heat capacity in  $\text{J g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. Curve-fitting JANNAF data gave the following equation for liquid hydrazine from 100 to 800 K [208]:

$$C_p = 80.957 + 5.2929 \times 10^{-2}T + 3.384 \times 10^{-5}T^2$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin, or, in mass units,

$$c_p = 2.5263 + 1.6517 \times 10^{-3}T + 1.056 \times 10^{-6}T^2$$

where  $c_p$  is the heat capacity in  $\text{J g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin.

Data on the heat capacity of pure liquid hydrazine are also contained in the following section on the heat capacity of hydrazine mixtures. The reader in search of hydrazine data is thus advised to review the following data on hydrazine mixtures

as well. Additional molar heat capacity data on liquid and gaseous hydrazine are contained in Tables 24 and 28, together with the heat of formation and other thermochemical data. See also [294].

### 2.2.1.2 Heat Capacity of Hydrazine Vapor

Some of the first heat capacity data derived from IR spectra of hydrazine vapor were those reported by Fresenius and Karweil [217] and Eucken and Krome [295]. The data from the two sources at 313 and 340 K (40 and 67 °C) were in good agreement.

Averaging experimental data from Fricke [210] and Scott et al. [107], as was done by Haws and Harden [172], the following polynomial function was obtained for the heat capacity of hydrazine vapor, but it turned out to be inconsistent with data shown in Table 3, Column 3 of Haws and Harden [172], a mistake that unfortunately was carried through two editions of the hydrazine book without being corrected in a timely manner. The incorrect equation is shown here as a warning (Do not use!):

$$c_p = 0.137857 + 5.2715 \times 10^{-5} T - 1.19907 \times 10^{-7} T^2$$

where  $c_p$  was the heat capacity in unspecified units and  $T$  was the temperature in unspecified units. This equation cannot be made to fit the Table 3, Column 3 data by assuming the temperature units are °C, °F, K, or °R or by changing the minus sign between the second and third terms to a plus sign.

JANNAF heat capacity data for hydrazine vapor from 300 to 1000 K [290] can be curve-fitted by equations derived by [208]:

$$C_p = 31.8832 - 5.397 \times 10^{-3} T + 3.13325 \times 10^{-4} T^2 - 4.16306 \times 10^{-7} T^3 + 1.69082 \times 10^{-10} T^4$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin, or, in mass units,

$$c_p = 9.9495 \times 10^{-1} - 1.6842 \times 10^{-4} T + 9.7777 \times 10^{-6} T^2 - 1.2991 \times 10^{-8} T^3 + 5.2764 \times 10^{-12} T^4$$

where  $c_p$  is the heat capacity in  $\text{J g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin.

### 2.2.1.3 Heat Capacity of Solid Hydrazine

Frozen hydrazine is not a good rocket propellant. Frozen hydrazine usually signifies a problem that may jeopardize mission success or even constitute a hazard to the population at large. The mission success of SOHO was in limbo for several months while hydrazine in propellant tanks was frozen [296]. A military satellite, referred to as USA 193, was launched into a low orbit in December 2006 but went out of control soon after, causing its load of hydrazine to freeze. There was concern that the chunk of frozen hydrazine in a spherical tank could survive uncontrolled re-entry in populated areas, so the satellite was shot down in February 2008 as a preventive measure. Calculations predicting the survival of the chunk of hydrazine needed to be based on the heat capacity and the heat of fusion of solid hydrazine.

**Table 24:** Heat capacity of solid and liquid hydrazine.

| Temperature                         |       |       | Heat capacity                         |       |                        |
|-------------------------------------|-------|-------|---------------------------------------|-------|------------------------|
| K                                   |       |       | K                                     |       |                        |
| J mol <sup>-1</sup> K <sup>-1</sup> |       |       | cal mol <sup>-1</sup> K <sup>-1</sup> |       |                        |
| Solid                               |       |       | Liquid                                |       |                        |
| 12                                  | 0.29  | 0.07  | 90                                    | 28.12 | 6.72                   |
| 13                                  | 0.39  | 0.095 | 95                                    | 29.54 | 7.06                   |
| 14                                  | 0.48  | 0.115 | 100                                   | 30.86 | 7.375                  |
| 15                                  | 0.58  | 0.14  | 110                                   | 33.39 | 7.98                   |
| 16                                  | 0.69  | 0.165 | 120                                   | 35.73 | 8.54                   |
| 17                                  | 0.86  | 0.205 | 130                                   | 37.95 | 9.07                   |
| 18                                  | 1.05  | 0.25  | 140                                   | 40.04 | 9.57                   |
| 19                                  | 1.26  | 0.30  | 150                                   | 42.02 | 10.045                 |
| 20                                  | 1.46  | 0.35  | 160                                   | 44.35 | 10.60                  |
| 25                                  | 2.84  | 0.68  | 170                                   | 45.75 | 10.935                 |
| 30                                  | 4.62  | 1.105 | 180                                   | 47.53 | 11.36                  |
| 35                                  | 6.71  | 1.605 | 190                                   | 49.27 | 11.775                 |
| 40                                  | 8.91  | 2.13  | 200                                   | 51.02 | 12.195                 |
| 45                                  | 11.19 | 2.675 | 210                                   | 52.76 | 12.61 ext <sup>a</sup> |
| 50                                  | 13.45 | 3.215 | 220                                   | 54.52 | 13.03 ext              |
| 55                                  | 15.65 | 3.74  | 230                                   | 56.25 | 13.445 ext             |
| 60                                  | 17.70 | 4.23  | 240                                   | 58.01 | 13.865 ext             |
| 65                                  | 19.66 | 4.70  | 250                                   | 59.75 | 14.28 ext              |
| 70                                  | 21.53 | 5.145 | 260                                   | 61.50 | 14.70 ext              |
| 75                                  | 23.26 | 5.56  | 270                                   | 63.26 | 15.12 ext              |
| 80                                  | 24.96 | 5.965 | 274.69                                | 64.06 | 15.31 ext              |
| 85                                  | 26.59 | 6.355 | —                                     | —     | —                      |
| Liquid                              |       |       |                                       |       |                        |
| 274.69                              | 97.44 | 23.29 | 310                                   | 99.58 | 23.80                  |
| 280                                 | 97.78 | 23.37 | 320                                   | 100.2 | 23.96                  |
| 290                                 | 98.37 | 23.51 | 330                                   | 101.0 | 24.14                  |
| 298.16                              | 98.82 | 23.62 | 340                                   | 101.8 | 24.34                  |
| 300                                 | 98.95 | 23.65 | —                                     | —     | —                      |

<sup>a</sup> ext = extrapolated

Data source: [107]

The only complete set of heat capacity data for solid hydrazine is the ancient one based on the data by Scott et al. from 1949 [107], summarized in Table 24. Audrieth and Ackerson-Ogg [7], pages 68–69, have developed six different curve-fitted equations that can be used to calculate the heat capacity in selected temperature ranges and can be used to integrate for the enthalpy changes in frozen hydrazine as it warms or cools between different temperatures.

No other experimental determination of solid N<sub>2</sub>H<sub>4</sub> specific heat has ever been attempted since the Scott et al. [107] investigation. There have been examinations of



density, compressibility, and thermal conductivity of solid hydrazine [113], but no further work on heat capacity.

#### 2.2.1.4 Heat Capacity of Hydrazine/Water Mixtures

Hydrazine/water mixtures are encountered during the production of hydrazine (hydrate) and need to be concentrated and dehydrated before a useful rocket propellant is obtained. Some hydrazine/water mixtures with 70% hydrazine are used as monopropellants in gas generators. The formation of unusual hydrates and associated clusters at certain hydrazine:water ratios, which already documented itself in unusual melting-point and viscosity behavior, is also partially reflected in the heat capacity of such mixtures. Hydrazine concentrations in boiler feedwater or in fuel cells are much lower than those in rocket propellants, but the physical properties of dilute solutions are included here and in many other publications.

The specific heats of hydrazine/water mixtures at the bubble-point pressure were determined in a stainless-steel bomb calorimeter for mixtures containing 48.3, 70.4, 90.3, and 99.9 mass-% hydrazine in water [297]. The temperature ranges for these mixtures were approximately 328 to 361 K, 316 to 361 K, 300 to 344 K, and 294 to 328 K (130 to 190, 110 to 190, 80 to 160, and 70 to 130 °F), respectively. This experiment should have included the 64%  $\text{N}_2\text{H}_4$  mixture, which corresponds to HH100. The heat capacity data of the binary hydrazine/water system are summarized in Table 25, which also shows data for pure hydrazine.

**Table 25:** Isobaric heat capacity of liquid hydrazine/water mixtures.

| Composition         | Heat capacity <sup>a</sup>         | Temperature, K |        |        |        |        |        |
|---------------------|------------------------------------|----------------|--------|--------|--------|--------|--------|
| Hydrazine<br>Mass-% | Units                              | 313            | 323    | 333    | 343    | 353    | 363    |
| 50                  | $\text{J g}^{-1} \text{K}^{-1}$    | 3.561          | 3.600  | 3.666  | 3.7417 | 3.818  | 3.894  |
| 50                  | $\text{cal g}^{-1} \text{°C}^{-1}$ | 0.8511         | 0.8605 | 0.8761 | 0.8943 | 0.9126 | 0.9306 |
| 60                  | $\text{J g}^{-1} \text{K}^{-1}$    | 3.494          | 3.516  | 3.576  | 3.629  | 3.675  | 3.718  |
| 60                  | $\text{cal g}^{-1} \text{°C}^{-1}$ | 0.835          | 0.8403 | 0.8546 | 0.8673 | 0.8783 | 0.8887 |
| 70                  | $\text{J g}^{-1} \text{K}^{-1}$    | 3.411          | 3.443  | 3.478  | 3.516  | 3.549  | 3.579  |
| 70                  | $\text{cal g}^{-1} \text{°C}^{-1}$ | 0.8152         | 0.8230 | 0.8313 | 0.8404 | 0.8483 | 0.8554 |
| 80                  | $\text{J g}^{-1} \text{K}^{-1}$    | 3.306          | 3.341  | 3.371  | 3.403  | 3.432  | 3.455  |
| 80                  | $\text{cal g}^{-1} \text{°C}^{-1}$ | 0.7902         | 0.7985 | 0.8057 | 0.8134 | 0.8203 | 0.8258 |
| 90                  | $\text{J g}^{-1} \text{K}^{-1}$    | 3.193          | 3.230  | 3.262  | 3.290  | 3.317  | 3.342  |
| 90                  | $\text{cal g}^{-1} \text{°C}^{-1}$ | 0.7632         | 0.7721 | 0.7796 | 0.7864 | 0.7927 | 0.7987 |
| 100                 | $\text{J g}^{-1} \text{K}^{-1}$    | 3.083          | 3.114  | 3.145  | 3.177  | 3.207  | 3.239  |
| 100                 | $\text{cal g}^{-1} \text{°C}^{-1}$ | 0.7368         | 0.7443 | 0.7517 | 0.7593 | 0.7665 | 0.7742 |

<sup>a</sup> Smoothed values.

Data Source: [176]

The data at 294.8 K (71 °F) are 0.03 cal/g higher than those reported by Scott et al. In a first, crude approximation, the heat capacity data of Table 25 can be represented by

$$c_p = 1.1300 - 0.26551X - 4.15746 \times 10^6 T^{-3}$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{°C}^{-1}$ ,  $X$  is the weight fraction of hydrazine, and  $T$  is the temperature in kelvin. An alternative curve fit gave

$$c_p = 0.54994 + 0.36032X - 1.8398 \times 10^{-3}XT + 1.8398 \times 10^{-3}T \\ - 1.73667 \times 10^7 T^{-3} + 3.85528 \times 10^9 T^{-4}$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{°C}^{-1}$ ,  $X$  is the weight fraction of hydrazine, and  $T$  is the temperature in kelvin. Neither of the two equations matches the data in Table 25 accurately, and they deviate after the second place after the decimal point. The heat capacities of comparatively dilute solutions (up to 0.69 molal  $\text{N}_2\text{H}_5\text{OH} = 2.18 \text{ mass-}\% \text{ N}_2\text{H}_4$ ) were determined as part of a study on the heats of solution of hydrazine in water, the apparent molal heat capacity of the mixture, and partial molal heat capacities of the solute and the solvent [298]. These data, summarized in Table 26, cover only the lower end of the concentration range of hydrazine-water mixtures.

**Table 26:** Heat capacity of dilute hydrazine hydrate solutions.

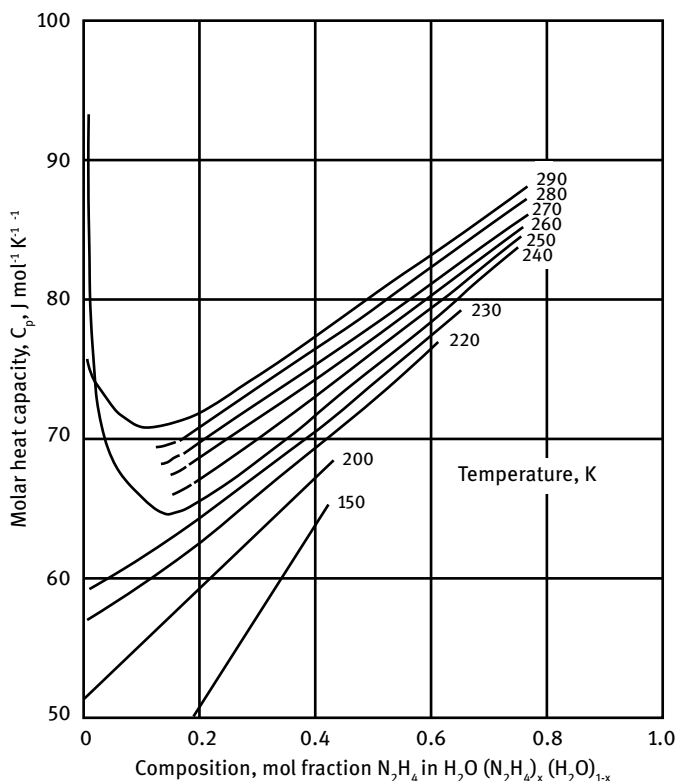
| $\text{N}_2\text{H}_5\text{OH}$<br>molality <sup>a</sup> | Composition                  |                               | Heat capacity                   |                                      |
|----------------------------------------------------------|------------------------------|-------------------------------|---------------------------------|--------------------------------------|
|                                                          | Mol-% $\text{N}_2\text{H}_4$ | Mass-% $\text{N}_2\text{H}_4$ | $\text{J g}^{-1} \text{K}^{-1}$ | $\text{cal mol}^{-1} \text{°C}^{-1}$ |
| 0.0000                                                   | 0                            | 0                             | 4.175                           | 0.9979                               |
| 0.1310                                                   | 0.23                         | 0.41                          | 4.161                           | 0.9944                               |
| 0.1537                                                   | 0.28                         | 0.50                          | 4.158                           | 0.9939                               |
| 0.1559                                                   | 0.28                         | 0.50                          | 4.158                           | 0.9938                               |
| 0.2269                                                   | 0.41                         | 0.73                          | 4.151                           | 0.9922                               |
| 0.3731                                                   | 0.67                         | 1.19                          | 4.139                           | 0.9892                               |
| 0.3762                                                   | 0.67                         | 1.19                          | 4.138                           | 0.9891                               |
| 0.6949                                                   | 1.24                         | 2.18                          | 4.115                           | 0.9834                               |

<sup>a</sup> Number of mols of  $\text{N}_2\text{H}_5\text{OH}$  per 55.508 mols of unreacted water.

Data source: [298]

Hydrazine has been used as a “diluent” for water in an effort to study the abnormal heat capacity behavior of supercooled water as its temperature approaches 228 K. The heat capacity of hydrazine/water mixtures was determined in a differential scanning calorimeter [299, 300]. Most of the interpretation of the data was concerned with the

effect of water rather than hydrazine in the mixture, as well as in comparison with the effect of hydrogen peroxide. The isotherms for the molar heat capacity of solutions are shown in Figure 32. The shape of the 240 K isotherm is truly extraordinary because heat capacity increases rapidly as the concentration approaches zero per cent hydrazine. This deviation from ideality has been attributed to the formation of association structures like those found in supercooled water [301]. Similar structures are most likely also responsible for the tendency of hydrazine/water mixtures to form viscous mixtures and glassy solids on approaching the freezing point, making it very difficult to determine freezing points and melting points of such mixtures.



**Figure 32:** Heat-capacity isotherms for water/hydrazine solutions. (Reproduced and modified from [300].)

Most publications deal only with the heat capacity of hydrazine solutions as a function of concentration and temperature. Additional investigations have also studied the effect of pressure on heat capacity of hydrazine solutions. High pressures may be encountered in steam power plants, although the hydrazine concentrations in boiler

feedwater are usually only very low. The heat capacity (thermal capacity) of aqueous hydrazine hydrate solutions in the temperature range 313–450 K and pressure range 0.101–49.1 MPa was measured, and generalized equations were obtained to calculate the thermal capacities of these solutions [302, 303]. The measurements were made along isobars with pressure steps of 4.9–9.8 MPa. The heat capacity of a solution containing 90% hydrazine hydrate and 10% water at 293 K decreased from  $3032 \text{ J kg}^{-1} \text{ K}^{-1}$  at 0.101 MPa down to  $2986 \text{ J kg}^{-1} \text{ K}^{-1}$  at 49 MPa. The heat capacity as a function of temperature at atmospheric pressure increased linearly with temperature from  $3032 \text{ J kg}^{-1} \text{ K}^{-1}$  at 293 K to  $3120 \text{ J kg}^{-1} \text{ K}^{-1}$  at 343 K.

### 2.2.2 Enthalpy of Formation of Hydrazine

Exact knowledge of thermodynamic data, including enthalpy of formation, free energy of formation, and entropy is important for the calculation of the theoretical performance of hydrazine in several practical applications, such as rocket engines or fuel cells. Besides from calorimetric determinations, these data are usually obtained from IR, Raman, or microwave spectroscopic observations and calculation of molecular vibrations. This requires knowledge of the structure of the hydrazine molecule, which is discussed in more detail in Section 2.3. See also [304, 305].

#### 2.2.2.1 Enthalpy of Formation of Hydrazine Liquid

Various numbers, not always in agreement, have been reported for the enthalpy of formation of liquid anhydrous hydrazine in recent decades. Historical data are summarized in Table 27.

**Table 27:** Comparison of enthalpy of formation data for liquid hydrazine.

| Enthalpy of formation |          |        | References |
|-----------------------|----------|--------|------------|
| kJ/mol                | kcal/mol | cal/g  |            |
| +50.41                | +12.049  | +376   | [306]      |
| +53.76                | +12.85   | +401   | [306]      |
| +50.38                | +12.041  | +375.7 | [307]      |
| +50.63                | +12.101  | +377.6 | [291]      |

Molecular mass: 32.0452 g/mol

The first accurate determination of the enthalpy of formation of liquid hydrazine was performed in 1939 using the heat of combustion measured in a calorimeter [308]. The heat of reaction when forming hydrazine hydrate from liquid hydrazine and liquid water is  $(\Delta H)_{298} \text{ N}_2\text{H}_5\text{OH(L)} = 43.09 \text{ kJ/mol}$  (10.30 kcal/mol), but the heat of formation of hydrazine hydrate from the elements is  $-209 \text{ kJ/mol}$  ( $-58.018 \text{ kcal/mol}$ ). There has been some confusion about the definition of the enthalpy of formation of hydrazine

hydrate in the literature, and earlier books contained incorrect numbers. The experimentally measured heats of combustion at 298 K were  $19404 \pm 4.6 \text{ J/g}$  ( $4637.6 \pm 1.1 \text{ cal/g}$ ) and  $12281 \pm 2.5 \text{ J/g}$  ( $2935.2 \pm 0.6 \text{ cal/g}$ ) for hydrazine and hydrazine hydrate, respectively. Depending on which heat of combustion is used, two slightly different enthalpies of formation of anhydrous hydrazine can be obtained. With a standard heat of formation of  $\text{H}_2\text{O}(\text{L}) = -68.315 \text{ kcal/mol}$  ( $-285.83 \text{ kJ/mol}$ ), a standard heat of formation of  $(\Delta H)_{298}^{\text{f}} \text{N}_2\text{H}_4(\text{L}) = 50.229 \text{ kJ/mol} = +12.005 \text{ kcal/mol}$  is obtained from the first number. With the heat of hydration of hydrazine from [298] and the second number, an enthalpy of formation of  $(\Delta H)_{298}^{\text{f}} \text{N}_2\text{H}_4(\text{L}) = +50.639 \text{ kJ/mol} = +12.103 \text{ kcal/mol}$  is obtained. An average of these two sets of data would be  $(\Delta H)_{298}^{\text{f}} \text{N}_2\text{H}_4(\text{L}) = +50.434 \text{ kJ/mol} = +12.054 \text{ kcal/mol}$ , a value that is recommended by numerous authors.

The heat of combustion of hydrazine was measured as  $629.68 \text{ kJ/mol}$  ( $150.497 \text{ kcal/mol}$ ) in a calorimeter, corrected for 298 K [309]. In the same apparatus, a heat of combustion of MMH was measured as  $1303$  to  $1305 \text{ kJ/mol}$  ( $311.5$  to  $311.8 \text{ kcal/mol}$ ). A later measurement in the same apparatus gave a heat of combustion of hydrazine of  $621.8 \text{ kJ/mol}$  ( $148.619 \text{ kcal/mol}$ ), corrected for 298 K [310].

Sets of thermodynamic properties have been reported as compiled in Table 28. This table also contains data on a few hydrazine salts. The origin of some of these data is not quite clear, but it is assumed that the National Bureau of Standards has checked them for accuracy.

An excellent summary of the thermodynamic data on hydrazine, including data on the heat of formation and liquid-vapor phase change, was presented in a series of papers [103–106]. On closer examination of data published earlier, several inconsistencies were discovered. Some of the inconsistencies may be a result of the low quality of anhydrous hydrazine used by some of the early investigators. Despite the widespread use of hydrazines, very few thermochemical data have been determined within the last 30 years. Many of the older data need to be verified using modern methods of calorimetry and pure starting materials. Another source of potential errors for the EOSs derived from the PVT data is the indiscriminate use of “bastard” units, mixing metric and nonmetric units in the same equation.

### 2.2.2.2 Enthalpy of Formation of Hydrazine Vapor

Using the enthalpy of formation of the liquid and the antiquated heat of vaporization ( $42.677 \text{ kJ/mol} = 10.2 \text{ kcal/mol}$  at 298 K) from [206], the heat of formation of hydrazine vapor was calculated as  $(\Delta H)_{298}^{\text{f}} \text{N}_2\text{H}_4(\text{G}) = +93.09 \text{ kJ/mol} = +22.25 \text{ kcal/mol}$  by Hughes, Corruccini, and Gilbert 1939, which was in good agreement with a classical, theoretical calculation by Pauling [312],  $+92.5 \text{ kJ/mol}$  ( $+22.10 \text{ kcal/mol}$ ), and with later determinations by Scott [107]:  $+95.2 \text{ kJ/mol}$  ( $+22.75 \text{ kcal/mol}$ ). NIST Chemistry WebBook lists the  $(\Delta H)_{298}^{\text{f}} \text{N}_2\text{H}_4(\text{G})$  as  $+95.35 \text{ kJ/mol}$  [291].

**Table 28:** Thermodynamic properties of hydrazine compounds.

| Compound                                                      | $(\Delta H)^f_{298}$ |          | $(\Delta G)^f_{298}$ |          | $S^0_{298}$                          |                                        | $C^0_{p, 298}$                       |                                        |
|---------------------------------------------------------------|----------------------|----------|----------------------|----------|--------------------------------------|----------------------------------------|--------------------------------------|----------------------------------------|
|                                                               | kJ/mol               | kcal/mol | kJ/mol               | kcal/mol | J mol <sup>-1</sup> °C <sup>-1</sup> | cal mol <sup>-1</sup> °C <sup>-1</sup> | J mol <sup>-1</sup> °C <sup>-1</sup> | cal mol <sup>-1</sup> °C <sup>-1</sup> |
| N <sub>2</sub> H <sub>4</sub> (L)                             | +50.63               | +12.10   | +149.2               | +35.67   | 121.2                                | 28.97                                  | 98.87                                | 23.63                                  |
| N <sub>2</sub> H <sub>4</sub> (G)                             | +95.40               | +22.80   | +159.3               | +38.07   | 238.4                                | 56.97                                  | 49.58                                | 11.85                                  |
| N <sub>2</sub> H <sub>4</sub> (aq.) <sup>a</sup>              | +34.31               | +8.20    | +128.0               | +30.6    | 138.1                                | 33                                     | —                                    | —                                      |
| N <sub>2</sub> H <sub>5</sub> <sup>+</sup> (aq.) <sup>a</sup> | -7.53                | -1.8     | +82.42               | +19.7    | 150.6                                | 36                                     | 49.4                                 | 11.8                                   |
| N <sub>2</sub> H <sub>5</sub> OH (L)                          | -242.7               | -58.01   | —                    | —        | —                                    | —                                      | —                                    | —                                      |
| N <sub>2</sub> H <sub>5</sub> OH (G)                          | -205.0               | -49.0    | -79.08               | -18.9    | 263.6                                | 63                                     | —                                    | —                                      |
| N <sub>2</sub> H <sub>5</sub> OH (aq.)                        | -251.5               | -60.11   | -109.2               | -26.1    | 207.9                                | 49.7                                   | 73.2                                 | 17.5                                   |
| N <sub>2</sub> H <sub>5</sub> NO <sub>3</sub> (aq.)           | -215.1               | -51.41   | -28.91               | -6.91    | 297.1                                | 71                                     | —                                    | —                                      |
| N <sub>2</sub> H <sub>5</sub> Cl (aq.)                        | -174.9               | -41.8    | -48.95               | -11.7    | 207.1                                | 49.5                                   | —                                    | —                                      |
| N <sub>2</sub> H <sub>5</sub> ClO <sub>4</sub> (aq.)          | -261.8               | -62.58   | -87.99               | -21.03   | 295.4                                | 70.6                                   | —                                    | —                                      |

Data source: [311]

The calculation of thermodynamic functions of hydrazine from spectroscopic data was the first thorough source of reliable data [313]. This work has been superseded by the JANNAF thermochemical tables, which present thermodynamic functions in 100-K intervals for liquid and gaseous hydrazine (Table 29). The JANNAF thermochemical tables are based on the critical evaluation of data from multiple sources.

**Table 29:** Thermodynamic functions of liquid and gaseous hydrazine.

| $T$<br>K      | $C_p^0$<br>J mol <sup>-1</sup> K <sup>-1</sup> | $S_0$   | $-(G_0 - H_0^{298})/T$ | $H_0 - H_0^{298}$<br>kJ/mol | $\Delta H_0^f$ | $\Delta G_0^f$ | $\log K_p$ |
|---------------|------------------------------------------------|---------|------------------------|-----------------------------|----------------|----------------|------------|
| <b>Liquid</b> |                                                |         |                        |                             |                |                |            |
| 100           | 87.236                                         | 21.037  | 205.395                | -18.436                     | 48.895         | 82.918         | -43.312    |
| 200           | 93.094                                         | 83.302  | 130.399                | -9.419                      | 49.613         | 116.715        | -30.483    |
| 298.15        | 98.840                                         | 121.544 | 121.544                | 0                           | 50.626         | 149.440        | -26.181    |
| 300           | 98.952                                         | 122.156 | 121.546                | 0.183                       | 50.649         | 150.054        | -26.127    |
| 400           | 107.361                                        | 151.693 | 125.516                | 10.471                      | 52.208         | 182.975        | -23.894    |
| 500           | 116.566                                        | 176.639 | 133.305                | 21.667                      | 54.619         | 215.406        | -22.503    |
| 600           | 125.771                                        | 198.705 | 142.398                | 33.784                      | 57.895         | 247.270        | -21.527    |
| 700           | 134.976                                        | 218.784 | 151.896                | 46.822                      | 62.013         | 278.518        | -20.783    |
| 800           | 144.181                                        | 237.409 | 161.435                | 60.779                      | 66.957         | 309.120        | -20.183    |
| <b>Vapor</b>  |                                                |         |                        |                             |                |                |            |
| 0             | 0                                              | 0       | Infinite               | -11.528                     | 109.430        | 109.430        | Infinite   |
| 100           | 34.368                                         | 195.185 | 277.002                | -8.182                      | 103.876        | 120.484        | -62.934    |
| 200           | 40.658                                         | 220.673 | 243.020                | -4.469                      | 99.290         | 138.917        | -36.281    |
| 250           | 45.534                                         | 230.252 | 239.526                | -2.318                      | 97.193         | 149.070        | -31.146    |
| 298.15        | 50.813                                         | 238.719 | 238.719                | 0                           | 95.353         | 159.232        | -27.897    |
| 300           | 51.019                                         | 239.034 | 238.720                | 0.094                       | 95.287         | 159.628        | -27.794    |
| 350           | 56.531                                         | 247.315 | 239.362                | 2.784                       | 93.621         | 170.487        | -25.444    |
| 400           | 61.702                                         | 255.207 | 240.853                | 5.742                       | 92.205         | 181.567        | -23.710    |
| 450           | 66.379                                         | 262.749 | 242.870                | 8.946                       | 91.023         | 192.811        | -22.381    |
| 500           | 70.544                                         | 269.963 | 245.221                | 12.371                      | 90.050         | 204.175        | -21.330    |
| 600           | 77.562                                         | 283.469 | 250.487                | 19.789                      | 88.626         | 227.144        | -19.775    |
| 700           | 83.302                                         | 295.869 | 256.096                | 27.841                      | 87.760         | 250.305        | -18.678    |
| 800           | 88.202                                         | 307.320 | 261.793                | 36.422                      | 87.326         | 273.560        | -17.862    |
| 900           | 92.511                                         | 317.962 | 267.449                | 45.462                      | 87.240         | 296.848        | -17.229    |
| 1000          | 96.356                                         | 327.912 | 273.004                | 54.908                      | 87.439         | 320.130        | -16.722    |

Data source: [290]

### 2.2.2.3 Enthalpy of Formation of Solid Hydrazine

The absolute enthalpy (enthalpy above absolute zero, not enthalpy of formation) and entropy of solid hydrazine are listed in Table 30.

**Table 30:** Absolute enthalpy and entropy of solid hydrazine.

| Temperature<br>K | Absolute enthalpy $H_s - H_s^0$ |         | Entropy                             |                                        |
|------------------|---------------------------------|---------|-------------------------------------|----------------------------------------|
|                  | J/mol                           | cal/mol | J mol <sup>-1</sup> K <sup>-1</sup> | cal mol <sup>-1</sup> °C <sup>-1</sup> |
| 25               | 16.7                            | 4       | 0.92                                | 0.22                                   |
| 60               | 368                             | 88      | 8.83                                | 2.11                                   |
| 100              | 1356                            | 324     | 21.17                               | 5.06                                   |
| 170              | 4067                            | 972     | 41.38                               | 9.89                                   |
| 275.16           | 9845                            | 2353    | 67.53                               | 16.14                                  |

Data source: [7], pp. 75 and 77

#### 2.2.2.4 Enthalpy of Formation of Hydrazine Solutions

Enthalpy-concentration diagrams for a binary system can be prepared for fixed pressure, and to be complete, they should include data on the solid, liquid, and vapor phases. Such charts are useful for calculations involving heat balances with accompanying concentration changes, such as those that may occur in aqueous solutions of hydrazine [314].

#### 2.2.2.5 Computations of Enthalpy of Formation of Hydrazine

Computational methods for predicting enthalpies of formation based on the number of chemical bonds and the molecular structure usually yield data only for molecules in the gaseous state, and it is more difficult to obtain enthalpies of formation for the same molecules in condensed states.

The enthalpies of formation of  $N_2H$ , diazene (*cis*- and *trans*- $N_2H_2$ ),  $N_2H_3$ , and hydrazine  $N_2H_4$ , as well as their protonated species (diazonium,  $N_2H_3^+$  and hydrazinium  $N_2H_5^+$ ), have been calculated using a high-level electronic structure theory [315]. Energies were calculated using coupled cluster theory with a perturbative treatment of the triple excitations and employing augmented correlation consistent basis sets to perform a complete basis set extrapolation for the energy. Geometries were optimized with different basis sets. The enthalpies of formation at 0 and 298 K are listed in Table 31. In addition, the enthalpies of formation of  $CH_3NH_2$ ,  $CH_3NNH$ , and  $CH_3HNNHCH_3$  were calculated using isodesmic reactions.

The enthalpies of formation,  $\Delta H_f^{298}$ , of hydrazine, in both the gas and condensed phases, and the enthalpies of sublimation or vaporization have been estimated using quantum-chemical methods, and similar calculations were made for 36 hydrazine derivatives. The composite G4 method has been used along with isodesmic reaction schemes to derive a set of self-consistent, high-accuracy gas-phase enthalpies of formation [316]. To estimate the enthalpies of sublimation and vaporization with reasonable accuracy (5–20 kJ/mol), the method of molecular electrostatic potential (MEP) has been used. A value of  $\Delta H_f^{298}(H_2NNH_2, G) = 97.0 \pm 3.0$  kJ/mol was determined from 75 isogyric reactions involving about 50 reference species, where



**Table 31:** Predicted enthalpies of formation of gaseous hydronitrogen compounds at 0 and 298 K

| Compound                                    | Predicted |     |          |       | Measured |     |            |      |
|---------------------------------------------|-----------|-----|----------|-------|----------|-----|------------|------|
|                                             | kJ/mol    |     | kcal/mol |       | kJ/mol   |     | kcal/mol   |      |
| Temperature, K                              | 0         | 298 | 0        | 298   | 0        | 298 | 0          | 298  |
| N <sub>2</sub> H                            | 254       | 251 | 60.8     | 60.1  | —        | —   | —          | —    |
| <i>cis</i> -N <sub>2</sub> H <sub>2</sub>   | 230       | 223 | 54.9     | 53.2  | —        | —   | —          | —    |
| <i>trans</i> -N <sub>2</sub> H <sub>2</sub> | 209       | 201 | 49.9     | 48.1  | 204      | —   | 48.8 ± 0.5 | —    |
| N <sub>2</sub> H <sub>4</sub>               | 111       | 97  | 26.6     | 23.1  | —        | 95  | —          | 22.8 |
| N <sub>2</sub> H <sub>3</sub>               | 235       | 224 | 56.2     | 53.6  | —        | —   | —          | —    |
| N <sub>2</sub> H <sub>3</sub> <sup>+</sup>  | 969       | 958 | 231.6    | 228.9 | —        | —   | —          | —    |
| N <sub>2</sub> H <sub>5</sub> <sup>+</sup>  | 783       | 764 | 187.1    | 182.7 | —        | —   | —          | —    |

Data source: [315]

for most of these species, the accurate  $\Delta H_f^{298}(\text{G})$  values were available in the Active Thermochemical Tables (ATcT) [317]. The calculated value was in excellent agreement with the reported results of the most accurate models based on coupled cluster theory (97.3 kJ/mol, the average of six calculations). However, the difference between the values predicted by high-level theoretical calculations and the experimental value of  $\Delta H_f^{298}(\text{H}_2\text{NNH}_2, \text{G}) = 95.55 \pm 0.19$  kJ/mol recommended in the ATcT and other comprehensive reference sources is quite large and requires further investigation.

In a subsequent examination of published experimental and computational predicted values for the enthalpy of formation of hydrazine vapor, the accuracy of the long-standing experimental enthalpy of formation of gas-phase hydrazine, fully confirmed in earlier versions of the ATcT, was reexamined in light of new high-end calculations of a different variety [318]. An overly optimistic determination of the vaporization enthalpy of hydrazine, which created an unrealistically strong connection between the gas-phase thermochemistry and the calorimetric results defining the thermochemistry of liquid hydrazine, was identified as the probable culprit of deviations. The new enthalpy of formation of gas-phase hydrazine, based on balancing all available knowledge, was determined to be  $111.57 \pm 0.47$  kJ/mol at 0 K ( $97.42 \pm 0.47$  kJ/mol at 298.15 K), which agreed with the ATcT data. ATcT version 1.11218 listed a  $\Delta H_f(0 \text{ K})$  of  $109.66 \pm 0.19$  kJ/mol;  $\Delta H_f(298.15 \text{ K}) = 95.51 \pm 0.19$  kJ/mol. The more recent ATcT version 1.118 value was only slightly different,  $\Delta H_f(0 \text{ K}) = 109.71 \pm 0.19$  kJ/mol; ( $\Delta H_f(298.15 \text{ K}) = 95.55 \pm 0.19$  kJ/mol). In both versions, the enthalpy is rather similar to the values listed in the NIST-JANAF tables ( $109.43 \pm 0.8$  kJ/mol at 0 K or  $95.35 \pm 0.8$  kJ/mol at 298.15 K).

### 2.2.3 Heat of Evaporation of Hydrazine

The literature offers a rather shaky choice of data for the enthalpy of vaporization (or latent heat of evaporation) of hydrazine. A striking observation is the lack of a genuinely experimental nature and reliability of the published data. They have all

been unconditionally estimated via approximate methods and accurate calorimetric determinations are lacking. Literature data for the enthalpy of vaporization were given only for one or, at most, two temperatures, far from the critical point. Data were all derived from the Clausius-Clapeyron equation and the slope of the vapor pressure curve, sometimes assuming ideal gas behavior for hydrazine vapor, which it certainly is not. A critical review of the rationale used by various investigators was performed by Giordano in 2001 [105]. It was emphasized that available vaporization-enthalpy data do not possess a sufficient degree of experimental purity. Their reliability could be undermined by overlooked inconsistencies and/or unverified inaccuracies.

The heat of vaporization is usually obtained from the slope of vapor pressure curves using the Clapeyron equation. Using Scott's [107] vapor pressure curve,  $(\Delta H)_{298}^{\text{vap}} \text{N}_2\text{H}_4 = 44.769 \pm 0.314 \text{ kJ/mol} = 10.700 \pm 0.075 \text{ kcal/mol}$  is obtained. Hieber and Woerner [206] calculated  $(\Delta H)_{296}^{\text{vap}} \text{N}_2\text{H}_4 = 42.68 \text{ kJ/mol} = 10.2 \text{ kcal/mol}$ . Hieber and Appel [319] measured a heat of vaporization at 273 K as  $48.1 \text{ kJ/mol} = 11.5 \text{ kcal/mol}$ . Using the combined vapor pressure curve given in Section 2.1.9.1, a value of  $(\Delta H)_{298}^{\text{vap}} = 43.43 \text{ kJ/mol} = 10.38 \text{ kcal/mol}$  is obtained. At the normal boiling point, the heat of vaporization is lower, only  $39.08 \text{ kJ/mol} = 9.34 \text{ kcal/mol}$ .

Trouton's rule states that the entropy of vaporization is almost the same value, about  $85$  to  $88 \text{ J K}^{-1} \text{ mol}^{-1}$ , for various kinds of non-associated liquids at their boiling points. The entropy of vaporization is defined as the ratio between the enthalpy of vaporization and the boiling temperature. The Trouton constant of hydrazine of  $24.1 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$  ( $100.8 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is indicative of a strongly associated liquid. Audrieth [7] listed a Trouton constant of  $25.23 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$  ( $105.6 \text{ J mol}^{-1} \text{ K}^{-1}$ ), equally different from the value of  $21 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1}$  ( $87.9 \text{ J mol}^{-1} \text{ K}^{-1}$ ) expected for nonassociated liquids. A positive deviation from the theoretical value for nonassociated liquids is indicative of association in the liquid phase. This deviation is, of course, even more pronounced for water than for hydrazine (water:  $26 \text{ cal mol}^{-1} \text{ }^\circ\text{C}^{-1} = 109 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

If one accepts the heat of evaporation at 298 K from Scott as  $10.7 \text{ kcal/mol}$ , the following equation can give the heat of evaporation as a function of temperature between 275 and 390 K. The original equation exactly as shown on page 74 of Audrieth and Ackerson-Ogg [7] is

$$\Delta H_{\text{vap}} = 15879 - 28.296T + 0.054525T^2 - 0.000068528T^3 \\ + 0.00000003125T^4 - 0.00000000008333T^5$$

where  $\Delta H_{\text{vap}}$  is the heat of evaporation in cal/mol and  $T$  is the temperature in kelvin. This equation can be converted to SI units, and then it reads

$$\Delta H_{\text{vap}} = 66438 - 118.39T + 0.228133T^2 - 2.8672 \times 10^{-4}T^3 \\ + 1.3075 \times 10^{-7}T^4 - 3.4865 \times 10^{-11}T^5$$

where  $\Delta H_{\text{vap}}$  is the heat of evaporation in J/mol and  $T$  is the temperature in kelvin. At the normal boiling point (386.6 K), which is outside the valid temperature range for this equation, this equation gives a heat of vaporization of 40.83 kJ/mol (9.758 kcal/mol).

### 2.2.3.1 Passivating Hydrazine Propellant Tanks in Outer Space

The heat of evaporation of hydrazine is the key parameter when constructing thermal models to predict the rate at which hydrazine propellant tanks empty themselves at the end of a mission when the propellant lines are opened to the vacuum of space to dump residual propellant. In the wake of some upper-stage (kick stage) explosive fragmentation events that created a cloud of orbital debris, mission planners now design spacecraft so that all residual hydrazine can be vented before the spacecraft reenters or overpressurizes when the hydrazine is locked up [320]. The PEGASUS Hydrazine Auxiliary Propulsion System (HAPS) fragmentation event demonstrated the importance of passivating spacecraft and upper stages at the end of missions by draining all propellant [321]. The sensible heat carried with room-temperature liquid-phase hydrazine isolated droplets in vacuum allows for the vaporization of a maximum of 30% of the liquid, with the rest remaining in the solid phase. The rate of sublimation of the cold hydrazine solid is much slower than the rate of evaporation of the liquid.

The thermodynamic properties of hydrazine, including the heat of evaporation, have been gathered in support of computations to predict how long it would take for a hydrazine propellant tank to empty and inert (passivate) itself to below the detonable partial pressure of hydrazine vapor. A numerical method (pressure-correction method using a staggered grid) was coupled to a thermodynamic model for compressible liquid hydrazine and applied to the venting of liquid hydrazine into space, during which the fluid underwent a large pressure drop [322–324]. Below the saturation pressure, vaporization occurs but insufficient energy is available for complete conversion to vapor. Some of the hydrazine will freeze and cause problems. Vaporization takes place near the outlet and induces variations of temperature, which may cause solidification and pipe clogging. To assess the risk of phase changes, numerical simulations of the venting line have been performed using a quasi-one-dimensional approach. The numerical method can handle compressible flows of fluids with nonconvex EOSs at the low Mach numbers that occur during hydrazine venting. A numerical study of the liquid behavior during sudden depressurization was performed for the tanks of the reaction control system of Ariane 5 upper stage, and the method was validated using experimental data and allowed for the prediction of the pressure profile and vaporization location along the pipe. It was deduced from these considerations that when one achieves the disposal of hydrazine reservoirs in vacuum after the operation of Ariane 5 upper-stage SCA, some risks of icing in piping exist, as well as obstruction of the exit orifice. The flow to be computed has a low Mach number:  $\text{Ma} < 0.03$ . Computations for an initial tank pressure of 25 bar indicated that liquid flashing occurred only near the outlet.

### 2.2.3.2 Flash Evaporation of Hydrazine in Vacuum

In addition to computer modeling, tank depressurization and passivating experiments have been conducted with simulated flight hardware in vacuum chambers on the ground, often using water as a surrogate liquid for hydrazine [325–328]. The shape and particle size of the hydrazine droplet-snow flake crystal spray emanating from the orifice sprayed into vacuum was studied with high-speed cinematography. It would have been of interest to examine whether this spray was associated with the buildup of static electricity.

The depressurization and emptying of a tank of liquid hydrazine once it is exposed to vacuum is aided by the effervescence of dissolved pressurant gas, like the opening of a champagne bottle. When hydrazine droplets are formed by flash evaporating liquid hydrazine into a vacuum and forming an aerosol, the sudden cooling does not allow crystals to order themselves, and the undercooled droplets consist of mixtures of disordered and crystalline phases [36]. Such clouds of hydrazine snow may exist on the planet Jupiter [35]. See also [329].

## 2.3 Molecular Structure of Hydrazine

The unique properties of hydrazines can be better understood by studying the nature of the chemical bonds that hold them together. The N–N bond is unique in being borderline between stable and labile. This provides for a wide range of possible reactions. Once individual bond energies are known, the enthalpies of formation of different molecules in the vapor state can be calculated by simply adding up the number of N–N, N–H, N–C, and C–H bonds in a molecule.

Many of the physical and thermodynamic properties summarized in the preceding chapter are closely interrelated with the molecular structure of hydrazine. Likewise, many molecular properties are related to the optical and electrical properties of hydrazines, which are discussed in subsequent sections of this chapter.

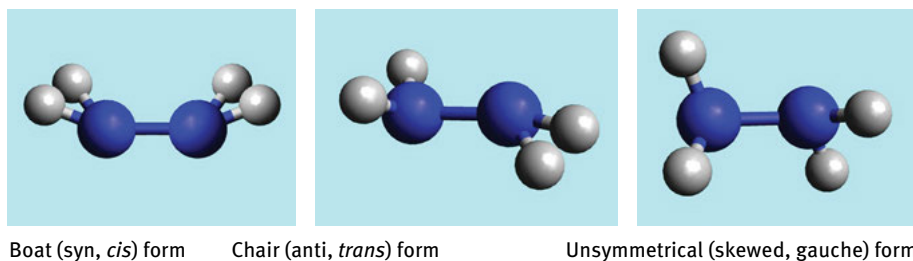
The peculiarity of hydrazine as a highly energetic compound has its origin in the molecular structure of this “dinitrogen tetrahydride.” The molecular structure, the bond strength, the bond length, and the geometric arrangement of hydrazine and some of its simpler derivatives thus deserve detailed discussion. One question that arises at this point is why the higher hydronitrogen homologues of hydrazine are so much less stable than hydrazine and why nitrogen is not capable of forming long-chain and ring compounds analogous to carbon compounds.

The molecular structure of hydrazine in its salts is slightly different from that of the parent molecule. Hydrazyl radicals are unique and partially responsible for the reactivity of hydrazine. The free radicals and intermediates in hydrazine decomposition are discussed in Section 4.4.2. One of the key parameters used in describing molecular structures is the bond length. Bond lengths are commonly measured in Ångstrom

units, which are not SI units. Nevertheless, for ease of conversion, the numerical values of molecular dimensions are reported in units of  $10^{-10}$  m, which is identical to 1 Å.

In an early quantum-mechanical study of hydrazine, it was theorized that the  $2s^2$  shell of the nitrogen atoms is not inactive in establishing a bond between the two nitrogen atoms, as one would first assume [330, 331]. Instead, a  $2s2p^3$  hybridization is assumed to occur that is like the tetrahedral arrangement in a saturated carbon atom and energetically favored. A pair of “lone” electrons with opposite spins occupies the place usually inhabited by a ligand in a carbon tetrahedron. Calculations showed that free rotation cannot occur in either of these molecules at ordinary temperatures and that the only stable forms are those in which the azimuth of one half of the molecule with respect to the other is twisted by approximately  $90^\circ$ . The essential feature of the argument is that the electrons of the two central atoms arrange themselves to form the strongest possible bonds and in so doing render the charge density on these atoms unsymmetrical about the axis of the molecule. The interaction of the two electronic clouds is the dominant factor in determining the azimuth of one group relative to the other.

In contradistinction to its organic analog, ethane, which can exist in only two conformations (eclipsed and staggered), hydrazine can theoretically exist in three conformations by rotating one half of the molecule around the N—N bond. As shown in Figure 33, a boat form, a chair form, and a totally unsymmetrical form can be drawn up for the  $N_2H_4$  molecule.



**Figure 33:** Possible hydrazine conformations

There are comparatively few compounds with the singly bonded  $>N-N<$  backbone because such systems are destabilized by the repulsion of the lone electron pairs on the two nitrogen atoms. The parent compound,  $HHN-NHH$ , is kinetically stable but thermodynamically unstable. The  $C_2$  symmetry *gauche* conformation of  $N_2H_4$  is known experimentally and theoretically to be the most stable structure. Rotation around the N—N bond as an axis leads to the less stable staggered (*anti*)  $C_{2h}$  conformer and an eclipsed (*syn*) structure. The latter conformation corresponds to a transition state, whereas the former is a local minimum on the energy potential surface.

### 2.3.1 Rotational Barriers in Hydrazine

Based on spectroscopic observations [217] and dipole measurements [332], the  $\text{NH}_2$  groups are not freely rotating around the N—N bond, but a rotational barrier of 25–41 kJ (6–10 kcal) must be overcome. This increase in energy leads to decomposition before spectra of the freely rotating molecule can be recorded. Instead of rotating freely, the two  $\text{NH}_2$  groups twist and oscillate against each other in the gas-phase molecule at room temperature. The rotational barrier compares to 10.7–13.8 kJ/mol (2.56–3.3 kcal/mol) for ethane; thus, the ethane rotation is “thawed” at room temperature and contributes to the specific heat of ethane gas. Dipole moment measurements of hydrazine (Section 2.8.2) also indicated that the molecule does not rotate freely [331]. Theoretical calculations based on three different variations of the molecular orbital theory have allowed prediction of the magnitude of rotational barriers [333]. The rotational barriers have been explained by the interaction of “lone-pair” orbitals of the lone electrons on neighboring nitrogen atoms.

If the two halves of the hydrazine molecule were rotating freely around the N—N axis, a tautomeric “amine-imide” form  $\text{H}_3\text{N}^+ - \text{NH}^-$  would be required to explain the dipole moment of hydrazine. However, this structure is highly unlikely.

The nuclear quadrupole coupling constants of the  $^{14}\text{N}$  nuclei for hydrazine were calculated by an *ab initio* SCF and by a CI calculation method. Rotational isomerism becomes evident as a form of energy state/line splitting in several spectra of hydrazine, including nuclear quadrupole coupling nuclear magnetic resonance (NMR) spectra [334] (Section 2.9) and electron spectroscopy for chemical analysis (ESCA), also called X-ray photoelectron spectroscopy (XPS), spectra (Section 2.6).

It was shown that an important consequence of nonrigid motions observed in the hydrazine molecule is the mixing of stereoisomers, although the geometrical symmetry group, taking into account these motions, similarly to the point group of one equilibrium configuration, has no improper transformations of the molecule as a whole [335, 336]. An important point is that the geometrical group of a nonrigid molecule is the so-called noninvariance dynamical group. The effect of mixing of stereoisomers on the total picture of nonrigid motions was considered using symmetry methods. It was shown that a nonrigid molecule exhibits properties of a symmetric top, whereas a rigid molecule represents an asymmetric top.

### 2.3.2 Bond Lengths and Bond Angles

Bond lengths and bond angles of the hydrazine molecule obtained by different authors using a variety of experimental methods and theoretical calculations are summarized in Table 32.

Besides the bond energy, the bond length and bond angles are also of interest to explain the behavior of hydrazine under certain conditions. These data are usually

**Table 32:** Bond lengths and bond angles of hydrazine.

| Bond  | Length ( $10^{-10}$ m) | Method | References |
|-------|------------------------|--------|------------|
| N—H   | 1.014                  | IR     | [337]      |
| N—H   | 1.022                  | IR     | [338]      |
| N—H   | 1.020 to 1.025         | IR     | [339]      |
| N—N   | 1.5                    | IR     | [337]      |
| N—N   | 1.449                  | IR     | [338]      |
| N—N   | 1.45                   | IR     | [340]      |
| N—N   | 1.46                   | X Ray  | [341]      |
| N—N   | $1.453 \pm 0.005$      | IR     | [339]      |
| Bond  | Angle (°)              | Method | References |
| N—N—H | 108                    | IR     | [337]      |
| N—N—H | 112                    | IR     | [338]      |
| N—N—H | 112 to 112.5           | IR     | [339]      |
| N—N—H | 112                    | IR     | [340]      |
| H—N—H | $105^{\circ}50'$       | IR     | [339]      |

derived from spectroscopic data. The following bond lengths were calculated for the ground-state molecule [337]:

$$\begin{aligned} \text{N—H} & 1.014 \times 10^{-10} \text{ m} \\ \text{N—N} & 1.500 \times 10^{-10} \text{ m} \end{aligned}$$

All bond angles are  $108 \pm 10^{\circ}$  as expected in a tetrahedral arrangement (theoretical angle  $109.5^{\circ}$ ). The following bond lengths and angle data were obtained from electron diffraction measurements:  $d(\text{N—N}) = (1.449 \pm 0.004) \times 10^{-10}$  m,  $d(\text{N—H}) = (1.022 \pm 0.006) \times 10^{-10}$  m, and bond angle  $\angle \text{NNH} = 112.0^{\circ}$  [338]. These results agreed well with IR data. Earlier IR spectra indicated an  $\angle \text{HNNH}$  angle of  $105^{\circ}50'$  [339]. The distance from the nitrogen to the nearest hydrogen belonging to a neighboring hydrazine molecule is  $(2.063 \pm 0.015) \times 10^{-10}$  m. There is active hydrogen bonding between the molecules.

### 2.3.3 Bond Energies of Hydrazine

The bond energy of individual linkages that hold the atoms together in a molecule determines the stability of the molecule and the amount of energy released when the molecule breaks apart. This process is what makes hydrazine a good monopropellant. Obviously, hydrazine is not a very stable molecule, and some explanation for this behavior is sought by studying the bond energies of hydrazine and its decomposition products. Bond energies can be derived from the natural frequency of atoms oscillating in the molecular skeleton by extrapolation of spectroscopic data, from ionization

and appearance potentials, or from calorimetric data. Bond energies are identical with dissociation energies required to break a particular bond (but there may be contributions by energy stored in other degrees of freedom of the molecule). Table 33 presents a summary of bond dissociation energy data in hydrazines. There is a wide scatter of dissociation energy data.

**Table 33:** Bond dissociation energies in hydrazines and ammonia.

| Bond                                     | Dissociation energy |          |          | References |
|------------------------------------------|---------------------|----------|----------|------------|
|                                          | kJ/mol              | kcal/mol | eV       |            |
| <i>Hydrazine and hydrazine fragments</i> |                     |          |          |            |
| H—N <sub>2</sub> H <sub>3</sub>          | 318 ± 21            | 76 ± 2   | 33 ± 2   | [342]      |
| H—N <sub>2</sub> H <sub>3</sub>          | 481                 | 115      | 50       | [343]      |
| H—N <sub>2</sub> H <sub>3</sub>          | 326                 | 78       | 34       | [344, 345] |
| H—N <sub>2</sub> H <sub>3</sub>          | 389                 | 93       | 40       | [346, 347] |
| H—N <sub>2</sub> H <sub>3</sub>          | 368                 | 88       | —        | [348]      |
| H—NHNH                                   | 226 ± 21            | 54 ± 5   | 23 ± 2   | [349, 350] |
| H—N <sub>2</sub> H                       | 314 ± 21            | 75 ± 5   | 33 ± 2   | [350]      |
| H—N <sub>2</sub>                         | −88 ± 21            | −21 ± 5  | −9 ± 2   | [350]      |
| H <sub>2</sub> N—NH <sub>2</sub>         | 242 ± 38            | 58 ± 3   | 25 ± 4   | [342]      |
| H <sub>2</sub> N—NH <sub>2</sub>         | 251 ± 13            | 60 ± 3   | 26 ± 3   | [351]      |
| H <sub>2</sub> N—NH <sub>2</sub>         | 226                 | 54       | 23       | [352, 353] |
| H <sub>2</sub> N—NH <sub>2</sub>         | 251                 | 60       | —        | [348]      |
| For comparison:                          |                     |          |          |            |
| H—NH <sub>2</sub>                        | 443 ± 13            | 106 ± 3  | 46 ± 1.3 | [342]      |
| H—NH <sub>2</sub>                        | 435 ± 8             | 104 ± 2  | 45 ± 0.9 | [354]      |
| H—NH                                     | 368 ± 17            | 88 ± 4   | 38 ± 1.7 |            |
| H—N                                      | 368 ± 25            | 88 ± 6   | 38 ± 2.6 |            |

Many bond energy data were obtained as a valuable byproduct of mass spectrometric analysis of hydrazine and hydrazine derivative decomposition kinetics. When studying the decomposition products of hydrazine in a microwave-induced glow discharge, dissociation energies were derived from the appearance potential of NH<sub>2</sub><sup>+</sup>, N<sub>2</sub>H<sub>3</sub><sup>+</sup> in the mass spectrometer [342]. The bond dissociation energies were 443 ± 12 kJ/mol (106 ± 3 kcal/mol) for D(H—NH<sub>2</sub>) in ammonia, in good agreement with 435 ± 8 kJ/mol (104 ± 2 kcal/mol) reported earlier [354]. The dissociation energy of the N—N bond in hydrazine D(H<sub>2</sub>N—NH<sub>2</sub>) was calculated to be 318 ± 21 kJ/mol (58 ± 9 kcal/mol), in agreement with a previous, more precise, determination of 251 ± 12 kJ/mol (60 ± 3 kcal/mol) [351]. The dissociation energy required to form hydrazyl radicals was estimated to be D(H—N<sub>2</sub>H<sub>3</sub>) = 318 ± 21 kJ/mol (76 ± 5 kcal/mol), significantly below that for an N—H bond in ammonia.



Data for a dissociation energy  $D(\text{N}_2\text{H}_3-\text{H})$  of 481 kJ/mol (115 kcal/mol) [355] was rather high and was later revised. In a consecutive reevaluation of the accuracy of the use of appearance potentials or ionization potentials in mass spectrometers for determination of bond dissociation energies, the lower value,  $D(\text{N}_2\text{H}_3-\text{H}) = 326$  kJ/mol (78 kcal/mol), was later confirmed based on an independent empirical relationship by deriving the enthalpies of formation of nitrogenous free radicals from similarity laws [344, 345]. From the dissociation energies of isoelectronic molecules  $\text{CH}_3\text{CH}_2-\text{H}$  (406–410 kJ/mol = 97–98 kcal/mol) or  $\text{HOO}-\text{H}$  (372–376 kJ/mol = 89–90 kcal/mol), one would expect that the dissociation energy of  $\text{H}_2\text{NNH}-\text{H}$  is on the order of 372 to 410 kJ/mol or 89 to 98 kcal/mol.

The adiabatic ionization potential of  $\text{N}_2\text{H}_3$  was found to be  $7.61 \pm 0.01$  eV. This observation leads to  $D_0(\text{H}_2\text{NNH}-\text{H}) = 338 \pm 1.2$  kJ/mol =  $80.8 \pm 0.3$  kcal/mol, and  $D_0(\text{HN}=\text{NH}-\text{H}) \approx 183 \pm 4.6$  kJ/mol =  $43.8 \pm 1.1$  kcal/mol [356].

An *ab initio* study of the ionization potential of hydrazine calculated the equilibrium geometries and harmonic vibrational frequencies of the  $C_{2h}$  and  $D_{2h}$  conformers of the hydrazine ion ( $\text{N}_2\text{H}_4^+$ ) [357]. Extrapolation of the best results gave ionization potentials equal to 8.07 and 7.81 eV, which were close to experimental data, reported by others as  $8.1 \pm 0.15$  eV.

The dissociation energy of  $\text{N}_2\text{H}_3-\text{H}$  can be calculated from the difference of the appearance potential of the  $\text{N}_2\text{H}_3^+$  ion and the ionization potential of the  $\text{N}_2\text{H}_3$  radical:

$$D(\text{N}_2\text{H}_3-\text{H}) = A(\text{N}_2\text{H}_3^+) - I(\text{N}_2\text{H}_3)$$

This assumption is true only if  $A$  does not involve excess energy terms and if  $I$  is the adiabatic value, that is, corresponds to the 0–0 electronic transition. The equal sign should be replaced by a “less than or equal to”  $\leq$  sign if one wishes to be more accurate. Disregarding the effect of excess energy and adiabatic values may lead to the erroneous result initially obtained by Dibeler. An N–N bond energy of 251 kJ/mol (60 kcal/mol) and an N–H bond energy of 368 kJ/mol (88 kcal/mol) were assumed [348].

Nitrogen-hydrogen single-bond dissociation energies in hydrazine can also be estimated from the energy of activation in the abstraction of hydrogen atoms by methyl radicals [347]. These data favor a  $D(\text{H}-\text{N}_2\text{H}_3)$  on the order of 377 kJ/mol (90 kcal/mol), definitely weaker than the  $\text{H}-\text{NH}_2$  bond in ammonia.

It is very educational to compare the bond dissociation energy of N–H and N–N bonds in hydrazine to those in ammonia or molecular nitrogen. The bond dissociation energy of the N–H bond decreases with each consecutive hydrogen stripped off from ammonia, from 435 kJ/mol ( $104 \pm 2$  kcal/mol) in the first  $\text{H}_2\text{N}-\text{H}$  bond to 368 kJ/mol in the  $\text{HN}-\text{H}$  radical and finally 368 kJ/mol ( $88 \pm 6$  kcal/mol) in the  $\text{N}-\text{H}$  radical dissociation [354]. The same trend is observed with  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , or  $\text{H}_2\text{O}$ . The heats of formation for gas-phase species have also been calculated:  $\text{NH}_3$  –46.2 kJ/mol (–11.04 kcal/mol),  $\text{NH}_2$  +171 kJ/mol ( $+41 \pm 2$  kcal/mol), and  $\text{NH}$  +322 kJ/mol ( $+77 \pm 6$  kcal/mol). The corresponding values for radicals obtained by successive abstraction

of hydrogen from hydrazine have been determined beyond those for the hydrazyl radical [350]. These  $N_2H$  radicals would not be very stable because the N—N bond usually breaks before more than two hydrogens can be removed from hydrazine. The theoretical enthalpy of formation, heat capacity, and entropy of hydrazine vapor and a dozen other small molecule fragments was calculated using an isodesmic procedure [358, 359]. The calculated heat capacities and entropies agreed quite well with experimental data ( $C_p = 12.09$  calculated vs.  $12.20 \text{ cal mol}^{-1} \text{ K}^{-1}$  measured,  $S_0 = 55.46$  calculated vs.  $57.10 \text{ cal mol}^{-1} \text{ K}^{-1}$  measured).

The heat of dissociation of  $N_2$  has been a subject of considerable controversy for several years. It is very difficult to determine, because common spectroscopic methods fail as a result of the symmetry and lack of dipole moment of the molecule. Estimates for the N—N dissociation energy in  $N_2$  range from a low  $942 \text{ kJ/mol}$  ( $225.2 \text{ kcal/mol}$ ) to a high  $1138 \text{ kJ/mol}$  ( $272 \text{ kcal/mol}$ ). Because of this uncertainty, the heat of formation of NH cannot be calculated very accurately.

The N—N stretching force constants of diazene, hydrazine, and hydrazinium ions were calculated from spectroscopic data using a normal coordinate analysis and a modified valence force field method [360]. The N—N force constants in  $N_2H_2$ ,  $N_2H_4$ ,  $N_2H_5^+$ , and  $N_2H_6^{2+}$  were 10.22, 4.74, 4.80, and  $5.35 \text{ mdyn/\AA} = 1022, 474, 480$ , and  $535 \text{ N/m}$ , respectively.

### 2.3.4 Molecular Structure of Frozen Hydrazine

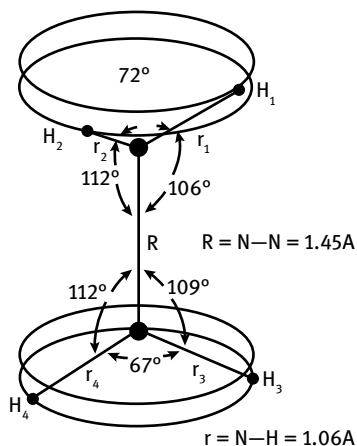
Frozen hydrazine may exist in the white clouds on Jupiter. The molecular structure in frozen hydrazine was measured by XRD [341]. The crystal structure of crystallized hydrazine is monoclinic  $C_{2h}^2 - P2_1/m$ , with two  $N_2H_4$  molecules in a unit cell of dimensions  $a = 3.56$ ,  $b = 5.78$ , and  $c = 4.53 \times 10^{-10} \text{ m}$ . The face angle is  $109.5^\circ$ . The N—N bond lies in the mirror plane, and the nitrogen atoms are  $1.46 \times 10^{-10} \text{ m}$  apart. The structure suggests the eclipsed configuration for the hydrazine molecule in the crystal, but hydrazinium salts assume a staggered configuration. Even if the hydrazine molecule has the eclipsed form in the crystal, there may be some reasonable doubt if this constellation survives if the molecule is vaporized. The spectroscopic data, at least until 1951, did not determine uniquely if the hydrogen atoms are in the opposed (*trans*) or eclipsed (*cis*) position.

Nuclear quadrupole relaxation spectroscopy of frozen hydrazine provided additional information about the lattice arrangement [361]. Six resonance lines due to two non-equivalent positions for each  $^{14}\text{N}$  nucleus in addition to the nonaxial symmetry of the crystalline field gradient, which gives rise to three resonance transitions were observed, and experiments of saturation recovery were carried out for these lines at liquid nitrogen temperature.

Numerous investigations attempted to resolve the question as to whether frozen hydrazine crystallizes in the  $C_{2h}^2 - P2_1$  space group or the  $C_{2h}^2$  space group. X-ray investigations first suggested a  $C_{2h}^2$  space group [341]. NMR [362–364] and far-IR [365] spectra

were shown to be consistent with a  $C_2^2 - P2_1$  structure instead. However, Raman spectra suggested another possible structure that is a monoclinic unit cell described by one of the  $C_{2h}$  space groups and containing four molecules located in general positions [366]. Only the positions of the nitrogen atoms have been established. More sophisticated proton spin-lattice relaxation measurements and some diffraction studies [367] now make the  $C_2^2$  space group more likely.

The molecular structure and molecular parameters of solid hydrazine are illustrated in Figure 34.



**Figure 34:** Molecular structure and molecular parameters of hydrazine molecule in solid state. (Reprinted and modified from [367], with permission from ©1975 Elsevier; permission conveyed through RightsLink)

It is surprising to learn that in frozen hydrazine between 200 and 260 K, the molecules have enough freedom of motion to exchange nitrogen nuclei between two nonequivalent crystallographic sites. This exchange has been detected by relaxation measurements of  $^{14}\text{N}$  nuclei by quadrupole NMR [368]. Line widths and spin-lattice relaxation times of the six nuclear quadrupole resonance lines of  $^{14}\text{N}$  in hydrazine were measured from 200 to 260 K using a pulse technique. It was shown that in this temperature range the dominant relaxation mechanism is a molecular motion that interchanges nuclei between the two nonequivalent crystallographic sites. The molecular motion has an activation energy of  $59.8 \pm 1.7 \text{ kJ/mol}$  ( $14.3 \pm 0.4 \text{ kcal/mol}$ ) and a rate of  $\sim 2500 \text{ s}^{-1}$  at 250 K.

The hydrazine monohydrate crystal is trigonal (space group  $P3_1$ ), with three molecules in a hexagonal unit cell.  $^{14}\text{N}$  NQR (nuclear quadrupole resonance) in hydrazine monohydrate has been investigated from 4.2 to 140 K [369]. A molecular motion with an activation energy of about 7.5 kcal/mol became active at about 120 K.

In frozen hydrazine hydrate, each hydrazine molecule is linked by six hydrogen bonds to the surrounding water molecules, and all nitrogen atoms in the unit cell occupy equivalent sites [370]. Each hydrazine molecule is separated from the nearest hydrazine molecule by six water molecules and allows a quasi-isolated two-spin system.

### 2.3.5 Computational Chemistry of Hydrazine Structures

Many chemists who never want to get their hands wet and have never taken a good whiff of hydrazine fumes have now resorted to computational modeling of hydrazine structures, working from the safe and convenient comfort of their offices. Ideally, these people should be able to design a new hydronitrogen rocket propellant and then give the blueprint to the lab chemists for further experimentation. Understanding the molecular structure of hydrazine helps to explain its reactive behavior in decomposition chambers in rocket engines. There are many different methods of modeling the molecular structure and predicting the physical properties of hydrazine and similar molecules [313, 371].

Anharmonic vibrational spectra of *gauche* conformers of hydrazine and hydrazine-d<sub>4</sub> were studied using vibrational self-consistent field and correlation-corrected vibrational self-consistent field methods within second-order Møller-Plesset perturbation theory [372]. Wavenumbers and intensities of both fundamental and overtone transitions were computed in different basis sets. Anharmonic spectra calculated on one potential energy surface were in much better agreement with experimental data than those obtained in another basis, but the energy sequence of  $\nu(\text{N-H})$  stretching modes was preserved in both basis sets. The wavenumber of the torsional mode was overestimated by 80 and 34  $\text{cm}^{-1}$  above its experimental position, respectively. The anharmonic spectrum of hydrazine-d<sub>4</sub> computed at the same level of theory also provided an adequate description of the experimental data, with the position of torsional vibration only 9  $\text{cm}^{-1}$  above the observed one.

Force field calculations for hydrazine were able to reproduce a range of equilibrium properties, including vapor-liquid coexistence densities, vapor pressures, enthalpies of vaporization, and critical properties [373]. Several dynamic properties, including self-diffusion coefficients and rotational time constants, were reported and found to be qualitatively consistent with experimental viscosities. Using this as a basis, a force field was also developed for the protonated form, i.e., hydrazinium-based cations.

#### 2.3.5.1 Calculations of Lone Electron Pair Interactions by Molecular Orbital Methods

The role of the two lone electron pairs on adjacent nitrogen atoms in preventing free rotation around the N—N bond has been investigated both experimentally through spectroscopic methods and computationally through molecular orbital and quantum-chemical methods.

It was once assumed that directional interactions of lone-pair orbitals make a significant contribution to the barrier energy [374], whereas others believed that lone pairs behave like ligands [375]. However, this would be in contradiction to the “rabbit-ear” effect of orbital interaction observed in hexahydropyrimidine. A single rotamer was predicted for  $\text{N}_2\text{H}_4$  at  $94^\circ$  with *cis* and *trans* barriers of 40.3 and 15.3 kJ/mol (9.64 and 3.67 kcal/mol) [376, 377].

Rotational barriers for hydrazine were calculated by an *ab initio* method and approximating complete neglect of differential overlap (CNDO) and intermediate neglect of differential overlap (INDO) methods. It was noted that the semi-empirical molecular orbital (MO) method results in barrier energies that are too low and in wrong torsional angles.

An attempt was made to explain the reasons for this discrepancy by recalculating the hydrazine molecule with the aid of the CNDO, INDO, and neglect of diatomic differential overlap (NDDO) methods, and an energy partition analysis was performed to account for the interaction of the lone electron pairs. [333]. The total energy and individual energy components were calculated and plotted as a function of the torsional angle. A minimum in the energy curve indicates the most stable position of the two  $\text{NH}_2$  groups in relation to each other. The difference between the peak and the valley gives the height of the rotational barrier. It was found that only the NDDO method made it possible to reproduce the results of the *ab initio* method and remain in agreement with experimental results.

Experimental results had indicated that the *gauche* form of hydrazine with a torsional angle of  $90^\circ$  is the most stable form [378]. The rotational barrier based on incomplete microwave studies was calculated to be approximately 13.14 kJ/mol (3.14 kcal/mol). The NDDO calculations by Wagner [376] and Koehler [333] gave 15.35 and 15.48 kJ/mol (3.67 and 3.70 kcal/mol) and  $94^\circ$  and  $\sim 100^\circ$ , respectively, in good agreement with each other.

Single Gaussian basis functions can represent lone-pair orbitals in contracted basis calculations. Using Pople's STO-4G and Dunning's *s-p* contracted basis sets, it was shown that optimum positions of lone-pair functions near the nitrogen nuclei are relatively insensitive to the molecular environment [379].

Improved bond-orbital calculations of rotation barriers in hydrazine and hydroxylamine using a STO-3G method looked at eleven different conformations of these molecules [380]. The results obtained using bond orbitals variationally optimized with respect to hybridization and polarity parameters showed that in the cases of lower local symmetry ( $\text{N}_2\text{H}_4$ ) second-order delocalization was essential for a correct description of the dependence of molecular energy on the dihedral angle.

Lone-pair interactions are also observed in other molecules like  $\text{HOOH}$ ,  $\text{H}_2\text{NOH}$ , or  $\text{H}_2\text{PPH}_2$ . For more information on conformational isomerism and force fields in the hydrazine molecule, see also [381–384]. Hydrazine is not a rigid rotor. Torsional wagging during rotation can lead to unexpected phenomena like tunneling of phonons [385, 386].

Others completely disregarded all references to previously published work and continued to calculate rotational barriers using a perturbation theory [340]. Lone-pair electrons associated to atoms located on the axis of rotation were effectively included in the model as additional nonbonded atoms. The researchers claimed that exchange interactions between the nonbonded atoms of the extended cluster were solely responsible for the observed conformation and rotation barriers. Their poten-

tial energy curve showed a minimum at  $\Theta = 75^\circ$  and a second less stable minimum at  $\Theta = 180^\circ$ . With respect to the equilibrium position, the *cis* and *trans* barriers were 25.15 and 10.5 kJ/mol (5.01 and 2.51 kcal/mol) high, respectively.

Other calculations for hydrazine and 10 hydrazine derivatives were performed using the intermediate retention of differential overlap (IRDO) MO method [387]. The repulsion of the lone pairs appears to be significant, favoring the form with perpendicular lone pairs over the *syn* and *anti* forms.

This agrees with gas electron-diffraction measurements [388]. Microwave measurements have also shown that hydrazine has a skew configuration with an equilibrium dihedral angle of  $90^\circ$  [389].

The modified intermediate neglect of differential overlap (MINDO/2) method was used to calculate conformations of hydrazine derivatives and compare them to results from XPS [390].

Molecular computational models for hydrazine, MMH, and UDMH molecules were derived to study the fluid phase behavior over a wide range of temperatures [239, 240, 391]. A parameterization of the classical molecular interaction models was carried out using quantum-chemical calculations and subsequent fitting to experimental vapor pressure and saturated liquid density data. To validate the molecular models, vapor/liquid equilibria for the pure hydrazines and binary hydrazine mixtures with water and ammonia were calculated and compared with available experimental data. The results for saturated densities, vapor pressure, and heat of vaporization obtained with this model were compared to the available experimental data and to the simulation results by Gutowski et al. Predicted critical point properties were  $T_c = 647.6$  K,  $p_c = 13.04$  MPa, and  $\rho_c = 10.16$  mol/L. In addition, the Henry's law constant for the physical solubility of argon, nitrogen, and carbon monoxide in liquid hydrazine, MMH, and UDMH was computed. In general, the simulation results were in very good agreement with the experimental data.

### 2.3.5.2 Calculations of Conformations and Lone Electron Pair Interactions by *ab initio* Methods

It has been pointed out that theoretical rotation barriers calculated for hydrazine by *ab initio* methods are probably too high [392]. The barrier to internal rotation in hydrazine has been calculated for values of 0, 60, 120, 180, and  $94^\circ$  (equilibrium conformation with energy minimum) of the dihedral angle, with all other bond angles and bond lengths fixed. The theoretical dihedral angle  $94^\circ$  was in good agreement with experimental indications of  $90$ – $95^\circ$ . The computed rotation barriers were 48.1 kJ/mol (11.5 kcal/mol) for the *cis* position and 20 kJ/mol (4.7 kcal/mol) for the *trans* position. Similar results were obtained using *ab initio* LCAO-MO-SCF wave functions [393]. Previously an energy minimum for  $\Theta = 90^\circ$ , a *cis* barrier of 46.23 kJ/mol (11.05 kcal/mol), and a *trans* barrier of 26.0 kJ/mol (6.21 kcal/mol) had been reported using an *ab initio* method [394].

Based on microwave spectra, a *gauche* conformation as the energy minimum ( $90^\circ < \theta < 95^\circ$ ), and assuming that both *cis* and *trans* barriers are equal, a barrier energy of 13.2 kJ/mol (3.15 kcal/mol) was predicted [378]. This did not agree too well with earlier results from other investigators [395, 396], who had used an *ab initio* restricted linear combination of atomic orbitals/molecular orbital/self-consistent field (LCAO-MO-SCF) method with bond functions. It was found that in its equilibrium conformation, the molecule had a dihedral angle of  $95^\circ$ . The barrier to pyramidal inversion at one nitrogen was 25.5 kJ/mol (6.1 kcal/mol) and the *syn* (eclipsed) and *anti* (staggered) rotational barriers were 50 kJ/mol (12.0 kcal/mol) and 6.7 kJ/mol (1.6 kcal/mol), respectively. The researchers' calculations indicated that during rotation over the *anti* barrier the bond angles contracted from their average equilibrium value of  $109.5\text{--}105.3^\circ$ .

A series of *ab initio* calculations was performed on hydrazine, 1,2-dimethylhydrazine, formamide, and its hydrogen-bonded dimer, 1,2-diformylhydrazine [397]. All systems were assumed to be planar. To study the changes in these bonds with variations in the ligands, the C—O, C—N, and N—N bond lengths were optimized in all cases. A systematic variation was found for the N—N bond when going from hydrazine via dimethylhydrazine to diformylhydrazine.

*Ab initio* SCF-MO calculations for  $\text{H}_2\text{NNH}_2$ ,  $\text{H}_2\text{NPH}_2$ , and  $\text{H}_2\text{PPH}_2$  showed that only the *gauche* conformation is a minimum energy level on the rotational curve of  $\text{H}_2\text{NNH}_2$  [398]. The pyramidal inversion barrier of hydrazine is slightly higher than that of ammonia.

Bond distances, bond angles, and total energies for the *gauche* and *anti* conformations of hydrazine in comparison to MMH were calculated using a modified Pulay's force method [399]. The predicted N—N distance of  $1.4509 \times 10^{-10}$  m of the *gauche* conformation is closer to the measured distance of  $1.45 \times 10^{-10}$  m than the value calculated for the *anti* conformation ( $1.5066 \times 10^{-10}$  m).

*Ab initio* calculations of the electronic spectrum and ionization potentials of hydrazine showed that all the first transitions appeared to belong to the first two Rydberg series, without any overlap with the valence transitions (which were expected to be above 11 eV) [400]. Comparing computer results to reported vacuum ultraviolet (VUV) spectra [401, 402] of hydrazine, the calculated splitting between the first two vertical ionization potentials is always lower than the experimental values. A rotation-torsion-inversion Hamiltonian function has been used to show that the inversion-torsion coupling in hydrazine is minimal and the inversion-inversion coupling is very strong [403, 404]. The barrier to inversion of  $2072\text{ cm}^{-1}$  is slightly higher than that in ammonia (which is a well-known microwave resonator). The barrier to an internal rotation of  $934\text{ cm}^{-1}$  calculated now is relatively high but lower than that reported by previous investigators using one-dimensional models.

Geometries, anharmonic vibrations, and torsion-wagging multiplets of hydrazine and its deuterated species were studied using high-level *ab initio* methods [405]. To describe the splitting patterns caused by tunneling in torsion-wagging states, the 3-D potential energy surface for the large-amplitude torsion-wagging modes was

constructed. The determined energy barriers, including the contributions from the small-amplitude vibrations, to the tunneling of the symmetric and anti-symmetric wagging mode of 1997 and  $3454\text{ cm}^{-1}$ , respectively, were in reasonable agreement with the empirical estimates.

*Ab initio* molecular orbital calculations and vibrational analysis confirmed that the *gauche* form with a dihedral angle close to  $90^\circ$  is the equilibrium conformation and that the *syn* form, which lies  $39.8\text{ kJ/mol}$  above the *gauche* form, is a transition conformation [406]. The energy level of the *anti* form, a weak equilibrium species, lies in a shallow minimum only  $7.7\text{ kJ/mol}$  above the *gauche* form. The *syn* form is only a transition structure for internal rotation, the barrier for which is  $36.9\text{ kJ/mol}$ . The barrier of inversion at one nitrogen atom is estimated to be somewhere around  $23\text{ kJ/mol}$ . Other *ab initio* calculations included the properties of molecular fragments of hydrazine and diazene (diimine) [407]. In discussing molecular structure and rotational barriers in hydrazine, its behavior has been repeatedly compared to that of its electron analogs hydrogen peroxide [379, 408, 409] and hydroxylamine, and MO/*ab initio* calculations were performed for all these molecules [410].

Equilibrium geometries and harmonic vibrational frequencies of the  $C_{2h}$  and  $D_{2h}$  conformers of the hydrazine ion  $\text{N}_2\text{H}_4^+$  were calculated using an *ab initio* method [357]. Valence and all electron correlation calculations were carried out using the correlation-consistent core and valence polarization triple-zeta basis set. The adiabatic ionization potential of hydrazine was calculated using two different methods, and the best predictions were  $8.07$  and  $7.81\text{ eV}$ , which were close to the experimental data, measured as  $8.1 \pm 0.15\text{ eV}$ .

The structural and spectroscopic properties of hydrazine were investigated by means of *ab initio* molecular dynamics, *ab initio* path integral molecular dynamics, and *ab initio* ring polymer molecular dynamics simulations in conjunction with electronic structure calculations [411]. Whereas the former method relies on the classical approximation of nuclear motion, quantum effects on structure and dynamics were considered at finite temperatures by *ab initio* path integral and *ab initio* ring polymer molecular dynamics, respectively. It was shown that quantum-mechanical fluctuation effects of the nuclei, in addition to their purely thermal activation, cause significant configurational fluctuations due to strongly anharmonic vibrations and, thus, increase the explored regions on the Born-Oppenheimer potential energy surface at room temperature. Including these effects, in turn, leads to significant improvements in the computed spectra compared to stick spectra obtained at the equilibrium structure by means of harmonic normal-mode analysis, as well as by classical *ab initio* molecular dynamics.

Optimized equilibrium geometries, harmonic frequencies, and rotational constants of the *gauche* conformer ( $C_2$  symmetry) of hydrazine were calculated employing a large series of basis sets and several *ab initio* methods [412]. The computed equilibrium geometries of the molecular structure were  $r_{\text{NN}} = 1.434\text{ \AA}$ ,  $r_{\text{NH}_1} = 1.013\text{ \AA}$ ,  $r_{\text{NH}_0} = 1.010\text{ \AA}$ ,  $\angle\text{NNH}_1 = 111.3^\circ$ ,  $\angle\text{NNH}_0 = 106.8^\circ$ , and  $\angle\text{H}_1\text{NNH}_0 = 89.7^\circ$ .



### 2.3.5.3 Dipole Moment Predictions of Hydrazine Molecule

Comparison of dipole moment measurements with INDO-calculated dipole moments for hydrazine vapor between 10 and 1000 K showed good agreement [413]. Calculations of free electron pairs in localized CNDO/2 wave functions of nitrogen compounds for hydrazine gave information on the type of hybridization of nitrogen “lone-pair” orbitals and free electron pair interactions in various N—N compounds [414].

Quantum Monte Carlo (QMC) calculations of the electric dipole moment and ground-state total energy of hydrazine used two QMC techniques: variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) techniques [415–417]. The electric dipole moment of the  $\text{N}_2\text{H}_4$  molecule was calculated using only the DMC technique. This gave an electric dipole moment value of 2.0 D, which was in good agreement with the experimental value of 1.85 D. Similarly, the ground-state total energy of the  $\text{N}_2\text{H}_4$  molecule was calculated using both VMC and DMC methods.

### 2.3.5.4 Computational Chemistry of Hydrazine Decomposition

Most theoretical CNDO, SCF-MO, LCAO-MO, MINDO, and other calculations discussed earlier are concerned with only the intact, vibrating, and rotating molecule of hydrazine. They will eventually indicate the limit of stability where the molecule will begin to break apart. Other calculations have taken the CNDO/INDO technique one step further and calculated potential energy surfaces for N—N bond rupture in hydrazine [418]. The calculation results agree with experimental data that indicate that amino radical recombinations occur without activation energies. Two amino radicals approaching each other do not have to overcome energy potential barriers in the approach as long as the two  $\text{NH}_2$  are oriented such that the  $\text{NH}_2$  flap angles with respect to the line joining the two nitrogen atoms are more than  $20\text{--}30^\circ$ . Computationally, the easiest pathway for photodecomposition of  $\text{N}_2\text{H}_4$  is through N—H rather than N—N bond rupture (in agreement with experimental results). In a different mathematical exercise, the results obtained with 62122 mixed basis sets were closer to the experimental values of the  $\text{N}_2\text{H}_4$  molecule than those obtained with standard basis sets as the single configuration level [419].

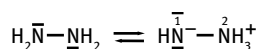
The decomposition of hydrazine ions in the beam of a mass spectrometer leads to different fragments. The unimolecular chemistry of  $\text{NH}_2\text{NH}_3^+$  formation and decomposition has been investigated experimentally and theoretically [420]. In accordance with experiments, losses of  $\text{H}_2$  and  $\text{H}^\bullet$  were calculated to be the dominant low-energy processes. A weak signal due to loss of  $\text{NH}$  with the formation of  $\text{NH}_4^+$  was also observed. The reaction dynamics of the  $\text{H}_2$  loss was investigated in great detail. This process has a substantial reverse barrier and a large non-statistical translational energy release. An *ab initio* direct dynamics calculation provided some insight into the process and was in agreement with the experimentally determined translational energy release. The proton affinity of  $\text{H}_2\text{NNH}_2$  was calculated and found to agree with experimental numbers.

### 2.3.5.5 Computational Chemistry of Hydrazine Cluster Formation, Hydration, Association, and Dissociation

Much of the interaction between hydrazine molecules and their surroundings is influenced by hydrogen bonding. Hydrazine would boil at a lower temperature close to that of its structural analog ethane if it did not have intermolecular hydrogen bonds. The diffusion properties and hydration structure of hydrazine in an aqueous solution were investigated through molecular dynamics simulations and split-flow pulse injection diffusion experiments [421]. The simulations were performed based on ambient conditions along the liquid side of the liquid-vapor coexistence curve, up to the critical point, and in the supercritical region at temperatures of 673, 773, 873, and 973 K and at densities ranging from 0.1 to 0.8 g/cm<sup>3</sup>. Such conditions may exist in steam power plants. The spatial distribution functions for hydrated water were derived. Under ambient conditions, hydrazine is hydrated by 24 water molecules with about 1.6 H-bonds being donated to each nitrogen atom. The hydration number decreases with temperature along the coexistence curve and is seen to increase with system density in the supercritical region. Under low-density supercritical conditions, hydrazine has no appreciable hydration structure and is surrounded by only two water molecules at 873 K and 0.1 g/cm<sup>3</sup>. The diffusion coefficients for hydrazine at subcritical state conditions agreed with Stokes-Einstein and Wilke-Chang predictions. The diffusion coefficients in the supercritical region were found to correlate more closely with the overall fit to the Dymond equation.

### 2.3.6 Isohydrazine and Ylide Structures

Besides resonance structures for hydrazine and its derivatives, in which electrons occupy different places in the molecule, tautomeric unsymmetrical ylide forms have been proposed, in which the hydrogen atoms are no longer equivalent if they are attached to two different atoms. Tautomeric amide-imide forms (“iminoammonium”) have been drawn up by theoretical chemists, but never proven to exist for hydrazine itself:



Tautomerism of this kind may play a role in intramolecular rearrangements found with aromatic hydrazine derivatives, but not hydrazine itself. Using the STO-3G method, bond lengths and angles for the hypothetical isohydrazine have been calculated: N<sup>1</sup>—H 1.037 × 10<sup>-10</sup> m, N<sup>1</sup>—N<sup>2</sup> 1.643 × 10<sup>-10</sup> m, N<sup>2</sup>—H 1.069 × 10<sup>-10</sup> m, angle ∠HN<sup>1</sup>H 106.5°, angle ∠N<sup>1</sup>N<sup>2</sup>H 94.0° [422, 423]. It has been pointed out that the isohydrazine molecule is isoelectronic with methanol, an otherwise very stable molecule. However, in isohydrazine the axis of the H<sub>3</sub>N pyramid is not in line with the N—N bond. The two axes are inclined against each other by 5.6°. Another set of

*ab initio* calculations concluded that isohydrazine, once formed, would be relatively stable since the barriers for its unimolecular isomerization and decomposition are relatively high [424]. But HNNH<sub>3</sub> is unlikely to be isolated in measurable amounts since bimolecular tautomerization takes place very rapidly. It should at least be considered an intermediate in hydrazine reactions.

The possibility of electron binding to the HNNH<sub>3</sub> or H<sub>2</sub>NNH<sub>2</sub> tautomers of hydrazine was examined at the coupled cluster level of theory with single, double, and noniterative triple excitations in an *ab initio* study [425]. The HNNH<sub>3</sub> tautomer, with a dipole moment of 5.4 D, binds an electron by 1076 cm<sup>-1</sup>, whereas the H<sub>2</sub>NNH<sub>2</sub> tautomer forms neither a dipole- nor valence-bound anionic state. A valence-bound anionic state for either the *gauche* or staggered conformations of H<sub>2</sub>NNH<sub>2</sub> or for HNNH<sub>3</sub> was not found. The dipole moment of 2.0 D for the *gauche* structure is too small to substantially bind an excess electron. The results indicate that the HNNH<sub>3</sub> tautomer of hydrazine can bind an electron, whereas the well-known H<sub>2</sub>NNH<sub>2</sub> tautomer cannot. This suggests a possible practical route to the formation of the HNNH<sub>3</sub> tautomer through photodetachment of an excess electron from N<sub>2</sub>H<sub>4</sub><sup>-</sup>. The neutral and anionic HNNH<sub>3</sub> are predicted to be kinetically stable with respect to tautomerization (having barriers of 98.7 and 107 kJ/mol, respectively), though thermodynamically unstable by 182 and 169 kJ/mol (with respect to the neutral H<sub>2</sub>NNH<sub>2</sub>), respectively.

Recombination of two amidogen radicals, NH<sub>2</sub> + NH<sub>2</sub> → N<sub>2</sub>H<sub>4</sub>, is relevant to hydrazine formation, ammonia oxidation and pyrolysis, nitrogen reduction (fixation), and a variety of other N/H/X combustion, environmental, and interstellar processes [426]. A comprehensive analysis of the N<sub>2</sub>H<sub>4</sub> potential energy surface, using a variety of theoretical methods, with thermochemical kinetic analysis and master equation simulations used to treat branching to different product sets in the chemically activated NH<sub>2</sub> + NH<sub>2</sub> process showed that iminoammonium ylide (NH<sub>3</sub>NH), the less stable isomer of hydrazine, may be involved in the multitude of N<sub>2</sub>H<sub>4</sub> formation and decomposition reactions. A termolecular reaction is an entropically disfavored path, but it does describe a new means of nitrogen fixation by activating the notoriously unreactive N<sub>2</sub>.

### 2.3.7 Molecular Structures of Other Hydronitrogens

The molecular structures of other hydronitrogens, such as diazene (“diimine”), triazane, tetrazene, hydrogen azide, hydrazinium cations, and hydrazine-derived free radicals, have been studied by computational chemistry because these compounds are either short-lived intermediates in the decomposition of hydrazine or were considered building blocks for other, more energetic hydrogens. A summary of the molecular structures of these entities is given in [427] and in *Encyclopedia of Liquid Fuels*, chapter “Hydronitrogens.”

## 2.4 Optical Properties of Hydrazine

This section deals with the interaction of hydrazines with electromagnetic radiation in a wavelength range of 100 nm to 20 cm. Correspondingly, the section is subdivided into UV absorption, IR absorption, and microwave absorption. The spectra obtained in these spectral ranges are of interest in the clarification of the molecular structure of hydrazine and measurement of the energies of the atomic/molecular bonds in it. Since the hydrazine N—N bond (as opposed to the azo bond N=N and its many azo dyes) is not a chromophore, there is nothing to report on the light absorption of hydrazine derivatives in the visible range. Practical applications of hydrazine spectra are in the analytical methods for measuring hydrazine concentrations in water or in air and for tracking the environmental fate of hydrazine that has been released into the atmosphere but is quickly destroyed by light and autoxidation.

The only spectra recorded for hydrazine are absorption and fluorescence spectra. The molecule is so unstable that it decomposes prior to the emission of characteristic molecular emission spectra when excited in an electric glow discharge. However, hydrazine as a lasing medium is a new research area and offers additional insight into the nature of the molecule. The emission spectra of fragments have been observed and are discussed in the following section.

### 2.4.1 UV Absorption Spectra of Hydrazine

It is very difficult to measure the UV spectra of hydrazine because the same radiation required to analyze the sample will also cause photolytic decomposition. In most cases, the UV spectra of hydrazine are intermixed with those of decomposition products. Reference to the UV absorption spectra is made in Section 4.6.2 on the UV photolysis of hydrazine. Once the absorption spectra of the decomposition products are subtracted, the absorption of the parent molecule can be mathematically derived.

The UV spectrum of hydrazine vapor consists of five or six nearly equidistant absorption maxima at about 232.6, 232, 227.6, 225, and 222.5 nm, followed by a continuous absorption below 220 nm extending all the way into the quartz-UV region [428, 429]. No rotation structures can be seen in the band absorptions at 5.4 Å per mm dispersion. Extending these measurements to shorter wavelengths, vacuum UV spectra of hydrazine vapor at up to 0.9 mbar were recorded in a 20-cm cell with a LiF entrance window and a quartz exit window [430, 431]. The absorption increased from 200 to 105 nm with two peaks at 190 and 170 nm, a weak peak at 153 nm, and a barely visible shoulder around 200 nm. Hydrazine vapor flowed through the cell at such a rate that photolysis decomposition products could not accumulate in the cell. An attempt was made to correlate the peaks with transitions predicted by the coupled electron pair approximation method [432]. Absorption at 165 to 210 nm was predicted to be dissociative. Although it has been observed that hydrazine mainly photodissociates to  $\text{N}_2\text{H}_3^\bullet$  and  $\text{H}^\bullet$  with a quantum yield near unity, emissions from fragments like excited

NH or  $\text{NH}_2$  may interfere with the hydrazine spectra. Complete knowledge of the UV spectra of the  $\text{NH}_2$  radical is needed to understand the spectra of hydrazine decomposition intermediates and products. Such information can be obtained by laser absorption spectrometry [433, 434]. Since the bond energy of N—D bonds differs from that of N—H bonds, UV spectra of deuterated hydrazine would result in absorption at different wavelengths [435]. Vacuum UV absorption coefficients for hydrazine, MMH, and UDMH were measured from 115 to 185 nm to determine interference with UV sensors in space applications [436]. Similar measurements of UV absorption cross sections at 191 to 291 nm determined the hydrogen atom quantum yield at 248 nm [437]. For the UV absorption of  $\text{N}_2\text{H}_4$  at 213.9 nm a UV absorption cross section of  $\sigma = 220.5 \times 10^{-20} \text{ cm}^2/\text{mol}$  was assumed for hydrazine photolysis and autoxidation studies in the atmosphere.

Vacuum UV absorption coefficients for hydrazine, MMH, and UDMH were measured from 115 to 185 nm to determine interference of leaked propellants with UV sensors in space applications [436]. Vacuum UV absorption coefficients for  $\text{N}_2\text{H}_4$ ,  $\text{CH}_3\text{HNNH}_2$ , and  $(\text{CH}_3)_2\text{NNH}_2$  were measured for wavelengths between 115 and 185 nm with an estimated experimental error of  $\pm 15\%$ . The measurements were made in a hydrazine-compatible flow-cell apparatus at room temperature.

Whereas ammonia has a distinct band structure of absorption bands between 120 and 200 nm, hydrazine essentially shows a continuum absorption in this range without much structure [438]. Measurements were made at a pressure of 0.8 to 1.5 mm Hg, and a flow of hydrazine was passed through the absorption cell to purge out photolysis products. A hydrogen lamp served as light source; it emits a continuum down to 165 nm and a mix of continuum and line or band structures between 165 and 120 nm. The VUV spectrum of hydrazine vapor showed three poorly defined shoulders at 218, 178, and 155 nm [401, 402]. The band shapes can be attributed to planarization of the Rydberg states. When the  $C_2$  pyramidal *gauche* geometry of the neutral molecule changes to  $D_{2h}$  planar geometry after losing a proton and becoming an ion, structural relaxation energies allow many energy states and wash out the sharp edge of photolysis threshold. The determination of absorption spectra of hydrazines in the vacuum UV region is complicated by premature photolysis.

A frequently observed intermediate in hydrazine decomposition or oxidation reactions is diazene (“diimine”)  $\text{HN}=\text{NH}$ . It has a distinct UV absorption spectrum with  $\lambda_{\text{max}}$  near 400 nm [439–441].

#### 2.4.2 IR Absorption Spectra of Hydrazine

IR spectra of hydrazine are extremely useful in identifying contaminants or verifying the absence of contaminants. Such spectra give information on the molecular structure of the  $\text{N}_2\text{H}_4$  molecule and allow the calculation of thermodynamic properties. It is common practice to describe spectra by giving wave numbers and intensities of absorption bands. The following abbreviations are in use for peak heights: **vs**, very

strong; **s**, strong; and **w**, weak. Wave numbers (in  $\text{cm}^{-1}$ ) can be converted to wavelength (in  $\mu\text{m}$ ) by forming the reciprocal

$$\lambda = \frac{10000}{\nu}$$

A common unit for wave numbers is reciprocal centimeters,  $\text{cm}^{-1}$  = kayser. This gives the number of wavelengths that fit into 1 cm. A chapter on IR spectroscopy could also be subdivided by the experimental technique used, of which there are quite a few: transmission, reflectance, attenuated total reflectance, vapor absorption, liquid absorption, mulls, emulsions, solid films, solid matrix isolation, adsorbed state on solid surfaces, complexed state in ligand spheres, isotope substitution, Fourier transform enhanced, and many more. Almost all of these methods have been applied to measure the IR spectra of hydrazine and hydrazine derivatives at one time or another. The following sections are subdivided by the physical state of the hydrazine for which IR spectra are being reported. Raman spectroscopy and IR spectroscopy complement each other, so there is some overlap.

IR spectra of hydrazine have been reported and interpreted in numerous publications, including [217, 442]. It would be difficult to provide a listing of all the IR spectra handbooks that include hydrazine. With the recent advent of online databases on the Internet (a few of these available for free), IR spectra and other physical data are now becoming available to computer users with the click of a mouse. This is the easiest way to obtain the most recent spectra in digital form.

Early efforts to assign frequencies and determine the symmetry of the hydrazine molecule were hampered by the lack of data for the corresponding deuterated molecule. All that could be said at that time based on a comparison of calculated (calculated for  $\theta = 0, 60, 90, 120$ , or  $180^\circ$  rotational distortion) and measured IR data was that the most likely angle of rotation from one  $\text{NH}_2$  group to the next was  $\theta = 90^\circ$ , which speaks for a *gauche* conformation of the molecule [443]. An initial summary of frequency assignments for hydrazine  $\text{N}_2\text{H}_4$  in the solid, liquid, and gaseous state is shown in Table 34, based on data from [313, 444–447].

The IR spectra of tetradeuterated hydrazine in the solid, liquid, and gaseous state were measured from 250 to  $4000\text{ cm}^{-1}$ , which allowed more specific assignments of absorption bands. To present a complete set of data, the Raman spectra of liquid  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{D}_4$  were also measured and included in the discussion and frequency assignments, as shown in Table 35.

For researchers studying molecular vibrations and their relations to absorption spectra, also applying quantum-mechanical computations for the molecular structures, the hydrazine  $\text{H}_2\text{NNH}_2$  molecule offers more of a challenge than comparable, simpler molecules like  $\text{HO}-\text{OH}$  or  $\text{H}_3\text{C}-\text{CH}_3$ . Molecular orbital calculations were aimed at interpreting the first excited state of the anti-symmetric wagging vibration [451], the R branch of the anti-symmetric wagging vibration at  $1002$  to  $1006\text{ cm}^{-1}$  [452], and a torsional-wagging tunneling problem in hydrazine vapor [385].

**Table 34:** Vibrational spectra data of hydrazine.

| IR                 |                     |                    | IR spectra of matrix<br>[447] |                  | Raman spec-<br>tra of liquid<br>[313] | Vibration and<br>symmetry type<br>assignments |            | Refer-<br>ences,<br>assign-<br>ments |
|--------------------|---------------------|--------------------|-------------------------------|------------------|---------------------------------------|-----------------------------------------------|------------|--------------------------------------|
| Vapor<br>frequency | Liquid<br>frequency | Solid<br>frequency | First<br>choice               | Second<br>choice | Frequency                             | Depolarization                                |            |                                      |
| —                  | —                   | —                  | 394(m)                        | 394(m)           | —                                     | —                                             | $\nu_7$    | [446]                                |
| 780(s)             | 800                 | 795                | 832(s)                        | 748(w)           | 783(vw)                               | —                                             | $\nu_6$    | [446]                                |
| —                  | 873                 | 885                | 1087(ms)                      | 875              | 882(s)                                | 0.5                                           | $\nu_5$    | [446]                                |
| 933(vs)            | —                   | 1072               | —                             | —                | —                                     | —                                             | —          |                                      |
|                    | 1038                | —                  | 982(vs)                       | 982(vs)          | —                                     | —                                             | $\nu_{12}$ | [447]                                |
| 966(vs)            | —                   | 1078               | —                             | —                | —                                     | —                                             | —          |                                      |
| 1098(m)            | —                   | 1124               | 1312(m)                       | 1087(ms)         | 1111(vs)                              | 0.3                                           | $\nu_4$    | [446]                                |
| 1275(w)            | 1280                | 1320               | 1265(m)                       | 832(s)           | 1295(vw)                              | —                                             | $\nu_{11}$ | [447]                                |
| 1493(w)            | —                   | —                  | —                             | 1312(m)          | 1628(s)                               | 6/7                                           | $\nu_3$    | [446]                                |
| 1628(m)            | —                   | —                  | —                             | 1265(m)          | —                                     | —                                             | $\nu_{10}$ | [447]                                |
| —                  | —                   | —                  | —                             | —                | 3190(s)                               | —                                             | —          |                                      |
| —                  | —                   | —                  | —                             | —                | 3261(vs)                              | —                                             | $\nu_2$    | [446]                                |
| 3280               | —                   | —                  | —                             | —                | —                                     | 0.2                                           | —          |                                      |
| 3314(m)            | 3200                | 3204               | 3297(mw)                      | 3297(mw)         | 3273(vs)                              | —                                             | $\nu_9$    | [447]                                |
| 3325(vw)           | —                   | —                  | 3390(mw)                      | 3390(mw)         | —                                     | —                                             | $\nu_1$    | [446]                                |
| 3350(m)            | 3338                | 3315               | 3356(mw)                      | 3356(mw)         | 3336(s)                               | 6/7                                           | $\nu_8$    | [447]                                |

Compiled from multiple data sources

Every line of the R branch splits into four components. Explicit expressions for torsional-wagging rotational Hamiltonian matrix elements, also in comparison to hydrazine-like molecules, and a Fourier transform spectrum of the second torsional band of hydrazine were given by [453, 454]. Torsional-wagging-rotational matrix elements for the three large-amplitude vibrational and rotational problem in hydrazine were derived in a more convenient form and in more detail using a separate treatment of the large-amplitude vibration and the overall rotation [386]. Torsional-wagging-rotational basis set functions were defined for each symmetry species of the permutation-inversion group  $G_{16}$ , and  $\Delta K = 0, \pm 1, \pm 2$ , and  $\pm 4$  Hamiltonian matrix elements constructed from these basis sets were given in terms of tunneling parameters, which can be used directly in a least-squares fitting procedure of spectra of hydrazine-like molecules.

The Fourier transform spectrum of the anti-symmetric amino-wagging band of hydrazine has been reanalyzed [455]. About 1700 transitions from 18 sub-bands with  $K'$  from 0 to 6 were newly assigned. In place of a global fit, which proved unsuccessful, individual sub-band fits were made for each  $K'$  value to obtain sublevel parameters for each  $K$  sublevel of the anti-symmetric amino-wagging state.

In the far-IR spectrum of hydrazine vapor, torsional vibration bands with centers at 376.7, 665.9, and 289.5  $\text{cm}^{-1}$  correspond to transitions  $0 \rightarrow 1$ ,  $0 \rightarrow 2$ , and  $1 \rightarrow 2$ , respec-

**Table 35:** Fundamental frequencies of hydrazine N<sub>2</sub>H<sub>4</sub>.

| Vibra-<br>tion<br>number | Initial description                              | More recent<br>assignment | IR spectra |           |       |        |       | Raman<br>spectra |
|--------------------------|--------------------------------------------------|---------------------------|------------|-----------|-------|--------|-------|------------------|
|                          |                                                  |                           | Matrix     | Ar Matrix | Solid | Liquid | Vapor | Liquid           |
| <b>a Species</b>         |                                                  |                           |            |           |       |        |       |                  |
| 1                        | NH <sub>2</sub> anti-symmet-<br>rical stretching | s-a-HNH stretch           | 3297       | 3390      | 3310  | 3332   | 3325  | 3277             |
| 2                        | NH <sub>2</sub> symmetrical<br>stretching        | s-s-HNH stretch           | 3207       |           | 3200  | 3189   |       | 3189             |
| 3                        | NH <sub>2</sub> deformation                      | s-scissor                 | —          |           | 1603  | 1806   | 1493  | 1628             |
| 4                        | NH <sub>2</sub> wagging                          | s-HNH twist               | 1312       | 1299      | 1304  | 1283   |       | 1295             |
| 5                        | N—N stretching                                   | N—N stretch               | 1087       | 1086      | 1126  | 1098   | 1098  | 1111             |
|                          |                                                  | + s-wag                   |            |           |       |        |       |                  |
| 6                        | NH <sub>2</sub> rocking                          | s wag                     | 832        | 810       | 884   | 871    | 780   | 882              |
|                          |                                                  | + N—N stretch             |            |           |       |        |       |                  |
| 7                        | Torsion                                          | torsion                   | 377        | 388       | 627   | —      | 377   | —                |
| <b>b Species</b>         |                                                  |                           |            |           |       |        |       |                  |
| 8                        | NH <sub>2</sub> anti-symmet-<br>rical stretching | a-a-HNH stretch           | 3390       | 3398      | 3310  | 3332   | 3350  | 3336             |
|                          |                                                  | + a-s-stretch             |            |           |       |        |       |                  |
| 9                        | NH <sub>2</sub> symmetrical<br>stretching        | a-s-HNH stretch           | 3356       | 3313      | 3310  | 3332   | 3297  | 3336             |
|                          |                                                  | + a-a-stretch             |            |           |       |        |       |                  |
| 10                       | NH <sub>2</sub> deformation                      | a-scissor                 | —          |           | 1655  | 1608   | 1608  | 1628             |
| 11                       | NH <sub>2</sub> wagging                          | a-HNH twist               | 1265       | 1262      | 1350  | 1324   | 1275  | 1295             |
| 12                       | NH <sub>2</sub> rocking                          | a-wag                     | 982        | 953       | 1066  | 1042   | 937   | 1000             |

Compiled from multiple sources, including [313, 444–450].

tively [339, 456]. The fine structure of rotational-vibrational bands is divided into two series, one with  $\Delta J = 0$ ,  $\Delta K = \pm 1$ , the other with  $\Delta J = \pm 1$ ,  $\Delta K = \pm 1$ . The Q branch is irregularly spaced near the center of the band, indicating that the symmetry factor is very small. The characteristic deformation vibrations of a pyramidal NH<sub>2</sub> consist of bending, twisting, and wagging modes. The bending and twisting modes correspond to the degenerate deformations of ammonia [457]. Hydrazine has three large-amplitude motions, two NH<sub>2</sub> wagging vibrations, and a torsional vibration. The torsional band in a range of 200 to 450 cm<sup>-1</sup> is ideal for testing theoretical models since it is the lowest vibration in the hydrazine molecule and is far from the higher-frequency vibrations, which might interfere. The torsional band of hydrazine is a b-type band, having the rotational selection rules  $\Delta K_a = \pm 1$ ,  $\Delta J = 0, \pm 1$ . The most distinctive feature of this band is a series of nearly equidistant Q-branch heads that degrade slightly toward the red. Under high resolution, one can resolve many regular series of R-branch lines [453]. However, P-branch lines could not yet be assigned. The barrier height for internal rotation was estimated to be approximately  $2100 \pm 50$  cm<sup>-1</sup>. Because tunneling splitting complicates the spectrum badly, it is difficult to give a more accurate estimate based on IR spectra alone. Some of the tunneling parameters in the torsionally excited state



were determined precisely. The torsional splitting in the torsionally excited state is 1824 MHz, compared to 5.8 MHz in the ground state. The inversion splitting found in the torsionally excited state is 7976 MHz. It is surprisingly smaller than the inversion splitting of the ground state, which is 16040 MHz.

Far-IR absorption lines of hydrazine can be assigned by a laser technique. Far-IR laser transitions for hydrazine can be generated by optical pumping with known laser lines [458]. For  $\text{N}_2\text{H}_4$ , assignments have been found for 14 new transition systems and verified for 5 others.

With 228 known far-IR (FIR) laser emissions, hydrazine is one of the most prolific laser active molecules after methanol. But due to the complexity of its rovibrational spectrum, only a few assignments of hydrazine FIR laser transitions are found in the literature [459, 460].

Rotational barriers are evident from two-dimensional inversion on the potential function for hydrazine determined from rotation-vibration spectra. The two-dimensional potential function for the inversion of the amino groups in hydrazine was obtained from a fit to the available IR and microwave data [403]. The barriers of 3408 and 2016  $\text{cm}^{-1}$  were calculated for the symmetric and anti-symmetric inversions of both amino groups, respectively. Contrary to earlier assumptions, a large potential coupling between the inversions of the amino groups was found [404]. The strong bands at 780 and 937  $\text{cm}^{-1}$  were assigned to the symmetric and anti-symmetric amino-wagging vibrations, respectively. When examining the 937  $\text{cm}^{-1}$  band of hydrazine vapor with a resolving power of 0.3  $\text{cm}^{-1}$ , it was found that every vibration-rotation band split into four components and that the amount of splitting depended only slightly upon the rotational quantum number [450]. At such a high resolution, described in IR spectroscopy lingo, the IR spectrum of hydrazine looks like the proverbial “picket fence.” This fine structure was explained by a vibration in which the wagging motions of the two amino groups take place anti-symmetrically with respect to the  $C_2$  axis, that along this axis an appreciable inversion takes place, and that such an inversion results in four equivalent equilibrium conformations. The barrier height between every two adjacent equilibrium conformations was 2620  $\text{cm}^{-1}$ .

A convenient source of IR for various analytical applications is the diode laser. Absorption measurements of pure hydrazine and MMH were recorded in an optical absorption cell (3 passes, 50 cm/pass) at low pressure (0–35 mm Hg) using a tunable external-cavity diode laser (ECDL), operating in a range of 6350 to 6650  $\text{cm}^{-1}$  (1.49 to 1.58  $\mu\text{m}$ ) [461, 462]. Peak absorption cross-sectional measurements of hydrazine and MMH, as determined from fixed-wavelength absorption measurements recorded at various pressures, were found to be  $\alpha_e/\nu = 0.163 \pm 0.003 \text{ cm}^{-1} \text{ atm}^{-1}$  at 6495  $\text{cm}^{-1}$  ( $\lambda = 1539.6 \text{ nm}$ ) and  $\alpha_e/\nu = 0.152 \pm 0.003 \text{ cm}^{-1} \text{ atm}^{-1}$  at 6560  $\text{cm}^{-1}$  ( $\lambda = 1524.4 \text{ nm}$ ), respectively. The measurements represent the first high-resolution survey spectra of these hydrazines in the near IR. These measurements will form the basis for the design of a diode-laser-based leak detection system for the Space Shuttle launch pad.

IR line positions, line strengths, and pressure-broadening coefficients are required to determine absolute trace gas concentrations from high-resolution absorption spectra. These values were measured for the IR absorption lines in the  $\nu_{12}$  band (anti-symmetric wag) of hydrazine between 965.4 and 965.7  $\text{cm}^{-1}$  using a high-resolution tunable diode laser system with 0.0006  $\text{cm}^{-1}$  spectral resolution and an 18-m pathlength multiple-pass absorption cell [463]. A continuous flow of hydrazine diluted to 100–500 ppm in nitrogen at pressures between 0.013 and 6.7 kPa (0.1 and 50 mm Hg) was used to prevent decomposition in the sampling cell. These results were used to construct a HITRAN-format line list that can be used both to spectroscopically distinguish hydrazine from other components and to determine its concentration in complex gas mixtures. See also [464].

The amino-wagging tunneling process in hydrazine was treated using the generalized internal-axis-method-like method developed by Hougen and Coudert, and Hamiltonian matrix elements were derived for each symmetry species in the combined group-theoretical and IAM-like treatment [465]. Ground-state microwave absorption transition data of hydrazine were analyzed again in this treatment to determine axis-switching angles for the amino-wagging tunneling process.

A high-resolution IR spectrum of hydrazine has been recorded in the 729–1198  $\text{cm}^{-1}$  region (the  $\nu_{12}$  anti-symmetric wagging band) with a resolution of 0.002  $\text{cm}^{-1}$  [466]. About 1350 transitions with  $K'$  from 7 to 13 have been assigned, and about 2350 transitions with lower values of  $K'$  were reanalyzed with the improved precision. The effective parameters were calculated separately for each value of  $K'$  using the Hougen-Ohashi Hamiltonian for hydrazine. The extended assignment completed the analysis of the  $\nu_{12}$  band of hydrazine.

In addition, 472 new rotational transitions in the vibrational ground state of hydrazine have been measured in the submillimeter range from 345 to 410 GHz [467]. Most recorded lines form eight  $K = 2 \leftarrow 1Q$  branches with  $J \leq 30$ , each branch being split due to internal rotation in hydrazine. New rotational transitions together with 443 that were previously known have been fitted to an effective group-theoretical Hamiltonian originally developed by Hougen 1981. For all 915 rotational transitions an overall standard deviation of the fit of 0.59 MHz was obtained using 32 parameters. These were 14 asymmetric rotor constants, 16  $\text{NH}_2$  inversion parameters, and 2 internal rotation parameters.

A very weak N–N stretching band ( $\nu_5$ ) in the IR spectrum of hydrazine was unambiguously assigned [468]. Almost 1500 transitions with a resolution of 0.002  $\text{cm}^{-1}$  for  $K'$  from 0 to 6 and for all symmetry species have been analyzed. The band center was determined at 1077  $\text{cm}^{-1}$ , much higher than previously expected.

A weak fundamental symmetric amino-wagging band,  $\nu_6$ , was assigned in the high-resolution FTIR spectrum of hydrazine [469]. An analysis of the Fermi-type resonance between the  $\nu_6$  and the third excited torsional state,  $3\nu_7$ , was performed, and a global fitting was carried out taking into account 3392 lines of the  $\nu_6$  band (for  $K'$  from

0 to 10 and for all symmetry species) and 428 lines of the  $3\nu_7$  band (for  $K'$  from 3 to 9 and only for the symmetry species in resonance). For all 3820 rovibrational transitions an overall standard deviation of the fit of  $0.019\text{ cm}^{-1}$  was obtained. The band centers of the symmetric wagging state and the third torsional were determined at  $795.137$  and  $860.138\text{ cm}^{-1}$ , respectively. IR and Raman spectra allow the distinction between singly and doubly protonated hydrazinium ions [470].

#### 2.4.2.1 IR Spectra of Solid Hydrazine, Adsorbed Hydrazine, and Matrix-Isolated Solid Hydrazine

Thin films of hydrazine or MMH or their decomposition products that may condense on cryocooled germanium optical windows of sensors on satellites in outer space might block IR transmittance. Therefore, IR absorption spectra of thin films of frozen  $\text{N}_2\text{H}_4$  or MMH on cold germanium windows were measured and interpreted by Fourier transform analysis [471, 472]. The substrate holders were cooled to 80 K (liquid nitrogen) or 20 K (cold helium gas) [473]. A dual-angle laser interference technique was used to determine the thickness and the refractive index of the thin hydrazine films. In addition, a quartz crystal microbalance was used to weigh the amount and give the average loading density. Plume contamination by unreacted propellants or combustion products is a concern for many satellite and space probe missions using hydrazine propellants.

The lack of some IR absorption bands reported by other investigators for crystalline  $\text{N}_2\text{H}_4$  suggested that the thin films deposited at very low pressures ( $10^{-7}\text{ mm Hg}$ ) were actually supercooled liquids and not truly crystalline hydrazine. The same has been observed in hydrazine droplets formed by flash evaporating liquid hydrazine into a vacuum and forming an aerosol [36]. The sudden cooling did not allow crystals to order themselves and the droplets consisted of mixtures of disordered and crystalline phases. A disordered phase was observed at initial cell temperatures of 230 to 180 K, and a transition to a crystalline phase occurred around 175 to 180 K. The gas (and particles suspended in it) was approximately 10 K warmer than the vacuum cell. At lower temperatures the IR bands at  $3000$  to  $3400\text{ cm}^{-1}$  became progressively sharper, indicating that the regularity in the crystals improved as the temperature was lowered to 110 K. At the lowest temperature, the two peaks split into doublets. Some self-annealing (due to the heat of condensation released at the moment of phase change) occurred before the particles had a chance to impinge on the wall of the chamber or bump into another particle with a different temperature. Such studies were initially started to study hydrazine clouds in planets with ammonia atmospheres but may also find application in detecting rocket propellant leaking from satellites in space or looking at the cloud generated when hitting a wayward satellite with an antiballistic missile.

#### 2.4.3 Raman Fluorescence Spectra of Hydrazine

Raman spectra are mostly of scientific interest and are not used for actual practical analytical methods like IR spectroscopy. Raman spectra, in combination with IR spectra, are useful in identifying fundamental vibrations in hydrazine molecules.

### 2.4.3.1 Raman Spectra of Liquid Hydrazine

Two sets of five sharp lines were observed in liquid hydrazine excited with the 404.7 or 435.9 nm lines of mercury [429, 439]. Two lines were at shifts of 90 and 112  $\text{cm}^{-1}$ , and three lines were at shifts of 3212, 3289, and 3339  $\text{cm}^{-1}$ . The latter three agreed very well with the triplet observed in liquid ammonia and have been assigned to N—H vibrations. The first two were unique to hydrazine. The weak line at 900  $\text{cm}^{-1}$  could have been caused by residual water in the sample. Raman and IR spectra were obtained on samples of  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{D}_4$  of identical purity and are shown in Table 36 for comparison [474].

**Table 36:** Raman and IR spectra of liquid  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{D}_4$ .

| $\text{N}_2\text{H}_4$        |                        |                               |                        | $\text{N}_2\text{D}_4$        |           |                               |           |
|-------------------------------|------------------------|-------------------------------|------------------------|-------------------------------|-----------|-------------------------------|-----------|
| Raman                         |                        | IR                            |                        | Raman                         |           | IR                            |           |
| Wave-number, $\text{cm}^{-1}$ | Intensity <sup>a</sup> | Wave-number, $\text{cm}^{-1}$ | Intensity <sup>b</sup> | Wave-number, $\text{cm}^{-1}$ | Intensity | Wave-number, $\text{cm}^{-1}$ | Intensity |
| 875                           | 6                      | 872                           | s                      | 365                           | 0         | —                             | —         |
| 1041                          | 1.5                    | 1045                          | vs                     | 745                           | 0.5       | —                             | —         |
| 1109                          | 7                      | 1130                          | s                      | 799                           | 1         | 720–830                       | m         |
| 1290                          | 1                      | —                             | —                      | 831                           | 0         | —                             | —         |
| 1325                          | 1                      | 1323                          | m                      | 885                           | 0.5       | 873                           | w         |
| 1625                          | 6                      | 1607                          | vs                     | 941                           | 7         | 935                           | vw        |
| 1756                          | 1.5                    | —                             | —                      | 959                           | 1         | 968                           | vw        |
| 1913                          | 0                      | —                             | —                      | 1010                          | 0         | 991                           | m         |
| 2125                          | 0                      | —                             | —                      | 1030                          | 5         | 1026                          | w         |
| 2922                          | 1                      | 2940                          | m                      | 1088                          | 0         | 1121                          | s         |
| 2968                          | 1                      | —                             | —                      | 1164                          | 0.5       | 1150                          | s         |
| 3187                          | 10                     | 3189                          | vs                     | 1201                          | 5         | —                             | —         |
| 3256                          | 10                     | 3270                          | vs                     | —                             | —         | 1371                          | vw        |
| 3332                          | 9                      | 3310                          | vs                     | 1473                          | 1         | 1462                          | s         |
|                               |                        |                               |                        | 2352                          | 10        | 2330                          | vs        |
|                               |                        |                               |                        | 2417                          | 10        | 2397                          | vs        |
|                               |                        |                               |                        | 2490                          | 9         | 2477                          | vs        |
|                               |                        |                               |                        | 3278                          | 1.5       | 3273                          | m         |
|                               |                        |                               |                        | 3325                          | 1         | —                             | —         |

<sup>a</sup> Intensity on a scale from 0 to 10 (estimated)

<sup>b</sup> Intensity on a scale from very weak to very strong (estimated)

Data source: [474]

The 435.8-nm line of mercury was used for excitation and the spectra were recorded on photographic plates and with an electric photometer. The agreement between the two sets of data for the two isotopomers was quite good. See also [475, 476].

Raman displacements, relative intensities, and depolarization factors for liquid hydrazine were measured at room temperature [313]. All available literature data con-

cerning the structure, Raman and IR spectra, frequency assignments, and dipole moment measurements were collected and examined in a search for the most reliable values. The results of normal coordinate treatment based on the  $C_2$  model were reported, and frequency assignments were reviewed. Also, calculated thermodynamic properties for 273.16 to 1000 K based on the rigid rotator harmonic oscillator approximation were provided.

#### 2.4.3.2 Raman Spectra of Solid Hydrazine

Since earlier Raman spectra of crystalline  $N_2H_4$  and  $N_2D_4$  had been obtained only with mercury line excitation [366], the spectra of both compounds were reinvestigated using the 514.5-nm line of an argon ion laser, resulting in good agreement between the two sets of data (Table 37) [445]. New, weak, previously not observed lines were reported at 818, 994, and  $1028\text{ cm}^{-1}$  for  $N_2H_4$  and at 333, 778, and  $852\text{ cm}^{-1}$  for  $N_2D_4$ .

Raman spectra provide information on the crystal structure of solid hydrazine. If solid hydrazine crystallized in the  $C_{2h}^2$  space group (see space group assignments based on X-ray and NMR data, Section 2.3.4), one should expect only six Raman-active lattice modes. An inspection of the Raman spectrum in the lattice region shows five strong, sharp lines and three weak, sharp lines for  $N_2H_4$  and six strong, sharp lines with an additional four weaker ones for  $N_2D_4$ . There does not appear to be any way in which these lines can be assigned as three libration and three translations, even if one considers phonon bands. Therefore, the  $C_{2h}^2$  space-group symmetry with two molecules per unit cell must be ruled out. It is possible to reconcile the Raman spectra with a  $C_{2h}$  space group with  $Z = 4$ . Phase transitions in solid hydrazine/water mixtures result in changes of the Raman spectra of the solid samples [123].

#### 2.4.3.3 Raman Spectra of Hydrazine Vapor

Based on measurements obtained using the 514.5-nm line of an argon ion laser [445], the Raman spectra of hydrazine  $N_2H_4$  vapor has five pronounced, polarized lines at 3398, 3329, 3302, 3266, and  $1076\text{ cm}^{-1}$ . For a molecule with  $C_2$  symmetry one expects two N—H stretching vibrations, resulting in polarized Raman bands.

Unlike in earlier studies, the Raman line at  $3398\text{ cm}^{-1}$  (a normal mode) is assigned to the  $NH_2$  anti-symmetric stretch of symmetry " $a$ " and the line at  $3329\text{ cm}^{-1}$ , the strongest line in the Raman spectrum, is assigned to an  $NH_2$  symmetric stretch of the corresponding symmetry. The band at  $1076\text{ cm}^{-1}$  is the N—N stretch. Two lines at 3302 and  $3266\text{ cm}^{-1}$  are overtones of two  $NH_2$  deformations. The strongest Raman line was reported at  $1564\text{ cm}^{-1}$  in [477], but Durig et al. did not observe any Raman scattering in this region. The two weaker lines at 1076 and  $3332\text{ cm}^{-1}$  agreed well among the two groups of authors. In the Raman spectrum of  $N_2D_4$  vapor, the lines at 2442, 2422, and  $2358\text{ cm}^{-1}$  were assigned to  $\nu_1$ ,  $\nu_2$ , and  $2\nu_3$ , respectively. The line at  $1031\text{ cm}^{-1}$  is the N—N stretch. The line at  $930\text{ cm}^{-1}$  is an  $ND_2$  wagging vibration. Isotope substitution has again proven to be a valuable tool in achieving assignments of frequencies to molecular vibrations. The various lines for both  $N_2H_4$  and  $N_2D_4$  are summarized in Table 38.

**Table 37:** Observed Raman spectra of crystalline  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{D}_4$ .

| Frequency, $\text{cm}^{-1}$ |    | Assignment and description |    |                                                            |
|-----------------------------|----|----------------------------|----|------------------------------------------------------------|
| $\text{N}_2\text{H}_4$      |    | $\text{N}_2\text{D}_4$     |    |                                                            |
| 3301                        | vs | 2464                       | vs | $\nu_1(a)\text{NH}_2(\text{ND}_2)$ anti-symmetric stretch  |
| 3194                        | m  | 2416                       | m  | $\nu_8(b)\text{NH}_2(\text{ND}_2)$ anti-symmetric stretch  |
| 3188                        | m  | 2403                       | m  | $\nu_9(b)\text{NH}_2(\text{ND}_2)$ symmetric stretch       |
| 3169                        | vs | 2332                       | vs | $\nu_2(a)\text{NH}_2(\text{ND}_2)$ symmetric stretch       |
| 3032                        | vw | —                          | —  | —                                                          |
| 1788                        | vw | —                          | —  | —                                                          |
| 1762                        | vw | —                          | —  | —                                                          |
| 1662                        | m  | 1226                       | mw | $\nu_{10}(b)\text{NH}_2(\text{ND}_2)$ deformation          |
| 1638                        | m  | 1218                       | mw | crystal splitting of $\nu_{10}$                            |
| 1609                        | mw | 1198                       | mw | $\nu_3(a)\text{NH}_2(\text{ND}_2)$ deformation             |
| —                           | —  | 1188                       | w  | crystal splitting of $\nu_3$                               |
| 1350                        | vw | —                          | —  | crystal splitting of $\nu_4$                               |
| 1335                        | mw | 1032                       | mw | $\nu_4(a)\text{NH}_2(\text{ND}_2)$ wag                     |
| 1318                        | mw | 1020                       | mw | $\nu_{11}(b)\text{NH}_2(\text{ND}_2)$ wag                  |
| 1302                        | vw | —                          | —  | crystal splitting of $\nu_{11}$                            |
| 1144                        | mw | —                          | —  | crystal splitting of $\nu_5$                               |
| 1133                        | mw | 955                        | w  | crystal splitting of $\nu_5$                               |
| 1114                        | vs | 938                        | m  | $\nu_5(a)\text{N—N}$ stretch                               |
| —                           | —  | 852                        | vw | crystal splitting of $\nu_{12}$                            |
| 994                         | w  | 832                        | vw | $\nu_{12}(b)\text{NH}_2(\text{ND}_2)$ rock                 |
| —                           | —  | 778                        | vw | crystal splitting of $\nu_6$                               |
| 905                         | w  | 768                        | mw | crystal splitting of $\nu_6$                               |
| 884                         | s  | 748                        | m  | $\nu_6(a)\text{NH}_2(\text{ND}_2)$ rock                    |
| 818                         | vw | —                          | —  | —                                                          |
| 534                         | vw | 396                        | vw | $\nu_7(a)\text{NH}_2(\text{ND}_2)$ torsion or lattice mode |
| 510                         | vw | 377                        | vw | $\nu_7(a)\text{NH}_2(\text{ND}_2)$ torsion or lattice mode |
| —                           | —  | 333                        | vw | lattice mode                                               |

Data source: [445]

#### 2.4.4 Refractive Index of Hydrazine

The measurement of the index of refraction is a quickly performed test for purity of liquid compounds or for the quantitative analysis of binary mixtures. The results are summarized in Table 39.

Additional index of refraction data for alkyhydrazines are in the chapters on dimethylhydrazines and methylhydrazine. The index of refraction of hydrazine has been determined for hydrazine at various temperatures using several different wavelengths. The results are summarized in Table 40. The refractive index of hydrazine can be plotted as a function of temperature, and a linear relationship is obtained (Figure 35).

**Table 38:** Raman spectra of hydrazine and tetradeuterohydrazine vapor.

| $\text{N}_2\text{H}_4$        |           |                           | $\text{N}_2\text{D}_4$        |           |                           | Assignment                                                       |
|-------------------------------|-----------|---------------------------|-------------------------------|-----------|---------------------------|------------------------------------------------------------------|
| Wave-number, $\text{cm}^{-1}$ | Intensity | Polarization <sup>a</sup> | Wave-number, $\text{cm}^{-1}$ | Intensity | Polarization <sup>a</sup> |                                                                  |
| 3398                          | m         | p                         | 2442                          | s         | p                         | $\nu_1(a)\text{NH}_2(\text{ND}_2)$ anti-symmetric stretch        |
| 3329                          | vvs       | p                         | 2422                          | vvs       | p                         | $\nu_2(a)\text{NH}_2(\text{ND}_2)$ symmetric stretch             |
| 3302                          | m         | p                         | 2358 <sup>b</sup>             | s         | p                         | $2\nu_{10}$ overtone of $\text{NH}_2$ deformation                |
| 3266                          | m         | p                         | —                             | —         | —                         | $2\nu_3$ overtone of $\text{NH}_2$ deformation                   |
| 2958 <sup>c</sup>             | —         | —                         | 3072                          | —         | —                         | —                                                                |
| 2925                          | mw        | ?                         | 2939                          | w         | p                         | impurity?                                                        |
| 2890                          | —         | —                         | 2885                          | —         | —                         | —                                                                |
| —                             | —         | —                         | 2054                          | m         | p                         | $2\nu_5$ overtone ( $2 \times 1031 = 2062$ )                     |
| —                             | —         | —                         | 1218                          | vw        | ?                         | $\nu_{10}(a)\text{ND}_2$ deformation                             |
| 1642                          | vvw       | ?                         | 1126                          | m         | dp                        | $\nu_3(b)\text{NH}_2(\text{ND}_2)$ deformation                   |
| 1076                          | s         | p                         | 1031                          | s         | p                         | $\nu_5(a)\text{N}-\text{N}$ stretch (mixed w. $\text{ND}_2$ wag) |
| —                             | —         | —                         | 1009                          | w         | dp                        | $\nu_{11}(b)\text{ND}_2$ wag (?)                                 |
| —                             | —         | —                         | 930                           | s         | p                         | $\nu_4(a)\text{ND}_2$ wag (mixed w. $\text{N}-\text{N}$ stretch) |
| —                             | —         | —                         | ~805                          | w         | dp                        | $\nu_{12}(b)\text{ND}_2$ rock                                    |
| —                             | —         | —                         | 749                           | m         | p                         | $\nu_6(a)\text{ND}_2$ rock                                       |
| —                             | —         | —                         | 238                           | —         | —                         | Beginning of pure rotational wing                                |

<sup>a</sup> p = polarized, dp = depolarized<sup>b</sup> possibly  $2\nu_3$ , Fermi resonance?<sup>c</sup> Intensity of these lines varies with purification, most likely due to impurities

Data source: [445]

**Table 39:** Index of refraction of hydrazine and hydrazine compounds.

| Compound                         | Temperature, K | $n_D$            | References |
|----------------------------------|----------------|------------------|------------|
| Hydrazine                        | 293.1          | 1.47074          | [171]      |
|                                  | 295.4          | 1.46979          | [478]      |
|                                  | 298            | 1.46899          | [479]      |
|                                  | 298.1          | 1.46867          | [171]      |
|                                  | 298.1          | 1.4679           | [480]      |
|                                  | 298.1          | 1.4683           | [207]      |
|                                  | 298.1          | 1.4686           | [481]      |
| Hydrazine hydrate                | 308.1          | 1.46444          | [167]      |
| Hydrazinium nitrate, crystalline | 298            | $\alpha = 1.458$ | [482]      |
|                                  | 298            | $\beta = 1.605$  | —          |
|                                  | 298            | $\gamma = 1.620$ | —          |

Table 40: Index of refraction data for hydrazine at different wavelengths.

| Temperature, K | Spectral line (Wavelength, nm) |        |        |         |                   |            |
|----------------|--------------------------------|--------|--------|---------|-------------------|------------|
|                | H $\alpha$                     | (365)  | (435)  | (546.1) | H $\beta$ (486.1) | Li (656.3) |
| 295.4          | 1.46675                        | —      | —      | —       | 1.47715           | 1.46624    |
| 308.1          | —                              | —      | —      | —       | 1.47108           | 1.46207    |
| 298.1          | —                              | 1.4980 | 1.4837 | 1.4714  | —                 | —          |

Data sources: [167, 481]

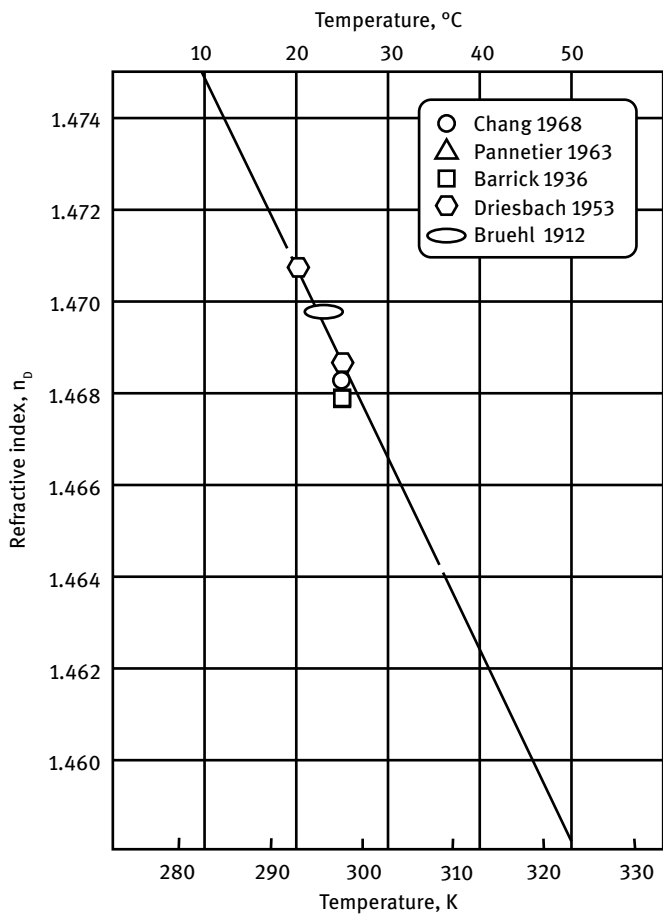
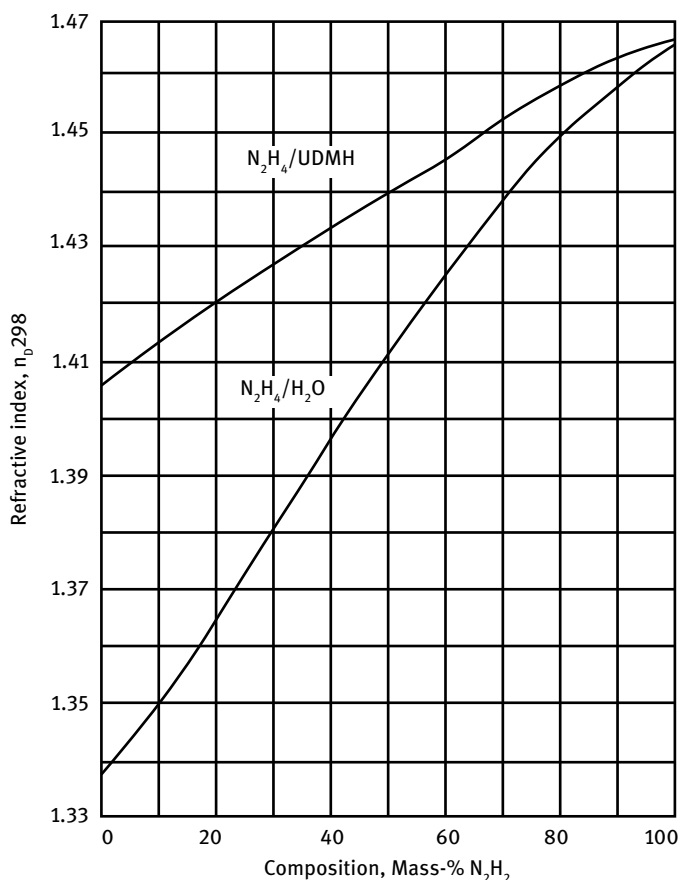


Figure 35: Refractive index of anhydrous hydrazine at sodium D line (5893 Å). (Reproduced and modified from [171].)



The molecular refraction of hydrazine at the D-line wavelength is 8.892 [167]. Very few good summaries of the refractive index and molecular refraction data of hydrazine derivatives exist [483].

The index of refraction of binary hydrazine mixtures can be used as a method of quick quantitative analysis. A calibration curve must be prepared first. A refractometric method of analysis of binary hydrazine-water or hydrazine/UDMH mixtures has been described [480]. The index of refraction data was measured at two temperatures, 293 and 298 K, over the entire range of compositions. Only the 298 K data are illustrated here (Figure 36).



**Figure 36:** Refractive index of hydrazine mixtures at 298 K. (Reprinted and modified from [480].)

The refractive index of  $N_2H_4$ /UDMH mixtures will be described further in the chapter on dimethylhydrazines. As can be seen in the preceding graph, comparison of the slopes of the two curves revealed that the  $N_2H_4$ / $H_2O$  system showed a more pro-

nounced variation of the refractive index as a function of composition than did the  $\text{N}_2\text{H}_4/\text{UDMH}$  system. The refractive index has been considered as an analysis method for hydrazine/water mixtures [484]. The advantage of the method is that it can be performed by untrained personnel. The disadvantage is that it is not specific to water or hydrazine in the presence of other contaminants. Also, it takes a relatively long time for the instrument and sample to attain constant temperature. The refractive index has been proposed as a field analysis method for a hydrazine propellant blend nominally containing 30% water [485]. A graph for the refractive index of aqueous HN solutions at 298 K was already shown in *Encyclopedia of Oxidizers*, in the chapter “Hydrazinium Salt Oxidizers.”

## 2.5 Microwave Spectra of Hydrazine

Microwave spectra extend the IR toward very long wavelengths on the order of millimeters instead of micrometers. Because of the lesser quantum energy, microwave spectra reveal details of low-energy molecular transitions, such as individual rotation energy states and their thawing temperatures. Microwave absorption of hydrazine would have to be known for the design of microwave-powered initiation of hydrazine decomposition in monopropellant thrusters.

Because ammonia and amino radicals have already been detected in interstellar gas, it should come as no surprise if one of these days hydrazine is also identified in interstellar gas by its microwave absorption.

Molecules with large-amplitude vibrational motions such as inversion or internal rotation show very complicated IR and microwave spectra. In hydrazine, three large-amplitude motions are possible, two inversions and an internal rotation of the two amino groups. Based on repeated microwave measurements, a revised theory of the rotational energies in the ground vibrational state was developed. The eight series of the Q-branch transition  $\Delta J = 0, K = 1 \leftarrow 0$  of hydrazine vapor were observed at frequencies up to 130 GHz [486, 487]. The inversion splitting for the  $J_K$  level may be expressed by

$$\nu = 16040.2 - 1.53J(J+1) - 25.9K^2, \quad \nu \text{ in MHz}$$

The rotational constants are

$$A = 143467.6 \text{ MHz}$$

$$B = 24083.0 \text{ MHz}$$

$$C = 24070.1 \text{ MHz}$$

The height of the internal barrier of rotation was found to be equivalent to  $1240 \pm 50 \text{ cm}^{-1}$ , assuming a twofold potential barrier. Other authors found the rotational barrier to be approximately 13.14 kJ/mol (3.14 kcal/mol) [378]. In a range of 4.7 to 30 GHz,

about 200 lines were found, and all exhibited quadratic Stark effects [488]. The spectrum is complicated by the internal rotation of one amino group with respect to the other and by the inversion of each amino group like motions in ammonia or methylamine [378]. For some lines the hyperfine structures due to the nuclear quadrupole coupling of two nitrogen nuclei with the overall and internal rotation of the molecule could be observed. It is possible to excite selective vibrations with IR radiation and then conduct double-resonance spectroscopy of selected molecule segments, e.g., the anti-symmetric amino group wagging with microwaves [489]. The anti-symmetric amino-wagging band lies in the 10- $\mu\text{m}$  region. Nearly 200 microwave transitions were measured in a frequency range of 6–60 GHz using  $\text{N}_2\text{O}$  and isotopic  $\text{CO}_2$  masers as the radiation source. Among the microwave transitions, 27 were assigned as those of the ground vibrational state and 9 as those of the vibrationally excited state. About 20 IR absorption lines were assigned based on the double resonance measurements. The excited-state rotational constants, the internal rotation splittings, the inversion splittings, and even Coriolis splittings were determined accurately.

Hydrazine can serve as a lasing medium. In addition to microwave absorption, microwave emission in the submillimeter range has also been observed with hydrazine molecules excited by radiation from a carbon dioxide laser [490, 491].

Water, hydrazine, and hydrogen peroxide all have a tendency to supercool. Dielectric relaxation studies of aqueous solutions of hydrazine and hydrogen peroxide in the neighborhood of their glass transition temperatures,  $T_g$ , showed that these solutions behave in a rather simple manner [492]. Their relaxations near  $T_g$  were more nearly exponential than in most other cases, and they showed essentially no secondary relaxations. Supercooled hydrazine solutions were the more stable solutions of the three.

Microwave spectra of deuterium-substituted hydrazine  $\text{N}_2\text{D}_4$  or HDNNDH helped in the assignment of vibrational bands [493]. When measuring the microwave spectrum of  $\text{N}_2\text{D}_4$  in a range of 8 to 100 GHz, an inversion splitting was observed at 443 MHz (compared to 7974 MHz for  $\text{N}_2\text{H}_4$ ) [494]. The rotational constants for  $\text{N}_2\text{D}_4$  were

$$A = 74724.3 \text{ MHz}$$

$$B = 18501.9 \text{ MHz}$$

$$C = 18437.5 \text{ MHz}$$

The barrier height to inversion was  $2120 \text{ cm}^{-1}$ .

## 2.6 Photoelectron (ESCA, XPS) Spectra of Hydrazine

ESCA (or XPS) is a spectroscopic method that can be applied to vapors and solid surfaces. Depending on the objective of the analysis and the range of atomic weights to be scanned, resonance lines of noble gases in vacuum UV or monochromatic X-

rays (magnesium or aluminum) are used to excite photoelectrons that are then passed through a monochromator, and their energy and intensity are measured. In solid materials, only a very thin surface layer is analyzed, usually only 5 nm deep. For gaseous samples, less energetic photons (vacuum UV as opposed to X-rays) are used to excite electron spectra. Hydrazine XPS spectra have been measured with the 30.4-nm He(II) resonance line [495, 496], 58.4-nm He(I) line [497], or magnesium  $K_{\alpha}$  lines [498, 499]. The high-resolution photoelectron spectrum of hydrazine vapor shows two pairs of overlapping bands. The experimental vertical ionization energies are 9.91, 10.64, 15.61, and 16.66 eV. The splitting of the two bands indicates the energy variation of electrons coming from two different rotational structures of hydrazine. The letters represent the originating orbitals [ $n(\text{N})$ ,  $\sigma(\text{N}-\text{N})$ ,  $\pi(\text{NH}_2)$ ] assigned to the respective electrons in the photoelectron spectrum.

Photoelectron spectroscopy has developed into a very useful tool for conformational analysis, and ESCA-XPS spectra permit quantitative determination of the interaction of molecular orbitals by measuring the ionization energies of various molecular valence orbitals with high precision. Different conformations are characterized by different energy states and usually show up as separate or split peaks in the ESCA spectrum. A splitting of 38.59 kJ/mol (0.4 eV) in the nitrogen nonbonding orbitals of hydrazine was derived from the initially obtained low-resolution spectra [500]. More sensitive instrumentation has allowed refinement of these data to 70.04 kJ/mol (0.73 eV) [496]. The measured energy was assigned to specific orbital interactions, and splitting of the peaks was derived by CNDO/2 and MINDO/2 calculations using a “sum rule” [497]. The sum rule states that the sum of experimental ionization energies may be reproduced by the sum of localized-orbital ionization energies. For a dihedral angle of  $95^\circ$ , the CNDO/2 method is more accurate than the MINDO/2 method.

## 2.7 Neutron and Electron Diffraction Spectra

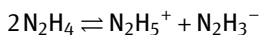
In addition to XRD, neutron and electron diffraction spectra have been used to investigate the structure of hydrazine and its compounds. Electron diffraction studies of hydrazine vapor showed no evidence of dimerization [501]. The N—N bond distance was  $(1.47 \pm 0.02) \times 10^{-10}$  m, the N—H bond distance was  $(1.04 \pm 0.06) \times 10^{-10}$  m, and the N—N—H bond angle was  $108 \pm 8^\circ$ . See also [388].

## 2.8 Electrical Properties of Hydrazine

### 2.8.1 Electrical Conductivity of Hydrazine

Hydrazine is an electrolyte, and any dissolved salt will greatly increase its electrical conductivity. Often trace amounts of contaminants, such as water or carbon dioxide,

will increase its conductivity. The small conductivity in ultrapure hydrazine may be due to autodissociation. Like water or ammonia, hydrazine undergoes molecular autoionization to form its acid and base conjugates:



### 2.8.2 Dielectric Constant of Hydrazine

The dielectric constant (abbreviation DC, symbol  $\epsilon$ ) of hydrazine has been determined to be between 58.5 and 51.7 between 273 and 298 K [502, 503]. The data, also compiled in Table 41, can be represented by the following equations:

$$\epsilon = 58.5 - 0.3253t + 2.8 \times 10^{-3}t^2 - 2.67 \times 10^{-5}t^3$$

where  $\epsilon$  is the dielectric constant (dimensionless) and  $t$  is the temperature in  $^{\circ}\text{C}$ , or

$$\epsilon = 266.82 - 1.2153T + 11.6565 \times 10^{-3}T^2$$

where  $\epsilon$  is the dielectric constant (dimensionless) and  $T$  is the temperature in kelvin.

**Table 41:** Dielectric constants of hydrazines.

| Compound                        | Temperature, K | Dielectric constant | References      |
|---------------------------------|----------------|---------------------|-----------------|
| $\text{N}_2\text{H}_4$          | 273            | 58.5                | [502]           |
|                                 | 278            | 56.9                |                 |
|                                 | 283            | 55.5                |                 |
|                                 | 288            | 54.2                |                 |
|                                 | 293            | 52.9                |                 |
|                                 | 298            | 51.7                |                 |
|                                 | 293            | 52.9                | [504]           |
|                                 | 308            | 49.5                |                 |
|                                 | 323            | 46.5                |                 |
| $\text{N}_2\text{H}_5\text{OH}$ | 298            | 61.2                | [504]           |
|                                 | 308            | 58.2                |                 |
| MMH                             | 288.7          | 19.2                | Olin Corp. 1986 |
|                                 | 305.3          | 17.3                |                 |
|                                 | 298            | 19.0                | [171]           |

The DC of hydrazine is quite high, 51.7 at 298 K, compared to 15 for ammonia or 81 for water. Electrolytes dissolved in hydrazine will thus become ionized almost as easily as in water. As a result, the electrical conductivity of hydrazine changes drastically as soon as minor impurities, such as carbazic acid formed from carbon dioxide in the air, become dissolved in it.

## 2.9 Nuclear Magnetic Resonance Spectra of Hydrazine

NMR spectra of hydrazine, either from the nitrogen nuclei or the hydrogen nuclei (protons), are useful for determining the structure of hydrazine molecules and the amount of proton exchange and hydrogen bonding among them. The machines used to perform this type of analysis and their magnets are usually very heavy, so this is not an analytical method suitable for portable toxic vapor analyzers.

The measurements of  $^{14}\text{N}$  nuclear quadrupole resonance cross relaxation in hydrazine [362, 389] and hydrazine hydrate [369, 505] have helped to elucidate the internal structure of these molecules. By varying the temperature of a solid hydrazine sample from 274 down to 77 K, four resonance lines were observed with almost equal intensity. At 77 K, the resonance frequencies were 1.8910, 1.9950, 2.6470, and 2.6717 MHz, respectively. When the sample was allowed to thaw, they faded out at 300 K.

On further study using a saturation recovery method, six resonance lines due to two nonequivalent positions for each  $^{14}\text{N}$  nucleus in addition to the nonaxial symmetry were observed [361, 506]. The observed frequencies were 4.611, 2.617, and 1.994 MHz for system II at 77 K. The spin-lattice relaxation of the nuclear spin is caused by the thermal transitions between the energy levels of  $\Delta m = \pm 1$  and  $\pm 2$ . It has been proposed that the crystal force field around the  $^{14}\text{N}$  nuclei deviates strongly from the axial symmetry. Together with data derived from X-ray analysis, this suggested that the crystal is a monoclinic (space group  $C2_2$ ) having two molecules in a unit cell.

With improved resolution, the fine structure of NQR lines of  $^{14}\text{N}$  in a solid hydrazine single crystal could also be observed [507]. The fine structure was found in all six lines. The line splitting in the two lines with the highest frequency was especially clear and well resolved. The fine structures consisted of at least four lines spreading over a bandwidth of 420 to 680 Hz. This fine-splitting was attributed to interaction with neighboring hydrogen atoms. It was too great to be interpreted by the direct nuclear magnetic dipole-dipole interaction between nitrogen and surrounding nuclei. Electron-coupled nuclear spin interaction was successfully applied to explain the fine-line structure of other molecules. The temperature dependence of spin-lattice relaxation correlates with the temperature dependence of fluid viscosity [508]. The quadrupole hyperfine structure in hydrazine, a molecule that exhibits significant tunneling splittings as a result of large-amplitude inversion and internal rotation motion, may be caused by tunneling motions [509]. The following quadrupole coupling constants were derived from  $^{14}\text{N}$  line widths:  $\Delta H_{\text{ms}} = 0.41 \pm 0.01 \text{ G}$ ,  $T_2 = 2.52 \times 10^{-3} \text{ s}$ ,  $(e^2qQ)/h = 4.8213 \text{ MHz}$ ,  $\eta = 0.8070$ ,  $\tau_q = 0.95 \times 10^{-12} \text{ s}$ ,  $\tau_c = 0.78 \times 10^{-11} \text{ s}$ ,  $\tau_c/\tau_q = 12.2$  [510].

The  $^{14}\text{N}$  NQR spectrum of hydrazine hydrate between 4.2 and 140 K consists of two high-frequency lines (4550 kHz at 4 K) and a low-frequency line (2560 kHz) [369, 511]. Both lines weaken and become extinct above 140 K. The activation energy of this molecular motion (most likely rotation or switching motion of a hydrogen bond),

which becomes active at about 120 K, is 31.4 kJ/mol (7.5 kcal/mol). One can also observe an echo envelope modulation due to intramolecular dipolar coupling. This molecular motion is different from that of anhydrous hydrazine, whose activation energy is 59.8 kJ/mol (14.3 kcal/mol), where a hydrazine molecule begins a type of turnover motion about an axis perpendicular to the N—N bond at temperatures above 245 K (Zussman and Alexander 1968). See also [512, 513].

Nuclear quadrupole magnetic resonance measurements can supply important information on internal motion in solids. Line width and spin relaxation time measurements of nuclei are especially helpful. Measurements of the  $^{14}\text{N}$  atom in frozen hydrazine between 200 and 260 K have shown that molecules remain sufficiently mobile to interchange  $^{14}\text{N}$  nuclei between two crystallographically nonequivalent sites. The molecular motion had an activation energy of  $59.8 \pm 1.7$  kJ/mol ( $14.3 \pm 0.4$  kcal/mol) and proceeded at a rate of  $\sim 2500\text{ s}^{-1}$  at 250 K [368]. A continuation of this study provided relative orientations of the electric field gradient (EFG) tensors [514]. The two nonequivalent nitrogen atoms in hydrazine interchange sites. Spin-lattice relaxation measurements on all six  $^{14}\text{N}$  NQR lines were done at 228 K. According to these measurements, there are two molecules in a unit cell related to each other by inversion. The two nitrogen atoms in the molecule are nonequivalent and have slightly different quadrupole parameters. At 228 K these are  $e^2q^I Q = 4.745$  MHz,  $\nu^I = 0.820$ ,  $e^2q^{II} Q = 4.738$  MHz, and  $\nu^{II} = 0.785$ . The angles between the tensor directions are  $\Phi_{XX} = 93.7^\circ$ ,  $\Phi_{YY} = 16.7^\circ$ , and  $\Phi_{ZZ} = 91.0^\circ$ .

## 2.10 Redox Potential of Hydrazine in Solution

The use of dilute hydrazine hydrate solutions in fuel cells opens new applications for hydrazine as an energy carrier. Electrochemical methods for the analysis and detection of hydrazine will be discussed in Section 3.6.10.

Based on experimental evidence obtained during the oxidation of hydrazine in acid and alkaline media it was concluded that the oxidation of hydrazine occurs not primarily via a hydrogen oxidation mechanism, as previously suggested, but via a sequential oxidation of radicals (intermediates) derivable from hydrazine [515]. It was furthermore concluded that the electrode surface characteristics affect the potential of oxidation, while the rest potential is controlled by the subsequent formation of radicals.

## 3 Chemical Properties of Hydrazine

### 3.1 Reactions of Hydrazine

#### 3.1.1 Reactions of Hydrazine with Inorganic Compounds

Hydrazine is very reactive and reacts with a multitude of inorganic compounds. Hydrazine as a base forms a wide range of hydrazinium salts, several of which are discussed in *Encyclopedia of Oxidizers*, in the chapter “Hydrazinium Salt Oxidizers.” Hydrazine and hydrazine derivatives as ligands in metal complexes open up an entire new chapter of hydrazine compounds, best summarized in a book by Patil and Ratan [516].

##### 3.1.1.1 Oxidation of Hydrazine (Hydrate) in Solution

Although the two adjacent nitrogen atoms in hydrazine should favor the formation of nitrogen when the hydrogen is abstracted by oxidation, this seemingly simplest path of reaction is hardly ever followed during oxidation reactions. The oxidation of hydrazine in aqueous solutions can happen in many ways, depending on the pH and the presence or absence of trace amounts of transition metals, which act as catalysts. A summary contains sections on thermochemical properties of hydrazine, reaction stoichiometry and kinetics studies, and studies of reaction intermediates [517]. Depending on the type of oxidant used, molecular nitrogen was found only in a few cases to be the sole oxidation product [518]. The multiplicity of oxidation products also made it very difficult to find an oxidizing agent that would react in stoichiometric ratios with hydrazine and could be used for quantitative oxidimetric volumetric analysis. In addition to molecular nitrogen, the compounds ammonia, hydrazoic acid, and diazene have been observed as oxidation products of hydrazine, depending on the type of oxidizer used.

##### 3.1.1.2 Kinetics of Hydrazine Reactions with Oxygen and Ozone

The kinetics of the reaction of hydrazine vapor with oxygen or ozone are of interest when one must predict the environmental fate of hydrazine released into the atmosphere. Because hydrazine is a strong reducing agent and hydrazine vapor will autoignite with oxygen (at higher than atmospheric pressure) and ozone (over a wide pressure range down to very low pressures), kinetic studies must be done outside the range of autoignition. This can be achieved either by working at very low pressures or by dilution with an inert gas.

Hydrazine-oxygen and hydrazine-ozone reactions in aqueous solutions are of interest for the design of wastewater treatment plants. Sometimes oxygen or ozone wastewater treatment is combined with other agents (UV, ultrasound, microwaves, catalysts) to speed up the reaction. This application will be discussed in Section 7.12.1.3.



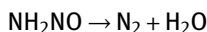
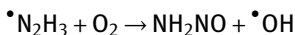
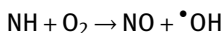
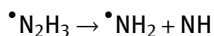
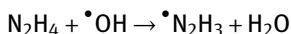
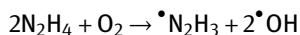
The main industrial application of hydrazine hydrate is for boiler feedwater de-oxygenation in steam power plants. This reaction is done mostly with the addition of water-soluble catalysts and is outside the scope of this book on rocket propellants.

Oxygen-hydrazine reactions can lead to spontaneous ignition and have been the cause of a few accidents. Under elevated pressure, dioxygen is a very active oxidant for hydrazine. The flammable range and autoignition temperatures of hydrazine in air and hydrazine in oxygen will be covered in Section 8.1. Flame speeds of hydrazine flames are described in Section 4.14.1. The current section deals only with academic treatises on hydrazine oxidation kinetics, experiments conducted at low pressures or in high dilution, and computational models for such reactions.

### 3.1.1.3 Vapor-Phase Autoxidation Reactions

Early studies of the reaction of hydrazine vapor with oxygen led to the conclusion that oxidation proceeds by a series of successive radical mechanisms and does not seem to involve either long or branching chains [519]. But the reaction slowed down by the increase of glass surface : volume ratios and/or the addition of ethylene as a radical scavenger. The reaction was studied at 373–433 K and up to 1.32 kPa (10 mm Hg) pressure. These results were confirmed in a later study [520]. The thermal gas-phase reaction showed none of the chain reaction characteristics found with hydrocarbon oxidation. It was found to be predominantly a bimolecular surface reaction with an activation energy of 26.9 kJ/mol (6.430 kcal/mol) (below 373 K). The rate increased linearly with the oxygen concentration. Nitrogen or water-vapor addition had no effect on the kinetic rates.

The explosive oxidation of hydrazine (and ammonia) was studied by flash photolysis and kinetic spectroscopy [521]. The main reaction, which resulted in nitrogen as the end product, was suggested to proceed as a series of progressive dehydrogenation steps without fission of the N–N bond:



The hypothesis of nitrosamine formation in the oxidation of hydrazine was adopted by later investigators. Nitrosamine could be detected in the reaction of atomic oxygen and amino radicals. Another intermediate that has been so far neglected in the study of hydrazine flames but that was shown to occur in other flames and was blamed for high  $\text{NO}_x$  formation is the NNH fragment [522]. It is likely to be an intermediate in  $\text{NO}_x$  formation in hydrazine flames.

Measurements of hydrazine decay in air were done in Pyrex glass vessels, but the data were not yet fitted to a kinetic model [523]. A few years later, other investigators fitted the University of Leeds data to a kinetic model and found good agreement between measurements and predictions of the surface catalysis model [524].

Because of the strong nitrogen dilution, the oxidation of hydrazine vapor with oxygen in an adiabatic flow reactor was not accompanied by a luminous flame, but this experimental arrangement allows a more in-depth study of the kinetics than an atmospheric pressure flame [525]. The reaction rate was found to be dependent on the first power of hydrazine concentration but independent of oxygen concentration. The data indicated that decomposition and oxidation occurred simultaneously and at the same rate. The oxidation reaction rate was between that of dry and “wet” hydrazine decomposition. The activation energy of  $156 \pm 10 \text{ J/mol}$  ( $37.2 \pm 2.4 \text{ kcal/mol}$ ) was very similar to that of hydrazine decomposition ( $151 \text{ kJ/mol} = 36.2 \text{ kcal/mol}$ ). The pre-exponential factor was  $10^{9.91 \pm 0.54}$ . The adiabatic reaction temperature in these tests was 950–1010 K, the initial hydrazine concentration was  $0.4\text{--}1.4 \times 10^{-7} \text{ mol/cm}^3$ , and the hydrazine : oxygen equivalence ratio was 0.2–0.5 (lean mixtures). A mechanism by way of fission of the N–N bond and chain propagation through  $\text{HNO}$ ,  $\text{N}_2\text{H}_3$ ,  $\text{H}_2\text{NNO}$ , and  $\cdot\text{OH}$  radicals was proposed, but very little proof was offered [525]. The addition of NO, usually an active radical scavenger, failed to bring about a distinct change of the reaction rate. Thus, amino and hydrazino radicals may not play the same role in hydrazine oxidation as in hydrazine decomposition, or the decomposition of  $\text{H}_2\text{NNO}$  may generate new radicals. The ignition and combustion of hydrazine in dioxygen was interpreted as a branched chain reaction with some indication of self-inhibition [526]. At higher pressures, the critical conditions of ignition were determined by a competition of chain branching and wall-catalyzed recombination reactions.

The environmental fate of hydrazine vapors in the atmosphere of Earth, which is an autoxidation reaction, has been studied in laboratory chambers under carefully controlled conditions (see Section 10 on Environmental Effects). It was difficult to obtain reproducible results due to interaction of hydrazine vapors with the chamber wall material, outward diffusion of hydrazine through the polymer foils used as chamber materials, and inward diffusion of oxygen from the laboratory air into the test chambers.

The adsorption and autoxidation of hydrazine vapor on polymeric and metallic surfaces was often ignored during the design and operation of laboratory test animal exposure chambers in hydrazine toxicity studies, resulting in overdosing the poor animals [527].

Peroxide radicals formed by reactions of atomic hydrogen (and possibly hydrazyl radicals) with dioxygen were trapped from a low-pressure  $\text{O}_2/\text{N}_2\text{H}_4$  flame onto a cold finger situated in the resonator cavity of an electron proton resonance (EPR) spectrometer [528]. The flame temperature was 860 K at 1.56 kPa. The free radical survival was

enhanced by coating the walls of the apparatus with boric acid. A graphite capillary was used to intercept and eliminate atomic hydrogen between the flame and the cold finger, thus assuring that the EPR signal of  $\text{HOO}^\bullet$  could be recorded without interference from  $\text{H}^\bullet$ .

Dioxygen activation reactions which propagate through a four center two electron (4c-2e) bound species were computed using static DFT and *ab initio* quantum-chemical techniques and showed an oxidation pathway for hydrazine and its methylated analogues with dioxygen which involved formation of this unconventional 4c-2e bonded species in route to the oxidation products [529].

It has been inferred from experimental data that hydrazine oxidation and decomposition reactions occur via a branched-chain and a nonbranched-chain mechanism, respectively. The chain nature of these processes helps explain the observed regularities under the critical autoignition conditions, including their “anomalous” character and the combustion-to-explosion transition [530].

The kinetics and mechanisms of atmospheric reactions of hydrazine vapor and molecular dioxygen on singlet and triplet potential energy surfaces have been investigated using *ab initio* and DFT methods [531]. The results showed that a direct hydrogen abstraction mechanism is the most important pathway of reaction. Three pre-reactive complexes on the singlet and triplet potential energy surfaces were formed between hydrazine and molecular dioxygen. Seven different products were suggested, all of which have sufficient thermodynamic stability. The production of  $\text{HN}=\text{NH} + \text{H}_2\text{O}_2$  and  $\text{H}_2\text{N}_2(\text{OH})_2$  were the main reaction channels from a thermodynamic viewpoint. From a kinetic point of view, an  $\text{H}_2\text{NN} + \text{H}_2\text{O}_2$  adduct (on singlet state) and  $2\text{N}_2\text{H}_3 + 2\text{HO}_2$  adducts (on singlet and triplet states) after passing one corresponding low-level transition state were the most favored pathways of reaction.

#### 3.1.1.4 Liquid-Phase Autoxidation Reactions in Aqueous Solution

Autoxidation of dissolved hydrazine in water by interaction with atmospheric oxygen would occur in holding ponds, where hydrazine-contaminated wastewater is held while it awaits permanent decontamination. Autoxidation of aqueous hydrazine solutions is accelerated by dissolved transition metal ions, which are typically present as natural contaminants in tap water and most surface waters [532–535].

It is surprising to learn that hydrogen peroxide, an oxidant, has been found among the reaction products of hydrazine (a reductant) with air [536]. The presence of  $\text{H}_2\text{O}_2$  was proved by reaction with titanil sulfate. The autoxidation reaction seemed to be heterogeneous (surface catalyzed). The rate of oxidation was at a maximum in 0.01–0.03 M NaOH and dropped again in stronger alkaline solutions.

Studies of the reaction between hydrazine and oxygen at 298 and 343 K (25 and 70 °C) in alkaline solutions have shown that the observed rate is due to catalysis by traces of impurities [537]. Copper(II) and manganese(II) were the most active catalysts, and, under certain conditions, the copper(II)-catalyzed reaction appeared to be homogeneous. Manganese(II) salts will catalyze autoxidation of hydrazine in water [538].

Free radicals have been observed in the metabolic oxidation of hydrazine in blood during the oxidative metabolism of hydrazine in rat liver microsomes [539]. This observation suggests the involvement of the cytochrome P-450 enzyme system in the formation of hydrazine radicals, which may be a precursor of diimide during microsomal oxidation of hydrazine.

Hundreds of catalysts have been patented for the use of hydrazine hydrate for the boiler feedwater deoxygenation in steam power plants. Some of these compounds may also be useful for the decontamination of hydrazine-polluted wastewaters by autooxidation in ponds at atmospheric pressure and ambient temperature.

If hydrazine is spilled into environmental waters, once the dissolved oxygen is depleted by the reacting hydrazine, the only means of continuing the reaction is by diffusion of atmospheric oxygen across the air-water interface [540]. Many publications did not consider the diffusional source of oxygen when predicting the rate of survival of hydrazine when spilled into surface waters.

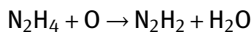
Most of the studies cited in the preceding discussion were performed with very dilute hydrazine hydrate solutions. The following reference deals with much higher concentrations. When 100% hydrazine hydrate (64% hydrazine) was stored in contact with air in Pyrex glass containers at room temperature, the concentration decreased from 64 to 45% within 160 d [541]. The hydrazine concentration of a 10% NaOH solution in hydrazine hydrate decreased at approximately the same rate. See also [517, 518].

#### 3.1.1.5 Kinetics of Reactions with Atomic Oxygen

Numerous investigators have studied the reaction of atomic oxygen with hydrazine vapor. This reaction will occur if hydrazine is released into the upper atmosphere and stratosphere. This reaction is peculiar in that not only does it exhibit chemiluminescence, but mass spectrometric studies have also shown that oxygen preferentially abstracts two hydrogen atoms from opposite ends of a molecule with the resulting formation of diazene [349]. Some of these studies were conducted using oxygen atoms and, in separate tests, hydrogen atoms to initiate hydrazine decomposition and comparing the results and different modes of hydrogen abstraction from hydrazine. In the remaining pages of this chapter, mass spectrometric studies are discussed first, followed by emission spectroscopic studies. The chemiluminescence of the reaction of atomic oxygen with hydrazine vapor can be used for the detection and analysis of hydrazine.

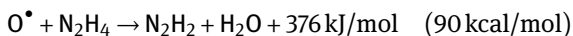
The thermochemical and kinetics properties of hydrogen abstraction from the hydrazine molecule by atomic oxygen were computed using high-level *ab initio* methods [542]. The properties along the reaction path were obtained using a dual-level methodology to build the minimum energy path with the potential energy surface method and thermochemical properties results. The thermal rate constants were calculated in the framework of variational transition-state theory. Energy wells on both sides of the reaction (reactants and products) were found and considered in the chem-

ical kinetics calculations. Additionally, the product yields were investigated by means of a study of the triplet and singlet surfaces of the reaction

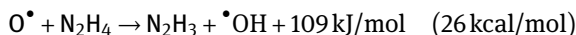


### 3.1.1.6 Mass Spectra of Reaction Products of Atomic Oxygen with Hydrazines

When studying the  $\text{O}^\bullet + \text{N}_2\text{H}_4$  reaction in crossed molecular beams, it was noted that the reaction



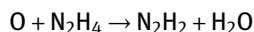
in which two hydrogens are removed, occurs at a substantially higher rate than the expected simple single hydrogen abstraction [349]:



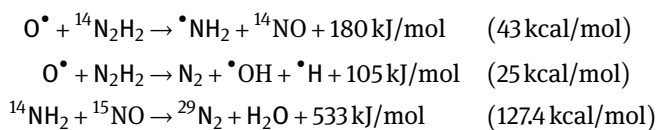
Diazene formation requires the removal of hydrogen atoms from opposite ends of the hydrazine molecule, which at first glance seems very unlikely, in particular because the neighboring hydrogen atoms in an amino group are only 0.157 nm apart (which is very close to the 0.152 nm in the water molecule), whereas two hydrogen atoms at opposite ends of the hydrazine molecule are at least 0.22 nm apart. One way to test this theory was to use UDMH or MMH in place of hydrazine. When UDMH was reacted with atomic oxygen under the same conditions, no dimethylaminonitrene  $\text{N}-\text{N}(\text{CH}_3)_2$  radicals or products of possible rearrangement, such as azomethane,  $\text{CH}_3\text{N}=\text{NCH}_3$ , were observed. Instead, only some  $\text{HN}^\bullet\text{N}(\text{CH}_3)_2$  was identified by the mass spectrometer, which indicated that the hydrogen abstraction reaction remained at this initial step of reaction, rather than proceed further and result in abstraction of both hydrogens from the same nitrogen atom. Further evidence became available from the crossed molecular beam bombardment of MMH with oxygen atoms. In these tests the ion current at a mass-to-charge ratio ( $m/e$ ) of 44, corresponding to  $\text{HNNCH}_3^+$ , increased drastically. Some radicals ( $\text{HN}^\bullet\text{NHCH}_3$  or  $\text{H}_2\text{NN}^\bullet\text{CH}_3$ ) formed by the abstraction of a single hydrogen atom were also observed at  $m/e$  45. In previous tests with UDMH decomposition by hydrogen atoms, the compound with  $m/e$  44 could be identified as  $\text{HN}=\text{NCH}_3$  and exhibited a surprising stability, in that it could be frozen out from the reacting mixture on a cold finger and would reappear when the condensate thawed. Based on the appearance potential of  $\text{HNNHCH}_3^+$  from MMH, a bond dissociation energy  $D(\text{H}-\text{NHNHCH}_3)$  was calculated as  $276 \pm 21 \text{ J/mol} = 66 \pm 5 \text{ kcal/mol}$ . This was somewhat lower than the hydrogen bond dissociation energy in hydrazine itself,  $D(\text{H}-\text{NHNH}_2) = 318 \pm 21 \text{ J/mol} = 76 \pm 5 \text{ kcal/mol}$ . Bond energies were already discussed in Section 2.3.3. In additional tests with oxygen atoms generated from the reaction  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$  rather than by glow discharge in  $\text{O}_2$  gas, it could be proved that the reactive species is indeed  $\text{O}^\bullet$  and not excited atomic or molecular states of oxygen.

A discharge flow system with two independently movable reactant inlet tubes coupled to a time-of-flight (TOF) mass spectrometer was used to study the formation and

destruction of NO in the H-N-O system, as well as with isotope labeling of the reactants [543]. The formation of nitric oxide in the reaction of oxygen atoms with hydrazine is likely to proceed through fission of the diazene N=N bond, since the principal step



preserves the hydrazine N—N bond [544]. The buildup of NO may also be related to the formation of  $\bullet\text{NH}_2$  radicals, which could be observed in large amounts in the  $\text{O}^\bullet + \text{N}_2\text{H}_4$  reaction. When this reaction was carried out in the presence of an excess of  $^{15}\text{NO}$  and the reaction products analyzed in the mass spectrometer, an increase of  $m/e$  29 ( $^{14}\text{N}^{15}\text{N}$ ) and a decrease of  $m/e$  28 ( $^{14}\text{N}^{14}\text{N}$ ) could be observed. This can be explained by the simultaneous reactions



In addition, a significant increase at  $m/e$  45 was observed that is due to nitrosamine  $\text{H}_2^{14}\text{N}^{15}\text{NO}$ . The weak peak at  $m/e$  44 ( $\text{H}_2^{14}\text{N}^{14}\text{NO}$ ) disappeared after  $^{15}\text{NO}$  addition. This was the first conclusive evidence that  $\text{H}_2\text{NNO}$  is an intermediate product in the combustion of hydrazine.

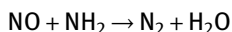
### 3.1.1.7 Emission Spectra of Reaction Products of Atomic Oxygen with Hydrazines

In low Earth orbits, reactions of atomic oxygen (or hydroxyl radicals) with hydrazine vapors oozing from a thruster during evaporation of the dribble volume can cause chemiluminescence and interfere with sensitive optical systems on observation satellites. Similar chemiluminescence can be observed in the contrails of spacecraft re-entering the atmosphere destructively or destroyed on purpose to prevent spread of contamination if they have unused propellant on board. For this reason, reactions of atomic species with hydrazine vapors have been thoroughly investigated. Ground-state atomic oxygen  $\text{O}(^3\text{P})$  makes up 70% of the atmosphere at 300 km. Under conditions in orbit, the collision energy is increased by the orbital speed of the spacecraft colliding with a thermal cloud of atomic oxygen with Maxwellian energy distributions, causing surface glow of adsorbed propellant vapors.

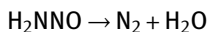
The free radicals formed by the interaction of atomic oxygen (or hydrogen) with hydrazine or ammonia have been identified by emission spectroscopy [545]. The atomic gases were generated in a glow discharge and reacted with hydrazine vapor at a pressure of 133 kPa (1 mm Hg). The main emissions observed with  $\text{O}^\bullet + \text{N}_2\text{H}_4$  were those of  $\text{NH}_2$ ,  $\text{NH}$ ,  $\text{OH}$ , and  $\text{NO}$ . All four emission bands were very intense, and no undecomposed hydrazine or ammonia was found in the condensate. The luminous zone of the  $\text{O}^\bullet + \text{N}_2\text{H}_4$  atomic flame is very narrow compared with that of other atomic flames at the same pressure. This showed that the reaction between  $\text{O}^\bullet$  and  $\text{N}_2\text{H}_4$

proceeded very quickly. When ammonia was substituted for hydrazine, only the NH band was observed as a very weak emission, and 90% of the ammonia was destroyed. Corresponding experiments with atomic hydrogen were discussed in Section 4.7.4.1.

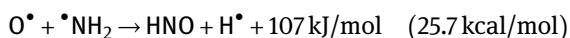
One of the reaction products of hydrazine with atomic oxygen is nitric oxide NO. NO is formed as an intermediate in the reaction, and some may persist and show up as a byproduct of this reaction [546, 547]. Spectroscopic studies have focused on NO emission spectra from  $O^\bullet + N_2H_4$  flames at 0.46–4 Pa (3.5–30  $\mu\text{m}$  Hg) hydrazine or atomic oxygen partial pressure. This work is of particular interest in view of the possible application of hydrazine as an internal combustion engine or scramjet fuel, where NO would be an undesirable contaminant. Once the formation of NO in hydrazine flames is fully understood, corrective action can be taken in combustion engines to avoid its formation by changing the mixture ratio or going to staged combustion. The intensity of the NO bands (due to the  $A^2\Sigma \rightarrow X^2\Pi$  transition) increased strongly by the addition of NO. This suggested that the excited NO was not a primary product of the reaction but rather became excited by energy transfer from another molecule, most likely active dinitrogen in an  $A^3\Sigma$  metastable state. The same dinitrogen was also shown to excite the 253.7-nm line if a trace of mercury vapor was added to the reaction mix. The formation and destruction of nitric oxide in  $O_2/NH_3$  and  $O_2/N_2H_4$  flames and the rate of the reaction



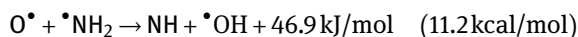
were measured directly for the first time [543]. This reaction is closely related to the decomposition of nitrosamine



postulated as an intermediate product in the combustion of hydrazine. For the first time nitrosamine could be identified as a reaction product of oxygen (atoms) and hydrazine by mass spectrometry [543]. The experimental setup was used to generate atomic species and radicals consisting of a flash-photolysis arrangement with a glow discharge system. Oxygen atoms were continuously generated in a microwave discharge and were present in excess in relation to the amino radicals produced by the photolysis of ammonia. To avoid radical-radical reactions and maintain isothermal conditions, the radicals were diluted with large quantities of inert gas. The decay of the amino radical concentration as a result of reaction with oxygen was measured by time-resolved absorption spectrometry at 597.9 and 516.6 nm. No decay was observed in the absence of oxygen atoms at  $10^{-11}$  mol amino radicals/ $\text{cm}^3$ . With an excess of oxygen atoms, the decay of  $NH_2$  concentration was strictly first order, and the rate constant was  $k = 2.1 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 298 K. The reaction can proceed through

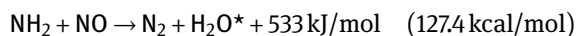


or

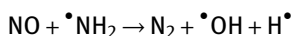


Data on the reaction of  $\text{O}^\bullet$  with  $\text{NH}_3$  support the first path, but even with an optical path of 20 m, no definite absorption could be observed that could be attributed to  $\text{HNO}$ .

The large amount of energy released in the reaction



results in vibrationally excited water molecules that could be identified by IR emission bands. Other theoretically possible products of this reaction could be eliminated because no hydrogen atoms were found by electron spin resonance (ESR) spectroscopy:



Hydrazines will quench the atomic oxygen singlet  $\Sigma$  emission at 1270 nm [548]. Twenty-five different hydrazines were tested in this reaction, and the emission at 1270 nm was measured as a function of time. The quenching mechanism includes electron transfer, electronic  $\rightarrow$  vibrational transfer, and contact charge transfer. It has been suggested that it might be possible to detect hydrazine leakage from satellites in low orbits, where the natural atomic oxygen concentration is high enough ( $10^9$  atoms  $\bullet\text{O cm}^{-3}$ ) to cause chemiluminescence [549].

Not only collisions with atomic oxygen, but also  $\text{O}^+$  ions at suprathermal energies (4–50 eV) result in the chemiluminescence of hydrazine vapors [550, 551]. Collision energy cross sections were measured as a function of the collision energy, using a quadrupole mass spectrometer (QMS) with chopped beams. Emissions detected in the 250–850 nm range were  $\text{OHA}^2\Sigma^+ \rightarrow \text{X}^2\Pi$  at 306 nm and  $\text{NHA}^3\Pi_i \rightarrow \text{X}^3\Sigma^-$  at 336 nm. The OH emission intensity decreased with increasing collision energy, while the NH intensity increased with increasing collision energy. In addition to  $\text{O}^+$ , other ions ( $\text{Ar}^+$ ,  $\text{Kr}^+$ ,  $\text{CO}^+$ ,  $\text{CO}_2^+$ ) were also aimed at hydrazine vapor for comparison. The  $\text{O}^+/\text{N}_2\text{H}_4$  high-mass product reaction sections sum to 15–20 Å<sup>2</sup>.

Laboratory measurements of 1.5 to 5  $\mu\text{m}$  FTIR spectra from  $\bullet\text{O}$  flames with hydrazine, MMH, or UDMH identified several species, among them OH,  $\text{H}_2\text{O}$ , CO,  $\text{CO}_2$ , HNO,  $\text{H}_2\text{CO}$ . It was suggested that  $\bullet\text{O}$  reacts with methylhydrazine to form  $\text{H}_2\text{CO}$  and  $\text{N}_2\text{H}_4$ , which then decomposes through well-established channels. For additional publications on atomic oxygen-hydrazine reactions, see [544, 552–555], also on the use of ESR spectroscopy for the identification of intermediates.

The reactions between hydrazine and atomic oxygen and free hydroxyl radicals were studied under laboratory conditions. The gas phase kinetics of  $\text{O}(^3P)$  and OH reactions with  $\text{N}_2\text{H}_4$ ,  $\text{CH}_3\text{NHNH}_2$ , or  $(\text{CH}_3)_2\text{NNH}_2$  were studied in a discharge flow-tube apparatus [555, 556]. The reactions were studied in 267 Pa (2 mm Hg) of He dilution under pseudo-first-order conditions in the transient species concentration with a known



excess of hydrazine concentration. The steady-state concentration temporal profiles of the transient species were directly monitored by fluorescence techniques to deduce the absolute second-order reaction rate coefficients. The Arrhenius expression

$$k = (7.35 \pm 2.16) \times 10^{-13} \exp(640 \pm 60)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

in the temperature range 252–640 K was obtained for the reaction of  $\text{O}(^3P)$  with  $\text{N}_2\text{H}_4$ . The corresponding expression

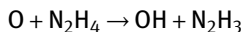
$$k = (1.25 \pm 0.19) \times 10^{-11} \exp(315 \pm 55)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

in the range 232–374 K was determined for the  $^{\bullet}\text{OH}$  reaction. The total yield of  $\text{OH}(X^2\Pi)$  formation in the  $\text{O} + \text{N}_2\text{H}_4$  reaction of  $(0.15 \pm 0.05)$  at 298 K (of which ~50% was found to be produced hot with vibrational excitation up to the limit of reaction exothermicity) and the observed experimental kinetic trends suggested that the initial addition of  $\text{O}(^3P)$  and  $^{\bullet}\text{OH}$  to the hydrazine molecule followed by rapid dissociation to products is an important process step in the atmospheric degradation of hydrazine. In a later study [556] with direct laser-induced fluorescence monitoring of  $[\text{OH}]$  temporal profiles in a known excess of hydrazine yielded the following absolute second-order OH rate coefficient expression:

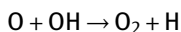
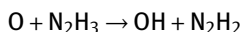
$$k_1 = (2.17 \pm 0.39) \times 10^{-11} \exp(160 \pm 30)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1},$$

for reactions with  $\text{N}_2\text{H}_4$  in the temperature range 232–637 K.

An ESR study of the reaction of atomic oxygen with hydrazine at 420 K, 0.7 mm Hg, and contact time of  $5 \times 10^{-3}$  s gave a rate constant of  $(3 \pm 0.8) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [557, 558]. The initial step is



followed by

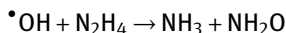


Most publications on reactions of atomic oxygen with hydrazine deal with gas-phase reactions at very low pressures that do not involve solid surfaces. It should be mentioned that adsorbed molecular oxygen on a platinum single crystal (111) face is likely to dissociate into adsorbed atomic oxygen and react rapidly with hydrazine vapor [559].

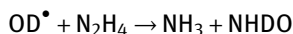
### 3.1.1.8 Kinetics of Gas-Phase Reactions of Hydrazine with Hydroxyl Radicals and Ions

Besides  $\text{O}^{\bullet}$  atoms, hydroxyl radicals  $^{\bullet}\text{OH}$  are presumed to play an important role in hydrazine combustion. The reaction of  $^{\bullet}\text{OH}$  with  $\text{N}_2\text{H}_4$  could be studied individually by

the crossed molecular beam method [560]. Whereas the attack by  $\text{H}^\bullet$  or  $\text{O}^\bullet$  leaves the N—N bond of hydrazine intact, the reaction with  $\bullet\text{OH}$  proceeds mainly under fission of the N—N bond:



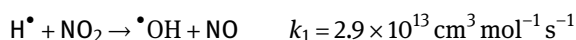
The identification of  $\text{NH}_2\text{O}$ , a little-known species, by mass spectrometry was difficult because its  $m/e$  coincides with that of hydrazine at 32. Its existence could be proved using OD instead of OH radicals, in which case the reaction proceeded as follows:



and the  $m/e$  of NHDO is distinctly different from that of undecomposed hydrazine.

A study of the action of hydroxyl radicals (Fenton reagent) on hydrazine in aqueous solution is described in Section 3.1.1.1 on the oxidation of hydrazine in solution, and, in addition, as a result of hydroxyl radicals formed by the radiolysis of water. Tetrazene and triazene are some of the species identified as intermediates in this reaction.

The temperature and concentration profiles of OH,  $\text{NH}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and NO across the reaction zone of oxygen-ammonia flames were measured for three different mixture ratios in premixed flames [561]. In addition to the reaction of hydroxyl radicals with hydrazine (or ammonia) and mass spectroscopic analysis of the reaction products in the gas phase [560], the reaction has also been investigated by ESR. The ESR spectrum is specific to the free electrons in free radicals, such as  $\bullet\text{OH}$  or  $\bullet\text{NH}_2$ . However, the accuracy with which spectra can be measured is inversely proportional to the lifetime of the free radicals. In one arrangement, the reactions of  $\bullet\text{OH}$  radicals with ammonia or hydrazine were studied in an isothermal flow reactor at pressures around 266 Pa (2 mmHg) with helium as carrier gas [562]. The fast reaction



has been used for generating hydroxyl radicals. Only small  $\bullet\text{OH}$  concentrations were used in order to avoid recombination with itself or uncontrolled wall reactions. The  $\bullet\text{OH} + \text{NH}_3$  or  $\bullet\text{OH} + \text{N}_2\text{H}_4$  mixtures were then flowed through the cavity of an ESR spectrometer. The flow rate and the ratio of reacting species could be varied to determine a time-resolved reaction profile. The reaction rate for  $\bullet\text{OH} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{H}_2\text{O}$  was measured at 298–669 K and found to be  $k = (3.2 \pm 0.5) \times 10^{12} e^{(-920/T)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The reaction



was measured at ambient temperature (298 K) only, and a rate of  $k = (1.3 \pm 0.3) \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  was found. In the overall reaction,  $2.5 \bullet\text{OH}$  radicals were removed for every  $\text{N}_2\text{H}_4$  consumed, leading to  $\text{N}_2$  and  $\text{H}_2\text{O}$  as the main final products. The rate con-

stant measured in the gas phase is like that measured in solution ( $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} = 1.4 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) [563]. Gas-phase reactions of  $\bullet\text{OH}$  with ammonia or hydrazine share some of the intermediates [564].

The reaction of  $\text{N}_2\text{H}_4$  with hydroxyl  $\bullet\text{OH}$  free radicals that gives  $\text{N}_2\text{H}_3$  as the major product has been investigated by quantum-chemical calculations [565]. The results showed that the hydrogen abstraction mechanism is more feasible than the substitution mechanism thermodynamically. The calculated rate constants agreed with the available experimental data. The calculated results showed that the variational effect is small at lower temperatures, while it becomes significant at higher temperatures. The calculated rate constants showed a negative temperature dependence at temperatures below 500 K, which was in accordance with reports that a slightly negative temperature dependence was found over the temperature range of 258–637 K.

Activation energies of reactions of hydrazine with  $\text{CH}_3$  and  $\text{OOH}$  radicals including hydrogen abstraction and substitution reactions were calculated using quantum-mechanical computational methods [566]. The activation energies of hydrogen abstraction from  $\text{N}_2\text{H}_4$  by  $\text{CH}_3$  and  $\text{OOH}$  radicals were 21.89 and 25.24 kJ/mol, respectively. Generally, activation energies of the hydrogen abstractions were smaller than those of substitution reactions. The rate constants of the reactions were calculated using the transition state theory in a temperature range of 200–2500 K. The rate constants of hydrogen abstraction from hydrazine by  $\text{CH}_3$  and  $\text{OOH}$  radicals were  $3.47 \times 10^{-13}$  and  $6.79 \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively, at 298 K. Hydrogen abstractions were exothermic, while almost all the substitution reactions were endothermic. One of the  $\text{NH}_2$  groups of  $\text{N}_2\text{H}_4$  can be replaced with  $\text{CH}_3$  or  $\text{OOH}$  radicals, which leads to  $\text{H}_2\text{NCH}_3$  or  $\text{H}_2\text{NOOH}$  products, respectively. The formation of  $\text{H}_2\text{NCH}_3$  was exothermic, while the formation of  $\text{H}_2\text{NOOH}$  was an endothermic reaction.

The energy profile of reactions of  $\text{H}_2\text{NN}\bullet\text{H}$  and  $\text{H}_2\text{NNH}_2^{\bullet+}$  with  $\text{HO}\bullet$  in the gas phase was studied using a modified *ab initio* method [567]. During the attack of  $\text{HO}\bullet$  on  $\text{H}_2\text{NNH}_3^+$  in the gas phase, the rate of formation of  $\text{H}_2\text{NNH}_2^{\bullet+}$  by H abstraction from the  $\text{NH}_3^+$  end of the molecule has a very low activation energy and is preferred over H abstraction from the  $-\text{NH}_2$  end. Most redox reactions of hydrazine in the liquid phase in the alkaline state involve hydroxyl anions  $\text{HO}^-$ . Comparatively little is known about reactions of hydrazine with hydroxyl ions in the gas phase. The energy potentials of 40 possible reactions in the presence of  $\text{HO}^-$  were calculated using a semi-empirical MNDO method and used to characterize most likely (least resistance) reaction paths of  $\text{HO}^-$  with  $\text{N}_2\text{H}_4$  vapor in the gas phase [568].

The low-pressure, vapor-phase reaction of hydrogen peroxide with hydrazine hydrate probably involves the intermediate formation of hydroxyl radicals formed by the decomposition of hydrogen peroxide [569]. At higher pressures this reaction would result in ignition.

The reaction mechanism of the  $\text{N}_2\text{H}_4 + \bullet\text{OH}$  reaction was examined by *ab initio* calculations for a wide range of conditions (i.e.,  $T = 200\text{--}3000 \text{ K}$  and  $P = 1\text{--}$

7600 mmHg) [570]. The kinetic rate model included corrections of the hindered internal rotor and tunneling effects. The calculated rate constants were in agreement with the latest experimental data [556], which helped to resolve the discrepancy between the previous experimental and theoretical studies. The reaction mechanism was revealed as follows: **(1)** the H-abstraction channel is more thermodynamically favorable than the OH-substitution mechanism; **(2)** non-Arrhenius behaviors and slightly positive pressure-dependence at low temperature ( $T = 500\text{ K}$ ) of the rate coefficients are observed; and **(3)** the hindered internal rotor treatment plays a substantial role in obtaining the reliable rate constants.

### 3.1.1.9 Kinetics of Gas-Phase Reactions of Hydrazine with Ozone

Hydrazine vapors released in the high atmosphere or stratosphere are surrounded by ozone, resulting in the rapid destruction of the hydrazine. Ozonizers have been used for chemiluminescence detection of hydrazine and nitrogen oxides in the effluent of gas chromatographs. The kinetics of the reactions of hydrazines with ozone are difficult to separate from the previously discussed reactions with atomic oxygen. Quite often atomic oxygen is the first product of ozone decomposition, and from then on the kinetics are the same as discussed previously. The current section would therefore only have to deal with the initiation steps.

The reactions of ozone with hydrazines are of practical interest: They take place in the atmosphere following the inadvertent release of hydrazine vapors in the atmosphere (Section 3.1.1.7). Ozonization is an attractive method for the disposal of unwanted hydrazines (Section 7.12.1.3). Ozone chemiluminescence is used in hydrazine analyzers (Section 3.6.11.5). Ozone is a convenient source of atomic oxygen for kinetic studies (*vide supra*). The current section deals with the kinetics of those reactions.

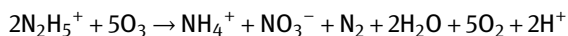
The homogeneous gas-phase reaction of hydrazine with ozone in air at atmospheric pressure is a convenient source for hydroxyl radicals [571]. The hydroxyl radicals can then be characterized by reactions with organic compounds for which rate constants were already known (based on the use of different hydroxyl generation methods). This reaction will most likely precede ignition when hydrazine is burned in ozone.

Hydrazine that has escaped to the high atmosphere where it is close to the ozonosphere is expected to be rapidly oxidized to nitrogen and water. Measurements were made of the reactions between ozone and hydrazine, MMH, and UDMH [572]. Measurements were carried out at room temperature, under pseudo-first-order conditions (hydrazines in excess), in a flow system designed to minimize diffusion limitations and wall reactions. Second-order rate constants were measured for each of the reactions. The measured values of the rate constants for the reactions of ozone with  $\text{N}_2\text{H}_4$ , MMH, and UDMH were  $3.4 \pm 0.4 \times 10^{-15}$ ,  $4.5 \pm 0.5 \times 10^{-14}$ , and  $5.5 \pm 1.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. The reaction is chemiluminescent.

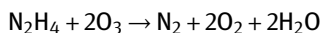
### 3.1.1.10 Hydrazine Reactions with Ozone in Aqueous Solutions

Modeling of the kinetics of hydrazine ozonolysis showed that fuel destruction rates were limited by the rate of ozone input [573]. Using a stopped-flow technique, it was shown that while overall, global destruction was rapid, observed “rate constants” were five to six orders of magnitude lower than the true kinetic rate constants ( $10^7$  to  $10^9 \text{ L mol}^{-1} \text{ min}^{-1}$ ). Initial mol ratios of fuel to ozone consumption were about two to five, and this ratio decreased to less than unity or even less than unity as the ozonolysis proceeded.

The oxidation of hydrazinium salts in solution by gaseous (dissolved) ozone proceeds independently of the anion (nitrate or sulfate) present. When oxidizing  $10^{-2} \text{ M}$  solutions of hydrazinium(1+) nitrate or hydrazinium(2+) sulfate with ozone, ammonium and nitrate ions were found in the reaction products [574]. The amount of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  formed was proportional to the amount of ozone consumed. The pH also decreased due to the additional hydronium ions formed. In a first approximation, the stoichiometry of the reaction can be represented as



Surprisingly, hydrogen peroxide can be identified as an intermediate while the ozone oxidation and autooxidation of hydrazine is in progress. Hydrogen peroxide concentration reaches a stationary level and drops off as soon as all hydrazinium ions are consumed. At that point, hydrogen peroxide itself is oxidized by ozone to form water and oxygen. Hydrogen azide or nitrous acid could not be found as intermediates, since either one would be rapidly oxidized to nitrate under the conditions of the test. When hydrazine hydrate is oxidized with ozone, only traces of ammonia and nitrate ion are found, and the main products are nitrogen, oxygen, and water:



As previously in the oxidation of hydrazinium salts, hydrogen peroxide was again found as an intermediate in the solution.

The use of ozone for the destruction of hydrazine(s) in wastewater usually occurs in combination with UV illumination and/or catalysts [575]. See Section 7.12.1.3.

### 3.1.2 Heterogeneous Surface-Catalyzed Reactions

The heterogeneous oxidation of hydrazine vapor by oxygen and oxygen/ozone mixtures on  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  surfaces was studied at 173 to 193 K in a flow reactor [576]. The reaction was zero order at ~70% conversion, and the activation energy was 38 kJ/mol. The oxidation rate for the case of  $\text{O}_2$  is an order of magnitude slower than for the  $\text{O}_2/\text{O}_3$  mixture. The vapor-phase reaction of ozone and hydrazine is more of interest for atmospheric chemistry than a practical means of hydrazine disposal.

All discussion in this section has centered around homogeneous gas-phase reactions of oxygen species with hydrazines, often initiating reactions leading to ignition

and combustion. Heterogeneous catalytic ignition of oxygen/hydrazine mixtures is possible but has not been studied in detail. A study of model catalytic oxidation reactions of dioxygen with hydrogen, ammonia, and hydrazine on Rh(111) single crystal surfaces in comparison to Pt(111) was one step in this direction [577].

Studying the autoxidation of hydrazine or methylhydrazines in confined atmosphere chambers in the laboratory is difficult. Hydrazine and oxygen may permeate through thin plastic walls. Metal walls may catalyze autoxidation [578].

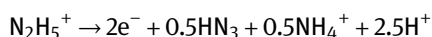
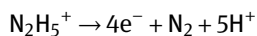
### 3.1.3 Catalytic Ignition of Oxygen-Hydrazine Reactions

It is known that activated charcoal wetted with hydrazine will inflame spontaneously as soon as air is admitted. Likewise, oxygen-saturated activated charcoal or graphite oxide will react spontaneously or even explosively with hydrazine vapor. Graphite oxide, also called graphitic oxide or graphitic acid, is a compound of carbon, oxygen, and hydrogen in variable ratios, obtained by treating graphite with strong oxidizers. The maximally oxidized bulk product is a yellow solid with a C:O ratio between 2.1 and 2.9, and it retains the layer structure of graphite but with a much larger and more irregular spacing. It is spontaneously reactive with hydrazine [579]. Graphene can be made by the reduction of graphite oxide monolayer films by hydrazine with annealing in argon/hydrogen and an almost intact carbon framework that allows efficient removal of functional groups. This reduction would have to be done in dilute aqueous solutions to prevent ignition.

### 3.1.4 Reactions of Hydrazine with Hydrogen Peroxide in Solution

Hydrazine reacts readily with hydrogen peroxide in aqueous solution to yield nitrogen and water. Reactions of hydrazine with hydrogen peroxide are of interest for several reasons: The combination of hydrogen peroxide with mixtures of hydrazine hydrate and methanol is hypergolic and was the first liquid rocket bipropellant to be used in a piloted rocket plane, the Me-163B. In more dilute solutions, hydrogen peroxide is used for the treatment of hydrazine-polluted wastewater (Section 4.6).

It was discovered that the oxidation of hydrazine with hydrogen peroxide in acidic solution resulted in the formation of hydrogen azide [580]. This discovery has spurred numerous other investigators in an effort to predict the reaction products as a function of the oxidizing agent used. Azide formation occurred only in acidic solution. Three distinct reactions could be identified:



For example, the first reaction occurs when the oxidizing agent is acidic iodate, neutral iodine, or alkaline cyanoferrate(III). The second reaction is approximated with

iron(3+) or manganate as the oxidizer. Many oxidants give both first and second reactions simultaneously. The third reaction occurs predominantly if hydrazine is oxidized in hot, concentrated sulfuric acid with hydrogen peroxide.

A study of the effect of concentration, pH, temperature, ionic strength, and surface area ratio on the uncatalyzed rate of reaction of hydrazine and hydrogen peroxide in dilute solutions showed that, for the concentration range studied, the uncatalyzed reaction proceeded at a very slow rate as a first-order reaction in both hydrazine or hydrogen peroxide [581]. The reaction rate was very slow below pH = 8 but rose sharply above pH 8, and the fastest rate was observed at pH 10. At higher pH values, it dropped off again. A mechanism involving hydrazinium salts and diazene was proposed to explain the pH dependence. In this study, neither hydrogen azide nor ammonia was found in the gaseous products or in solution, although they probably can form when more concentrated solutions are reacted at low pH. See also [582, 583].

Transition metal ions catalyze the reaction of hydrazine with hydrogen peroxide [584, 585]. The rate of the  $\text{H}_2\text{O}_2 + \text{N}_2\text{H}_4$  reaction as measured by the rate of nitrogen evolution was quite erratic. Using a solution that was 0.4 molar in hydrogen peroxide and 0.2 molar in hydrazine and a temperature of 298 K (25°C), the initial rate of the reaction varied from 0.6 to 0.8 mL/s. The reaction was found to be first order in peroxide and zero order in hydrazine. The rate of the reaction depended on the purity of the water that was used as solvent. The addition of very small amounts of ethylene diamine tetraacetic acid (EDTA), a metal ion complexing agent, completely suppressed the reaction [586].

A thorough investigation of copper(II) catalysis showed that the rate-determining step of the catalyzed reaction involves hydrogen peroxide and copper ion [587, 588]. Since copper(II) has been shown to react slowly with hydrogen peroxide, the copper ion is probably complexed with hydrazine. It is this complex that then reacts with hydrogen peroxide. The rate coefficient for the catalyzed reaction is seven orders of magnitude higher than that of the uncatalyzed reaction, indeed a very pronounced effect! This also illustrates the importance of working with pure reagents in hydrazine chemistry because trace amounts of contaminants, such as  $\text{Cu}^{2+}$ , can give drastically altered results. The following rate law has been proposed for this reaction:

$$\frac{d[\text{N}_2]}{dt} = \frac{k_1 K [\text{N}_2\text{H}_4] [\text{H}_2\text{O}_2] [\text{Cu}^{\text{II}}]_{\text{T}}}{1 + [\text{N}_2\text{H}_4]}$$

where  $[\text{Cu}^{\text{II}}]_{\text{T}}$  represents the total concentration of copper. The enthalpy of activation and the entropy of activation of this reaction between 288 and 308 K were  $24.3 \pm 0.8 \text{ kJ/mol}$  ( $5.8 \pm 0.2 \text{ kcal/mol}$ ) and  $117 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$  ( $28 \pm 1 \text{ cal mol}^{-1} \text{ K}^{-1}$ ), respectively.

Copper ions are the most active catalysts in this reaction [589]. It was shown that the reaction involves both radical ( $\cdot\text{N}_2\text{H}_3$ ) and nonradical ( $\text{HN}=\text{NH}$ ) intermediates. Free-radical reactions are often characterized by one-half- and three-half-order kinetics, rarely integer-order kinetics [590]. It is assumed that Cu(II) is first reduced to Cu(I), which forms a complex with  $\text{N}_2\text{H}_4$  [591].

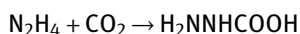
The decomposition of hydrazinium ion acidic solutions by hydrogen peroxide solutions in a temperature range of 323 to 353 K (50 to 80 °C) was examined as a method for decontamination of hydrazine-containing wastewater from a nuclear power plant [592]. The presence of copper(II) ions  $[\text{Cu}^{2+}]$  substantially increased the decomposition reaction rate of hydrazine. The decomposition reaction rate of hydrazine also increased with the increase of temperature and the solution pH. Even an excess of hydrogen peroxide could not decompose the hydrazine efficiently at lower pH. The study neglected the possible formation of azide in acidic solutions. The oxidation of hydrazine with hydrogen peroxide leads to diazene, which has found widespread application as a selective reducing agent in organic chemistry.

### 3.1.5 Reactions of Hydrazine with Carbon Oxides

#### 3.1.5.1 Reactions with Carbon Dioxide

Reactions of hydrazine with atmospheric carbon dioxide, mostly through negligence in incompletely closed storage containers, have been the cause of numerous contamination incidents because the carbazic acid formed as the first step in this reaction and its hydrazinium salt are very corrosive and form a series of corrosion product salts when in contact with metals in storage containers. Not all these complex metal salts are hydrazine-soluble, and some may precipitate and cause clogging of narrow passages in the propulsion systems. Other complex metal carbazate salts are soluble in hydrazine but precipitate where hydrazine evaporates, such as on valve seats or in injectors. Hydrazine can react with one or, in the presence of an excess of carbon dioxide, two molecules of  $\text{CO}_2$ , forming a monocarbazic acid (or its hydrazinium salt) or a dicarbazic acid (or its hydrazinium salts). Carbazic acid itself is not stable, but many of its salts are stable and well characterized.

The reaction of hydrazine and carbon dioxide, the anhydride of carbonic acid, does not lead to hydrazinium carbonate, as one would expect. Instead, if carbon dioxide is bubbled through anhydrous hydrazine, a syrupy material results that is not inclined to crystallize and does not behave like a salt at all. If an excess of carbon dioxide is passed into hydrazine hydrate, a sparingly soluble precipitate is obtained; this was assumed to be hydrazinocarboxylic acid, also called carbazic acid [593]:



Reacting dry ice under conditions of supercritical carbon dioxide with hydrazine in an autoclave at 353 K (80 °C) and 100 bar for 10 h resulted in a solid product that was recrystallized and characterized by XRD as a zwitterionic compound  $\text{H}_2\text{N}^+\text{NHCOO}^-$ , like hydrazinium carbazate [594].

Carbon dioxide sequestration from industrial exhaust stack gases would be one way to alleviate global warming due to carbon dioxide release into the atmosphere. Reversible carbon dioxide absorption in industry is usually done with low-volatility organic amines, mostly for  $\text{CO}_2$  removal from synthesis gas and natural gas. It is not



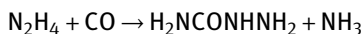
known why anyone would want to use the more expensive hydrazine hydrate for that purpose, but it appears that CO<sub>2</sub> absorption into hydrazine hydrate can be readily reversible and that CO<sub>2</sub> release from the saturated liquid can be achieved at lower temperatures than with aliphatic amines [595–597]. Reaction mechanisms involved in CO<sub>2</sub> absorption into hydrazine hydrate solutions were identified using <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectroscopy and compared to predictions from first-principles quantum-mechanical calculations. Both hydrazine monocarbazate (NH<sub>2</sub>–NH–COO<sup>–</sup>) and hydrazine dicarbazate (<sup>–</sup>OOC–NH–NH–COO<sup>–</sup>) were found, with the latter becoming prevalent with increasing CO<sub>2</sub> loading.

Hydrazinium carboxylate in concentrated solutions acts as a low-molecular-mass gelator, which self-assembles and in doing so traps unreacted hydrazine. The properties and molecular structures of the gels were investigated by means of elemental analysis, DSC/TGA, heteronuclear (<sup>1</sup>H, <sup>15</sup>N, and <sup>13</sup>C) NMR spectroscopy, and cryo-immobilized high-resolution SEM [598].

If anhydrous hydrazine (25 mL in a dish with 16.3 cm<sup>2</sup> surface area) is left standing exposed to the atmosphere, rapid absorption of CO<sub>2</sub> will increase the CO<sub>2</sub> (carbazate) content to 30% within 4 d [241]. At the same time, water content increases to 50%. The initial rate of CO<sub>2</sub> absorption is 50 ppm/min. This fast rate of CO<sub>2</sub> absorption is the reason anhydrous hydrazine must be kept blanketed with nitrogen at all times and contact with air must be avoided if one wants to maintain a corrosion-free system.

### 3.1.5.2 Reactions with Carbon Monoxide

The reaction of hydrazine with carbon monoxide at high pressure (91 MPa) and 314–320 K in the presence of iron pentacarbonyl leads to semicarbazide [599, 600]:



1,2-Dihydro-*s*-tetrazin-3(4*H*)-one is formed as a byproduct. If the reaction time is extended, 4-amino-1,2,4,4*H*-triazole-3(2*H*)-one and 4-amino-1,2,4,4*H*-triazole are obtained as ultimate products [601].

### 3.1.6 Reactions of Hydrazine with Nitrogen Oxides

Hydrazine reacts with numerous other nitrogen compounds [602]. Because hydrazine is the hydronitrogen with the strongest reducing power, these reactions invariably result in the oxidation of hydrazine.

The gas-phase reaction of hydrazine with nitrogen oxides is of practical importance in NO<sub>x</sub> removal from stack gases of combustion power plants prior to discharge into the atmosphere. Hypergolic ignition of N<sub>2</sub>O<sub>4</sub> with several propellant hydrazines is key to one of the most important applications of hydrazine as a bipropellant fuel (to be presented in a future *Encyclopedia of Hypergolic Bipropellant Combinations*). Reactions of hydrazine with nitrite ion, nitrite esters, and occasionally also nitrate ion

sometimes result in the unwanted formation of azides. Many azides are explosive hazards.

In the presence of moisture, the reactions of hydrazine (hydrate) with nitrogen oxides often involve reactions of hydrazine with nitrous acid and nitric acid. The reaction of anhydrous hydrazine or methylhydrazines with concentrated WFNA or even red fuming nitric acid (RFNA) leads in most cases to spontaneous ignition. These combinations have thus been investigated as hypergolic rocket propellants. The noncombustion reaction product of hydrazine and RFNA in a rocket chamber typically formed during evaporation of the liquids retained in the dribble volume, has been analyzed by IR and visible and mass spectrometry and was found to consist of at least 95% hydrazinium nitrate [603]. There was no evidence of hydrazinium nitrite. It has also been suggested that the nonignition residues contain ammonium nitrate or nitramine [604].

### 3.1.7 Reactions of Hydrazine with Nitrogen Dioxide or Dinitrogen Tetroxide

The vapor-phase reactions of hydrazine(s) with nitrogen dioxide often precede the ignition of such gas mixtures. Some of those pre-ignition reactions will be discussed in Section 4.15.1.1.

For a long time, pure hydrazine itself was not used as a fuel in bipropellant combinations because it is not suitable as a regenerative coolant. The pre-ignition or partial noncombustion reactions of hydrazine and methylhydrazines with NTO have been extensively investigated in an effort to explain occasional hard starts, pressure spikes, or rocket engine explosions as a result of accumulation of unreacted propellants and their partial reaction products in injector passages or dead corners of the combustion chamber. This problem required investigations of hard start phenomena and the chemical reactions of NTO with hydrazines, both in the liquid and in the vapor state [605–609]. For instance, hydrazine vapor and nitric acid vapor will not ignite below a certain partial pressure. Instead, a deposit of explosive hydrazinium nitrate will accumulate in the chamber. The same thing occurs after the propellant valves have closed and the combustion has ceased, when the propellants in the hold-up volume (“dribble volume”) between the valve and the injectors slowly evaporate. Reactions of hydrazine(s) with NTO and nitrogen dioxide leading to ignition will be discussed in a future *Encyclopedia of Hypergolic Bipropellant Combinations*, in the chapter “Hypergolic Combinations with Nitrogen Oxides.” IR spectra taken during the thawing of a mixture of  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{H}_4$  condensed on a sodium chloride window cooled to 77 K showed that all of the original material had reacted by the time the sample reached 163 K, whereas an exotherm in the DTA experiments was not observed until a temperature of 215 K was reached [610].

Another potential problem situation is the slow back-leakage of oxidizer through check valves into the helium pressurant of bipropellant rocket systems. The permeability of  $\text{NO}_2$  vapors through Teflon valve seats is relatively high. Since in some space-

craft designs fuel and oxidant share the pressurant helium supply, premature reaction may occur in the lines leading from the pressurant to the propellant tanks. This mechanism was suspected in the loss of the Mars OBSERVER space probe in 1993. Although that space probe used NTO and MMH, similar problems might occur in NTO/N<sub>2</sub>H<sub>4</sub> systems. Learning from the Mars OBSERVER fiasco, later space probes had separate oxidizer and fuel pressurant gas tanks.

The non-ignition reaction products of hydrazine and NTO contain hydrazinium(1+) nitrate (HN) [608, 611, 612] or hydrazinium azide [613, 614], as shown by IR analysis and comparisons of the spectra with authentic samples. A free-radical mechanism has been proposed to explain the other reaction products in addition to hydrazinium nitrate, namely, water, nitrogen, nitric oxide, nitrous oxide, and ammonia. An intermediate nitrosamine ONNH<sub>2</sub> has been postulated, but nitrosamine could not be detected because it is very unstable.

### 3.1.8 Reactions of Hydrazine with Nitrate Ion

The reduction of nitrate ion to nitrite ion by hydrazine in alkaline solution constitutes an important step in the analysis of atmospheric nitrogen oxides by wet microanalytical methods. The reduction of nitrate to nitrite ion in alkaline aqueous solutions in the presence of Cu<sup>2+</sup> and Zn<sup>2+</sup> catalysts is also used for the determination of trace nitrate in surface waters, sea water, or drinking water at concentrations below 10 mg nitrogen/m<sup>3</sup>. Following the reduction of nitrate, the nitrite is determined by using spectrophotometric sensitive reagents such as sulfanilic acid with *N*-(1-naphthyl)ethylenediamine (Saltzman reagent), *p*-amino acetophenone with azulene, or 8-anilino-1-naphthalene sulfonic acid (ANSA). The addition of a trace of copper(II) sulfate accelerates the reduction of nitrate.

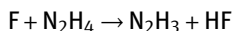
The reaction of hydrazinium ions with nitrate ions limits the storage stability of aqueous hydrazinium nitrate solutions [615]. Azide formation is highly undesirable. Procurement specifications for hydrazinium nitrate solutions must include a maximum tolerable limit of azide.

### 3.1.9 Reactions of Hydrazine with Halogens and Hypochlorite

The most common method for the destruction of unwanted hydrazine, as well as hydrazine decontamination in diluted hydrazine spills, is by reaction with sodium hypochlorite (chlorine bleach) or calcium hypochlorite (HTH<sup>®</sup>, a swimming pool sanitizing agent) in dilute solutions. This method can also be used to decontaminate MMH or UDMH but may result in the formation of traces of chloroform, an unwanted, even more persistent contaminant. Reactions of hydrazine with halogens and interhalogens result in the formation of nitrogen and hydrogen halides [616].

The hypergolic combination of liquid fluorine with hydrazine has been evaluated as propellant for upper stages. This application will be described in a future *Ency-*

*lopedia of Hypergolic Bipropellant Combinations*, in the chapter “Hypergolic Combinations with Fluorine.” The kinetics of the reaction of fluorine with hydrazine may involve hydrogen abstraction as the first step of the reaction. The low-pressure gas-phase reaction between  $\text{N}_2\text{H}_4$  and F atoms is predicted to have three possible reaction channels. Calculated results revealed that the first two primary channels



are equivalent and occur synchronously via the formation of a pre-reaction complex rather than via direct H abstraction [617].

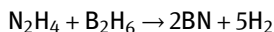
### 3.1.10 Reactions of Hydrazine with Boron Compounds

Hundreds of reactions of hydrazine(s) with boron halogenides, hydrides, alkali metal boranates, and alkyl boron derivatives have been reported. Many hydrazine and boron compounds have been tested as rocket propellant ingredients, mostly for solid propellants. The reason for the versatility of hydrazine-boron interactions is the charge-transfer bond formed in many of these compounds between the free electron pairs of the nitrogen atoms in hydrazine with the electron-deficient boron atom. The information is arranged in sequence by the number of boron atoms involved. Boron hydrides (boranes) are discussed first, followed by alkyl boron compounds, boron halogenides, and boric acid and boric acid esters.

Many boron compounds form Lewis-type adducts with hydrazine and hydrazine derivatives. Many boron compounds crystallize with excess molecules of hydrazine as solvate.

Hydrazinoborane, diborylhydrazine,  $\text{H}_2\text{B}-\text{NH}-\text{NH}-\text{BH}_2$  can be prepared by pyrolysis of a hydrazine-diborane adduct [618]. Alkylated homologs can be prepared by the treatment of tetraalkyldiboranes with hydrazine at 373–423 K [619].

Hydrazine and diborane react hypergolically with a hot flame:



The flame reaction has actively been investigated as a rocket propellant combination. The flame speed of the stoichiometric mixture on a 28-mm burner was 5 m/s [620, 621]. The premixed  $\text{N}_2\text{H}_4/\text{B}_2\text{H}_6$  flame could be stabilized only at pressures below 6.6 kPa (50 mm Hg) because solid adducts often clogged the orifices at higher mixing pressures [622].

Hydrazine borine  $\text{BH}_3 \cdot \text{N}_2\text{H}_4$  can be obtained by reacting dihydrazinium(1+) sulfate  $(\text{N}_2\text{H}_5)_2\text{SO}_4$  with lithium borohydride in ether or, even better, with sodium borohydride in dioxane [618]. The reaction between hydrazinium sulfate and sodium borohydride is very slow and requires 5–15 h at 300 K. The product crystallizes from the dioxane filtrate. Its precipitation can be accelerated by adding petroleum ether, in which hydrazine borine is insoluble. The compound crystallizes in colorless columnar crys-

tals and melts at 334 K. It is soluble in water, alcohol, ether, hydrazine, and other polar solvents. It is stable in aqueous solution and will not decompose unless the solution is acidified below  $\text{pH} = 4$ .

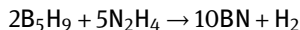
Hydrazine bisborane can be prepared by the reaction of alkali metal borohydrides with hydrazinium salts [623, 624] or by the reaction of trimethylamine borane with hydrazine [625]. The reaction of hydrazine bisborane  $\text{H}_2\text{B}-\text{NH}-\text{NH}-\text{BH}_2$  with hydrazinium perchlorate gives complex salts of the  $\text{N}_2\text{H}_4\text{BH}_2\text{ClO}_4$  type, which can be used as rocket propellants [626].

Various adducts of hydrazine and alkali metal or aluminum borohydrides have been patented as rocket propellants, either as solids or as solutions in hydrazine. Adducts of aluminum, zirconium, or beryllium borohydride with hydrazine, UDMH, *O*-methyl hydroxylamine, or *N*-methoxy methylamine dissolved in ether are said to be hypergolic with nitrogen tetroxide [627].

Solutions of lithium borohydride in hydrazine lower its freezing point and increase the specific impulse when burned with oxygen as a rocket propellant [628]. Thus, solutions with 5.25, 6.1, 12.25, 13.25, or 15% by weight lithium borohydride in hydrazine lower the freezing point to 250, 246, 229, 226, and 235 K, respectively. The specific impulse of hydrazine with oxygen can be increased from 270 to 300 s by the addition of lithium borohydride. In the absence of solvents such as ether or dioxane, hydrazinate adducts of the type  $\text{LiBH}_4 \bullet \text{N}_2\text{H}_4$  are obtained that are soluble in excess hydrazine and, when crystallized, can be used as a rocket propellant [629].

Lithium borohydride and aluminum borohydride form hydrazinates and *N,N*-dimethylhydrazinates with hydrazine or UDMH, which can be used as rocket fuels [630]. With lithium borohydride in ether, the following compounds were isolated:  $\text{LiBH}_4 \bullet \text{N}_2\text{H}_4$ ,  $\text{LiBH}_4 \bullet 2\text{N}_2\text{H}_4$ , and  $\text{LiBH}_4 \bullet \text{H}_2\text{NN}(\text{CH}_3)_2$ . The compounds are white crystals that can be handled under air without danger, even though they are very hygroscopic. In contrast, the hydrazinates of aluminum borohydride are very sensitive to oxygen and must be handled in an inert atmosphere. Aluminum borohydride accepts up to four hydrazine molecules as solvates:  $\text{Al}(\text{BH}_4)_3 \bullet 4\text{N}_2\text{H}_4$ . Solutions of hydrazinium decaboranate in hydrazine can be used as hypergolic fuels [631, 632].

One of the most unusual liquid rocket propellant combinations is that of hydrazine with pentaborane. On contact, the components react in a highly exothermic reaction, and a combustion-like reaction can be sustained in a rocket engine. The reaction leads to boron nitride and hydrogen:



The low molecular weight of the exhaust gases (mainly hydrogen) results in a very good specific impulse of this propellant combination, which will be further discussed in a future *Encyclopedia of Hypergolic Bipropellant Combinations* [633].

### 3.2 Electrooxidation of Hydrazine in Solution

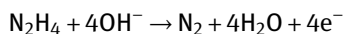
Electrooxidation of hydrazine in solution is a key step in using hydrazine hydrate solutions in air-fuel cells. Automobiles with air/hydrazine hydrate fuel cells would be a pollution-free mode of transportation. In the anodic oxidation of hydrazine in solution, the oxygen that would have evolved at the anode in plain (acidified) water does not evolve but is immediately desaturated by reaction with hydrazine. The electrooxidation of hydrazine is the basis of coulometric analysis of hydrazine and other electrochemical analysis methods (Section 3.6.10). A thorough discussion of the kinetics of electrooxidation and importance of electrode selection can be found in [634]. Practical applications of electrooxidation of hydrazine(s) are discussed in Section 3.6.15.12.

Hydrazine is an excellent solvent and can serve as the electrolyte for many reactions. Because anhydrous hydrazine is an electrolyte due to autodissociation, the electrooxidation of hydrazine in the absence of a solvent is possible. That method has been considered as a method for the controlled release of gases for micropropulsion in satellites.

The oxidation of hydrazine in acid and alkaline aqueous media has been examined. It was concluded that the oxidation of hydrazine occurs not primarily via a hydrogen oxidation mechanism, as was previously suggested, but via a sequential oxidation of radicals (intermediates) derivable from hydrazine. It was also concluded that electrode surface characteristics affect the potential of oxidation, while the rest potential is controlled by the subsequent formation of radicals [515].

Hydrazine can be oxidized by electrooxidation in liquid ammonia as the electrolyte and solvent. Potential sweep investigations of the electrochemical oxidation of hydrazine on platinum in liquid ammonia electrolytes yielded current-potential curves that depended markedly on the nature of the electrolyte anion present [635]. These anion effects were interpreted in terms of the principle of soft and hard acids and bases and specific adsorption at the electrode. Low-temperature studies showed that hydrazine can be electrochemically oxidized in liquid ammonia at 213 K (60 °C), demonstrating the high reactivity of this fuel. The oxidation of hydrazine on platinum appears to be a diffusion-controlled, highly irreversible reaction.

It was stated that the amount of nitrogen released on oxidation of 0.5 M  $\text{N}_2\text{H}_4$  in 5 M KOH at 293 K on platinum electrodes corresponded to the quantity calculated from the number of coulombs passed through the system [636]. Using palladium-black coated electrodes, it is possible to electrolyze hydrazine in alkaline solution per



without the chemical decomposition of hydrazine [637]. The anode gas thus obtained is mostly nitrogen free from hydrogen.

It was suggested that the hydrazine electrode is essentially a low-pressure hydrogen electrode, and it was verified that the hydrogen pressure is a function of the hydroxide ion concentration since it is roughly proportional to its third power [638]. It

was assumed that the hydrazine molecule was first adsorbed on the platinum electrode, where it underwent a decomposition to nitrogen and hydrogen.

The electrochemistry of hydrazine electrooxidation at platinum electrodes has been re-evaluated by an investigation using microelectrodes [639]. Platinum oxides remaining on the electrodes from preceding oxidative scans will facilitate hydrazine oxidation occurring at up to ca. 400 mV more cathodic potentials than at an oxide-free Pt electrode. The observed voltammetry at oxidized or “activated” platinum electrodes was found to be a function of the immersion time (time elapsed since “activation”) and pH. Although hydrazine is known to react with bulk Pt oxide, the loss of activation with time was found to be independent of hydrazine concentration and was instead a function of pH and supporting electrolyte.

During a study of the effects of the supporting electrolyte on electro-catalytic oxidation of hydrazine hydrate on a platinum ultramicroelectrode, it was found that the  $H^+$  electric field generated during the catalytic process could partly hinder the reactants from participating in the catalytic reaction using low-concentration supporting electrolytes, which resulted in a final steady current value that was less than the theoretical value [640]. On the other hand, the supporting electrolyte has a regulatory effect on both concentrations of  $N_2H_4$  and  $N_2H_5^+$  involved in the catalytic reaction, which in turn affects the intensity of steady-state currents and the value of each steady-state current generated in the reaction. In this case, the effect of neutral salts did not change with concentration variations. By contrast, when different concentrations of sulfuric acid or sodium hydroxide are used as the electrolytes, the intensity of steady-state currents and the value of each steady-state current were mainly determined by the original and the subsequently produced  $H^+$  concentration around the electrode. This information assists in the choice of supporting electrolyte and catalytic potential in the determination of hydrazine concentrations by amperometric methods and in catalytic reactions with hydrazine hydrate as the reducing medium.

### 3.3 Nitride Formation with Metals

At very high temperatures, such as those occurring in hydrazine decomposition monopropellant reactors, nitride formation with structural metals may lead to premature degradation, embrittlement, and failure of structural elements such as catalyst bed retention screens, bed plates, injectors, nozzles, and chamber materials. Traces of carbon can aggravate the nitride formation. Metallurgists had to go through a long period of trial-and-error evaluation of candidate metals for hydrazine rocket engines and gas generators before alloys were found that could resist the harsh environment in hydrazine decomposition reactors. While metal nitriding is highly undesirable, nitriding of semiconductor elements under carefully controlled high-vacuum conditions has developed into a new application for ultra-high-purity hydrazine.

### 3.4 Reactions of Hydrazine with Organic Compounds

Reactions of hydrazine with organic compounds can be grouped into the following categories: hydrazination reactions, cyclization reactions, and hydrogenation reactions. Hydrazination reactions generally leave part of the molecule, maybe one  $\text{—NH}_2$  group, unreacted, and the products share many of their properties with hydrazine, including the ease of becoming oxidized. On cyclization, frequently as part of the formation of heterocyclic ring systems, the properties of hydrazine disappear altogether, and the products are frequently much more stable than hydrazine by itself [641]. In hydrogenation reactions, the hydrazine is consumed, and the hydrogen is transferred to carbon. Reactions of hydrazine with organic compounds leading to alkyl- or arylhydrazines will be discussed in the chapters “Alkylhydrazines,” “Methylhydrazine,” and “Dimethylhydrazines.” Many of the reactions discussed here, such as the reaction with acyl halides, are observed with alkylhydrazines (MMH, UDMH) and hydrazine alike [642].

Reactions of hydrazine with organic compounds serve as analytical methods for qualitative and quantitative analysis of hydrazine(s). Reactions of hydrazine with organic compounds can also be useful to trap hydrazine, to reduce its vapor pressure, and to convert it to less toxic compounds. Such reactions would be useful for wastewater and spill decontamination. A more detailed summary of reactions of hydrazine with organic compounds is published in [643].

### 3.5 Hydrazinium Salts

Hydrazine forms two types of salts with acids, giving either monoprotonated hydrazinium(1+) or diprotonated hydrazinium(2+) salts. In aqueous solutions, normally only the hydrazinium(1+) salts are formed with a variety of acids. Hydrazinium(2+) salts form only with strong acids and/or in anhydrous media. Summaries of the properties of hydrazinium salts are provided in [644, 645]. Hydrazinium salts are useful sources of nitrogen in gas generant formulations. Hydrazinium salts of oxidizing acids are described in more detail in *Encyclopedia of Oxidizers*, in chapter “Hydrazinium Salt Oxidizers.”

### 3.6 Analysis of Hydrazine

The analysis of hydrazines is of importance in the production, quality control, application, occupational hygiene, and environmental control of these compounds. For most applications, the analysis methods will have to be quantitative.

Several monographs and survey articles appeared several decades ago [646, 647] which make a separate chapter on hydrazine analytical methods in this book almost



unnecessary. One frequently cited reference on this subject is a very specific book on the determination of hydrazino-hydrazide groups [648]. One book on the analysis of rocket propellants contains several chapters on hydrazine analysis [649]. A study was published on new methods for the analysis of hydrazine compounds and the use of hydrazine as an analytical reagent [650]. A chapter in the *Encyclopedia of Industrial Chemical Analysis* [651] provides a summary of analysis methods for hydrazine. Both books and the encyclopedia chapter contain detailed cookbook-style instructions for analysis and are suitable for use in the laboratory, whereas the book at hand is not. The objective here is only to provide an overview of analytical methods. Previous summaries on analytical methods such as those published in [22] are repeated here only in abbreviated form. In many cases, the user will not be spared the arduous walk to the library if more detailed step-by-step instructions for hands-on analytical methods are required. Hydrazine can be used as a reductant and analytical reagent [652].

The objective here is to arrange this chapter on chemical analytical methods by the method used, rather than by the application. This arrangement of subject sections in a logical sequence is not always easy to carry out consistently because many good surveys have been published that reviewed several candidate analysis methods for a given application, such as the analysis of water in hydrazine [653], the analysis of hydrazine in boiler feedwater [654, 655], or the analysis of hydrazines in body tissues or body fluids [656]. The wide-ranging use of hydrazine derivatives in growth retardants, pesticides, and pharmaceuticals made it necessary to test many of these consumer products for hydrazine residues. In the wake of growing consumer concern over pesticide residues on fruits and vegetables, methods of conducting trace analyses for hydrazine derivatives have yielded important information that served as the basis of environmental policies. The former National Bureau of Standards has compiled a summary of recommended methods for the analysis of hydrazines on crops [657].

Frequently, analytical surveys are conducted to find suitable analysis methods for hydrazines under field conditions, such as traces of hydrazine in the air (Section 3.6.15.1) or water (Section 3.6.14.1). Also, hydrazine fuels ready for loading into a spacecraft or aircraft frequently must be analyzed in the field without the luxury of having a well-equipped chemical laboratory nearby. Such field analysis instruments must be self-contained, be rugged, and give fast, unambiguous, and reliable “yes” or “no” answers with regard to the acceptability of a fuel within a given specification limit. For instance, rapid analysis methods are being sought for the field (flight line) analysis of the H-70 fuel mixture (70% hydrazine, 30% water) [485]. See also [658].

### 3.6.1 Qualitative Analysis of Hydrazine

Qualitative tests frequently give only a “yes” or “no” answer to the question as to whether a given sample (air, water, solid) contains hydrazine or not. Not all qualitative tests are suitable for quantitation.

In addition to *p*-dimethylaminobenzaldehyde (PDAB), other aldehydes such as salicylaldehyde can be used not only for gravimetric analysis, but also for spot plate tests identifying hydrazine in small quantities [659, 660]. The condensation reaction of salicylaldehyde and hydrazine in a 2:1 molar ratio usually gives initially a mixture of the three geometrical isomers of salicylaldazine [661].

A test tube/spot plate test for hydrazine uses a cacotheline reagent in 7–12N sodium hydroxide [662]. It gives a blue color that is stable for 1 h. The sensitivity is approximately 2 µg/mL. A red addition product is formed by the reaction of hydrazine with glutaconaldehyde as spot plate reagent [663]. The color formation is specific to hydrazine with selenous acid and 1-naphthylamine [664–666]. One hundred and thirteen organic substances, including alkyl hydrazines, alkyl-, and arylhydrazides, did not interfere. Some of these color-forming ingredients can be packaged by adsorption on resin beads that can be stored as solids and are easy to add to the solution to be tested. The reduction of silver diammino hydroxide by hydrazine gives a black spot on a paper chromatogram, but it is not specific [667]. Other reducing agents will cause the same reaction.

Hydrazines and amines form intensely colored adducts (Meisenheimer complexes) with aromatic nitro compounds that may be suitable for qualitative detection of hydrazine, MMH, or UDMH [668]. Many amines give similar colors, with the colors ranging from yellow to purple to black. One of the nitro compounds recommended for this test is trinitrobenzene [669].

*peri*-Naphthindan-2,3,4-trione hydrate is a sensitive reagent for the detection of hydrazine in spot plate tests [670] as well as spectrophotometric quantitative analysis [671]. The compound becomes reduced to a purple conjugated diol. The detection limit is 0.3 µg.

Various chemicals, including PDAB, pH indicators, and potassium tetrachloroaurate (KAuCl<sub>4</sub>), were tested for the detection of hydrazine or MMH vapors [672]. These indicators have been tested for the detection of hydrazine under various conditions: pure liquid fuel, aqueous fuel solution, saline aqueous fuel solutions, vapor fuel, and 3-month shelf life study, which included UV exposure, temperature extremes, and normal storage conditions.

### 3.6.2 Specifications for Hydrazine

Propellant specifications are important in the procurement and quality control of hydrazines. The rationale in setting specification limits is to achieve reproducible performance of rocket propulsion systems by carefully controlling the purity of propellant hydrazines. It is obvious that there must be a compromise between the propellant purity that can be achieved at reasonable cost and the level of inevitable contamination that the propellant user gets away with without getting into serious trouble. Excessively tight specification limits will result in many rejected propellant batches and additional expense both to the user and the propellant manufacturer. Quite often

specification limits were set arbitrarily without enough prior statistical process control studies. Table 42 is a summary of MIL-SPEC propellant specifications relating to hydrazine. A similar evolution has taken place for MMH specifications.

**Table 42:** Military specifications for hydrazine.

| MIL-SPEC Number              | Date        | Reason for revision, changes made                                                                                                                         |
|------------------------------|-------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|
| MIL-H-45701 (ORD)            | 20 Mar 1959 |                                                                                                                                                           |
| MIL-P-26536A                 | 31 Jul 1959 |                                                                                                                                                           |
| MIL-P-26536B                 | 13 Mar 1964 |                                                                                                                                                           |
| MIL-P-26536C                 | 23 May 1969 | Raise $N_2H_4$ assay from 97.5 to 98% min; lower $H_2O$ from 2.5 to 1.5% max                                                                              |
| Suppl.Data Sheet             | 15 Jun 1972 | Raise $N_2H_4$ assay from 98 to 98.5% min; lower $H_2O$ from 1.5 to 1.0% max; add particulate, Cl, Fe, NVR, $CO_2$ , organics limits                      |
| Amendment 1 (1 page)         | 25 Jul 1974 | Introduce new monopropellant grade with aniline limit of 0.5% max                                                                                         |
| Amendment 2                  | 1 Feb 1982  | Introduce new high-purity grade with aniline limit of 50 ppm max, NVR of 10 ppm max and $CO_2$ of 30 ppm max                                              |
| MIL-P-26536D (27 pp.)        | 27 Jul 1987 | Lower high-purity grade $NH_3$ from 0.4 to 0.3% max                                                                                                       |
| Amendment 1                  | 5 Jun 1995  | Specify range of $H_2O$ from 0.5 min to 1.0% max                                                                                                          |
| MIL-PRF-26536E-BASE (23 pp.) | 24 Sep 1997 |                                                                                                                                                           |
| Amendment 1                  | 10 Jan 2000 | Delete the minimum of 0.5% $H_2O$ requirement                                                                                                             |
| MIL-PRF-26536F (36 pp.)      | 1 Apr 2011  |                                                                                                                                                           |
| MIL-PRF-26536G (33 pp.)      | 11 Jul 2017 | Eliminate provisions for standard grade hydrazine; specify carbonaceous material to include <b>all</b> organic materials that give an FID response in GC. |

These specifications are frequently updated, and the user is advised to check the most recent status of the specification in question. Collections of most of the military specifications MIL-SPECs (as well as some previous revisions) are now available on government and commercial web sites. It is of interest to follow the historical evolution of hydrazine propellant MIL-SPECs as they exist today (Table 43).

The first hydrazine specification ever issued, MPD-139C, dates to 3 February 1955 and required only 95% hydrazine and allowed up to 1.5% aniline and *n*-heptane [673]. The purity requirements for hydrazine became more severe as the adverse effects of typical contaminants on monopropellant decomposition catalysts became better understood. Most hydrazine decomposition catalysts are very sensitive to contaminants that may act as catalyst poisons. A significant amount of effort has thus been devoted to identifying catalyst poisons and establishing tolerable levels of carbon-containing contaminants.

A comparison of different hydrazine specifications, especially for use in small thrusters, showed that the non-volatile residue (NVR) tolerance in monopropellant-grade hydrazine needed to be tightened further to prevent flow blockage in capillary feed tubes [674]. Non-volatile residue levels of 50 ppm in monopropellant Amendment A-grade and 30 ppm in so-called VIKING-grade hydrazine may still be too much for delicate injector capillary tubes of 0.44 N catalytic or electrothermal thrusters. Since the NVR limit cannot be lowered below the detection limit of the analytical method used, 10 ppm will be a reasonable limit if extremely low NVR levels are required. A 1-L hydrazine sample will have to be evaporated for each NVR determination, making this analysis more expensive and time consuming. The MIL-PRF requirements for H-70, a 70% hydrazine/30% water fuel mix used in the F-16 EPU, are listed in Table 44 [675].

### 3.6.3 Gas Chromatographic Analysis Methods for Hydrazine

Chromatographic methods are only separation methods that facilitate the subsequent identification of analytes in a mixture of substances. Identification of the analyte is made by retention time and comparison to an authentic sample or by applying a secondary identification method (spectrophotometry, mass spectrometry) to the enriched spot or eluate.

Gas chromatography (GC) is the most versatile method for both quantitative and qualitative (quality control) analysis of hydrazines. Most hydrazines are of sufficient volatility to allow separation from each other and from other constituents. However, the tendency of most hydrazines to undergo thermal or catalytic decomposition severely limits the operating temperatures and the choice of materials in a GC system. GC is also used for the analysis of gaseous decomposition products of hydrazine. Most GC applications use a liquid stationary phase, and the exact abbreviation of this would be GLC. Suffice it here to say that GC and GLC are intended to serve as abbreviations for the same analytical methods.

Water, MMH, and hydrazine were nicely separated at 383 K on a 1/4-in.-diameter  $\times$  6-ft.-long column filled with 10% Dowfax 9N9 on 60-80-mesh Teflon-6 [676, 677]. The fractogram also revealed traces of nitrogen and ammonia. For calibration purposes, response factors for water in hydrazine or MMH were determined by analyzing calibration mixtures of known composition. The reciprocal response ratio for water in hydrazine remained fairly constant (1.05) in the range 10–50% H<sub>2</sub>O. Likewise, it remained constant (1.15–1.20) for mixtures with 16–72% H<sub>2</sub>O in MMH. The column did not give satisfactory separation of UDMH from water in any of these mixtures and showed no loss of separating power after 200 injections. The addition of 1% sodium hydroxide to the stationary phase did not improve hydrazine separation, and better results were achieved in columns without NaOH.

The gas chromatography analysis method for hydrazine specified in MIL-PRF-26536G uses a 60- or 30-m  $\times$  0.53-mm, 1- $\mu$ m, DB-WAX capillary column, a thermal conductivity detector, with a split injector and an ultra-inert, deactivated, glass wool

Table 43: Historical evolution of specification limits for anhydrous hydrazine.

| Specification (Date)            | MIL-P-265361B (13 Mar 1964) | MIL-P-26536C (23 Mar 1969) | MIL-P-26536C Amendment 1 (25 Jul 1974) | MIL-P-26536C Amendment 2 (1 Feb 1982) | MIL-P-26536D (27 Jul 1987) | MIL-P-26536D Amendment 1 (5 Jun 1995) | MIL-PRF-26536E <sup>c</sup> Amendment 1 (10 Jan 2000) | MIL-PRF-26536G (11 Jul 2017) |
|---------------------------------|-----------------------------|----------------------------|----------------------------------------|---------------------------------------|----------------------------|---------------------------------------|-------------------------------------------------------|------------------------------|
| Constituent                     | Standard Grade <sup>a</sup> |                            |                                        | Monopropellant Grade <sup>b</sup>     | High-Purity Grade          | High-Purity Grade                     | High-Purity Grade                                     | Mono Grade                   |
| Hydrazine, % by weight, min     | 97.5                        | 98                         | 98                                     | 98.5                                  | 99.0                       | 99.0                                  | 99.0                                                  | 98.5                         |
| Water, % by weight              | 2.5 max <sup>b</sup>        | 1.5 max                    | 1.5 max                                | 1.0 max                               | 1.0 max                    | 0.5 min–1.0 max                       | 1.0 max                                               | 1.0 max                      |
| Ammonia, % by weight, max       | —                           | —                          | —                                      | —                                     | 0.4                        | 0.3                                   | 0.3                                                   | —                            |
| Particulate (>10 µm), mg/L, max | 10                          | 10                         | 10                                     | 1.0 max                               | 1.0                        | 1.0                                   | 1.0                                                   | 1.0                          |
| Chloride, % by weight, max      | —                           | —                          | —                                      | 0.0005                                | 0.0005                     | 0.0005                                | 0.0005                                                | 0.0005                       |
| Aniline, % by weight, max       | —                           | —                          | —                                      | 0.5                                   | 0.005                      | 0.003 max                             | 0.003                                                 | 0.50                         |

Table 43: (continued).

| Specification (Date)                                                                    | MIL-P-265361B (13 Mar 1964) | MIL-P-26536C (23 Mar 1969)        | MIL-P-26536C Amendment 1 (25 Jul 1974) | MIL-P-26536C Amendment 2 (1 Feb 1982) | MIL-P-26536D (27 Jul 1987) | MIL-P-26536D Amendment 1 (5 Jun 1995) | MIL-PRF-26536E <sup>c</sup> Amendment 1 (10 Jan 2000) | MIL-PRF-26536G (11 Jul 2017) |
|-----------------------------------------------------------------------------------------|-----------------------------|-----------------------------------|----------------------------------------|---------------------------------------|----------------------------|---------------------------------------|-------------------------------------------------------|------------------------------|
| Constituent                                                                             | Standard Grade <sup>a</sup> | Monopropellant Grade <sup>c</sup> | Monopropellant Grade <sup>b</sup>      | High-Purity Grade                     | High-Purity Grade          | High-Purity Grade                     | High-Purity Grade                                     | High-Purity Grade            |
| Iron, ppm by weight, max                                                                | —                           | —                                 | 30                                     | 20                                    | 4                          | 4                                     | 4                                                     | 4                            |
| Non-volatile residue, mg/L, max                                                         | —                           | —                                 | 50                                     | 50                                    | 10                         | 10                                    | 10                                                    | 10                           |
| Carbon dioxide, % by weight, max                                                        | —                           | —                                 | 0.02                                   | <b>0.003 max</b>                      | 0.003                      | 0.003                                 | 0.003                                                 | 0.003                        |
| Other volatile carbonaceous material (total as MMH and UDMH, alcohol), % by weight, max | —                           | —                                 | 0.02                                   | 0.02                                  | 0.005                      | 0.005                                 | 0.005                                                 | <b>0.005</b>                 |

min = minimum, max = maximum, Changes in either limits or methods are highlighted in **bold** type.

<sup>a</sup> Standard-grade requirements remained unchanged through Rev. E(1) in 2000

<sup>b</sup> Monopropellant requirements remained unchanged through Rev. E(1) in 2000

<sup>c</sup> MIL-PRF-26536E Orig. (27 Sep 1997) did not change spec. limits, only methods of analysis

**Table 44:** Specification requirements for H-70 per MIL-PRF-87930B

| Properties                                                                              | Limits     | Method                                                      |
|-----------------------------------------------------------------------------------------|------------|-------------------------------------------------------------|
| Hydrazine (% by weight)                                                                 | 69–70      | GC                                                          |
| Water (% by weight)                                                                     | 30 min     | GC                                                          |
| Particulate (mg/L)                                                                      | 1.0 max    | Gravimetry                                                  |
| Chloride (% by weight)                                                                  | 0.0005 max | Colorimetry, specific ion electrodes, or ion chromatography |
| Aniline (% by weight)                                                                   | 0.40 max   | Spectrophotometry or GC                                     |
| Iron (% by weight)                                                                      | 0.002 max  | Atomic absorption or spectrophotometry                      |
| Non-volatile residue (mg/L)                                                             | 40 max     | Gravimetry                                                  |
| Carbon dioxide (% by weight)                                                            | 0.002 max  | GC                                                          |
| Other volatile carbonaceous material (total as either MMH or UDMH/alcohol, % by weight) | 0.02 max   | GC                                                          |

packed split liner with dual temperature programming at two different rates, 10°/min between ambient and 100 °C and 20°/min between 100 and 185 °C.

For the analysis of water and ammonia in the H-70 fuel blend, a 3.17-mm × 0.61-m (0.125-in. × 2-ft.) column packed with 10% polyethylene glycol on 60- to 80-mesh Fluoropak was at one time recommended [678]. In calculating the results, corrections must be made for aniline that hangs up in the column. Aniline is determined separately by a spectrophotometric method. As an alternative to the spectrophotometric method, aniline in H-70 can also be analyzed by GC, using a 1.7% Amine 220/34% Apiezon L on 60–80 mesh silanized diatomaceous earth columns. With a GC-FID (flame ionization detector), the peak area must be calibrated from a known standard since water does not show in the FID. A later revision of the MIL PRF procedure specified a 60-m × 0.53-mm, 1-μm film thickness Agilent DB-WAX capillary column, a TCD, with a split injector and a glass wool packed split liner [675].

Three different columns – polyphenyleneoxide = Porapak Q; 20% loading of a mixture of 72% diethanolamine, 18% lauryl alcohol, 10% sodium iodide on Chromosorb W 80–100; 9% Carbowax MOA on Fluoropak – were tested for the separation of water, hydrazine, and its decomposition products [679]. Hydrogen in the mixture was determined in a separate injection with nitrogen as carrier gas and vice versa, requiring repeated injections of the same sample.

A review of existing methods for determining hydrazine and its short-alkyl and acyl derivatives with the use of different types of chromatography examined the selectivity and sensitivity of many different methods [680, 681]. Possible ways to increase the sensitivity of hydrazine determination were suggested and evaluated against examples of analyses of real samples.

### 3.6.3.1 GC Analysis Without Prior Derivatization

Improved separation of all three hydrazines and water was achieved using a stationary phase that is chemically similar to hydrazine [682]. In this case, 2-hydrazinopyridine, a polar liquid of low volatility, was used as the stationary phase in 10% concentration on Fluoropak 80. An attractive feature of the fractogram of a synthetic blend consisting of 27.9%  $\text{N}_2\text{H}_4$ , 27.9% MMH, 22.2% UDMH, and 21.9%  $\text{H}_2\text{O}$  depicted in [682] is the symmetry of the peaks, devoid of the tailing that is so characteristic (and disturbing) of  $\text{H}_2\text{O}$  and  $\text{N}_2\text{H}_4$  on other polar stationary phases. The constituents elute in the sequence UDMH,  $\text{H}_2\text{O}$ , MMH, and  $\text{N}_2\text{H}_4$ . 2-Hydrazinopyridine is strongly alkaline and will rapidly absorb  $\text{CO}_2$  from the air if the column is left open to the atmosphere. The column had to be stored tightly sealed while not in use. Even if kept in the GC under a flow of helium, the columns were operable for only 10 d. Significant vaporization losses ("bleeding") of the stationary phase occurred if the column was heated above 353 K.

Apparently some Third World countries in their quest for UDMH resorted to the direct methylation of hydrazine with dimethyl sulfate and obtained mixtures containing four methylated derivatives of hydrazine: MMH, UDMH, SDMH, and trimethylhydrazine, with some unreacted hydrazine and water that needed to be analyzed by GC [683]. Several columns with different stationary phases under different experimental conditions (temperature ramping, carrier gas flow, split/splitless injection) were used, but clearly resolved peaks of proper peak shape and integration could not be obtained.

GC analysis of water in hydrazine should be a fairly simple, straightforward procedure [684]. A packed column used for hydrazine analysis was replaced by a capillary column with improved results [269]. See also [685].

### 3.6.3.2 GC Analysis of Impurities in Hydrazine

Several attempts have failed so far to identify a column stationary phase/packing material that separates all contaminants commonly found in hydrazine equally well. Although satisfactory columns are available for MMH or UDMH, none was capable of simultaneously separating carbon dioxide, ammonia, water, MMH, UDMH, and 2-propanol (isopropanol = IPA) from the hydrazine. Normally, propellant-grade hydrazine contains only water, aniline, ammonia, and carbon dioxide. Sometimes MMH, UDMH, and IPA are accidentally introduced by careless transfer, storage, and cleaning procedures. A dual-column technique using three separate columns, namely, a 1-m  $\times$  6-mm 33% Carbowax 400 (PEG 400) on 90-100-mesh Anakron AB column (Column A), a 1.8-m  $\times$  6-mm 10% Dowfax 9N9 on 60-80-mesh TeeSix (Analabs) (Column B), and a 1.8-m  $\times$  6-mm 50-80-mesh Porapak PS column (Column C) was developed to achieve complete separation [686]. Column A did not separate UDMH/IPA or water/MMH. Column B did not separate water/UDMH or MMH/IPA. When A and B were used in combination, UDMH and IPA were still not quite separated. When combining columns B and C, six well-resolved peaks were obtained



in the fractogram of hydrazine spiked with all five contaminants, but this time hydrazine and MMH were not separated. With two separate injections on two different combinations of columns, a complete analysis could be achieved. Another alternative would have been to use a dual-column setup and backflush one of the unresolved pairs of peaks into another column for complete separation. At a column temperature of 373 K, aniline would always hang up in the column or at best elute as a very broad peak, causing gradual baseline shifts.

A column packing of 20% Ucon Oil 550X on Fluoropak-80 has been used for the analysis of small (0.5–2%) quantities of water in hydrazine [687, 688]. A ¼-in. × 10-ft. column at 376 K (103 °C) with 80-mL/min He at 172 kPa (25 psig) gave satisfactory separation of hydrazine from ammonia, methylamine, ethylamine, UDMH, and MMH.

### 3.6.3.3 GC Analysis Following Prior Derivatization

The detection limit for toxic or otherwise troublesome contaminants by GC has generally been improved by several orders of magnitude through the introduction of the FID. It is known that the FID is “blind” to hydrazine that combusts only to nitrogen and water. Alkylhydrazines give only a weak signal because they contain very little carbon. Sensitivity for the detection of hydrazine(s) by GC-FID can be improved by converting hydrazine(s) to volatile, thermally stable organic derivatives with high carbon (or even some halogen or silicon) content, such as hydrazones or azines. Similarly, the electron capture detector is very sensitive to halogen, and halogen-containing derivatizing agents improve the detection limit dramatically. The methods can also be adapted to analyze MMH or UDMH.

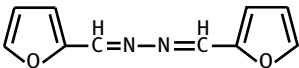
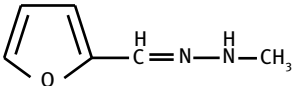
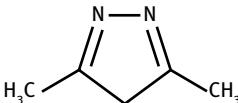
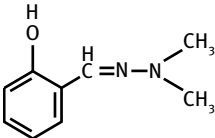
The following Table 45 summarizes some of the derivatizing agents used for GC and the types of derivatives formed. In search of additional derivatizing agents, it may be useful to scan the list of derivatizing agents used for high-performance (high-pressure) liquid chromatography (HPLC) (Section 3.6.4.2). Some derivatizing agents work equally well for GLC and HPLC. Many of the derivatizing agents that have been tested for the analysis of hydrazine derivatives (pharmaceuticals, growth retardants) can be applied to the analysis of hydrazine itself.

Details of GC analytical methods with derivatizing agents are described in [689]. The derivatizing agents used (in alphabetical order, allowing prefixes such as *ortho* or *para* as part of the name) included acetone [690–698]; benzaldehyde [699, 700]; 2-furaldehyde [701–713]; chloroformate esters [714]; 2,4-dinitrobenzaldehyde [715], *ortho*-phthalaldehyde [716], *para*-chlorobenzaldehyde, [717–719], pentafluorobenzaldehyde [720, 721]; 2,4-pentanedione [722–724]; and 3-butenone (E)-1,1,1-trifluoro-4-(3-thienyl) [725].

### 3.6.3.4 Thin-Layer and Column Liquid Chromatography

These analytical methods have been used extensively for the concentration and identification of natural products such as sugars and amino acids. There are only comparatively few applications of these methods in the analysis of hydrazines. Column chro-

**Table 45:** Derivatizing agents for GC and derivatives thus formed.

| Reagent Used               | Type of Hydrazine Analyzed | Derivative Formed                                                                                      |
|----------------------------|----------------------------|--------------------------------------------------------------------------------------------------------|
| Acetone                    | Hydrazine                  | $(\text{CH}_3)_2\text{C}=\text{N}-\text{N}=\text{C}(\text{CH}_3)_2$                                    |
| Acetone                    | MMH                        | $\text{CH}_3\text{NH}-\text{N}=\text{C}(\text{CH}_3)_2$                                                |
| Acetone                    | UDMH                       | $(\text{CH}_3)_2\text{N}-\text{N}=\text{C}(\text{CH}_3)_2$                                             |
| Benzaldehyde               | Hydrazine                  | $\phi\text{HC}=\text{N}-\text{N}=\text{C}\phi\text{H}$                                                 |
| 2,4-Dinitrobenzaldehyde    | Hydrazine                  | $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CH}=\text{N}-\text{N}=\text{CHC}_6\text{H}_3(\text{NO}_2)_2$ |
| 2,4-Dinitrobenzaldehyde    | MMH                        | $\text{CH}_3\text{NH}-\text{N}=\text{CHC}_6\text{H}_3(\text{NO}_2)_2$                                  |
| 2,4-Dinitrobenzaldehyde    | UDMH                       | $(\text{CH}_3)_2\text{N}-\text{N}=\text{CHC}_6\text{H}_3(\text{NO}_2)_2$                               |
| Furaldehyde                | Hydrazine                  |                       |
| Furaldehyde                | MMH                        |                       |
| 2-Nitrobenzaldehyde        | UDMH                       | $(\text{NO}_2)\text{C}_6\text{H}_4\text{CH}=\text{N}-\text{N}(\text{CH}_3)_2$                          |
| Pentane-2,4-dione          | Hydrazine                  |                       |
| Pentane-2,4-dione          | MMH                        |                                                                                                        |
| Pentane-2,4-dione          | UDMH                       | $\text{H}_3\text{CCOCH}_2\text{C}(\text{CH}_3)=\text{N}-\text{N}(\text{CH}_3)_2$                       |
| Pentafluorobenzaldehyde    | UDMH                       |                                                                                                        |
| Pentafluorobenzoylchloride | UDMH                       | $(\text{C}_6\text{F}_5\text{CO})_2\text{N}-\text{N}(\text{CH}_3)_2$                                    |
| Salicylaldehyde            | UDMH                       |                     |

matography is often used as a method of sample preparation to separate the analyte from complex mixtures, such as in biological specimens. Once concentrated, other analysis methods, such as GC, in particular GC or HPLC with prior derivatization, can be used to further identify and quantify the hydrazine derivative extracted from the enriched section of the column.

As little as 0.5  $\mu\text{g}$  hydrazine can be detected by paper chromatography using *n*-butanol/6N HCl as mobile phase [726]. Picryl chloride is better than ninhydrin for developing paper chromatograms when looking for hydrazines.

A rapid and efficient procedure for determining traces of hydrazine in recovered solvents is the thin-layer chromatography (TLC) of the intensely colored azine with PDAB [727]. Hydrazine concentrations as low as 0.002% in aqueous and alcoholic media can be determined with a minimum of interference. The sensitivity of the test is enhanced by observing the TLC plate under UV light after spraying the plate with Dragendorff's spray reagent. As little as 0.2 µg will give a recognizable spot on the plate.

Hydrazine, MMH, SDMH, and UDMH as their dichloride salts can be separated by TLC on cellulose powder on glass plates, using 2-propanol/water/concentrated HCl in a volume ratio of 130:40:30 as the eluent [728]. Folin-Ciocalteu reagent was used to develop the plates and formed distinct blue spots equally well with all four hydrazines; PDAB does not react with SDMH. Using 366-nm UV light to stimulate fluorescence, hydrazine could be detected at the nanogram level after reaction with fluorescamine and isomeric phthalaldehydes [729].

### 3.6.4 High-Performance Liquid Chromatography

Essentially all methods previously described for paper or TLC can be adapted to HPLC by choosing suitable derivatives, eluents, column stationary phases, and detectors. These methods have proved particularly useful for trace contaminant/crop residue analysis. A discussion has evolved about the interpretation of the letter P in HPLC. It has been pointed out that the latest developments of the method are not using high pressure and do not deserve the attribute "high performance," since other, more efficient methods have become available. Nevertheless, we summarize the HPLC methods here that have at one time or another been used for the analysis of hydrazine and hydrazine derivatives.

#### 3.6.4.1 HPLC Analysis Without Prior Derivatization

Picogram quantities of hydrazines in the effluents of HPLC columns can be detected by chemiluminescence with ozone [730]. Because hydrazine is a reducing agent, its presence in the effluent from HPLC columns can be detected by electrochemical oxidation [731]. Regardless of which hydrazine must be analyzed, derivatized or not, miniaturized electrochemical detectors for these and similar HPLC-EC applications made the analysis more specific.

A hydrophilic interaction liquid chromatography (HILIC) method for the simultaneous determination of hydrazine, MMH, and UDMH in natural waters and soils was based on a combination of HPLC chromatographic separation on a zwitterionic sulfo-betaine stationary phase with amperometric detection and used a mixture of 78 vol. parts of acetonitrile with 22 parts of an aqueous phosphate buffer solution of pH 2.5 with an ionic strength of 20 mM as the mobile phase [732]. Detection in the direct current mode was performed at a working electrode potential of 1.1 V. The advantages of the method are the high efficiency of separation, speed, high sensitivity, and a wide

dynamic range of analyte concentrations, covering four orders of magnitude. The limits of detection were in the range 0.07–0.13 µg/L, which was two orders of magnitude lower than those achievable in previously used methods of ion chromatography with electrochemical or mass spectrometric detection.

#### 3.6.4.2 HPLC Analysis Following Prior Derivatization

Just as with GC, derivatization of hydrazine stabilizes it as a derivative for the subsequent separation and analysis by liquid chromatographic methods. The methods can also be adapted for the analysis of MMH or UDMH.

Many of the methods described here were used to determine traces of hydrazine that could be present in pharmaceutical drugs as contaminants or form in the body of patients as the hydrazine-derived drugs are metabolized. Traces of hydrazine (i.e., hydrazinium sulfate) in sulfuric acid (residual excess hydrazine after removal of NO<sub>x</sub> and free chlorine) can be determined by derivatization liquid chromatography [733].

Details of HPLC analytical methods with derivatizing agents are described in [734]. The derivatizing agents used included benzaldehyde [735–739]; salicylaldehyde [731, 740, 741]; *p*-hydroxybenzaldehyde [742]; *p*-tolualdehyde [743]; *p*-anisaldehyde [744]; naphthalene-2,3-dialdehyde [745, 746]; 2-hydroxynaphthaldehyde [747]; and 2-nitrobenzaldehyde or 5-nitro-2-furaldehyde [748, 749].

#### 3.6.5 Ion Chromatography

Ion chromatography is often performed in the same equipment as HPLC, just using ion-exchange resins instead of solid sorbents as the stationary phase. Ion chromatography can use cation-exchange resins or anion-exchange resins.

Hydrazine and hydroxylamine in aqueous solution may be determined using a Nucleosil 10SA cation-exchange column with 2mM citrate and 2mM ethylenediamine at pH 4.5 as eluent with a copper electrode [750]. Detection limits were in the range 2–10 nmol for the species examined. Alkali metal ions, ammonium ion, and hydrazinium(1+) ion can be determined simultaneously in less than 10 min. on an HPIC-CG3 column with 0.015 M HCl as the eluent [751].

A major drawback of the commonly used derivatizing agents for either GC or HPLC is that they rarely allow analysis of all three propellant hydrazines in one shot. It was therefore of interest when it was found at the NASA White Sands Test Facility (WSTF) that all three hydrazines, underivatized but in the state of their cations, could be separated by HPLC on a cation-exchange resin column using an acidic potassium phosphate buffer as the eluent [752]. DC amperometry of the eluent at a platinum electrode is specific for hydrazines since they are easily electrooxidized. Detection limits of 1 µg/L were achieved in clean wastewater samples. The only sample preparation was filtering, a substantial savings of labor over competing derivatizing/extracting methods. Similar results are possible with a gold electrode [753].

Ion chromatography with amperometric detection was applied for the direct determination of UDMH, hydrazine, MMH, and SDMH in water [754]. Selectivity of two column materials – (1) reversed phase silica modified by dodecylbenzenesulfonic acid and (2) silica with chemically bonded sulfonic acid groups – was investigated with conductivity detection. The method was used to analyze soils contaminated by spilled UDMH from crashed PROTON launch vehicles. Hydrazine and MMH were detected as decomposition products of UDMH in the soil.

An ion-exclusion chromatography method with ion-exchange enhancement of conductivity was developed for the selective separation and sensitive determination of hydrazinium ion from alkali/alkaline earth metal cations and ammonium ion [755]. Hydrazinium ions were separated by ion-exclusion/penetration effect from other cations on a weakly basic anion-exchange column in the  $\text{OH}^-$  form (TSKgel DEAE-5PW). Two different ion-exchange resin columns were inserted between the separating column and conductimetric detector in order to improve the sensitivity of hydrazinium ion. As a result, the sensitivity of hydrazinium ion using two conductivity enhancement columns could be 26 times greater than using the separating column alone. The detection limit of hydrazine ions in this system was 0.64 parts per billion (ppb).

Several methods exist for the direct determination of hydrazines in water, including ion, ion-pair, ion-exclusion, and hydrophilic interaction chromatography [756]. The separation selectivity and sensitivity of detection for each method depends on the type of sample. Direct methods are simpler than those requiring prior derivatization of samples, as was demonstrated with examples of hydrazine determination in real samples.

### 3.6.6 Capillary Electrophoresis Chromatography

Another modern analysis method suitable for the analysis of ionized compounds is capillary electrophoresis (CE). The CE method in combination with electrochemical detection (called CEEC) allows for the simultaneous determination of hydrazine, MMH, and other hydrazines in one injection without prior derivatization [757–759]. Detection of hydrazines in eluent was achieved with a palladium-modified carbon fiber microdisc array electrode. The detection limits for hydrazine or MMH were 1.2 or 2.1 pg, respectively. This is several orders of magnitude more sensitive than other chromatographic methods. Hydrazine and methylhydrazines could be separated and detected by CEEC at 1 millimol/L concentrations in a borate buffer at pH 7.18 [760].

CEEC can be used for the simultaneous detection of hydrazine and MMH using a 4-pyridyl hydroquinone self-assembled microdisc platinum electrode [761]. Such an electrode has very high catalytic capability for hydrazines, and they were detectable even at a potential of 0.0 V. The responses for hydrazine and methylhydrazine were linear over three orders of magnitude in the range 0.2–400  $\mu\text{M}$  hydrazine or MMH with

correlation coefficients of 0.9998 and 0.9991, respectively. The detection limits were  $0.1\text{ }\mu\text{M}$ .

A miniaturized analytical system for separating and detecting hydrazines was based on the coupling of micromachined CE chips with removable thick-film amperometric detectors and offered rapid (2 min) low-potential (+0.5 V vs. Ag/AgCl) simultaneous detection of hydrazine, MMH, UDMH, and phenylhydrazine at the  $1.5 \times 10^{-6}\text{ M}$  level, with linearity over the  $2 \times 10^{-5}\text{ M}$  to  $2 \times 10^{-4}\text{ M}$  range [762].

Non-aqueous capillary electrophoresis (NACE) with electrochemical detection (NACE-ED) can be used for the separation and quantitative determination of hydrazine and its methyl derivatives. The best performance of NACE-ED was achieved when using 4 mM sodium acetate/10 mM acetic acid/methanol/acetonitrile as the running buffer, with a bare platinum working electrode set at +1.0 V in an end-column amperometric detection cell [763]. The limits of detection for hydrazine, MMH, SDMH, and UDMH were 5, 2, 12, and 1 ng/mL, respectively. This is between one and two orders of magnitude lower than that achieved by previously reported CEEC methods in aqueous buffer systems in conjunction with various types of chemically modified electrodes.

Poly(methylmethacrylate) (PMMA) microchip electrophoresis separations with contactless conductivity detection, which integrates all separation and detection components in a compact portable device, enables the separation of hydrazine, MMH, and UDMH within <30 s at a separation voltage of 3.8 kV using a L(-)-histidine/2-(*N*-morpholinoethanesulfonic acid) buffer (25:50 mM, pH 5.87) [764]. The contactless conductivity detection enabled detection limits for hydrazine, MMH, and UDMH of 11.9, 35.5, and 337.8 ng/mL, respectively, with linear concentration dependence up to  $10\text{ }\mu\text{g/mL}$ . In complex matrices such as soil samples or river water, interferences were eliminated by implementing ultrasound-assisted headspace single-drop micro-extraction under strongly alkaline conditions, which led to improved limits of detection for hydrazine, MMH, and UDMH of 6.5, 15.3, and 11.4 ng/mL, respectively.

A multitude of different electrochemical detection electrode materials, many based on carbon fiber electrodes, have been developed for these CEEC hydrazine analysis applications. The same electrodes can be used for amperometric titrations (Section 3.6.10.8).

### 3.6.7 Gravimetric Methods for Analysis of Hydrazine

Gravimetric methods are a thing of the past and consume time and lack accuracy. At best, precipitation of insoluble hydrazine derivatives can be used for pre-concentrating the analyte. Benzalazine precipitates quantitatively from solutions of hydrazine and benzaldehyde [765]. Because the azine melts at 366 K, it must be dried at low temperature in a vacuum desiccator. In concentrated solutions with 50% methanol, even the intensely yellow azine formed from hydrazine with PDAB can be precipitated and weighed. It melts at 537 K and can be dried at higher temperature than the ben-

zalazine. An insoluble yellow azine precipitates from 2-nitro-1,3-indandione and hydrazine [766]. It melts at 498 K (225 °C) under decomposition.

Because the boiling points of hydrazine and ammonia are so disparate, it has been possible to do quick (but not very accurate) analyses of hydrazine/ammonia mixtures with up to 27% hydrazine by low-temperature thermogravimetry [767]. In this method, a weighed sample is slowly heated from 228 to 423 K, while the weight of the sample is recorded by an electronic balance. A typical sample weight was 40 mg. Carbon dioxide must be carefully excluded, since its potential interference by the formation of less volatile carbazic acid has not been investigated thoroughly enough.

### 3.6.8 Volumetric Analysis Methods for Hydrazine

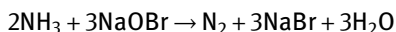
Just like gravimetric methods, volumetric analysis methods are slowly becoming a thing of the past because they consume time and lack accuracy and require operator training. Volumetric analysis methods have traditionally been the daily chore of the analytical chemist before wet chemistry was eventually replaced by automated titrators and instrumental methods of analysis where one does not have to wash dishes afterward. As they are listed here, they only differ by the type of reaction and endpoint indication.

#### 3.6.8.1 Acidimetric Analysis Methods for Hydrazine

Acidimetric titrations are rarely used to determine any hydrazines individually, but several methods have been developed to analyze hydrazine mixtures by multi-step acidimetric titrations. Several complications are to be expected in attempts to titrate hydrazine directly acidimetrically: **(1)** A dilute alkaline solution of hydrazine will rapidly autoxidize if air is not carefully excluded prior to and during titration; **(2)** the choice of a suitable indicator is difficult since hydrazine is an even weaker base than ammonia, and salts with strong acids hydrolyze to form acidic solutions; and **(3)** hydrazine has two protonization levels. The true inflection point in less than 0.4 M solutions falls in the lower range of methyl red and in the upper range of methyl orange [768]. If the sample contains ammonia and hydrazine, it can be titrated acidimetrically first and iodometrically second to obtain numbers for both constituents.

When hydrazine is removed prior to ammonia analysis, in this case with 0.04–0.4 mM ammonia in solutions containing 0.7 mM hydrazine, there is a method where ammonia can be determined by Kjeldahl distillation and acidimetric titration following destruction of all the hydrazine with iodate in acidic solution [156, 769]. The standard deviation obtained from seven repetitive analyses was only  $\pm 0.5\%$  for ammonia in the vicinity of 8 mg of  $\text{NH}_3$  in  $\text{N}_2\text{H}_4$ . The method has also been applied to alkyl- and arylhydrazines without additional ammonia generation during the removal of the hydrazines.

Mixtures of 5–10% hydrazine in ammonia, such as those expected to be formed by nucleofission synthesis of hydrazine from ammonia, can be analyzed by first reacting the hydrazine only in acidic solution with bromine (liberated in solution by mixing potassium bromate and potassium bromide solution) [770]. Excess bromine is then converted to free iodine by the addition of potassium iodide, and the iodine is backtitrated with sodium thiosulfate to a starch (or potentiometric) endpoint. One mol of hydrazine is equivalent to four equivalents of bromate. Next, a second sample is also mixed with bromate and bromide, acidified to liberate bromine (this is done in a bromination flask or an iodine number flask with tightly sealing ground glass stopper), and then rendered alkaline to form hypobromite by adding 6N NaOH until the color of the solution changes from brown to pale yellow. The reaction of hypobromite with ammonia



varies slightly with alkalinity. When samples contain both ammonia and hydrazine, hydrazine is analyzed first in acidic solution and then subtracted from the total equivalents of bromate consumed in the second reaction in alkaline medium. The relative standard deviation in either ammonia or hydrazine results was on the order of 0.22–0.36%.

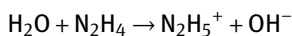
### 3.6.8.2 Acidimetric Titration Following Reaction with Organic Compounds

The pKs of hydrazine and UDMH or MMH are too close to allow simultaneous titration of two or three bases in aqueous solution. Following derivatization of hydrazine and UDMH, however, the acidity of the resulting azines when titrated in non-aqueous media (acetic acid) with perchloric acid in dioxane is distinctly different. Derivatization allows separate titration of different hydrazines and may also help in achieving sharper endpoints. Carbonyl compounds used to derivatize hydrazines in this application include salicylaldehyde [771–773] and acetone [774].

Instead of forming derivatives with salicylaldehyde, the different rate of acetylation of hydrazine and UDMH or hydrazine and MMH with acetic anhydride provides the basis for a method to analyze binary hydrazine mixtures [775–778]. In acetonitrile, both hydrazine and MMH react almost immediately, whereas the acetylation of UDMH proceeds very slowly. Total basicity of an unacetylated sample is determined by titration with standardized perchloric acid in acetic acid with quinaldine red indicator.

Hydrazine and its methylated derivatives can be differentiated not only by reaction with acetylating agents or azine-forming reagents but also by acidimetric titration before and after reaction of the sample with isocyanates [779].

Traces of water in hydrazine are strongly ionized



and form the acid hydrazinium ion. Small amounts of water in hydrazine can be determined by titrating this “acid” with a strong base, such as standardized 0.1 molar



sodium hydrazide in hydrazine [780]. This reaction must be carried out under the exclusion of air. Endpoint indication is possible with a potentiometer, a platinum electrode, and a Cd/CdSO<sub>4</sub>/0.2M H<sub>2</sub>SO<sub>4</sub> reference electrode. Special precautions are required when preparing the sodium hydrazide solutions to avoid explosions.

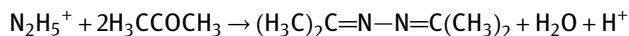
Hydrazinium salts of weak or medium-strength acids may have acidic or basic properties, depending on the solvent used. They can be titrated in non-aqueous media with potentiometric endpoint indication. Thus hydrazinium(1+) nitrate can be titrated as an acid in pyridine solvent using tetrabutylammonium hydroxide as the titrant. A glass/thallium amalgam electrode pair was used to sense the equivalence potential. If hydrazinium(1+) nitrate is to be determined as an acid, dimethyl sulfoxide or glacial acetic acid can be used as the solvent. In the case of glacial acetic acid, the preferred titrant is 0.05 N perchloric acid in acetic acid [781–783].

A combination of derivatization with salicylaldehyde and acidimetric titration with potentiometric endpoint indication in non-aqueous solvents used perchloric acid in acetonitrile, nitrobenzene, or acetic acid [784]. The Schiff base formed with hydrazine was the least basic azine of the ArCH=N(CH<sub>2</sub>)<sub>n</sub>N=CHAr series (*n* = 0 to 4) tested. An increase in the number of central —CH<sub>2</sub>— groups increased the basicity of the Schiff bases.

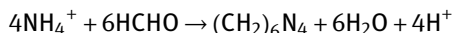
Mixtures of hydrazine, MMH, or UDMH with diethylene triamine can be analyzed in a non-aqueous titration system using methanol as a solvent, hydrochloric acid in methanol as the titrant, and bromocresol green as indicator [785]. The method uses the reactions of salicylaldehyde, which forms neutral azine with hydrazine, neutral hydrazones with MMH and 1,1-dimethylhydrazine, and a basic Schiff base with diethylene triamine. The total basicity of the admixtures is determined on separate aliquots of the mixtures before and after the addition of salicylaldehyde.

Mixtures of hydrazine, hydrazinium nitrate, ammonia, and water can be analyzed by titrating the mixture with standard acid before and after reacting it with acetone or, in a separate test, with formaldehyde [786, 787]. The procedure employs successive acidimetric titrations on a single sample as follows:

- Neutralization of the sample with standard acid to determine the total basic components (hydrazine and ammonia).
- Reaction of the hydrazinium ion with excess acetone forming dimethylketazine, and titration of the acid liberated with standard base. This determines the sum of free and combined hydrazine (hydrazine and hydrazine salt):



- Reaction of ammonium ion with excess formaldehyde forming hexamethylenetetramine and titration of the acid liberated with standard base. This determines ammonia:



- d. Subtracting the result for ammonia from the result for total basic components determines hydrazine. Subtracting the result for hydrazine from the result for free and combined hydrazine determines hydrazine salts. The remainder of the sample was assumed to be water. The results were then compared with titrating the total hydrazine with potassium iodate in hydrochloric acid solution.

### 3.6.8.3 Redox Titration Analysis Methods for Hydrazine

Because of the multitude of oxidizers that have been more or less successfully tried as oxidants for the redox titrations of hydrazine, a systematic approach must be followed in discussing these analysis methods. The following discussion covers redox titrations in the sequence of groups in the periodic table of elements, arranged by the active atom that changes its state of oxidation. The review starts with group VIII and proceeds from right to left toward group I. In this arrangement, the halogens and halogenates are discussed first, and copper(II) sulfate (group Ib) is discussed last.

In evaluating several different methods for the analysis of hydrazine and its methyl derivatives, both iodate and bromate titrations were conducted for hydrazine, MMH, UDMH, and SDMH [788]. In the iodate titration using chloroform extraction of purple iodine as a visual indicator, hydrazine reacted on a 1:1 molar basis, but UDMH reacted on an iodate:UDMH = 1:2 ratio. As an alternative, the four hydrazines can be titrated potentiometrically with 0.016 M  $\text{KBrO}_3$  when the samples are dissolved in 20 mL concentrated HCl containing 2 g KBr.

### Redox Titrations with Visual and Other Non-Electric Endpoint Indication

Analysis methods for hydrazine by redox titrations have been evaluated as early as 1924. Iodic acid, iodine, bromine, and hypochlorite were tried as oxidants, but iodic acid or potassium iodate in acidic solution was quickly recognized as the most desirable oxidizer [789]. Only the methods of endpoint indication were initially very cumbersome, and usually the excess oxidant had to be backtitrated iodometrically. The methods listed in this first section operate without electronic endpoint indication, but they would work just as well or even better with electronic endpoint indication. Methods that depend on electronic instrumentation for endpoint indication are summarized in a following section. For a more detailed summary of analytical methods for hydrazine(s) using a variety of oxidants, see [790]. That thorough resource contains sections on the following oxidizers: potassium hexacyanoferrate(III), bromine monochloride, bromine, potassium chlorate, sodium hypobromite, potassium bromate, iodine, potassium iodate, potassium permanganate, potassium peroxodisulfate, selenous acid, potassium dichromate, chloramine-T, *N*-bromosuccinimide, potassium or ammonium vanadate, cerium(IV) nitrate or cerium(IV) sulfate, and methods for visual endpoint indication. The endpoints of redox titrations can also be recognized by thermometric titrimetry [791, 792].

Hydrazine has been determined by its oxidation to nitrogen with a known excess of bromine. Bromine in acidic medium bleaches the dye methyl red. A known excess of bromine when treated with hydrazine is reduced to bromide, and the unreacted bromine is determined spectrophotometrically using methyl red [793–795]. The molar absorptivity of methyl red was calculated to be  $9.95 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The method obeys Beer's law in the range 0–6  $\mu\text{g}$  of hydrazine in an overall aqueous volume of 25 mL with a correlation coefficient of 0.999. The detection limit was 0.25  $\mu\text{g}$ . The method has been successfully applied for the determination of hydrazine in boiler feedwater samples. The results obtained with the bromine-methyl red method compared well with the PDAB method.

### Redox Titrations with Potentiometric or Amperometric Endpoint Indication

Potentiometric or amperometric endpoint indication is more accurate than visual endpoint indication and can be applied to titrations with most of the oxidizers listed in the preceding section. Redox titrations with potentiometric or amperometric endpoint indication are summarized in [796], where additional information on redox titrations can be found.

Oxidizers used for redox titrations with potentiometric or amperometric endpoint indication include iodine, iodine(I) chloride, potassium iodate, potassium periodate, potassium bromate, potassium permanganate, molybdates, chromates, chloramine-T, chloramine-B, cerium(IV) nitrate, cerium(IV) perchlorate, and cyanogen bromide.

Depending on the pH and the amount of additional hydrochloric acid present during titration, the reduction of iodine(V) by hydrazine sulfate can proceed to different states of oxidation, and the three different equivalence points (resulting in iodine monochloride, free iodine, or iodide ion) can be visualized by plotting the electrochemical potential against a reference electrode [797]. Sometimes a layer of chloroform is used to extract the free iodine and make it visible by its purple color for visual endpoint indication.

The endpoint during the titration of hydrazine with iodine or iodate can also be recognized using an iodide-selective electrode [798, 799]. As little as 13 ng hydrazinium(2+) chloride has been determined by this method in the absence of other reducing agents. The reproducibility was like that of the direct potentiometric methods (2–3% in  $10^{-5} \text{ N}$  solutions).

### 3.6.9 Gasometric and Manometric Analysis Methods

Many hydrazine compounds give quantitative yields of dinitrogen gas on treatment with iodate in a Warburg apparatus. The ready availability of high-purity hydrazinium(2+) sulfate caused several investigators to choose this salt as a standard for the calibration of their gasometric apparatus. The reaction proceeds rapidly with hydrazine, MMH, and numerous monoacyl hydrazides of industrial and pharmacological interest [800]. With hydrazine in the form of hydrazinium(2+) sulfate, the

mean nitrogen recovery of four subsequent analyses was 99.5% with a standard error of  $\pm 1.2\%$ . See also [801]. Other hydrazine derivatives can be analyzed by gasometric microdetermination by oxidation in basic media [802, 803].

### 3.6.10 Electroanalytical Methods for Hydrazine

Electrochemical analysis methods are becoming increasingly popular because they can be automated and made to interface with digital data acquisition and data reduction. Electrochemical analysis methods include coulometric, potentiometric, and amperometric methods.

#### 3.6.10.1 Coulometric Analysis Methods for Hydrazine

Because of the different routes of hydrazine oxidation in acidic, neutral, or alkaline solutions, coulometry is a suitable method for the direct oxidation of hydrazine, provided that all conditions are kept constant. The mechanism of the electrooxidation of hydrazine was already discussed in Section 3.2.

Hydrazine in the presence of ammonia in aqueous acidic solutions could be determined with a relative standard deviation of 0.09% by direct coulometry in 1 M sulfuric acid with a platinum analytical electrode, a platinum wire helix auxiliary electrode, and a mercury/mercury(I) sulfate reference electrode [804, 805]. The oxidation was carried out at a potential of +0.410 V versus the mercury/mercury(I) sulfate reference electrode. This method was used to determine less than 10% hydrazine formed in anhydrous ammonia in a chemonuclear reactor. The amount of hydrazine in the analysis cell ranged from 55 to 440  $\mu\text{g}$ . Measured coulombs consumed for the oxidation were linear with concentration within this range.

Electrogenerated iodine or bromine performed equally well in the coulometric titration of hydrazine [806]. Electrogenerated iodine in methanol as a solvent and in the presence of potassium acetate as a buffer allows the coulometric determination of hydrazine [807]. Iodine in the plus one state of oxidation  $\text{I}^{+1}$  can be electrogenerated from iodobenzene or 4-iodonitrobenzene in 0.2-M  $\text{HClO}_4/\text{AcOH}$  solutions on a Pt electrode and used for coulometric titration of hydrazine and hydrazine compounds [808].

A rapid and automatic coulometric titration procedure for the determination of hydrazine and monosubstituted hydrazines in the 3- to 5-mg range with electrolytically generated bromine had a standard deviation of approximately  $\pm 1\%$  [809]. The use of anodically generated chlorine in place of bromine did not result in any improvements. An acetic acid/water/methanol/mercury(II)acetate/potassium bromide solvent was used for most of the compounds titrated. Other solvents tested were aqueous 0.3 M hydrochloric acid with 0.1 M potassium bromide and 80% acetic acid/20% water 1.0 M in hydrochloric acid with potassium bromide. The choice of solvent depends on the type of hydrazine to be titrated. Hydrazine, MMH, phenylhydrazine, and acetylhydrazine consumed close to four equivalents of bromine, and the reaction was rapid. UDMH consumed close to six (5.88) equivalents, and the results were repro-

ducible. A similar method in a microcell holding a tiny 0.5 mL sample volume has extended the sensitivity range to micromol quantities of hydrazine [810].

All three propellant hydrazines (hydrazine, MMH, UDMH) from sulfuric acid-impregnated air sampling tubes or wastewater samples can be analyzed and titrated coulometrically with electrically generated chlorine or bromine, but the method does not differentiate between the three hydrazines [811]. This method is faster than many competing methods since it does not require derivatization or internal standards for calibration. At the lower limit of sensitivity, nanomols of hydrazines can be detected, which translates to ppb concentrations in air samples. Coulometric titration does not differentiate between hydrazines and hydrazones, which are contaminants in samples. In samples that contain MMH and UDMH autoxidation and partial oxidation products, various amounts of formaldehyde hydrazones will be found that may also consume some of the oxidizer. Formaldehyde (a UDMH oxidation product) and its hydrazones are also oxidized by either free chlorine or bromine, but the stoichiometry is different from that with pure hydrazines. In samples with large amounts of methylhydrazines and their autoxidation products, the coulometric titration results can be corrected by determining formaldehyde (from the hydrolysis of the methylhydrazones) colorimetrically with chromotropic acid in concentrated sulfuric acid.

Electrogenerated bromine allows the side-by-side determination of ammonia and hydrazine in boiler feedwater with biamperometric or bipotentiometric endpoint indication [812]. The electrolysis cell is separated by a glass diaphragm. At first the hydrazine is titrated at pH 0.5 to 7 in 0.3 N  $\text{H}_2\text{SO}_4$ , then a borax buffer is added, and ammonia is titrated at pH 8.2 to 8.5.

Direct coulometric titration of hydrazine, MMH, or acetylhydrazine with electrically generated bromine in acetic acid gave good results [813]. 0.9 M  $\text{CH}_3\text{COONa}$  or  $\text{CH}_3\text{COOK}$  in glacial acetic acid provided a good anode electrolyte. Contamination by no more than 4% water could be tolerated, but none by acetanhydride. Similar conditions, also in acetic acid, were used to titrate hydrazine with electrically generated  $\text{Pb}(\text{CH}_3\text{COO})_4$  [814].

A coulometric flow titration with electrogenerated bromine was combined with chemiluminescent and amperometric flow detection to determine small concentrations of hydrazine and ammonium. Hydrazine could be titrated in a range between 2  $\mu\text{M}$  and 1.1 mM with chemiluminescence detection of the equivalence points [815]. The lowest concentration of hydrazine that could be titrated was 60 nM. Ammonia concentrations lower than 0.5 mM did not influence the titration results. Between pH 1 and 7 hydrazine can be selectively titrated in the presence of ammonium. The sum of hydrazine and ammonia/ammonium can be titrated at pH 8.3 with amperometric detection. Hydrazine and ammonia were titrated precisely in their mixtures and in concentration ranges between 20  $\mu\text{M}$  and 0.5 mM.

### 3.6.10.2 Polarographic Analysis Methods for Hydrazine

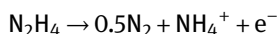
Polarography is a subclass of voltammetry where the working electrode is a dropping mercury electrode. Voltammetry is the study of current as a function of applied potential. The potential is varied arbitrarily either step by step or continuously, and the current value is measured as the dependent variable.

The polarographic behavior of hydrazine has been studied by many researchers, and there is general agreement that polarography is not a suitable method for the quantitative estimation of hydrazine itself in solution. Nevertheless, polarography can be applied after the hydrazine is converted to organic derivatives, such as benzalazine. This conversion is quantitative, and the azine can be analyzed by polarography just like many other reducible or oxidizable compounds. Another topic discussed in this section is polarography in hydrazine or hydrazine hydrate as a solvent.

It was shown that neither the half-wave potential nor the ratio of limiting current to hydrazine concentration was independent of the hydrazine concentration, which makes it impossible to obtain exact analytical results [816]. Dinitrogen was identified as the main product of anodic oxidation of hydrazine in alkaline solutions [817]. None of the methods was useful for the quantitative analysis of hydrazine.

An attempt was made to explain the mechanism of the electrooxidation of hydrazine that is responsible for the irregularities in polarography [818]. Dinitrogen is the main product of electrooxidation of hydrazine at a mercury-coated platinum electrode. Under some conditions, ammonia is also formed as a result of diimide dimerization.

The complex mechanism of the anodic oxidation of hydrazine has been extensively studied with respect to the use of hydrazine in fuel cells. Whereas sharp half-wave potentials cannot be achieved for hydrazine in aqueous solution, both hydrazine and hydrazine hydrate gave well-defined one-step anodic chronopotentiograms in dimethyl sulfoxide (DMSO) as a solvent [819]. The oxidation of hydrazine in aprotic solvents proceeds as a one-electron process:



When mercury electrodes are used in hydrazine polarographic studies, it must be kept in mind that hydrazinium ions, like many alkali metals and organic “onium” ions, can form an amalgam with mercury. The amalgam formation may change the electrode potentials.

Even though the results may not have been reproducible enough to be useful for quantitative analysis, the half-wave potentials of hydrazine on a rotating platinum disc electrode were measured in neutral and acidic solutions [820]. The hydrazine concentrations were  $8 \times 10^{-5}$  to  $1.3 \times 10^{-3}$  M. Two oxidation half-waves were observed: The first occurred at a potential of  $-0.2$  to  $+0.4$  V, depending on the supporting electrolyte ( $0.5$ – $8$  M  $\text{H}_2\text{SO}_4$ ,  $1$  M  $\text{HNO}_3$ ,  $\text{AcOH-AcO}^-$  buffer at pH 4.6). The second occurred at or above  $+0.7$  V, but only if the hydrazine concentration was in excess of  $6 \times 10^{-4}$  M. The magnitude of the current depended on the surface state of the platinum, which

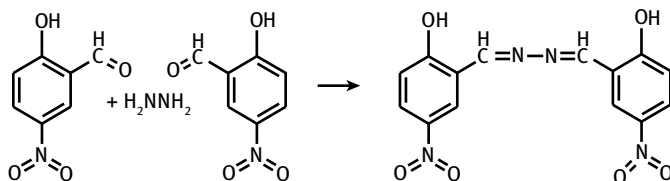
changed because of adsorption of  $N_2H_4$  or its oxidation products. All data indicated that the oxidation reaction is diffusion controlled.

Polarization curves of the electrooxidation of hydrazine on mercury, silver, and gold electrodes in alkaline solutions on a mercury drop electrode were obtained varying concentration, ionic strength, and pH of the solution and on rotating silver and gold disc electrodes varying concentration and pH of the solution, and speed of rotation of the electrode [821]. Polarization curves on the silver electrode seemed to be independent of pH. The half-wave potential of the oxidation of hydrazine on the mercury electrode was independent of the potential difference across the diffuse double layer. The process at the silver electrode was direct discharge of the hydrazine molecule. The rate-controlling process in the oxidation at the mercury and gold electrodes was either a two-electron electrode reaction with the participation of hydroxide ions or a chemical volume or surface reaction of the product of a one-electron reversible oxidation.

One method for the voltammetric determination of hydrazine and hydroxylamine involves conducting a sweep to measure the current plateau at pH 5.0 with a rotating Pt electrode before and after the addition of acetone [822]. This method was used to determine the two hydronitrogens in concentrations from 0.32 to 5.7 mg/L with standard deviations of 2 to 5%.

Hydrazines can be determined by voltammetry, based on their hydrogen catalytic wave in formaldehyde-platinum-sulfuric acid media [823]. Adsorption of the platinum-formazone complex on the hanging mercury drop electrode enhanced the sensitivity, allowing convenient measurement of micromolar and submillimolar concentrations of simple hydrazines. The selectivity was better than that of conventional (anodic) measurements of hydrazine(s) because oxidizable compounds did not interfere. The sensitivity was also greatly improved at concentrations down to  $10^{-6}$  M. The hydrazine response was evaluated with respect to pre-concentration time, concentration dependence, platinum and formaldehyde concentrations, reproducibility, and other variables. The relative standard deviation (at  $2 \times 10^{-5}$  M) was 1.6%.

Another polarographic method used 5-nitrosalicylaldehyde to derivatize hydrazine prior to polarographic determination [824]. The method is suitable for hydrazine concentrations in a range of 0.25–5 mg/L. The aldazine that is formed by the reaction



is insoluble in water. It is filtered and re-dissolved in 0.1 N NaOH. Polarography is then carried out in this solution and is free from interference. Neither MMH nor UDMH interferes.

A nanoporous gold electrode demonstrated a high sensitivity to hydrazine oxidation. Hydrazine was detected by hydrodynamic chronoamperometry at +0.2 V (vs. Ag/AgCl) [825]. The steady-state oxidative current exhibited a linear dependence on the hydrazine concentration in a concentration range of 5.00 nM–2.05 mM, and the detection limit was 4.37 nM. This detection limit is lower than the detection limits reported in the literature.

### 3.6.10.3 Anhydrous Hydrazine as Solvent for Polarographic Studies

In addition to polarographic studies where hydrazine becomes oxidized, there are also numerous studies where hydrazine or its aqueous solutions merely serve as a solvent. These measurements of current-potential curves discussed here relate closely to the study of the corrosion mechanism of metals in hydrazine and solutions of hydrazinium salts in hydrazine.

Polarographic curves of numerous metals as electrodes have been measured in anhydrous hydrazine solutions with hydrazine as solvent. The objective of these studies was to find materials that are compatible as storage tank containers or resist corrosion when used as fuel cell electrodes or electrodes in hydrazine electrolysis units. For the latter application, electrodes with low overpotential were also sought. A cadmium reference electrode prepared by the deposition of cadmium from cadmium sulfate in 2M H<sub>2</sub>SO<sub>4</sub> or hydrazine was used to study anhydrous hydrazine as a solvent [826]. This electrode had a potential of –0.246 V against the normal hydrogen electrode in hydrazine.

The reduction of Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup> ions in anhydrous hydrazine and in hydrazine-water mixtures was measured, but attempts to measure the potentials of alkaline and alkaline earth metal ions in anhydrous hydrazine were not successful because the potential was below –0.7 V [827]. The most sudden potential jump was observed in the reduction of Ni<sup>2+</sup>. The polarization currents resulted in a linear function when plotted against nickel concentration.

A potentiostatic setup with three electrodes was used to study the electrochemical behavior of nickel electrodes in anhydrous hydrazine [828]. A solution that was 1 molar in hydrazinium chloride was highly corrosive, and the solution turned pink. A similar reaction was observed with hydrazinium azide. In neutral medium or when potassium chloride instead of hydrazinium chloride was added, the nickel was not corroded by hydrazine. The authors have also recognized the contribution of carbazic acid to the corrosion of nickel in hydrazine. Carbazic acid is formed by the absorption of atmospheric carbon dioxide into the hydrazine if the solution is not protected from air during the experiment.

Currently, both chloride and carbon dioxide are analyzed in MIL-SPEC high-purity grade hydrazine to show compliance with this propellant specification. The main con-



cern is that these contaminants contribute to the corrosion of tanks and valves in flight systems. However, both carbon dioxide and chloride are poor indicators of hydrazine corrosivity. Both may exist in hydrazine as inactive species or active species. The actual active species in both cases is thought to be the hydrazinium ion, which may also be formed by the addition of water to anhydrous hydrazine. So far, there is no specific and reliable method for the analysis of  $\text{N}_2\text{H}_5^+$  in hydrazine. An attempt was made to analyze  $\text{N}_2\text{H}_5^+$  in hydrazine by polarographic techniques [829]. Such methods have the advantage that they can work with small (2-mL) samples and give an almost immediate readout that indicates the level of contamination in the hydrazine. A mercury drop electrode was used, and a range of 0.0 to  $-0.5\text{ V}$  was swept each time. Pure hydrazine was spiked with known levels of contaminant in an attempt to identify the various peaks observed. No assignments were made to the anions, such as carbazate, carbamate, carbonate, chloride, or sulfate. The polarogram wave ("peak") heights at  $-0.64$  and  $-0.74\text{ V}$  were proportional to the amount of dry  $\text{CO}_2$  gas added in the range below 30 ppm by weight in hydrazine. This appears to be a useful range for analysis. When copper(II) sulfate was added to anhydrous hydrazine that also contained some previously added HCl, a well-defined wave was observed for  $\text{Cu}^{2+}$  at  $-0.16\text{ V}$ . See also [248, 830].

#### 3.6.10.4 Potentiometric Analysis Methods

Potentiometric analysis methods passively measure the potential of a solution between two electrodes, causing no changes to the solution in the process, so that it is a non-destructive measurement. One electrode serves as the reference electrode and has a constant potential, while the other one is an indicator electrode whose potential changes with the composition of the sample. The difference in potential between the two electrodes gives a signal proportional to the concentration of the analyte in the solution. Potentiometry usually uses indicator electrodes made to be specifically sensitive to the ion of interest, such as fluoride in fluoride-selective electrodes, so that the potential depends solely on the activity of this ion of interest.

There are electrochemical sensors for hydrazine vapors in air that are an important part of leak detection and workplace air surveillance and monitoring. The instruments can continuously record the hydrazine concentration in air and trigger an alarm if a certain threshold concentration is exceeded. The electrodes in these instruments are embedded in a non-volatile, gelled electrolyte and separated from the air by a semi-permeable membrane. These instruments will be described in Section 3.6.15.12.

#### 3.6.10.5 Redox Potential Measurements in Aqueous Solutions

In the absence of other oxidants or reductants, the redox potential of a properly activated electrode in relation to a standard electrode may serve as an indicator of the amount of hydrazine present. The main application of hydrazine redox potential measuring electrodes is for metering hydrazine hydrate for the deoxygenation of boiler

feedwater. Similar instruments could be used to measure hydrazine in wastewater, but they would work only in the absence of other reducing contaminants.

Commercially available boiler feedwater analyzers with platinum/stainless-steel electrodes have been adapted to analyze hydrazine vapor concentrations in air [831].

#### 3.6.10.6 Ion-Selective Electrodes for Analysis of Hydrazine

Ion-selective electrodes have become increasingly popular during the past decade because they offer the possibility for fast analysis of ions in solutions. Although many ions interfere and the electrodes are not always as selective as one would wish, these electrodes have already been used in the analysis of hydrazine. The excess of chloramine-T remaining after complete reaction of hydrazine can be determined with a chloramine-T ion-selective electrode [832]. With this method 0.06 to 3 mg of hydrazine could be determined with a relative standard deviation of 2%.

Hydrazine in the absence of other reducing media can be determined indirectly after reaction with excess iodate using an iodide-selective electrode [799]. Hydrazinium(2+) dichloride can be determined at concentrations of 13 ng  $\text{N}_2\text{H}_6\text{Cl}_2/\text{mL}$  with this method.

A similar method established a detection limit of  $5 \times 10^{-5}$  mol/L by reacting hydrazine hydrate solutions with iodine in an alkaline medium, then determining the iodide at pH 2 to 5 [833]. Excess free iodine was extracted with chloroform prior to the iodide measurement. The calibration curve was linear from  $5 \times 10^{-5}$  to  $5 \times 10^{-3}$  mol/L.

Chloride in H-70 fuel mix can be analyzed with ion-selective electrodes after dissolving the NVR in 1-N  $\text{H}_2\text{SO}_4$  and neutralizing with 1-N NaOH [675]. Calibration standards must be prepared in solutions of identical ion strength.

The fluorine atom in 1-fluoro-2,4-dinitrobenzene is sufficiently activated that it reacts directly with hydrazine, releasing fluoride ions. The fluoride ion can subsequently be determined with an ion-selective electrode, and its concentration is directly proportional to the original amount of hydrazine in the sample [834]. Calibration was linear over a range from  $10^{-4}$  to  $10^{-2}$  M.

#### 3.6.10.7 Chronopotentiometric Analysis Methods for Hydrazine

A variant of potentiometry is chronopotentiometry, which consists in using a constant current and measurement of potential as a function of time. Study of the depolarization kinetics of an anodically polarized electrode was the basis for a quantitative method for analysis of hydrazine by chronopotentiometry [835]. When plotting the logarithm of the potential versus the logarithm of time, straight lines are obtained for constant hydrazine (= hydrazinium sulfate in 1-N  $\text{H}_2\text{SO}_4$ ) concentration. The location of these well-defined parallel lines is determined by the amount of hydrazine present. The slope of the lines is dependent on the electrolyte and is not affected by the concentration of added reductants. Platinum is a suitable electrode material for chronopotentiometric oxidation of hydrazine [836]. In a study of the effect of electrode pre-treatment on the anodic oxidation of hydrazine in sulfuric acid solutions,

reaction occurred with the smallest activation overpotential at a platinized electrode over a concentration range of 0.5 to 25 mM hydrazine. Several possible mechanisms for this variation, involving adsorption of hydrazine, bubble formation, occurrence of an intermediate chemical reaction, and catalytic decomposition of hydrazine at the electrode surface, were considered.

#### **3.6.10.8 Electrodes for Electrochemical Analysis of Hydrazine in Water Flow Injection Analysis with Electrochemical Detectors**

Hydrazine solutions can be analyzed continuously by a flow injection analysis method with an amperometric detector (Pt electrode, Ag tube) [837]. The hydrazine calibration curve covered the concentration range  $10^{-4}$  to  $10^{-3}$  mol/L with 20  $\mu$ L samples.

Continuous, online flow injection analysis of hydrazine or semi-carbazide is possible by first reacting with a freshly HCl acidified, previously neutral iodate/iodide solution, and then analyzing the eluent amperometrically at a platinum electrode [838]. In this method, iodine is produced online in a flow injection system by the injection of hydrochloric acid or sulfuric acid into neutral or slightly alkaline iodide/iodate eluent and is determined amperometrically at a platinum electrode. Compounds like hydrazine that can be oxidized or iodinated by iodine are determined by injecting them, in acid solution, into the iodide/iodate eluent and the excess of iodine after reaction with organic compound is determined by flow injection analysis amperometry at a platinum electrode.

A bromine stream can be used to titrate a hydrazine stream and any excess bromine determined as previously [839]. Ammonia and hydrazine in the range  $0.05 \times 10^{-3}$  to  $0.7 \times 10^{-3}$  M were determined with a relative error of <5% by reaction with  $1 \times 10^{-3}$  M hypobromite in phosphate buffer solution (pH 9.8) and determining the excess of hypobromite by flow injection voltammetry. Hydrazine is then calculated as the difference between the two voltammetric readings.

#### **Electrodes for Other Electroanalytical Applications**

In addition to flow injection analysis, flow-through amperometric detectors have found widespread use for the measurement of electroactive, reducible, or oxidizable species in the effluent of liquid chromatographs (Section 3.6.4), ion chromatographs (Section 3.6.5), or capillary electrophoresis chromatographs (Section 3.6.6). Hydrazine and most of its organic derivatives are oxidizable and readily detected by electrooxidation. Besides being specific to hydrazines, electrochemical detectors in this application offer excellent sensitivity, wide linear range, and low dead volume. A problem with many analytes is that they undergo electrooxidation only at electrode potentials substantially different from their redox potentials predicted from thermodynamic calculations. One method to minimize overpotential is the use of chemically modified electrodes with catalytic properties. A wide variety of electrode materials has been tested for this application. Initially those were mostly platinum

group metal electrodes, but later many other conductive and catalytically active materials were used as electrodes. Several of these electrode materials were already summarized in [840]. That information need not be repeated here. A few more recent additional examples are listed here for updates and improvements on those electrode materials and analysis methods. Many of these electrode materials are also of interest for electrodes in fuel cells.

Much effort has been devoted to facilitating the amperometric detection of hydrazines, including using pre-anodized glassy carbon electrodes and various chemically modified electrodes. Electrode materials for the electrocatalytic oxidation of hydrazine included single crystal surfaces of platinum [841, 842]; various polycrystalline metal electrodes (Ni, Co, Fe, Cu, Ag, Au, and Pt) [843];  $\text{Ni}_{0.87}\text{Zn}_{0.13}$ ,  $\text{Ni}_{0.95}\text{La}_{0.05}$ , and  $\text{Ni}_{0.85}\text{La}_{0.15}$  [844–846]; glassy carbon or vitreous carbon [847–871]; carbon fiber and carbon nanotube electrodes [872–888]; metal-phthalocyanine-coated electrodes [889–903]; or hexacyanometallate (Prussian Blue) coated electrodes [847, 849, 904, 905]. Electrodes with nanosize metal particles [906–910] or metal oxide electrodes [911, 912] have been examined. See also [853, 913–915].

### 3.6.11 Spectrophotometric Analysis Methods for Hydrazine

Of all analytical methods, spectrophotometric methods offer the most versatile applications, and they are easily adapted to different reagents [916]. Most of these methods operate in absorption, but a few also operate by analyzing light emitted by fluorescence from the sample undergoing analysis.

#### 3.6.11.1 UV-Visible Spectrophotometric Analysis Methods for Hydrazine

Direct UV spectrophotometric methods without the addition of color-forming reagents can be used for hydrazine itself (in the absence of any colored organic contaminants) or for the analysis of contaminants like aniline in standard-grade hydrazine. For direct UV spectrophotometric analysis of hydrazine hydrate in water (in the absence of other contaminants) some investigators have attempted to use the absorption at 280 nm without being aware that until the year 2000, H-70 propellant-grade hydrazine typically contained some aniline since it was usually made by diluting anhydrous standard propellant-grade hydrazine with water [917]. It must be assumed that the absorption at 280 nm shown was actually that of aniline and not of hydrazine (cf. spectra reported in Section 2.4.1).

Aniline in hydrazine can be determined by UV spectrophotometry. The aniline absorption peaks at 280 nm and appears as a shoulder of a broader hydrazine peak located at shorter wavelengths [918]. The exact location of the shoulder depends on the hydrazine dilution. One must extrapolate to an imaginary baseline or use Fourier transform peak analysis to obtain the contribution of aniline at that wavelength, which makes this a difficult analysis to perform. This analysis method was described in several editions of the military specification MIL-P-26536, summarized in Table 42.

Attempts have been made to extract the aniline from hydrazine with cyclohexane (by multiple extraction) and measure the aniline UV absorption in the hexane extract.

**Visible Light Spectrophotometric Analysis Methods for Hydrazine.** Many of the spectrophotometric methods operating in the visible range have the advantage that they are easy to perform, are specific to hydrazines, and do not require very costly equipment. Therefore, for the analysis of trace quantities of hydrazine in air or water, spectrophotometric methods are frequently used either for routine analysis or to calibrate electronic direct-reading instruments that are based on non-spectroscopic principles. They typically involve the reaction of a sample in water with a color-forming reagent that is more or less specific to hydrazine. These methods are not suitable for performing assays on pure hydrazines because of the large dilution required to bring the absorbance into the range of the instrument and the need to stay within the linear range of the calibration.

Because of the large number of color-forming reagents available, the material in the following section had to be arranged somehow in a systematic order. The methods and reagents are listed here in alphabetical order by reagent name. The prefix *p*- or *o*- is recognized as the letter of the alphabet by which the reagents are sorted in alphabetical order. Similar color-forming reagents are available for the analysis of MMH or UDMH (chapters “Methylhydrazine” and “Dimethylhydrazines”). This arbitrary alphabetical arrangement does not necessarily reflect the order of importance of the respective method. If ranked by importance and frequency of use, the PDAB methods should probably be listed first.

A review of the main approaches to determining hydrazine and its derivatives by spectrophotometric and fluorometric methods included 122 references to the literature [919]. Reagents for the spectrophotometric analysis of hydrazine(s) include benzofuroxazan reagents [920–922]; bindone [671, 923]; 1-chloro-2,4-dinitrobenzene [924]; chromium [925, 926]; glutaconaldehyde [663, 927–929]; colloidal gold, nanogold [930]; 2-hydroxy-1-naphthaldehyde [931–933]; molybdenum blue [934]; molybdatophosphoric acid, phosphomolybdic acid [935–938]; 5-nitro-2-furaldehyde [939]; PDAB [940–972]; picryl chloride [973]; potassium permanganate [974]; thiophene-3-carboxaldehyde (3-thienaldehyde) [975]; vanillin (4-hydroxy-3-methoxy-benzaldehyde) [972, 976, 977]; and veratraldehyde [978].

Indirect spectrophotometric methods proposed for the analysis of hydrazine, MMH, and several hydrazides would not be specific to hydrazine but would respond to all reducing agents. It also would not work if the hydrazine already contained some iron. This method is based on the reaction of a nitrogenous reducing substance with ferric iron at 358 K (85 °C) in acetate buffer solution containing 2,2'-bipyridyl and on the determination of the resulting ferrous-bipyridyl complex spectrophotometrically [979].

### 3.6.11.2 Infrared Absorption Spectrophotometric Methods

The IR absorption of water in hydrazine, MMH, or UDMH obeys Beer's law [980]. Using the 1.9- $\mu\text{m}$  absorption band of water, an IR-spectrophotometric analysis method has been worked out that is applicable to mixtures containing 0.1–15% water. Dimethylamine and nitrosodimethylamine do not interfere, but methanol and ethanol would interfere if they were present in concentrations greater than 1%. Quartz cells measuring 1 cm were used for these tests. The results can be expressed by  $P = a + bA$ , where  $P$  represents weight percent of water in the mixture,  $A$  is 100 times the absorbance, and  $a$  and  $b$  are constants as follows (all data for 1-cm pathlength):

$$\text{N}_2\text{H}_4 \quad a = -0.053 \quad b = 0.1057$$

If the sample temperature differed by less than 2 K from that used during calibration, only minor deviations (<1%) were encountered. Oxygen must be excluded from the solutions to prevent autoxidation and the formation of additional water.

In an extension of this method, IR spectrophotometry was used for the analysis of both water at 1.9  $\mu\text{m}$  and aniline at 6.66  $\mu\text{m}$  [981]. The absorbance of the aniline peak at 6.66  $\mu\text{m}$  depends on the amount of water present. Before quantitative aniline results can be obtained, absorbance must be corrected for water content. This can be done by measuring the valley at 6.5  $\mu\text{m}$ . The method is applicable not only to binary water/hydrazine or aniline/hydrazine mixtures, but also to ternary hydrazine/water/aniline mixtures with up to 2.5% aniline and up to 7% water. The absolute error is  $\pm 0.05\%$  for either of the two contaminants. Best results were obtained with a cell with calcium fluoride windows and a 0.1-mm pathlength.

Atmospheric contaminants can be detected remotely without sample physical contact by **Light Detection And Ranging (LIDAR)**. Differential absorption LIDAR (DIAL) is a powerful remote sensing technique for the rapid detection of many toxic agents present in the atmosphere due to industrial and vehicular exhausts, rocket propellants, chemical warfare agents, and so forth. In a DIAL system, the concentration of the agent is determined from the ratio of strengths of return signals at two close-by wavelengths, known as online and offline wavelengths, such that the agent has strong absorption at the former wavelength and relatively weak absorption at the latter wavelength. A typical LIDAR system has a transmitter, receiver, microcontroller, and data acquisition and data processing units. A 50-cm-diameter Cassegrain telescope can be used to collect the backscattered signal. The transmitting and receiving telescopes, which are coaxially aligned, are mounted on gimbals. The receiving telescope is connected to the detector box that contains spectral filters and detectors. There are two detectors, one each for the detection of signals in the 2- to 5- $\mu\text{m}$  and 9- to 11- $\mu\text{m}$  regions.

Remote sensing of hydrazine, MMH, or UDMH vapors using a dual mini Transversely Excited Atmospheric (TEA) carbon dioxide laser DIAL system can detect 100 ppb hydrazine over a distance of less than 3 km (2 mi) [982–985]. The measurements involved LIDAR returns from a topographic target located 2.7 km

from the laboratory, but it was found during these experiments that atmospheric fluctuations were the major factor limiting the sensitivity of these measurements.

The  $^{12}\text{C}^{16}\text{O}_2$  laser can produce over 100 different discrete wavelengths between 9.1 and 11  $\mu\text{m}$  where there is very little interference from atmospheric water or carbon dioxide. Hydrazine, MMH, and UDMH have characteristic absorption bands in this regime, so their vapors in air can be detected by laser absorption or even by remote sensing techniques using LIDAR [986–989], also in combination with photoacoustic measurements [990]. The high-resolution laser radiation absorption cross sections of hydrazine, MMH, UDMH, and their oxidation products were determined first in order to assess the value of the laser techniques. In addition to IR absorption or LIDAR fluorescence, photoacoustic detection of hydrazines has been studied by pumping modulated laser energy into selected wavelengths of hydrazine vapors in a cell with a microphone and searching for sound waves with the same frequency [991]. Absorption of energy causes a temporary pressure pulse (=sound), which can be picked up by the microphone. With a laser output at 1 W/line, the photoacoustically detectable levels were 0.2, 0.3, and 0.3 ppb for hydrazine, MMH, and UDMH, respectively. In comparison, for simple long-path-length (100-m cell) absorption, the sensitivities would be “only” 70, 140, and 130 ppb, respectively. For LIDAR, remote sensing detection limits for the three hydrazines vary between 20 and 90 ppb. With polluted urban air as background, detection limits would be significantly worse. Most laser methods would suffer one to two orders of magnitude in sensitivity if hydrazines had to be detected against a background of urban atmospheric pollutants. Another IR method (so far used mostly for the detection of chemical warfare agents) relies on the blackbody radiation of buildings, rocks, or soil in the background of a radiometer-scanned area to provide a source of radiation. A hydrazine vapor cloud drifting between the background horizon and the observation site can be detected by its IR absorption [992].

Calculations for a 200-m-thick cloud of vapor showed that the minimum detectable concentrations at a distance of 5 km with a laser pulse of 200 mJ are 0.886, 1.166, and 1.737 ppm as the values of  $N_{\text{min}}$  for hydrazine, UDMH, and MMH, respectively. There are also upper limits where the incoming laser light is absorbed completely such that no energy is reflected [993].

Besides analyzing undecomposed hydrazine in various matrices, sometimes the chemist needs to analyze hydrazine decomposition products consisting of ammonia, nitrogen, and hydrogen, depending on the degree of ammonia dissociation in a catalytic reactor. Ammonia is the only IR absorber in this mixture. The ammonia dissociation is often a design variable in the design of rocket engines (see *Encyclopedia of Monopropellants*, chapter “Hydrazine Monopropellants”). Ideally, one would want an analysis method that gives an instant readout, instead of taking a grab sample and waiting several days for the results to come back from the lab. A non-dispersive infrared (NDIR) analyzer was used to monitor the ammonia and water content of hydrazine decomposition products in the gaseous state [994]. The analyzer was calibrated with two gas mixtures of known composition.

### 3.6.11.3 Spectrofluorescence Analysis Methods for Hydrazine

The fluorescence of solid or liquid samples excited with light of shorter wavelength can be very specific for certain hydrazine derivatives and is suitable for the detection of trace quantities, such as hydrazine derivatives on a thin-layer chromatography plate. The reagents that can form fluorescing compounds with hydrazine are 5-chlorosalicylaldehyde [995]; fluorescamine {4-phenylspiro-[furan-2(3H),1'-phthalan]-3,3'-dione} [729]; 3-(6-hydroxynaphthalenyl)-1-(4-nitrophenyl) prop-2-en-1-one [996]; 2,3-naphthalenedicarboxaldehyde [997–1001]; 1,2-naphthoquinone-4-sulfonic acid [1002]; and PDAB [1003].

### 3.6.11.4 Fluorescence Detection and Imaging of Hydrazine

Fluorescence detection of hydrazine and imaging of hydrazine distribution, even in living cells under the microscope, constitute a new analytical technique for hydrazine that is useful for tracing the path of hydrazines and the metabolic fate of hydrazine-derived pharmaceuticals in living organisms. The fluorescent dyes typically change their emission spectra after they are exposed to traces of hydrazine. Different techniques have been used, one called “turn on” fluorescence. Another technique is comparing emissions at two frequencies using a ratiometric method. Ratiometric fluorescence detection measures the ratio of fluorescence intensities at two different wavelengths. Very little comparable work has been done on any of the methylhydrazines. Many hydrazine-based pharmaceutical drugs metabolize and release hydrazine in the body. There is some justification for developing more sensitive analysis techniques to study the pharmacodynamics and toxicokinetics of hydrazine-based drugs and their metabolic products. But the worldwide use of hydrazine-based pharmaceutical drugs is declining over concern about hydrazine toxicity.

Fluorescence methods include rhodamine B [1004, 1005]; trifluoroacetyl acetate naphthalimide [1006]; cyanine dye derivative [1007, 1008]; dichlorofluorescein and resorufin acetate [1009]; 2-(4-((4-(benzo[d]thiazol-2-yl)phenyl)ethynyl)benzylidene)-malononitrile [1010]; carbazole based malononitrile [1011]; trifluoroacetyl acetate and coumarin [1012]; dibenzothiazole [1013]; 4-amino-1,8-naphthalimide [1014]; [4-phthalimide-N-(4'-methylcoumarin) naphthalimide] [1015]; resorufin [1016]; merocyanine 1,2,2,4-tetramethyldihydroquinoline [1017]; 4-bromobutyrate/fluorescein [1018, 1019]; azobenzene derivative-naphthalenediimide [1020]; coumarin-based fluorescent probe [1021]; 2-[4-(3,5-diphenyl-4,5-dihydro-pyrazol-1-yl)-benzylidene]-malononitrile [1022]; quinoline [1023]; condensation product of *N,N*-dimethylamino cinnamaldehyde with [1024]; combination of coumarin and benzopyrylium [1025]; coumarin and hemicyanine [1026, 1027]; tricyanofuran [1028]; naphthalimide and 4-hydroxynaphthalimide [1029]; 1,8-naphthalimide [1030, 1031]; pyrene- and anthracene-based compounds [1032]; 2-(9-ethyl-9*H*-carbazol-3-yl) isoindoline-1,3-dione [1033]; and chalcone cyclization [1034]. See also [1035–1040]. These methods have been used to detect and localize hydrazine in living mice and fish.



### 3.6.11.5 Chemiluminescence Analytical Methods

The chemiluminescent reaction of hydrazine oxidized by *N*-bromosuccinimide in the presence of dichlorofluorescein as a sensitizer has been used for the flow injection analysis of hydrazine solutions in a concentration range from  $1 \times 10^{-6}$  to  $5 \times 10^{-5}$  M [1041]. The detection limit was  $5 \times 10^{-7}$  M. A similar method used oxidation by hypochlorite and could detect  $10^{-5}$  M hydrazine [1042]. Some metal ions inhibited luminescence while others activated it. Another flow injection determination of hydrazine using a fluorimetric endpoint detection method involving the oxidation of hydrazine by thallium(III) had a detection limit of 20 ng/mL [1043].

Luminous oxidation with acidic permanganate was found to be usable for chemiluminescence determination of hydrazine and its derivatives [1044]. The sensitivity was high enough to determine hydrazine in workroom air. The linear range was  $3.0 \times 10^{-5}$  to  $1.0 \times 10^{-7}$  g/mL.

A chemiluminescence flow system for the determination of hydrazine was based on the enhancement effect of hydrazine on the chemiluminescence reaction between luminol and  $\text{BrO}^-$  in alkaline media [1045]. The oxidant  $\text{BrO}^-$  was online electrogenerated by constant current electrolysis, resulting in the elimination of the inconvenience of its instability. Hydrazine can be determined in the range of 0.01–10  $\mu\text{g/mL}$  with a detection limit of 0.003  $\mu\text{g/mL}$ . A complete analysis could be done in 1 min with a relative standard deviation of 3.7%. The method is suitable for the automatic and continuous online monitoring of low levels of hydrazine, for instance, in drinking and river waters.

The oxidation of hydrazine by potassium hexacyanoferrate(III) in alkaline luminol solution leads to chemiluminescence. This can be used to determine individual hydrazines using flow injection systems [1046]. The system has been successfully applied to the determination of hydrazine in air.

The oxidation of hydrazine by either sodium dichloroisocyanurate or trichloroisocyanuric acid in alkaline medium caused chemiluminescence and the emission intensity was greatly enhanced if dichlorofluorescein was added as a sensitizer [1047]. The parameters for the determination of hydrazine were optimized and the optimized method yielded  $3\sigma$  detection limits of  $2 \times 10^{-7}$  to  $3 \times 10^{-7}$  M for hydrazine.

### 3.6.12 Mass and Ion Mobility Spectrometric Analysis of Hydrazine

Mass spectrometric analysis of hydrazines is used extensively for trace detection, for the identification of the effluent of chromatographic separations, for the study of kinetic mechanisms, or for the determination of molecular bond dissociation data. The detection of hydrazine in air by mass spectrometry based on the parent ion alone is difficult since both hydrazine and oxygen have a molecular mass of 32 atomic mass units (amu). To make the problem worse, methanol has the same amu. The compounds must be identified by their ionized fragments in addition to the parent ions. Because hydrazine and ammonia have identical breakdown products in the mass spectrometer

ion source, it is impossible to differentiate between ammonia-derived and hydrazine-derived amino radicals  $\text{NH}_2$ . This section summarizes some of the experimental techniques used in obtaining mass spectra for hydrazines. The ionization and appearance potentials of hydrazine molecule fragments are listed in Table 46 below. The ionization and appearance potentials of several alkylhydrazine molecule fragments are summarized in Table 37 in the chapter “Methylhydrazine.” These tables will be an aid to future investigators in the identification of  $m/e$  peaks.

**Table 46:** Summary of appearance potentials of hydrazine.

| Species                                      | Parent compound        | Appearance potential, eV | References |
|----------------------------------------------|------------------------|--------------------------|------------|
| $\text{N}_2\text{H}_4^+$                     | $\text{N}_2\text{H}_4$ | 10.07                    |            |
| $\text{N}_2\text{H}_4^+(2\text{B})$          | $\text{N}_2\text{H}_4$ | 10.64                    | [497]      |
| $\text{N}_2\text{H}_4^+(2\text{A})$          | $\text{N}_2\text{H}_4$ | 15.61                    |            |
| $\text{N}_2\text{H}_4^+(2\text{B}2\text{A})$ | $\text{N}_2\text{H}_4$ | 16.66                    |            |
| $\text{N}_2\text{H}_4^{+*}$                  | $\text{N}_2\text{H}_4$ | 24.5                     | [496]      |
| $\text{N}_2\text{H}_4^{+**}$                 | $\text{N}_2\text{H}_4$ | 30.0                     |            |

Some of the appearance potentials were determined by photoelectron methods and not by electron impact ionization in a mass spectrometer. A very useful summary was published on the mass spectrometry of inorganic radicals, including those formed by hydrazine decomposition [349].

In many instances in a mass spectrometer, not only is the hydrazine molecule dissociated, but the ion is also left in a state of excitation from which a photon may be emitted. The state of excitation is indicated either by letters in parentheses or by an asterisk following the formula of the ion. The calculated ionization potential of  $\text{N}_2\text{H}_4$  is 7.54 eV, in agreement with experimental data [425].

Most mass spectrometric investigations of hydrazine used electron bombardment for sample ionization. A gentler ionization method that causes less random fragmentation can be achieved by field ionization [1048, 1049] or photoionization [356, 495]. A comparison of the fragmentation patterns is given in [22], Table 5.20, Section 5.4.1.2. The hydrazinium dication is well known in liquid acidic solutions, but less well characterized in the gas phase, where it has shown surprising stability [1050].

It is very difficult to obtain an accurate quantitative analysis of argon-diluted hydrazine/ammonia mixtures by mass spectrometry because varying amounts of hydrazine hang up in the inlet system of conventional mass spectrometers [1051]. Hydrazine and ammonia can be separated from the permanent gases by first condensing them in a cold trap at 119 K. Subsequently, after analyzing the gases passing through the cold trap, the cold trap is thawed, and hydrazine and ammonia are quantitatively decomposed into the elements in a glow discharge. The hydrogen : nitrogen ratio of the decomposition products then gives the hydrazine : ammonia ratio in the condensate.

Mass spectrometry is well suited for the analysis of volatile contaminants in liquid hydrazine. Various contaminants have been observed in this manner but could not always be identified. In hydrazine that had been dried and distilled over calcium hydride, a contaminant at  $m/e = 60$  has been observed that could not be removed by passing the vapor through molecular sieves at 340 K [353, 1052].

### 3.6.13 Electron Spin Resonance Analysis of Hydrazyl Free Radicals

ESR analysis is widely used to identify free radicals, the short-lived ones involved in the decomposition of hydrazine and the stable ones obtained by dissociation of tetraphenyl hydrazine and other aromatic hydrazines. Hydrazyl free radicals were identified by ESR in the decomposition of a hydrazino nitroso ferrate complex in aqueous solution [1053] and during autoxidation of hydrazine in solution [1054].

### 3.6.14 Trace Analysis of Hydrazine

#### 3.6.14.1 Trace Analysis of Hydrazine in Water

The sensitivity of analytical methods for the analysis of hydrazine in environmental water samples can be improved by adsorbing the hydrazine-PDAB aldazine onto solid sorbents and then extracting it with hydrochloric acid [1055]. The limit of detection for the method was 0.2 mg/L. The method was used to determine hydrazine in freshwater, seawater, and wastewater.

Hydrazine concentrations in solutions used in the PUREX nuclear fuel reprocessing process can be measured remotely by fiber optic cables where the exposed section of the bare fiber is coated with a gel containing PDAB [1056, 1057]. A similar fiber optic sensor used fibers coated with 4-nitrobenzaldehyde in a gel of polyethylene oxide [1058].

#### 3.6.14.2 Analysis of Trace Contaminants in Hydrazine

Many applications of hydrazine require a very pure product and will not tolerate contaminants in the hydrazine used. Examples of such applications are the use of hydrazine as reductant in the production of laser crystals or the use of hydrazine as a monopropellant in rocket engines on long-term missions. Hydrazine that has been purified to meet strict purity requirements will have to be analyzed for trace contaminants before and after the purification process. Contaminants can be organic or inorganic in nature. The most bothersome contamination caused by the absorption of atmospheric carbon dioxide and leading to hydrazinium carbazate probably should be classified as an inorganic contaminant, although other carbonic acids are considered organic compounds. The military propellant specifications contain detailed methods for the analysis of trace contaminants in hydrazines and hydrazine blends. This section contains a few additional methods not yet covered in the MIL-SPEC.

**Chloride.** Excess hydrazine must be removed by reaction with 3% hydrogen peroxide before chloride can be determined with the diphenylcarbazone/mercury(II) nitrate or the mercury(II) thiocyanate spectrophotometric method [485].

Chloride is often determined in concentrated NVR instead of liquid hydrazine because this eliminates the interference by hydrazine and affords orders-of-magnitude improvements of detection limit. Because of the volatility of hydrazinium chloride under conditions of NVR determination, some chloride-free AR-grade sodium hydroxide must be dissolved in hydrazine prior to distillation. Samples of monopropellant-grade hydrazine were spiked with various levels of standard aqueous hydrogen chloride to measure percent recovery by this method [1059]. Two NVR analysis methods were compared using three different chloride determination techniques. The major source of variation in chloride recovery from hydrazine appeared to be due to the mechanical loss of material during the open beaker evaporation step of one NVR method.

**Fluoride.** An electrochemical method was used to analyze trace fluoride in hydrazine [1060]. Other than this, there is no standard test method for the analysis of fluoride in hydrazine. Several colorimetric methods for fluoride in water do not work in the presence of hydrazine interference [1061].

**Total Carbon.** Instead of specifying individual limits for carbon dioxide and organic contaminants in hydrazine, some agencies have begun specifying limits on total carbon in hydrazine. Early vintage (1955) hydrazine was allowed to have up to 1.5% aniline and hydrocarbon (typically *n*-heptane remaining from the distillation process). Total carbon was analyzed initially by combusting the sample in air over a roll of oxidized copper wire gauze in a 25 × 910 mm Vycor tube [673]. The carbon dioxide was absorbed in a U tube filled with Ascarite and Anhydrone and weighed in the same manner as in an ordinary CH elementary analysis. Because relatively large samples (up to 1.4 g) were used, the weighing errors could be kept small, and good accuracy was achieved. A more recent version of a combustion technique for determining total carbon content in hydrazine also uses large samples (1 cm<sup>3</sup>) of hydrazine and combusts them in a stream of oxygen over a copper oxide catalyst at 1123 K [1062]. The carbon dioxide in oxygen (and water) is collected in a 16-L tank at 340 kPa and analyzed by an IR method. The precision of this method is ±20% in the 20- to 40-ppm total carbon range.

Total carbon analyzers and total organic carbon (TOC) analyzers that were developed mostly for water analysis can be used for dilute, nonflammable hydrazine solutions. EPA methods analyze one sample directly, the other sample after dispelling all mineral carbonates by acidification with a non-volatile acid. TOC is calculated as the difference between the two numbers. Organic contaminants that were leached from container materials (bladders, diaphragms) used for storage or expulsion of hydrazine can be determined by this method. Organic contaminants carried over from hydrazine hydrate that was made by the ketazine or hydrogen peroxide method and then dehydrated to make anhydrous hydrazine can be analyzed by this method.

**Carbon Dioxide.** Carbon dioxide absorption is a problem not only with hydrazine but also alkylhydrazines and resulting in corrosion problems. Methods recommended for the analysis of CO<sub>2</sub> in alkylhydrazines can probably be used for hydrazine itself as well [1063, 1064].

**Trace Metals.** Trace levels of titanium that has been leached from the wall of titanium tanks during long-term storage of hydrazine can be determined by atomic absorption spectrophotometry (AAS) following flash evaporation of the hydrazine and re-dissolving the residue in 0.2% nitric acid [1065]. The AAS spectrophotometer used a graphite furnace lined with a coating of pyrolytic graphite, in which a 10-μL sample was dried at 423 K, charred at 2070 K, and atomized at 3070 K. The titanium spectral line used for absorption was the one at 365.4 nm. The method is sensitive down to 2 ng/μL = 2 mg/L = 2 ppm. The average error in this range was 15%. The same method should be applicable to a wide range of other trace metals in hydrazine. Unfortunately, the flash evaporation is associated with a (relatively constant) loss of material that must be determined in a separate experiment prior and in addition to calibration samples. In the example given, 12 ng Ti was lost, and this number had to be arbitrarily added to the results on each sample. Elevated metal losses during the charring step may occur in the presence of fluoride since most fluorides are volatile.

High levels of cadmium were discovered in some samples of high-purity hydrazine. Cadmium may have leached from some of the equipment in which hydrazine is dehydrated and distilled at the manufacturer. The highest level of cadmium detected in hydrazine was 0.38 ppm, and it caused clogging in cavitating venturi [269].

Excessively high alkali metal concentrations in either the oxidizer or the fuel could lead to high ionization in the exhaust and radio-frequency interference in plumes of bipropellant missiles, launch vehicles, and spacecraft. A highly ionized plume will shield radio waves. Potassium and sodium in typical Aerozine-50 was analyzed by AAS and found to be on the order of 0.07–0.18 ppm Na and 0.82–1.13 ppm K [1066]. There is no MIL-SPEC specification limit for alkali metals in bipropellant fuels. Similar tests were conducted on sodium and potassium in UDMH or NTO [1067].

**Silicon.** Organic silicon compounds leached from elastomers (diaphragms, bladders) immersed in hydrazine in positive expulsion tanks can be analyzed by IR in a spherical chamber with multiple reflections [1068].

### 3.6.14.3 Trace Analysis of Hydrazine in Air

Because the olfactory threshold for hydrazine vapor is above the concentration at which permanent damage can be caused by continued hydrazine vapor inhalation, it is very important to monitor workplaces with sensitive analytical devices. One cannot rely on the human sense of smell alone to receive a warning when dangerous hydrazine concentrations are exceeded. This applies to hydrazine itself as well as many volatile hydrazine derivatives. The methylhydrazines have a more pronounced (“fishy”) odor and are more readily detected than hydrazine itself.

The olfactory threshold for hydrazines is discussed in Section 9.12. What is now needed are analytical methods that are more sensitive than our noses and provide a more quantitative answer. The sensitivity requirements for hydrazine detection instrumentation are inevitably tied in with the TLVs and emergency exposure limits (EELs) established by various government agencies for the protection of workers inside and the general public outside of factories and rocket test sites. The two sets of numbers seem to “leapfrog” each other where the government regulators are reasonable enough not to establish limits so low that they cannot be verified but nevertheless often set them so low that each lowering constitutes a new challenge to the instrument industry. The limits for hydrazines have been lowered twice by several orders of magnitude in the two decades preceding the 1990s. Therefore, the instrument industry was constantly struggling to come up with instruments that could reliably detect the new TLVs or even fractions of the new TLVs to provide some level of confidence or to be prepared for the next imminent lowering of the TLV (justified or not). To the uninvolved bystander it sometimes looked as if the availability of more sensitive detection methods (more sensitive than the current TLV) spawned a new round of calls from the occupational hygiene community for additional lowering of the TLVs and EELs. The cost:benefit ratio of those actions was never shown, and nobody knows how many lives have been saved or extended.

The words *sensor* and *detector* can be used interchangeably and refer to the part of the system that is exposed to vapors. A *monitor* consists of a sensor or detector connected to some electric circuitry that can be adjusted to a certain threshold above which an alarm will sound to alert the workers. A single central monitor can interrogate many remote sensing stations in sequence by a rotary switch. A recording monitor keeps a continuous and permanent record of the concentration profile as a function of time.

Detectors and monitors for hydrazine and hydrazine derivatives must be both sensitive and specific. Unfortunately, many detection methods that are sensitive to hydrazine(s) will also respond to the presence of other vapors in air. Many sensors respond to ammonia. Ammonia is a typical hydrazine decomposition product but is also produced by many other biological processes (e.g., in a horse stable or outhouse). Many hydrazine sensors suffer interference (false readings, low readings) from the presence of other contaminants in air. Some are affected by the level of humidity. Many launch sites are in coastal areas where the humidity is always high.

In addition to detectors and monitors that sound an alarm if a preset threshold concentration is exceeded, it has become increasingly important to develop instruments that give a continuous recording of hydrazine concentration on chart paper or magnetic tape. Such stationary instruments are recommended for production and test installations using hydrazines to show compliance with OSHA regulations at places of employment and to protect the employer from later liability suits.

The main application of these instruments is to monitor work areas where personnel are potentially exposed to and may inhale hydrazine vapors. Additional applica-

tions for these instruments are leak detection in propellant storage areas, in spacecraft or submarines, and in test installations. Other needs are the monitoring of propellant clouds released from controlled spill tests in uninhabited areas to study plume dispersion and atmospheric decay of propellant vapor clouds [1069].

Progress in the area of toxic missile propellant vapor detection has been significant in recent decades, necessitated by the concern about a wide range of adverse effects caused by hydrazines. In the US, most of the work performed on propellant vapor detectors was aimed at the detection of the more volatile MMH, which was used in the Space Shuttle Orbital Maneuvering System (OMS) and in the Minuteman and Peacekeeper intercontinental ballistic missiles (ICBM) third stages stored in missile silos. Relatively little work has been conducted specifically on the less volatile hydrazine. The use of UDMH or Ae-50 in the US has been phased out. Surveys of missile propellant vapor detectors have been published in the literature from time to time and are summarized in Table 47. Some candidate analytical methods included in these surveys never advanced past the experimental stage and did not result in commercially viable products. Surveys of commercially available instruments are quickly outdated because some manufacturers went out of business and others changed names or were bought out by or merged with competitors.

A review was conducted of commercially available sensors that are able to detect hydrazine or MMH concentrations from as low as 10 ppb up to several parts per million and that are most commonly used as either leak detectors or personnel monitors [1083].

A wide range of chemical interactions between hydrazine and organic reagents have been reviewed for their adaptability to microsensors for hydrazine vapors [1084]. The microsensors generally consist of a physical probe and a coating that has specific affinity toward hydrazines. Some of the microsensors now tested with hydrazine(s) were derivatives of existing sensors originally intended for the detection of toxic chemical warfare agents. The sensing principles considered were (1) surface acoustic waves on piezoelectric crystals, (2) optical wave guides, and (3) chemiresistors. The optical waveguide methods involve color-changing reactions. The reactions suitable for specific sensing of hydrazines include those of (1) aldehyde and ketone carbonyl compounds, (2) nucleophilic aromatic displacements, (3) organic compound and metal ion redox reductions, and (4) organic dyes. It has been proposed to study second-derivative spectrometry and ion cluster spectrometry as a means for continuous measurement of hydrazines in concentrations down to 0.05 ppm.

Wet flow injection/amperometric analysis methods where hydrazine vapor in air first had to be absorbed into aqueous solutions were compared to both surface acoustic wave (SAW) devices and quartz crystal microbalances (QCMs) with the objective of being able to detect hydrazine vapor at concentrations below 1 ppm [1085].

**Table 47:** Historical summary of publications on hydrazine(s) vapor detector technology.

| Author(s)                      | Topic                                                                                                                | Year | References |
|--------------------------------|----------------------------------------------------------------------------------------------------------------------|------|------------|
| Annand, Chang, and Hurd        | Evaluation of physicochemical methods, very early study, no instruments yet                                          | 1961 | [1070]     |
| Ricca                          | NASA efforts for leak detection (not personnel monitoring)                                                           | 1966 | [1071]     |
| London, Sappington, and Widman | Evaluation of field instrumentation for Minuteman missile silos                                                      | 1969 | [1072]     |
| Luskus                         | USAF SAM Brooks AFB survey paper on measuring hydrazine vapor in air                                                 | 1978 | [1073]     |
| Luskus                         | USAF SAM Brooks AFB activities on measuring hydrazine vapor in air                                                   | 1981 | [1074]     |
| Loper                          | Technical interchange meeting sponsored by Aerospace Corp.                                                           | 1981 | [1075]     |
| Hannum and Loper               | CPIA survey on hypergolic vapor detector technology                                                                  | 1981 | [1076]     |
| Hannum                         | NASA-Air Force Workshop on Hypergolic Vapor Detectors                                                                | 1981 | [1077]     |
| Rose and Holtzclaw             | NRL evaluation of three types of commercially available instruments                                                  | 1983 | [1078]     |
| Young and Travis               | NASA KSC experience with three types of instruments                                                                  | 1987 | [1079]     |
| Young, Helms, and Travis       | NASA KSC evaluation of 6 least promising techniques and 2 most promising techniques (paper tape and ion mobility MS) | 1990 | [1080]     |
| Anonymous                      | Hypergolic vapor detection technology, a bibliography with 96 references                                             | 1991 | [1081]     |
| Hammond et al.                 | Hypergolic propellant vapor detection systems                                                                        | 1991 | [1082]     |
| Meneghelli                     | Review of hydrazine sensors                                                                                          | 1999 | [1083]     |

### 3.6.15 Hydrazine in Air Sampling Methods

The following sections are subdivided by active and passive sampling methods. By *active* we understand that the system needs a pump to force air through the apparatus. *Passive* samplers or badges depend on the diffusion of ambient air and air movements (often the draft of the working person moving through the working environment). Passive methods have the advantage that they do not require a portable power source, but they are probably not as accurate as active samplers. Other systems to subdivide a chapter on trace analyzers would be by *direct reading* and *non-direct-reading* instruments.



There are passive and active analyzers in both groups. A passive analyzer can be direct reading if the color change of a reagent button alarms the person wearing and looking at it. Non-direct reading instruments are usually samplers that have to be taken to a laboratory at the end of the work period, where the samplers are extracted, and the extract is analyzed to obtain a number. Another approach to subdividing this section would be by portable and stationary instruments. All personal samplers/detectors/badges must be portable by definition. The instruments must be small enough that they do not prevent propellant technicians from doing their job.

The least expensive, most accurate, but more manpower-intensive method of sampling air in contaminated areas is by bubbling a known amount of air through dilute sulfuric acid (0.1M) in impingers (bubble flasks), followed by analysis of the dissolved hydrazinium sulfate in aqueous solution. Many different analysis methods are available for that step of the process.

The efficiency of impingers may depend on the design of the apparatus (glass orifice, fritted glass plate diffuser). Concerns have been raised over the repeatability of air analysis with impingers depending on the geometric variations (orifice size, liquid depth, air flow rate) of the equipment. In an effort to correlate variances in the geometric parameters of “identical” (same part number) impingers to the repeatability of chemical analyses,  $N_2H_4$ , MMH, and UDMH were used as test vapors. Nominal concentrations of 80 ppb  $N_2H_4$ , MMH, and UDMH were generated. Ultimately, it was found that orifice size did not have a significant effect on the repeatability of the analysis [1086]. By hooking up two impingers in series, it was shown that any difference in the measured vapor concentrations observed between various impingers was not due to vapor breakthrough from the first impinger.

Instead of air sampling with liquid absorbents, usually with dilute acids in impingers (“bubblers”), it is more practical to use solid absorbents, which can consist of inert granular ceramic carriers impregnated with an acid, held in sampling tubes through which air is drawn at a controlled rate and for a known length of time. Some of these solid sorbent tubes and the subsequent spectrophotometric analysis capture hydrazine as well as MMH and UDMH [1087]. With this particular method, the relative error of measurement was less than 17%, and the recovery rate was better than 80%. Hydrazine in air was collected in a tube filled with 2,4-pentanedione and the 3,5-dimethylpyrazole thus formed was extracted with methanol and analyzed by means of GC-MS [1088].

### 3.6.15.1 Surveys and Laboratory Evaluation of Commercially Available Analyzers

In trying to decide which instrument to buy for a specific monitoring application, it is difficult to maintain an up-to-date “Buyer’s Guide” for hydrazine monitoring instruments. Unfortunately (fortunately if improvements are incorporated into new instruments), the market is constantly changing, which means this section will be one of the first sections of this book to become obsolete. One may still have to conduct one’s own market survey or even a side-by-side laboratory or field evaluation of several in-

struments to find the one that suits specific needs. An introduction to hydrazine vapor monitoring instruments was given in [1089] with more than 100 references to the literature but that is now only of historical interest. Section headings in that summary were

- Calibration Methods and Vapor Generation Chambers
- Materials Selection to Avoid Sampling Losses due to Wrong Materials for Air Sampling Tubing
- Colorimetric Detectors and Monitors
- Passive Personal Dosimeter Badges (Direct Reading)
- Actively Pumped Gas Detector Tubes and Paper Tape (Direct Reading)
- Gas Detector Tubes
- Impregnated Paper Analyzers
- Personal Passive Samplers (Not Direct Reading)
- Personal Active Samplers and Solid Sorbents (Not Direct Reading)
- Impinger Methods – Wet Chemistry (Not Direct Reading)
- Active Recording Detectors (Direct Reading, Portable, but not Lapel-Mounted)
- Fiberoptic-Colorimetric and Waveguide Methods
- Noncolorimetric Detectors and Monitors
- Ionization and Photoionization Chambers for Detection of Hydrazines
- Mass Spectrometric and Ion Mobility Detection Methods
- Electric Conductometric and Differential Temperature Detectors
- Optical Direct IR Absorption Methods for Detection of Vapors
- Open-Path IR Absorption Methods, also with Lasers as the Light Source
- Laser Photoacoustic Spectroscopy
- Laser Raman/Surface-Enhanced Raman Spectroscopy (SERS)
- Optical-Emission Chemiluminescence Detectors and Monitors
- Electrochemical Potentiometric Detectors and Monitors
- Thin-Film Redox Electrodes as Hydrazine Vapor Detectors
- Coated Carbon and Graphite Electrodes in Hydrazine Vapor Detectors

That summary needs to be updated from time to time. In the following pages, only a few of the sections listed above are expanded and updated, mostly with publications published after the year 2000. No assurance is given that this review is complete, and it would require a substantial effort to keep it up to date. In this volume, *Encyclopedia of Liquid Fuels*, the chapters “Methylhydrazine” and “Dimethylhydrazines” contain a similar summary of instruments for the detection of MMH or UDMH vapors in air. Some of those instruments will also respond to hydrazine itself.

As part of an effort to upgrade the sensor technology background information, NASA requested information from a total of 27 manufacturers of portable multi-gas instruments [1090]. A set of criteria was established to determine which vendors would be selected for laboratory evaluation. Each of the 27 manufacturers of multi-gas analyzers was sent a copy of the criteria and asked to fill in the appropriate information

pertaining to their instrumentation. Based on the results of the sensor criteria worksheets, a total of 9 vendors out of 27 surveyed manufactures were chosen for evaluation.

### **3.6.15.2 Calibration Methods and Vapor Generation Chambers**

An instrument setup for calibrating model MDA 7100 paper tape cassette hydrazine detectors in the USAF inventory consisted of a Kintek 491 permeation tube reference gas generation system, a humidifier/mixer system (which combines the dry reference hydrazine gas with humidified diluent or carrier gas to generate the required humidified reference for calibrations), and a gas sampling interface [1091]. The Kintek reference gas generation system itself was periodically calibrated using coulometric titration to verify the hydrazine concentration of the sample atmosphere in the interface module. The Kintek reference gas was then used to calibrate the hydrazine monitors. Thus, coulometric titration is only used to periodically assess the performance of the Kintek reference gas generation system and is not required for hydrazine monitor calibrations. One advantage of using coulometric titration for verifying the concentration of the reference gas is that it is a primary standard (if used for simple solutions). The report also contains a description of the hydrazine calibration system used by the MDA 7100 instrument's manufacturer, Zellweger Analytics.

### **Material Selection to Avoid Sampling Losses due to Wrong Choice of Materials for Air Sampling Tubing**

Many of the McEwen and Vernot animal inhalation toxicity data in the 1980s are invalid due to long sampling lines made from absorbent plastics. A single central hydrazine analyzer served several animal exposure chambers and was connected to those chambers with long, thin plastic hoses. Much of the hydrazine leaving the exposure chambers never arrived at the analyzers due to absorption into and diffusion through the plastic. As a result, the animals were exposed to much higher hydrazine concentrations than what was read on the analyzers and reported in the literature.

### **3.6.15.3 Passive Personal Dosimeter Badges (Direct Reading)**

An automated system for reading the exposure levels of personal dosimeters worn by personnel at rocket test sites and archiving exposure data for subsequent evaluation has been developed [1092, 1093]. The reading of personnel dosimeter badges for exposure to potentially harmful vapor concentrations of hydrazines is usually performed visually at the end of the work shift by comparing the color developed by the badge with a calibrated color comparator chart. The badge reader also stores bar-code data unique to each badge, as well as bar-code information on the user, as part of the permanent badge record.

A single-spot dosimeter for real-time, colorimetric detection of hydrazine in air mounted on a passive badge consisted of a dosimeter card containing a vanillin so-

lution coated on a thin paper substrate [1094]. The active patch consisted of a thick cellulose substrate coated with a vanillin solution. When placed in a plastic sample holder attached to a personnel pump, up to 5 L/min could be drawn through the active badge substrate. The vanillin hydrazone formed in the reaction was yellow. The spot color intensity was proportional to the dose. When exposed passively to hydrazine, the experimental detection limit was  $20 \text{ ppb} \times \text{h}$ . Extrapolated results indicate that a detection limit of  $5 \text{ ppb} \times \text{h}$  for long sampling periods should be possible. RH effects on badge response were minor. High humidity enhanced the color development on the vanillin badge, while low humidity had no effect on badge response.

A two-spot passive dosimeter badge developed and tested by the Naval Research Laboratory (NRL) and GeoCenters was extensively used at NASA Kennedy Space Center (KSC) for personnel monitoring of  $\text{N}_2\text{H}_4$  and MMH. This badge, manufactured by Bacharach (former GMD), utilizes two chemistries: PDAB and vanillin impregnated on filter paper. A color must be observed on both spots of the badge as verification of the presence of toxic vapors. In the case of both  $\text{N}_2\text{H}_4$  and MMH, the PDAB spot turns orange, while the vanillin turns yellow. There was no observable color when the badge was exposed to UDMH vapors. The minimum detectable doses of  $\text{N}_2\text{H}_4$  and MMH for this badge were  $25 \text{ ppb} \times \text{h}$  and  $50 \text{ ppb} \times \text{h}$ , respectively. Cross interferences of several organic and inorganic substances known as normal satellites of hydrazines, including up to 25 ppm ammonia, were examined. None of the tested substances showed any effect on the performance of the hydrazine systems. The hydrazine and MMH systems use the same sensor. This sensor is 10 times more sensitive to hydrazine and MMH than to UDMH.

The K and M Environmental Corporation has developed a simple, direct-read, one-spot passive badge for all three hydrazines ( $\text{N}_2\text{H}_4$ , MMH, and UDMH) [1095]. The badge operates on the same principle of diffusion. The presence of  $\text{N}_2\text{H}_4$ , MMH, or UDMH is indicated by the formation of a color change in the shape of an exclamation mark inside a triangle on the front of the badge. Unlike the Bacharach/GMD/NRL badges, which were made from impregnated filter paper, the K&M sensors are fabricated from a uniformly coated indicator layer placed on an inert surface. This alternative construction causes the sensor to be more sensitive and consistent in its color formation. The minimum detectable levels (MDLs) for  $\text{N}_2\text{H}_4$ , MMH, and UDMH were 4.5, 6, and  $10 \text{ ppb} \times \text{h}$ , respectively. Personal dosimeters for hydrazine or MMH are also available from DOD Technologies under the ChemLogic trade name.

### **Actively Pumped Paper Tape (Direct Reading, Portable or Stationary)**

A common feature of continuously operating vapor sensors available from several instrument suppliers is a spool of reagent-impregnated paper tape that is held between two tubes through which air flows at a known rate. The paper tape is advanced at certain time intervals and color changes are measured in reflected light. The discoloration is proportional to the concentration of toxic agent in the air. The impregnating reagents that have been used by various instruments include molybdatophosphoric

acid [937, 1074], PDAB, and potassium tetrachloroaurate [1096]. Instruments of this type were (are) made by MDA Scientific, later acquired by Zellweger Analytics, currently operated by Honeywell Analytics. This includes the CM4 Chemcassette, SPM Flex, and ChemKey TLD Toxic Gas Detectors.

One of the first paper tape instruments was the AutoStep hydrazine analyzer made by GMD, a company that was later absorbed by Bacharach [1097]. The GMD MK-2 is a microprocessor-controlled instrument with direct liquid crystal display meter readout and full data storage facilities. Some of the performance requirements established for the detector were an accuracy of  $\pm 1$  ppb tested at 10 ppb, linear range of 0 to 400 ppb, zero and span drift of  $\pm 2$  ppb in 4 h, response time of less than 4 min to 90% tested at 10 ppb, error due to temperature change from 273 to 313 K (0 to 40 °C) at 45% RH within  $\pm 20\%$ , and error due to humidity change from 10 to 80% within  $\pm 25\%$ . Evaluation tests, other than the RH test, were performed using hydrazine, MMH, and UDMH vapors ranging from 1 to 400 ppb at 298 K (25 °C) and 45% RH.

### Actively Pumped Gas Detector Tubes and Badges

An MSA ProLite Turbo personal sampling pump was used at NASA KSC to draw air samples through filter paper treated with a mixture of vanillin and 0.5% phosphoric acid [1098]. The pump was orificed to draw 1 L air/min. At this flow rate, the TLV (1992) threshold of 10 ppb MMH could be detected within 10 min. The paper disc was held between two O-rings in a Lexan housing to which the suction hose of the pump was connected. This is essentially like the passive vanillin badges, except instead of relying on convection and movement of the personnel wearing the badge, a constant air flow is drawn through the paper similar to the portable or stationary recording instruments. The colors were read by inserting the card from the badge into a Minolta CR-200 Chroma color-light meter.

An active hydrazine vapor sampler was developed to detect vapors of hydrazine and MMH in air at ppb concentration levels [1099]. The sampler consisted of a commercial personal pump that draws ambient air through paper tape treated with vanillin (4-hydroxy-3-methoxybenzaldehyde). The paper tape is sandwiched in a thin cardboard housing inserted in one of the two specially designed holders to facilitate sampling with two 1.5-cm-diameter windows in the front and back. Contaminated air reacts with vanillin to develop a yellow color. The intensity of the color is proportional to the concentration of hydrazine or MMH. This device can detect 10 ppb in less than 5 min.

An active vanillin badge patch consists of a thick cellulose substrate coated with a vanillin solution [1094]. When placed in the sample holder attached to a personal pump, flow rates up to 5 L/min can be drawn through the active badge substrate. The detection limit for hydrazine at a flow rate of 5 L/min was below 100 ppb.

The color transition temperature of some liquid crystal chemicals changed after the chemicals had been exposed to hydrazine, UDMH, or nitrogen dioxide at concentrations of less than 10 ppm. Attempts have been made to develop a dosimeter badge based on this reaction [1100].

### Personal Passive Samplers (Not Direct Reading)

A badge personal dosimeter has been adapted to hydrazine monitoring, and the results of the dosimeter were compared to results obtained with GC methods with prior derivatization with furaldehyde [1074, 1101]. The best results were obtained with hydrazine and PDAB, but analysis of UDMH was more difficult. The badge contained a diffusion-controlled absorption element containing 5N  $\text{H}_2\text{SO}_4$  on non-woven porous polypropylene sheets or firebrick granules. The absorbed hydrazine, bound as hydrazinium sulfate, was subsequently extracted and analyzed colorimetrically with PDAB. Linear response in the range 0.1–10 ppm was demonstrated with a statistically significant number of samples. As an alternate method, derivatization with furaldehyde, followed by GC analysis, was attempted with moderate success for hydrazine alone. Exposed dosimeters could be stored refrigerated for up to 7 d without loss of hydrazine.

#### 3.6.15.4 Impinger Methods – Wet Chemistry (Not Direct Reading)

For the analysis of hydrazine in air at places of employment in the UK, the recommended method is sampling either onto acid-coated glass fiber filters followed by solvent desorption or directly into modified impingers with dilute sulfuric acid, followed by analysis by liquid chromatography after derivatization with benzaldehyde [1102].

#### 3.6.15.5 Fiber Optic-Colorimetric and Waveguide Vapor Detection Methods

It is more reliable to have a multitude of remotely operating colorimetric sensors out in the field and connect them via fiber optic cable to a central processor. The task is to make the “multitude of sensors” cheap enough that an entire multi-node network can be set up to spatially monitor, for instance, a drum yard where hydrazine is stored.

An optical waveguide sensor using oxazine perchlorate dye initially intended for ammonia detection has been modified to detect hydrazine vapors [1103, 1104]. It was hoped that this system would be reversible, but initially reversibility had been demonstrated only for ammonia and not for hydrazine. Even if the chemical reaction and color change at the end of the fiber optic cable was irreversible, there would be potential applications for such a remote sensing network.

Distributed multi-site fiber optic chemical sensors for real-time monitoring of hydrazine, MMH, and UDMH down to the 10 ppb concentration level based on evanescent wave interaction at the fiber optic surface using triphenylmethane dyes immobilized onto the surface of silica fiber may be susceptible to other amine or ammonia vapors [1105].

Fiber optic chemical sensors were developed for the remote detection of hydrazine propellant vapors in a network of sensor stations. The sensors contained a color-changing indicator (phosphomolybdic acid) that reacted selectively and irreversibly with hydrazines to yield chemical compounds that absorb laser light launched into a fiber optic network. The sensors were fabricated by dispersing the reagent within either a porous cladding or a porous gelled distal end coating. Remote

field-scale detection of hydrazine vapor in regime of a few hundred ppb  $\times$  min integrated dose was demonstrated with a network that was approximately 1 km in length and used a low-power (10-mW) diode laser [1106–1109]. Hydrazine detection fiber optic dosimeters were tested for periods of up to 3 months at Cape Canaveral Air Force Station (CCAFS) to determine the effect of the local environment on lifetime and sensitivity [1110]. The dosimeters were deployed at a diverse group of sites, including fuel, oxidizer, and hydrocarbon fuel storage and transfer locations. In addition, a group was set aside in a sealed enclosure for control purposes. The dosimeters were retrieved at monthly intervals and exposed to measured doses of hydrazine vapor to determine the effects of the field exposure on their hydrazine response. The analysis indicated that 90% of the exposed dosimeters were able to sense hydrazine at a dose detectivity of less than 15 ppb  $\times$  h, a value that meets the current hydrazine sensing requirement. The reaction of hydrazine with phosphomolybdic acid is irreversible, but similar fiber optic sensors were evaluated that contained 2,4,7-trinitrofluorenone, an electron acceptor compound that selectively formed chemically reversible, colored intermolecular charge transfer complexes [1111].

Evanescent wave fiber optic sensors for hydrazine, MMH, and UDMH capable of detection below 10 ppb were prepared by removing the cladding from commercial multi-mode fibers and coating the exposed core with a hydrazine-sensitive triphenylmethane dye immobilized in an inert polymer matrix, typically poly(vinyl chloride) [1112]. Triphenylmethane dyes bleach reversibly in the presence of hydrazines, enabling colorimetric sensing. The linear dynamic range was typically 0–300 ppb and the overall dynamic range was up to ca. 5 ppm. Sensors optimized for hydrazine were only as much as a factor of 45 less sensitive to MMH and UDMH, suggesting that the sensor film would require optimization for each analyte. Saturation response and relaxation times were on the order of 5–8 min, but measurable signals for 10 ppb hydrazine could be obtained in under 30 s.

A fiber optic hydrazine and NO<sub>2</sub> sensor used an acid-base indicator that underwent color changes depending on which gas was present [1113, 1114]. Bromothymol blue bromocresol green mixture (1/1) in hydrogel (1/1) produced a blue-green indicator for hydrazine and/or NO<sub>2</sub>. The sensor was tested several times over a period of 8 weeks, and the response was consistent when exposed to 52 and 18 ppm hydrazine or 400 and 200 ppm NO<sub>2</sub>.

A hydrazine fiber optic reversible sensor used commercial silica fibers and a pentacenediquinone (PDQ) and polymer mix, with an index of refraction adjusted to closely match that of silica as an active sensing material replacing the cladding of a silica core optical fiber [1115]. The optical signal passing through this modified cladding-type fiber sensor exhibited a reversible intensity change in the presence of hydrazine at different concentrations. The sensor contained a PDQ/organic compound mix as an active sensing element in a 5-cm-long modified cladding fiber sensor [1116]. The refractive index of this modified cladding was adjusted to 1.492 to closely match that of the silica fiber core. When the PDQ reacted with

hydrazine, oxygen atoms from the PDQ were replaced by a molecule of hydrazine. This replacement resulted in a significant increase in the absorption spectra of the mix, specifically at wavelengths between 1331 and 1430 nm as well as at 1550 nm.

### 3.6.15.6 Ionization and Photoionization Chambers

Other methods investigated for possible use in hydrazine or UDMH vapor detection and monitors include ionization chambers with  $^{90}\text{Sr}$  isotope as  $\beta$ -radiation source [1117]. Photoionization by UV light can be a very sensitive detection method for contaminant levels from a few ppb to 1000 ppb with decent linearity over the entire range, which is a very desirable feature. Photoionization detectors (PIDs) are often used in the effluents of gas chromatographs after a mixture of chemicals has been first separated. One of the unique properties of hydrazines in comparison to other flammable or toxic vapors is the low ionization potential in comparison to other photoionizable molecules. However, without prior separation by GC, the PID is not specific to hydrazines and has shown significant humidity interference and occasional lamp window contamination.

Commercially available photoionization gas detectors, mostly used for the detection of flammable gases, can be modified to detect hydrazines. Instruments of this type are made by RAE Corporation with brand names such as ToxiRAE, UltraRAE, and MultiRAE, some portable ones even feature wireless transmission of results to a central receiving station. In the UltraRAE, an 8.1-eV lamp was suggested for hydrazine in order to screen out as many interfering compounds as possible.

A xenon lamp with photons of 8.44 eV selectively ionizes only species with ionization energies below this level [1118]. Hydrazine has an ionization potential of 8.4 eV, MMH 8.0 eV, and UDMH 7.8 eV. Many organics, such as amines, will, unfortunately, interfere. The non-selectivity disadvantage of the PID can be overcome by combining a PID with a modulated ON/OFF or IN/OUT decomposition or absorption filter in the sample inlet [1119].

A photoionization gas sensor for hydrazines that can also measure other volatile organic compounds and other gases in concentrations from sub-ppb to 10000 ppm was capable of giving real-time readings and monitoring continuously [1120]. The design of a micro ionization chamber and signal detection circuits was integrated with a single-chip microcomputer. This instrument was portable and small and had high accuracy, fast response, and continuous operation capability.

### 3.6.15.7 Mass Spectrometric and Ion Mobility Detection Methods

A miniature mass spectrometer with a focal plane geometry was developed at the Jet Propulsion Laboratory [1121]. The miniature mass spectrometer has the potential to meet the government requirements of 10-ppb sensitivity for hydrazine detection, as well as the requirements for instant response, portability, and low maintenance. The sensitivity of the instrument was increased by installing a new ionizer and by increasing the voltage from 600 to 1450 V.



In ion mobility spectrometers, a small portion of an air sample that is drawn over the surface of a semi-permeable membrane and transferred to the detector side of a membrane through solution, diffusion, and evaporation mechanisms. Molecules that pass through the membrane are transferred to an ionization region and mixed with a secondary sample of air containing a dopant. A radioactive source generates high-energy particles that cause the formation of positively and negatively charged ion clusters. These ions are eventually separated, collected, and quantified using TOF differences like those in a TOF mass spectrometer.

Ion mobility spectrometry (IMS) has the advantage that it does not require a hard vacuum like conventional mass spectrometers but can operate at atmospheric pressure. IMS separates ions by time differences it takes them to drift through a gas at atmospheric pressure in an applied electrostatic field. The drift tube is the central part of the instrument. At the inlet to the drift tube is an ionizer, most commonly a  $^{63}\text{Ni}$  radioactive foil like the one used in some household fire alarms/smoke detectors. In the air sample, the  $\beta$  particles ionize compounds with high proton affinity such as hydrazines to become positive ions, whereas other compounds such as halocarbons with high electron affinity form negative ions. Ammonia, hydrazine, and MMH have characteristic drift times and arrive at the collector electrode at the downstream end of the drift tube at different times. With response times from 0.1 to 1 s, reported sensitivities for other toxic contaminants from 0.1 to 10 ppb, simplicity of operation, and the potentially compact size of the instruments, this method has been subjected to intense investigation as a method for the detection of hydrazine and MMH. Early evaluation was done with laboratory-built one-of-a-kind instruments, and later testing was conducted with commercially available units. In early laboratory testing, it was demonstrated that the limits of detection for hydrazine and MMH were near  $0.01\text{ mg/m}^3$  and that the response was linear between 0 and  $0.05\text{ mg/m}^3$  but became flat above  $0.1\text{ mg/m}^3$  [1122]. A modified hand-held ion mobility spectrometer manufactured by Graseby Ionics has been evaluated as a field analyzer for  $\text{N}_2\text{H}_4$  and MMH. During initial testing, the minimum detection level for MMH was found to be 6 ppb with a 0 to 1 ppm total analytical range and an insensitivity to humidity. The initial observed ammonia interference was decreased by changing the internal dopant to 5-nonanone from acetone [1123].

Hydrazine, MMH, and UDMH in air can be detected and identified by IMS at low concentrations, but with interference from ammonia [1124]. The optimum spectrometer operating conditions for the detection of hydrazine, MMH, and UDMH in the presence of ammonia were incorporated into a hand-held portable instrument capable of near real-time detection. Ammonia is still an interferent in the IMS detection of the parent hydrazine. The use of ketones as dopant chemicals has been shown to be effective in the ion mobility spectrometric determination of hydrazines.

An ion mobility spectrometer was flown on two Space Shuttle missions: STS-37 and STS-49 [1125–1128]. The external side of the space suit of astronauts returning from EVA work was sniffed in the airlock before the astronauts were allowed to return to the crew cabin. No hydrazines were detected.

### 3.6.15.8 Thin-Film Electric Conductometric Detectors

Chemiresistors change their electric conductivity in the presence of certain chemicals. The Spire Corp. and Spectral Sciences Inc. initially developed a conductive polymer-based dosimeter using poly(3-hexyl) thiophene-based sensing elements [1129].

Thin films of the electrically conducting polymer, poly(3-hexylthiophene) (P3HT), were developed as sensors for hydrazine vapor at the part-per-billion level [1130–1132]. The P3HT films were fabricated by a spin-coating technique onto quartz substrates incorporating gold-interdigitated electrodes and were rendered conductive by doping with an NOPF<sub>6</sub> solution. The sensors responded strongly and instantaneously to hydrazine concentrations as low as 1 ppb with a measurement accuracy of  $\pm 20\%$ . In addition, the sensors exhibited excellent environmental stability and a long shelf life and were free from interference by contaminants.

The original sensor demonstrated a minimum detectable dose of approximately 1 ppb  $\times$  h and a saturation dose of approximately 250 ppb  $\times$  h as measured in dry conditions. In a humidified environment with greater than 60% RH, the output of the sensor changes significantly [1133].

Two thin-film electronic noses, the Cyranose (a commercial product) electronic nose and an electronic nose developed at JPL, both consisting of an array of 32 sensors made of polymer-carbon composite films, were tested to determine their utility for detecting hydrazine and MMH [1134]. The devices were exposed to concentrations of hydrazine from 0.5 to 52 ppm, and 14 ppm and 1 ppm MMH. The Cyranose sensors responded to hydrazine at 52 and 18 ppm; the JPL developmental ENose sensors responded to hydrazine at 3 ppm. The response of the Cyranose to 1.1 ppm hydrazine was not measurable; the response of the JPL ENose sensors to 0.5 ppm was evident but was obscured by a humidity change. The Cyranose sensors responded to 14 ppm and 1.1 ppm MMH.

A poly(3-hexylthiophene) conducting polymer-based thin-film microsensor for a real-time detection of hydrazine vapor at ambient pressure consisted of a rectangular shaped inert substrate and gold electrode pairs [1135]. A layer of poly(3-hexylthiophene) thin film was coated onto the sensor platform using a spin-coating method, and nitrosonium hexafluorophosphate (NOPF<sub>6</sub>) was used to dope the poly(3-hexylthiophene) thin film to increase its electrical conductivity and form the finished sensor. The results showed that the sensor responded to hydrazine vapor in less than a few seconds, attained orders of magnitude change in normalized resistance during hydrazine exposure, and was not easily saturated. When exposed to 1 ppm of hydrazine vapor, the compensation interaction between the reducing hydrazine gas and p-type doped poly(3-hexylthiophene) leads to a five-order-of-magnitude increase in the resistance of the device [1136]. The sensor can detect hydrazine in concentrations from tens of ppb to tens of ppm. The sensitivity of the sensor increased with increasing hydrazine concentration and decreasing polymer film thickness.

A review article covered the main applications of conducting polymers in chemiresistor sensors for sensing hypergolic liquid propellant vapors and toxic exhaust plume acidic vapors of solid rocket motors at TLV concentration levels [1137]. This included NO<sub>2</sub> and mixed oxides of nitrogen (MON-3), hydrazine, MMH, UDMH, and HCl. Discussion of key features of the sensors such as conducting mechanisms during sensing, thickness of the sensing layer, factors that influence conductivity, response time, recovery time, detectable range, and minimum detectable limit constitutes a good introduction to this topic.

Thin films containing bis(diethylaminodithiobenzil) nickel films and stearyl alcohol in a 1:1 molar ratio are electrically conductive. Chemiresistor sensors were fabricated by depositing thin layers onto interdigital electrodes [1138, 1139]. The current passing through these sensors increased by three orders of magnitude on exposure to parts-per-billion levels of hydrazine, with high signal-to-noise ratios. Exposure to potential interferents such as ammonia at 29 ppm or 60% RH at room temperature caused current increases of only 10- to 20-fold. These sensors hold promise for use in alarm devices for hydrazine.

#### 3.6.15.9 Differential Temperature Detectors

A hydrazine vapor detector has been proposed that consists of an alumina pellet with 28–36% iridium, similar to Shell 405 catalyst [1140]. When N<sub>2</sub>H<sub>4</sub>, MMH, or UDMH vapor comes into contact with the catalyzed pellet, the temperature change resulting from hydrazine decomposition and oxidation is sensed by a thermistor and compared to that of a non-promoted reference alumina pellet in a Wheatstone bridge type circuit. This type of sensor would respond to hydrogen and numerous other flammable vapors as well.

Electrochemical hydrazine detectors typically saturate at levels above 500 ppm and cannot be used for the detection of flammable levels of UDMH or MMH vapors. Instead, a Bacharach Model 301 Portable Combustible Gas Detector was modified for the detection of flammable levels of hydrazine fuels, mostly UDMH and MMH [1141]. The vapor/air sample is drawn through a cell with two heated platinum thermistor elements in a Wheatstone bridge circuit, like thermal conductivity detectors in gas chromatographs. One thermistor is coated with an inert material to prevent its reaction with combustible vapor, the other is in contact with the vapor/air stream, allowing catalytic combustion to take place on its surface and thus upsetting the balance of the Wheatstone bridge. Since the instrument was designed for methane detection, which oxidizes only at higher temperatures than UDMH, the current to the thermistors and their surface temperature had to be reduced.

A hydrazine leak sensor was developed based on chemically reactive thermistor beads [1142]. The sensor consisted of a thermistor bead coated with copper(II) oxide (CuO) dispersed in a clay or alumina binder. The CuO-coated thermistor was one of a pair of closely located thermistors, the other being a reference. On exposure to hydrazine the CuO reacted exothermically with the hydrazine and increased the temper-

ature of the coated thermistor by several degrees. The temperature rise was sensed by a resistive bridge circuit and an alarm triggered by data acquisition software.

### 3.6.15.10 Optical Direct IR Absorption Methods for Detection of Vapors

The MIRAN SapphiRe, manufactured by the Foxboro Corporation, is a portable ambient air analyzer capable of analyzing for over 100 individual chemicals [1079, 1080]. Using an optical filter and a variable pathlength gas cell (0.5 to 1.5 m), the SapphiRe can measure both parts-per-billion and parts-per-million concentrations of chemical vapors. In the case of  $\text{N}_2\text{H}_4$ , the measurement range is 0 to 50 ppm, with a detection limit of approximately 500 ppb. A SAPPHIRE Portable Gas Detector is also offered by Enmet.

### Open-Path IR Absorption Methods, also with Lasers as Light Source

A lead-salt tunable diode laser cooled to 85 K and operating near  $962\text{--}966\text{ cm}^{-1}$  was used to record direct absorption and second-derivative spectra of hydrazine at several pressures to study the sensitivity to low levels of hydrazine [1143]. Spectra of  $\text{NH}_3$  and  $\text{CO}_2$  were used for wavelength identification of the scanned region. Measurements were made in a 50-cm quartz cell with multiple reflections. With a cumulative pathlength of 80 m, detection sensitivities of about 1 ppb were achieved for hydrazine in dry nitrogen at a cell pressure of 10 mbar. For spectroscopic detection of  $\text{N}_2\text{H}_4$  using the  $10.6\text{-}\mu\text{m}$  band, spectral regions including strong  $\text{NH}_3$  lines or  $\text{CO}_2$  lines must be avoided. Ammonia was always present when the hydrazine concentration was measured. The ammonia signal was at least an order of magnitude stronger than the hydrazine signal. This particular laser diode could only cover narrow regions near 962 and  $965\text{ cm}^{-1}$ , where strong ammonia interferences were expected. However, the high resolution ( $0.001\text{ cm}^{-1}$ ) of the TDL spectrometer allowed individual lines of hydrazine to be identified far from interferences from either ammonia or carbon dioxide, especially at lower pressures. A hydrazine line at  $961.75\text{ cm}^{-1}$  was identified that was free from ammonia absorption interference and that would be suitable to monitor hydrazine levels.

### Laser Photoacoustic Spectroscopy

In photoacoustic spectroscopy, the gas to be analyzed is irradiated by intermittent light of a preselected wavelength coincidental with an absorption band of the analyte, such that the gas will absorb part of the light and warm up. The heat generated by the absorbed light causes the gas to expand and results in a local pressure rise. By chopping the light, the pressure alternately increases and decreases and generates an acoustical signal. This signal is subsequently detected by a microphone and amplified.

### 3.6.15.11 Optical-Emission Chemiluminescence Detectors and Monitors

Chemiluminescence reactions can occur in the gas, liquid, and solid phases. The light emitted from chemiluminescent reactions has differing degrees of intensity, lifetime, and wavelength. The wavelength can extend across the entire spectrum from near UV through the visible and into the near IR. Solution phase chemiluminescent reactions that have found analytical application often produce light in the visible region.

Tris (2,2'-bipyridine) ruthenium (III) ( $\text{Ru}(\text{bpy})_3^{3+}$ ) is an electrogenerable, chemiluminescent reagent that is electrochemically reversible and is a reagent for the detection of gas-phase hydrazine, MMH, and UDMH [1144, 1145]. The electrochemical oxidation of  $\text{Ru}(\text{bpy})_3^{2+}$  to  $\text{Ru}(\text{bpy})_3^{3+}$  creates a strong oxidizer, whose reduction back down to  $\text{Ru}(\text{bpy})_3^{2+}$  by reaction with a reducing analyte is characterized by the emission of photons of light centered at 610 nm. Portable and semi-portable instruments that rely on the chemiluminescent reactivity and reversibility of the  $\text{Ru}(\text{bpy})_3^{3+}$  reagent have been designed and tested. Detection limits for hydrazine and its derivatives were in the low-ppb regime, while response times were on the order of seconds to several minutes, depending upon the analyte being examined.

A chemiluminescence analysis method for hydrazine combined with flow-injection technique used luminol and hexacyanoferrate(III), both of which were immobilized on an anion-exchange column [1146, 1147]. The chemiluminescence signal produced by the reaction between luminol and hexacyanoferrate(III), which were eluted from the column through sodium phosphate injection, was decreased in the presence of hydrazine. The decrease in chemiluminescence intensity was linear with hydrazine concentration in a range from 0.1 to 100 ng/mL, and the detection limit was 0.04 ng/mL ( $3\sigma$ ).

### 3.6.15.12 Electrochemical Potentiometric Detectors and Monitors

In hydrazine electrochemical sensors, the measured current is generated by the oxidation of  $\text{N}_2\text{H}_4$ , MMH, or UDMH in an electrolytic cell. The output current of the detector is directly proportional to the concentration of the hydrazine vapors that pass by a sensing electrode. The specificity of the electrochemical system can be improved by properly selecting the sensing electrode, supporting electrolyte, and the potential difference between the reference and sensing electrodes. Some electrochemical systems employ a third electrode, or counterelectrode, to provide added stability.

The Interscan series 4000 series 2-electrode electrochemical monitor was supposed to be capable of detecting  $\text{N}_2\text{H}_4$  and MMH vapor concentrations at the 10-ppb level. This analyzer has somewhat high maintenance needs since it requires the periodic addition of water to the electrochemical cell [1080, 1148]. The depletion of the water from the cell is due to the evaporation of supporting electrolyte as sample air is pumped across the surface of the sensing electrode. The overall life of the cell is decreased due to the intrusion of atmospheric  $\text{CO}_2$  into the cell and the subsequent formation of carbonates. Although the formation of carbonates cannot be stopped, the substitution of cesium hydroxide ( $\text{CsOH}$ ) for potassium hydroxide ( $\text{KOH}$ ) has led

to a more soluble carbonate species and helped to prevent plugging of the sensor membrane. However, the Interscan 4187 often did not read zero when clean air was passed through the instrument, and NASA KSC is phasing out the use of the Interscan 4187 instrument.

NASA has developed an area vapor monitor that has the capability to continuously monitor and detect hydrazine vapor concentrations in the workplace that might be present at both the proposed 10 ppb TLV level, as well as at leak levels as high as 10 ppm. Commercially available boiler feedwater analyzers with platinum/stainless-steel electrodes have been adapted to analyze hydrazine vapor concentrations in air [831, 1149, 1150]. A prototype area monitor analyzer system based on the MDA/Hach Polymetron 9186 or 9586 Hydrazine Analyzer capable of meeting these requirements and operating unattended for 90 d (24 h/d) on a continuous basis was demonstrated. This analyzer is a three-electrode liquid analyzer typically used in boiler feedwater applications. For air monitoring, the system incorporated a dual-phase sample collection/transport method that simultaneously pulled ambient air samples containing hydrazine and a very dilute sulfuric acid solution (0.0001M) down a length of 1/4 in.-outer-diameter tubing from a remote sampling site to the analyzer. The hydrazine-laden dilute acid stream is separated from the air, and the pH is adjusted by the addition of a dilute caustic solution to a pH greater than 10.2 prior to analysis. See also [1151].

## 4 Decomposition of Hydrazine

In most of this book's chapters, the decomposition of any given rocket propellant is discussed as part of the chemical properties of a given substance. In deviating from this format, in the current chapter the decomposition of hydrazine has been moved to a section of its own, not as a subsection of chemical properties, because it is such an important property of hydrazine and has generated a flood of publications. There are many different modes of initiating the decomposition of hydrazine, including thermal, photolysis, radiolysis, and catalytic decomposition.

This section on hydrazine decomposition and combustion comprises a relatively large fraction of the total volume of this chapter because so many industrial applications depend on controlled hydrazine decomposition on command. Also, safety hazards can be caused by unexpected, accidental, and catastrophic hydrazine decomposition events that need to be prevented by a better understanding of decomposition mechanisms and triggers. Therefore, a better understanding of handling safety can be obtained and possibly new applications identified if all decomposition properties of hydrazine and its mixtures and derivatives are known and thoroughly understood. This includes decomposition in the absence of catalysts and controlled decomposition with the aid of catalysts. Only if the decomposition of hydrazine is completely understood from all points of view (i.e., academic and engineering points of view) will it be

possible to develop methods for the controlled decomposition of hydrazine and acquire a better understanding of conditions to avoid being a casualty of unexpected hydrazine explosions. Because the decomposition of hydrazine is important for most of its industrial uses, the fundamentals of decomposition kinetics are covered in this chapter, which includes such topics as kinetic rates, activation energy, free radicals, and isotope labeling.

Ever since the discovery of hydrazine (and hydrazine hydrate), its decomposition has undergone a very thorough investigation. This has resulted in a flood of publications beyond those modest eight initial works referenced in Audrieth's first monograph on hydrazine several decades ago [7]. It is difficult to organize all this material in a systematic, user-friendly fashion. The experimental methods for studying hydrazine decomposition differ as widely as the results, and it is not always easy to draw final conclusions when the data obtained by different methods agree with or contradict each other. In this chapter, the material was arranged by the mode of decomposition. Information on the decomposition of hydrazine derivatives, such as methylhydrazines, will be discussed in *Encyclopedia of Liquid Fuels* in the chapter "Methylhydrazine." The decomposition of hydrazinium salts was already presented in a separate section on the thermal stability of hydrazinium salts in *Encyclopedia of Oxidizers*, chapter "Hydrazinium Salt Oxidizers." Applications of hydrazine as a monopropellant that depend on controlled decomposition will be discussed in *Encyclopedia of Monopropellants*, in the chapter on monopropellants.

Most academic investigators have studied the vapor-phase decomposition of pure or diluted hydrazine at low partial pressures in glass or quartz apparatus. This may be useful for kinetic studies, but it does not reflect the actual operating pressure of hydrazine decomposition reactors for industrial applications. A significant fraction of hydrazine in a modern design rocket engine reactor decomposes catalytically, and only a small fraction decomposes thermally. Relatively few papers have examined the mechanism of hydrazine decomposition on the surface of heterogeneous catalysts because at higher temperatures, so many different mechanisms take place in parallel and simultaneously.

Throughout the various efforts to study the kinetics of hydrazine decomposition, the use of isotope-labeled hydrazine has proved very useful. The isotope-labeled hydrazines are not useful as rocket propellants. However, we regard them only as a means to obtain kinetics results and shall review them at the appropriate section depending on the mode of decomposition. Nitrogen-15-isotope-labeled hydrazine has been used in photolysis [1152, 1153], thermal decomposition, and oxidation [518] studies of hydrazine. The use of  $^{15}\text{N}$  isotope marking is very convenient because the isotope is not radioactive and does not require special safety precautions. Nitrogen-15-labeled hydrazine has also been used for studying the quadrupole moment and molecular structure of hydrazine. Other than replacing nitrogen atoms at the backbone of the molecule, isotope labeling of hydrazine could also be accomplished by the replacement of hydrogen with deuterium. This method has

been widely used in IR and Raman spectroscopic studies of the hydrazine molecule. The decomposition rate of  $N_2D_4$  has been shown to be markedly different from that of  $N_2H_4$  as a result of the isotope effect [1154]. The use of  $\bullet OD$  radicals instead of  $\bullet OH$  radicals has facilitated identification of intermediate products of the hydrazine oxidation flame [560].

Throughout the discussion of the kinetics and thermodynamics of hydrazine decomposition it is very important to know the bond dissociation energies (Section 2.3.3), because unless sufficient energy is pumped into the system to break at least one of the bonds, no decomposition may occur, at least not thermodynamically. Molecules are reluctant to dissociate if they have the same bond energy as carbon in diamond. The activation energy is a barrier to decomposition. In order for hydrazine to decompose on command, the most frequently used method is the lowering of the activation energy. The lowering of the activation energy by catalysis is discussed in Section 4.12.

#### 4.1 Slow and Accelerated Liquid-Phase Decomposition During Storage

The main interest in the slow liquid-phase decomposition of hydrazine stems from practical concern about unwanted pressure buildup during storage and the effect of various materials of construction on the rate of such pressure buildup. Some of the concern has carried over from the previous historical use of hydrogen peroxide as a monopropellant, where liquid-phase decomposition and pressure buildup during storage was and remains a serious design limitation. It has been proved that hydrazine can be stored for several decades without excessive pressure buildup or loss of performance. For instance, VOYAGERS 1 and 2 are still operational after 46 years in space.

The current section deals only with the slow decomposition of liquid hydrazine(s) during storage. Liquid-phase decomposition during conditions other than room-temperature storage is discussed in Section 4.2. Liquid-phase decomposition under catastrophic conditions (bonfire test) will be discussed in Section 8.12.

Experimental techniques used to study the effect of materials of construction, contaminants, or stabilizers on the decomposition of liquid hydrazine during storage include gas evolution/pressure buildup, differential thermal calorimetry, microcalorimetry, and chemical analysis of hydrazine(s) before and after long-term storage.

##### 4.1.1 Effect of Container Materials

A more detailed summary of suitable materials of construction is given in Section 5.3. The current discussion centers only on materials for laboratory experiments in which the slow decomposition of pure hydrazine is studied, preferably without any interference from the wall material. Since the liquid must somehow be contained under



terrestrial conditions to keep it from flowing away, container wall effects are difficult to avoid. For laboratory tests, the least interference is generally encountered with the use of borosilicate (e.g., Pyrex) glass or quartz.

The kinetic rate data of homogeneous hydrazine decomposition obtained by different authors and using different methods were combined on an Arrhenius plot, and fortunately all fell on the same straight line [1155]. The kinetics of the homogeneous decomposition of hydrazine did not change over a wide temperature range (~240 °C) and an extremely wide range of the rate constant (approximately nine orders of magnitude). The expression for the rate constant is

$$k = 5 \times 10^{6.0 \pm 0.2} \exp\left(\frac{-26800 \pm 800}{RT}\right)$$

where  $k$  is the rate constant in  $\text{s}^{-1}$  and  $T$  is the temperature in kelvin. These tests were repeated for the heterogeneous decomposition of hydrazine in contact with various materials of construction. The kinetic constants for these conditions are summarized in Table 48.

**Table 48:** Kinetic rate constants for heterogeneous decomposition of hydrazine on surface of materials of construction.

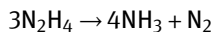
| Material                   | Temperature |        | Pre-exponential factor | Activation energy |
|----------------------------|-------------|--------|------------------------|-------------------|
|                            | K           | °C     | $\text{cm s}^{-1}$     | kJ/mol            |
| Stainless steel H18N10T    | 303–533     | 30–260 | 13                     | 66.7              |
| Stainless steel 12H18N10T  | 313–403     | 40–130 | 380                    | 76.7              |
| Nickel-based alloy El654   | 313–403     | 40–130 | 15                     | 72.9              |
| Stainless steel 12H21N51   | 313–403     | 40–130 | 29                     | 72.1              |
| Teflon film                | 323–368     | 50–95  | 25                     | 82.9              |
| Aluminum-based alloy AMG-6 | 323–403     | 50–130 | 12                     | 90.8              |

Data source: [1155]

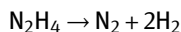
The inseparable interaction of liquid-phase and vapor-phase thermal decomposition of hydrazine is evident [1156]. Borosilicate glass tubes 3 to 7 mm in diameter were used in this study. A weighed amount of liquid hydrazine was inserted above a plug of mercury, taking care to prevent gas bubbles. The movement of the mercury column as a function of time, temperature, additives, and pressure was then measured. Since the initial ullage was zero, the initial vapor space must result from the decomposition of pure liquid hydrazine. After the vapor space was produced, decomposition could occur in either phase. The data did not reveal whether either of the two decomposition modes was heterogeneous. After a constant initiation period, the decomposition rate remained constant, whereas the surface area to which vapor was exposed changed continuously. The rate of decomposition was independent of the tube diameter. The

tubes could be placed in a pressurized chamber environment to compensate for the vapor pressure of hydrazine. The rate of decomposition increased from  $10^{-4}$  to 1%/h over a temperature range of 448–523 K. An activation energy of 304.2 kJ/mol (72.7 kcal/mol) was obtained from an Arrhenius plot of the data. However, this value is significantly higher than the activation energy obtained for hydrazine in the vapor phase by numerous other investigators (Section 4.3). The discrepancy is most likely due to different mechanisms of decomposition in the liquid and vapor phases. The generation of a small gas bubble under Lucien's conditions acted quasi-autocatalytically, in that decomposition in the vapor phase occurs more rapidly than in the liquid phase at identical temperatures. This is illustrated by the pressure effect on hydrazine decomposition: at 495 K, a change in pressure from 2.06 MPa (300 psi) to 2.96 MPa (430 psi) reduced the rate of decomposition from 1.8 to 0.04%/h. The higher pressure delayed the formation of a bubble by keeping the decomposition gases dissolved for a longer period of time until the liquid was saturated. Ammonia addition had a distinct retarding effect on hydrazine decomposition: at 495 K and 2.06 MPa, the rate decreased from 1.8 to 0.4%/h when 2.5% ammonia was added. The nitrogen : hydrogen ratio was dependent on reaction time, pressure, or ammonia concentration and was inversely proportional to all these variables.

Regarding the stoichiometry of the liquid-phase decomposition, the decomposition proceeds mainly through



Only small amounts of hydrogen are observed as a result of



It was concluded that hydrazine is “relatively stable” under the conditions described [1156]. One question was not discussed in that paper – the possibility of interaction between hydrazine and the mercury used to seal the sample. Hydrazine decomposition is catalyzed by many metals, and a catalytic contribution of mercury (or its contaminants) to the observed results cannot be excluded. The activation energy derived from an Arrhenius plot of gas evolution rate measurements between 343, 353, and 363 K was 66.3 kJ/mol in glass, 61.1 kJ/mol in aluminum, and 50.6 kJ/mol in CRES-304 [1157, 1158]. It is a misrepresentation of physical and hazard properties of hydrazine to state that “... the liquid (hydrazine) is relatively stable at temperatures to 300 °C” [1159]. The source quoted for this statement [9] originally said, “Anhydrous hydrazine decomposes on heating in the absence of oxygen at a temperature above 300 °C.” This does not preclude that unexpected, unwanted, but potentially catastrophic decomposition may occur far below 300 °C. The upper temperature limit of storability depends to a large extent on the materials of construction, the size of the container, and the surface : volume ratio. For the hazards caused by the lack of thermal stability, see Section 8.12.

On the basis of 10-year storage tests in an all-glass apparatus, the rate of decomposition of hydrazine at 316 K (110 °F) is 0.015%/year in the absence of metal surfaces and catalytic contaminants [1160–1162]. The rate of decomposition was identical for MIL-SPEC monopropellant-grade and high-purity-grade (“VIKING-grade”) hydrazine. In the presence of the most inert metal specimens (Ti-6Al-4V), the rate of decomposition increased to 0.15%/year. In the same test, MMH decomposition was only 0.02–0.1%/year.

The gas evolution rate of hydrazine in a glass isoteniscope at 294–305 K was slightly above  $3.67 \times 10^{-15} \text{ m}^3 \text{ g}^{-1} \text{ s}^{-1}$  [1163]. The gassing rates of MMH and UDMH were of the same order of magnitude. When plotting the logarithm of the gas evolution rate of hydrazine against reciprocal temperature, the slope of the curve changed abruptly at 300 K, showing steeper slopes at higher temperatures.

The sealed vial storage stability tests by Rocketdyne [1164–1170] were later repeated (with smaller surface : volume ratios) at Stanford Research Institute (SRI), also in comparison to the decomposition of MMH [1171]. Although the Rocketdyne tests showed that added glass surface had little or no accelerating effect on the decomposition of propellant-grade hydrazine, the SRI apparatus with only 6% of the surface area also had only 10% of the rate of decomposition. At 448 K, 2.55% of the hydrazine was decomposed after 572 h. The decomposition products consisted of 78.8% ammonia, 17.8% nitrogen, and 3.4% hydrogen. The average rate of decomposition was 0.0045%/h.

Hydrazine decomposition reactions in dilute aqueous, oxygen-free solutions at very high, supercritical pressures in water, up to 703 K (430 °C) and 35.5 MPa (350 atm), were studied by Raman spectroscopy in a high-pressure optical cell with diamond windows [1172]. The decomposition reaction appeared to be a first-order reaction. The effective first-order rate constant at 673 K was  $0.32 \text{ s}^{-1}$ . This study is of interest for the application of hydrazine solutions as boiler feedwater additive.

Many satellites have electric heaters wrapped around or traced alongside hydrazine propellant lines to prevent freezing while the spacecraft is pointing away from the Sun or while it is in the shadow of the planet or moon around which it revolves. One of the possible failure modes involves a stuck thermostat relay and accidental overheating of the lines. Line heater simulation tests have heated hydrazine in CRES-321 line sections to as high as 538 K (510 °F) without explosion [1173]. Laboratory tests simulated the situation where both primary and redundant heater thermostats failed in the closed (energized) position. Thermal analysis predicted that this situation could result in heating the propellant to 538 K (510 °F). To simulate this condition, in a first series of tests, 27.9 cm (11 in.) of propellant line upstream of a valve were traced with strip heaters, instrumented, and insulated. After initial tests at 422, 450, and 477 K (300, 350, 400 °F) were uneventful, the experimenters were more “gutsy,” and tests at 505 and 538 K (450 and 510 °F) were added to the test matrix. The hot section of the line slowly filled with gaseous decomposition products and the liquid/vapor front receded to cooler zones. Thruster firing tests were conducted

at 422, 450, 477, 505, and 538 K (300, 350, 400, 450, and 510 °F). The propellant was held in the heated tubing for 24 h prior to the firing. Other than reduced thrust due to gas bubble ingestion, the thrusters worked normally, and no explosions occurred on shutdown. The valve was solidly thermally shunted to the mounting plate, such that the valve never heated to the temperature of the first slug of incoming propellant. Subsequent fresh propellant cooled both the lines and the valve. In a second test series, stagnant propellant in a 53-cm (21-in.) line was heated such that two-thirds of the line were at temperature for up to 4 weeks and the ullage pressure was monitored. These tests did not produce any explosions either.

Previously, to obtain measurable thermal effects with conventional DTA, DSC, or ARC equipment, the samples had to be heated to at least 373 K. With the advent of more sensitive microcalorimetry, the rate of decomposition of hydrazine could be measured at room temperature for the first time [1174]. Microcalorimetry has been used to determine battery life, exothermic corrosion, or storage stability of rocket propellants. Microcalorimetry is approximately 10000 times more sensitive than other techniques (DTA, DSC, ARC). Microcalorimetry instruments measure heat flow in a range from 298 to 328 K. Some instruments can measure heat flows as low as  $0.5 \mu\text{J/s}$ , which corresponds to a hydrazine decomposition rate of  $4 \times 10^{-12} \text{ mol/s}$  (4 picomol/s). The samples (3 mL hydrazine and metals under investigation) were typically loaded into a 9-mL titanium bulb. The bulbs were identical to those used in ARC studies and can resist internal pressure of up to 9 MPa. Steady-state heat flux measurements were made at three temperatures, 298, 313, and 328 K. When converting heat flow data to rate of hydrazine decomposition, the theoretical heat of reaction had to be corrected for the heat of solution of ammonia in hydrazine. The metals under study were added as powders, and the surface area of each sample was measured beforehand. In this way, the reaction rate could be normalized by the wetted surface area to eliminate variations due to different particle size. The steady-state heat evolution rates were sorted by increasing catalytic activity at 328 K, as summarized in Table 49. The catalytically most active metals were molybdenum and nickel.

**Table 49:** Heat evolution and kinetic rate data of metal powders in liquid hydrazine.

| Metal powder | Heat evolution, $\mu\text{J s}^{-1} \text{ m}^{-2}$ |          |          | Frequency factor <i>A</i>           | Activation energy |
|--------------|-----------------------------------------------------|----------|----------|-------------------------------------|-------------------|
|              | at 298 K                                            | at 313 K | at 328 K | $\mu\text{J s}^{-1} \text{ m}^{-2}$ | kJ/mol            |
| Chromium     | 1.5                                                 | 22       | 30       | $2.70 \times 10^7$                  | 74                |
| CRES-304L    | 2                                                   | 8        | 54       | —                                   | —                 |
| Tungsten     | 82                                                  | 323      | 967      | $9.94 \times 10^6$                  | 63                |
| Hastelloy-C  | 360                                                 | 2445     | 6272     | $1.77 \times 10^{11}$               | 78                |
| Molybdenum   | 719                                                 | 3323     | 8579     | $4.96 \times 10^8$                  | 67                |
| Nickel       | 350                                                 | 2219     | 9265     | $1.41 \times 10^{12}$               | 89                |

Data source: [1174]

An attempt was made to correlate hydrazine decomposition data obtained from different thermal stability measurement methods (NASA NHB8060.1C Test 15, ARC and microcalorimeter) since they are all the result of the same hydrazine decomposition mechanism (Table 50). One such attempt to correlate thermal stability/exothermicity measurements led to the development of a computer program called HYKIN [1175], which is useful for data reduction and data correlation from all three methods and for making predictions for real-life situations outside the temperature range tested in the laboratory. The data were converted to a common denominator unit as  $\text{mol s}^{-1} \text{m}^{-2}$  (or  $\text{picomol} = \text{pmol cm}^{-2} \text{s}^{-1}$ ) and then compared. When plotted in an Arrhenius plot, data from the three methods for molybdenum showed good agreement. Less satisfactory agreement was found when plotting the Hastelloy-C data, which differed by a factor of 2 to 3, but at least they were of the same order of magnitude.

**Table 50:** Liquid hydrazine decomposition rates measured by different methods.

| Material sample | Decomposition rate, $\text{pMol cm}^{-2} \text{s}^{-1}$ |                              |                              |              |
|-----------------|---------------------------------------------------------|------------------------------|------------------------------|--------------|
|                 | Long-term ampoule<br>at 298 K                           | Microcalorimeter<br>at 298 K | Microcalorimeter<br>at 298 K | NASA Test 15 |
| Background      | 0.024 (glass)                                           | N/D                          | < 0.01 (Ti)                  | —            |
| CRES-304L       | 0.1                                                     | 0.3                          | —                            | —            |
| Hastelloy-C-276 | 1.1                                                     | 1.2                          | 2.2                          | 176          |
| Inconel 600     | > 1.2                                                   | 0.8                          | 2.3                          | —            |

Data source: [1174]

The acceleration of thermal decomposition of hydrazine caused by metals was measured using a differential scanning calorimeter and SuperCRC [1176]. The DSC measurements revealed that the exothermic reactions of  $\text{N}_2\text{H}_4$  depended on the type of sample cells. The onset temperature in a differential scanning calorimeter with a gold pan was 485.2 K and that with a glass capillary was 620.5 K. The activation energy of the thermal decomposition of  $\text{N}_2\text{H}_4$ , calculated from the Kissinger and Ozawa methods, were  $38 \pm 2 \text{ kJ/mol}$  in the gold pan and  $141 \pm 8 \text{ kJ/mol}$  in the glass capillary. A heat flow profile was observed with SuperCRC during the mixing of  $\text{N}_2\text{H}_4$  and a metal ion solution at 298 K. The maximum heat flow was related to the metal ion oxidative characters. The higher oxidative characters would provide a faster acceleration for the exothermic behavior than the lower oxidative ions. Mn(VII) and Cr(VI) solutions exhibited strongly oxidative characteristics during mixing with  $\text{N}_2\text{H}_4$ .

#### 4.1.2 Hydrazine Hydrate Slow Liquid-Phase Decomposition

The decomposition of hydrazine hydrate during storage in sealed vials was measured [541]. As long as air was excluded, the concentration of the 100% hydrazine

hydrate (64% hydrazine) did not change when stored in Pyrex containers at up to 343 K, even in the presence of 10% sodium hydroxide or potassium hydroxide. However, if the glass stopper was allowed to leak in air, hydrazine concentrations dropped from 64% to 42% in 155 d at room temperature. It is important to clean glass vessels before long-term tests with hydrazine. Pre-test cleaning with one of four solutions (10%  $\text{K}_2\text{Cr}_2\text{O}_7$  in  $\text{H}_2\text{SO}_4$ , 50%  $\text{HNO}_3$ /50%  $\text{H}_2\text{SO}_4$ , 42% aqueous KOH, or 3%  $\text{KMnO}_4$ / $\text{H}_2\text{SO}_4$ ) showed that all four solutions worked equally well and did not make any difference as long as the vessels were thoroughly rinsed with distilled water before use with hydrazine hydrate.

#### 4.1.3 Effect of Contaminants and Catalysts

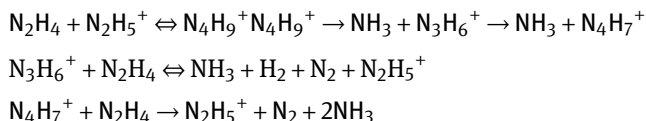
Proton donors appear to destabilize hydrazine. The effect of acidity on the rate of hydrazine decomposition was studied in a simple microcalorimeter at temperatures of 426–474 K with the use of hydrazinium nitrate as an additive [1177]. The reaction velocity is proportional to the concentration of hydrazine *and* its nitrate:

$$\frac{dC_{\text{N}_2\text{H}_4}}{dt} = k_t C_{\text{N}_2\text{H}_4} C_{\text{N}_2\text{H}_5\text{NO}_3}$$

The rate constant is a function of the temperature:

$$k = 10^{12.5 \pm 0.5} e^{\frac{-37000 \pm 1000 \text{ cal}}{RT}} \text{ mol}^{-1} \text{ s}^{-1}$$

Nitrate ions do not influence the kinetics because sodium nitrate addition did not increase the rate of decomposition. The following mechanism was proposed:



No proof has been offered for the existence of any of these intermediates, and the mechanism seems to be quite speculative. The rate constant for the decomposition of pure liquid hydrazinium nitrate where the principal reaction is the catalytic decomposition of hydrazine was previously found to be

$$\frac{dC_{\text{N}_2\text{H}_4}}{dt} = C_{\text{N}_2\text{H}_5\text{NO}_3} \times 10^{12.2} \times \exp\left(\frac{-3800 \text{ cal}}{RT}\right)$$

The increase of the rate of liquid hydrazine decomposition in glass containers with the addition of carbazic acid or ammonium chloride was attributed to the hydrazinium ion formed in either case by protonation of hydrazine. In sealed Pyrex vials, the rate of decomposition of propellant-grade hydrazine acidified with 1% hydrazinium(1+) chloride at 448 K was 40 times higher than that of the control without chloride addition [1171].

Iron(II) carbazate  $\text{N}_2\text{H}_5[\text{Fe}(\text{H}_3\text{N}_2\text{COO})_3]$  is a likely corrosion product when  $\text{CO}_2$ -contaminated hydrazine is stored in steel containers. Addition of the iron(II) carbazate complex  $\text{N}_2\text{H}_5[\text{Fe}(\text{H}_3\text{N}_2\text{COO})_3 \cdot \text{H}_2\text{O}]$  to hydrazine at concentrations equivalent to up to 173 ppm  $\text{CO}_2$  caused an increase in the rate of decomposition in glass vials at 324 K (51 °C) from 0.03 to 0.11  $\text{cm}^3/\text{d}$  [1178–1180]. On adding the iron(II) dicarbazato dihydrazino complex to hydrazine in glassware at 316 K (43 °C), there was no increase in the rate of decomposition of hydrazine. At 316 K (43 °C), addition of the iron carbazate had no measurable effect. The addition of tricarbazatochromium(III) dihydrate to hydrazine in a glass tube at 333 K (60 °C) did not produce an increase in propellant decomposition relative to the undoped hydrazine. Dicarbazatohydrazine nickel(II) was not sufficiently soluble in hydrazine to be included in this test series. Chromium(II) complexes can be oxidized to chromium(III) complexes by hydrazine in anhydrous hydrazine. In solution in anhydrous hydrazine the stable oxidation state of chromium is +3. It has been suggested that the ease with which chromium oscillates between the oxidation states of +2 and +3 in hydrazine is the key to its catalytic activity in the slow decomposition of hydrazine contaminated by chromium ions leached from the walls of stainless-steel drums [1181]. The carbazate salts by themselves are not nearly as active as solutions to which acidic hydrazinium salts have been added [1180]. In tests measuring the rate of gas evolution at 316 and 323 K with and without addition of Mn and Cr carbazate complexes  $[\text{Cr}(\text{H}_3\text{N}_2\text{COO})_3] \cdot 2\text{H}_2\text{O}$ , both individually and together, the addition of acid to hydrazine containing the metal complexes resulted in significant increase of decomposition, higher than either complexes in hydrazine (without acid) or acid in hydrazine (without metals). The mechanism responsible for high rates of gas evolution may be one involving Cr and Mn contaminants in combination with hydrazinium ion. Hydrazinium ion generated from  $\text{CO}_2$  addition to hydrazine in glass vials did not give a linear relationship between carbazic acid content and hydrazine decomposition rate as it was observed in steel containers. The rate of hydrazine decomposition leveled off above approximately 100 ppm  $\text{CO}_2$  equivalent. When  $\text{CO}_2$ -containing hydrazine with a high rate of decomposition that had already spent time in a CRES-304 tank was transferred to a glass bottle at the same temperature, the rate of gas evolution dropped only 20%. This indicated that the majority of the hydrazine decomposition in contaminated, aged hydrazine occurred in the homogeneous phase and only a small fraction of it was catalyzed heterogeneously by the metal surface.

In one study, 100 ppm nickel or cobalt added to purified hydrazine at 303 K in the form of soluble chlorides enhanced decomposition rates to such a degree that the tubes burst from internal overpressure within a week [241]. The pressure rise rate at 9% ullage was 70–100 kPa/week. Iron was a less effective contaminant than nickel or cobalt. Aluminum, titanium, chloride, or sulfate addition caused decomposition rates like the control tubes without contaminant addition.

Hydrazine is indefinitely stable in anhydrous ammonia solution as long as the solution is neutral or acidic, but as soon as sodium amide or sodium metal is added

to create alkaline conditions, hydrazine decomposes rapidly, forming hydrogen and nitrogen gas in a 2:1 molar ratio [1182]. The energy of activation of the uncatalyzed reaction is approximately 54 kJ/mol (13 kcal/mol). Kinetic studies have shown that the liquid-phase decomposition proceeds through an apparent one-half-order reaction. Steel, rust, platinum, or graphite accelerated the decomposition reaction, whereas increasing the Pyrex glass surface : volume ratio had no effect.

#### 4.1.4 Stabilizing Additives

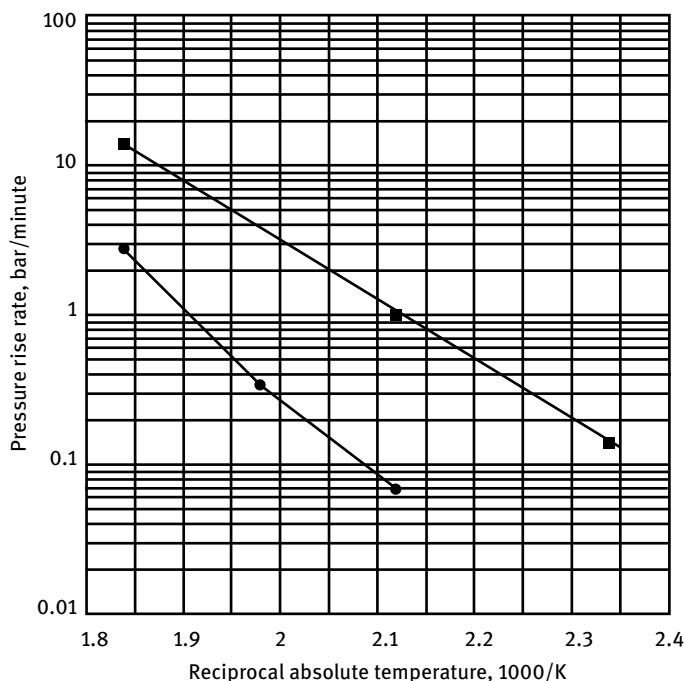
The slow, barely measurable decomposition of hydrazine in contact with common materials of construction may cause a design problem due to pressure buildup during long-term storage. The problem is far less severe with hydrazine than with hydrogen peroxide, which was previously used for space propulsion and continues to decompose at very high rates despite the addition of stabilizers. Following the tradition of hydrogen peroxide problem solving, stabilizers have been sought for hydrazine as well, but none really proved to be effective, nor was one necessary. The search for stabilizers for hydrazine is now a thing of the past. Stabilizers became unnecessary once the propellant handlers understood the importance of impeccable cleanliness requirements for hydrazine systems and once designers stuck to a list of compatible and approved materials for propellant tanks and flow control components.

The rate of propellant-grade hydrazine decomposition can be suppressed by a factor of 0.01 by pre-treatment with barium oxide; however, the same treatment is less effective for MMH. Barium oxide treatment cuts the rate of MMH decomposition only in half [1183].

Ethanol was said to have a stabilizing effect on anhydrous hydrazine, and no loss of hydrazine was measurable after 477 d in a 63 mass-% hydrazine/ethanol mixture [187]. However, the decomposition rates shown for anhydrous hydrazine stored in glass bottles are questionable. More recent data indicate that anhydrous hydrazine can be stored in glass bottles for several years with only minimal decrease in hydrazine and increase in ammonia concentration. In addition to extending the long-term storage duration of hydrazine at room temperature, attempts have also been made to extend the short-term upper temperature limit of safe use of liquid hydrazine to beyond 800 K by addition of stabilizers. These efforts have had only marginal success. The situation is different from that with hydrogen peroxide where several stabilizers are capable of extending the storage life of this notoriously unstable propellant.

Cadmium acetate was said to stabilize liquid hydrazine [1184]. Tests with decomposing hydrazine in a CRES-347 bomb with 60% ullage at 463, 475, 500, and 522 K (375, 395, 440, and 480 °F), 688–12380 kPa (100–1800 psia) for up to 120 min. showed that cadmium plating of the inside wall of the cylinder and addition of cadmium salts to the hydrazine substantially reduced the rate of hydrazine decomposition. In Figure 37, the upper heavy solid line describes the plain steel and the lower light solid line the cadmium-plated cylinder with cadmium acetate added to the liquid.





**Figure 37:** Effect of cadmium plating on hydrazine decomposition rates. (Image created by Schmidt 2020 based on data from [1184])

#### 4.1.5 Decomposition in Aqueous Solutions in the Absence of Oxygen

One of the main applications of hydrazine hydrate solutions is in boiler feedwater deoxygenation. Under these conditions, hydrazine decomposition competes with hydrazine oxidation as an undesirable side reaction. Tests with hydrazine hydrate solutions in dioxygen-free water at high temperatures and pressures have shown that hydrazine hydrate is remarkably stable under these conditions [1185].

In studies with hydrazine hydrate in pure, dioxygen-free water, at least 97% of the initial hydrazine was recovered after 3 h at temperatures between 373 and 573 K at saturation pressures in a passivated CRES-316 reactor [1186]. This means that simple cooking of hydrazine solutions as a means of decontaminating wastewater will not be effective.

The thermal decomposition of hydrazine in sub- and super-critical water at 25 MPa was measured in a super-critical water flow-through test facility [1187]. The thermal stability of hydrazine in aqueous solution was examined along the 25-MPa isobar from 473 to 725 K. The obtained first-order rate constant for the thermal decomposition of hydrazine increased from  $3.73 \times 10^{-4} \text{ s}^{-1}$  at 473 K to about  $0.31 \text{ s}^{-1}$  at 725 K.

## 4.2 Accelerated Liquid-Phase Decomposition

In most cases the rate of decomposition at room temperature is too slow, and the miniscule changes are difficult to measure. To accelerate storage life tests, the samples are stored at two or three elevated temperatures below the thermal runaway temperature, but above room temperature, and the rates of decomposition are plotted against the reciprocal absolute temperature in order to obtain kinetic parameters that will allow us to make predictions about the storage life at lower temperatures. Frequently it is difficult to avoid the effect of container materials on the rate of decomposition. If a totally inert container material cannot be found, the tests must be repeated with different volume:surface ratios so that the surface effect can be zeroed out. Even glass or quartz may have an effect on the rate of decomposition of anhydrous hydrazine.

Occasionally hydrazinium salts are stored as aqueous solutions, in particular if they are shock or friction sensitive, like hydrazinium nitrate, and they cannot be shipped in the solid state. The thermal decomposition of aqueous solutions of hydrazinium salts was already discussed in *Encyclopedia of Oxidizers*, in the chapter "Hydrazinium Salt Oxidizers."

Solutions of hydrazinium nitrate in hydrazine have been tested as monopropellants, liquid gun propellants, and explosives. While these solutions offer higher energy output than monopropellant hydrazine, concern over the lack of thermal stability has prevented their widespread use.

## 4.3 Homogeneous Vapor-Phase Decomposition

Of all various modes of hydrazine decomposition, the homogeneous decomposition of hydrazine vapor is the easiest to study (if one maintains a low pressure in the apparatus). The slow decomposition of liquid hydrazine was already described in Section 4.1. In both cases it is very difficult to study the truly homogeneous reaction without contributions from the reactor walls. The following modes and methods of gaseous hydrazine decomposition have been studied: thermal, hot-wire, photolysis,  $\alpha$ -radiolysis,  $\gamma$ -radiolysis, X-ray radiolysis, shock waves in shock tubes, glow discharges, and catalytic surfaces (thin-film, single-crystal, and polycrystalline surfaces). Test methods may include static tests in a thermostatted chamber with pressure measurement or dynamic tests where vapor flows from a vaporizer or vapor reservoir over a heated (presumably noncatalytic) reactor packing. The dwell time can be varied with the flow velocity.

The various modes of decomposition have several reaction steps in common. To facilitate comparison and discussion of results, a consecutive numbering system for reactions is used throughout this chapter to identify the many possible reaction steps. There is hardly any decomposition reaction of hydrazine(s) that proceeds by a one-step reaction. Many hydrazine decomposition reactions proceed by several pathways in parallel and via short-lived, unstable intermediate products.

A table in [1188] gives a historical survey of the various publications on liquid hydrazine homogeneous decomposition in chronological order. It lists the publications with the operating pressure and temperature range and the method of experimentation used. A schematic of possible reaction steps is shown in Figure 38. The numbers placed next to the arrows will be referenced in the following discussions.

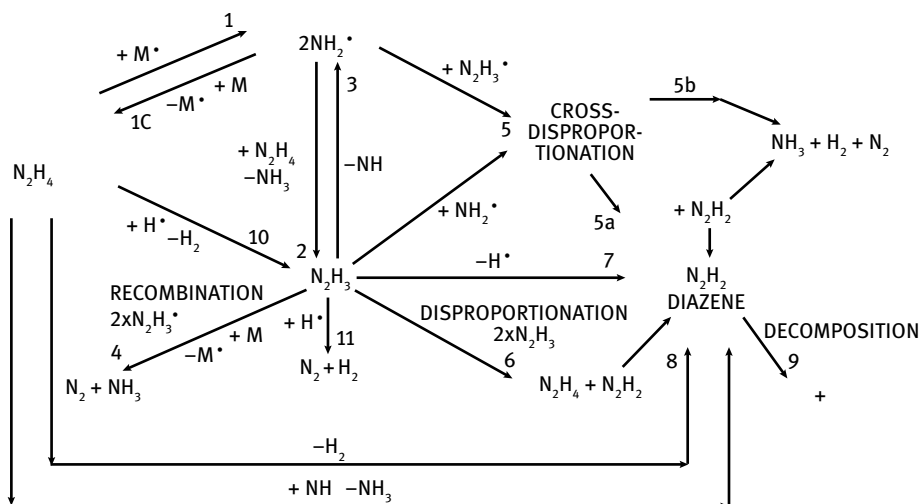


Figure 38: Schematic of hydrazine decomposition reactions

The kinetic parameters for thermal decomposition of hydrazine vapor in oxygen and nitrogen atmospheres were determined by a non-linear isoconversional method [1189]. From thermographic data at heating rates of 5, 10, and 20 °C/min, kinetic parameters could be determined in nitrogen ( $E_{act} = 47.3 \pm 3.1$  kJ/mol,  $\ln A = 14.2 \pm 0.9$ , and  $T_b = 342$  K = 69 °C) and oxygen ( $E_{act} = 64.9 \pm 8.6$  kJ/mol,  $\ln A = 20.7 \pm 3.1$ , and  $T_b = 348$  K = 75 °C) atmospheres. It was not possible to identify a specific kinetic model for hydrazine thermal decomposition due to high heterogeneity in reaction.

#### 4.4 Thermal Decomposition of Hydrazine

The following sections attempt to separate the inevitable effects of wall materials from the kinetics of hydrazine decomposition in the absence of catalysts. Of all the many modes of hydrazine decomposition, the thermal and heterogeneous catalytic decomposition of hydrazine are the two with the most practical importance.

Unfortunately, thermal initiation does not initiate only one specific reaction (as selected wavelength photolysis would do), but a host of competing reactions are ini-

tiated and proceed to varying levels of completion at the same time once the temperature is high enough. Once the critical energy threshold is exceeded, the remainder of the decomposition proceeds in a self-accelerating, avalanche-type fashion. It is difficult to maintain isothermal conditions under these circumstances. The following sections are subdivided by the physical state of hydrazine undergoing the decomposition, hydrazine vapor, hydrazine liquid, and hydrazine solutions.

#### 4.4.1 Thermal Decomposition of Hydrazine Vapor

Most academic thermal decomposition studies (as well as those with other modes of initiation) were conducted with hydrazine vapor. The most dangerous part of these experiments if they are conducted in a flow reactor is the possibility that decomposition may propagate upstream from the reaction zone into the hydrazine vapor reservoir. One will therefore want to minimize the size of the reservoir and use methods where liquid hydrazine is vaporized rapidly without accumulating more vapor than needed to achieve temperature equilibrium before entering the reaction zone. Very little is known about the purely thermal decomposition of the liquid because it only occurs at temperatures where there is already a significant fraction of vapor in the system. A frequent problem is the interaction with the container material, and different results are obtained depending on the type of containment. The current section summarizes decomposition studies with thermal heating (stationary or dynamic flow reactors). Shock-tube studies, essentially also a mode of thermal decomposition but with the heating provided by rapid compression, are summarized in Section 4.4.10.

The use of  $^{15}\text{N}$  isotope-labeled hydrazine has proved very useful in several hydrazine decomposition kinetics studies, including thermal decomposition. In thermal as well as in photolytic decomposition, two different hypotheses have been proposed for the mechanism, and arguments have been advanced to support or disprove each of these possible mechanisms. Even though some of the work referenced in this summary on hydrazine decomposition may already have been superseded by later publications, it is still useful to illustrate the difficulty in obtaining conclusive proof of the decomposition mechanism. With regard to some of the questions, the discussion is still in full swing and the mechanism of hydrazine decomposition is still being actively investigated.

When comparing thermal hydrazine decomposition in a flow reactor to that induced by an alternating current-glow discharge in a flow reactor, the existence of a threshold level of decomposition was a new observation [1190]. The threshold level and experimental data could be explained with a mechanism consisting of three regimes. The first regime is responsible for threshold phenomena, the second regime for the reformation of hydrazine, and the third for the slow decomposition.

Unimolecular rate constants for hydrazine dissociation by thermal and chemical activation have been calculated according to the Rice Ramsperger Kassel Marcus (RRKM) theory [1191]. The two activated complex models used in the calculations rep-

resent plausible upper and lower bounds to the rate constants. The calculations were mainly directed at establishing expected decomposition to stabilization ratios of  $\text{N}_2\text{H}_4$  produced by the (re)combination of  $\text{NH}_2$  radicals; however, a general comparison with available experimental data for hydrazine dissociation was also made.

A useful summary of rate constants reported by various investigators has been compiled as shown in Table 51 [1192]. The results for the rate constant, pre-exponential factors, and activation energies vary widely, depending on the experimental technique used. Note that the gas constant  $R$  has already been combined with the activation energy in the dividend above the line of the quotient that makes up the exponent of  $e$ . Despite the wide scatter of data, several investigators obtained similar activation energies for the overall reaction at high pressures, near 225 kJ/mol.

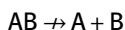
**Table 51:** Activation energy of hydrazine vapor decomposition.

| Temperature, K           | Rate constant $k$                   | Order       | References |
|--------------------------|-------------------------------------|-------------|------------|
| 935–1085                 | $3.5 \times 10^8 \exp(-15800/T)$    | 1 (or 1/2?) | [1193]     |
| 750–1000                 | $2.2 \times 10^{10} \exp(-18200/T)$ | 1           | [1194]     |
| 1100–1600                | $5 \times 10^{12} \exp(-26170/T)$   | 1           | [1195]     |
| 1100–1600                | $4 \times 10^{15} \exp(-20640/T)$   | 2           | [1196]     |
| $T_{\text{initial}} 333$ | $10^{17} \exp(-17861/T)$            | 2           | [1154]     |
| 1100–1400                | $4 \times 10^{13} \exp(-26700/T)$   | 1           | [1197]     |
| 1100–1650                | $10^{16.25} \exp(-32300/T)$         | 1           | [1198]     |

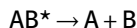
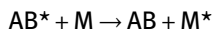
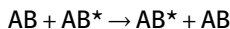
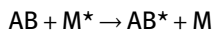
#### 4.4.2 Free-Radical Mechanisms

One of the questions regarding the decomposition mechanism of hydrazine was whether free radicals are involved. In the following sections, free radicals are indicated by the symbol for the free electron  $\bullet$  added to their formula. Prior to the advent of sophisticated electronic equipment, ortho conversion of para-hydrogen was usually taken as an indication for the presence of free radicals in a reaction. However, no *para-ortho* conversion was detected when hydrazine and parahydrogen were heated to 473 K [1199]. This was initially interpreted as evidence against a radical mechanism [1200]. Szwarc also identified the first step of the hydrazine decomposition to be a dissociation into amino radicals and later proved the presence of amino radicals by reactions with toluene. It is now generally assumed that the thermal and photolytic decomposition of hydrazine involves free radicals.

In a thermal decomposition reaction in the gas phase, the molecules obtain the energy for initiating decomposition by collisional energy transfer. In general terms, a compound AB, such as  $\text{N}_2\text{H}_4$ , does not decompose directly to A and B

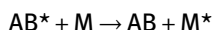


Instead, collisions with third bodies M or already excited AB molecules raise AB to an excited state  $AB^*$ , from which it can either deactivate itself by collision with another molecule M or undergo decomposition:

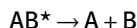


The asterisk \* is used in these equations to identify excited molecules with a statistically significant number of higher states of excitation populated.

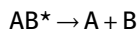
The deactivation



and decomposition

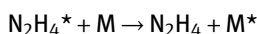
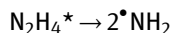
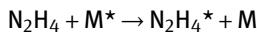


reactions compete for the activated  $AB^*$  molecules. The rate of the reaction will be quite different at high pressures, where intermolecular collision is frequent, as opposed to low pressure, where decomposition

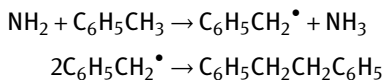


is allowed to proceed because the time between collisions is long compared to the half-life time of the excited state. Consequently, one can differentiate between low-pressure and high-pressure mechanisms. The effect of the nature of diluents (third body M) is more pronounced at low pressures than at high pressures. At the high-pressure limit, the effectiveness with which the third body M transfers energy into a collision is of little consequence because statistically there are sufficient collisions taking place to maintain a stationary concentration of  $AB^*$ . However, at low pressure, differences in the effectiveness of  $M^*$  become more pronounced.

The decomposition of hydrazine is presumed to be a chain reaction that, not unlike other chain reactions, can achieve explosive force. All free-radical chain reactions include four fundamental steps: initiation, propagation, branching, and termination. In the case of hydrazine, the first step is the dissociation into  $^{\bullet}NH_2$  radicals (reaction number 1 in Figure 38):



In a study of the bond strength of the N—N bond, hydrazine was decomposed in the presence of toluene in a heated tubular flow reactor presumed to be isothermal [1200]. Toluene served as a radical scavenger for the amino radical by way of



By analyzing the reaction product (dibenzyl) concentration, Szwarc calculated the rate of formation of  $\text{NH}_2$  radicals from  $\text{N}_2\text{H}_4$ :

$$\frac{d[\text{N}_2\text{H}_4]}{dt} = 4 \times 10^{12} e^{\frac{-60000}{RT}} [\text{N}_2\text{H}_4] \quad \text{s}^{-1}$$

Based on this equation, Szwarc [1200] postulated a homogeneous, unimolecular first-order gas reaction. The fraction of hydrazine decomposing to ammonia, nitrogen, and hydrogen was proportional to the surface: volume ratio of the reactor. However, the dibenzyl yield was independent of the surface ratio, which would indicate that the first step is a vapor-phase reaction, whereas consecutive steps leading to hydrazine decomposition depend on the presence of a surface. Szwarc concluded that the reaction does not depend on  $\bullet\text{NH}_2$  free radicals because the presence of a surface would accelerate hydrazine decomposition, but not the rate of  $\text{NH}_2$  radical (and dibenzyl) formation.

In later studies, some doubt was thrown on Szwarc's data by pointing out that the inlet portion of his reactor was not truly isothermal [1201, 1202]. An attempt was made to re-interpret Szwarc's results by assuming that the formation of  $\bullet\text{NH}_2$  radicals is a second-order rather than a first-order reaction. The re-evaluation of the same experimental data gave a rate constant and a reaction order that is, again, consistent with the results obtained from flame data:

$$k = 10^{19} e^{\frac{-60000}{RT}} \quad \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$$

The experimental results obtained by Szwarc have been discussed and interpreted (or misinterpreted) by numerous investigators, but only one experimental work has become known to check the validity of Szwarc's initial results. The pyrolysis of hydrazine, MMH, and benzylamines was studied by the toluene-carrier technique [1203]. Whereas Szwarc calculated the rate constants for the decomposition of hydrazine from the amount of dibenzyl produced, the exhaust gas composition was now used to calculate the rate constants. The later work discovered that the rate constant  $k_1$  was markedly dependent on toluene pressure, whereas this dependence was previously dismissed as unimportant. The value  $k_1$  is nearly proportional to pressure, whereas Szwarc has postulated independence of the rate on pressure. The pressure dependence of  $k_1$  supports Gilbert's conclusion that the unimolecular reaction forming  $\text{NH}_2$  radicals in the hydrazine flame reaction is in the second-order region. It substanti-

ates his reappraisal of Szwarc's results based on a non-isothermal reactor [1201, 1202], also [1204]. The Arrhenius plot equations by [1205] and [1200] agree closely:

$$\log k_1 = 11.70 - \frac{54150}{2.3RT} \quad (2)$$

$$\log k_1 = 11.39 - \frac{54000}{2.3RT} \quad (3)$$

The following heats of formation have been calculated by equating activation energies with the strengths of bonds broken [1203]:

$$(\Delta H)_f^\circ \quad \bullet\text{NH}_2 \quad 39.8 \text{ kcal/mol} = 166 \text{ kJ/mol}$$

$$(\Delta H)_f^\circ \quad \text{CH}_3\text{NH}\bullet \quad 34.5 \text{ kcal/mol} = 144 \text{ kJ/mol}$$

$$(\Delta H)_f^\circ \quad (\text{CH}_3)_2\text{N}\bullet \quad 29.5 \text{ kcal/mol} = 123 \text{ kJ/mol}$$

This indicated that methyl substitution has a greater weakening effect on N—H and N—N bonds than on the corresponding C—H and C—C bonds.

Because the amino radical plays a key role in the decomposition of hydrazine, its thermochemical and kinetic properties should be thoroughly understood. In another study, it was found that the heat of formation of the amino radical is actually 197 kJ/mol (47.2 kcal/mol), which leads to a dissociation energy  $\text{DH}_0(\text{NH}_2\text{—H})$  of 460 kJ/mol (110 kcal/mol), considerably higher than the value assumed in previous studies [1206].

The decomposition of hydrazine vapor in a quartz tube at 1123 K and 66 Pa and the trapping of decomposition products on a liquid-nitrogen-cooled cold finger moved different distances from the reaction zone resulted in the formation of yellow, short-lived deposits thought to contain hydrazyl radicals and tetrazene [1207]. The yellow material was stable in the solid state at 78 K but decomposed rapidly on thawing. A color change from yellow to white occurred at 95 K. Unfortunately, the investigator overlooked the possibility of forming diazene. Labeling studies with the simultaneous decomposition of  $^{15}\text{N}_2\text{H}_4$  and  $^{14}\text{N}_2\text{H}_4$  showed complete randomization, explained by the presence of hydrazyl radicals.

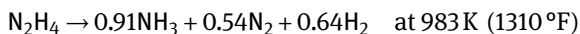
Hydrazine vapor decomposition tests in an all-quartz isothermal reactor at ambient overall pressure but very low hydrazine partial pressures (achieved by dilution with argon as the inert gas) showed that under these conditions the decomposition is completely heterogeneous over the entire temperature range 542–910 K [1208]. Hydrazine concentrations were on the order of 0.1–4 mM/L, and contact times were on the order of 1 s. The decomposition products consisted mainly of ammonia and nitrogen, with some hydrogen observed only at higher temperatures. Since ammonia itself would not decompose in this apparatus at the highest temperature tested, the source of hydrogen had to be a side reaction of hydrazine decomposition, and not secondary ammonia decomposition. The reactor itself had a surface:volume ratio of  $2.5 \text{ cm}^{-1}$ . When the surface:volume ratio was increased by a factor of 7 to a ratio of  $18 \text{ cm}^{-1}$ ,



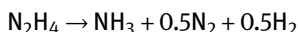
the rate of decomposition increased by a factor of up to 23-fold. This indicated that the reaction is very sensitive to surface condition and that the quartz rods inserted to increase the surface may have been of a purity (level of catalytic activity) different from that of the quartz tube from which the reactor was built. The activation energies of the decomposition reactions in the empty and packed reactor were also slightly different. Since this ancient, early (1951) study did not use anhydrous hydrazine, but only a 95.5%  $\text{N}_2\text{H}_4$ /4.5%  $\text{H}_2\text{O}$  mix, rate constants and activation energies would be different from those of pure hydrazine anyway. Decomposition rates were the same, regardless of whether argon or nitrogen was used to dilute the hydrazine vapor.

The discussion about the validity of Szwarc's results illustrates the difficulty in choosing a proper experimental technique. The Princeton adiabatic flow reactor offers significant advantages over an isothermal reactor but is considerably more complex [348]. It does not suffer from mixing and temperature non-uniformity problems encountered in isothermal bombs and isothermal flow reactors. The adiabatic flow reactor provides data in a reaction rate regime that is too slow for shock tubes and too fast for isothermal bombs. Even in a very comprehensive study, one can read the statement that *"Despite all work done on hydrazine decomposition, the overall mechanism by which this decomposition proceeds is still not understood. For the case of hydrazine derivatives, the situation is even worse"* [348]. In the 58 years since publication of this statement (1964), the reaction has been studied intensively but is still not completely understood, in particular as soon as one leaves the low-pressure regime of a few mm Hg pressure.

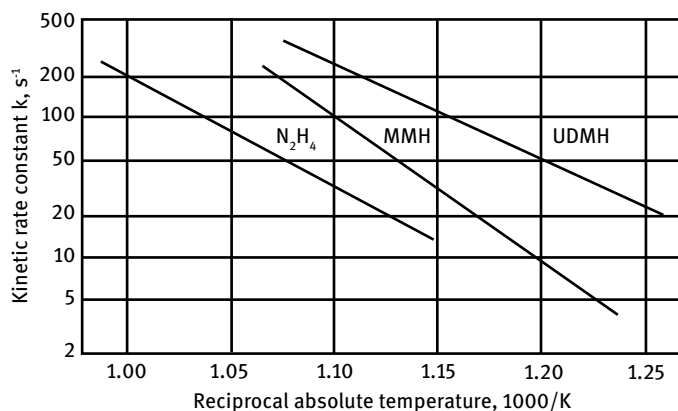
The most comprehensive study of thermal gas-phase decomposition of hydrazine and its methyl derivatives was conducted at Princeton University [348, 1209]. The Princeton adiabatic flow reactor was made entirely of quartz to minimize decomposition of hydrazine in the injector portion [348]. In an earlier model with stainless-steel injector and reactor, the hydrazine decomposed prematurely by contact with the walls. The flow conditions were highly turbulent to promote rapid mixing of injected hydrazine with the carrier gas stream to prevent back diffusion. The molar fraction of reactant in diluent helium or nitrogen gas rarely exceeded 0.02. Different duct diameters (7.5 or 10 cm = 3 or 4 in.) were used to vary the heat loss/heat compensation condition and to verify that the system was truly adiabatic. The overall stoichiometry could be described by the following equation:



Similar decomposition product compositions had been observed in flame studies, such as those by [1210] discussed in Section 4.9:



The results of this study show (Figure 39) the rate constants of thermal decomposition of hydrazine and its methyl derivatives as a function of reciprocal absolute temperature. The activation energy can be derived from the slope of the lines.



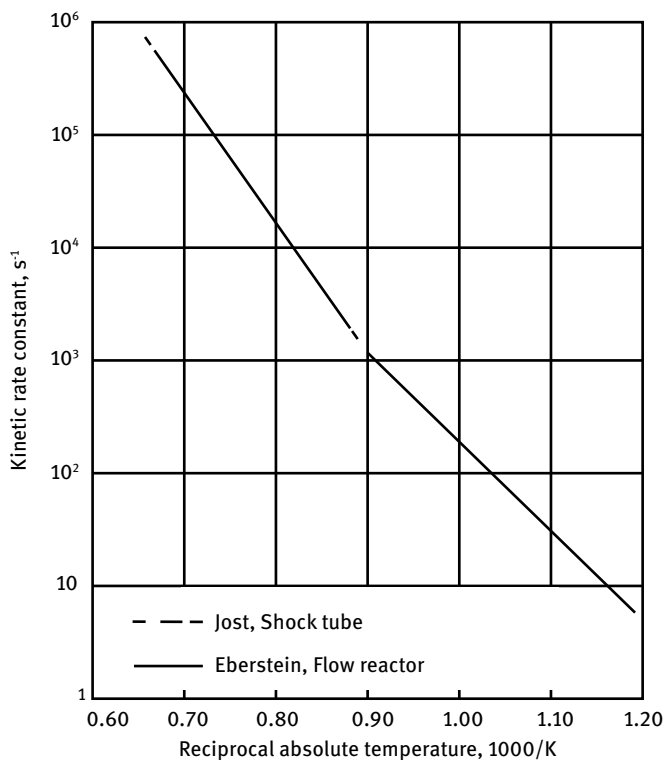
**Figure 39:** Comparison of decomposition rates of hydrazine, MMH, and UDMH vapor in 76-mm reactor. (Reproduced and modified from [348].)

One seeming contradiction is the fact that the rate constant for UDMH at a given temperature is higher than that of MMH or hydrazine, although in other parts of this book it was stated that the thermal stability of hydrazine increases in the order hydrazine, MMH, and UDMH. Apparently, additional factors become important in the decomposition of hydrazine at higher concentrations than those studied in the Princeton reactor. The decomposition of methylhydrazine will be discussed in the chapter “Methylhydrazine.”

Figure 40 shows that the adiabatic flow reactor and shock-tube results complement each other very nicely and good agreement exists in the overlapping temperature range.

The overall mechanism of hydrazine decomposition can be broken down into the 10 equations that are shown in Table 52 along with the rate constants suggested by Eberstein [348]. All 10 equations were combined in a computer program and solved for temperatures and constant concentrations and for concentrations at constant temperatures. The combined rate of hydrazine consumption agreed well with experimental shock tube and adiabatic flow reactor data.

In interpreting the results of his study, Eberstein [348] cautioned that the assumption of one generally valid reaction order and the application of the relatively simple Arrhenius equation may lead to oversimplification of a complex reaction mechanism. Also, the effect of impurities must be considered. The hydrazine used in his study had a surprisingly high content of ammonia (8.3% NH<sub>3</sub>, 0.5% H<sub>2</sub>O, 0.3% C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, 90.9% N<sub>2</sub>H<sub>4</sub>), and one wonders what effect this high initial ammonia concentration might have had on the exhaust composition. In addition, nitrogen (which may have contained traces of oxygen) was used as a carrier gas to dilute the incoming hydrazine vapor and may have contributed to some of the decomposition products. Experiments eliminating any impurities and participation of the carrier gas have been suggested.



**Figure 40:** First-order rate constants for hydrazine vapor decomposition in flow reactors and shock tubes. (Reproduced and modified from [348].)

Amino radical  $\text{NH}_2$  profiles were measured in a discharge flow reactor at ambient temperature by monitoring reactants and products with an electron impact mass spectrometer [1211]. At the low pressures used (0.7 and 1.0 mbar) the gas-phase self-reaction was dominated by a “bimolecular”  $\text{H}_2$ -eliminating exit channel with a rate coefficient of  $k_3$  (300 K) =  $(1.3 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and leading to  $\text{N}_2\text{H}_2 + \text{H}_2$  or  $\text{NNH}_2 + \text{H}_2$ . The heterogeneous recombination reaction along the walls yields  $\text{N}_2\text{H}_4$  molecules.

One of the reactions for hydrazine decomposition is its splitting into two amino radicals. The rate constant for the reverse reaction, the rate of recombination of two amino radicals, was measured in  $\text{CF}_4$ ,  $\text{N}_2$  or Ar carrier gases at  $293 \pm 2 \text{ K}$  over a pressure range of 0.27 to 1.33 kPa (2 to 10 mm Hg) [1212]. The  $\text{NH}_2$  radicals were produced by the 193 nm photolysis of  $\text{NH}_3$  diluted in the carrier gas. The low-pressure rate constant showed a linear dependence on pressure. The slope of the pressure dependence was dominated by a recombination rate constant for  $\text{NH}_2 + \text{NH}_2$  given by  $(8.0 \pm 0.5) \times 10^{-29}$ ,  $(5.7 \pm 0.7) \times 10^{-29}$ , and  $(3.9 \pm 0.4) \times 10^{-29} \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  in  $\text{CF}_4$ ,  $\text{N}_2$ , and Ar diluent

**Table 52:** Mechanism of hydrazine decomposition.

| Reaction number     | Reaction                                         | Rate constant                                                    |
|---------------------|--------------------------------------------------|------------------------------------------------------------------|
| <i>Initiation</i>   |                                                  |                                                                  |
| (1)                 | $X^* + N_2H_4 \rightarrow X + 2^*NH_2$           | $k_1 = 10^{19} e^{(-60000/RT)}$                                  |
| <i>Propagation</i>  |                                                  |                                                                  |
| (2)                 | $N_2H_4 + ^*NH_2 \rightarrow ^*N_2H_3 + NH_3$    | $k_2 = k_4 = 10^{13} e^{(-7000/RT)}$                             |
| (3)                 | $^*N_2H_3 + X \rightarrow N_2 + H_2 + H^* + X^*$ | $k_3 = 10^{13} e^{(-20000/RT)}$                                  |
| (4)                 | $H^* + N_2H_4 \rightarrow NH_3 + ^*NH_2$         | $k_4 = k_2$                                                      |
| <i>Branching</i>    |                                                  |                                                                  |
| (5)                 | $^*N_2H_3 + X \rightarrow NH + ^*NH_2 + X$       | $k_5 = 10^{12.8} e^{(-18000/RT)}$                                |
| (6)                 | $N_2H_4 + NH \rightarrow ^*NH_2 + ^*N_2H_3$      | $k_6 = 10^{14} e^{(-10000/RT)}$                                  |
| <i>Termination</i>  |                                                  |                                                                  |
| (7)                 | $^*NH_2 + ^*N_2H_3 \rightarrow NH_3 + N_2 + H_2$ | $k_7 = 10^{12.5} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   |
| (8)                 | $^*N_2H_3 + ^*N_2H_3 \rightarrow 2NH_3 + N_2$    | $k_8 = 10^{12.3}$                                                |
| (9)                 | $^*N_2H_3 + ^*H \rightarrow N_2 + H_2$           | $k_9 = 10^{15}$                                                  |
| (10)                | $^*NH_2 + ^*NH_2 \rightarrow N_2H_4$             | $k_{10} = 10^{13}$                                               |
| <i>Deactivation</i> |                                                  |                                                                  |
| (11)                | $^*N_2H_3^* + X \rightarrow ^*N_2H_3 + X^*$      | $k_{11} = 10^{6.5} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |

Data source: [348]

gases, respectively. The average of the three independent measurements of the sum of the disproportionation rate constants (the zero pressure rate constant) was  $(3.4 \pm 6) \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

Recombination of two amidogen  $NH_2$  radicals is relevant to hydrazine formation, ammonia oxidation and pyrolysis, nitrogen reduction (fixation), and a variety of other N/H/X combustion, environmental, and interstellar processes. A comprehensive analysis of the  $H_2NNH_2$  potential energy surface was performed using a variety of theoretical methods, with thermochemical kinetic analysis and master equation simulations used to treat branching to different product sets in the chemically activated  $NH_2 + NH_2$  process [426]. Iminoammonium ylide ( $NH_3NH$ ), the less stable isomer of hydrazine, was included in the kinetic modeling of  $H_2NNH_2$  decomposition. A new, low-energy pathway was identified for the formation of  $NH_3$  plus triplet  $NH$ , via initial production of  $NH_3NH$ . This reaction channel resulted in the formation of dissociated products at a relatively rapid rate at even moderate temperatures. Another pathway for the decomposition of activated  $H_2NNH_2$  eventually leads to the formation of the simple products  $N_2 + 2H_2$  via  $H_2$  elimination to *cis*- $HN=NH$ . This process, referred to as “dihydrogen catalysis,” may have significant implications in the formation and decomposition chemistry of hydrazine and ammonia in diverse environments. In this mechanism, stereoselective attack of *cis*- $HN=NH$  by molecular hydrogen results in decompo-

sition to  $N_2$  with a fairly low barrier. The reverse termolecular reaction leading to the gas-phase formation of  $cis\text{-HN=NH} + H_2$  achieves non-heterogeneous catalytic nitrogen fixation with a relatively low activation barrier ( $322\text{ kJ/mol} = 77\text{ kcal/mol}$ ), much lower than the  $523\text{ kJ/mol}$  ( $125\text{ kcal/mol}$ ) barrier reported for bimolecular addition of  $H_2$  to  $N_2$ .

The recombination rate constants for the reactions  $NH_2 + NH_2 \rightarrow N_2H_4$  (reaction  $k_1b$ ) and  $NH_2 + H \rightarrow NH_3$  (reaction  $k_2b$ ) with  $N_2$  as a third-body have been measured as a function of temperature and pressure in a temperature range of 292 to 533 K and a pressure range of a few mm Hg up to 40–53 kPa (300–400 mm Hg), well within the pressure fall-off region [1213]. The  $NH_2$  radicals were produced by 193-nm pulsed-laser photolysis of  $NH_3$  in a temperature-controlled flow chamber. The pressure and temperature dependence of  $k_1b$  could be represented by a group of parameters.

If hydrazyl radicals exist as intermediates in the hydrazine decomposition, they themselves will soon undergo further decomposition, and attempts were made to obtain a rate constant for this process [1214].

#### 4.4.3 Water Vapor as Inhibitor of Hydrazine Decomposition

Another common contaminant or sometimes a desirable additive to hydrazine is water. The effect of water on the rate of decomposition has been studied repeatedly [348, 1215]. It was found that the rate of decomposition of hydrazine/water mixtures (25%  $H_2O$  and 50%  $H_2O$ ) was 10 times slower than that of anhydrous hydrazine [348]. Surprisingly, it is independent of the amount of water added. The 25 and 50%  $H_2O$  mixtures behaved kinetically like wet hydrazine samples with 0.8 or 0.9%  $H_2O$ , respectively.

It was noted that wet hydrazine and hydrazine/water mixtures decompose at a rate that appeared to be independent of the surface:volume ratio. The effect of water on the decomposition rate goes beyond that of a simple diluent and would indicate some kind of inhibition on a rate-determining step. It has been hypothesized that water is 100 times more active in absorbing vibrational energy from vibrationally excited species with which it collides than, for example, nitrogen. Water has more freedom of vibration and, if colliding with an activated  $N_2H_3^*$  radical or  $N_2H_4^*$  molecule that otherwise would decompose forming chain-propagating  $^{\bullet}NH_2$  radicals, will deactivate that molecule or radical.

#### 4.4.4 Inhibiting Effects of Permanent Gases

The decomposition of hydrazine vapor in equilibrium with hydrazine liquid and the effect of hydrogen, nitrogen, or argon on the decomposition limits were studied in a glass apparatus using electrical arc ignition with tungsten electrodes [1216]. Decomposition flames were obtained in saturated vapor above 310 K, corresponding to a vapor pressure of 3.16 kPa (23.8 mm Hg). For unsaturated conditions, the threshold

pressure increased with temperature, which is somewhat surprising since the opposite trend should be expected from kinetic data. Of the three gases evaluated as potential decomposition-inhibiting blanketing gases for hydrazine distillation, hydrogen was the most active, nitrogen intermediate, and argon the least active diluent. The difference in activity is thought to be related to their heat capacity, not a kinetic interaction with the decomposition mechanism.

#### 4.4.5 Inhibiting Effects of Organic Vapors

In a similar way, organic vapors were tested as additives in a decomposition apparatus [1217]. The vapor concentration of additive above which hydrazine vapor mixtures will not decompose explosively decreases in the order argon (71.9), nitrogen (64.8), hydrogen (45.9), benzene (27.9), toluene (24.0), xylene (20.0), butane (17.3), hexane (12.8), and heptane (11.9). Organic vapors are thus more effective at suppressing hydrazine vapor decomposition than are inorganic gases. Aniline was also tested, but its effectiveness depended on the total pressure in the system because its boiling point is so different from that of hydrazine. Heptane is a useful blanketing fluid for the distillation of anhydrous hydrazine. Additional studies on the effect of diluents and inhibitors on the explosive decomposition limits of hydrazine vapors are discussed in Section 8.4.2. These tests relate more to the handling safety of hydrazine than to the elucidation of the decomposition mechanism of hydrazine, to which this chapter is devoted.

Subsequent investigators have analyzed Eberstein's data and attempted to fit them to their own kinetic models (in particular those providing overall kinetics) and tried to expand the range of validity of kinetic equations to higher hydrazine partial pressures up to atmospheric [1218]. Using an asymptotic analysis based on large differences among the rate constants of several elementary reactions, it was shown that the Eberstein-Glassman mechanism for the thermal decomposition of hydrazine could be expressed by an overall rate equation between 750 and 1000 K. Data on the rate constants of homogeneous hydrazine decomposition are summarized in Table 53. Depending on the technique used, the results differ widely, even in the assignment of a reaction order for the global decomposition rate equation. At high pressure, the activation energy seems to be on the order of 225 kJ/mol.

#### 4.4.6 Isotope Effects on the Decomposition of Hydrazine

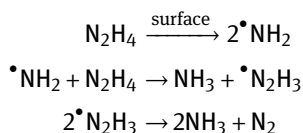
A study on the thermal decomposition of  $^{15}\text{N}$ -labeled hydrazine was somewhat hampered by the fact that the  $^{15}\text{N}$  isotope concentration in the starting material was only 32% [1224]. The results agree with a later study on the photolysis of hydrazine [1153] in that in neither case was randomization of nitrogen observed. Kant and McMahon [1224] share the opinion of Szwarc [1200] that free radicals are not involved in the thermal decomposition of hydrazine. Since it is very difficult to eliminate the effects of the surface of the reaction vessel, at least part of the thermal decomposition of hydrazine

**Table 53:** Rate constants of homogeneous hydrazine decomposition.

| Reaction                                                                                                   | Rate constant <i>k</i>                                                              | References |
|------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|------------|
| $\text{H}^\bullet + \text{N}_2\text{H}_3 \rightarrow 2^\bullet\text{NH}_2$                                 | $(1.6 \pm 0.8) 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K       | [1219]     |
| $^\bullet\text{NH}_2 + \text{N}_2\text{H}_4 \rightarrow \text{NH}_3 + ^\bullet\text{N}_2\text{H}_3$        | $(3.1 \pm 0.4) 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300 K       | [1219]     |
| $^\bullet\text{NH}_2$ recombination : disproportionation ratio $k_1/k_2 = 4.710^6 \text{ cm}^3/\text{mol}$ |                                                                                     | [1219]     |
| Global reaction rate $\text{N}_2\text{H}_4$                                                                | $10^{10.33} e^{(-36200/RT)} \text{ s}^{-1}$                                         | [330]      |
| Global reaction rate $\text{N}_2\text{H}_4$                                                                | $410^{13} e^{(-26700/T)} \text{ s}^{-1}$ <sup>b</sup>                               | [1197]     |
| Global reaction rate $\text{N}_2\text{H}_4$                                                                | $510^{12} e^{(-26170/T)} \text{ s}^{-1}$ <sup>b</sup>                               | [1195]     |
| Global reaction rate $\text{N}_2\text{H}_4$                                                                | $2.210^{10} e^{(-18200/T)} \text{ s}^{-1}$ <sup>b</sup>                             | [1194]     |
| For comparison:                                                                                            |                                                                                     |            |
| Global reaction rate MMH                                                                                   | $10^{8.84} e^{(-26700/RT)} \text{ s}^{-1}$                                          | [348]      |
| Global reaction rate UDMH                                                                                  | $10^{13.4} e^{(-47000/RT)} \text{ s}^{-1}$                                          | [348]      |
| $\text{N}_2\text{H}_4 \rightarrow 2^\bullet\text{NH}_2$                                                    | $410^{12} e^{(-60000/RT)} \text{ s}^{-1}$                                           | [1200]     |
| $\text{N}_2\text{H}_4 \rightarrow 2^\bullet\text{NH}_2$                                                    | $10^{15.6} e^{(-41000 \pm 2000/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$   | [1220]     |
| $\text{H}^\bullet + \text{N}_2\text{H}_4 \rightarrow ^\bullet\text{N}_2\text{H}_3 + \text{H}_2$            | $1.310^{13} e^{(-2500/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$            | [1219]     |
| $\text{H}^\bullet + \text{N}_2\text{H}_4 \rightarrow ^\bullet\text{N}_2\text{H}_3 + \text{H}_2$            | $1.510^{12} e^{(-1300 \pm 200/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$    | [1221]     |
| $\text{H}^\bullet + \text{N}_2\text{H}_4 \rightarrow ^\bullet\text{N}_2\text{H}_3 + \text{H}_2$            | $\text{Be}^{(-2000/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$               | [1222]     |
| $\text{H}^\bullet + \text{N}_2\text{H}_4 \rightarrow ^\bullet\text{N}_2\text{H}_3 + \text{H}_2$            | $9.87 \pm 1.17 10^{12} e^{(-2380/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | [1223]     |

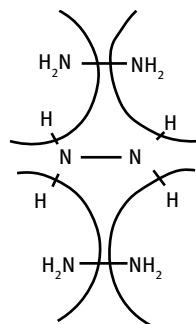
<sup>a</sup> All activation energies in cal/mol.<sup>b</sup> It appears that the gas constant *R* has already been factored into the denominator

may proceed by means of a heterogeneous surface reaction. If it did proceed through the following sequence of reactions,

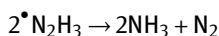


complete randomization of nitrogen would have to be expected. Instead, the non-occurrence of randomization was temporarily explained by a transition complex involving three hydrazine molecules, from which nitrogen would evolve without breaking an N—N linkage.

The dashed lines in the following scheme indicate the fashion in which this transition complex would break up. An arrangement of this kind would be achieved only on surfaces, not in the gas phase. If randomization had been observed, it would be important to know whether it occurred during hydrazine decomposition or was a reaction that dinitrogen molecules underwent after they were formed. However, dinitrogen molecules are thermally very stable, and nitrogen isotope randomization can be achieved only at temperatures above 970 K.



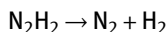
At the time of that study, the ratio of disproportionation : recombination of hydrazyl radicals according to



was not yet known. Later photolytic studies have shown that this ratio is surprisingly high and accounts for the non-randomization, even though hydrazyl radicals are involved [1152]. The ratio of disproportionation : recombination of hydrazyl radicals was found to be approximately four. To explain this mechanism, it is necessary to assume that two hydrazyl radicals must collide in the proper sterical arrangement for the disproportionation to take place. The mechanism may also be favored by an (only transient) stability of an intermediately formed tetrazane. Nevertheless, it is more likely to have two hydrazyl radicals in proper arrangement than three hydrazine molecules, as postulated by the Szwarc surface mechanism. The ratio of disproportionation to combination for hydrazyl radicals is nearly 30 times larger than that for the analogous  $^{\bullet}\text{C}_2\text{H}_5$  radical.

A transition or hybrid mechanism between thermal and photolytic decomposition has been postulated for the flash photolysis of hydrazine [521, 1225]. The high-intensity flash was only used to raise temperature of the vapor rapidly to a desired decomposition temperature, and short wavelengths were filtered out. With this method, undesirable interference by hot surfaces can be eliminated. The conversion is small, generally below 10%, as opposed to thermal experiments, which usually allow the decomposition to go to completion.

The decomposition of  $^{15}\text{N}$ -isotope-labeled hydrazine by flash photolysis showed that no nitrogen randomization occurred and the yield of  $^{14}\text{N}^{15}\text{N}$  was very low [1226]. This agrees with previous thermal [1224] and photolytic [1153] isotope studies and heterogeneous decomposition results discussed in Sections 4.6.1 and 4.6.4. It has also been observed that the ratio of hydrogen : nitrogen was always close to 1.0. This can be explained by assuming that hydrogen and nitrogen are formed by the decomposition of diazene:





while at the same time maintaining the isotope distribution in nitrogen. The  $\text{N}_2$  formed by the flash photolysis of hydrazine was found to be only 17% randomized (compared to 13% for photolytic decomposition). An excess of  $^{14}\text{N}_2$  formed in the decomposition of 1:1 mixtures of  $^{14}\text{N}_2\text{H}_4$  and  $^{15}\text{N}_2\text{H}_4$  remained unexplained. The photolysis of hydrazine at 133 Pa (1 mm Hg) in a 75-mL cylindrical quartz vessel with a single jolt of 720 J resulted in the decomposition of approximately 10% of the hydrazine present [1153, 1227].

Besides isotope labeling, the addition of radical scavengers sometimes provides insight into the radical mechanisms of thermal as well as the photolytic decomposition of hydrazine. Most studies of this type have been conducted in relation to the photolysis of hydrazine, but it was also used to study the slow thermal decomposition of hydrazine vapor [1228]. The decomposition rate of  $\text{N}_2\text{D}_4$  has been shown to be markedly different from that of  $\text{N}_2\text{H}_4$  as a result of the isotope effect [1154].

#### 4.4.7 Effects of Wall Materials on Decomposition of Hydrazine

It would be important to find wall materials that will not only not catalyze the decomposition of hydrazine but even retard the unwanted decomposition that may occur when hydrazine is distilled. The effect of various reaction vessel materials and surface coatings on the thermal decomposition of hydrazine was studied in an early investigation [1229–1231]. Calcium oxide and cadmium sulfide increased the rate of decomposition between 570 and 770 K in a flow system more than did Pyrex. A zinc oxide/potassium hydroxide/water glass surface acted like uncoated Pyrex glass. A mixture of aniline and toluene has been suggested as additive to inhibit the unwanted thermal (homogeneous) or catalytic (heterogeneous) decomposition of hydrazine vapor during hydrazine manufacturing operations [1232, 1233].

#### 4.4.8 Diazene as Intermediate in Hydrazine Decomposition

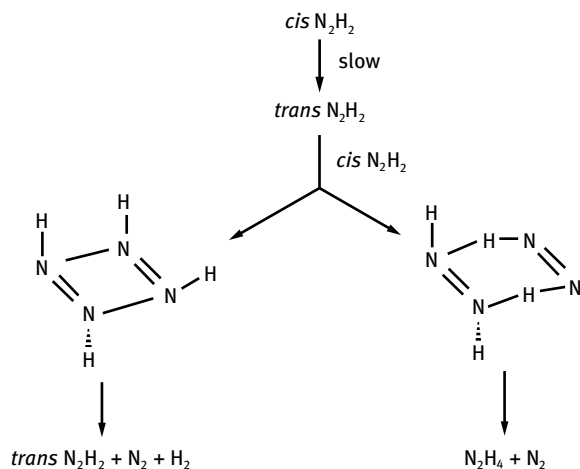
A complete understanding of the decomposition of hydrazine must include the nature of the intermediates that play a role in the decomposition mechanism. Obviously, many nitrogen-hydrogen free radicals and short-lived molecules, such as diazene, play an important role in the decomposition of hydrazine, regardless of whether it is initiated thermally, photolytically, or by any other means. The same is true for the oxidation of hydrazine in both gas phase and solution. Several publications deal with the properties of these radicals and short-lived molecules regardless of their path of formation or decay. Some of these papers are referenced here because they may aid the more seriously interested reader in locating additional information on hydrazine formation and decomposition and its intermediates such as imidogen NH radicals [1234, 1235] or hydrazido  $\text{N}_2\text{H}_3$  radicals [1053, 1236].

Trying to find hydrazine in ammonia-laden interstellar or planetary environments may not be possible by detecting hydrazine itself but only its fragments that are re-

leased following a short-lived existence and inevitable decomposition. One can only indirectly prove that hydrazine may have existed in those mixtures of decomposition products, including ammonia and diazene.

Most of the earlier studies on diazene as an intermediate in hydrazine decomposition were done in the liquid phase. One study identified diazene as an intermediate of the thermal, surface-catalyzed gas-phase decomposition of hydrazine or ammonia at 180–500 K on polycrystalline rhodium foil [1237, 1238]. They identified diazene based on mass spectrometry of the parent ion at 30 amu and a single-dehydrogenation fragmentation product at 29 amu that is present at 6% of the abundance of its parent. Adsorbed NH was proposed as an intermediate residing on the surface. Co-adsorption of hydrogen increased and co-adsorption of oxygen decreased the diazene yield.

In the gas phase, diazene decomposition showed a first-order dependence on the concentration of diazene,  $k_{\text{obs}} = 2.45 \times 10^{-3} \text{ s}^{-1}$  at 296 K (23 °C) [1239]. A rate-limiting step in this mechanism may be the *trans*-*cis* isomerization (illustrated in the following schematic Figure 41, patterned after a similar schematic in [1240]).



**Figure 41:** Competitive pathways in gas-phase decomposition of diazene

The reactive *cis*-diazene interacts with another *trans*-diazene via a cyclic  $\text{N}_4\text{H}_4$  intermediate (“diazene dimer”) to form either nitrogen and hydrogen with the restoration of some of the diazene (left pathway) or hydrazine and nitrogen (right pathway). The difference between the two ring structures is the orientation of the *cis* member, one facing the nitrogen atoms, the other facing the hydrogen atoms and allowing some hydrogen bridging. Although *trans*-diazene is thermodynamically unstable, its symmetry provides it some stability advantages and less reactivity compared to the *cis* isomer. The thermal decomposition of  $\text{N}_2\text{H}_2$  and  $\text{N}_2\text{D}_2$  follows a single first-order ki-

netic rate equation for most temperature and pressure conditions [1241]. It was suggested that the rate-determining step in the mechanism is a first-order homogeneous gas-phase isomerization of *trans*-diazene. The *trans* isomer is sterically hindered and less reactive than the *cis* isomer. Diazene decomposition usually leads to isomerization to the more reactive *cis* isomer first. The decomposition reaction shows a distinct isotope effect as shown below:

$$k(\text{N}_2\text{H}_2) = 1.8 \exp\left(\frac{-4.2}{RT}\right) \quad k \text{ in s}^{-1}, E_a \text{ in kcal/mol}$$

$$k(\text{N}_2\text{D}_2) = 1.0 \exp\left(\frac{-4.4}{RT}\right) \quad k \text{ in s}^{-1}, E_a \text{ in kcal/mol}$$

At temperatures above room temperature, self-heating leads to rapid run-away decomposition.  $\text{N}_2\text{H}_2$  decomposes to  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{N}_2\text{H}_4$ , whereas  $\text{N}_2\text{D}_2$  gives mostly  $\text{N}_2$  and  $\text{N}_2\text{D}_4$ . Azide or ammonia could not be detected at the detection limit of the methods used. The concentrations of  $\text{N}_2\text{H}_2$  and  $\text{N}_2\text{D}_2$  can be determined by measuring the absorption at 365 nm, and the optical density follows Beer's law at concentrations between 0.1 and 1.2 mMol/L. A calibration chart was provided by Willis, Back, and Purdon [1241].

The reaction of *cis*- or *trans*-diazene with dihydrogen leads back to hydrazine, but the stereoisomers react at different speeds. *Ab initio* calculations of the reactants and transition states have enabled us to predict kinetic barriers for this reaction [1242].

Diazene is often observed as an intermediate in the oxidation or decomposition of hydrazine. It can be easily characterized by its distinct absorption spectrum in the near UV. It can be trapped on a cold finger extending into a hydrazine decomposition chamber, e.g., a glow discharge. A convenient method to study the spectra of diazene at leisure without having to worry about premature decomposition is by trapping it in liquid ammonia. The near-UV absorption spectrum of diazene in liquid ammonia at 220 K is shifted by 50 nm to the long end of the wavelength scale compared to the gas-phase spectrum of diazene with a  $\lambda_{\text{max}}$  at 400 nm [440]. The spectrum in the liquid state is also broadened and the vibrational structure is largely obscured, most likely as a result of hydrogen bonding. Diazene decay in liquid ammonia follows a first-order kinetic rate equation  $r = 1.9 \times 10^3 \exp(-6.6/RT) \text{ s}^{-1}$  with an activation energy of 6.6 kcal/mol.

The thermochemical and kinetics properties of the hydrogen abstraction and addition processes of the *trans*- $\text{N}_2\text{H}_2 + \text{N}$  reaction were computed using high-level *ab initio* and DFT approximation methods [1243]. The results for classical barrier height were 54.8 and 62.8 kJ/mol (13.1 and 15.0 kcal/mol) for the abstraction and addition reactions, respectively. The thermal rate constants were calculated using the dual-level direct dynamics by variational transition state theory with the potential energy surface and thermochemical properties corrected. The calculated rate constants showed that the variational and tunneling effects play a relevant role only for the abstraction reaction.

#### 4.4.9 Tetrazane as Intermediate in Hydrazine Decomposition

The recombination of two hydrazyl free radicals forms tetrazane,  $N_4H_6$ . This is similar to tetrazene(2)  $N_4H_4$  with a double bond at the center of the molecule, which may be more stable than tetrazane. A yellow material was detected in the condensate that was flash frozen from thermally decomposing hydrazine onto a liquid-nitrogen-cooled finger [1207, 1244]. It was suggested that this material, which decomposed on warming, is tetrazane,  $N_4H_6$ . The gas evolved when the yellow material decomposed at 95 K was mainly (98.5%) nitrogen. This could indicate that the material is not amino radical  $\bullet NH_2$  or hydrazyl radical  $\bullet N_2H_3$ . This is also supported by the fact that the sample was not paramagnetic as would be expected from free radicals. The half-life of the yellow compound is on the order of 9 ms, much longer than that of other species, such as  $NH$ ,  $\bullet CH_3$ , or  $|CH_2$ . There have also been attempts to identify the mechanism of  $N_4H_6$  formation using  $^{15}N$ -labeled hydrazine. However, the low isotope content in the starting material and partial randomization made an interpretation of the results very difficult.

#### 4.4.10 Decomposition of Hydrazine in Shock Tubes

Shock-tube studies are well suited for the study of hydrazine decomposition kinetics. With a proper selection of experimental conditions, certain fast phenomena can be separated and studied individually. Thus shock-tube studies are for thermal decomposition what short-wavelength flash photolysis is for photolytic decomposition. The shock-tube technique allows a sample to be rapidly heated to a high temperature, held there for a few milliseconds, and then rapidly cooled by adiabatic expansion. During the short hot period, the decomposition is truly homogeneous without interference from heterogeneous wall reactions. Shock tubes typically consist of a high-pressure driver section filled with helium and a low-pressure test section, which is filled with the gas (vapor) under study. A small intermediate chamber, separated from either section by coined burst discs, can be rapidly evacuated, resulting in the rupture of the burst disc and release of a plane shock wave into the test section. The incident shock wave raises the temperature and pressure of the test gas instantly. The incident shock wave is reflected at the planar end of the shock tube and, in passing through the once-shocked medium in the opposite direction, again raises the temperature of the medium incrementally to an even higher temperature and pressure. The temperature and pressure behind the reflected shock wave remain constant for several hundred milliseconds, during which time period kinetic studies are carried out. Shock-tube decomposition studies with hydrazine have been conducted by numerous investigators during the past seven decades.

The temperatures achieved in a shock tube are significantly higher than those in externally heated devices. Nevertheless, good agreement has been obtained, for instance when comparing the results from an adiabatic flow reactor with those obtained in a shock tube (Figure 40 above).

The diagnostic methods of observation of the decomposition processes in shock tubes include schlieren photography, pressure transducers, mass spectrometers [1245, 1246]; UV absorption at 2300 Å [1195, 1220]; or NH radical emission spectrophotometry [1247, 1248].

One of the first shock-tube studies of hydrazine decomposition conducted in the United States was the one at Rocketdyne [1193]. The amount of decomposition and the composition of the reaction products was determined by drawing a gas sample into an evacuated flask immediately after passage of the shock wave. The gas sample was then analyzed in a mass spectrometer. It was assumed that no further change of composition occurred after the sample gas was transferred into the evacuated flask. The stoichiometry of the decomposition under these conditions could be expressed by



Moberly believed that his results supported a steady-state chain mechanism such as the one proposed by [1249]. Because many of the individual rate constants of reaction steps in this mechanism were not yet known in 1962, Moberly [1193] could not check his assumption against the global rate, which he had just measured and found to be

$$k = 10^{10.73} e^{\frac{-37500}{RT}} \text{ s}^{-1}$$

assuming a reaction of 1.5 order with a termolecular termination step. (From today's viewpoint, quite improbable). This assumption has not been confirmed by later investigators. It was expressly stated that this method of deciding on a reaction mechanism was very crude and could be taken only as a guess and that more work needed to be done to define the mechanism more precisely.

A study of the decomposition of hydrazine vapor diluted with argon at 1200–2500 K and 4.04–25 kPa (0.04–0.25 atm) total pressure in a shock tube used a TOF mass spectrometer to track the concentration of reactant, intermediates, and products [1245, 1246]. The time-resolved (25 μs) mass spectra showed the sequence of events as a shock wave passed through the gas. The major species observed were N<sub>2</sub>H<sub>4</sub>, NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>, and the •NH<sub>2</sub> free radical. The primary process in the dissociation of hydrazine was shown to be the rupture of the N–N bond to give •NH<sub>2</sub> radicals. The •NH<sub>2</sub> free-radical concentration was found to go through a maximum and then to decay within the same time as hydrazine. No radicals other than •NH<sub>2</sub> were observed. The rate constants measured by Diesen disagreed with the rate constant measured by Szwarc for thermal decomposition of hydrazine in toluene vapor [1200].

A controversy had developed at one time over the interpretation of hydrazine shock-tube data obtained by different groups. Michel and Wagner [1195, 1250, 1251] proposed a chain mechanism, whereas McHale [352, 353] claimed a simple non-chain mechanism. The first group (Michel and Wagner 1962–1965) studied the thermal decomposition of highly diluted hydrazine (0.03–0.5% N<sub>2</sub>H<sub>4</sub> in Ar or He) behind shock waves at temperatures of 1100–1600 K. At low temperatures and high concentrations, an induction period and a dependence of the half-lives of N<sub>2</sub>H<sub>4</sub> on the concentration

was observed, which is usually characteristic of chain reactions. The pyrolysis of ammonia was also investigated in the same apparatus to determine how the hydrazine decomposition product composition could be altered by undesirable post-shock reactions. The addition of oxygen to a 0.3% hydrazine/argon mixture did not cause significant acceleration unless the oxygen : hydrogen equivalence ratio exceeded two.

In continuation of these studies, a new shock tube was built at Göttingen, and the rate of decomposition of hydrazine at concentrations of  $2 \times 10^{-6}$  to  $3 \times 10^{-6}$  mol cm<sup>-3</sup> was measured at low and high pressures, also in comparison to that of ammonia [1252]. The effect of boundary-layer phenomena on the conditions behind the incident and reflected shock waves was also taken into consideration. The NH<sub>2</sub> and NH concentration profiles were measured as a function of time. The constants for low- and high-pressure decomposition of hydrazine are summarized in Table 54.

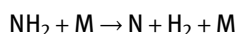
**Table 54:** Rate constants of hydrazine and ammonia decomposition in shock waves.

| Reactant  | Pressure regime | Rate equation         |                           |
|-----------|-----------------|-----------------------|---------------------------|
|           |                 | Pre-exp. factor       | Activation energy, kJ/mol |
| Hydrazine | Low             | $6.5 \times 10^{-17}$ | 233                       |
| Hydrazine | High            | $2.5 \times 10^{-16}$ | 281                       |
| Ammonia   | Low             | $4.0 \times 10^{-16}$ | 393                       |
| Ammonia   | High            | $5.5 \times 10^{-15}$ | 451                       |

Data source: [1252]

This work gave an enthalpy of formation for the amidogen radical of 196 kJ/mol, which was quite different from the one listed in the JANNAF tables (+167.8 kJ/mol). Perhaps the authors meant the formation of amidogen from hydrazine and not from the elements [1252]. The formation and decomposition of NH<sub>2</sub> and NH radicals as well as H and N atoms during the thermal decomposition of hydrazine in shock tubes was investigated over a wide temperature range [1253]. The decomposition of hydrazine already started behind the incident shock wave. For the first time frequency-modulated spectroscopy was used for the detection of NH<sub>2</sub> radicals behind shock waves. In comparison with the dual beam laser absorption technique, the detection limit was improved by 1.5 orders of magnitude. A premixed oxygen/ammonia flame was used as a stationary, constant source of NH<sub>2</sub> and NH radicals and the reference beam of a dual-beam laser absorption spectrometer passed through it. The rate constants are summarized in Table 55.

The experimental apparent activation energies were found to be in good agreement with theoretical calculations and recommended enthalpies of formation for NH<sub>2</sub> and NH. The competing NH<sub>2</sub> decomposition channel



**Table 55:** Rate constants of  $\text{NH}_2$  and  $\text{NH}$  decomposition.

| Reaction                                                             | Temp. range, K | Rate constant $k$                                                                                                |
|----------------------------------------------------------------------|----------------|------------------------------------------------------------------------------------------------------------------|
| $\text{NH}_2 + \text{M} \rightarrow \text{NH} + \text{H} + \text{M}$ | 2200–4000      | $(1.2 \pm 0.5)10^{15} \exp [ - (318 \pm 10)\text{kJ mol}^{-1}/RT ] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
| $\text{NH} + \text{M} \rightarrow \text{N} + \text{H} + \text{M}$    | 2500–3400      | $(1.8 \pm 0.8)10^{14} \exp [ - (313 \pm 15)\text{kJ mol}^{-1}/RT ] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |

Data source: [1253]

was shown to be only of minor importance ( $\leq 5\%$ ). The publication contains an up-to-date summary of 26 reactions of  $\text{NH}$  species involved in the decomposition of hydrazine listing the pre-exponential factors  $A$ , reaction orders  $n$ , and activation energies  $E_{\text{act}}$  of these reactions, along with literature references [1253].

The results by McHale and co-workers [352, 353] contradicted those of Michel and Wagner and many other researchers. It was generally accepted as an almost undisputed fact that the decomposition of hydrazine proceeds by way of a chain mechanism. However, in many cases this assumption was adopted by some authors without experimental verification of their own. Similar errors such as the true mechanism of the iodine plus hydrogen reaction have perpetuated themselves over decades until some probing independent researcher took an unbiased approach. The same might be true for hydrazine. In view of this, the study by McHale deserves special attention. The experimental study used a single-pulse shock tube at 970–1120 K and 232–867 kPa (2.3–8.6 atm) with approximately 1 mol-% hydrazine in argon. Comparing the experimental conditions of the two conflicting studies side by side, the latter used lower temperatures over a narrower range of temperatures. The hydrazine concentrations were higher than those used by anyone else in shock-tube studies. This may be one of the reasons why the experimental results led the authors to the conclusion that the decomposition kinetics obeyed a simple non-chain mechanism. Possible chain mechanisms (mainly those proposed by Adams and Stocks) were examined in detail and found to be at variance with observations.

McHale's review of previous data is repeated here because it will aid in the subsequent discussion of advantages and disadvantages. There is hardly any discussion on hydrazine decomposition without reference to Szwarc's historical determination of the N–N dissociation energy [1200]. As discussed in Section 4.4.1 on thermal decomposition,  $\text{D}(\text{H}_2\text{N}–\text{NH}_2)$  was first determined by Szwarc to be 251 kJ/mol (60 kcal/mol). A re-evaluation of these data by Gilbert [1202] resulted in a significantly higher pre-exponential factor

$$k_1 = 10^{19} e^{\frac{-60000}{RT}}$$

If Gilbert's revision is correct, the activation energy, which should be close to the N–N dissociation energy, would have to be 305 kJ/mol (73 kcal/mol), which is excessively high compared to the  $243 \pm 37$  kJ/mol ( $58 \pm 9$  kcal/mol) found by Foner and Hud-

son [342]. In the opinion of McHale, the results obtained by Szwarc are dubious because heterogeneous decomposition was not prevented.

One interesting way to relate bond dissociation energies and activation energies with the molecular structure of hydrazine is to study the number of classical oscillators required to absorb the energy prior to dissociation. Each of these oscillators represents one internal degree of freedom and thus contributes  $0.5R$  to the heat capacity of the molecule. The total number of possible internal (valence and deformation) oscillations in hydrazine is 15. These considerations are also important for the interpretation of IR spectra (Section 2.4.2). McHale used the number of oscillators to assess the acceptability or impossibility of N–N dissociation energies proposed in the literature. His results indicate that  $D(\text{H}_2\text{N}–\text{NH}_2)$  is 226 kJ/mol (54 kcal/mol), and the unimolecular theory predicts that six classical oscillators contribute energy to the low-pressure decomposition. An activation energy of about 151 kJ/mol (36 kcal/mol) is predicted for the second-order reaction at 2000 K, in agreement with results by Allison in hydrazine liquid strand burning flames, that is, 167 J/mol = 40 kcal/mol [1254].

McHale and co-workers studied the effect of contaminants, water and carbon dioxide, on the rate of decomposition of hydrazine in a shock tube [352, 353]. Up to 3%  $\text{H}_2\text{O}$  or 1%  $\text{CO}_2$  had no measurable effect on the rate of decomposition. However, the discrepancy between their 1965 results and those of a previous investigation by one of the authors using the same apparatus [1255] was explained as being caused by impurities in the hydrazine. The rates differed by a factor of two depending on the method of drying the hydrazine,  $\text{CaH}_2$  distillation, or  $\text{CaH}_2$  distillation followed by passing the vapor through a molecular sieve Linde 3A column [99].

The advantage of shock-tube studies is that they can be performed over a wide range of pressures. The initial reactions can be studied free from interference from consecutive reactions. However, at low temperatures ( $<1200\text{ K}$ ) and high hydrazine concentrations ( $>10^{-7}\text{ mol/cm}^3$ ) evidence for a chain mechanism has been assumed in view of the induction periods observed [1195]. It is very difficult to interpret results because the order of



changes markedly with pressures between 0.1 and 1 MPa.

The previous measurements by the Göttingen group were extended over a wider range of pressures [1220]. Experiments at low pressure were conducted with incident shock waves and argon dilution at 0.2–0.5% hydrazine in argon and a total pressure of 20–404 kPa (0.2–4 atm). The temperature in the shock front was 1280–1580 K. The hydrazine concentration was measured by its UV absorption at 230 nm. Under the conditions used, the rate equation for hydrazine decay was

$$k = 10^{15.6} e^{\frac{-41000 \pm 2000}{RT}}$$

This agrees well with other data [1245, 1246]. At high pressures (up to 30.3 MPa = 300 atm), more dilute hydrazine mixtures (0.001–0.1%) in argon were used to avoid

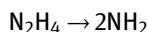


interference from the heat of reaction. The experimental first-order rate constants were found to be independent of the total pressure above 30.3 MPa (300 atm); the equation is

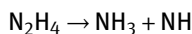
$$k_1 = 10^{13.7} e^{\frac{-54000 \pm 2000}{RT}}$$

At low pressure the rates fall off, and the fall-off curves ( $k$  vs.  $p$  with temperature as auxiliary parameter) are plotted in [1220] for these most recent data in comparison with data obtained from [353, 1052, 1195, 1245, 1246].

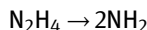
It was previously assumed that thermal hydrazine decomposition occurred through splitting into two amino radicals, similar to radiolysis [1220, 1256]:



However, this opinion had to be revised in view of other results [1196]. Based on unimolecular decomposition rates, a reaction enthalpy of 243 kJ/mol = 58 kcal/mol had to be assumed. However, a reaction by way of



would be more favored because it requires only a reaction enthalpy of approximately 188 kJ/mol = 45 kcal/mol. So far, ammonia and imino radicals were thought to be secondary rather than primary products of hydrazine decomposition. The enthalpy of formation of NH was determined by an independent method to be 197 kJ/mol (47.2 kcal/mol) [1206]. With this revised value,  $\Delta H$  of



would be 301 kJ/mol (72 kcal/mol), making it even less likely than before.

In three tests with 1% hydrazine in nitrogen at 1100 K/296 kPa, 1160 K/275 kPa, and 1190 K/220 kPa, induction periods were observed only at the two lowest temperatures [1192, 1257]. The induction period was not noticeable at 1190 K, about 50  $\mu\text{s}$  at 1160 K, and a little less than 200  $\mu\text{s}$  at 1100 K. For mixtures containing less than 2 mol-%  $\text{N}_2\text{H}_4$ , pressures above 500 kPa, and shock temperatures between 1100 and 1400 K, the rate constant was expressed as

$$k = (1.9 \pm 0.2) 10^{12} e^{\frac{-22900 \pm 500}{T}} \quad k \text{ in units of } \text{s}^{-1}, T \text{ in K}$$

Differences between more concentrated and more diluted mixtures of  $\text{N}_2\text{H}_4$  vapor in  $\text{GN}_2$  become more obvious at higher temperatures. The energy contribution from the decomposition in more concentrated mixtures increases the temperature and the system is no longer isothermal. With more concentrated mixtures between 1090 and 1400 K and for pressures above 500 kPa, the kinetic rate constant can be approximated by

$$k = (1.2 \pm 0.7) 10^{14} e^{\frac{-27600 \pm 700}{T}} \quad k \text{ in units of } \text{s}^{-1}, T \text{ in K}$$

Some of the nitrogen diluent in mixtures containing 0.5–2%  $\text{N}_2\text{H}_4$  was substituted with 20, 40, and 60% helium. The rate constants derived from the Arrhenius plots were

$$k = (4.5 \pm 1)10^{11} e^{\frac{-21300 \pm 700}{T}} \quad \text{for 20–40\% He}$$

$$k = (2 \pm 0.3)10^{11} e^{\frac{-20500 \pm 600}{T}} \quad \text{for 60\% He}$$

where  $k$  is the reaction constant in  $\text{s}^{-1}$  and  $T$  is the temperature in kelvin. The diameter of shock tubes is usually chosen well above the critical diameter below which detonations can no longer propagate through narrow tubes. The dynamic parameters of detonations are as follows:

- Critical detonation initiation energy  $E_c$
- Critical diameter  $d_c$ , corresponding to minimum diameter of a tube necessary to achieve propagation
- Characteristic dimension  $\lambda$  of detonation cells

Several empirical equations have been derived for all vapor detonations (not only for hydrazine) to correlate these parameters:  $E_c$  is roughly proportional to the cube of the cell diameter:

$$E_c \sim \lambda^3$$

the critical diameter is approximately 13 times the cell diameter:

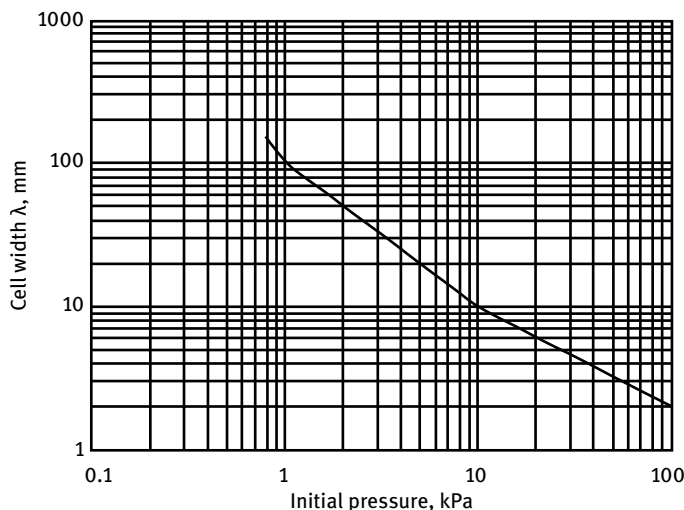
$$d_c \sim 13\lambda$$

and the cell diameter is approximately 29 times the length of the induction zone  $\Delta$ :

$$\lambda \sim 29\Delta$$

The cell diameter can be measured by depositing a thin layer of soot on the inside of the detonation tube. The passage of the detonation wave leaves a pattern of diamond-shaped crisscrossing lines where the high pressure has lifted the soot off the wall. It can also be measured by an optical method.

The detonation velocity and cell widths for hydrazine decomposition were measured over a wide range of temperatures and pressures [1258]. The detonation velocity in pure hydrazine vapor was within 5% of the calculated Chapman-Jouguet (C-J) velocity. The detonation cell width measurements were interpreted using the Zeldovich-von Neumann-Doring (ZND) model with a detailed reaction mechanism for hydrazine decomposition. Agreement with experimental data for pure hydrazine was obtained using the empirical relation that detonation cell width was equal to 29 times the kinetically calculated reaction zone length. Figure 42 presents the NASA WSTF data, showing the cell diameter of hydrazine as a function of the pressure with temperature as the auxiliary parameter. The cell diameter  $\lambda$  of hydrazine vapor detonations at 101 kPa and 393 K was extrapolated from low-pressure data to be 1.38 mm, a very, very small number indeed. The format in Figure 42 is like that derived by [1259].



**Figure 42:** Detonation cell width as a function of hydrazine vapor initial pressure. (Reproduced and modified from [1258], with permission from ©1988 American Institute of Aeronautics and Astronautics 7-Jul-2021.)

The cell diameter is typically predicted to be  $\lambda = 29\Delta$ , where  $\Delta$  is the length of the induction zone. These data are in good agreement with predicted theoretical numbers. The reaction zone length  $\Delta$  of the traveling detonation wave is dependent on the induction time. The pressure dependence of the reaction zone length illustrated in Figure 43 suggests that

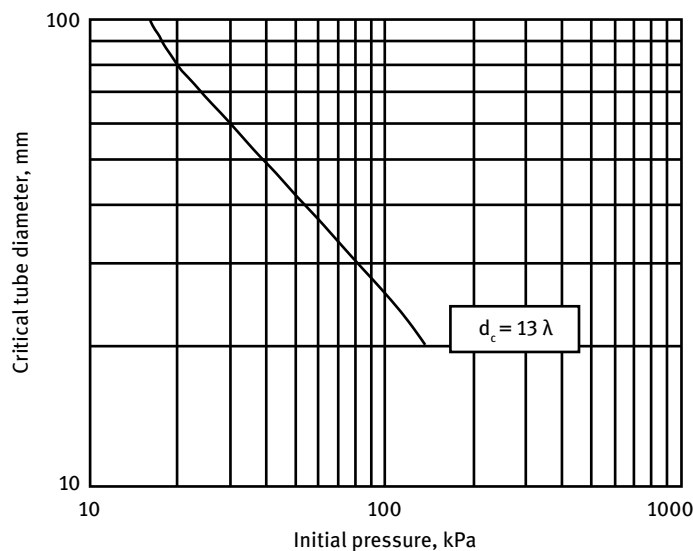
$$\Delta \approx p^{-0.8}$$

It was mentioned previously that empirical correlations for most gas detonations put the dependence of the critical tube diameter on the detonation cell width at

$$d_c \sim 13\lambda$$

This correlation is shown as a straight line in Figure 43, and data points fall not too far from this line.

Hydrazine vapor detonation data were obtained at NASA in an 150-mm-ID, 1.75-m-long stainless-steel tube with 7-mm-thick walls [1258]. The chamber could be evacuated, injected with liquid hydrazine, and heated to evaporate all the hydrazine. Two methods of initiation were used in these tests: For initial studies at higher pressures, an oxygen-acetylene driver section was used. For later tests, in particular those at lower pressures, hydrazine vapor ignition was achieved by a spark gap through which a capacitor bank holding up to 3 kJ was discharged. This initiation was faster and more reproducible than the acetylene driver. Detonation velocity and pressure was measured with four piezoelectric transducers at 0.4-m intervals along the tube. Detonation velocities (e.g., 2406 m/s at 60 kPa) were within  $\pm 10\%$  of the calculated velocity



**Figure 43:** Calculated reaction zone lengths for pure hydrazine vapor as a function of initial pressure. (Reproduced and modified from [1258], with permission from ©1988 American Institute of Aeronautics and Astronautics 7-Jul-2021.)

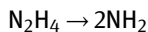
using the C-J equation. Other measured data (cell diameter) were in good agreement with predictions made with the ZND model described by Shepherd.

Shock-tube measurements of hydrazine decomposition were extended to high pressures and measurement of decomposition behind the reflected shock wave [1197]. The rate equation for the decomposition of 0.01–0.1% hydrazine vapor in argon at 10.1–30.3 MPa (100–300 atm) was very similar to that derived by previous authors [1220]:

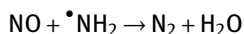
$$k_1 = 10^{13.6 \pm 0.4} e^{\frac{-53000 \pm 2000}{RT}} \text{ s}^{-1}$$

For additional shock-tube studies on hydrazine decomposition, see [1198, 1260]. Similar data are available on the decomposition of methylhydrazines in shock tubes (Chapter “Methylhydrazine”).

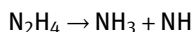
The addition of NO as a radical scavenger was expected to facilitate the clarification of the dispute between promoters of free-radical chain mechanisms in the decomposition of hydrazine vapor. If the reaction proceeded through



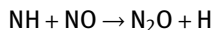
then a noticeable effect on the kinetic rate should be observed because NO reacts with  $\bullet\text{NH}_2$  more rapidly than  $\bullet\text{NH}_2$  does with hydrazine:



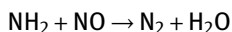
If hydrazine decomposed through



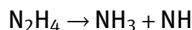
the intermediate NH would react with NO and form  $\text{N}_2\text{O}$ :



Amino radicals would also react quickly with NO:



and NO addition should slow down the reaction if amino radicals play a key role. The results obtained in a shock tube showed that the rate of hydrazine decomposition in a wide range of  $\text{N}_2\text{H}_4:\text{NO}$  ratios was indeed independent of NO addition, which speaks against the intermediacy of  $\cdot\text{NH}_2$  [1196]. The main products were  $\text{N}_2\text{O}$  and  $\text{NH}_3$ , whereas  $\cdot\text{NH}_2$  or NH could not be measured. Approximately 40% of the initially present hydrazine was converted to  $\text{NH}_3$ , and approximately half of it contributed to the formation of  $\text{N}_2\text{O}$ . All data were interpreted to favor a mechanism shown in



The addition of small amounts of UDMH (less than 1%) to hydrogen/air mixtures in a shock tube was found to decrease the delay periods usually observed after the passage of a shock front, whereas the addition of more than 3% UDMH increased the ignition delay [1261]. Apparently small UDMH concentrations release free radicals that trigger the  $\text{O}_2\text{-H}_2$  reaction.

## 4.5 Detonation of Hydrazine

The conditions under which the detonation of hydrazine liquid or vapor or foam may be initiated will be discussed under safety properties and detonability sensitivity in Section 8.4. The current section deals with mechanisms and kinetics that would enable the propagation of detonations, regardless of how they have been initiated.

### 4.5.1 Detonation of Hydrazine Vapor

The detonability of hydrazine vapor will be discussed again under safety properties in Section 8.4 of this chapter. The current section looks only at the kinetics of detonations in relation to thermal decomposition of hydrazine from an academic point of view.

The fundamental gas-dynamic characteristics of the detonation, instantaneous combustion (explosion) in constant volume, combustion at constant pressure, and deflagration for hydrazine, MMH, UDMH, SDMH, or trimethylhydrazine in mixtures with oxygen or air that are diluted with argon at varied initial pressure and temperature values were examined [1262, 1263]. Spray detonation is also potentially relevant to the study of pulse detonation engines (PDEs) and other hypersonic propulsion sys-

tems exploiting detonative reactions. The main parameters of these processes were analyzed both for the case of a gaseous propellant and for the case of a heterogeneous propellant where the propellant is a highly dispersed, sprayed aerosol cloud in an oxidant medium. Calculations were performed by means of the computer code SAFETY. Calculation results agreed with experimental data. For hydrazine by itself, detonation wave velocity was predicted to be  $D_0 = 2482$  m/s. For a stoichiometric mixture of gaseous hydrazine with oxygen the detonation wave velocity was predicted to be  $D_0 = 2595$  m/s. For a stoichiometric mixture of gaseous hydrazine with air the detonation wave velocity was predicted to be  $D_0 = 2003$  m/s. A poorly dispersed spray of liquid hydrazine aerosol in a stoichiometric proportion to oxygen was predicted to detonate at  $D_0 = 2534$  m/s.

An initial detailed kinetic model describing the hydrazine vapor detonation consisted of 33 reversible reactions and 13 species [1264]. A reduced kinetic model was then proposed using the principal component analysis of matrix F method as implemented in KINALC. It consisted of 26 reactions and 11 species. This model has been shown to be valid over a pressure range of 10 to 1010 kPa (0.1 to 10 atm). However, the predictions of the models were significantly affected by changes in the enthalpy of formation of  $N_2H_3$ , which was only known with poor accuracy. With the help of the full kinetic model, a value of  $A$ , the proportionality factor in the ZND model between the induction distance in the detonation wave and the detonation cell size, of  $27.5 \pm 3.0$  was derived considering that the collision efficiency of  $N_2H_4$  on the thermal decomposition of hydrazine is equal to that of  $N_2$ . The value of  $A$  for pure hydrazine detonation was shown to be strongly dependent on the value of the collision efficiency of  $N_2H_4$ . See also [1265].

#### 4.5.2 Detonation of Liquid Hydrazine

Despite numerous experiments testing the detonability of liquid, bubble-free hydrazine, it has not been possible to achieve detonation of liquid hydrazine. The propagation of induced shock waves in liquid hydrazine has been studied experimentally and modeled by computational methods, also in support of experiments measuring the effects of hypervelocity particle impacts on hydrazine tanks. The detonability of liquid hydrazine is discussed again under safety properties in Section 8.4 of this chapter.

The shock Hugoniot of liquid hydrazine was determined in a pressure range of 3.1 to 21.4 GPa (31 to 214 kbar) using an impedance matching technique [1266–1268]. Shock pressures were generated using a plane wave explosive driver system with different explosives and reference materials compared against the liquid hydrazine. The velocity of the shock wave in the liquid hydrazine and the free surface velocity of the reference materials were measured using different pin contact techniques. Shock velocities ranged from 3.72 to 6.76 km/s, depending on the type of donor charge and flat plate flyer. Plotting the shock wave velocity versus the surface wave velocity gave a linear function relationship. The experimental Hugoniot appeared smooth, and

there was no indication of a phase change. The shock Hugoniot of liquid hydrazine was compared against three other liquid Hugoniots – liquid ammonia, water, and carbon tetrachloride – and was closest to the Hugoniot for water and in between ammonia and carbon tetrachloride. The hydrazine Hugoniot was also compared to the “universal” Hugoniot for liquids. The universal Hugoniot for liquids is not a good approximation for the liquid hydrazine Hugoniot in the pressure range studied.

Several shock compression experiments have been conducted in an attempt to investigate the detonability of liquid hydrazine; however, the experimental results are not in agreement. Therefore, each experiment was reproduced numerically to evaluate in detail the shock wave profiles generated in the liquid hydrazine, including chemical kinetic experiments, chemical equilibrium calculations, and characterization of the EOS of liquid hydrazine [1269, 1270].

The parameters of shock-compressed liquid hydrazine were calculated within the framework of the approaches developed for studying shock compression of organic liquids and liquefied gases [1271–1274]. In the case when the mass velocities behind shock fronts do not exceed  $3.1 \text{ mm}/\mu\text{s}$ , it may be managed under an assumption of the retention of the unreacted, initial compound (hydrazine) behind a shock front. Detonation velocities of hydrazine solutions with such explosives as nitromethane and hydrazine nitrate correspond to the destruction of hydrazine to ammonia and nitrogen, which is accompanied by a noticeable energy release. The estimates demonstrated the possibility of detonation of liquid hydrazine at a velocity of  $8 \text{ mm}/\mu\text{s}$  with shock heating of the liquid to approximately 2000 K, which is comparable with the temperature observed behind a shock front during detonation of liquid explosives. Large values of the critical diameter of detonation (up to 1 m) are expected because of the large activation energy of hydrazine decomposition ( $223 \text{ kJ/mol} = 53.2 \text{ kcal/mol}$ ), which is almost 1.4 times larger than the activation energy of decomposition of standard explosives. In this case, their more rapid decomposition behind a shock front would result in a temperature increase that is enough for hydrazine destruction for peak times less than  $0.1 \mu\text{s}$ .

#### 4.6 Photolytic Decomposition of Hydrazine

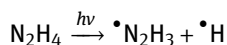
Of the various methods for the study of hydrazine decomposition, the one initiated by photolysis is probably most easily accessible to analysis of the disappearance of hydrazine and the appearance of decomposition products. Photolytic studies of hydrazine decomposition are done for various reasons. One reason would be to study the mechanism of hydrazine decomposition with a method where the initiating energy is easily dosed (metered) and can be delivered in discrete pulses of preselected duration and intensity, such as in flash photolysis. Selective states just short of dissociation can be excited by coupling monochromatic radiation, typically provided by a laser, to absorptive vibrations of the molecule. This is a difference from thermal decompo-

sition, where the decomposing hot molecules occupy a broad band of energy states and only those at the high-energy end of the band have enough energy to dissociate. Photolysis is very suitable for selectively dissociating bonds in molecules by choosing monochromatic light and identifying the intermediates. The photolysis of hydrazine may occur in planetary atmospheres that are rich in ammonia and may be responsible for limiting the hydrazine yield in ammonia photolysis reactions studies as a means of making hydrazine. The environmental fate of hydrazine vapors inadvertently released into Earth's atmosphere depends on its rate of destruction by photolysis. The photolysis of hydrazine is undesirable if one wants to obtain UV spectra of hydrazine that are free from decomposition products.

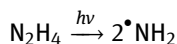
#### 4.6.1 Photolysis of Hydrazine Vapor

The earliest studies on the photolytic decomposition of hydrazine vapor date back to 1929 [1275, 1276]. Hydrazine vapor in a 150-mL quartz vessel at 1.06 kPa (8 mm Hg) pressure and  $298 \pm 1$  K was illuminated with UV light from a mercury arc in a quartz bulb, and the total pressure increase was measured as a function of time. Selected gas samples were analyzed for gas composition. Hydrazine vapor absorbed UV light appreciably below 244 nm. The photolytic decomposition was found to lead to hydrogen and nitrogen as the main products, resulting in a tripling of the pressure in the flask. It was assumed that any hydrogen found must come from the secondary photolysis of ammonia, but no proof was offered for this hypothesis. The photochemical decomposition of ammonia proceeds at approximately one-tenth the speed of hydrazine decomposition. The data have been interpreted to indicate that the photolysis of hydrazine under these conditions is a chain reaction. The quantum efficiency was on the order of 13 molecules reacted per quantum of light absorbed.

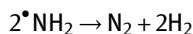
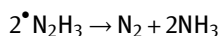
One of the objectives of studies of the photolytic decomposition of hydrazine is to identify intermediate products of decomposition. In the case of photolysis as well as other modes of initiation, free radicals are presumed to play an important role. For a long time, the photolysis of hydrazine was believed to proceed through one or both of two mechanisms:



or



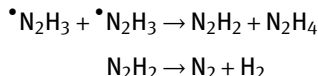
with nitrogen formation attributed to radical-radical reactions:



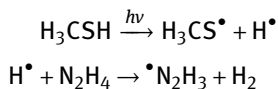
This hypothesis was temporarily contested by Stief and de Carlo [1153] as well as Kant and McMahon [1224] using  $^{15}\text{N}$ -isotope-labeled hydrazine. When a 50:50 mixture of  $^{14}\text{N}_2\text{H}_4$  and  $^{15}\text{N}_2\text{H}_4$  was irradiated,  $^{15}\text{N}_2$  and  $^{14}\text{N}_2$  were formed in approximately equal



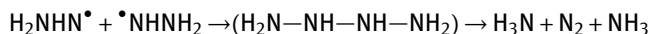
proportions, whereas very little randomized  $^{14}\text{N}^{15}\text{N}$  could be observed [1153]. If the decomposition occurred by  $\bullet\text{N}_2\text{H}_3$  or  $\bullet\text{NH}_2$  free radicals, an approximately even statistical distribution of the isotopes should have occurred. An alternative explanation of the lack of randomization would be the disproportionation of  $\bullet\text{N}_2\text{H}_3$  radicals:



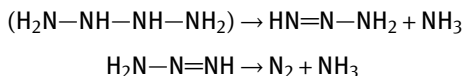
Depending on the (initially unknown) ratio of disproportionation to recombination for the  $\bullet\text{N}_2\text{H}_3$  radical, only 50% randomization could be expected via this mechanism. For the observed 13% randomization this ratio would have to be at least 2.8, which is very high in comparison to other free radicals. The authors concluded that, contrary to previous suggestions, the major portion of the dinitrogen in the photolysis of hydrazine formed by molecular elimination. However, a later, more detailed, study of the ratio of disproportionation of recombination of hydrazyl radicals showed that this number is indeed higher than 2.8, actually closer to 4.0 [1152]. Identifying randomization of isotopic nitrogen with the combination  $\text{N}_2\text{H}_3$  and non-randomization with the disproportionation of  $\text{N}_2\text{H}_3$ , the ratio of disproportionation to combination was approximately 4. This was an unexpectedly large value, being nearly 30 times larger than that for the analogous hydrocarbon radical  $\text{C}_2\text{H}_5$ . Hydrogen atoms generated by the photolysis of methyl mercaptan were used to abstract hydrogen from hydrazine and form hydrazyl radicals without thermal or photolytic excitation of hydrazine molecules.



Several alternative mechanisms were discussed. The combination of two hydrazyl radicals with the unknown tetrazane and splitting of terminal  $\text{NH}_2$  groups would explain only complete (100%) randomization because two different  $\bullet\text{N}_2\text{H}_3$  radicals are likely to combine:

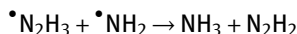


Since the experimentally observed randomization is 50%, some other mechanism must be contributing. Based on studies of the oxidation of hydrazine in aqueous solution, decomposition of the tetrazane to triazene was proposed, which is at least as unstable as tetrazane [518, 1277]:

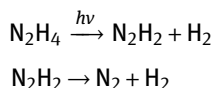


Stief assumed that this mechanism would come into play in the gas phase as well and that it accounted for the 50% randomization observed. Certainly, efforts have been made to identify the tetrazane and triazene intermediates postulated by these au-

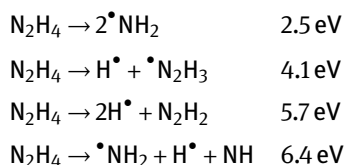
thors [342]. Some of this work is discussed in the chapter “Hydronitrogens.” The experimentally determined disproportionation : combination ratio is  $4.0 \pm 0.6$  with certain experimental errors due to insufficient isotopic purity of the starting materials. To a certain extent, radical cross-disproportionation may further cloud the issue:



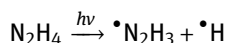
In the direct photolysis of hydrazine (as opposed to that using methyl mercaptan as “sensitizer”), the direct formation of hydrogen and nitrogen via



cannot be disregarded and may well contribute to the overall very complex mechanism. When studying the energy transfer from metastable, electronically excited  $\text{N}_2$ , Ar, Kr, Xe to hydrazine and isoelectronic organic molecules, it was an unexpected result to find that cleavage of the weak central bond is much less likely than that of the stronger terminal bonds [1278]. The threshold energies for dissociation channels by reaction with  $\text{N}_2^*$  are as follows (an asterisk \* denotes excited species):



The data for hydrazine were difficult to interpret because of the speed of secondary reactions. Time-resolved studies have shown that  $\bullet\text{NH}_2$  is not a primary product of photodissociation at 193 nm, consistent with the prevailing dominant reaction pathway [1279–1281]



The photolysis of hydrazines occurs inadvertently while trying to determine absorption spectra in the vacuum UV region. Photoionization thresholds of ammonia, hydrazine, MMH, and UDMH were measured in a molecular-beam apparatus [401, 402]. The ionization thresholds of hydrazines are very broad, as opposed to a sharp ionization threshold of ammonia at 10.16 eV. The measured photoionization threshold potentials are 8.32 eV for hydrazine, 8.05 eV for MMH, and 7.87 eV for UDMH.

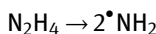
The dependence of the relative  $\bullet\text{NH}_2$  yield on fluence (in a range of 0.1 to  $100 \text{ J cm}^{-2}$ ) of laser radiation from a  $\text{CO}_2$  laser and pressure of hydrazine vapor (from 1.4 to  $2.6 \text{ Pa} = 10^{-3}$  to  $0.02 \text{ mm Hg}$ ) was examined using the 935, 944, and  $953 \text{ cm}^{-1}$  laser lines [1282]. A photon at  $935 \text{ cm}^{-1}$  corresponds to an energy of 11.9 kJ/mol. The three initiating lines were in the vicinity of the  $937 \text{ cm}^{-1}$  absorption band of hydrazine, which is attributed to the anti-symmetric wagging mode. While shock-wave studies

point to ammonia as a co-dissociating intermediate and source of  $\bullet\text{NH}_2$ , it does not appear to be a major contributor here under conditions of “collisionless” multi-photon dissociation at pressures of low collision frequency, nor is the direct dissociation of hydrazine to nitrogen and hydrogen, which is very exothermic.

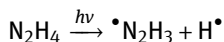
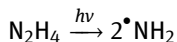
In addition to free radicals as energetic species, many of the molecular species leaving the hydrazine decomposition reaction are in an electronically excited state from which they may lase if a population inversion prevails. The production of species in electronically excited states was observed during the photolysis of  $\text{N}_2\text{H}_4$  or  $\text{N}_2\text{D}_4$  at 193 nm [1283]. The visible spectrum in the region 420–900 nm showed a broad and largely unstructured continuum emission upon which was superimposed a large number of well-resolved spectral features corresponding to  $\text{NH}_2(\text{A})$  or  $\text{ND}_2(\text{A})$ . The population of the excited states may depend on the initial temperature of the hydrazine vapor. This was demonstrated by photolyzing hydrazine vapor at 573 K in comparison to hydrazine vapor at 296 K and the cross sections for  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$ ,  $\text{NH}(\text{A}^3\Pi)$ , and  $\text{NH}_2(\text{A}^2\text{A}_1)$  were determined at the same time [1284]. See also [433, 434].

#### 4.6.2 Effect of Wavelength of Incident Light

The ratio of amino to hydrazyl radicals formed in the photolysis of hydrazine changes with the wavelength of the incident radiation. It has been suggested [1281] that at  $\lambda > 200$  nm cleavage to amino radicals



occurs preferentially, whereas at  $\lambda < 200$  nm hydrazyl radicals are formed first (which is  $\text{N}_2\text{H}_4 \rightarrow \bullet\text{N}_2\text{H}_3 + \text{H}\bullet$ ):



At 200 nm  $\text{N}_2\text{H}_4 \rightarrow 2\bullet\text{NH}_2$  slightly predominated, with 55% of all hydrazine decomposing via this route [1281]. On the other hand, at 105 nm,  $\text{N}_2\text{H}_4 \rightarrow \bullet\text{N}_2\text{H}_3 + \text{H}\bullet$  was found to predominate [1285]. At 123.6 and 147 nm  $\text{N}_2\text{H}_4 \rightarrow \bullet\text{N}_2\text{H}_3 + \text{H}\bullet$  was shown to be present because only that reaction can be inhibited by deuterioethylene  $\text{C}_2\text{D}_4$  addition [1286].

Monochromatic 199-nm radiation from a condensed aluminum spark passed through a monochromator was used to study the quantum yield of the photochemical decomposition of gaseous hydrazine, but the researchers' findings disagreed with those of Elgin and Taylor, possibly as a result of analysis errors in decomposition product composition [1287]. In the low-pressure range at 265 Pa (2 mm Hg), the quantum yield was 1 and increased to 1.7 at 1866 Pa (14 mm Hg). The composition of the reaction products was dependent on the initial hydrazine pressure. More hydrogen was formed at the low hydrazine pressures than at higher pressures.

When pure hydrazine was photolyzed with krypton resonance lines (123.6 and 116.5 nm), an emission was observed at 336 nm that was attributed to the  $\text{NH}$  radi-

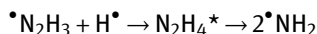
cal [1286, 1288]. Except for some  $\cdot\text{OH}$  due to water present in the hydrazine, no other emissions were noted initially between 200 and 700 nm. Only after several minutes was ammonia emission at 324 nm detected. The 336-nm emission can be used as an indicator of the NH concentration in the reaction mixture. The NH concentration (336-nm intensity) decreased with time, whereas the 324-nm emission (presumed to belong to ammonia) increased with time. No emissions were observed when the xenon resonance line at 147 nm was used in the hydrazine photolysis.

The absorption coefficients of ammonia and hydrazine at four different wavelengths (116.5, 123.6, 129.5, and 147 nm) and emission spectra due to  $\text{NH}^*$  were measured in the vacuum UV range [1289]. Xenon and krypton emission lines were used to initiate the photolysis of hydrazine at pressures close to 26.6 Pa (0.2 mm Hg) in both static and flow systems. In the flow system, only the  $\text{NH}^*(^3\Pi \rightarrow ^3\Sigma)$  band was observed, whereas in the static system a  $\text{NH}(^1\Pi \rightarrow \Delta)$  began to appear after a short time of illumination, which must be due to the ammonia formed in the hydrazine decomposition.

Continuous photolysis was achieved with the 206.2-nm resonance line from an iodine lamp [1290, 1291]. The hydrazine partial pressure was 266–1063 Pa (2–8 mm Hg) in xenon gas at up to 36 kPa (270 mm Hg). The inert heavy gas helped to maintain isothermal conditions during the photolysis reactions. For flash photolysis, a flash of 5000 J was discharged within 5  $\mu\text{s}$  into hydrazine vapor that was contained in a cell 56 mm in diameter and 1 m in length. For isothermal reaction conditions, inert gas was again added to the hydrazine vapor, this time argon at a ratio of 100 : 1.2. Approximately 5% of all the hydrazine was decomposed after a single flash discharge under isothermal conditions. Time-resolved spectra of the photolysis products showed:

- (1) The well-known absorption spectrum of  $\text{NH}_2$  radicals that lasted for several hundred microseconds
- (2) NH radicals at 336 nm that lasted for approximately 18  $\mu\text{s}$
- (3) Continuous absorption across the entire UV range, lasting for only around 10  $\mu\text{s}$ , which was attributed to the  $\cdot\text{N}_2\text{H}_3$  radical
- (4) Ammonia formation beginning after 50  $\mu\text{s}$

The formation of amino radicals is assumed to be a secondary effect of photolysis:



Lasers offer the opportunity to study the effect of wavelength on the photolysis of hydrazine with very high accuracy as to the energy of the incident radiation. An argon fluoride excimer laser emitting at 193 nm was used to study the photolysis of hydrazine [1279, 1280]. A secondary tunable dye laser scanned through a range near  $18400\text{ cm}^{-1}$  as a diagnostic tool. Amino radical fluorescence was observed at 597 and 571 nm. The dependence of laser-induced fluorescence due to  $\cdot\text{NH}_2$  on the initial hydrazine pressure was linear from 0 to 107 Pa (0 to 800  $\mu\text{m Hg}$ ). Amino radicals are not a major primary product of the laser photolysis of hydrazine. The intensity of visible fluorescence emission at 450–600 nm was linearly proportional to the initiating laser energy

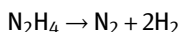
from 0 to 8 mJ/pulse. Strong two-photon absorption from  $\text{NH}(\text{A}^3\Pi)$  was also observed and attributed to secondary absorption by the  $\bullet\text{N}_2\text{H}_3$  primary photoproduct. While some authors favored the secondary photolysis of  $\text{N}_2\text{H}_3$  and the mechanism for the excitation of  $\text{NH}$ , other investigators suspected that another intermediate might be involved. In later studies, also with an argon excimer laser at 193 nm, the photolysis of hydrazine resulted in triplet emission of  $\text{NH}$  imidogen [1292, 1293]. Similar observations had been made earlier with the same laser aimed at ammonia, hydrogen azide, hydrazine hydrate, or methylamine. Relatively strong emission was observed from the first rotational level of  $\text{NH}(\text{A}^3\Pi)$ . Of all the molecules tested, the largest relative population of the first vibrational state ( $v = 1$ ) was found with hydrazine. In the rotationally resolved spectrum, emissions from rotational levels up to  $N' = 28$  were observed. The fluorescence intensity of the  $\text{NH}(\text{A}^3\Pi \rightarrow \text{X}^3\Sigma)$  emission was found to depend on the 1.8<sup>th</sup> power of the laser intensity, suggesting that absorption of at least two photons is required to generate an excited  $\text{NH}^*$  species.

#### 4.6.3 Flash Photolysis of Hydrazine Vapor

The flash photolysis of hydrazine was also studied as part of the investigation of the explosive oxidation of ammonia and hydrazine [521]. The composition of the decomposition products varied with the flash intensity. Assuming two overall reactions



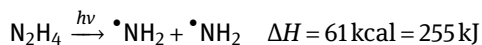
and



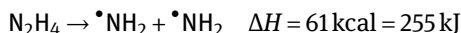
it was found that with a flash energy of 1150 J, 75% of the hydrazine was decomposed and the ratio (1):(2) was 54:46. The possibility of secondary thermal or photolytic ammonia dissociation was ruled out because ammonia added to the system was not thermally decomposed. The differences in the final product analysis were attributed to the varying stability of the  $\bullet\text{N}_2\text{H}_3$  radical at different temperatures. These results agreed with Ramsay's interpretation of hydrazine photolysis [1225, 1294] based on the absorption of hydrazine in its photolysis.

A re-investigation of the flash photolysis of hydrazine in an excess of inert gas revealed a new absorption band of the  $\text{NH}$  radical and a previously unknown continuous absorption below 400 nm that has been attributed to the  $\bullet\text{N}_2\text{H}_3$  radical [1295]. Dilution by a large amount of inert gas served to maintain isothermal conditions during the reaction. The experimenters used a flash of shorter duration ( $t_{1/2}$  approximately 5  $\mu\text{s}$ ) than those used by previous investigators. An optical path of up to 16 m was achieved by multiple reflection of the analyzing beam in a cylindrical cell with a diameter of 55 mm.  $\text{NH}$  absorption was measured at 336 nm ( $\text{A}^3\Pi \rightarrow \text{X}^3\Sigma$  with a half-life of 18  $\mu\text{s}$ ), and  $\text{NH}_2$  absorption was measured at 597.6 nm.  $\text{NH}_2$  absorption was visible for several hundred microseconds.

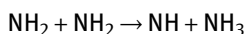
In view of results obtained during the photolysis of hydrazine at 2062 Å in the presence of ethylene [1296], it has been postulated that of the four possible photolytic reactions



the reaction  $\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2$  does not provide the main contribution, as was originally assumed. Instead, the reaction



is the main initial step in the photolysis of hydrazine. The improved experimental techniques were now used to investigate the origin of  $\text{NH}_2$  in the isothermal flash photolysis of hydrazine following the formation and decay of this radical, as evidenced by its absorption in the 597.6-nm band [1295]. It is unlikely that  $\text{NH}$  forms by the reaction



because  $\text{NH}$  disappears with a half-life time of 18  $\mu\text{s}$ , whereas  $\bullet\text{NH}_2$  sticks around much longer. Between 0 and 250  $\mu\text{s}$  the rate of disappearance of  $\bullet\text{NH}_2$  in photolyzed hydrazine was much slower than in photolyzed ammonia, despite the initially higher  $\bullet\text{NH}_2$  concentration in hydrazine. Ammonia, whose photolysis has already been exhaustively investigated, was also used in this study in some flash photolytic experiments in the same setup as a baseline for comparison. Based on these flash photolysis experiments, the authors concluded that  $\bullet\text{NH}_2$  plays only a minor role in the photolysis of hydrazine [1295]. Amino  $\bullet\text{NH}_2$  radicals play an important role in the attempted preparation of hydrazine by the photolysis of ammonia, possibly also occurring in the atmospheres of planets with ammonia atmospheres, and in the photolytic decomposition of hydrazine. The rates of recombination of amino radicals for bimolecular and trimolecular reactions are summarized in Table 56. The rate of disappearance of the  $\text{NH}_2$  radicals is immediately tied to the rate of formation of hydrazine.

The rate of amino radical disappearance is proportional to the square of the amino radical concentration:

$$\frac{d[\text{NH}_2]}{dt} = 2k_1[\text{NH}_2]^2$$

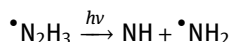
When studying the effect of pressure on  $k_1$ , it was noted that the reaction proceeds by “self-exciting collisions” [1299]. The decay profile of  $\bullet\text{NH}_2$  radicals at 598 nm,  $\text{NH}$  radicals at 336 nm, and yet unidentified species (believed to be  $\text{N}_2\text{H}_3$  radicals) at 290 nm has been measured for up to 300  $\mu\text{s}$  after the initial photolysis flash. Attempts were

**Table 56:** Reaction rates for recombination of amino radicals.

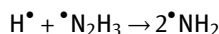
| Rate expression                                                      | Temperature, K | Pressure, mm Hg | Diluent         | Reaction type |
|----------------------------------------------------------------------|----------------|-----------------|-----------------|---------------|
| $(1.00 \pm 0.50)e^{18} \text{ cm}^6 \text{ mol}^{-1} \text{ s}^{-1}$ | 300–500        | 0–20            | Ar              | termolecular  |
| $(1.00 \pm 0.50)e^{19} \text{ cm}^6 \text{ mol}^{-1} \text{ s}^{-1}$ | 300–500        | 0–20            | NH <sub>3</sub> | termolecular  |
| $(1.50 \pm 0.75)e^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | 300–500        | 1000            | N <sub>2</sub>  | bimolecular   |
| $6.19e^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$            | 298            | 250–1520        | NH <sub>3</sub> | bimolecular   |

Data source: [1297, 1298]

made to check the validity of Beer's law for the 597.6-nm band of the  $\bullet\text{NH}_2$  radical by plotting the optical density as a function of optical pathlength. The law is not fulfilled, and a straight line could not be obtained. This is probably because more than one line or band contributes to the absorption at this wavelength. This had already been observed by other authors [1298]. The unexplained continuum at 290 nm showed some correlation with the concentration of NH radicals. If the continuum is due to  $\bullet\text{N}_2\text{H}_3$ , then secondary photolysis of  $\bullet\text{N}_2\text{H}_3$  could form some NH:

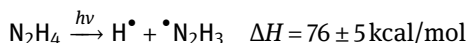


This reaction and hydrogenolysis



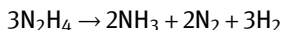
are secondary sources for NH<sub>2</sub> in the hydrazine photolysis, but  $\text{N}_2\text{H}_4 \rightarrow \bullet\text{NH}_2 + \bullet\text{NH}_2$  has now been eliminated as a possible source. This conclusion is also supported by the observation that NH<sub>2</sub> concentration reached its maximum only several microseconds after the flash, at a time when the continuum (possibly N<sub>2</sub>H<sub>3</sub>) was already decaying.

A similar study on the flash photolysis and photolysis with continued irradiation of hydrazine, both under adiabatic and isothermal conditions, led to the conclusion that at 200 nm the primary step is the hydrogen abstraction leading to hydrazyl radicals [1291]:



Laser flash photolysis of hydrazine vapor at 296 K from a 248.3-nm laser resulted in the formation of H atoms, which were directly measured using a continuous-wave-resonance fluorescence detection of H(<sup>2</sup>S) technique at 121.6 nm. Other species were studied by their absorption at 253.65 nm [1300]. Initially, the primary quantum yield of H formation was reported as  $0.85 \pm 0.15$  or near unity when tested at additional wavelengths of 193, 222, and 248 nm. By repeating the primary reaction of H atoms with hydrazine at various temperatures between 222 and 296 K, it was possible to determine the Arrhenius rate equation (and the activation energy) of this reaction to be  $k_1 = (7.57 \pm 1.55) \times 10^{-12} \exp(-1150 \pm 50/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This was consistent with a metathetical reaction in which the reaction proceeds via H-atom abstraction in hydrazine to give H<sub>2</sub> and N<sub>2</sub>H<sub>3</sub> as the major products. Later tests gave the quantum yield

at 193 nm as  $1.01 \pm 0.12$  and at 222 nm as  $1.06 \pm 0.16$  [1301]. The high yield of H atoms observed in the photolysis was consistent with the continuous UV absorption spectrum of hydrazine. A second-order rate constant of hydrogen abstraction from hydrazine by atomic hydrogen was determined from a series of experiments with varying hydrazine concentrations in helium. From these tests, the rate equation was derived as  $k_1 = (11.7 \pm 0.7) \times 10^{-12} \exp(-1260 \pm 20/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , somewhat different from the older equation published earlier [1302]. Whereas only 5% of the hydrazine was destroyed under isothermal conditions, each flash discharge destroyed more than 80% of the hydrazine under adiabatic conditions at 106–930 Pa (0.8–7 mm Hg). The stoichiometry under these conditions was



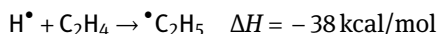
#### 4.6.4 Photolysis in the Presence of Additives

Sometimes short-lived intermediate species can be trapped or a key mechanism can be inhibited by conducting the photolysis of hydrazine in the presence of additives. Nitric oxide [1227, 1303, 1304], ethylene  $\text{C}_2\text{H}_4$  [1296], deuterioethylene  $\text{C}_2\text{D}_4$  [1286], and propylene [1303] have been used as additives and radical scavengers. Other additives generate additional free radicals and initiate additional chain reactions. Methyl mercaptan was already mentioned. Dimethyl mercury has been used for the same purpose.

The addition of hydrogen, nitrogen, or ammonia to the hydrazine did not affect its rate of photolytic decomposition [1275, 1276]. When the hydrazine vapor was sensitized with mercury vapor and then irradiated with light from a mercury lamp, hydrazine decomposition occurred much more rapidly than under any other condition tested. The photosensitized decomposition of hydrazine was 40 times faster than that of ammonia under identical conditions. The rate of the sensitized decomposition was directly proportional to the incident light intensity.

Photolysis in the presence of water vapor would be dominated by the interaction of hydroxyl radicals with hydrazine. Hydroxyl radicals are a strong oxidizing agent and will destroy hydrazine. This reaction is believed to be responsible for the destruction of hydrazine or MMH vapor in the troposphere [1305] (Section 10.4.3). The photolysis of aqueous hydrazine solutions will produce some dihydrogen gas [1306, 1307], whereas none is produced during slow liquid-phase decomposition of hydrazine solutions.

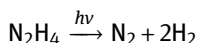
**Effect of Radical Scavengers.** When hydrazine/ethylene mixtures are photolyzed, ethylene will scavenge hydrogen atoms and compete with reaction (10) in Figure 38 [1296]. Accordingly, the hydrogen yield decreases with increasing ethylene pressure:



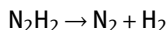
At the wavelength at which this experiment was conducted (206.2 nm), ethylene is transparent and will not become electronically excited. Ethylene pressures of 20–



11400 Pa (0.15–86 mm Hg) were used, whereas the hydrazine pressure was kept constant at 1.2 kPa (9.3 mm Hg). The quantum yield for  $\text{H}_2$  formation dropped from 1.2 without ethylene to 0.1 for an ethylene : hydrazine molar ratio of 8 [1296]. A similar effect was observed when using deuterated ethylene  $\text{C}_2\text{D}_4$  instead of  $\text{C}_2\text{H}_4$  [1286]: the quantum yield of hydrogen by photolysis at 147 nm and 66 Pa (0.5 mm Hg) dropped from 0.72 to 0.55 at a hydrazine : deuterioethylene ratio of 5. Perhaps the  $\text{C}_2\text{D}_4$  test should be repeated at higher scavenger : hydrazine ratios (up to 8) like those used with  $\text{C}_2\text{H}_4$ . The quantum yield of nitrogen in this experiment remained unchanged (0.5). The remaining hydrogen formed in this test was attributed to reactions not involving hydrogen radicals, such as the direct molecular elimination of hydrogen

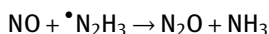
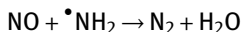


or decomposition of diazene

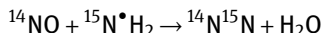


The latter reaction was initially thought to be very likely because, in the presence of  $\text{C}_2\text{D}_4$ , the quantum yields for  $\text{H}_2$  and  $\text{N}_2$  are equal. However, later studies by the same authors [1227, 1304] with the addition of NO instead of  $\text{C}_2\text{D}_4$  reversed this conclusion.

In the same way that ethylene acts as a selective scavenger for hydrogen atoms, nitric oxide acts as a scavenger for amino and hydrazyl radicals [1303]:



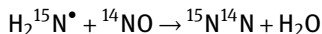
If  $^{15}\text{N}_2\text{H}_4$  is used for the  $^{14}\text{NO}$ -inhibition study, the nitrogen formed in the preceding reaction will have a molecular weight of 29 [1227, 1304]:



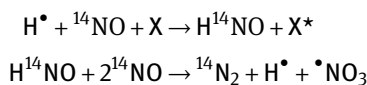
As was discussed in earlier sections on the thermal and photolytic decomposition of mixtures of  $^{14}\text{N}_2\text{H}_4$  and  $^{15}\text{N}_2\text{H}_4$ , the lack of randomization of nitrogen indicated a molecular elimination of nitrogen with only a minimum of radical disproportionation. The formation of  $^{15}\text{N}_2$  in the presence of  $^{14}\text{NO}$  is then attributed to the direct molecular process. Complete scavenging of  $^{15}\text{N}\bullet\text{H}_2$  and  $^{15}\text{N}_2\text{H}_3\bullet$  radicals must be achieved by adding enough  $^{14}\text{NO}$  to suppress all radical disproportionation. One objective of the investigation was to determine how much NO was required to achieve a complete suppression of chain reactions.

The effect of NO addition on the rate of decomposition product formation is expressed as a percent of the rate observed with  $^{15}\text{N}_2\text{H}_4$  alone without NO addition. The  $^{15}\text{N}_2\text{H}_4$  partial pressure was 66 Pa (0.5 mm Hg), and 147 nm UV light was used for photolysis. The addition of 5–50% NO reduced the rate of  $^{15}\text{N}_2$  formation drastically to 25% of its value in the absence of NO. It was found that 5% NO was enough to bring about this effect, and the rate of  $^{15}\text{N}_2$  formation did not change between 5 and 50% NO. The

addition of  $^{14}\text{NO}$  also led to the formation of  $^{14}\text{N}^{15}\text{N}$ . Its rate of formation increased to 25% of that for  $^{15}\text{N}_2$  in the photolysis of hydrazine alone with the first 5% NO addition. Its rate remained constant at 5–50% NO. These two results indicated that 5–10% NO was enough to scavenge all amino radicals via the reaction

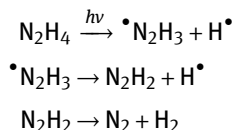


Substantial amounts of  $^{14}\text{N}_2$  were also formed in the photolysis. For instance,  $^{14}\text{N}_2$  did not show up until 5%  $^{14}\text{NO}$  addition was exceeded and increased linearly with the NO concentration. The delay in the formation of  $^{14}\text{N}_2$  is explained by the fact that  $^{14}\text{NO}$  reacts preferentially with  $^{15}\text{NH}_2$ , and only after all amino and hydrazyl radicals are scavenged is NO available to enter into other reactions, presumably a chain reaction involving hydrogen atoms and hyponitrous acid:

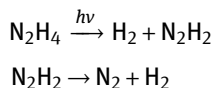


However, as the previous tests with  $\text{C}_2\text{D}_4$  had shown, the supply of hydrogen atoms is insufficient to explain the large amount of  $^{14}\text{N}_2$  formed unless a chain reaction constitutes part of the mechanism. A delayed increase in the rate of  $^{14}\text{N}_2$  formation was also observed in the photolysis of ammonia in the presence of NO. Since no  $^\bullet\text{N}_2\text{H}_3$  radicals are formed in this system, the preferential interaction of NO with  $^\bullet\text{NH}_2$  is given further credence.

It has been shown that the addition of NO decreased the  $^{15}\text{N}_2$  formation to 25% of its original value. This 25% was evidently formed by direct molecular elimination, whereas the remaining 75% was formed by radical disproportionation. The hydrogen:nitrogen ratio gave further evidence of the mechanism by which this molecular elimination occurred. Whereas, based on preliminary results with  $\text{C}_2\text{D}_4$ , it was previously assumed to occur via

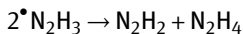


with an  $\text{H}_2:\text{N}_2$  ratio of 1, the later measurement of an  $\text{H}_2:^{15}\text{N}_2$  ratio of 2.3 made a direct split of the hydrazine molecule to diazene more likely:

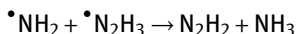


The NO inhibition tests also allow a statement on the ratio of disproportionation:combination of radicals. The uncertainty regarding this ratio had previously

made it difficult to interpret the results of mixed  $^{15}\text{N}_2\text{H}_2$ — $^{14}\text{N}_2\text{H}_4$  tests. The disproportionation of  $\text{N}_2\text{H}_3$

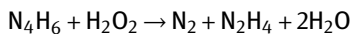
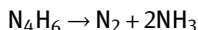
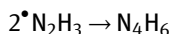
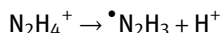
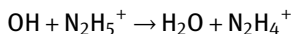


or cross-disproportionation of  $\bullet\text{NH}_2$  and  $\bullet\text{N}_2\text{H}_3$



results in the production of non-randomized  $^{15}\text{N}_2$  (the disappeared 75%). The randomized nitrogen (see [1153]) resulted from the combination of radicals. The ratio of disproportionation to combination was now found to be 5, in good agreement with a ratio of 4 previously deduced from other measurements [1286].

Some early investigators had reported the formation of hydrogen peroxide during the decomposition of hydrazine in the presence of water. Although this could not be confirmed by later investigators, it was of interest to investigate the photolysis of hydrazine (hydrazinium ion) in the presence of added hydrogen peroxide and vice versa [1308]. Free hydroxyl radicals formed by the photolysis of  $\text{H}_2\text{O}_2$  above 220 nm are hypothesized to attack hydrazinium(1+) ions as follows, but experimental proof is lacking:

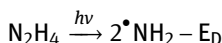


Of course, hydrogen peroxide reacts with hydrazine (at higher pH) also without stimulation by photolysis and sometimes hydrogen peroxide forms as an intermediate in the autoxidation and radiolysis of hydrazine solutions.

#### 4.6.5 Initiation of Explosive Decomposition by Flash Photolysis

Whereas kinetic and photolysis experiments are usually conducted with very low and, hence, safe partial pressures of hydrazine, another way to study the photolysis of hydrazine is to operate at the brink of explosive vapor concentrations. Only minimal decomposition occurs in the vapor during the pre-irradiation period. However, the energy added by a flash of exactly timed duration is sufficient to make the vapor explode. This mode of hydrazine decomposition has been thoroughly investigated [1309–1311]. This work is unique because it studied the time-dependent phenomena that led to the explosion of hydrazine vapor when irradiated with a flash, rather than trying to solve the problem with quasi-steady explosion theory, which was found to be of little use in this case. Employing a kinetic scheme, some reaction paths resulting from the UV flash irradiation of initially quasi-steady samples of hydrazine were formulated. Calcula-

tions showed that under certain conditions (100%  $\text{N}_2\text{H}_4$  at  $1.7 \times 10^{-3} \text{ g/cm}^3$  and 400 K, 6-cm pathlength,  $\lambda = 225 \text{ nm}$ ) flash durations below  $300 \mu\text{s}$  will not initiate an explosive instability, whereas longer flashes will input sufficient activation energy to initiate an explosion. Similar calculations were also performed for MMH and UDMH [1311]. The results were also compared to those obtained with ozone, which decomposes more readily than any of the hydrazines. For identical initial conditions, the half-life of hydrazine was the longest, 295 vs.  $184 \mu\text{s}$  for MMH or  $148 \mu\text{s}$  for UDMH. The dissociation energy for the photodissociative step of hydrazine



was assumed to be  $240 \text{ kJ/mol}$  ( $57.1 \text{ kcal/mol}$ ). Five selected cases were assumed to be typical borderline cases, and differential equations were established to determine whether photolysis would lead to explosion:

1. The optically thin sample is subjected to an arbitrarily short, intense UV pulse.
2. The optically thin sample is subjected to constant, steady-state UV flux.
3. The optically thin sample is subjected to a non-steady-state UV flux that ultimately becomes steady.
4. The optically thick sample is subjected to an arbitrarily short, intense UV pulse.
5. The optically thick sample is subjected to a steady-state UV flux.

The explosive decomposition of hydrazine is characterized by free-radical chain processes in which the variety of different chemical substances appears more significant than the details of the energetics of their reactions. Very rapid data acquisition with spectrometers is required to resolve the concentration-time profile of reacting species in the photolytic initiation of hydrazine or ozone explosive decomposition. Low sample pressures and long absorption paths make it possible to sample every millisecond, fast enough to be comparable to the mean time between intermolecular collisions. The spectra of at least four different substances were observed during the photolysis of hydrazine and photolytically initiated explosions [1312]. In this study,  $\text{NH}_2$  was characterized by a system of lines in the 400- to 600-nm region,  $\text{NH}$  by lines in the vicinity of 300 nm. A weak continuum around 300 nm is associated with hydrazine. A transient, diffused spectrum was observed in the 600-nm region and was tentatively attributed to the hydrazyl radical  $^\bullet\text{N}_2\text{H}_3$ .

#### 4.6.6 Other Photolytic Reactions

Hydrazine photolysis takes place as a yield-limiting step in the photolysis of ammonia that was intended as a method for making hydrazine. If hydrazine forms by the photolysis of ammonia in the atmosphere of Jupiter, its equilibrium concentration will be limited by the photolytic decomposition of hydrazine. Study of the photolysis of ammonia at 184.9 nm revealed that the extinction coefficient of hydrazine is at least six times as large as that of ammonia at the same wavelength [1313, 1314]. Any energy ra-

diated into the system would thus be preferentially absorbed by hydrazine and lead to its decomposition, unless a large excess of ammonia is maintained. A hydronitrogen compound that decomposes even more readily than hydrazine and whose photolysis has also been thoroughly investigated is hydrogen azide,  $\text{HN}_3$ . Some of the intermediate species involved are the same for both hydrazine and hydrogen azide. Some of the experimental techniques described in these references may be useful for the study of the photolysis of hydrazine as well.

#### 4.7 Radiolytic Decomposition of Hydrazine

The decomposition of hydrazine by radiation is of practical interest because it limits the yield during various hydrazine synthesis processes through radiolysis of ammonia. Also, for hydrazine applications in outer space, exposure to cosmic radiation or even intense radiation as in the van Allen belt may result in an increased rate of decomposition and pressure buildup in hydrazine propellant tanks. Hydrazine as a boiler feedwater additive in nuclear power plant primary steam circuits is subjected to a wide array of radiation, mostly neutron radiation and  $\gamma$  radiation, but possibly also including  $\beta$  radiation. Any one of these radiations will decompose hydrazine.

On long-term deep-space missions, radioisotope thermoelectric generators (RTGs) provide electric power from the heat generated by the decomposition of radioactive isotopes. Although RTGs are shielded and placed on extendable booms away from the spacecraft core, some radiation penetrates the shielding. Propellant tanks close to the RTGs are still exposed to nuclear radiation. Because oxidizers are less sensitive to radiation damage than fuels, it would be best to design spacecraft such that the oxidizer tank is between the radiation source and the fuel tank, serving as a radiation shield. Hydrazine radiolysis in a high-radiation environment may cause the propellant tank pressure to increase [1315, 1316].

##### 4.7.1 Decomposition of Hydrazine by X-Ray Radiation

X-rays act in many ways like  $\gamma$  radiation, even though they constitute the “soft” low-energetic range of  $\gamma$  radiation. As long as the energy is high enough to penetrate structural materials, cosmic X-rays may also contribute to the decomposition of hydrazine propellant being stored in spacecraft. In a NASA study, hydrazine vapor at 2 kPa (15 mmHg) was irradiated with X-rays from a 250-kV source at 90–100  $\text{rad}^1/\text{min}$  [1317]. A total dose of 590 krad resulted in approximately 3% decomposition. Hydrogen, nitrogen, and ammonia were found in the decomposition products. A similar test with ammonia resulted in traces of hydrazine being formed

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<sup>1</sup> rad = radiation dose absorbed, 1 rad = 0.01 J/kg; 1 R = 1 roentgen = 0.0002 Coulomb/kg

from ammonia. In a continuation of this work both hydrazine and 1,1-dimethylhydrazine were investigated [1318]. Higher dose rates (100–1000 rad/min.) and higher total absorbed doses (up to 2.3 Mrad = 23 kJ/kg) were used in this later study. The total dose of X-rays was selected to be equivalent to that potentially received through 0.38 mm (0.015 in.) of stainless steel for 2 years at 0.6–1.0 astronomical units from the Sun. Hydrazine vapor at 1.79 kPa (13.5 mm Hg) decomposed faster than UDMH (vapor or liquid) or hydrazine liquid, whereas hydrazine liquid decomposed at the slowest rate of all propellants and physical states examined in this series of tests. The primary radiolysis products from hydrazine were again nitrogen, hydrogen, and ammonia, but also traces of unidentified less volatile products were observed by GC. Although ground experiments have shown the effect of radiation on hydrazine decomposition, there are no reports from actual space missions where cosmic radiation contributed to an excessively fast rate of pressure buildup in hydrazine tanks. Usually other materials' incompatibility problems overshadow the effect of cosmic radiation. The  $G$  value for the decomposition of hydrazine vapor was proportional to the vapor density and (surprisingly) the 1.9<sup>th</sup> power of the glass surface per weight of vapor. In other reactions, the presence of surface quenched chain reactions. For liquid hydrazine, the surface area per unit weight entered only as approximately the 0.6<sup>th</sup> power. The extent of decomposition of the liquids was directly proportional to the total radiation dose and was independent of the dose rate. In hydrazine, decomposition stopped immediately with the discontinuation of irradiation.

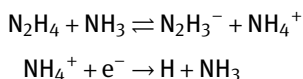
#### 4.7.2 Hydrazine Decomposition by $\alpha$ , $\beta$ , and $\gamma$ Radiation

Long-term storage of hydrazine propellants in spacecraft subjects the propellant tanks to cosmic radiation. Some of the radiation may be energetic enough that it penetrates the tank walls. Cosmic radiation is energetic enough to penetrate propellant tank walls, which are usually made of titanium/aluminum alloys, which are a poor radiation shield. Irradiation experiments have been conducted to simulate this unusual storage condition. The results of hydrazine radiolysis depend on the energy content of the radiation, the radiation intensity, the hydrazine concentration, and the medium in which the reaction is carried out. They also depend on the physical state of the hydrazine to be irradiated. Hydrazine has been irradiated in the solid, liquid, dissolved, and gaseous states.

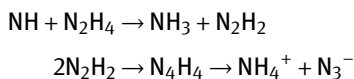
The decomposition of  $\text{N}_2\text{H}_4$  is accelerated by ionizing radiation such as electrons, protons, neutrons, or gamma radiation, most of which are found in cosmic radiation [1319, 1320]. The transient spectrum that can be observed on nanosecond pulse radiolysis of liquid anhydrous hydrazine showed a broad absorption band from 500 to 1000 nm, which has been attributed to solvated electrons.

During the radiolysis of polar amines and hydrazine, solvated electrons disappear by recombination with cations in the solvent. In hydrazine, solvated electrons disappear by reaction with the  $\text{N}_2\text{H}_3$  radical. There is a very low probability of survival of

more energetic electrons in solvents for which the efficiency of electron-radical recombination is low [1321–1323]. The recombination rate constant for recombination of the solvated electron with hydrazinium ions was  $(5 \pm 3) \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$  and was not diffusion controlled. The electron yield can be determined by scavenging with biphenyl, and for nanosecond pulses it was on the order of  $G = 3.4$ . The extinction coefficient of solvated electrons in hydrazine at 1000 nm is  $18500 \text{ mol}^{-1} \text{ cm}^{-1}$ . Irradiated hydrazine also has a small absorption band in the UV range that is like the one observed in irradiated ammonia [1324]. To study reactions between hydrazine and solvated free electrons, therefore, hydrazine has been introduced into deeply colored solutions of alkali metals in liquid ammonia [1325, 1326]. The reaction between hydrazine and ammoniated electrons was followed by absorption measurements, and it was shown that it is not a simple single-step reaction but a two-step reaction in which hydrazine acts as a weak acid in ammonia:



From these kinetic measurements, the pK of hydrazine in ammonia was calculated as pK = 13. This agreed quite well with earlier potentiometric measurements at 213 K. The radiolysis of hydrazine in ammonia forms azide ions. By measuring the  $G$  values for the disappearance of hydrazine in relation to those for the formation of nitrogen and azide, it was noted that the sum of the three  $G$  values is not constant. The following mechanism by way of imide and diazene was proposed to explain the azide formation:



The recombination rate constant of solvated electrons with acidic ions  $\text{N}_2\text{H}_5^+$  is  $(5 \pm 3) \times 10^7 \text{ mol}^{-1} \text{ s}^{-1}$ , and the reaction is not diffusion controlled.

Samples of 2.8, 7, and 10 mL anhydrous hydrazine were vacuum degassed and loaded into 14-mL metal bomblets under argon for radiolysis tests in a  $^{60}\text{Co}$  source [1327–1329]. Bomblets were made from Ti-6Al-4V alloy. At a dose rate of  $6 \times 10^5 \text{ rad/h}$ , 1.6% of the hydrazine was decomposed after 118 h, as indicated by a pressure rise to 303 kPa absolute (44 psia). The rate of gas formation was approximately 0.1 mL gas STP  $\text{Mrad}^{-1} \text{ g}^{-1}$ . Low-dose-rate experiments at 5600 rad/h for 189 d for a total dose of 24.9 Mrad indicated  $G$  values of 7.7, much higher than in the high-dose-rate experiments. The pressure increase in a control bomblet without irradiation was only 10% of that in the irradiated sample. In subsequent experiments, bomblets made of CRES-347, Al-1100, and Al-6061 were tested in addition to those made of Ti-6Al-4V. A series of experiments was conducted for irradiating anhydrous hydrazine in Ti-6Al-4V vessels filled as described previously. All radiation exposures were at 295 K (22°C) and a dose rate of  $6.16 \times 10 \text{ rad/h}$ . Several different sample volumes were used so that the

liquid-vapor ratio was varied. Hydrazine vapor was the only gas present over the liquid during irradiation. The range of volumes of liquid samples was 3–10 mL, which corresponds to 20 to 66% of the total vessel volume. The results showed that the formation of gaseous products not condensable at 195 K (–78.5 °C), i.e.,  $N_2$  and  $H_2$ , was unaffected by a change in ullage. In addition to anhydrous hydrazine, a fuel mixture composed of 24% HN and 1%  $H_2O$  in  $N_2H_4$  was tested for compatibility and radiation resistance. The pressure buildup due to irradiation was independent of container material, but CRES-347 was not compatible with the nitrate mix even without irradiation. The pressure rose in the CRES-347 bomblet eight times faster than in the other bomblets. The rate of radiation-induced decomposition of the nitrate fuel mix was 50–60% higher than the rate of neat hydrazine.

In de-aerated aqueous solutions,  $\gamma$  radiation decomposed hydrazine to ammonia and nitrogen [1330]. The results have been interpreted assuming that radiolysis of the solvent produced  $\cdot OH$  and  $H\cdot$  radicals, which abstracted hydrogen from hydrazine-forming hydrazyl radicals, which disproportionated to  $N_2 + 2NH_3$ . In distinctly alkaline solution, hydrazyl might also dissociate into  $N_2H_2^-$  and  $H^+$ . Aerated solutions decompose with the same  $G$  yield if the pH is below 9. In this case nitrogen is the sole reaction product. It is assumed that an  $HOO\cdot$  radical is formed that is as active as  $H\cdot$  in the destruction of hydrazine. The amount of gas formed by the radiolysis of liquid hydrazine could not be reduced by the addition of olefinic radical scavengers [1331].

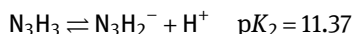
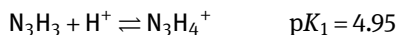
The effect of irradiation is of importance for rocket propellants as well as structural materials and for the two in contact with each other. Gamma radiation instead of X-ray radiation was used for material-radiation compatibility studies to qualify hydrazine for long-term space missions. In one test at JPL with  $^{60}Co$  radiation with hydrazine in a titanium tank, more gas was formed at a low dose rate (5600 rad/h) than at a high dose rate (6160 rad/h) [1332]. After 10 Mrad, 60–80  $\mu mol$  of gas had formed per gram of hydrazine.

Gamma radiation was used to dissociate hydrazine and UV was used as a diagnostic tool to change the excited states of the free radicals thus formed. Hydrazyl free radicals were first generated in frozen hydrazine in sealed quartz ampoules at 77 K by  $\gamma$ -irradiation, then photolyzed by UV light in a wavelength where undissociated hydrazine does not absorb and then measured by EPR. The UV used was filtered to provide maximum intensity between 280 and 400 nm or between 340 and 400 nm. Hydrazine does not absorb in these regions. When the frozen samples were exposed to UV light, the hydrazyl radical concentration decreased. The radical concentration and the concentration-time profile were observed at 77 to 194 K, and the activation energy of the recombination reactions could be determined [1333]. Although the free radicals were immobilized in a matrix of frozen hydrazine, there appeared to be a chain reaction by way of proton or electron exchange migration. The light-excited hydrazyl radical dissociated with the formation of diazene and a hydrogen atom, which abstracted another hydrogen from frozen hydrazine and propagated the chain reaction.



#### 4.7.2.1 Gamma-Ray Radiolysis of Hydrazine Solutions

The radiolysis of water produces  $\bullet\text{OH}$  radicals. The attack of  $\bullet\text{OH}$  radicals on hydrazine produced a short-lived intermediate with absorption at 230 nm, thought to be the hydrazyl radical. The half-life time was approximately 50  $\mu\text{s}$ . Extended observation showed that there existed another longer-lived species that absorbed at the same wavelength and decayed by a first-order acid- or base-catalyzed reaction with a half-life time of approximately 5 ms. There was supportive evidence that the species could have been triazene [1334]. Triazene can participate in the following acid-base equilibria:



The  $\text{p}K$  values were determined from the dependence of the first-order rate constant on pH, from the dependence of initial absorbance on pH, and from the dependence of the first-order rate constant on temperatures at constant pH. The rate constants for the decomposition of the acidic and basic forms of triazene in solution were

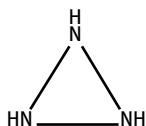
$$\text{triazenium ion} \quad k = 1.97 \times 10^{11} e^{(-12600/RT)} \text{ s}^{-1}$$

$$\text{triazenide ion} \quad k = 2.14 \times 10^{14} e^{(-19200/RT)} \text{ s}^{-1}$$

Triazene itself, which is relatively stable in comparison to its conjugate acid and base forms, has a rate constant of approximately  $0.001 \text{ s}^{-1}$  at 297 K. The global rate constant can be expressed as a function of pH by

$$k = \frac{133}{\left(1 + \frac{K_1}{[\text{H}^+]}\right)} + \frac{2}{\left(1 + \frac{[\text{H}^+]}{K_2}\right)} \text{ s}^{-1}$$

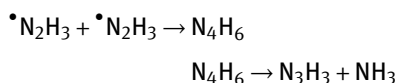
where  $K_1 = 1.12 \times 10^{-5}$  and  $K_2 = 4.27 \times 10^{-12}$  ( $\text{p}K_1 = 4.95$  and  $\text{p}K_2 = 11.37$ ). The decomposition of triazene is catalyzed by phosphate ions. If one assumes that triazene has a linear structure as shown in the preceding reaction scheme, a rapid proton migration or tautomerism must occur. On the other hand, since the spectrum of the reaction mixture showed no absorption characteristics of the  $-\text{N}=\text{N}-$  azo group (which brightens the world of dyestuff chemistry with such beautiful colors), the cyclic structure cyclo-triazene



cannot be ruled out. However, isotope distribution in the products did not support this theory.

The kinetics of oxidation of hydrazine and some of the intermediates can be identified by generating an oxidant in an aqueous solution *in situ* by pulse radiolysis. In an aqueous solution, pulse radiolysis generates hydroxyl radicals,  $\bullet\text{OH}$  [563]. The rate of reaction of hydrazine with hydroxyl radicals was found to depend on the state of protonation of hydrazine or hydrazinium ions, respectively:  $k(\text{OH} + \text{N}_2\text{H}_4) = 1.4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , whereas  $k(\text{OH} + \text{N}_2\text{H}_5^+) = 1.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Various intermediates were observed by UV absorption spectrometry and tentatively identified as hydroxyl radical, tetrazane, and triazene. Up to that time, these intermediates had not yet been observed in solution, but only in the gas phase. The radiolysis products, ammonia and hydrogen, have a pronounced effect on the overall reaction rate, because in their absence the radiolysis of hydrazine is much faster.

If the radiolysis is conducted at pH = 9, an intermediate that absorbs at 230 nm and decays through a second-order reaction is observed, presumed to be the hydrazyl radical. In neutral or acidic solutions, not only hydrazine, but also the hydrazyl radical becomes protonated. Its pK is 7.1, somewhat less basic than hydrazine itself (pK = 8.07). The second-order decay of hydrazyl radicals is postulated to form tetrazane, which decomposes in unimolecular reaction to triazene and ammonia:



Triazene decays by first-order kinetics, presumably to ammonia and nitrogen. The decay rate is markedly dependent on pH, resulting in more rapid decomposition of  $\text{N}_3\text{H}_3$ , or rather  $\text{N}_3\text{H}_4^+$  in acidic solution.

According to Lefort and Haissinsky [1330], the irradiation of hydrazine in deoxygenated water with  $\gamma$  radiation leads to the formation of ammonia and nitrogen. The radiolysis products of water ( $\bullet\text{H}$  and  $\bullet\text{OH}$  radicals) are assumed to react with hydrazine to form a hydrazyl radical  $\bullet\text{N}_2\text{H}_3$ , which then undergoes further decomposition. If oxygenated aqueous solutions are irradiated, the sole product is nitrogen. At pH levels above 9, an  $\text{HOO}\bullet$  radical is also assumed to take part in the reaction, and the mechanism may be like that of hydrazine autoxidation. Some solutions were also irradiated with  $\alpha$  particles in place of  $\gamma$  radiation, but in these tests ammonia was always observed as a product.

The  $\gamma$  radiolysis of hydrazine solutions in water leads to both hydroxyl radicals and hydrogen peroxide. For continued radiolysis, a stationary  $\text{H}_2\text{O}_2$  concentration develops, and  $\text{H}_2\text{O}_2$  itself acts as radical scavenger. The hydrogen yields in acidic and neutral solutions can be explained by the equation [1325]

$$G(\text{H}_2) = G_{\text{H}_2} + G_{\text{red}} - G_{\text{H}_2\text{O}_2}$$

where the component  $G_{\text{red}}$  is contributed by radiolysis of hydrazine:

$$G(-\text{N}_2\text{H}_4)^* = G_{\text{red}} + G_{\text{OH}} = 5.2$$

The rate constant  $k(\text{N}_2\text{H}_5^+ + \text{H}^\bullet)$  has been found to be  $2.5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$  at pH = 0 and  $1.2 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$  at pH = 6. For comparison, the rate constant of ion recombination  $k(\text{N}_2\text{H}_5^+ + \text{e}^-_{\text{aq}})$  at pH = 6 is equal to  $1.5 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ . The low yields of radiolysis in very alkaline (pH = 13) solutions can be attributed to the slow rate of the reaction  $\text{N}_2\text{H}_4^+ + \text{e}^-_{\text{aq}}$ .

The Arrhenius plot for reaction rates of  $\bullet\text{OH}$  with  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{H}_5^+$  did not give a straight line, and activation energies could not be derived. The products of the  $\bullet\text{OH}$  reactions are  $\bullet\text{N}_2\text{H}_3$  and  $\bullet\text{N}_2\text{H}_4^+$ . Recombination of  $\bullet\text{N}_2\text{H}_3$  has the same temperature dependence as the recombination of  $\bullet\text{OH}$  free radicals ( $k = 2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  at 293 K) and leads to tetrazene. Tetrazene then decomposes first by a first-order process to triazene and then to nitrogen and ammonia. Decomposition of triazene does not go directly from the neutral species but only via the cationic or anionic forms,  $\text{N}_3\text{H}_4^+$  or  $\text{N}_3\text{H}_2^-$ . The decomposition of triazene is acid- and base-catalyzed over the entire temperature range tested from 293 to 473 K. The absorption maximum of solvated electrons increases from 700 nm at 288 K to 970 nm at 473 K.  $\bullet\text{N}_2\text{H}_3$  has a maximum absorbance at 230 nm and  $\bullet\text{N}_2\text{H}_4^+$  has a weaker absorbance also at 230 nm. Triazene absorbed with a  $\lambda_{\text{max}}$  at 225 nm.

Rate constants for the reactions of  $\text{e}^-_{\text{aq}}$  and  $\bullet\text{OH}$  with  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{H}_5^+$  in liquid water at temperatures up to 473 K (200 °C) have been measured by pulse radiolysis [1335, 1336]. Linear Arrhenius plots for the reactions of  $\text{e}^-_{\text{aq}}$  gave  $k(293) = 10^6$  and  $1.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , and  $E_a = 13.5$  and  $18.2 \text{ kJ/mol}$ , respectively. H is the product of the reaction with  $\text{N}_2\text{H}_5^+$ . The  $\text{pK}_a$  of  $\text{N}_2\text{H}_5^+$  decreased linearly with temperature from 8.1 at 293 K (20 °C) to 4.2 at 473 K (200 °C). The products of the  $\bullet\text{OH}$  reactions were  $\bullet\text{N}_2\text{H}_3$  and  $\bullet\text{N}_2\text{H}_4^+$ , respectively, and the  $\text{pK}_a$  of  $\bullet\text{N}_2\text{H}_4^+$  also decreased with increasing temperature. The self-reaction of  $\bullet\text{N}_2\text{H}_3$  showed the same temperature dependence as that of  $\bullet\text{OH}$  with  $k(293) = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The product of this reaction was tetrazene. Up to 473 K (200 °C) the data were consistent with successive eliminations of  $\text{NH}_3$  to form triazene and then  $\text{N}_2$ . The pH-dependent kinetics of these processes indicated that the decomposition of triazene  $\text{H}_2\text{NN}=\text{NH}$  is acid- and base-catalyzed over the whole temperature range.

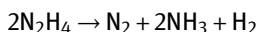
The rate of reaction of oxygenated water with hydrazine in a pulse radiolysis reactor at pH = 10.3 was  $k = (3.8 \pm 0.1) \times 10^6$  and the activation energy was unusually low [1337]. This low value was interpreted to indicate the formation of  $\bullet\text{N}_2\text{H}_3\text{O}_2$ . In irradiated oxygenated solutions, hydrazine could be destroyed by a short chain reaction that may be terminated by radical-radical reactions. Complexing metal ions by adding EDTA shortened the chain. Metal ions present as contaminants accelerated the chain propagating reactions more than the termination steps.

The radiation-induced decomposition by  $^{60}\text{Co}$   $\gamma$  rays of oxygen-saturated aqueous solutions of hydrazine has been measured over the pH range 3.5 to 11.7 [1338]. A reaction set has been proposed that accounts for the experimental observations based on the decomposition proceeding by a pH-dependent chain reaction propagated by hydrazyl radicals (specifically  $\bullet\text{N}_2\text{H}_3$ ) reacting with  $\text{O}_2$  and the resulting

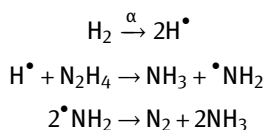
$\text{HO}_2/\text{O}_2^-$  radicals oxidizing the hydrazine to hydrazyl radicals ( $\bullet\text{N}_2\text{H}_4^+/\bullet\text{N}_2\text{H}_3$ ). Chain termination is probably via the self-reactions of  $\text{HO}_2/\text{O}_2^-$ . The pH dependence of the chain length was consistent with (a)  $\text{HO}_2/\text{O}_2^-$  having different reactivity toward  $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5^+$  in the propagating step and (b) the known pH dependence of the termination reaction. There was no evidence that  $\bullet\text{N}_2\text{H}_4^+$  is a chain carrier.

#### 4.7.2.2 Decomposition of Hydrazine by $\alpha$ Radiation

The decomposition of hydrazine by  $\alpha$  rays leads to nitrogen, ammonia, and hydrogen:



It has been proposed that in the presence of a large excess of hydrogen atomic hydrogen is formed first, which then results in the protolysis of hydrazine [1339]:



#### 4.7.3 Hydrazine Decomposition in Glow Discharges

As already mentioned in the section on hydrazine synthesis from ammonia or from the elements in a glow discharge, hydrazine will decompose under these conditions of synthesis very rapidly, and at best a low stationary concentration of hydrazine can be obtained by passing ammonia through a glow discharge. Glow discharges with and without internal electrodes have been used to study the decomposition kinetics of hydrazine at low pressure in the gas phase. It was possible to prove the existence of tetrazene,  $\text{N}_4\text{H}_4$ , and triazene,  $\text{N}_3\text{H}_3$ , by the mass spectrometry of hydrazine glow discharge products [342]. If hydrazine vapor was decomposed by electrodeless discharge near the sampling orifice of a mass spectrometer, the following species were observed:  $\text{H}\bullet$ ,  $\text{H}_2$ ,  $\text{N}$ ,  $\bullet\text{NH}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{N}_2\text{H}_2$ ,  $\text{N}_2\text{H}_4$ , and  $\bullet\text{N}_2\text{H}_3$ . If the products of the microwave glow discharge were first condensed in a liquid nitrogen trap and then fractionated by evaporation after removing the liquid nitrogen from the cold trap, tetrazene  $\text{N}_4\text{H}_4$  could be observed in addition to the aforementioned species. Since no tetrazene was present in the gaseous products of the direct sample, it must have formed by recombination in the condensate as the condensate thawed out. Diazene  $\text{N}_2\text{H}_2$  was also observed as a discrete mass peak that had about the same volatility as ammonia. It was found that  $\text{N}_4\text{H}_4$  evaporated at a somewhat lower temperature than  $\text{N}_3\text{H}_3$ . The least volatile species in the cold trap was the undecomposed hydrazine. Studies of the ionization potentials of various NH compounds in the mass spectrometer also allowed estimation of bond energies (Section 2.3.3).

Diazene has been obtained by the decomposition of hydrazine in a glow discharge and condensing the decomposition products immediately on a liquid-nitrogen-cooled calcium fluoride window [1340]. The yellow deposit, which contained up to 20% di-

azene in a matrix of ammonia, was indefinitely stable at liquid nitrogen temperature. The IR spectrum of the solid at 82 K agrees with the planar structure predicted for diazene, and the molecule appears to be principally in the *cis* form. A cold trap cooled with dry ice was inserted between the glow discharge tube and the liquid-nitrogen-cooled window. When the condensate on the window was allowed to warm up, the absorption bands characteristic of diazene, such as those at 2898, 3095, and  $3205\text{ cm}^{-1}$ , disappeared. Mass spectrometric analysis of the evolved gas showed diazene, ammonia, hydrogen, and nitrogen.

Even at room temperature, diazene vapor diluted with ammonia (prepared by microwave discharge in hydrazine) was surprisingly long lived [1239]. Based on absorption measurements at 345 nm, a wavelength characteristic of  $\text{N}_2\text{H}_2$ , the half-life time was on the order of several minutes. The fact that  $\text{N}_2\text{H}_2$  is not strongly paramagnetic and other data indicate the possibility of a singlet rather than a triplet for the ground state of the molecule.

A yellow deposit has also been observed on a cooled surface in the electrodeless discharge (0.2 MHz) in flowing (10 cm/s) hydrazine vapor [1341]. It has been postulated that this deposit is tetrazane, formed by the recombination of two hydrazyl radicals. A mass spectrometer analysis showed it consisted of 84 vol.-% nitrogen and 16% hydrogen. However, no further proof for this hypothesis was offered, and the compound decomposed on warming.

In another series of glow discharge experiments, hydrazine vapor was decomposed at 1.93 kPa (14.5 mm Hg) and 298 K with 19–60 W of power applied to electrodes 75 mm apart [1342, 1343]. The discharge current (19 to 60 W) and the residence time (0.4 to 2.8 s) were varied, and measurements were made of the light emission at different wavelengths, the fraction of hydrazine decomposed, and the decomposition product composition. Sixty-five percent of the hydrazine was found to decompose within 0.16 A s. The strongest line in the decomposition spectrum was the  $\text{N}_2$  emission at 337.13 nm. Adjacent to this line was strong NH emission at 336.0 nm. Two weak lines at 516.62 and 570.7 nm were assigned to the  $\cdot\text{NH}_2$  radical. These do not stem from ammonia decomposition, because ammonia has a higher dissociation energy (4.52 eV) than hydrazine (3.30 eV), and insufficient energetic electrons were available to decompose ammonia. Also, the hydrazine glow discharge could be sustained only above a threshold voltage applied to the electrodes. Below this voltage no glow discharge was observed, whereas above this voltage at least 64% of the hydrazine decomposed. The decomposition mechanism proposed by Logan agrees with photolytic decomposition studies.

Besides by electrode-supported and electrodeless discharges, hydrazine can be decomposed in silent discharges. The emission spectra obtained from silent discharge in hydrazine have been recorded and compared to those of ammonia [1344]. Between 500 and 800 nm three previously unreported diffuse peaks were reported, with maxima at 525, 638, and 756 nm, which came most likely from molecules with more than

two atoms, possibly  $\text{N}_2\text{H}_3$ ,  $\text{N}_2\text{H}_2$ , or  $\text{N}_2\text{H}_4$  itself. Several papers on the decomposition of hydrazine in a high-frequency glow discharge plasma have been published [1345–1348].

The plasma generated in the glow discharge of hydrazine vapor can be exhausted through a nozzle in a plasma thruster operating on hydrazine decomposition products [1349, 1350]. Preliminary tests were conducted to examine a reaction mechanism using pulsed or stationary AC discharge plasma instead of pelletized catalysts in a rocket-type reaction chamber. In the reaction chamber filled with hydrazine, a sudden increase in temperature and pressure was observed immediately after the activation of a plasma discharge.

#### 4.7.3.1 Hydrazine Decomposition by Electron Beams

In a glow discharge electrons undoubtedly contribute effectively to hydrazine decomposition, but it is not possible to separate their effect from those of the other ions in the plasma. As part of the studies on hydrazine formation by the pulse radiolysis of ammonia, the decomposition of hydrazine by  $\beta$  radiation was also studied. It is this unwanted decomposition reaction that limits the hydrazine yield in the pulse radiolysis of ammonia.

Ionization of a molecular beam of hydrazines by electron bombardment is the most common method for the preparation of a sample for analysis by mass spectrometry. Under these conditions, not only will the parent molecule become ionized, but, depending on the energy of the electrons, the molecule will also be fragmented into smaller radicals and short-lived intermediates. The appearance potentials of various  $m/e$  peaks are summarized in Section 3.6.12 on mass spectrometric analytical methods.

#### 4.7.3.2 Electron Beam Bombardment of Pure Hydrazine in Condensed Phase

Hydrazine was sublimed on a liquid-nitrogen-cooled cold finger and subjected to the discharge from a Tesla coil with approx. 20-keV electrons and a mix of anions of undetermined energy [1351]. The frozen hydrazine did not discolor permanently, even after the longest exposure to radiation. It did appear to turn slightly blue for an instant, but this color could not be stabilized. Even when replacing the  $\text{LN}_2$  with liquid helium, the bombarded frozen hydrazine remained colorless. The cold finger condensate could be fractionated by allowing the most volatile species to sublime first. The reactions occurring during thawing were interrupted by refilling the cold finger with  $\text{LN}_2$  and the absorption spectra in the visible range were recorded after each step and showed distinct changes as the thawing progressed. The  $\text{N}_2/\text{H}_2$  ratios in the ultimately evolved gas depended on the thawing sequence. This indicated that the gases formed not as a result of particle beam irradiation, but as a result of some intermediates that were stable at 77 K but followed different decomposition paths, depending on the thawing sequence.

Although  $\gamma$  radiolysis and fast electron radiolysis by pulsed radiation in the microsecond range was observed previously, the first pulsed electron radiolysis investigation of hydrazine in the nanosecond range found that 3-ns pulses of 600-keV electrons provided about  $10^{14}$  electrons per pulse [1323]. A spectrum in the range 300–1100 nm was recorded immediately after the pulse and again 4  $\mu$ s later. The transient spectrum measurement was not extended below 310 nm because of the strong absorption of hydrazine. The maximum of the spectrum that was recorded immediately after passage of the pulse was located beyond 1100 nm, outside the range of the spectrometer. A similar spectrum had previously been observed using a 4.5- $\mu$ s electron pulse and attributed to the solvated electron in hydrazine [1236]. This assignment was now confirmed using biphenyl as an electron scavenger. The ions present had a stronger effect on the electron decay than electron-hydrazine solvent interaction. Whereas solvated electrons can easily be generated and observed forever in anhydrous liquid ammonia by dissolving some alkali metal, the blue color due to the solvated electron can be observed in hydrazine for only a few seconds. Hydrazine very rapidly forms hydrazides of the alkali metals that are very explosive, even in solution. There is thus no easy way to observe solvated electrons in hydrazine other than by using equipment that operates in the microsecond range or faster. In the solution that contained hydrazinium(1+) chloride, there was also an absorption band from 330 to 450 nm with a peak at 370 nm. This band has not yet been identified. A similar, weaker one could also be observed in pure hydrazine.

#### 4.7.3.3 Electron Beam Bombardment of Hydrazine Vapors

Electron bombardment of hydrazine vapors has practical implications: The data may be useful in optimizing the sensitivity of mass spectrometers in the analysis of hydrazine in air or other atmospheres. Electron bombardment ionization or low-pressure samples in the sample inlet of mass spectrometers precedes the separation of ions in crossed electrostatic and magnetic fields.

Nearly monochromatic electron beams can be generated with good uniformity of energy levels and aimed at the vapor of  $X-NH_2$  molecules ( $X = H, NH_2, OH, CH_3$ ) capable of splitting off amino radicals or ions. When setting (fixing) a QMS to the  $m/e$  of  $NH_2^-$  ions and tuning the energy level of the electron beam, it is possible to generate a maximum intensity of  $NH_2^-$  at a certain resonant energy level of low-energy (0.1–10 eV) electrons where electrons preferentially attach themselves to the dissociated molecular fragment, rather than splitting it into smaller pieces. Surprisingly, ammonia, hydrazine, hydroxylamine, and methylamine all gave very similar  $NH_2^-$  appearance potentials, in contrast to potentials predicted from theory that would essentially parallel the  $H_2N-X$  bond energy [1352]. In crossed-beam experiments with ammonia or hydrazine at up to 23 eV, fluorescence from excited fragments was observed at low pressure and the emitting species were identified by spectroscopic measurements [1353]. The threshold energies at which certain fragments began to appear are listed in Table 57.

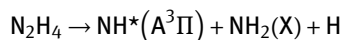
**Table 57:** Threshold energies for appearance of light-emitting species in glow discharges.

| Vapor                         | Primary reaction                                                                                                                   | Energy, eV |
|-------------------------------|------------------------------------------------------------------------------------------------------------------------------------|------------|
| N <sub>2</sub> H <sub>4</sub> | N <sub>2</sub> H <sub>4</sub> → NH <sub>2</sub> *( <sup>2</sup> A <sub>1</sub> ) + NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> ) | 3.87       |
| N <sub>2</sub> H <sub>4</sub> | N <sub>2</sub> H <sub>4</sub> → NH*( <sup>3</sup> Π) + NH <sub>3</sub>                                                             | 5.92       |
| N <sub>2</sub> H <sub>4</sub> | N <sub>2</sub> H <sub>4</sub> → NH*( <sup>3</sup> Π) + NH( <sup>3</sup> Σ) + H <sub>2</sub>                                        | 10.07      |
| N <sub>2</sub> H <sub>4</sub> | N <sub>2</sub> H <sub>4</sub> → NH*( <sup>3</sup> Π) + NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> ) + H                         | 10.42      |
| N <sub>2</sub> H <sub>4</sub> | N <sub>2</sub> H <sub>4</sub> → N <sub>2</sub> *( <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> ) + e <sup>-</sup> + 2H <sub>2</sub>    | 18.7       |
| N <sub>2</sub> H <sub>4</sub> | N <sub>2</sub> H <sub>4</sub> → NH*( <sup>3</sup> Π) + NH <sub>2</sub> ( <sup>2</sup> B <sub>1</sub> ) + H*( <i>n</i> = 4)         | 23.1       |
| NH <sub>3</sub>               | NH <sub>3</sub> → NH <sub>2</sub> *( <sup>2</sup> A <sub>1</sub> ) + H                                                             | 5.70       |
| NH <sub>3</sub>               | NH <sub>3</sub> → NH*( <sup>3</sup> Π) + H <sub>2</sub>                                                                            | 7.62       |
| NH <sub>3</sub>               | NH <sub>3</sub> → NH*( <sup>1</sup> Π) + H <sub>2</sub>                                                                            | 8.95       |

Data source: [1353]

It was thought remarkable that the (<sup>1</sup>Π) state of NH is not produced by electron impact on hydrazine. Similar appearance potential measurements are important for the optimization of mass spectrometers as analytical instruments.

Electron-impact dissociation of other nitrogen species, including hydrogen azide or methylamine in addition to hydrazine or ammonia, also produced excited NH(A<sup>3</sup>Π) or NH(c<sup>1</sup>Π) radicals [1354]. The triplet excited state of the parent compound contributes to the formation of the triplet NH(A<sup>3</sup>Π) near the threshold. The threshold of the reaction



was observed at 10.4 eV, in agreement with the results of theoretical calculations and experimental results reported by other investigators. More energetic electrons up to 50 eV were used to study the formation and internal energy distribution of NH fragments produced from dissociation of hydrazine or methylamine at 0.013 Pa (~10<sup>-4</sup> mm Hg) [1355]. Both NH(A<sup>3</sup>Π) and NH(c<sup>1</sup>Π) were found in either reaction and identified by their emission spectra at 336 nm. In the electron-impact dissociation of hydrazine, the observed rotational temperature of the *v*' = 0 level of the NH(A) state was about twice as high as that of the NH(c) state. The onsets of NH(A<sup>3</sup>Π) and NH(c<sup>1</sup>Π) formation from hydrazine were at 10.8 ± 0.6 and 11.9 ± 0.7 eV, respectively. Even higher electron energies (10–270 eV) were used to study the electron-impact dissociative ionization of ammonia, hydrazine, and MMH [402]. The apparatus consisted of (1) pulsed electron and molecular beams, (2) a field-free ionization volume, (3) two-stage high-voltage ion extraction, and (4) multi-channel mass detection. Thirty-five parent and fragment ions were detected and the appearance potentials for electron impact ionization were compared to those obtained by photoionization. All measurements were made in a crossed electron-molecular beam apparatus using pulsed extraction and time-of-flight mass detection to ensure field-free excitation and high collection efficiency for energetic ions. The molecular beams were jet-cooled to obtain uniform



initial energy levels. The measured cross sections for total ionization at 70 eV were  $2.35 \text{ \AA}^2$  for ammonia,  $3.76 \text{ \AA}^2$  for hydrazine, and  $4.20 \text{ \AA}^2$  for MMH. In a continuation of this study, electron energies for electron impact dissociative ionization were varied from the ionization thresholds to 260 eV [1356]. Molecules at room temperature underwent more fragmentation upon ionization, and the distribution of partial cross sections shifted toward smaller fragment ions. The partial cross sections of energetic ions need to be corrected for detection (in)efficiency, which drops for higher-energy ions.

In the gas phase, the radiolysis of hydrazine leads to hydrogen, nitrogen, and ammonia [1357]. Hydrazine vapor was irradiated under dynamic conditions at a pressure of  $6 \times 10^{-3} \text{ mm Hg}$  (0.8 Pa) by a beam of electrons, the energy of which could be varied between 10 and 100 eV. Another series of experiments was carried out by the irradiation of hydrazine vapor under static conditions at a pressure of 14 mm Hg (1.9 Pa) by  $\alpha$  rays in an apparatus that also enabled the effect of an electric field on the radiolysis to be determined. The results obtained seemed to indicate that the radiolytic decomposition of  $\text{N}_2\text{H}_4$  was initiated by two primary acts: an excitation producing  $\text{N}_2$  and  $\text{H}_2$ , and an ionization producing  $\text{N}_2$  and  $\text{NH}_3$ . At low pressures these two mechanisms are of comparable importance; at higher pressures the latter one initiating a chain reaction becomes predominant.

Different approaches have been proposed for the study of bond breakage probabilities under electron impact, including the calculation of stabilities, rupture coefficient, and indices of fragmentation [1358].

#### 4.7.4 Hydrazine Decomposition by Atomic Hydrogen

Most studies on the decomposition of hydrazine under the influence of proton beams ( $\beta$  radiation) were conducted in the vapor phase. However, with the use of hydrazine hydrate in the primary steam loop of nuclear reactors, interaction with atomic hydrogen in the liquid aqueous phase was becoming of increasing interest.

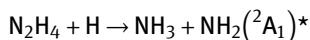
##### 4.7.4.1 Hydrazine Decomposition by Atomic Hydrogen in Vapor Phase

Atomic hydrogen can be used as a selective reagent to initiate hydrazine decomposition, and numerous publications deal with this method. Actually, these papers should be listed among the methods used to generate hydrogen atoms, such as glow discharge or photolysis [1301]. However, the method is sufficiently unique to deserve a section of its own. In a similar fashion, atomic oxygen is also used to initiate decomposition of hydrazine with the subsequent formation of water. These studies are discussed in the section on hydrazine combustion mechanisms (Section 4.14). A convenient source of atomic hydrogen is the photolysis of hydrazine [1301].

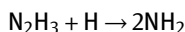
Numerous publications deal with the decomposition of hydrazine under the influence of hydrogen atoms [545, 1199, 1219, 1221, 1222, 1359]. Over the years, experimental

techniques have been refined, and new methods of analysis, such as ESR, have been applied to study the free radicals formed in the process.

The luminescent reaction of hydrazine with atomic hydrogen was studied in flowing gas systems [1360, 1361]. The emission is due to  $\text{NH}_2$  radicals apparently produced by the process

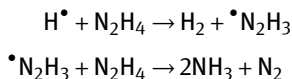


Estimates of the emission quantum yield showed that this is a relatively minor process. The absorption spectrum showed an unexpectedly high concentration of  $\text{NH}_2$  radicals in the reaction zone. This is consistent with the other known facts if the process



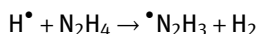
becomes important when the  $[\text{H}]/[\text{N}_2\text{H}_4]$  ratio is large.

When hydrogen atoms generated in a glow discharge were mixed with a molecular beam of hydrazine vapor, a reaction with the formation of ammonia and permanent gases ( $\text{N}_2 + \text{H}_2$ ) took place. At the point of impingement of the jets, a weak green fluorescence could be observed [1359]. The mixing zone also heated up considerably from the heat liberated by the reaction. The hydrogen atom concentration was measured by the heat of recombination when a platinum foil (Langmuir probe) was exposed to the gas. The first attempt to explain the mechanism of atomic hydrogen reactions with hydrazine followed the path of thoughts previously established during ammonia photolysis:



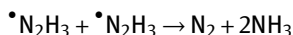
One convenient way to study free radicals involved in reactions is by recording their emission spectra. Hydrogen atoms were generated in a glow discharge and interacted with a molecular beam of hydrazine vapor at a pressure of 133 Pa (1 mm Hg) [545]. An  $\text{NH}_2$  band of medium intensity and  $\text{NH}$  bands of weak intensity were observed in emission. Hardly any undecomposed hydrazine was found in the condensate, but 30–55% of the theoretically possible ammonia was condensed as such. No emission spectra could be recorded when ammonia was substituted for the hydrazine. With atomic oxygen very intense emission spectra were observed.

ESR was used to measure the rate of reaction of hydrogen atoms with hydrazine [1221]. Although a reaction stoichiometry was not deduced because no gas analysis was performed, a possible reaction sequence is also being proposed for this mode of hydrazine decomposition. The first step is most likely a hydrogen abstraction



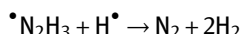
(Reaction (10) in Figure 38

The hydroxyl radical can then follow one of two reaction paths



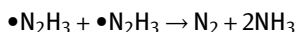
(Reaction (4) in Figure 38

or



(Reaction (11) in Figure 38

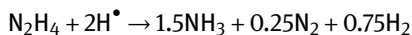
Since the experimental conditions were such that the hydrazine concentration was much higher than the hydrogen atom concentration,



was considered more likely. Because it lacks an exact stoichiometry, the pre-exponential factor obtained in this study is less accurate than the activation energy. The activation energy was obtained from the slope of the rate constant straight line in an Arrhenius plot and agreed well with those reported by other authors (Table 51). The main difference in the pre-exponential factor may be due to the use of a fast flow system in [1219] and [1221], as opposed to a stirred reactor used by previous investigators [1222]. In a similar study in which a stream of atomic hydrogen was generated by subjecting a mixture of 0.5%  $\text{H}_2$  and 99.5% He to a high-frequency electrodeless discharge (2375 MHz, 100 W), the reaction of hydrogen atoms with hydrazine vapor was studied in a flow system by ESR spectroscopy at 304–505 K and 0.23–0.33 kPa with contact times from 0.5 to 10 ms [1362]. By repeating the test at different temperatures, the activation energy of the reaction was determined by a discharge flow method and ESR as  $9.2 \pm 0.9$  kJ/mol [1363].

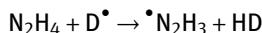
The absolute rate parameters of the reaction of atomic hydrogen with hydrazine were measured using flash photolysis and measurement of atomic hydrogen by means of resonance fluorescence [1223]. No secondary reactions involving hydrogen atoms as a reactant or product interfered with these measurements.

It was difficult to determine rate constants for several reactions of importance in hydrazine decomposition [1219]. The results were already summarized in Table 53. The hydrogen atoms were generated in a separate chamber by microwave induction and then mixed with hydrazine vapor at 213–473 K and 133–1330 Pa (1–10 mm Hg) in a flow system. The composition of the decomposition products varied with the ratio of atomic hydrogen to undecomposed hydrazine. As long as this ratio did not exceed 5, the following stoichiometry of the decomposition reaction was observed:



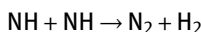
When the effluent of the mixing zone was monitored with a TOF mass spectrometer at  $m/e = 16$  (the molecular weight of the amino radical), it increased slightly from a background current to an intermediate value if hydrazine only was introduced. How-

ever, as soon as the hydrogen discharge was energized, the  $\bullet\text{NH}_2$  radical concentration jumped to more than twice this value. This is a distinct proof for the presence of  $\bullet\text{NH}_2$  radicals as the result of hydrogen atom interaction with hydrazine. Besides  $\bullet\text{NH}_2$ ,  $\bullet\text{N}_2\text{H}_3$  and  $\text{NH}$  radicals were observed in smaller concentrations;  $\bullet\text{N}_2\text{H}_3$  could be identified by monitoring mass number 31 while reacting molecular beams of hydrogen atoms and hydrazine. Further proof of the hydrogen abstraction from hydrazine was provided using deuterium instead of hydrogen atoms:



In this test the ion current at  $m/e = 3$  increased as soon as the experiment was initiated.

The rate constant obtained for the reaction  $\text{H}\bullet + \text{N}_2\text{H}_4 \rightarrow \bullet\text{N}_2\text{H}_3 + \text{H}_2$  is shown in Table 53. Even though the activation energy is the highest of all reported to date, the rate constants reported by Gehring agree well with the results obtained by [1221] but do not agree with those by [1222]. A direct comparison is difficult because the conditions of reaction were slightly different. Gehring and co-workers [1219] deemed the direct decomposition of diazene [Reaction (9) in Figure 38] as very unlikely. Instead, they assumed a rate of  $5 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the reaction



to explain the disappearance of  $\text{NH}$  without intermediate formation of  $\text{N}_2\text{H}_2$ . Concentration profiles for nine species in the reaction  $\text{H}\bullet + \text{N}_2\text{H}_4$  were calculated for the first 3 ms of reaction time. Calculated curves agreed well with experimental TOF mass spectrometer data (to be compared also to the results obtained by abstraction of hydrogen from hydrazine [346, 347]).

The energy profiles of reactions of  $\text{H}_2\text{NN}\bullet\text{H}$  and  $\text{H}_2\text{NNH}_2^{\bullet+}$  with  $\text{H}\bullet$  in the gas phase were studied using a modified G2 (MP2) *ab initio* method. This method has been used to obtain bond dissociation energies, proton affinities, and heats of formation of hydrazine and radicals and radical ions derived therefrom [567]. During the attack of  $\text{H}\bullet$  on  $\text{H}_2\text{NNH}_3^+$ , the rate of formation of  $\text{H}_2\text{NNH}_2^{\bullet+}$  by H abstraction from the  $\text{NH}_3^+$  end of the molecule has a very low activation energy, but in aqueous solution, solvation effects will lead to attack at both ends in comparable intensity.

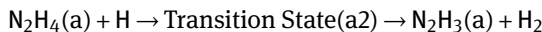
A study of the hydrogen abstraction reaction  $\text{N}_2\text{H}_4 + \text{H} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$  using a direct *ab initio* dynamics method predicted four possible reaction channels caused by different structures of  $\text{N}_2\text{H}_4$  and different positions of hydrogen atom attack [1364]. The structures and frequencies at the stationary points and along the minimum energy paths were determined by computations. Thermodynamic data for reactants and intermediates were further refined based on theory. The rate constants are calculated in a temperature range of 220–3000 K. The calculated results showed that in the lower temperature range, the most favorable reaction channels are



and



while in the higher-temperature range



and



predominated. The calculated total rate constants of the four reaction channels were in good agreement with the available experimental data.

#### 4.7.4.2 Hydrazine Decomposition by Atomic Hydrogen in Liquid Phase

Hydrogen atoms were generated in aqueous solution within an EPR spectrometer cavity by pulse radiolysis with 3-MeV electrons from a van de Graaff accelerator, and the irradiated fluid was flowing through the sample chamber at a rate sufficiently high to completely replace the liquid between pulses [1365]. At 314.7 K, a scavenging constant of  $(5.8 \pm 1.9) \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  was measured directly for the reaction of  $\text{H}^\bullet$  with  $\text{N}_2\text{H}_5^+$ . From data taken over the temperature range 314–355 K the activation energy could be calculated as  $61.4 \pm 1.2 \text{ kJ/mol}$ . Based on these measurements, the acidity constant of the  $\text{N}_2\text{H}_5^+$  ion over the range 273–353 K can be calculated from

$$\text{p}K_{\text{a}} = \frac{2600 \pm 30}{T} - (0.771 \pm 0.099) \quad T \text{ in K}$$

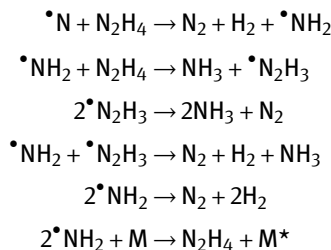
which gives  $\text{p}K_{\text{a}} = 7.95$  at 298 K. From the two preceding equations, then, the rate constant could be calculated for the reaction of  $\text{H}^\bullet$  with  $\text{N}_2\text{H}_4$  itself, which was found to be  $k = (6.74 \pm 0.23) \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$  at 297.6 K with an activation energy of  $16.29 \pm 0.80 \text{ kJ/mol}$ . The reaction rate of  $\text{H}^\bullet$  with  $\text{N}_2\text{H}_4$  is consistent with hydrogen abstraction as the first step, giving  $\text{H}_2$  and  $^\bullet\text{N}_2\text{H}_3$ , like the gas-phase reaction. However, based on the relatively high activation energy and entropy of the reaction of  $\text{H}^\bullet$  with  $\text{N}_2\text{H}_5^+$ , an addition-fragmentation process has also been discussed.

#### 4.7.5 Hydrazine Decomposition by Molecular Beams and Vibrationally Excited Dinitrogen

Electronically excited dinitrogen  $\text{N}_2(\text{A}^3\Sigma_{\text{u}}^+)$  and vibrationally excited “active” dinitrogen molecules do not contribute significantly to the decomposition of hydrazine molecules in the nitrogen afterglow if the reaction with nitrogen atoms is the main reaction [1366]. The reaction of hydrazine with excited dinitrogen molecules may be a yield-limiting reaction in the attempts to synthesize hydrazine from the elements or from ammonia in a glow discharge, since it reverses the desired direction of synthesis. It may also take place if hydrazine is vented in the high atmosphere in areas where the

nitrogen afterglow can be seen. Some of these reactions of hydrazine with molecular excited species or ions also take part in a glow discharge (Section 4.7.3), but they are difficult to isolate when a host of species is zipping around between the electrodes. It would be better to extract a narrow range of particles and particle energies from a glow discharge and let them impinge on hydrazine vapor. The ratios of luminous intensity in the absence of hydrazine to that in the presence of hydrazine, measured at 580 nm [yellow glow due to recombination of  $N(^4S)$  atoms] were taken as an indication of reaction of N atoms with hydrazine. Similar ratios were measured at 253.7 nm in active nitrogen sensitized with mercury vapor. In all cases, and over a wide range of glow discharge currents, the presence of hydrazine quenched the emission intensity to a third to a fourth of the baseline luminous intensity.

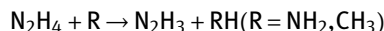
It was observed that hydrazine vapor was completely destroyed when bombarded with active nitrogen at a flow rate of  $9 \times 10^{-5}$  mol/s [1367]. The tests were performed at 423 and 753 K and the rate of decomposition was 14% faster at the higher temperature. The results were interpreted to indicate that amino radicals are formed in only secondary reactions. The most probable mechanism for the reaction was proposed as



When modeling the thermodynamics and kinetics of sequential hydrogen abstraction reactions from hydrazine by nitrogen atoms, the dehydrogenation was divided into three steps:  $N_2H_4 + N$ ,  $N_2H_3 + N$ , and  $N_2H_2 + N$  [1368]. The thermal rate constants were calculated within the framework of canonical variational theory, with zero and small curvature multi-dimensional tunneling corrections. The reaction paths were computed, and the thermochemical properties were improved using another method. The first dehydrogenation step presented the lowest rate constants, equal to  $1.22 \times 10^{-20} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 298 K.

#### 4.7.6 Hydrazine Decomposition Initiated by Hydrogen Abstraction

A direct *ab initio* dynamics study on the hydrogen abstraction reactions



predicted six possible reaction channels for  $NH_2$  abstraction and four for  $CH_3$  abstraction caused by the different  $N_2H_4$  isomers and various attacking orientations of foreign radicals in relation to  $N_2H_4$  [1369]. The structures and frequencies at the stationary points and the points along the minimum energy paths of all reaction channels were

calculated. The rate constants of these channels were calculated using the improved canonical variational transition-state theory with the small-curvature tunneling correction method. The calculated results showed that the favorable reaction channels were channels (n1) and (n4) as well as (c1) and (c3) in the whole temperature range. The rate constants of all channels for the two reactions were both in good agreement with the available experimental data, and corresponding three-parameter expressions in 220–3000 K are fitted as

$$k = 6.46 \times 10^{-15} (T/298)^{3.60} \exp(-386/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for  $\text{NH}_2$  abstraction and

$$k = 1.04 \times 10^{-14} (T/298)^{4.00} \exp(-2037/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for  $\text{CH}_3$  abstraction. Additionally, the long-range interaction between the H atom of X–H bond in foreign radicals and the lone pair on the non-reactive N atom of the transition states was further discussed to explain the various transition-state numbers of the two similar hydrogen abstraction reactions.

The kinetics of the reaction of  $\text{N}_2\text{H}_4$  with atomic oxygen depends on the initial conditions. In oxygen-rich systems, the rate constant shows a conventional positive temperature dependence, while in hydrazine-rich systems the dependence is negative in certain temperature ranges. A theoretical model was presented that adequately reproduced the experimental results for a hydrazine-rich environment, consisting of the hydrogen abstraction from the hydrazine dimer by an oxygen atom [1370]. The thermochemical properties of the reaction were computed using two quantum-chemical approaches. The kinetic data were calculated with the improved canonical variational theory using a dual-level methodology to build the reaction path. Energy potential wells on both sides of the reaction  $(\text{N}_2\text{H}_4)_2 + \text{O} \rightarrow \text{N}_2\text{H}_4 \dots \text{N}_2\text{H}_3 + \text{OH}$  were determined. A reaction path with a negative activation energy was found leading, in a temperature range of 250–423 K, to a negative dependence of the rate constant on the temperature, which was in good agreement with experimental measurements. The hydrazine dimer model provided significantly improved agreement with the experimental data and should be included in the mechanism of the global  $\text{N}_2\text{H}_4$  combustion process because it can be particularly important in hydrazine-rich systems.

#### 4.8 Analytical Mathematical Models of Hydrazine Decomposition

Besides the variety of experimental studies described in the preceding sections, some investigators have also conducted theoretical studies of mathematical models of hydrazine decomposition. These studies were greatly aided by the availability of digital computers in recent decades. The publications can generally be divided into equilibrium and non-equilibrium studies. Under practical conditions, such as in hydrazine decomposition reactors, equilibrium is rarely achieved, and the predictions of equi-

librium studies are of only limited value. On the other hand, non-equilibrium studies including kinetic rates for all reactions involved are not yet perfected, and, at best, rough approximations have been reported.

A theoretical kinetic study was conducted to investigate the effects of dihydrogen (present in pyro valve actuator blow-by gases) on hydrazine decomposition [1371]. Since hydrogen is a normal product of hydrazine decomposition, all reactions necessary to evaluate its effect on hydrazine decomposition chemistry were already in the original mechanism developed [1372]. The expanded kinetic mechanism consisted of 70 species interacting via a network of 452 reactions. Calculations indicated that  $H_2$  presence as an initial reactant in substantial amounts can dramatically impact the process of hydrazine decomposition. What was of particular interest, and somewhat surprising, was the extent to which molecular dihydrogen in the initial mixture was predicted to accelerate the decomposition of hydrazine. The change in hydrazine half-life from the baseline case (i.e., no  $H_2$  initially present) to the case where a 1 : 1  $H_2$ : $N_2H_4$  starting ratio exists was five orders of magnitude.

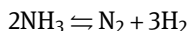
One of the kinetic analysis programs used for the study of hydrazine vapor decomposition was ReaxFF, which allows the valence interactions (bonds, angles, torsions) and charges to change continuously as bonds form and break in reactions. The instantaneous bond orders are determined from the bond distances that in turn determine the forces between the atoms. This program has been used to model the homogeneous decomposition of bulk hydrazine or MMH vapors, the decomposition of hydrazine in the presence of hydrogen peroxide, and the heterogeneous decomposition of hydrazine on catalytic surfaces Pt[100] and Pt[111] under various conditions [1373].

The most detailed and richly illustrated computational approach to date to hydrazine decomposition in the vapor phase and on the surface of iridium/alumina catalysts was based on gas-phase electronic structure theory calculations that included electron correlations and predicted that numerous molecular and free radical reactions could occur within the same energy range as the basic free radical pathways: N—N bond breaking around 272 kJ/mol (65 kcal/mol) and N—H bond breaking around 339 kJ/mol (81 kcal/mol) [1374]. The results suggested that a revision and more detailed approach to existing kinetics modeling were desirable, based on the energetics and the new elementary steps reported. A supported  $Ir_6$  octahedron model for the Shell 405 iridium catalyst was developed. Self-consistent field and electron correlation calculations (with core potentials and associated basis sets) illustrated a diverse chemistry for hydrazine on this catalyst model. The model catalyst enabled dramatically lower N—N and N—H bond cleavage energies and an even smaller barrier to breaking the N—H bond by  $NH_2$  abstractions. Thus, the low-temperature decomposition over the catalyst was interpreted in terms of consecutive  $NH_2$  abstractions to produce ammonia and nitrogen. The higher-temperature channel, which has  $H_2$  and  $N_2$  products, may be due to several simultaneous mechanisms. These mechanisms are successive N—H cleavages with surface H+H recombinations, and the same types of assisted  $H_2$  eliminations were found to occur in the gas phase.



#### 4.8.1 Equilibrium Calculations

Numerous thermochemical equilibrium computer programs have been described in the literature and applied to the problem of hydrazine and hydrazine derivative decomposition. The reason for discrepancies between equilibrium calculations and experimental results is that the equilibrium



is very slowly established, significantly slower than the hydrazine decomposition. In many cases the dwell time in a reactor is insufficient to establish equilibrium and the ammonia dissociation is lower than predicted by equilibrium calculations. There are also experimental errors, and it is difficult to obtain exact measurements of the degree of ammonia dissociation in the exhaust. Changes in the composition of the gas samples after they have been withdrawn from the reactor should not occur because the reaction is usually quenched by a cold probe, and the gases do not change composition when stored at room temperature.

Mollier-type diagrams have been calculated and graphed for hydrazine decomposition products at equilibrium temperatures of 865–1646 K and pressures up to 10 MPa, assuming 0–80% ammonia decomposition [1375]. These graphs have the advantage over other equilibrium calculations that a Beattie-Bridgeman-type EOS was used, which represents high-pressure data better than the ideal gas laws.

The highest operating temperature of actual hydrazine applications occurs in arcjets. Attempts have been made, with varying success, to model the plasma in the exhaust where hydrazine and ammonia are mostly dissociated, and the electron density is an important variable of the working medium. The residence time in an arcjet is usually too short to achieve equilibrium but, on the other hand, too long to assume frozen flow. Results of non-equilibrium numerical methods with separate electron and gas temperatures, including consideration of viscous flow properties and assuming laminar axisymmetric flow, were compared with experimental measurements of electron density with a Langmuir probe and heavy particle velocities with a TOF electrostatic probe [1376]. There are few reliable sets of thermodynamic and transport properties of nitrogen/hydrogen plasmas at very high temperatures and pressures. There are several more studies on arcjets, but they are beyond the scope of this chemistry book since the plasma could very well have started as a mixture of ammonia, nitrogen, and hydrogen instead of hydrazine, and one would not know the difference. One such model includes consideration of equilibrium dissociation/recombination, binary exchange, and ionization over a range of 1 MPa to 10 Pa and 300 to 15000 K [1377]. Equations are derived for electrical conductivity, viscosity, and thermal conductivity of the plasma flow.

## 4.9 Hydrazine Decomposition Flames

Many experimental investigations have been devoted to hydrazine decomposition flames. First, one could argue that this topic would be more accurately discussed in the preceding section under the overall heading “Homogeneous Vapor-Phase Decomposition.” However, hydrazine decomposition flames are discussed here because, although some investigators study the rate of combustion of *liquid* hydrazine strands, the rate-controlling phenomena still take place in the *vapor* phase. In a hydrazine decomposition flame, the liquid does not decompose *per se* but must vaporize first. The same is true for hydrazine combustion in the presence of oxidizers.

Unlike alkyl nitrate-based monopropellants like Otto Fuel II, hydrazine as a monopropellant is usually not burned in empty, hollow combustion chambers. As a minimum, if no catalyst is used to initiate and sustain hydrazine decomposition, there would be a thermal bed or a flame holder. Thus, flame speed studies have no practical value for hydrazine as a monopropellant and are done mostly to satisfy academic curiosity. Droplet decomposition of hydrazine sprays may have some practical applications in engines with discrete head spaces or in biplex engines where hydrazine is injected downstream of a catalytic pre-decomposition chamber and into a plenum chamber at very high pressures where it decomposes without the aid of a catalyst.

One significant advantage of liquid hydrazine over other monopropellants like nitromethane or some HAN-based monopropellants is that combustion does not propagate upstream from a hot reactor through the injector passages into the liquid propellant reservoir. The burning rate of hydrazine liquid through a liquid-filled line is too slow and the heat loss to the tubing wall will quench the propagation of a flame front (but only with small feed tube diameters). Nevertheless, when modeling flame front propagation through the feed system in real propulsion systems, the regression rate of liquid hydrazine flames must be known over the entire range of temperatures and pressures. This is important for scaled-up propulsion systems where tubing diameters may exceed 1 in. and more.

There are basically four methods for studying hydrazine decomposition flames: stabilization of a stationary vapor flame on a flame holder, photographic measurement of flame propagation in a closed vessel, liquid strand burning, and liquid droplet burning. Sometimes the term *hydrazine combustion* is used in a misleading fashion in reference to decomposition flames that do not involve an oxidizer and a fuel. In our terminology the term *combustion* is reserved for flames involving an oxidizer.

Experimental results of flame speed, quenching distance, critical pressure, and regression rate (“burning velocity”) of monopropellant hydrazine decomposition flames are discussed and compared in the following sections. In many cases the authors have attempted to relate the results of flame studies to kinetic data obtained at lower partial pressure in the non-flammable range. However, data that nicely agree with theoretical explanations at lower pressure fail to do so at higher pressures and temperatures.

The terminology and the difference between flame speed  $S_b$  and burning velocity  $S_v$  are explained by the fact that the flame speed is the speed at which the gases must flow if a stationary flame is to be obtained. The burning velocity relates to the combustion of the liquid, and, to avoid confusion, we prefer the term *regression rate*, which is borrowed from solid and hybrid rocket propellant combustion to describe this process.

Hydrazine decomposition flames were first observed during an investigation on the reaction of hydrazine with nitric oxide [1228]. It was one of the first compounds found to undergo controllable decomposition in the absence of an oxidizer.

Some additional information on hydrazine decomposition flames is contained in Section 8.1 on hydrazine safety. Sections 8.1.2 and 8.1.3 summarize information on the limits of propagation of hydrazine vapor decomposition at low pressures and with various diluents. Several of the papers discussed in the following sections discuss the pressure dependence of the flame speed  $S_b$  as an indication of the order of reaction  $n$ . The thermal theory of flame propagation predicts a relationship of

$$S_b \approx P^{\frac{(n-2)}{2}}$$

In a low-pressure regime, most investigators agree that the flame speed is independent of pressure. In the preceding equation, this would mean  $n = 2$ , a second-order reaction. Only at pressures above atmospheric pressure can an inverse square-root dependence be observed that is typical of a first-order reaction. Several purely analytical studies on flame propagation have endeavored to interpret the vast amount of experimental data, but this is not always easy. Experimental data on hydrazine flame speed are pressure-independent at low pressures [1204, 1378, 1379]. Thus, a second-order reaction mechanism was assumed to be controlling. Kinetics were given for a chain mechanism in which the  $\text{NH}_2$  radical is formed by a pseudo-unimolecular process, tending to first order at high pressures but second order at low pressures. The consequent set of flame equations could be solved using a chemical steady-state hypothesis. In this instance, however, the solution to the flame equation leaves both the flame speed and the overall chemical rate constant undetermined for hydrazine decomposition. Insertion of an experimental flame speed made it possible to obtain a value for this rate constant. It was also possible to calculate the second-order rate constant for the formation of activated  $\text{N}_2\text{H}_4$  radicals. The rate equation was

$$k_a = \sim 3 \times 10^{18} \exp(-60000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The unusually high value for this constant suggested energy transfer to the N—N bond from many vibrational modes of  $\text{N}_2\text{H}_4$ . Re-examination of earlier data of Szwarc on the formation of  $\text{NH}_2$  radicals treated as a first-order process indicated that a second-order process may be implied from the data and, also, a value for

$$k_a = 10^{19} \exp(-60000/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

may be deduced. Other authors provided only a review of existing flame reaction data [1380].

Several theories have been promoted for calculating and predicting flame speeds of monopropellant decomposition flames from the molecular and thermochemical properties of the reactant [1381–1384]. Usually far-reaching assumptions must be made to obtain all the input data to enter into such a computerized model, which often stands on shaky ground.

The flame speed of laminar decomposition flames has been described by an analytical model by first assuming that the steady-state assumption is justified for the concentration of radicals [1385]. Subsequently a model was developed for the computation of flame speed not including this assumption. Comparison of the results with experimental data from other authors indicated that a steady-state assumption was justified. Because the stoichiometry of hydrazine flames is simple in comparison to the combustion of pre-mixed reactants, hydrazine decomposition flames have frequently been used as model flames to validate various combustion models. For ambient pressure flames, good agreement was observed between calculated and measured values for laminar flame velocity (calculated: 1.84 m/s, measured: 1.85 m/s) and quenching distance (calculated: 0.5 mm, measured: 1.2 mm) of hydrazine decomposition flames in the absence of air [1386, 1387]. The ratio of flame velocity  $U_f$  to quenching distance  $D$  is proportional to the ratio of reaction rate  $w$  to initial fuel concentration  $A_0$ :

$$\frac{U_f}{D} \approx \frac{W}{A_0}$$

The general equations on laminar flame propagation in hydrogen, oxygen, and nitrogen mixtures are applicable to hydrazine combustion flames as well as decomposition flames [1388]. However, no numerical data were given for hydrazine flames. Some correlations allowed for the calculation of the burning velocity in pre-mixed laminar flames, including decomposition flames [1389].

An earlier flame model of the time-dependent laminar flame structure of decomposition flames, which was restricted to planar one-dimensional flames, was extended to the computation of cylindrical and spherical flames [1390]. Examples of flame speed and ignition energy for both planar and spherical flames were calculated, and an appreciable decrease in flame speed was computed when the flame radius was of the same order as the flame thickness. The theoretical model was then tested for hydrazine flames, and good agreement with other numerical results was obtained [1391]. A flame speed of 1.554 m/s in relation to the unburned hydrazine was calculated, compared to 1.54 m/s reported later [1392]. For a planar geometry, the model predicted that the reaction would complete within 0.4 mm from the origin of the flame front. The model calculated not only stationary flame speeds but also transient flame speeds during the ignition period. Thus, the model predicted that stationary flame speed would be achieved within 0.03 ms after ignition, certainly within a very short time. In addition to flame speeds and ignition transients, the model also calculated required ignition

energies. It specified the minimum size of a “hot gas pocket” serving as ignition center and the minimum energy required for ignition. If the pocket is too small, combustion does not propagate, and the flame becomes quenched after 80  $\mu$ s. If the pocket is twice as big, ignition occurs, and stationary conditions are attained within 40  $\mu$ s. The required minimum ignition energy is on the order of  $10^{-14}$  cal/cm<sup>2</sup> cross-sectional area of the hot gas bubble. It would be interesting to convert this number to the temperature required for ignition in a given volume in the absence of a surface. However, surface effects are difficult to eliminate.

Unsteady-state laminar flame theory was used to predict minimum ignition energies for hydrazine vapor and to predict flame speed, temperature profiles, and concentration profiles from ignition by spherical or elongated hot pockets to steady propagation of spherical flames [1393, 1394]. The time-dependent flame equations are solved in prolate spheroidal coordinates. It was shown that the minimum ignition energy was affected by the geometry of the ignition source and that the ignition energy passed through an absolute minimum as a function of the radius of the spark. The laminar flame velocity and minimum ignition energy calculations were repeated for hydrazine decomposition flames and resulted in profiles like those of Spalding and Bledjian. The ignition was assumed to occur by electric spark, and the electrode gap and spark temperature were among the several variables considered. Using the kinetics of two previous investigators, the vapor flame speed was calculated as a function of the distance from the point of initiation. For the starting conditions selected, the flame speed increased with distance from the point of ignition (e.g., a spark discharge or exploding wire) and did not become constant before it had traveled at least 1 cm. The flame speed approached the constant value asymptotically. The calculated flame speed of 1.52 m/s compared well with the 1.54 m/s reported earlier [1391] and the 1.554 m/s reported a few years later [1390]. Other reported flame speeds for hydrazine decomposition flames were 1.8 m/s on a 28-mm burner [620, 621].

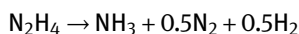
The initiation and transient behavior of hydrazine flames depends on the initial energy in the hot pocket between the electrodes. If the energy is less than the threshold energy, the energy in the hot pocket is dissipated into the surrounding cool gas, and ignition does not occur. Given sufficient energy, the temperature of the hot pocket (assumed to be on the order of 3100 K) drops immediately after ignition and approaches the adiabatic flame temperature asymptotically. As the initial hot pocket expands, its velocity decreases since the pocket cools by expansion and by divergence, undergoes a minimum after approximately 80  $\mu$ s, and reaches the planar flame speed after more than 1 s. If one calculates the fate of hot pockets of identical initial temperature (e.g., 5000 K) and energy density as a function of pocket radius, one can identify a minimum hot pocket radius below which the flame dies down. Calculations showed this critical hot pocket diameter to be on the order of 0.03 mm, indeed a very small diameter. The theoretical minimum ignition energy for temperatures from 2500 to 10000 K ranged from  $1.2 \times 10^{-7}$  to  $1.8 \times 10^{-7}$  J, depending on the hot pocket radius (0.03–0.052 mm). Most spark discharges between electrodes do not create a spherical hot pocket, but an elon-

gated (“prolate spheroidal”) discharge. It was thus important to extend the theoretical considerations to non-spherical geometries as well. The prolate spheroidal pocket is less likely to result in ignition than a spherical pocket of equal energy because it has a greater surface area: volume ratio than the sphere and has a smaller radius than the sphere; the greater divergence again results in greater heat transfer and more rapid cooling than a sphere. It was found by modeling calculations that prolate spheroidal flames with a half-axis ratio of  $a/b \geq 10$  indeed die while a sphere of the same volume and energy will propagate a flame. However, when plotting minimum ignition energy as a function of  $a/b$ , the semi-axis ratio, a minimum at or near  $a/b = 2$  was noted. The curve ascended again to the value of a sphere ( $a = b$ ) at about  $a/b = 9$ . Because ignition depends on three variables (hot pocket radius, semi-axis ratio, and ignition energy), the boundary between ignition and failure to propagate can be described as a curved surface in a three-dimensional coordinate system. A better understanding of ignition phenomena and the importance of spark geometry may lead to the design of improved ignition devices, not so much for hydrazine, but for combustible vapor (gasoline)/air mixtures. Hydrazine decomposition flames were only used as an example to test the model because the mechanism is simple compared to that of other combustion reactions.

#### 4.9.1 Stationary Hydrazine Decomposition Flames Stabilized on Flame Holders

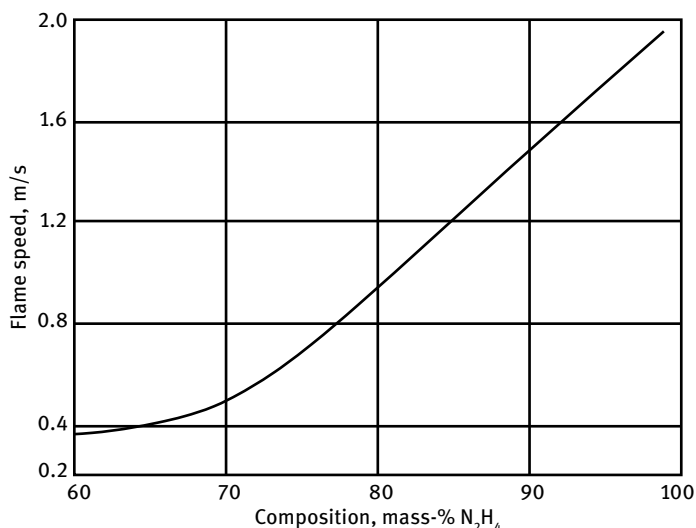
Whereas most other combustibles can be pre-mixed and burned in a Bunsen burner with a flame holder without special precautions, the attempt to stabilize a hydrazine monopropellant vapor decomposition flame requires special precautions to prevent flashback into the reservoir of hydrazine vapor. Accordingly, only a few experimenters have attacked this problem.

The flame speeds of hydrazine and hydrazine/water mixtures (60.0–97.2%  $\text{N}_2\text{H}_4$  in  $\text{H}_2\text{O}$ ) at 423 K (150 °C) and atmospheric pressure were measured by a burner method at atmospheric pressure [1210]. It was found that the flame reaction has the following stoichiometry:



It was assumed that the decomposition in the flame proceeded through a thermally activated first-order reaction, and on the basis of Szwarc’s results, an activation energy of 251 kJ/mol (60 kcal/mol) was suggested for the rate-determining step, believed to be the dissociation in amino radicals. However, as discussed in previous sections, this is not the true course of reaction. The all-glass experimental setup consisted of a hydrazine reservoir, a capillary flow meter, a vaporizer, a mixing section kept at 423 K, and a burner tube with an orifice. The same apparatus was also used to study hydrazine-oxygen and ammonia-oxygen flames (Section 4.14.1). Initially, some air was allowed to surround the diffusion flame, but some flames with high hydrazine concentrations did not need an air sheath and could be stabilized on the orifice without

external air supply. The orifice diameter was varied from 1.4 mm for 97%  $\text{N}_2\text{H}_4$  to 5 mm for 60.9%  $\text{N}_2\text{H}_4$ . The flames low in hydrazine could be stabilized only with a sheath of external diffusion combustion flame supported by air. The flame speed as a function of hydrazine concentration (remainder water) is shown in Figure 44.



**Figure 44:** Decomposition flame speeds in hydrazine-water vapor at 423 K. (Republished and modified from [1210], with permission of ©1951 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center, Inc.)

The flame speed can be expressed as volume of vapor burned per unit flame surface (from photographs) per second. The volume of vapor was calculated at 423 K and 101 kPa (atmospheric pressure). Flame temperatures were also measured and were found to be between those calculated with or without ammonia decomposition, respectively. The speed of the self-decomposition front in hydrazine with more or less water vapor decreased with increasing water content [1395]. This thorough study gave some early fundamental insight into flame speeds, but no information on the pressure dependence of the decomposition flame speed was obtained. The pressure dependence was later investigated by a different method by measuring the regression rate of a liquid surface in a capillary tube (Section 4.10.1).

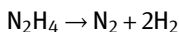
The measurements were later extended to the low-pressure range, where the burning velocity of 97% hydrazine at 393 K was determined at 4, 9.3, and 20 kPa (30, 70, and 150 mm Hg), respectively [1396]. The velocity remained constant over this range, close to 185 cm/s. It was very similar to the flame speed measured at atmospheric pressure. Besides flame speeds, emission spectra of the decomposition were recorded and compared to hydrazine and ammonia flames in oxygen and nitric oxide.

The flame speed of laminar flow flames seems to obey different reaction orders in different pressure regimes. It was found that below atmospheric pressure the flame speed was independent of pressure, which is indicative of a reaction of second order [1204]. A first-order reaction would predict an inverse square-root dependence on pressure. At higher pressure the flame speed was proportional to the reciprocal square root of the pressure, indicating an overall first-order reaction at higher pressures. As already discussed in Section 4.4.2, at lower pressure each collision leads to decomposition, whereas at higher pressure deactivating collisions are as frequent as activating collisions, and a stationary but small concentration of activated  $\text{N}_2\text{H}_4^*$  molecules prevails that decompose by a first-order reaction.

In a spectroscopic study of the hydrazine decomposition flame at 343, 353, and 363 K initial temperature and 1.86–3.46 kPa (14–26 mm Hg) pressure, only traces of excited NH radicals could be observed in absorption, indicating that the NH concentration in a hydrazine decomposition flame is significantly smaller than that in an oxygen-ammonia flame. The flame speed at 353 K and 1.86 kPa (14 mm Hg) was 152 cm/s. Besides emission and absorption spectra, mass spectra scans were also taken across the flame zone, showing  $\text{N}_2\text{H}_4$ ,  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$ . No  $\text{N}_2\text{H}_3$  could be observed with any of the methods, and therefore the authors prefer the mechanism



over the direct molecular decay



proposed by Husain and Norrish [521].

The concentration profile of  $\text{N}_2\text{H}_4$ ,  $\text{N}_2\text{H}_2$ , and  $\text{NH}_2$  in an orifice-stabilized hydrazine decomposition flame at 3.7 kPa (28 mm Hg) and 343 K was measured with a capillary quartz probe and a TOF mass spectrometer [1397]. The response factor of the mass spectrometer for diazene was not exactly known, but with some extrapolation and assumptions it was stated that the diazene concentration may be up to 0.7% of that of hydrazine prior to decomposition. This relatively high concentration would indicate that diazene plays an important role in the thermal and other modes of decomposition of hydrazine. The maximum of the  $\text{NH}_2$  and  $\text{N}_2\text{H}_2$  concentrations coincides with the zone in the flame where all hydrazine has disappeared (approximately 7 mm from the orifice at a flow velocity  $v_0 = 58$  cm/s).

Flame temperatures were measured in hydrazine/water mixtures in stationary decomposition flames and ranged from 1407 K at 60 mass-%  $\text{N}_2\text{H}_4$  to 1668 K at 82.5 mass-%  $\text{N}_2\text{H}_4$  [1215, 1398]. These temperatures are significantly higher than the theoretically possible maximum flame temperature at zero ammonia dissociation, and it may be assumed that some measurement error went undetected in this experiment.

Concentration profiles of  $\text{N}_2\text{H}_4$ ,  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  across hydrazine decomposition flames at 1.86 kPa (14 mm Hg) were measured by withdrawing samples from an



8-cm-diameter burner into a mass spectrometer [561]. The initial temperature of the hydrazine vapor was 343, 353, and 363 K and had little effect on the concentration profiles. A maximum temperature of 1350 K was measured with a thermocouple, substantially lower than the 1700 K expected from theoretical calculations. With a linear flow rate of 97 cm/s, about 9 mol-% of the hydrazine decomposed within the first millimeter of the burner. For higher stream velocities, 6 mol-% decomposed at 120 cm/s and only 1% decomposed at 152 cm/s.

The ignition of a combustible gas stream by a hot jet was modeled using a boundary layer approximation of aerothermochemistry assuming a one-step unopposed global reaction following any order reaction kinetics with temperature dependence according to the Arrhenius rate law [1399]. The Prandtl and Schmidt numbers were assumed to be equal, so a similarity between the equation of energy and the diffusion equation exists, greatly simplifying the analysis. This model was applied to the thermal decomposition of azomethane and the thermal decomposition of hydrazine, with numerical calculations done for the first-order approximation. Graphs showed the temperature profile along the axis of the flow for different ratios of cold and hot gas. For each set of given temperatures of the cold combustible gas and the hot gas, there exists a minimum jet width below which ignition cannot take place. It was confirmed that if the width of the jet is large enough, then the ignition always takes place at some point of the stream, but if the width of the jet is small, whether or not the ignition takes place depends on the width of the jet and the temperature of the hot gas.

A detailed N/H reaction mechanism has been developed and validated by comparing modeling results with measurements of hydrazine pyrolysis in shock waves and in hydrazine decomposition flames at low and atmospheric pressures [1400]. The mechanism consisted of 51 reactions with 11 species. Rate constants for several decomposition reactions were estimated employing updated thermodynamic data. Analysis of the reactions abstracting an H atom from  $\text{NH}_3$ ,  $\text{NH}_2$ ,  $\text{NH}$ , and  $\text{N}_2\text{H}_4$  from 1000 to 2000 K demonstrated that the Evans-Polanyi correlation [1401] held true for the radicals H, NH, and  $\text{NH}_2$ . This should probably also be valid for the radicals N, NNH, and  $\text{N}_2\text{H}_3$ . Several rate constants were estimated under this assumption. No further adjustment of the mechanism was attempted. The computer model correctly reproduced the experimental rate of decomposition of hydrazine and the product distribution. The initial decomposition of  $\text{N}_2\text{H}_4$  into two  $\text{NH}_2$  radicals and the subsequent reaction  $\text{N}_2\text{H}_4 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{N}_2\text{H}_3$  mainly govern the decomposition of hydrazine in dilute mixtures and together with the reaction  $\text{NH}_2 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_2 + \text{H}_2$  control the propagation speed of a hydrazine flame. The computed speeds of such decomposition flames agreed well with low-pressure and atmospheric-pressure experiments for pure hydrazine and its mixtures with Ar,  $\text{N}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ . The measured concentration profiles of major and minor species in low-pressure hydrazine flames were well reproduced. A sensitivity analysis identified the critical reactions under these experimental conditions.

### 4.9.2 Stationary Flames in Porous Media

Rather than burning liquid hydrazine at the tip of an open capillary, an attempt was made to stabilize liquid hydrazine decomposition in inert porous media. One such experiment used either crushed silicon carbide granules or bundles of parallel quartz rods of equal diameter in a 27-mm-ID, 250-mm-length quartz tube [1402, 1403]. Two granule sizes (1.0–1.2 and 2.0–2.5 mm) and several quartz rod diameters (1 to 5 mm) were tested. Liquid hydrazine was pushed in from one end of the tube and decomposition products passed through a section of the porous bed before leaving the tube at the opposite end. This method of combustion study is also called liquid infiltration combustion. The decomposition was initiated before starting hydrazine feed pump operation and a decomposition front propagated into the porous bed. The flow rate of hydrazine delivered by the feed pump was then adjusted such that the flame front remained stationary. The wave speed and the flow rate of the infiltrating fluid were similar, both on the order of 0.1 to 0.3 mm/s. Decomposition occurred in a stable planar reaction front at atmospheric pressure. Due to the high heat of evaporation, the pre-heat zone of hydrazine in the porous medium was wider than with other monopropellants. The axial temperature profile showed a sharp bend at the boiling point of hydrazine. One must remember that this was not a truly one-dimensional process, and capillary forces caused liquid to flow radially in addition to axially. The burning velocity decreased with the liquid feed velocity and the flame quenched below a lower limit. The burning velocity and the length of the gas-liquid zone decreased with increasing opening size of the porous medium (coarser granules or wider quartz rods).

Modeling the strand burning of liquid monopropellants in a capillary tube is also called filtration burning in the Russian literature because it simplifies the burning of a monopropellant in a porous medium or tube by looking at only one strand of liquid. Monopropellant burning in a porous medium (a packed bed of inert granules or rods or ceramic foam) was the original burning mode, which was called filtration combustion or filtration burning. A better description of the process would be infiltration combustion or infiltration burning. Filtration combustion of a monopropellant liquid is like filtration gas combustion in a low-velocity regime, which occurs under strong thermal interaction between the gas and the porous medium. A one-dimensional two-temperature model for the filtration combustion of liquid monopropellants was used to analyze the filtration combustion of liquid hydrazine in narrow tubes [1404, 1405]. This model described qualitatively the behavior of steady-state combustion waves of a liquid monofuel infiltrated into a porous medium or a capillary tube. A comparison of experimental data on the combustion of hydrazine in a porous medium and in narrow (5-mm quartz) tubes with calculations by the model showed that the model provided an adequate qualitative description of the infiltration combustion of liquid monopropellants. In a continuation of this study, two steady-state regimes were found [1406]. In regime I, the dominant mechanism of heat transfer from the combustion products in the pre-flame zone

was heat conduction in the gas, and in regime II, the dominant mechanism of heat transfer was interfacial convective heat transfer and heat conduction in the solid phase, the wall of the tube. Calculations using this model were in good agreement with experimental data on the combustion of liquid hydrazine in narrow tubes [1407].

#### 4.9.3 Hydrazine Vapor Decomposition Flames in Closed Vessels

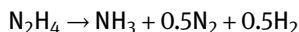
The decomposition of hydrazine vapor was first studied using 3- and 1.5-cm-diameter Pyrex tubes 10 cm in length [1228]. Ignition was achieved by an electric arc across tungsten electrodes. The tube was kept at 373 K to prevent hydrazine condensation. The lower pressure limit depended on the diameter of the tube. Thus, with reaction vessels with diameters of 1.5 and 3.0 cm, the lower explosion limits were reached at hydrazine pressures of 6.64 and 4.65 kPa (50 and 35 mm Hg), respectively. Later investigations in a 118-mL, 2.54-cm (1-in.) Pyrex tube found hydrazine decomposition flame propagation with spark ignition at even lower pressures [1408]. The minimum pressure for the spark ignition of hydrazine vapor was 1.6 kPa (12 mm Hg) at a bath temperature of 302 K (29 °C). This was somewhat lower than the value of 4.65 kPa (35 mm Hg) given by [1228].

The study of hydrazine decomposition flames in closed vessels requires the use of fast recording instrumentation, such as high-speed-film cameras and oscilloscopes. The phenomena are steady only for a short time, and after the flame front has propagated for a short length, the effect of the diffusion of decomposition products may become noticeable. Even though the initial temperature and pressure can be closely controlled, pressure will increase as soon as the reaction starts, and temperature will increase as a result of adiabatic compression. Thus, in a vessel diameter  $R$ , only the initial flame path up to  $0.3R$  is usually taken for calculating the flame speed.

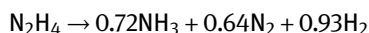
The propagation and stability of hydrazine decomposition flames were studied in a closed vessel and by the liquid strand method (see following section) [1409–1411]. A fourfold increase in pressure from 2.66 to 10.6 kPa (from 20 to 80 mm Hg) produced little variation in the flame speed of pure hydrazine. At 6.64 kPa (50 mm Hg) and 393 K the flame speed relative to the unburned gas was 117 cm/s, which agreed with a previous measurement of 200 cm/s at 423 K and atmospheric pressure, that reported by Murray and Hall [1210].

The addition of diluents (helium, argon, hydrogen, nitrogen, ammonia) decreased the speed of the decomposition flame. The effectiveness of decreasing the flame speed increased in the order listed previously in parentheses and (except for He) seems to relate to the heat capacity of these gases. This agrees with the conclusions drawn by others on the effect of diluent gases on the autodecomposition pressure limit of hydrazine [1216]. Because some secondary decomposition of ammonia may have occurred in the closed vessel after the flame front had propagated all the way through

the chamber, the gas composition was slightly different from that expected for the following equation:



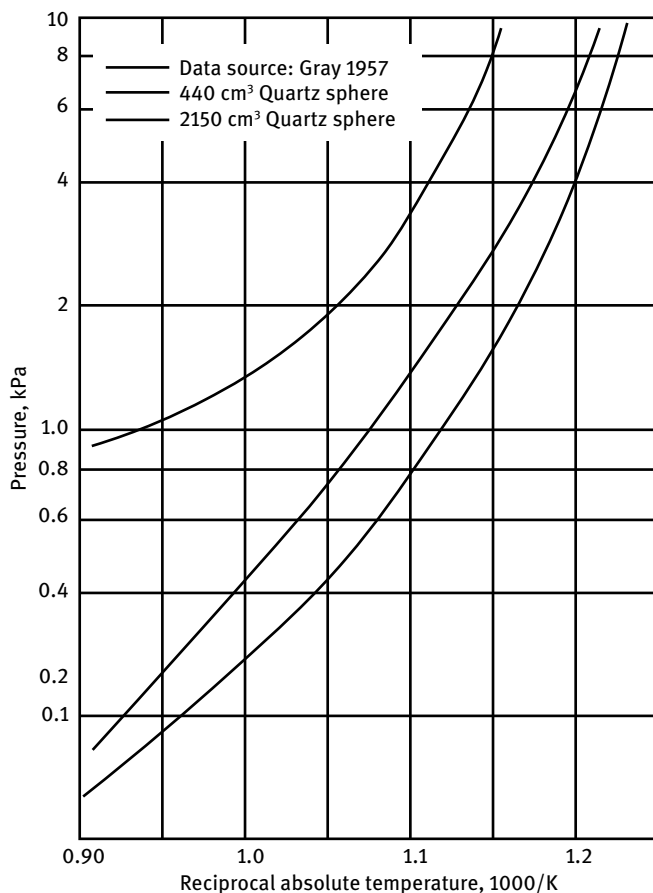
the actual composition being



One issue addressed by numerous investigators was to determine the cause of the relatively weak pressure dependence of the flame speed. It can be explained if the rate is determined by bimolecular activation, not by unimolecular decomposition.

The burning rate results of other authors were subjected to a critical review and attempts were made to fit them to a one-center chain reaction model that had been programmed on a computer in an effort to predict the effect of pressure on the speed of the hydrazine decomposition flame [1412]. Data were calculated from 1300 to 1900 K and 10 kPa to 10 MPa (0.1–100 atm). Although numerical results did not fully agree with experimental data, the computer model was at least able to predict the trends. The temperature coefficient of the flame speed was found to be independent of the assumptions made regarding the chain-terminating reaction. This was believed to be due to the fact that the rate of chain termination is small compared to the rate of chain propagation and that the activation energies of both are small compared to that of the initiating reaction (293 kJ/mol). Experimental results indicated that the temperature coefficient of flame speed corresponded to an overall activation energy of little more than half that of the initiating step (at that time still believed to be the decomposition of hydrazine into  $\text{NH}_2$  radicals) [1210, 1411]. The pressure dependence predicted by the computer for lower flame temperatures at pressures above atmospheric was very unusual. The calculated reaction order varied from 1.4 near atmospheric to 0.7 at a pressure of 1.5 MPa and increasing again to 1.0 at 10 MPa. No experimental data for vapor-phase flames are available to check these predictions. On the other hand, the authors conclude that the propagation reaction is almost certainly second order at all times. For the termination reaction they assumed a reaction second order in radical concentration but third order in total pressure. This is required for the assumed three-body recombination of free radicals, but the reaction may become second order at very high pressures when the time between collisions is shorter than the half-life time of an excited molecule. The explosive decomposition of anhydrous hydrazine vapor can be initiated with an electrostatic discharge (ESD) [1398].

Besides spark-ignited decomposition flames, thermally ignited spontaneous decomposition flames or, depending on the confinement conditions, explosions in closed vessels have also been studied [1413]. If hydrazine vapor is expanded from a reservoir into a hot, evacuated vessel, it will ignite as soon as its pressure exceeds the critical spontaneous ignition pressure for the given temperature of the vessel. Spontaneous ignition pressure results obtained with a quartz cylinder 3.7 cm in diameter  $\times$  250 cm<sup>3</sup> in volume  $\times$  300 cm<sup>2</sup> in surface area are shown in Figure 45.



**Figure 45:** Explosion limit of hydrazine. (Reprinted and modified from [1414], with permission from ©1962 Elsevier; permission conveyed through RightsLink.)

At sufficiently high pressures, the ignition of pure hydrazine was seen as a bright yellow flash with an induction period of less than 1 s. As shown in Figure 45, the initial pressure required for ignition decreased from 8.64 to 1.06 kPa (from 65 to 8 mm Hg) as the temperature was increased from 853 to 1083 K. Dilution (1:1 ratio) with helium or argon had only a negligible effect on the pressure limit (as long as only the partial pressure of hydrazine in the gas mixture is plotted). Helium increased and argon diminished the difficulty of ignition.

It is interesting to note that under the same experimental conditions, UDMH vapor would undergo spontaneous self-decomposition at lower initial temperatures than hydrazine, for example, 703 K at 8 kPa (60 mm Hg) as opposed to 873 K for hydrazine at the same pressure (Table 58).

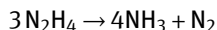
**Table 58:** Approximate autodecomposition temperatures.

| Compound  | Approximate autodecomposition temperature, K |      |                         |      |
|-----------|----------------------------------------------|------|-------------------------|------|
|           | Partial pressures kPa                        |      | Partial pressure, mm Hg |      |
|           | 8                                            | 0.8  | 60                      | 6    |
| Hydrazine | 873                                          | 1073 | 873                     | 1073 |
| UDMH      | 703                                          | 788  | 703                     | 788  |

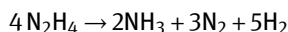
Data source: [1413]

A similar closed vessel apparatus, also filled by fast admission of hydrazine vapor to a pre-evacuated vessel, was used to study the borderline conditions for the initiation of hydrazine vapor explosions [1414]. Instead of igniting with an electric arc, the entire vessel was pre-heated to the ignition temperature. The admitted vapor usually warmed up to equilibrium temperature in 10–40 ms, depending on the size of the vessel. This was probably due to the convective heating of the incoming vapor stream and adiabatic compression of the first portion of vapor to enter the flask, the same effect that caused some interference in Gray's test. Instead of measuring flame speed, the pressure rise inside the vessel was recorded with a high-response pressure transducer and an oscilloscope. The explosion limit of hydrazine as a function of pressure and temperature is shown in Figure 45 for two different size vessels in comparison to data obtained by Gray [1411].

It was stated that whereas hydrazine decomposition does not show the usual properties of branched-chain explosions (multiple limits, extremely slow reaction below the limit, dependence on surface), it does not agree with the theory of thermal explosion, either. The addition of hydrogen or helium did not cause the change in the explosion limit predicted from their respective thermal conductivity. Ammonia lowers the explosion limit pressure  $p^*$  slightly. The amount of decomposition during the induction period was higher than predicted. The pressure rise during the induction period preceding the explosion was 15–20%. The stoichiometry of decomposition below and above  $p^*$  was markedly different. Below  $p^*$  it could be represented by



Above  $3p^*$  the yield of ammonia levels off:



Laminar and turbulent hydrazine decomposition flames in a closed vessel (70-mm diameter) were studied at 383 K and 80 kPa (600 mm Hg) [1415]. The combustion bomb had windows for schlieren cinematography and a pair of spark electrodes for initiating the decomposition. The flame speed was varied by dilution with nitrogen or water vapor and plotted as a function of the theoretical flame temperature  $T_h$ . It was noted that a significant fraction of hydrazine would decompose prematurely when hot hy-

drazine vapor was admitted to a hot, evacuated vessel. Apparently, some of the hydrazine molecules that were already heated close to the borderline of self-propagation reached high velocities on expansion into a vacuum as a molecular jet and the resulting increase in kinetic temperature caused them to decompose. When nitrogen was admitted first, followed by hydrazine vapor, only negligible decomposition was observed.

The authors noted that the difference in flame speed measured by the closed bomb and open burner flame method [1210] cannot be explained by the difference in initial temperature alone. The temperature dependence of the rate of laminar flame burning can be represented by the formula

$$S_B \propto T_0 T_h^{2.7} (T_h - T_0)^{-1.5} e^{\frac{-E}{2RT_h}}$$

where  $T_h$  is the adiabatic flame temperature (1904 K according to [1415]),  $T_0$  is the initial temperature in K, and  $E$  is the activation energy (generally assumed to be 37 kcal/mol). The ratio of flame speeds calculated with this equation for 423 and 335 K initial temperature, respectively, was 1.38, whereas the measured ratio was 1.7. In trying to explain this discrepancy, Karpov and Sokolik pointed out that a certain degree of turbulence cannot be avoided in a burner stabilized flame. They then determined flame speeds in a closed bomb with and without agitation by stirrers. Very similar energies of activation in the preceding equation were obtained for both types of flame, but the turbulent flame speed was higher than the laminar flame speed. In addition to the temperature dependence, the pressure dependence of laminar and turbulent flame speeds was measured in that study. It was shown that, in agreement with earlier results [1411], the order of reaction for both laminar and turbulent flames was approximately 2, resulting in an overall independence of flame speed from hydrazine pressure in the range 11.9–42.5 kPa (90–320 mm Hg). Whereas a thermal model was assumed to treat the steady laminar flame, pulsating combustion and periodic mixing of burned and unburned gas were assumed for turbulent flame propagation.

The effect of isotopic substitution on the decomposition flame speed of hydrazine was studied using the same closed-bomb technique previously described [1154]. The comparison was extended by measuring flame speeds for binary mixtures containing inert diluents. Increasing amounts of two diluents, argon and nitrogen, were added to a fixed partial pressure (6.7 kPa = 50.2 mm Hg) of  $N_2D_4$ , and flame speed was measured over the entire flammability range. The effect of the added diluents was to decrease the flame speed with increasing partial pressure of diluent and to extinguish the flame when the concentration of diluent exceeded ca. 50%. The effective activation energy was estimated from the dependence of flame speed on temperature for diluted mixtures. It was estimated to be  $146 \pm 8$  kJ/mol ( $35 \pm 2$  kcal/mol), based on

calculated values of adiabatic flame temperature and thermal conductivity, assuming a stoichiometry identical to that for  $\text{N}_2\text{H}_4$  decomposition. A large isotope effect of flame speed was apparent when the results were compared directly with those of a previous investigation of the  $\text{N}_2\text{H}_4$  flame, obtained in the same apparatus and under the same initial conditions. The speed of the hydrazine decomposition flame was halved when deuterium was substituted for hydrogen. The flame speeds relative to the burned gas were determined by schlieren photography. Flame speeds for pure  $\text{N}_2\text{D}_4$  were measured at an initial temperature of 335 K in the pressure range 2.6–9.3 kPa (20–70 mm Hg). In this pressure range the flame speed was virtually independent of pressure, indicating that the overall reaction was of second order [1316, 1411]. Substitution of deuterium for hydrogen in hydrazine has a very pronounced effect on the decomposition mechanism. The flame speed of the hydrazine decomposition flame is halved when deuterium is substituted for hydrogen. At least three parameters affecting flame speed are believed to be responsible for this change: transport properties, equilibrium thermodynamics, and kinetic factors. Isotopic changes in thermal conductivity contribute by a factor of 1.1 to the total effect, adiabatic theoretical flame temperature is off by a factor of 1.3–1.5, and kinetic isotope effects have the most pronounced effect,  $k_{\text{H}}:k_{\text{D}} = 1.5$ . This investigation was stimulated by the decades-old question as to whether the decomposition of hydrazine proceeds by way of a unimolecular or a radical mechanism. This question was already extensively discussed in Section 4.4.1 in view of recent shock-tube results. Although these results indicate a unimolecular mechanism at high pressures, the possibility of a radical mechanism, such as the one proposed by Adams and Stocks in 1953 [1249] and confirmed by many other investigators, still exists.

The most surprising effect of isotopic substitution was a 50% reduction of flame velocity when deuterium was substituted for hydrogen in hydrazine [1154]. For example, at an initial pressure of 6.67 kPa (50.2 mm Hg), the flame speed for  $\text{N}_2\text{H}_4$  decomposition was 1330 cm/s, whereas for  $\text{N}_2\text{D}_4$  it was 683 cm/s. With the use of a standard enthalpy of formation of 79 kJ/mol (+18.90 kcal/mol) for  $\text{N}_2\text{D}_4$  vapor, an adiabatic flame temperature of 1805 K was calculated compared to 1904 K for  $\text{N}_2\text{H}_4$ . Besides flame temperature, thermal conductivity is also lower for  $\text{N}_2\text{D}_4$  vapor than for  $\text{N}_2\text{H}_4$  vapor,  $712 \times 10^{-6} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ , compared to  $870 \times 10^{-6} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$ . All these differences contribute to the large isotope effect. The isotope effect in the hydrazine decomposition flame is higher than in any other flame reaction studied to date. The activation energy of the  $\text{N}_2\text{D}_4$  decomposition was found to be essentially identical to that of  $\text{N}_2\text{H}_4$  decomposition over the range studied, 146 kJ/mol (35 kcal/mol) in both cases. The interpretation of kinetic data led the authors to the conclusion that neither a radical nor a unimolecular reaction is clearly supported by the isotope flame speed results. It was suggested to perform a shock-tube study to obtain some more definite rate data.



#### 4.10 Liquid Strand Decomposition in Absence of Oxygen

Of all methods for studying hydrazine decomposition flames, the “burning” of liquid strands in tubes is most easy to perform safely. The term strand burning has been inherited from solid propellants where this technique is extensively used to determine linear burning rates. However, the flame speed in the vapor phase is in reality higher than the regression rate of the liquid because the vapor and the liquid surface are moving in opposite directions, and the volume of the vapor is many times that of the liquid from which it originates. Heat-transfer phenomena between the flame front and the vaporizing liquid may affect the regression rate more than kinetic changes in the flame front would. Also, the flame front has a different shape and different surface area than the liquid-vapor interface. At 1 g on the surface of Earth, the flame front is hardly ever disc shaped, which would be the easiest shape to treat mathematically. Wall effects and gravity cause it to assume dish and ogive shapes. Strand burning phenomena have been studied for many monopropellant candidates, in particular those containing organic nitro compounds and nitrate esters. Some of the same experimental techniques developed during the 1950s were later applied to hydrazine. It was one of the safety advantages of hydrazine that under normal operating conditions it does not have a tendency to strand burn, which would be highly undesirable if strand burning propagated in a rocket from the combustion chamber through the injector through the valve and into the propellant reservoir (as has happened in many instances with nitro and nitrate compounds). However, if hydrazine were to be used in a valveless design of an on-demand gas generator, there may be problems with burn-back at higher pressures.

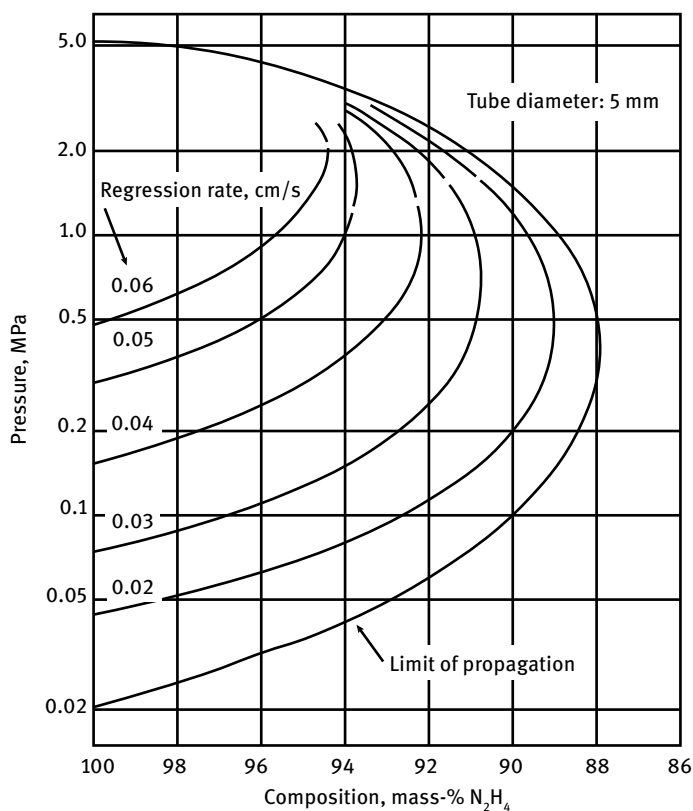
The walls exert a quenching effect on the flame, and some heat is lost to the walls. This quenching would be desirable for arresting unwanted propagation in flight applications, but it is undesirable for academic lab studies of burn rates. Lab tests have been conducted with heated capillary walls to compensate the heat loss. Attempts have also been made to calculate the quenching effect and correct the results for the expected heat loss. Nevertheless, despite all shortcomings of the capillary tube method for measuring burn rates, some interesting results can be obtained by this simple method, which is certainly not quite as dangerous as the Bunsen burner method, which involves large amounts of hydrazine vapor. The strand burning method has also been used to study the hydrazine combustion in oxidizing atmospheres.

##### 4.10.1 Monopropellant Strand Burning of Liquid Hydrazine (in Absence of Oxidizers)

The rate of monopropellant burning of hydrazine has been measured for a wide range of pressures (101–3500 kPa = 1–35 atm) and water dilutions [1249]. The liquid hydrazine is assumed to have been at room temperature, but no temperature measurements were given and there was no effort to maintain constant hydrazine temperatures. The regression rate was measured by observing the regression of

the liquid surface in a capillary tube. First, the effect of the tube diameter on the regression rate was studied in order to select a proper tube geometry for the experiment. It was found that the rate initially decreased and then leveled off beyond a 5-mm diameter. Therefore, most subsequent experiments used a 5-mm-diameter graduated tube. The rate of regression increased with increasing pressure, following roughly a square-root proportionality up to 1 MPa (10 atm), and then becoming independent of pressure above 1 MPa. Surprisingly, above a certain initial nitrogen pressure (4.4 MPa), the liquid will no longer ignite from a hot wire, or, if the pressure is raised during the burning experiment, the flame will extinguish at the same limit pressure. Apparently increased nitrogen dilution restricts flame propagation. For 98.9% hydrazine in a 5-mm tube, the regression rate increased from 0.28 mm/s at atmospheric pressure to 0.77 mm/s at 810 kPa (8 atm) and leveled off at this pressure until extinction occurred above 4.24 MPa (42 atm). As expected, water addition decreased the regression rate. The slope of the burn rate =  $f$  (concentration) curve becomes steeper with increasing water content [1386, 1387]. Strand burning rates as a function of pressure can be predicted for several hydrazine/water mixtures using the model developed by Gerstein [1387]. The agreement between experimental and calculated data for 98.9% hydrazine in a 5-mm tube at pressures of 20–1500 kPa was quite good. Between 20 and 1500 kPa, the regression rate of 98.9% hydrazine increased from 0.005 to 0.08 cm/s. The quenching distance was also calculated (0.05 cm) and measured (0.12 cm). Several of the conclusions drawn by early investigators [1249] in the interpretation of their own results and those of Murray and Hall [1210] turned out to be incorrect due to a lack of fundamental information on hydrazine decomposition that became available only during the following decades.

Gray and co-workers [1411] as well as Hall and Wolfhard [1396] extended the range of liquid hydrazine strand burning investigations into the region of low pressures. A lower limit extinction pressure was detected that is a counterpart to the high-pressure (dilution) extinction. The lower pressure limit for the propagation of the decomposition flame was measured in four tubes with diameters increasing from 3 to 10 mm. Also, the hydrazine concentration was varied from 91.4 to 97.7%  $\text{N}_2\text{H}_4$  (remainder water). The extinction pressure increased with tube diameter and hydrazine concentration. For a given tube, for example, 5 mm, the regression rate increased with pressure, whereas at constant pressure the rate was smaller in tubes of larger diameter. Combining the results of [1249] and [1411], the limits of stability and regression rate of liquid hydrazine decomposing in a 5-mm-diameter glass tube are illustrated in Figure 46 as a function of pressure and hydrazine concentration. In interpreting this graph, one must keep in mind that at pressures above atmospheric the increased pressure is by nitrogen pressurization, not true undiluted hydrazine pressure. The upper limit of propagation would not exist in a nitrogen-free system. The initial temperature of the hydrazine was ambient temperature, but some heat was transferred to the liquid from the tube as the flame traveled down the tube.



**Figure 46:** Limits of stability and regression rates of decomposition flame of liquid hydrazine. (Reprinted and modified from [1411], with permission from ©1957 Elsevier; permission conveyed through RightsLink.)

The law of mass conservation dictates the relationship for stable combustion

$$u_0 \rho_0 = u_c \rho_c$$

where  $u_0$  is the regression rate of the liquid surface,  $\rho_0$  is the density of the burning liquid,  $u_c$  is the velocity of the decomposition products relative to the flame front, and  $\rho_c$  is the density of the decomposition products. In a gravity field the buoyancy of the hot gases may result in the detachment of a bubble of hot gases from the surface of the burning liquid and the influx of cold gas from the sides. This phenomenon is called flame front separation. When the velocity of convective rise of the bubble exceeds the velocity of the decomposition products  $u_c$ , the combustion becomes unstable. The critical diameter and pressure above which the hydrazine flame is extinguished were calculated assuming a convective mechanism and compared with experimental values for different hydrazine concentrations in Table 59.

**Table 59:** Regression rate and critical pressure of hydrazine decomposition flame.

| $\text{N}_2\text{H}_4$ concentration,<br>% by mass | $\rho_c \times 10^4, \text{g cm}^{-3}$ | $p, \text{MPa}$ | $u_0$ Regression rate of liquid,<br>cm/s | $p_{cr}, \text{MPa}$ |
|----------------------------------------------------|----------------------------------------|-----------------|------------------------------------------|----------------------|
| 97                                                 | 1.40                                   | 2.12            | 0.125                                    | 4.44                 |
| 94.5                                               | 1.45                                   | 2.63            | 0.077                                    | 3.43                 |
| 89.5                                               | 1.55                                   | 1.11            | 0.023                                    | 1.46                 |

Data source: [1416]

At pressures above 1 MPa the reproducibility of the results became worse, and the average values of the burning rate tended to be independent of pressure. Hydrazine could not be ignited above a certain critical pressure  $p_{cr}$ , which could be predicted and calculated from the properties of the decomposition products.

Liquid hydrazine was fed from a reservoir through a peristaltic pump to a 5-mm-ID vertical quartz capillary with 1.1-mm walls in a decomposition chamber at 0.1 MPa and 293 K [1417, 1418]. Under normal conditions with a flow velocity of 5.9 mm/s, the regression rate was 4.8 mm/s in a tube with 1.1-mm walls. The slope of the regression rate  $u_0$  vs. fluid flow velocity  $v_0$  depends on the wall thickness and increased with increasing wall thickness. At low flow velocities ( $\leq 0.3$  mm/s) the combustion was steady, but at high flow velocities ( $\geq 0.8$  mm/s) it became turbulent and droplets were thrown out of the liquid interface into the space above. For a flow velocity of 0.6 mm/s, the flame front could be stabilized at the tip of the capillary, and the regression rate  $u$  of the interface was seemingly zero. In the transition regime bubbles began to appear at the interface. The regression rate as a function of wall thickness curves showed maxima at a wall thickness of  $\sim 1$  mm, in particular for flow velocities on the order of 0.2 mm/s. The curves all converged at a regression rate of 0.3 mm/s for very thin tubes. The quartz tube played an important role in the heat transfer between the decomposition front and the liquid. Under some conditions the quartz tube became bright red hot and its radiation accentuated its role as a flame holder.

When liquid hydrazine decomposed in glass tubes, an abrupt increase in the regression rate was observed as the pressure was increased [1419]. For 100% hydrazine in a 5.6-mm-diameter tube the regression rate increased from 0.02 cm/s at 101 kPa slowly and leveled off at 0.09 cm/s at 1.21 MPa (12 atm), until at 1.414 MPa (14 atm) a sudden increase to more than 0.2 cm/s was observed. No change in the smoothness of burning or any other parameter could be correlated with this discontinuity. The pressure at which this abrupt change occurs was called the break pressure, and its dependence on tube diameter and hydrazine concentration has been studied [1205, 1420]. The break pressure decreased linearly from 1.414 MPa (14 atm) to 0.4 MPa (4 atm) if the tube diameter was increased from 5.6 to 12.7 mm. The break pressure increased with decreasing hydrazine concentration.

The luminosity and gas temperature of the decomposition flame were also measured but did not change as abruptly as the regression rate. Therefore, there are no

changes in mechanism that could explain this phenomenon, and it was suggested that physical and not kinetic factors caused the change of reaction/regression rate. There is a certain risk in overinterpreting the liquid strand burning rate data. Adams and Stocks [1249] tacitly assumed that a first-order gas-phase reaction controlled the burning rate, even though some deviation at the high-pressure end was obvious. A study of the burning of hydrazine between 101 and 1818 kPa (1–18 atm) found a one-third power dependence of regression rate on pressure [1409]. Gerstein interpreted the results of previous investigators and proposed a model equation [1386, 1387]. It was later concluded that the regression rate of liquid hydrazine is controlled primarily by a second-order reaction in the gas phase and that in certain pressure ranges (depending on the tube diameter and the concentration of the liquid) the regression rate is limited by an evaporation rate [1419]. A good correlation could be obtained with a burning rate/pressure dependence equation originally developed for solid propellants.

If nitrohydrazines were stable (they are not), they would have very high burning rates, faster than those of HN or ammonium dinitramide (ADN) [1421].

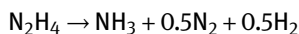
#### 4.10.2 Effect of Additives on Monopropellant Strand Burning of Liquid Hydrazine

In a study of the effect of additives on the strand burning rate of liquid hydrazine in a nitrogen atmosphere, it was found that the addition of water or other additives had two effects: **(1)** The regression rate at any pressure was lowered and **(2)** the pressure at which the regression rate increased abruptly was increased [1422]. One percent by volume solutions of the following additives were tested (listed in the order of increasing effect on regression rate): MMH, ethanol, ethylene diamine, *n*-amylamine, *tert*-butanol, pyridine, and *n*-butanol. Whereas MMH had no measurable effect, the effect of the other additives seemed to increase with the number of carbon atoms.

The strand burning characteristics of hydrazine were measured under both steady-state and imposed oscillatory conditions [1254]. Strand burning rates, liquid temperature distributions, and surface temperature were measured as a function of pressure in the range of 32 kPa to 4.2 MPa (0.32–42 atm). It was found that at sub-atmospheric pressures the burning rate varied as the square root of pressure, whereas for pressures greater than atmospheric the burning rate was a linear function of pressure. Attempts were made to explain this behavior by setting up a theoretical model and assuming a reaction order of 1 at sub-atmospheric and an order of 2 for super-atmospheric pressures. An oscillatory burning modification of the steady-state strand burning apparatus was built, and measurements in the oscillating mode were taken. Theory and experiment were found to be in good agreement (100–1000 kPa) if the hydrazine decomposition reaction was assumed to be second order with an activation energy of 167 kJ/mol (40 kcal/mol). The results showed an increase in the response of the combustion process to the same extent as interaction occurred with transient liquid-phase effects. There was a frequency range where the combustion process exerts enough amplifying power to drive a resonant oscillating system with

subsequent combustion instability. It is not known what implications this might have for monopropellant thrusters because most decomposition there occurs on the surface of catalysts rather than on the surface of liquid strands or droplets.

In addition to strand burning rates, the flame temperature and composition of decomposition products were also determined over a wide range of pressures (101–2626 kPa = 14.7–382 psia) [1423]. A remotely actuated sampling probe was inserted into the flame front for a very short time to withdraw gases for continuous mass spectrometer analysis. The probe dwelled in the flame only long enough to draw a sample, yet not too long to suffer damage from the high temperature. The linear regression rate in a 10.8-mm tube increased from 0.04 cm/s at atmospheric pressure to 0.32 cm/s at 2.6 MPa. The overall stoichiometry of decomposition products could be represented by



The ammonia concentration increased with increasing pressure from 1.023 to 1.095 mol of  $\text{NH}_3$  formed per mol of  $\text{N}_2\text{H}_4$  decomposed. The linear regression rate agreed closely with molar mass combustion rates (in units of  $\text{g mol cm}^{-2} \text{s}^{-1}$ ) predicted using the Belyaev-Zeldovich equation

$$u = \frac{RT_c^2}{QE} \sqrt{2\lambda\rho kc}$$

where  $u$  is the mass combustion rate ( $\text{g cm}^{-2} \text{s}^{-1}$ ),  $c$  the heat capacity ( $\text{cal g}^{-1} \text{K}^{-1}$ ),  $Q$  the enthalpy of reaction corrected for phase changes ( $\text{cal/g}$ ),  $k$  the rate constant of the reaction at combustion temperature ( $\text{s}^{-1}$ ),  $\lambda$  the thermal conductivity of vapor ( $\text{cal cm}^{-1} \text{s}^{-1} \text{K}^{-1}$ ),  $E$  the activation energy ( $\text{cal/mol}$ ),  $T_c$  the combustion temperature (K),  $\rho$  the gas density ( $\text{g/cm}^3$ ), and  $R$  the gas constant. The gas constant  $R$  is available in many units of measurement, e.g.,  $1.98 \text{ cal mol}^{-1} \text{K}^{-1}$ , and needs to be selected so the equation will balance. The liquid strand burning technique is useful for studying oxidizer-free decomposition flames and oxidation flames alike. The effects of additives, temperature, and oxidizing atmosphere on the combustion of liquid hydrazine in a paper straw tube were studied [1424]. The strand burning rate of hydrazine/water mixtures increased from 0.018 to 0.040 cm/s as the hydrazine content increased from 85 to 100 mass-%. Lead nitrate, potassium permanganate, nickel chloride, chromium chloride, and thallium(I) chloride were tested as burning rate catalysts. Their activity decreased in the previously given order, with lead nitrate being the most active catalyst, increasing the burning rate  $r$  to 0.062 cm/s. Combustion in oxygen, nitrogen dioxide, or nitric oxide occurred faster than in air, whereas nitrous oxide retarded combustion. When the logarithm of  $r$  was plotted against  $1/T$ , a straight line was obtained. An energy of activation was calculated from the slope of the line and was found to be only 12.5 kJ/mol (3 kcal/mol). The maximum temperature of the hydrazine-air flame measured was 1360 K.

#### 4.10.3 Effect of Hydrazinium Salts on Strand Burning of Liquid Hydrazine

Solutions of hydrazinium(1+) nitrate (HN) in hydrazine and water have been considered propellants for liquid propellant guns along with other monopropellants. The combustion of hydrazine/hydrazinium nitrate solutions in the breech of a liquid propellant gun would be without the aid of a catalyst. A mixture of 30% HN, 65% hydrazine, and 5% water was tested in 37-mm guns and as strand burners in a pressurized bomb [1425]. In 3.8- and 6-mm-diameter strands, the strand burning rate of this mixture at 200 MPa (29 kpsi) was approximately 25 cm/s. However, in a gun barrel, a liquid charge 19 cm long was combusted at the same pressure within 1 ms. This indicated that the burning surface must have been increased by internal droplet breakup (Taylor instability and Helmholtz mixing) to more than 6000 cm<sup>2</sup>. Unfortunately, the hydrazine-HN propellant and all other liquid gun propellants tested suffered from combustion variations, thus causing an intolerably wide scatter of muzzle velocities and projectile ballistics. A similar mixture consisting of 75% HN, 20% hydrazine, and 5% water had previously been tested without the desired success [1426]. These tests indicated that even for such high HN concentrations, stable combustion could not be sustained at pressures below 13 MPa.

#### 4.11 Decomposition of Hydrazine Droplets in an Atmosphere of Decomposition Products

The decomposition combustion of droplets is a process of great industrial importance. A review of 216 references on the combustion of droplets of liquid fuels and monopropellants summarized the theoretical background accumulated prior to 1973 [1427]. Decomposition and combustion flames with monopropellant droplets stand out with respect to the mechanisms involved and the combustion velocities. The study of monopropellant and, in particular, hydrazine droplet decomposition burning has contributed significantly to the understanding of droplet combustion in general.

Hydrazine was chosen as one of the fuels investigated in both monopropellant and oxidizing atmosphere droplet combustion studies [1428–1430]. The solving of the system of three nonlinear differential equations describing burning rate as a function of droplet diameter and pressure required a significant mathematical effort that cannot be repeated here. The agreement of calculated data with experimental results was satisfactory; however, combustion of monopropellant droplets in an absolutely inert atmosphere was not achieved. The droplets were suspended from a quartz capillary and were smaller than the droplets used by Rosser and Peskin [1431, 1432]. The latter authors used porous alumina spheres of various diameters (3–13 mm) to support hydrazine drops. The reaction vessel was a 15-cm (6-in.)-diameter Pyrex tube. The hydrazine was fed to the porous alumina sphere by a linear drive motor from a syringe and ignited by an electric arc. During burning, a gas stream of selected composition

flowed upward and past the burning liquid. The feed rate was adjusted so that the sphere was uniformly wetted but would not drip or run dry. No decomposition occurred inside the alumina sphere, and the measured temperature inside a drop of hydrazine was only 367 K. The mass burning rate was proportional to the square of the drop diameter, rather than the first power of the diameter, as for drop diffusion flames. The mass burning rate was proportional to the radius only for very low reaction rates or in the evaporative limit. For high reaction rates, the mass burning rate was proportional to the square of the radius. The ability to maintain decomposition flames was found to be dependent on the purity of the hydrazine. Aniline was identified as an inhibitor. Hydrazine with 1.5 mass-% aniline would not sustain a pure decomposition flame at atmospheric pressure with pure nitrogen flowing, but the addition of 8–10 vol.-% oxygen to the nitrogen was required. This would result in a secondary combustion flame downstream from the decomposition flame. The double flame stabilized the system and allowed measurements at lower pressures. Hydrazine of a higher quality with only 0.5% aniline would burn without oxygen addition. Up to 2.5 mass-% water in the fuel seemed to have no effect. The mass burning rate determined by the droplet method,  $2.2 \times 10^{-2} \text{ g cm}^{-2} \text{ s}^{-1}$ , agreed well with data determined by the strand burning method, for example,  $2.4 \times 10^{-2} \text{ g cm}^{-2} \text{ s}^{-1}$  [1411]. The droplet mass burning rate is proportional to pressure, in contrast to low-pressure burning of hydrazine in tubes, where the rate is independent of pressure [1411]. The flame speed of a pre-vaporized hydrazine flame (120 cm/s) is much higher than that calculated for vapor emerging from a hydrazine droplet (~21 cm/s for the 0.5% aniline and 15 cm/s for the 1.5% aniline-containing hydrazine). The authors believed that the presence of aniline inhibited radical chains and thus lowered the flame speed.

#### 4.11.1 Decomposition of Hydrazine Droplets in an Atmosphere of Hot Combustion Products

A study of the decomposition of hydrazine, MMH, or UDMH droplets in an atmosphere of hot combustion products used single droplets suspended from a 100- $\mu\text{m}$ -diameter quartz filament as well as porous Alundum spheres [1433–1435]. Droplet diameter could thus be varied from 0.11 to 1.91 cm. The fuel droplets were burned in the hot gaseous combustion products of a flat-flame burner to simulate bipropellant rocket engine operating conditions. The flat-flame burner could be fed with lean fuel mixtures, generating oxygen-rich hot gases in which secondary combustion of the droplet vapor decomposition products would take place. The conditions included 1660–2530 K at ambient pressure. The results of the tests with oxygen excess are discussed in Section 4.14. As far as the monopropellant burning is concerned, the following results were obtained for hydrazine: The hot gas velocity was low enough to avoid turbulent flow; the Reynolds numbers around the droplets were less than 38. In all suspended droplet tests, plots of diameter squared as a function of time were



reasonably linear. Decomposition flames were not luminous at all, but oxidation flames of all three fuels showed two distinct zones of luminosity.

A theoretical combustion and flame structure model was developed similar to and based on models suggested earlier [1436–1438]. In this method the monopropellant flame was assumed to be infinitely thin and located at a position where the unreacted gas flows into the flame at the laminar flame speed of the monopropellant vapor. The hybrid model (with another second flame front) reduced to pure monopropellant burning if no oxidizer was present. Assuming  $E_{\text{act}} = 0$ ,  $T = 2060$  K, and  $v_{\text{ambient}} = 55.7$  cm/s, good agreement of experimental and theoretical data was achieved. The hydrazine burning rate was relatively independent of ambient temperature between 1700 and 2400 K, in particular for large droplet diameters. Whereas the results of the hybrid model and a bipropellant evaporation model were quite different for hydrazine, the distinction was not as pronounced for MMH or UDMH. The droplet burning rates for hydrazine are presented in Figure 47.

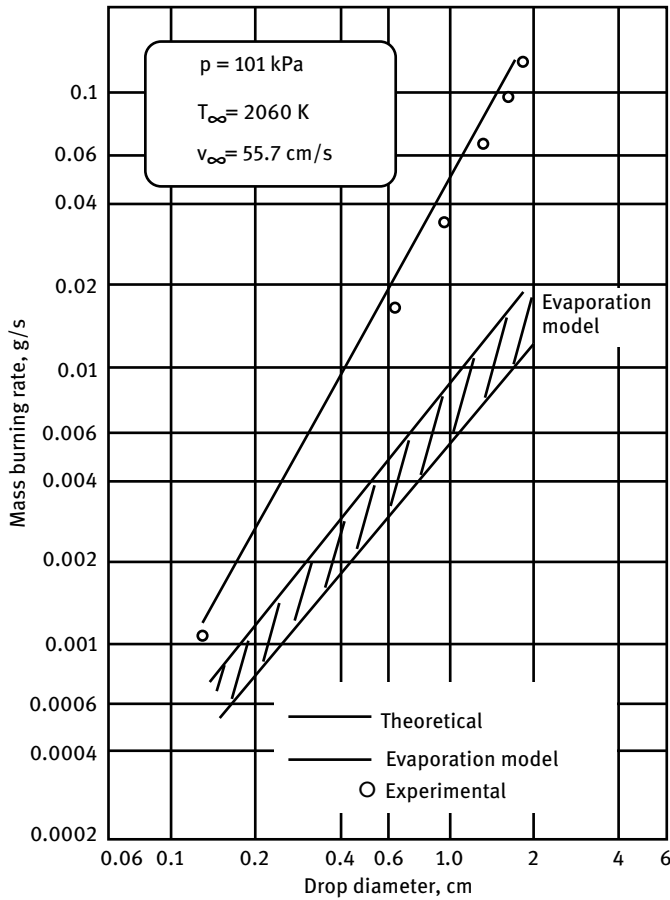
The mass burning rates predicted by the Allison-Faeth equation showed good agreement not only with experimental data of the same authors (Figure 47) but also with data from other investigators, such as [1431, 1432, 1439]. The data by Tarifa [1428] did not fit, and it was suspected that furnace radiation must be blamed for these high results.

Comparing the hydrazine and MMH decomposition rates of Figures 47 and 32 in the chapter on methylhydrazine, it is obvious that MMH monopropellant droplet burning proceeds more slowly than that of hydrazine in spite of higher volatility of MMH and increased luminosity of MMH decomposition flames.

#### 4.11.2 Other Studies on Droplet Combustion of Monopropellants

Imposed pressure oscillations may affect the burning rate of monopropellant droplets significantly. The phenomena can be described by a first-order perturbation analysis [1440]. A theoretical investigation was conducted on the open-loop combustion response of monopropellant droplets and sprays to imposed pressure oscillations. The theoretical model was solved as a perturbation analysis through first-order, yielding linear response results. Unsteady gas-phase effects were considered in some cases, but the bulk of the calculations assumed a quasi-steady gas phase. Calculations were conducted using properties corresponding to hydrazine decomposition. Zero-order results agreed with earlier measurements of hydrazine droplet burning in combustion gases. The droplet response was greatest (exceeding unity in some cases) for large droplets with liquid-phase temperature gradients; at frequencies near the characteristic frequency of the liquid-phase thermal wave. The response of a spray was less than that of its largest droplet; however, a relatively small percentage of large droplets provides a substantial response (exceeding unity in some cases).

Calculated steady combustion results and response predictions for large hydrazine droplets agreed favorably with earlier measurements [1441]. Droplet and



**Figure 47:** Hydrazine droplet monopropellant burning rate. (Reproduced and modified from [1433].)

spray response factors in excess of unity were found. High response was associated with high pressures (1–10 MPa), large droplets, large mean liquid temperature gradients, and frequencies near the characteristic frequency of the liquid phase thermal wave. Spray response factors are lower than the response factor of the largest injected drop; however, a small percentage of large drops can still provide substantial response for the combustion process [1442].

Depending on the geometry of the combustion chamber and the amount of attenuation provided, monopropellant droplet decomposition may lead to combustion instability and resonant effects [1443]. The burning-rate response of a condensed-phase fuel layer adjacent to a reacting gaseous boundary layer where the external flow has a longitudinal oscillation was examined to simulate the unsteady droplet burning in a liquid-propellant rocket and to try to isolate a physical mechanism that leads to in-

stability. The non-steady process is the heat transfer in the condensed phase. The results showed that the velocity-sensitive responses exhibited resonant phenomena at the proper frequency range and indicated that, under (un)favorable conditions, a liquid-propellant rocket can be driven to instability because of the thermal lag in the droplets.

There exists a large body of literature on the droplet combustion of monopropellants under various conditions in a combustion chamber. Some of these models are even applicable to the combustion of fuel sprays in a Diesel engine. Many of these publications apply to more than one monopropellant, but they are summarized here under hydrazine because this compound is the most important monopropellant, although it is rarely burned as a spray of droplets. For additional information on the theory and study of monopropellant droplet burning compare the following references: [1435, 1444–1473].

Most of these papers are quite general and only a few of them give data specifically applicable to hydrazine. Many of the experimenters had previously worked at one point or another with organic nitro compounds and nitrate esters as monopropellants and later used the same equipment and the same computer models to study hydrazine monopropellant droplet burning. Some of the droplet burning work was done to support the use of propylene glycol dinitrate/dibutyl sebacate mixtures as torpedo propellants.

A conventional formulation of quasi-steady radially symmetric burning of a pure spherical monopropellant droplet was re-examined assuming that the droplet undergoes adiabatic vaporization and exothermic direct one-step irreversible first-order decomposition burning [1474]. The singular near-equilibrium limit was examined by asymptotic analysis, and the dependence of the vaporization rate on the first Damköhler number was sought as that number becomes indefinitely large. In the near-equilibrium limit the flame was confined to a narrow spherical shell contiguous to the droplet. As the first Damköhler number became large without bound, some experimental and theoretical work has reported that the vaporization rate is proportional to the droplet radius squared, while other work has suggested that the vaporization rate is linearly proportional to the droplet radius. An analysis predicted that the maximum vaporization rate does not occur at chemical equilibrium (in contrast to bipropellant droplets). Further, in contradiction to previous work, it was indicated that for vaporization rate to be proportional to the droplet radius squared, the ratio of specific heat of vaporization to specific heat of combustion must be less than unity. It is this ratio which is important, not the non-dimensionalized droplet or ambient-state enthalpies.

#### 4.12 Heterogeneous Catalyzed Hydrazine Decomposition

Of all the possible modes of hydrazine decomposition, the catalytic mode is of prime practical importance. Countless (several thousand) satellites and space probes in op-

eration now use hydrazine for attitude control and orbit adjustment propulsion. All these spacecraft rely on the heterogeneous catalytic decomposition of hydrazine. Additional applications are for hydraulic and electric power in advanced fighter aircraft and, historically, at one time in both the US and Russian space shuttles. In many cases, the design of flightworthy hydrazine decomposition reactors relies on empirical design criteria, and very little helpful information can be derived from the few academic kinetic studies that have appeared to date. So far, nobody has been able to establish a reliable correlation between all the testing done with hydrazine decomposition in the laboratory at low pressures and the performance of hydrazine decomposition catalysts in rockets and gas generators at high pressures.

The low-pressure tests, mostly academic in nature, are useful in establishing the kinetics of heterogeneous hydrazine decomposition and establish a relative ranking of the catalytic activity of metals, working one's way all the way across the periodic table of elements (metals). Metals that have been identified as catalytically active must be avoided in materials of construction for hydrazine storage containers. The acceptability of steels containing less than 0.5% molybdenum remains a topic of discussion.

Hydrazine (hydrate) has been evaluated as a fuel for air-fuel cells. While catalytic decomposition of hydrazine as a monopropellant is highly desirable, it is very undesirable where hydrazine (hydrate) is in contact with electrodes in fuel cells, resulting in fuel loss even during idle periods of fuel cells.

A table in [1475] gives a chronological overview of the numerous publications devoted to the study of heterogeneous hydrazine decomposition. This table complements another table in [1188], which is restricted to homogeneous decomposition studies. A small number of these publications have practical applications. A complete review of all those publications would fill a book in its own right. A good summary of catalysts for rocket propulsion and gas generators, a first step in this direction, was written as a chapter of a handbook on heterogeneous catalysis [1476].

Heterogeneous decomposition of hydrazine has been studied in solution as well as in the vapor phase. The majority of these more academic investigations used a catalytic surface in ultra-high vacuum in combination with a mass spectrometer for product analysis. These studies relate only remotely to the decomposition of anhydrous hydrazine in a real-world reactor, whereas decomposition in solution may help to explain material compatibility or incompatibility of hydrazine with certain tankage materials. The metals under study and brought into contact with hydrazine were finely divided as a powder, as a skeleton catalyst, as a supported catalyst, as a wire filament, or as a freshly deposited thin film. A few metals were also tested as single crystals.

The main objective of many of the investigations discussed herein was to determine ground rules for the selection of more active decomposition catalysts, to study the decomposition mechanism, and to determine the activation energy of the decomposition of hydrazine in the presence of catalytic surfaces. Catalytic activity is closely related to the activation energy. Table 60 gives a summary of the activation energies

**Table 60:** Activation energy of heterogeneously catalyzed decomposition of hydrazine. (Metals in alphabetical order.)

| Metal     | Activation energy |              | Temp. range | Hydrazine partial pressure                          | References   |
|-----------|-------------------|--------------|-------------|-----------------------------------------------------|--------------|
|           | kcal/mol          | kJ/mol       | K           | mm Hg, or concentration                             |              |
| Ag        | 15 ± 1            | 63 ± 4       | 393–423     | 8 in Ar at 760                                      | [1477, 1478] |
| Co        | 16 ± 1            | 67 ± 1       | 353–393     | 8 in Ar at 760                                      | [1477, 1478] |
| Au        | 9.08 ± 0.48       | 38 ± 2       | —           | liquid                                              | [1176]       |
| Cr        | 20.7 ± 0.2        | 87 ± 0.8     | 369–549     | 10                                                  | [1479]       |
| Cu        | 16 ± 1            | 67 ± 1       | 393–423     | 8 in Ar at 760                                      | [1477]       |
| Fe        | 13.6 ± 0.2        | 57 ± 0.8     | 331–380     | 10                                                  | [1479]       |
| Ir        | 15.617 ± 0.038    | 65.34 ± 0.16 | 273–327     | 99% liquid                                          | [1480]       |
| Ir        | 15.636 ± 0.031    | 65.42 ± 0.13 | 273–327     | 31.7% aq.                                           | [1480]       |
| Ir        | 13.640 ± 0.035    | 57.07 ± 0.15 | 273–327     | N <sub>2</sub> H <sub>5</sub> Cl solution           | [1480]       |
| Ir        | 12 ± 1            | 50 ± 4       | 323–383     | 8 in Ar at 760                                      | [1477]       |
| Ir        | 20.5              | 86           | 310–320     | Liquid                                              | [1481]       |
| Ir        | 5.54              | 23           | 350–700     | 1–3% N <sub>2</sub> H <sub>4</sub> in He at 1 mm Hg | [1482, 1483] |
| Mn        | 14.7 ± 0.2        | 62 ± 0.8     | 336–510     | 10                                                  | [1479]       |
| Ni        | 15 ± 1            | 63 ± 4       | 343–383     | 8 in Ar at 760                                      | [1477]       |
| Ni Raney  | 17.1              | 71.5         | 274–323     | 96% liquid N <sub>2</sub> H <sub>4</sub>            | [1484]       |
| Ni on MgO | 14                | 58           | 298–423     | >10                                                 | [1485]       |
| Os        | 12.7 ± 0.2        | 53 ± 0.8     | 395–505     | 10                                                  | [1479]       |
| Pd        | 16 ± 1            | 67 ± 1       | 363–423     | 8 in Ar at 760                                      | [1477]       |
| Pd        | 29                | 121          | 320         | 10                                                  | [1486]       |
| Pd        | 21 ± 2.5          | 88 ± 10      | 413–493     | 10–100                                              | [1487, 1488] |
| Pd        | 10.66 ± 0.12      | 44.6 ± 0.5   | 273–323     | 30.1 M in H <sub>2</sub> O                          | [1489]       |
| Pt        | 7.69 ± 0.10       | 32.2 ± 0.4   | 273–323     | 30.8 M in H <sub>2</sub> O                          | [1489]       |
| Pt        | 17 ± 1            | 71 ± 4       | 343–383     | 8 in Ar at 760                                      | [1477]       |
| Re        | 13.7 ± 0.2        | 57 ± 0.8     | 383–483     | 10                                                  | [1479]       |
| Rh        | 9.87 ± 0.08       | 41.28 ± 0.33 | 273–323     | 30.8 or 45% in H <sub>2</sub> O; D-labeled          | [1490]       |
| Rh        | 12 ± 1            | 50 ± 4       | 333–373     | 8 in Ar at 760                                      | [1477]       |
| Ru        | 12 ± 1            | 50 ± 4       | 373–413     | 8 in Ar at 760                                      | [1477]       |
| W         | 14.4 ± 0.2        | 60.2 ± 0.8   | 338–474     | 10                                                  | [1479]       |
| W         | 9.4               | 39.3         | 440–487     | 1.5                                                 | [1491–1493]  |

on various metals and the conditions under which the measurements were obtained. This table focuses on metals for which activation energies have been reported and it gives numerical data for the activation energies and the conditions under which they were determined. The metal that achieves the most significant reduction of the activation energy of hydrazine (compared to data obtained in the absence of any catalyst) should make a good catalyst for future use in rocket engines.

These data may help in the development and selection of catalysts for hydrazine decomposition. In surveying the various metals that catalyze hydrazine decomposi-

tion, it was noted that transition metals having incomplete *d* subshells act as strong catalysts for hydrazine decomposition, whereas metals having no *d* subshells or completely filled *d* shells are not catalytic [1232, 1233]. It was theorized that electrons from the lone electron pairs in hydrazine interact with unfilled *d* orbitals in the early stages of adsorption and chemisorption of hydrazine. Other molecules with lone electron pairs, such as ammonia or aniline, block active sites and inhibit the catalytic decomposition of hydrazine.

#### 4.12.1 Heterogeneous Vapor-Phase Decomposition

The results to be discussed in this section can be subdivided and arranged in several ways: in chronological order, by experimental method, or by metal investigated. It has been decided to arrange the various references that are reviewed by experimental method and try to maintain a chronological sequence within each method. This can be done only at the expense of the clarity of the typical behavior of each of the metals investigated. The experimental methods used for studying heterogeneous vapor-phase decomposition include decomposition on thin films, single-crystal faces, polycrystalline wires, metal powders, or supported catalysts. The methods of monitoring the decomposition process include pressure rise, mass spectrometer analysis, field ion appearance spectroscopy, and electrical measurements. Electrical measurements include measuring the changing electric conductivity of thin films or the electron emission work function on metal wire tips while adsorption-desorption and decomposition is in progress.

#### 4.12.2 Vapor Decomposition on Thin Films

A high-vacuum apparatus was used to measure the rate of ammonia formation on a freshly deposited thin tungsten film at various temperatures in the range 195–273 K for study of the heterogeneous decomposition of hydrazine [1494]. The interpretation of the results was still based on the incorrect assumption that the dissociative adsorption of hydrazine would give amino radicals. This assumption was later shown to be wrong in view of results with <sup>15</sup>N-labeled hydrazine.

Subsequent investigations on the heterogeneous decomposition of hydrazine on tungsten and molybdenum films, respectively, were hampered by the lack of a mass spectrometer for product analysis [1495, 1496]. Instead, the authors had to rely on pressure rise measurements, fractionation of condensables, and selective adsorption on nickel films to draw conclusions on hydrazine decomposition mechanisms.

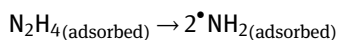
Hydrogen is selectively chemisorbed on freshly deposited nickel films, whereas nitrogen is not. The non-condensable gases passing through the liquid nitrogen trap could be analyzed in this fashion. The decomposition of hydrazine on tungsten films was explained as dissociative (as opposed to associative) chemisorption [1495]. A thin film usually contains all single-crystal planes in random mixture. It is not directly possible to state which face of the many crystals is more active than another face such as

is possible when a large single crystal is available to work with and the other faces can be isolated. From previous knowledge of the activity of tungsten single crystals in the adsorption of gases such as nitrogen, hydrogen, ammonia, and carbon monoxide, however, it was possible to derive which exposed crystal planes are most active in hydrazine decomposition. This was achieved by pre-adsorbing the four gases mentioned previously prior to the admission of hydrazine, in this fashion selectively blocking certain active sites. For instance, because the (110) plane of tungsten does not dissociatively chemisorb nitrogen from the gas phase, and carbon monoxide is adsorbed on this plane only subsequent to filling the more active (100) and (111) planes, the authors postulated that dissociative chemisorption of hydrazine occurred on the (100) and (111) planes, whereas molecular chemisorption took place on the (110) plane. Experimental evidence seemed to support this so-called two-plane theory.

Knowledge of the surface of the deposited metal film allows one to calculate the coverage of active sites by hydrazine. It follows that each  $\text{N}_2\text{H}_4$  molecule upon dissociative chemisorption on the (100) or (111) plane occupies four (H-adatom) sites. On the (110) sites the molecular adsorption may occur through a single hydrogen atom in the  $\text{N}_2\text{H}_4$  molecule. Thus, nitrogen and hydrogen are formed from decomposition on the (100) and (111) planes, whereas ammonia is formed without adsorption, most likely on the (110) plane.

In a similar study on hydrazine decomposition on molybdenum films, the results were qualitatively and quantitatively like those obtained on tungsten films [1496]. Both studies on tungsten and molybdenum were conducted at significantly lower temperatures than previous investigations. This may be one reason why results at higher temperatures included vapor-phase decomposition and indicated different mechanism. Other thin-film investigations measured the conductivity of nickel films prior to and during adsorption of hydrazine vapor [1497]. The change in resistance of Cu and Ni films during the decomposition of  $\text{H}_2\text{NNH}_2$  was studied between 297 and 423 K (24 and 250 °C) at partial pressures of  $\text{H}_2\text{NNH}_2$  ranging from 1.3 to 1.9 kPa (10 to 14 mm Hg). In the presence of  $\text{H}_2\text{NNH}_2$ , the resistance of the Ni film was found to increase rapidly owing to chemisorption of  $\text{H}_2\text{NNH}_2$ . Upon complete decomposition of  $\text{H}_2\text{NNH}_2$  the resistance was observed to decrease slightly, only to increase again, because a surface nitride  $\text{NiN}_3$  apparently was being formed.

Surprisingly, even hydrazine molecules adsorbed on aluminum, an otherwise totally inert metal, will dissociate at very low temperatures. Based on results with XPS, at 85 K both  $\text{NH}_3$  and  $\text{N}_2\text{H}_4$  are adsorbed molecularly, with N(1s) peaks at 400.5 eV [1498]. At 290 K hydrazine was initially adsorbed to give an N(1s) peak at 399 eV, but with time and additional exposure, the location of the peak shifted to lower photoelectron potentials, finally approaching 397 eV after heating the adatom layer to 390 K. One may assume that hydrazine underwent a slow dissociation



possibly with further decomposition to hydrogen adatoms that tenaciously adhere to the metal surface and prevent the adsorption of more hydrazine. As expected, ammonia dissociates more slowly than hydrazine. Hydrazine vapor will decompose on thin films of iron, nickel, or copper [1499]. Thin metal films were deposited inside a 240-mL glass flask by metal vapor deposition in high vacuum. The surface areas of the films were characterized by krypton adsorption prior to each test when varying amounts of hydrazine were admitted to the evacuated flask and the pressure recorded and the gas composition measured with a mass spectrometer within 1–3 min. after admission of the hydrazine. The temperature of the flask was varied from 273 to 393 K. The surface coverage  $\theta$  of hydrazine on the film was expressed in terms of multiples of the volume of the krypton monolayer and ranged from 0.6 for Fe to 0.73 for Ni and 1.5 for Cu at 243 K. Fast, dissociative chemisorption of hydrazine occurred on iron films at 243 K and the decomposition led to the evolution of  $N_2$  and  $NH_3$  within less than 1 min. Hydrogen became the main gaseous product above 393 K. Hydrazine adsorption and decomposition on nickel was like that on iron. Hydrazine as adsorbed on copper, but no decomposition occurred below 303 K. It was suggested that two-point attachment of the lone electron pairs in  $>N-N<$  to the copper crystal lattice could occur without a significant strain on the molecule.

A few tanks and expulsion diaphragms for some hydrazine-fueled satellites and missiles are made from stainless steel. Sometimes stainless steel is covered with thin films of rust in places where it has been welded and lost its passivity toward moisture in air, which is a problem. These rust films may cause accelerated decomposition of hydrazine (liquid or vapor) if the tank is not properly cleaned after the welding step. Quite often, residual pickling acids are left sitting in the hardware too long before they are cleaned out. In this case corrosion continues and salts are deposited in places where the acid/water solution dries out. In all these cases, it would be desirable to have a realistic non-destructive acceptance test to verify the compatibility of the tank with hydrazine before it is filled with liquid hydrazine. An all-up pre-flight test with liquid hydrazine would consume too much hydrazine and add to the headaches of removing all the hydrazine after the test, cleaning the tank, and keeping it clean prior to flight. Instead of using liquid hydrazine, a method has been devised that uses hydrazine vapor at very low partial pressures. In a carefully thermostatted chamber and with sensitive pressure transducers, contaminated tanks can be recognized by accelerated pressure rise [1500, 1501].

#### 4.12.3 Vapor Decomposition on Hot Wires and Metal Foil

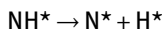
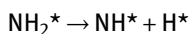
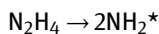
An activation energy of 39.3 kJ/mol (9.4 kcal/mol), a pre-exponential factor of  $1.79 \times 10^7 \text{ mol}^{-0.24} \text{ s}^{-1}$ , and a reaction order of 1.24 were measured in the catalytic decomposition of hydrazine vapor on tungsten filaments at an initial  $N_2H_4$  pressure of 202 Pa (1.52 mm Hg) and a temperature of 440–487 K [1491–1493].



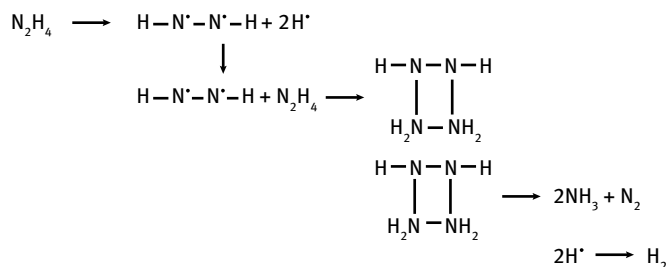
When hydrazine vapor was decomposed on an electrically heated platinum filament in a flow reactor at 13 mPa ( $10^{-4}$  mm Hg), several observations suggested the formation of diazene as an intermediate [1502]. Three molecules of hydrazine were decomposed for every molecule striking the filament. The hydrogen:nitrogen ratio in the non-condensable fraction of the reaction products was 2.5:1, suggesting that a compound with a H:N ratio of less than 2:1 had condensed in the cold trap. By attaching the platinum filament flow reactor to the inlet of a mass spectrometer, short-lived intermediates in the decomposition products could be identified, including mass 30 ( $\text{N}_2\text{H}_2^+$ ) and mass 29 ( $\text{N}_2\text{H}^+$ ).

When oxygen was mixed with hydrazine, heating of the catalyst produced an increase of  $m/e$  30 by a factor of 4. This was attributed to the formation of NO because there was no concurrent increase in  $m/e$  29. If both  $m/e$  30 and 29 had increased, diazene might have formed by partial oxidation of hydrazine on the surface of the catalyst.

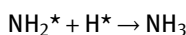
Using a  $0.0046 \times 0.07 \times 6.9$ -cm ribbon of polycrystalline iridium foil in an ultra-high vacuum system with an attached QMS, an attempt was made to identify adsorbed species that might interfere with the hydrazine decomposition activity of an iridium surface [1503]. The characteristics of the clean surface were studied first, followed by adsorption and desorption of nitrogen, hydrogen, and ammonia. Desorption spectra from the hydrazine-dosed iridium ribbon suggested that the dosed surface harbored nitrogen in three distinct binding states and hydrogen in two states. It also contained molecularly adsorbed ammonia. A common feature of the desorption spectra obtained from hydrazine-dosed and from ammonia-dosed iridium ribbons was the appearance of hydrogen and nitrogen peaks at and above temperatures close to 600 K. Less ammonia was recovered from the ammonia-dosed ribbon than from the hydrazine-dosed ribbon. The simultaneous appearance of hydrogen and nitrogen peaks at about 600 K suggested that they arose from a single-surface reaction step that involved a common intermediate, most likely adsorbed molecular ammonia. IR absorption observed by other authors had previously been attributed to adsorbed ammonia [1504, 1505]. Two modes of hydrazine decomposition have been postulated. In one mode, hydrazine dissociatively adsorbs on iridium degrading rapidly to  $\text{NH}^*$  (\* = adsorbed) nitrogen adatoms and hydrogen adatoms:



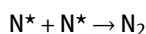
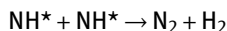
In the other mode, hydrazine molecules chemisorb by way of hydrogen abstraction and by way of subsequent interaction with another hydrazine molecule from the vapor phase to form ammonia and nitrogen:



These four reactions account for product stoichiometry observed at temperatures up to about 500 K. Between 500 and 600 K an ammonia-forming reaction such as



may take place, while above 600 K, ammonia formation virtually ceases, and nitrogen and hydrogen are formed by



and adsorbed ammonia rapidly decomposes to nitrogen and hydrogen. Adsorbed nitrogen in the  $\beta$  state has been shown to be responsible for the gradual loss of hydrazine decomposition activity of an iridium foil. The activity could be restored by heating to a temperature at which the  $\beta$   $\text{N}^*$  becomes desorbed. The persistence of  $\beta$  nitrogen on the iridium surface after exposure to hydrazine was verified by the examination of the catalyst with Auger electron spectroscopy (AES). The results obtained from the desorption from the iridium ribbon were useful for the interpretation of later results obtained by the same laboratory using Shell 405 catalyst (Section 4.13.2.2). The rate-determining step is the desorption of nitrogen from the catalyst surface. The activation energy for this step was determined to be 213 kJ/mol (51 kcal/mol), and the pre-exponential factor is  $1.1 \times 10^{-2} \text{ cm}^2/\text{s}$  [1503]. Dehydrogenated surface species such as  $\text{NH}$  and  $\text{NH}_2$  or  $\text{N}$  and  $\text{H}$  adatoms were also observed by XPS of hydrazine vapor decomposition on iron films [1506]. Iron is the main catalyst for industrial ammonia production. If hydrazine is formed as an intermediate in ammonia synthesis, it may adhere to iron surfaces differently than ammonia would.

The decomposition of hydrazine on iridium wire and a catalyst surface closely simulating that of Shell 405 was studied using a molecular beam method and a TOF mass spectrometer [1482, 1483]. One objective of the study was to determine the extent of active site occupation by hydrazine and its decomposition products at lower temperatures (<600 K). The desorption of these molecules above a certain temperature will cause a sudden increase in reaction rate with increasing temperature. The experiments were conducted in a flow reactor where helium with a small amount of

hydrazine (1–3%) was flowed past the helix-shaped catalyst at 130 Pa (1 mm Hg) pressure. After reaction, the gas mixture was passed through two skimmers and introduced directly into the mass spectrometer. The temperature of the bare wire or coated catalyst helix could be raised by passing an electric current through it. At the same time, its resistance was measured as a temperature indication. The global reaction rate of hydrazine decomposition on iridium wire was found to obey the following equation:

$$R_2 = 1.74 \times 10^{-4} \times e^{-\frac{5540}{RT}} \times C_{\text{N}_2\text{H}_4}^{1.39} \times C_{\text{H}_2}^{0.025} \times C_{\text{N}_2}^{0.00} \times C_{\text{NH}_3}^{0.05} \quad \text{mol s}^{-1} \text{cm}^{-2}$$

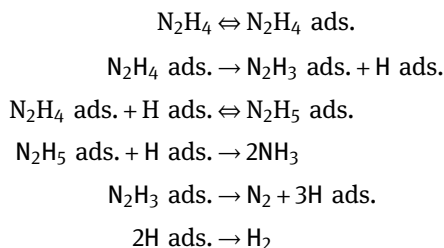
The activation energy was thus found to be 23 kJ/mol (5.54 kcal/mol) over a temperature range of 460–700 K. Below 430 K the rate was significantly lower, which was attributed to adsorbed hydrazine. The decomposition rate was weakly dependent on temperature, except in the range 450–500 K, where it was dependent on temperature. It was suspected that below this temperature a significant portion of the active surface area is covered with a strongly bonded species, which begin to desorb at 450 K. Similar phenomena had been observed on tungsten [1495] and molybdenum [1496]. For the alumina-supported iridium catalyst a similar rate equation was obtained, except that the activation energy is essentially zero. The order of the reaction is the same:

$$R_e = 2.7 \times 10^{-2} e^{-\frac{(1.6 \pm 1.09) \times 10^3}{RT}} C_{\text{N}_2\text{H}_4}^{1.33}$$

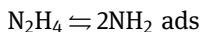
This equation was obtained in a lower temperature regime than that for bare iridium wire because the reaction became diffusion controlled above 500 K since the supported catalyst is more active than the bare wire. The degree of ammonia dissociation  $X$  (for a definition, see *Encyclopedia of Monopropellants*, in the chapter “Hydrazine Monopropellants”) was identical for both catalysts (0.25–0.35).

A molecular beam/hot-wire technique with a mass spectrometer was used to study the decomposition of hydrazine on polycrystalline palladium surfaces [1486], which was like the apparatus used in [1483]. The pressure was maintained below  $10^{-5}$  mm Hg. The palladium wire had a geometric surface of approximately  $3 \text{ cm}^2$  and could be heated by passing an electric current through it. The kinetics of hydrazine decomposition were investigated by deuterium exchange, thermal desorption spectra, and measurement of stationary decomposition conditions. Analysis of the percentage of  $\text{N}_2\text{H}_3\text{D}$  and  $\text{N}_2\text{H}_2\text{D}_2$  in the products of a  $\text{N}_2\text{H}_4 + \text{D}_2$  mixture passing over a palladium wire showed that some isotope exchange occurred even at room temperature. At 520 K, up to 25%  $\text{N}_2\text{H}_3\text{D}$  and close to 5%  $\text{N}_2\text{H}_2\text{D}_2$  were observed in the products, whereas the  $\text{N}_2\text{H}_4$  fraction decreased with temperature as a result of isotope exchange. The initial hydrazine  $\text{N}_2\text{H}_4$  partial pressure was extremely low,  $10^{-8}$  mm Hg. The rate of deuterium exchange as a function of deuterium:hydrazine ratio showed a maximum. At higher deuterium pressures the isotope exchange was inhibited by pre-adsorption of deuterium on the catalyst. This indicated that the exchange occurred with hydrazine in the adsorbed state. Thermal desorption spectra of decomposition products obtained after loading the metal wire with hydrazine at room temperature and heating rapidly (20 K/s) showed that nitrogen and hydrogen

formation are governed by the same rate-determining mechanism. Stationary decomposition was achieved with flowing hydrazine at approximately  $10^{-5}$  mm Hg. Hydrazine decomposition began already slightly above room temperature and was complete above 450 K. Nitrogen, hydrogen, and ammonia formation increased in this range until above 600 K, where the ammonia formation dropped off as a result of incipient ammonia decomposition. In interpreting the experimental results, the authors proposed the following mechanism consisting of a sequence of six reactions, in which the second reaction is the rate-determining step:



The formation of ammonia is attributed to stepwise progressive hydrogenation of hydrazine by way of the third and fourth reaction. The proposed mechanism acknowledges the results by Block [1048] and [1490], according to whom the dinitrogen is formed from nitrogen atoms in the same hydrazine molecule such as shown in the fifth reaction. The reaction on palladium was first order, in agreement with the foregoing mechanism, in particular the second reaction. However, in previous tests with a gallium arsenide catalyst, the authors postulated a one-half-order mechanism that would support Szwarc's repeatedly disputed mechanism



The decomposition mechanism is apparently strongly influenced by the substrate on which the decomposition occurs.

In studying the decomposition of hydrazine vapor on palladium foil at 413–493 K and 1.4–13.1 kPa in a circulating flow system, the investigators concluded that the kinetic data excluded a chain mechanism [1487, 1488]. At 413 K, nitrogen and hydrogen were the major products of decomposition. The activation energy was determined to 87.9 kJ/mol ( $21 \pm 2.5$  kcal/mol). At 493 K, ammonia formed along with nitrogen. A mechanism was proposed where sorption and surface intermediate complex formation constituted the rate-determining steps. Studies were also conducted on a semi-permeable palladium tube membrane. Hydrogen was found to inhibit the decomposition. The rate of nitrogen production was proportional to the hydrazine concentration to the 0.85<sup>th</sup> power and inversely proportional to the hydrogen concentration to the 1.4<sup>th</sup> power:

$$W_{\text{N}_2} = k \frac{p_{\text{N}_2\text{H}_4}^{0.85}}{p_{\text{H}_2}^{1.4}}$$

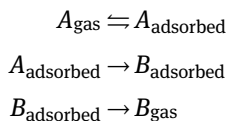
where  $W(\text{N}_2)$  is the rate of  $\text{N}_2$  production and  $k$  is a constant. The retardation of the reaction on palladium by hydrogen elevated to a power greater than 1 could not be explained by simply filling the surface with hydrogen. It must be related to the reversibility of intermediate steps in the reaction. The rate of ammonia formation was proportional to

$$W_{\text{NH}_3} = p_{\text{N}_2\text{H}_4}^{0.6} p_{\text{H}_2}^{0.14}$$

At 513 K on palladium foil, the amount of ammonia formed comprised only several percent of all the hydrazine decomposed. Since ammonia by itself does not decompose on palladium at 500 K, hydrogen must be formed directly by the decomposition of hydrazine.

A cross-flow filament reactor was used to study the partitioning of chemical energy release between solid catalysts and gaseous reaction products of hydrazine vapor decomposition [1507, 1508]. The platinum, iridium, or tungsten filaments (0.127 mm diameter) were heated to temperatures above 1000 K and measurements taken in a range of 900 to 2200 K. This technique allowed for isothermal conditions on the reacting surface, although conversions were very slight. The temperature of the impinging hydrazine vapor could be varied by an upstream, heater filament also made from Pt but kept at a much lower temperature so it would not enter into competition with the hotter, main filament. Not all reactions can proceed to equilibrium within the short contact time of hydrazine with the catalyst filament. Non-equilibrium desorption of  $\text{H}_2$  molecules from the catalysts was responsible for part of the exoergic reaction energy transport and removal. The hydrazine source was a 1-L flask in the thermostatted bath and kept at a low, constant vapor pressure ( $\pm 0.1$  mm Hg). At the temperatures of this study, no other intermediate ( $\text{NH}$ ,  $\text{N}_2\text{H}_2$ ) appeared to be involved in the decomposition, but the experimenters did not use a mass spectrometer and product analysis was only by thermoconductivity and gasometry.

The Langmuir-Hinshelwood mechanism assumes a single binding state with coverage-independent parameters (a Langmuir isotherm). A reaction  $\text{A} \rightarrow \text{B}$  is assumed to proceed via adsorbed species



In a study of hydrazine decomposition, residence time of hydrazine vapors in a 400-mL CRES reactor filled with hot, polycrystalline Pt or Rh wires at 1.3 to 93 Pa (10 to 700  $\mu\text{m}$  Hg) and 400 to 1700 K was 1 to 10 s [1509]. A sample of the reaction products was bled through a control orifice into a QMS for analysis. Unfortunately, additional cracking of hydrazine or ammonia occurred on the hot filaments of the mass spectrometer, and this amount of byproducts determined in a baseline test had to be subtracted from all results with the catalyst in place. Below 800 K, the rates of ammo-

nia and nitrogen formation were comparable, while nitrogen was the main product above 800 K. Above 800 K, the rates became temperature independent, most likely as a result of reactant flux/diffusion limitations. The results (rates of  $\text{N}_2$  and  $\text{NH}_3$  formation as a function of temperature) could be represented accurately by a Langmuir-Hinshelwood rate expression. In a similar study of polycrystalline iridium wires in the same apparatus, the rates of  $\text{N}_2$  and  $\text{NH}_3$  formation were measured at 300–1700 K and 1.3–40 Pa (0.01–0.3 mm Hg) [1510]. At high temperatures (>900 K), both rates were first order with respect to hydrazine pressure and were pressure independent at <700 K. The shape of the rate =  $f(T)$  curves could be represented accurately by Langmuir-Hinshelwood unimolecular rate expressions. The rate of  $\text{N}_2$  formation rose rapidly with temperature but became flux-limited above ~800 K.

The identification of diazene in the intermediates of hydrazine or ammonia vapor-phase decomposition may hint at one of the inhibiting species suspected to linger on hydrazine decomposition catalysts at temperatures around 400 K. Most of the earlier studies on diazene as an intermediate in hydrazine decomposition were done in the liquid phase. Now diazene has been identified as an intermediate of the thermal, surface-catalyzed gas-phase decomposition of hydrazine or ammonia at 180–500 K on a polycrystalline rhodium foil [1237, 1238]. The experiments were performed in an ultra-high vacuum system equipped with AES, low-energy electron diffraction, and a multiplexed mass spectrometer. Low and high levels of hydrazine coverage on the metal foil were studied. At higher hydrazine coverage (near monolayer coverage), diazene was found along with adsorbed hydrogen, nitrogen, and ammonia. Diazene was identified at foil temperatures above 220 K based on mass spectrometry of the parent ion at 30 amu and a single-dehydrogenation fragmentation product at 29 amu that is present at 6% of the abundance of its parent. Adsorbed NH was already proposed earlier as an intermediate residing on the surface, but its dimer had so far not been seen. Co-adsorption of hydrogen increased and co-adsorption of oxygen decreased the diazene yield.

A modulated molecular beam mass spectrometer incorporating TOF and threshold ionization capabilities was used to study the decomposition of hydrazine vapor on a platinum foil at 773–1373 K and <186 Pa (<1.4 mm Hg) [1511].  $\bullet\text{N}_2\text{H}_3$  radicals and diazene were found at 773–973 K, but no  $\bullet\text{NH}_2$  radicals.

#### 4.12.4 Vapor Decomposition on Surface of Single Crystals

Most catalytic decomposition studies of hydrazine vapors at low pressures were done on polycrystalline foils, thin films, or wires. It has been found that the different surfaces of a well-formed single crystal can have widely varying activities for the decomposition of hydrazine. Thus, for supported catalysts, it would be desirable to select deposition methods that maximize crystal surfaces with high activities [577, 1506, 1512–1529]. The decomposition studies on single-crystal surfaces help to explain the cat-

alytic decomposition kinetics of hydrazine decomposition and may even aid in the development of improved supported catalysts.

From experiments using  $^{15}\text{N}$ -labeled hydrazine it was concluded that the product  $\text{N}_2$  is always formed from a single hydrazine molecule, based on data obtained on platinum single crystals [1048]. Imidogen free radicals adsorbed on the (111) surface of nickel single crystals during the decomposition of hydrazine can be identified by their IR spectra [1516]. The same has been observed for diimine on the (100) surface of Ni single crystals [1518]. A lack of mobility of the reaction intermediates  $\text{NH}_2$ ,  $\text{NH}$ , and  $\text{N}$  favors the recombination of two nitrogen atoms originating from the same hydrazine molecule on alumina-supported catalysts [1530, 1531]. Co-adsorption of  $\text{CO}$  or  $\text{D}_2$  with hydrazine on  $\text{Rh}(100)$  surfaces was studied with TPS, XPS, and ultraviolet photoelectron spectroscopy (UPS) in an effort to identify the active sites [1521, 1522]. The metal-CO bond was weakened by the presence of nitrogen. At 500–550 K,  $\text{N}$  was the only species remaining on the surface. On the other hand, pre-adsorption of molecular oxygen enhanced the decomposition and oxidation of hydrazine on  $\text{Pt}(111)$  crystal faces [559, 1525]. There is something peculiar about the activity of iridium as a catalyst for the decomposition of hydrazine. A new method, called angularly resolved temperature-programmed decomposition on single-crystal surfaces, has been applied in an effort to identify the geometric arrangement of the reacting species on active sites [1532, 1533]. It has been noted that nitrogen molecules desorbing from a clean surface of an iridium single crystal after depositing hydrazine vapor at 80 K followed by quick (100 K/s) warming will not radiate uniformly as expected by a cosine distribution. Instead, one of the three temperature programmed desorption (TPD) peaks, the one desorbing first at 290 K, showed a strong angular dependence, such that most of the nitrogen is ejected perpendicularly to the surface. This sharp angular dependence indicated that the desorbing molecule experienced a strong repulsive potential as it left the surface. It also allows some speculation about the orientation of the hydrazine molecules from which the nitrogen molecules originated.

With the use of a supersonic molecular beam-scattering system, the decomposition of hydrazine on  $\text{Ir}(111)$  surfaces has been studied in the temperature range 200–1500 K [1523, 1529]. While the sensor was placed at an angle of  $45^\circ$  to the surface, there was a temperature interval in which essentially no nitrogen was produced. This is in direct conflict with the decomposition stoichiometry. It was found that the nitrogen emission (= effusion) between 200 and 320 K had an extremely strong angular dependence. This was the first time a pronounced angular dependence of nitrogen emission had been observed for surface decomposition.

Experiments and computer simulations of hydrazine decomposition on  $\text{Ir}(111)$  surfaces of single crystals were combined in order to gain a better understanding of the  $\text{N}_2\text{H}_4$  decomposition on Ir catalysts [1524]. Metallic Ir rather than  $\text{IrO}_2$  was identified as the active phase for hydrazine decomposition.

#### 4.12.5 Vapor Decomposition on Metal Powders and Supported Catalysts

Results obtained on thin films and single-crystal surfaces help to interpret the results obtained on more complex surfaces, such as on metal powders and supported catalysts, but they only work at very low pressures. This is where the practical value of these investigations comes to bear if they result in the discovery of more active or less expensive catalysts for the decomposition of hydrazine in energy conversion systems. The most important reaction is the heterogeneous decomposition of hydrazine on supported iridium catalysts. In addition to supported iridium catalysts, numerous other supported metal catalysts have been investigated. These publications can be subdivided into those on noble metal catalysts and those on non-noble metal (generally ferrous metal) catalysts. According to their importance, the noble metal catalysts are discussed here first.

A TOF mass spectrometer was used to study the decomposition of hydrazine in a 15-cm (6-in.)-long reactor at 2.7–10.6 Pa (20–80  $\mu$ m Hg) filled with Shell 405 pellets [1534]. Complete decomposition was achieved if the catalyst was heated to 770 K, whereas without catalyst (thermal decomposition only) some hydrazine remained undecomposed even at 1170 K. Certainly, the pressure in this experiment was so low that the collision rate was very small, and some hydrazine passed undecomposed. At higher pressure, such as in a gas generator, complete hydrazine decomposition would occur. Besides hydrogen, nitrogen, and ammonia,  $\text{NH}_2$ ,  $\text{N}_2\text{H}$ ,  $\text{N}_2\text{H}_2$ , and  $\cdot\text{N}_2\text{H}_3$  radicals were also observed in the reactor effluent. Another surprising observation was the tenacity with which carbon dioxide was held by the catalyst despite 20 h of degassing in vacuum at 770 K before use. This may have implications for the repeated use of hydrazine propulsion systems after landing on Mars or in other carbon-dioxide-laden planetary atmospheres.

Temperature-programmed desorption of hydrazine decomposition products from catalyst surfaces helps to elucidate the hydrazine decomposition mechanism. Comparison of hydrogen TPD spectra of hydrogen adsorbed on iridium powder and on alumina-supported iridium indicated that the supported iridium had four instead of only two peaks [1504, 1505, 1535, 1536]. This indicated the formation of new bonding states formed by the interaction of the active metal with the carrier. Although nitrogen was not adsorbed from the vapor phase between 298 and 973 K, desorption spectra recorded after adsorbing and decomposing of hydrazine showed a new desorption peak, which was attributed to nitrogen remaining adsorbed on iridium. This corresponds to a desorption activation energy of 58 kJ/mol and confirmed that the first step of decomposition is the formation of a bond between nitrogen atoms of the hydrazine molecule and the unfilled *d* orbitals of the metal. The IR spectra of catalyst surfaces and adsorbed intermediates and products have also helped to elucidate the decomposition mechanism.

The use of Shell 405 catalyst provided more surface area than did a plain metal ribbon to study the chemisorption and desorption of adspecies that were previously found to reduce the catalytic activity of an iridium metal ribbon [1503]. The catalyst

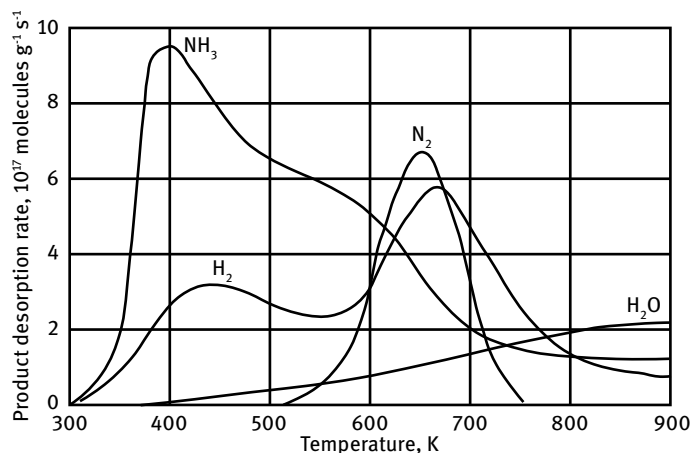


was particularly useful for this study because of its high active metal loading and relatively large iridium surface area. The objective of the work reported in a series of publications was to elucidate the causes of catalytic activity loss that occurs in operational monopropellant thrusters and to determine the mechanism of heterogeneous hydrazine decomposition on commercial catalysts [1537]. At room temperature the steady-state decomposition of hydrazine over an alumina-supported Ir catalyst was found to yield  $\text{NH}_3$  and  $\text{N}_2$ , while at temperatures above 800 K the products were  $\text{N}_2$  and  $\text{H}_2$ . Following exposure of the catalyst surface to  $\text{N}_2\text{H}_4$ , the adsorbed species were studied by a temperature-programmed desorption technique at a heating rate of 2 K/s. The desorption products included  $\text{N}_2$ ,  $\text{NH}_3$ , and  $\text{H}_2$  originating from different binding states. For the more strongly bound nitrogen [ $\text{N}_2(\beta 2)$ ] the kinetics of desorption following exposure to  $\text{N}_2\text{H}_4$  were of first order with a desorption rate constant of  $3 \times 10^7 \exp(-26800/RT) \text{ s}^{-1}$ . Pre-adsorption of oxygen on the iridium catalyst was found to decrease the nitrogen binding energy and increase the nitrogen coverage. The surface coverage of all adsorbed species was found to be significantly smaller on catalysts that had already been used in pulse-mode monopropellant thrusters. The differences observed were correlated with the loss in the metal surface area of the catalyst. However, no differences in the binding energies of the various adspecies were detectable between fresh catalyst and used catalyst [1538–1540].

It was suggested that the temperature region around 450 K was the most detrimental to catalyst life under laboratory conditions, possibly due to adsorption of a surface contaminant or intermediate. This could have been the effect of aniline in the hydrazine used but was not recognized as such (see *Encyclopedia of Monopropellants*, in the chapter “Hydrazine Monopropellants”).

In the experimental setup, a 0.1-g catalyst sample was held in a vacuum system close to the inlet of a mass spectrometer. The catalyst could be exposed to hydrazine and/or adsorbing gases and would be heated at predetermined heating rates. Throughout the hydrazine exposure and TPD the composition of the offgassing could be analyzed in short intervals and recorded along with the catalyst temperature. The catalyst had to be reduced by repeated injections of hydrazine before reproducible results could be obtained. After the reduced catalyst had been exposed to hydrazine to saturation level, it was subjected to TPD, and the concentrations of each gaseous product leaving the surface was recorded as shown in Figure 48.

Ammonia desorbed in two very broad peaks located at 373 and 628 K, hydrogen desorbed in two nicely separated peaks at 383 and 673 K, whereas nitrogen resulted in a single peak with a maximum at 663 K. Water began to come off only at very high temperatures, most likely as a result of progressive dehydration of the catalyst carrier, alumina. When the tests were repeated at lower initial coverages, only the hydrogen peak at the higher temperature was occupied, but with increasing surface loading, the low-temperature hydrogen peak also became filled. The nitrogen was formed by a first-order process, and the activation energy and pre-exponential factor of nitrogen desorption from Shell 405 were determined to be 112 kJ/mol (26.8 kcal/mol) and

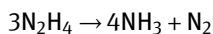
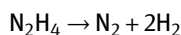


**Figure 48:** Temperature-programmed desorption peaks of ammonia, hydrogen, nitrogen, and water for hydrazine adsorption. (Reprinted and modified from [1537], with permission from ©1976 Elsevier; permission conveyed through RightsLink.)

$3 \times 10^7 \text{ s}^{-1}$ , respectively. Nitrogen desorption may be one of the rate-determining steps in hydrazine decomposition. The shape and location of the nitrogen peak was the same regardless of whether hydrazine or ammonia were adsorbed on the catalyst, but following ammonia adsorption, an additional small low-temperature nitrogen peak was observed, the origin of which is uncertain. The identity of the peaks and other observations support the conclusion that the hydrogen and nitrogen peaks formed during hydrazine decomposition at room temperature originate from an adsorbed ammonia intermediate. Studies by other authors with  $^{15}\text{N}$ -labeled hydrazine have indicated the absence of isotope mixing in the nitrogen formed from  $\text{N}_2\text{H}_4$  decomposition. The TPD results discussed here agree with the assumption that below 598 K the amount of ammonia decomposition is small, and the adsorption of hydrazine does not involve breakage of the N–N bond. There have been attempts to reduce the susceptibility of iridium on alumina catalysts (e.g., Shell 405) to inactivation by adsorbed products by depositing nickel on top of the iridium and alloying the two metals [1541]. Whereas rocket engine performance of alloy catalysts has so far always been inferior to Shell 405, laboratory studies using low partial pressures of hydrazine (2 vol.-%  $\text{N}_2\text{H}_4$  in He) showed that the mixed-metal catalyst system exhibited a pronounced activity maximum at a composition equivalent to 65 atom-% Ir/35% Ni. Whereas an all-iridium catalyst showed 52% activity loss after being exposed to  $3 \times 10^{-4} \text{ mol}$  at 448 K, the 65 Ir/35 Ni catalyst had lost only 27% of its activity under the same conditions. The results point to an electronic alloy effect. The affinity of a blocking intermediate to the surface is sufficiently decreased by the addition of Ni to prevent its accumulation on active sites. If pairs of iridium atoms in a specific steric arrangement were required

for the adsorption and decomposition of hydrazine, the progressive addition of nickel would dilute the iridium site density, but this is not what the experimental results indicate. It has been postulated that the decomposition of hydrazine may start with hydrazine dimers that are associated through hydrogen bonding, but there was very little proof for this theory [1542].

A very thorough investigation of the decomposition of hydrazine vapor on supported catalysts carrying metals of group Ib and group VIII of the periodic table of elements investigated iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, iridium, and platinum [1477, 1478]. The activity and selectivity of these metals in the decomposition of hydrazine vapor were measured in the temperature range 333–433 K. *Activity* expresses the disappearance of hydrazine due to reaction according to the combination of two or more possible equations:



*Selectivity* is defined as the ratio of the rate of  $\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2$  to the sum of the reactions  $\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2$  and  $3\text{N}_2\text{H}_4 \rightarrow 4\text{NH}_3 + \text{N}_2$ . The higher the selectivity, the more ammonia will be decomposed. Depending on the application, it is desirable to have catalysts with low selectivity (for space propulsion) or high selectivity (for undersea buoyancy). The catalyst samples were prepared by impregnating 0.2- to 0.4-mm alumina granules with aqueous metal salt solutions, drying, decomposing, slowly heating in a stream of hydrogen to 773 K, and reducing at this temperature for 10 h. The active metal loadings were chosen such that all catalysts would create about equal conversions of the hydrazine fed in argon at atmospheric pressure with hydrazine partial pressures of 1.3–1.5 kPa. For this reason, iridium and rhodium active metal loadings were very low (0.01–0.08%), whereas silver and copper were deposited to 5% by weight in the finished catalyst. In a baseline test with bare alumina carrier, it was determined first that thermal decomposition does not contribute significantly until a temperature of 453 K is exceeded. All catalyst work was thus conducted below this temperature.

It was noted that under isothermal steady-state conditions all catalysts except for copper, silver, and cobalt lost up to 50% of their initial activity over the course of 5 h. The activity of copper remained unchanged, whereas that of silver and especially cobalt increased with time. The deactivation was reversible and disappeared after heating in argon to 673 K for 8 h. It was most likely caused by adsorbed ammonia. Activation energies were determined by repeating tests at different temperatures. Although the activation energies were almost identical regardless of the metal, the pre-exponential factors vary by four orders of magnitude between platinum and copper. The activities and the range of selectivities of the various metals are summarized in Table 61, in which the data show that activity and selectivity do not necessarily go hand in hand.

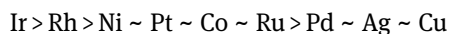
**Table 61:** Activity and selectivity of supported metals arranged by decreasing activity at 373 K.

| Metal | Activity <sup>a</sup>                                             | Selectivity range |                   |
|-------|-------------------------------------------------------------------|-------------------|-------------------|
|       | mol N <sub>2</sub> H <sub>4</sub> h <sup>-1</sup> g <sup>-1</sup> | At lower <i>T</i> | At upper <i>T</i> |
| Ir    | 25                                                                | 0.03              | 0.1               |
| Rh    | 7.5                                                               | 0.6               | 0.17              |
| Pt    | 1.7                                                               | 0.7               | 0.1               |
| Ni    | 1.7                                                               | 0.1               | 0.04              |
| Co    | 1.2                                                               | 0.008             | 0.025             |
| Ru    | 1.0                                                               | 0.03              | 0.06              |
| Pd    | 0.0025                                                            | 0.9               | 0.6               |
| Ag    | 0.002                                                             | 0.006             | 0.02              |
| Cu    | 0.0007                                                            | 0.01              | 0.04              |

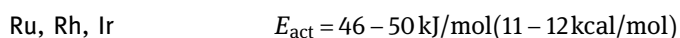
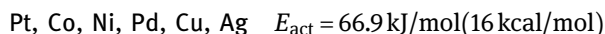
<sup>a</sup> Presumably normalized to grams of active metal, not grams of catalyst.

Data source: [1477]

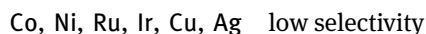
It should also be mentioned that the selectivity of Ru, Co, Ir, Cu, and Ag increased with temperature, whereas that of Ni, Rh, Pd, and Pt decreased with temperature. The latter three metals possess rather high selectivities in the vicinity of  $\gamma = 1.0$  at 333 K. When arranging the metals in order of decreasing activity, the sequence is



Iridium is 30000 times more active than copper at 373 K. *A priori* one might believe that rhodium is an equally good catalyst, but its increased selectivity may reduce practical interest [1477]. Similar relative rankings were derived from liquid-phase tests [1543]. The elements could be grouped into two groups by activation energy:



or by selectivity



The low activation energy in the group Ir, Ru, Rh explains, of course, why these metals are good hydrazine decomposition catalysts. If any of the metals formed stable nitrides, the hydrazine decomposition mechanism might be blocked. Of all metals listed in Table 61, only copper is known to form a stable nitride, which may be one explanation for its low activity.

In a continuation of these studies, one group of authors has concentrated on one representative catalyst from each group of high and low selectivity or activity, respec-

tively [1544, 1545]. In studying the kinetics, the researchers noted that under the conditions of their experiment, the order of hydrazine decomposition was zero in hydrazine on both iridium and platinum catalysts and regardless of temperature (333–423 K). Temperature had a marked effect on selectivity. That of platinum decreased from 0.8 to less than 0.1, and that of iridium increased from 0.03 to 0.08 when the temperature was increased from 323 to 422 K. Admixing of hydrogen or ammonia to the hydrazine feed had little effect on selectivity, whereas an increase in selectivity should have been expected based on existing theories. Both gases had an inhibiting effect, but activity recovered to normal levels as soon as the admixing of reaction products was discontinued. The authors concede that the mechanism is not yet completely understood.

The decomposition of hydrazine vapor on metal powders was studied at low pressures (10 mm Hg) [1479]. Two groups of three elements each were chosen to include neighboring transition elements within the same period of the periodic table of elements. The objective of the study was to study any possible periodicity of the catalytic activity of elements that differ by only one unit in the charge of their nucleus (atomic number). The catalytic activity was found to increase in the order  $\text{Cr} < \text{Mn} < \text{Fe}$  and  $\text{W} < \text{Re} < \text{Os}$ . One theory tried to explain this by the stability of the respective metal nitrides, which decreases in the same sequence, thereby facilitating the desorption of nitrogen and/or ammonia from the catalyst surface [1479]. Pre-adsorption of hydrogen on the metal powder resulted in more active catalysts. For this reason, hydrogen that formed during the decomposition also acted autocatalytically. The fraction of ammonia dissociation (for definition, see *Encyclopedia of Monopropellants*, in the chapter “Hydrazine Monopropellants”) was 0.1 for all metals. The activation energy decreased from Cr to Fe and from W to Os.

The activity of iridium catalysts was found to decrease by the accumulation of strongly adsorbed nitrogen-containing adspecies on the active sites [1503, 1537, 1538]. When testing alloy catalysts with up to 48 atom-% nickel (balance iridium) supported on alumina in a differential microreactor, it was shown that the activity of the catalyst could be maintained for a longer time than with pure iridium catalyst and that the degree of catalyst deactivation, caused by prolonged hydrazine exposure, could be greatly reduced [1546]. XRD indicated that annealing the Ni/Ir catalyst (Ni coated on Ir on  $\text{Al}_2\text{O}_3$ ) for 15 h in hydrogen at 723 K resulted in the formation of Ir/Ni alloy crystallites. AES revealed that the surface was enriched with iridium atoms. Based on these results, it was concluded that the surface bonding of NH and N adspecies to Ir is weakened by the addition of Ni atoms. Their presence in subsurface atomic layers affected the nature of the chemisorption bond between adsorbates and the active sites on the Ir-Ni crystallites.

Other studies on nickel catalysts supported on magnesium oxide showed that the activation energy is dependent on the absence or presence of dopants [1485]. On pure MgO the activation energy was 58.6 kJ/mol (14 kcal/mol). Doping of the carrier with gallium lowered the activation energy to 50 kJ/mol (12 kcal/mol), whereas doping with

lithium increased it to 70 kJ/mol (16 kcal/mol). Rare-earth metal oxide catalysts have been used extensively in the decomposition of hydrogen peroxide as a rocket propellant, but little is known about their utility for decomposition of hydrazines. Mixtures of lanthanide oxides with manganese oxide were patented for cleaning up hydrazine vapors vented from a tank, some containing 4000–5000 mg hydrazine/L in air and passing through the reactor at a space velocity of 10000/h [1547, 1548].

The decomposition of hydrazine vapor on supported iron catalysts had found sudden attention in view of the fact that it or some of the reactions involved in it may be intermediate steps in the industrial Haber-Bosch synthesis of ammonia, a reaction that is operated worldwide on a megatonnage scale every day [1549, 1550]. If the ammonia synthesis process could be quenched at a certain stage to isolate the intermediate hydrazine, and even if the yield was only 0.01%, that would drastically change the supply situation for this energetic chemical.

The reverse process, the hydrazine decomposition mechanism can be investigated by pulsed reaction chromatography [1551]. In this study, only ammonia and nitrogen, but no hydrogen, could be detected in the decomposition products of hydrazine on an iron catalyst supported on magnesium oxide at 473 K. Conclusive proof of the fact that the N–N bond of hydrazine is not split during the decomposition and formation of nitrogen was obtained by analyzing the decomposition products of  $^{15}\text{N}$ -labeled hydrazine on an MgO-supported iron catalyst with a mass spectrometer [1552]. No randomization was observed in this test that used a good quality  $^{15}\text{N}_2\text{H}_4$  of exceptionally high isotope content (better than 94.9%) mixed with  $^{14}\text{N}_2\text{H}_4$  of natural isotope distribution. The only  $^{14}\text{N}^{15}\text{N}$  in the decomposition products was that which originated from the 5.1%  $\text{H}_2^{14}\text{N}^{15}\text{NH}_2$  contamination in the  $^{15}\text{N}_2\text{H}_4$ . Despite the weak bond strength of the N–N bond, this bond remains intact when nitrogen  $\text{N}\equiv\text{N}$  is formed. No surface-adsorbed amino, imine, or atomic nitrogen species take part in the formation of nitrogen in the hydrazine decomposition as postulated by some authors, at least not on the iron [1552] and rhodium [1490] catalysts that have been used in isotope studies so far. However, surface-bonded amidogen (amino) and imidogen (imino) groups contribute to hydrogen and ammonia formation.

Partially  $^{15}\text{N}$ -enriched ( $\gamma = 0.463$ ) hydrazine diluted with known amounts of natural isotope distribution hydrazine ( $\gamma_0 = 0.0038$ ) was used to study the decomposition mechanism of hydrazine vapor at 4 kPa (30 mm Hg) on eight different catalytic metals supported on a low-surface-area  $\alpha$ -alumina [1530, 1531]. The active metals were Co, Cu, Ir, Ni, Pd, Pt, Rh, and Ru with active metal loading between 0.5 and 5 mass-%. In agreement with results obtained by other investigators on heterogeneously catalyzed or homogeneous vapor-phase decomposition of hydrazine, no randomization (“isotope scrambling”) was observed.

The hydrogenolysis of hydrazine vapor or decomposing on the surface of various supported metal catalysts allows further insight into the decomposition mechanism

of hydrazine. A pulsed microcatalytic GC technique was employed using helium or hydrogen as carrier gas [1553]. Selectivities defined by

$$S = \frac{[\text{NH}_3]}{[2\text{N}_2] + [\text{NH}_3]} 100$$

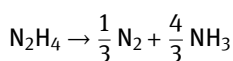
are listed in Table 62 for various metals and two different carrier gases.

**Table 62:** Activity and selectivity of supported metals arranged by decreasing activity at 373 K.

| Metal     | Selectivity with carrier gas |          |
|-----------|------------------------------|----------|
|           | Helium                       | Hydrogen |
| Co        | —                            | 76.2     |
| Fe        | 67.3                         | 77.2     |
| Fe(Al)    | —                            | 78.4     |
| Fe(Al, K) | 69.1                         | 80.9     |
| Ir        | 71.2                         | 85.0     |
| Mo        | —                            | 72.2     |
| Ni        | 72.6                         | 78.8     |
| Pt        | 69.8                         | 87.9     |
| Rh        | —                            | 83.0     |
| Ru        | 68.9                         | 85.1     |
| W         | 68.0                         | 74.2     |

Data source: [1553]

At a catalyst temperature of 473 K, the hydrazine decomposition was complete, but no hydrogen was detected. The theoretical selectivity for hydrazine decomposition through



is 66.67. The data with helium carrier gas were close to this number but were consistently higher. The deviation has been attributed to the retention of  $\text{NH}_3$  and  $\text{NH}_2$  or  $\text{NH}$  on the catalyst. When hydrogen was used as a carrier gas, the selectivity for ammonia formation was higher than the theoretical maximum, indicating that some nitrogen that otherwise would have ended up as molecular nitrogen became reduced to ammonia.

When the selectivity of nine of the metals was plotted against the enthalpy of formation of the oxides of these metals, a hyperbolic curve-shaped relationship was confirmed. Variation of catalyst temperature within  $\pm 40^\circ$  did not have a significant effect on selectivity. The interpretation of the hydrogenation results may help to explain the ammonia formation on ammonia synthesis catalysts, even though the mechanism of N—N bond splitting in hydrazine assumed by Aika, Okhata, and Ozaki [1553] has been proved wrong in the meantime.

Another method is to correlate selectivity with the enthalpy of adsorption of hydrazine on the catalyst. On catalysts with a low enthalpy of adsorption, hydrazine decomposition produced mostly  $N_2$  and  $H_2$ . On catalysts with a high enthalpy of adsorption ( $>520 \text{ kJ mol}^{-1}$ ), the reaction products were  $N_2$  and  $NH_3$  [1554].

The chemisorption of hydrazine precedes heterogeneous decomposition. The chemisorption of hydrazine on metals involves interaction with the electron orbitals, whereas chemisorption on non-conductors must occur by different mechanisms [1555]. In the presence of CO, the adsorption of ammonia or hydrazine on vanadium, iron, or nickel catalysts may result in the formation of isocyanate [1556].

The first attempt to measure exo-electron emission or structural changes in Shell 405 in a stream of hydrazine vapor at 1 Pa ( $10^{-5}$  mm Hg) in a scanning electron microscope was not successful, but this could be a useful method of observing active sites in action [1557–1560]. Thermal electron emission beginning at 523 K obscured the exo-electron effects that might have been observed as a result of hydrazine adsorption and decomposition.

Technetium is an unusual element; it is radioactive and does not occur naturally except in trace quantities as a decay product of other elements. In the periodic table of elements it is located between manganese and rhenium, both of which are catalytically active metals. One would not want to use supported technetium as a catalyst unless there was a special need, e.g., keeping the catalyst bed warm under its own power of radioactive decay [1561].

A chemically inert, ultra-high-vacuum-compatible, pulsed gas inlet system was used for studying decomposition of a hydrazine molecular beam on a planar  $Ir/Al_2O_3/NiAl(110)$  catalyst button [1562]. The inert, pulsed inlet system made it possible to measure decomposition products evolving from a small (2 mm) Ir-containing spot, despite the high propensity for hydrazine to prematurely decompose on the surfaces of inlet systems and vacuum chambers.

#### 4.12.6 Vapor Decomposition on Semiconductors or Organic Catalysts

Much of the electronic age owes its success to silicon semiconductors in transistors and integrated circuits and microprocessors on chips. It is interesting to note that these semiconductor devices are not only electronic conductors, but also catalysts. Under certain conditions, catalysis and electrical conductivity go hand in hand. Semiconductors can either be elements like silicon or germanium or compounds like gallium arsenide or certain metal oxides. Study of the decomposition of hydrazine on semiconductors can help in gaining a better understanding of the decomposition of hydrazine on metals where electrons flow more freely. However, these materials may not be suitable for operation at higher temperatures where metal oxides become reduced to the parent metals. Unfortunately, the thermal stability of these semiconductors and organic catalysts is insufficient to be of any use for hydrazine monopropellant reactors. They can potentially be used as electrode materials in fuel cells or electro-



chemical hydrazine vapor sensors. In view of the indicated catalytic activity of zinc oxide in semiconductor experiments, it may be a poor choice to include zinc oxide as a filler in diaphragm polymers for hydrazine tanks. Superconducting ceramic oxides can also catalyze the decomposition of hydrazine and hydrazinium ions.

#### 4.12.7 Computational Modeling of Catalyst-Hydrazine Interactions

Developing catalysts for any application, not only for the decomposition of hydrazine, is mostly an empirical process or trial and error. Attempts have been made to derive some guidelines for the selection of active catalysts based on the experience of generations of catalyst chemists. Modern computational chemistry based on quantum-chemical methods has been applied to model interactions between adsorbed hydrazine and catalytic surfaces, such as platinum [1563], copper [1513, 1564–1566], nickel [1567, 1568], silicon [1569], or iridium [1570].

The ReaxFF program was used to model the decomposition of hydrazine on catalytic surfaces Pt(100) and Pt(111) under various conditions [1373]. The presence of a Pt catalyst reduced the onset of decomposition temperature of hydrazine by about 50%. On single crystals, the Pt(100) surface was 20 times more active for hydrazine decomposition than the Pt(111) surface, in qualitative agreement with experiments.

The bond-order conservation method was used to examine the catalytic decomposition of  $\text{N}_2\text{H}_4$  on metal catalysts for the study of catalytic selectivity [1571]. Variation in the activation energy,  $E_{\text{act}}$ , of the most relevant steps was calculated as a function of the enthalpy of adsorption of nitrogen,  $Q_{\text{N}}$ , between 0 and 1250 kJ/mol. In the present case there are three ranges of enthalpy of adsorption of nitrogen, corresponding to different catalysts, each of which favors one route. Results suggested that below  $Q_{\text{N}} = 520$  kJ/mol the catalytic decomposition of  $\text{N}_2\text{H}_4$  produces mostly  $\text{N}_2$  and  $\text{H}_2$ . Above  $Q_{\text{N}} = 520$  kJ/mol,  $\text{NH}_3$  and  $\text{N}_2$  are the main products. Near  $Q_{\text{N}} = 520$  kJ/mol, a mixture of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  is obtained, in agreement with experimental results on different metals.

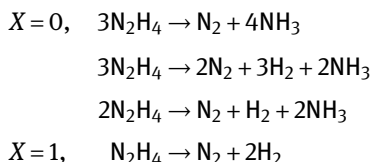
### 4.13 Heterogeneous Liquid-Phase Decomposition

Liquid-phase decomposition is often preceded by adsorption of the liquid on an active surface of a high-surface-area material and release of the heat of adsorption. In some cases, the energy released initially is sufficient to vaporize all hydrazine and then the decomposition continues as a vapor-phase decomposition.

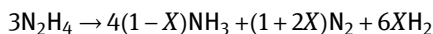
#### 4.13.1 Heterogeneous Thermal Decomposition of Hydrazine

Thermal decomposition of hydrazine can occur over a wide range of temperatures. By *thermal* we mean hydrazine by itself or in contact with an inert container wall as

long as one works in a gravity field. Thermal decomposition implies the absence of a catalyst. Catalytic decomposition of hydrazine in monopropellant reactors will be discussed in *Encyclopedia of Monopropellants*, in the chapter “Hydrazine Monopropellants,” of this book. Depending on the temperature environment, thermal decomposition can occur slowly or quickly. The slow, unwanted liquid-phase decomposition of hydrazine during storage was already discussed in Section 4.1. The current section deals with liquid hydrazine decomposition under conditions other than storage. In particular, here we are interested in very rapid liquid-phase reactions that precede the controlled catalytic decomposition of hydrazine when it comes into contact with a catalyst. These reactions are of considerable commercial interest. The mechanism of heterogeneous hydrazine decomposition in the liquid phase is very similar to that in the vapor phase, except it is sometimes very difficult to exclude solvent and surface interference. The mechanism of heterogeneous decomposition in anhydrous hydrazine is very difficult to study because measurements are restricted to less active catalysts. At low temperatures (room temperature), isothermal experiments often extend over months or years. The more active catalysts will immediately cause a temperature increase because of the strong exothermicity of the reaction, and it becomes impossible to maintain isothermal conditions needed to make kinetic measurements. On the other hand, the study of heterogeneous hydrazine decomposition is also closely related to liquid-phase stability studies described in Section 4.1, in particular material compatibility studies described in Section 5.3 and autodecomposition safety studies described in Section 8.2.3. At least four different equations can be used to describe the stoichiometry of the heterogeneous decomposition of hydrazine in solution:



Or, in more general terms, combining the four preceding conditions:



These reactions may take place simultaneously or preferentially, depending on the reaction conditions and the type of catalyst used. The thermal decomposition of hydrazine was studied in packed reactors filled with platinum-rhodium wire mesh or molybdenum beads [1572].

Another method to study strictly thermal decomposition of liquid hydrazine is in strand burners (Section 4.10.1) and in burners in which the flame is stabilized on a flame holder (Section 4.14.1) or in an inert porous medium (Section 4.9.2).

#### 4.13.2 Catalytic Decomposition of Liquid Hydrazine

When studying the catalytic decomposition of liquid hydrazine, be it unwanted decomposition in contact with container materials or desired controlled decomposition in a rocket engine, it is difficult to separate the effects of the wall materials of the test apparatus from the effects of the added material under study. For kinetic studies, it is difficult to maintain isothermal conditions because the heat of reaction immediately leads to a runaway temperature increase situation.

The production and characterization of catalysts for decomposition of hydrazine in rocket engines and gas generators will be discussed in more detail in *Encyclopedia of Monopropellants*, in the chapter “Hydrazine Monopropellants.” Here we are only looking at catalyst-hydrazine interactions from an academic point of view. There are many methods for producing more active and more durable catalysts for hydrazine decomposition. It is important to select the right type of carrier, the most active metal, and the optimum method for active metal deposition. All these more practical (less theoretical) aspects will be dealt with in *Encyclopedia of Monopropellants*.

##### 4.13.2.1 Catalytic Decomposition of Liquid Hydrazine on Metal Powders

The current section deals mostly with attempting to define the thermal stability of hydrazine in mathematical terms using kinetic theory, identifying intermediates and rate-determining reaction steps. This section deals with the decomposition of hydrazine at higher temperatures than are typically encountered during storage. The slow decomposition of liquid hydrazine during storage was already covered in Section 4.1. The two sections complement each other, and there may be some overlap. Both sections should be read side by side when trying to determine the likelihood of unwanted hydrazine decomposition under conditions of use. The current section helps in selecting materials that hydrazine may be exposed to in the hotter sections of a rocket engine, such as during heat soak back in the injector. It also deals with the problems mostly from an academic point of view, not necessarily related to specific hardware such as valves or rocket engine injectors. Data in the current section also help to identify metals with an undesirably high activity for catalyzing hydrazine decomposition in materials of construction but that may make good catalysts for hydrazine decomposition in monopropellant thrusters. One of these examples is molybdenum, which one must exclude from hydrazine storage tank materials, but it makes a modestly active catalyst (although less active than platinum-group metals).

Tests of highly concentrated (>90%) hydrazine with nickel, cobalt, iron, aluminum, copper, silver, or platinum had shown that only Raney nickel and Raney cobalt brought about rapid decomposition at room temperature [1484, 1573]. In particular, Raney nickel was a catalyst of reproducible quality, and its effect on the decomposition of hydrazine was studied in more detail. The decomposition of hydrazine was studied by measuring the rate of gas evolution. In these experiments, 0.003–0.5 g of Raney nickel was added to 3 mL hydrazine. The rate of gas evolution was directly proportional to the amount of catalyst added, typical for a heterogeneous

reaction. The rate remained constant over a 24-h period at 298 K. The results of measurements at six different temperatures between 274 and 323 K fitted nicely into an Arrhenius plot, and the slope of the line gave an activation energy of 71 kJ/mol = 17.1 kcal/mol. The decomposition products always contained some hydrogen. Tests with hydrazine-water mixtures revealed a maximum specific activity at eight molar hydrazine solutions. Hydrazinium salts, such as hydrazinium(2+) sulfate  $\text{N}_2\text{H}_6\text{SO}_4$ , caused an initial temporary acceleration, and rates of gas evolution sometimes dropped below those previously measured with pure hydrazine. Pre-treatment of Raney nickel with cyanide or sulfide (or admixture of sulfide or cyanide to the hydrazine) poisoned the catalyst, whereas platinum salts promoted its activity.

An advanced experimental method to study liquid hydrazine decomposition reactions is in an accelerating rate calorimeter (ARC). This method has now been complemented by the microcalorimeter, which can take heat flux data at lower temperatures than the ARC [1174]. While the ARC works at temperatures from 373 to 625 K, the microcalorimeter, owing to its increased sensitivity, operates at lower temperatures between 298 and 328 K. The ARC used at NASA WSTF for studying the acceleration of hydrazine decomposition reactions by various materials of construction was already described in Section 5.3.2 [1574]. It consisted of a 25-mm-diameter spherical sample holder vessel made of pure titanium weighing approx. 8 g by itself and 30 g with the adapter B-nut. Internal volume was 9 mL and surface area was 24 cm<sup>2</sup>. Gas evolved, causing the pressure buildup was analyzed for residual hydrazine and decomposition products after several runs. No residual hydrazine could be detected using a coulometric titration method. GC analysis showed the gas to consist of 81.7%  $\text{NH}_3$ , 18.2%  $\text{N}_2$ , and a trace (0.13%) of  $\text{H}_2$  (% numbers in vol.-%). Decomposition of 0.5 g hydrazine in the vessel caused a temperature increase of 115 K and a pressure increase to 12.5 MPa. The burst pressure of the titanium bulb was expected to be near 40 MPa. With hydrazine alone, the first detectable onset of exotherms was usually near 468 K [1575]. For the hydrazine-only baseline tests, the titanium bulbs were used only once to eliminate contamination and passivation effects. It was noted that the log temperature rate vs.  $1/T$  had a discontinuity and the log pressure vs.  $1/T$  curve had an inflection point near 515 K. It was shown that the discontinuity and the inflection point coincided with the point at which all liquid hydrazine was consumed and the remainder of the event took place in the vapor phase. While both liquid and vapor hydrazine are present and in equilibrium, the reaction has an apparent zero order and the activation energy in contact with titanium was  $98.3 \pm 1.7$  kJ/mol.

Metals in powder form were weighed into the sample holder and 0.5 mL hydrazine added in a glove box under nitrogen. With CRES-304L, the heat release rate for the sample holder vessel was proportional to the surface area of the stainless-steel powder added. The heat release rate (expressed as  $\text{J s}^{-1} \text{m}^{-2}$ , where  $\text{m}^{-2}$  is the reciprocal surface of the sample holder) was proportional to the surface area of the metal sample, when nickel powder, nickel turnings, and nickel foil were inserted into the titanium sphere. Surprisingly, chromium, aluminum, CRES-410L, and CRES-316L had very low

catalytic activity, which could not be discerned from the background effect caused by the titanium vessel alone. The catalytic effect of CRES-304L was distinct, but borderline. When normalized by the surface area, CRES-304L, iron, molybdenum, nickel, and cobalt had increasing catalytic activity in that order. Cobalt was the most active metal tested in this series at 353 K. In continuation of these studies, 0.5 mL hydrazine were mixed with 0.01–1.5 g of metal powders and tested in the ARC as above [1576]. The metals tested are summarized in Table 63 in order of decreasing activity.

**Table 63:** Relative activity of metal powders tested in accelerating rate calorimeter.

| Metal     | Activation energy, kJ/mol | Relative activity |
|-----------|---------------------------|-------------------|
| Co        | 43                        | 3900              |
| Ni        | 93                        | 310               |
| Mo        | 76                        | 94                |
| V         | 85                        | 66                |
| Fe        | 119                       | 33                |
| W         | 68                        | 11                |
| Au        | 74                        | 7.8               |
| Ti        | 95                        | 1.0               |
| CRES-304L | 100                       | 0.43              |
| Cr        | 105                       | 0.099             |
| Ta        | 106                       | 0.06              |

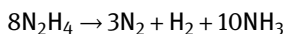
Data source: [1576]

The decrease in relative activity (calculated at 353 K from average activation parameters) parallels an increase in activation energy. The relative activity of iron stands out among the other metals, and its dissimilarity with nickel (one of the most active metals in the group) is remarkable. Nickel was also tested in four different particle sizes. The temperature rise rate was linearly proportional to the surface area of the particles.

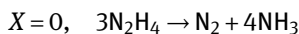
The surface area of the nanoparticles of nanometals is extremely high and offers ways to make very active catalysts. This may work fine with hydrazine solutions at room temperature for releasing hydrogen for use in fuel cells, but at the typical much higher operating temperature of hydrazine monopropellant reactors, the nanoparticles would quickly sinter into a solid mass with very little activity.

#### 4.13.2.2 Catalytic Decomposition of Liquid Hydrazine on Supported Catalysts

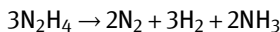
The gas composition obtained during the heterogeneous decomposition of liquid hydrazine (diluted with water) on a 20% ruthenium on alumina catalyst (on 1/8 × 1/8-in. pellets) indicated an overall stoichiometry of [1577]



This can come about by simultaneous contributions from



and



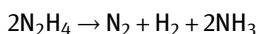
Both reactions are first order with respect to hydrazine. The rate equations are expressed as

$$v_1 = 8.7 \times 10^3 e^{-\frac{54444}{8.314T}} \text{ c mol } N_2 \text{ g}^{-1} \text{ s}^{-1}$$

and

$$v_3 = 3.0 e^{-\frac{34000}{8.314T}} \text{ c mol } (N_2 + H_2) \text{ g}^{-1} \text{ s}^{-1}$$

The rate-controlling step was assumed to be the reaction between one  $N_2H_4$  molecule in the liquid phase and the adsorbed  $NH$  radical to form nitrogen and ammonia. Similar results were obtained on supported palladium and platinum catalysts (20% Pt or Pd on 1/8-in. alumina pellets) using the same experimental technique [1578]. The reaction products corresponded to the following overall reaction:

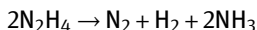


It was theorized that the initial, slow step is the dissociative chemisorption of hydrazine in the form of  $NH_2$  radicals. In accordance with the dual-plane theory of Cosser and Tompkins [1495], it was suggested that the adsorption process and subsequent reaction occur only on the active sites of these metals. Under certain conditions, such as with low hydrazine concentrations or during the beginning of a test, pre-adsorption of hydrogen on the palladium surface changed the stoichiometry of the evolved permanent gas. The observed kinetics were one-half order over the entire range of hydrazine concentrations (0.6 to 30.8M). On platinum catalysts, the order of reaction was also one-half at low concentrations but decreased to zero if hydrazine concentrations exceeded 25 mol/L. The hydrazine decomposition activity of the five noble metals tested by Sayer can be ranked in the sequence  $Ir \gg Ru > Rh > Pd > Pt$ .

One of the first of a long series of reports by Sayer et al. started looking at the reaction rates of hydrazine with 1, 2, or 4 Shell 405 catalyst pellets held in a rotating (300–350 rpm) basket with a retractable glass sheath [1579]. They used water dilution and three concentrations of hydrazine to slow down the reaction and extrapolate to 100%  $N_2H_4$ : 15.8, 29.8, 31.7, and 99%  $N_2H_4$  in  $H_2O$  and measured the rate of gas evolution as a function of initial temperature. From these data they derived an average activation energy of 65.4 kJ/mol (15.628 kcal/mol) and concluded that this is a heterogeneous first-order reaction, which is chemically controlled.

Subsequently, others studied the decomposition of hydrazine in aqueous solution (30.8 and 45 mass-%) on rhodium and iridium catalysts using  $^{15}N$ -labeled hydrazine [1480, 1490, 1580]. The most important result of this study was the finding that

the N—N bond of hydrazine remains intact when hydrazine decomposes on rhodium or iridium catalysts. The reaction mixture consisted of 30.8 mass-% hydrazine with a  $^{15}\text{N}_2\text{H}_4$  : normal  $\text{N}_2\text{H}_4$  molar ratio of 1 : 65.3. The  $^{15}\text{N}$ -isotope-labeled hydrazine contained 96.2 atom-%  $^{15}\text{N}$  and 3.8 atom-%  $^{14}\text{N}$ . A second dilution was made to obtain 45 mass-% hydrazine, in which the molar  $^{15}\text{N} : ^{14}\text{N}$  dilution ratio was 1 : 122.3. Gas chromatographic analysis showed that hydrogen and nitrogen were produced in equimolar quantities over the entire range of experimental conditions when the 20% rhodium on alumina catalyst was used. This would correspond to



However, with the Shell 405 catalyst (32% iridium on alumina), much less hydrogen was formed, as the molar ratio  $\text{H}_2 : \text{N}_2$  was only 1 : 200. Analysis of the nitrogen with a mass spectrometer showed that no randomization of the nitrogen isotopes had occurred and the amount of  $^{14}\text{N}^{15}\text{N}$  was equal to that initially present as  $\text{H}_2^{14}\text{N}^{15}\text{NH}_2$  in the mixture. However, as previously reported, Davis and Sayer had observed a 50% randomization during oxidation of hydrazine with cerium(IV) sulfate [1277]. As far as the reaction order is concerned, it was found to be dependent on hydrazine concentration in the experiments with rhodium catalysts. Over the concentration range 0–20 mass-% the rate of decomposition was approximately proportional to the square root of the hydrazine concentration. When the hydrazine concentration was increased, the reaction order changed from one-half to zero for concentrations in excess of 50 mass-%. This change indicated that the adsorption of hydrazine on the catalyst surface was a rate-determining step. Apparently, the decomposition products must desorb and diffuse away before more hydrazine can be adsorbed on the surface. The activation energy in the high-concentration range in which the reaction order is zero was determined as  $41.28 \pm 0.33 \text{ kJ/mol}$  ( $9.87 \pm 0.08 \text{ kcal/mol}$ ) with a pre-exponential factor of  $3.45 \times 10^2 \text{ mol g}^{-1} \text{ s}^{-1}$ .

The mechanism of heterogeneous hydrazine decomposition, in the words of Davis and Sayer

involves two hydrazine molecules, the two nitrogen atoms of one of these molecules form nitrogen gas without N—N bond fission, and the slow step in the reaction involves the dissociative chemisorption of the hydrazine molecule. The dissociative chemisorption of hydrazine gives adsorbed amide radicals, and these further dissociate to imine radicals and hydrogen atoms, the latter combine and are desorbed as hydrogen gas.

On the Shell 405 catalyst and in aqueous solution, activation energies of hydrazine decomposition were determined in three different conditions [1480]. A “well-stirred” reactor was used in this study by mounting the catalyst pellets on the end of a rotating shaft. The activation energies for iridium tabulated in Table 60 were determined in 31.7 and 99.0% hydrazine, respectively. The decomposition of aqueous hydrazinium chloride solution on the same catalyst had a slightly lower activation energy than that of pure hydrazine. The first-order reaction is assumed to be chemically controlled, not

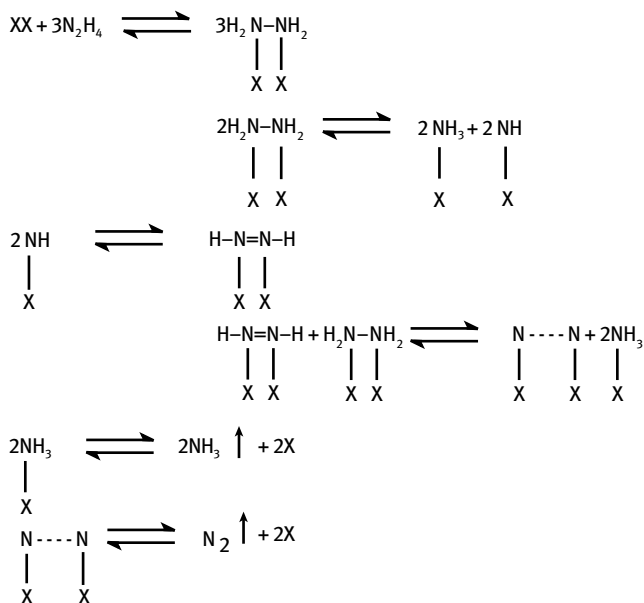
diffusion controlled, because activation energies of diffusion-controlled reactions are usually significantly lower, on the order of 8–16 kJ/mol (2–4 kcal/mol). The isotope labeling indicated that the N–N bond was not split during decomposition, either in free hydrazine or in hydrazinium chloride.

The rate of reaction of liquid hydrazine in contact with supported catalysts is determined by kinetics and in many instances by the diffusion of reactants to and products from the catalyst surface. In the case of hydrazine and Shell 405, the ignition delay is of crucial importance for the response of rocket thrusters and also for the survival of the catalyst itself. An excessive induction period allows liquid hydrazine to wick deeply into pores of the catalyst structure, and the sudden pressure increase caused by delayed hydrazine decomposition causes the catalyst to split. The induction period has been studied by high-speed cinematography [1581] and by pressure-rise measurements [1582]. Pressure-rise measurements gave decomposition rates of  $16.5 \times 10^{-4} \text{ mol g}^{-1} \text{ s}^{-1}$  at 310 K and an activation energy of  $12.7 \pm 1.1 \text{ kJ/mol}$  [1582]. The tests were conducted by dropping a 1/8 by 1/8-in. pellet into liquid hydrazine and measuring the pressure rise. Pre-adsorption of ammonia increased the induction period. The results of most of the tests are questionable because some catalyst samples were not fresh. Furthermore, tests with granular catalyst would have been more meaningful because pellets are very rarely exposed to liquid hydrazine in the inlet portion of hydrazine reactors. The effects of additives and contaminants on decomposition of hydrazine on Shell 405 were measured [1583].

In another study, a catalytic surface was prepared by pressing a mixture of pulverized Centre National d'Etudes Spatiales – European Space Research Organization (CNESRO) (Ir-Al<sub>2</sub>O<sub>3</sub>) catalyst, graphite, and polytetrafluoroethylene (PTFE) together. Because these pellets had fewer active sites, kinetics could be studied without interference from excessive heat or gas evolution [1481]. Also, the pellets had good thermal and electrical conductivity, allowing rapid heat dissipation and study of catalytic phenomena on surfaces with superimposed electric potentials. From an Arrhenius plot an activation energy of 86 kJ/mol (20.5 kcal/mol) was derived. This is much higher than the 65 or 48 kJ/mol previously obtained by Sayer [1480] or Santacesaria, Guiffre, and Gelosa [1584], respectively. The effect of dissolving electrolytes in the hydrazine could not be studied with unequivocal results, because hydrazinium(1+) chloride or potassium chloride caused premature swelling and breakup of the catalyst pellet. Potassium hydroxide left the catalyst intact but had no effect on the catalytic rates. Therefore, a 0.05-M KOH solution in hydrazine was used for the experiments with polarized catalysts. Cathodic polarization slowed the catalytic decomposition to a complete state of inactivity, whereas anodic polarization restored the initial activity of the catalyst. It is theorized that adsorbed hydrazide ions play a role in this mechanism because they occupy the electrophilic sites of the catalyst, preventing access of the lone electron pairs of hydrazine molecules. The attachment of lone electron pairs of nitrogen in hydrazine to the active sites is thought to be the first step in catalytic hydrazine decomposition.



An interesting study on the kinetics of liquid hydrazine on iridium-alumina catalysts was conducted using both Shell 405 and the CNESRO catalyst [1585]. Most results were obtained for Shell 405. The experiments used a small bomblet holding 0.5–1.0 g catalyst. Hydrazine was injected with a syringe, and temperature and pressure were recorded on an oscilloscope using thermocouples and a pressure transducer. The ignition delay was defined as the time at which 5% of maximum pressure was reached. The  $p = f(t)$  curve was characterized by an inflection point. The authors theorized that below this point the temperature of liquid in contact with the catalyst rose adiabatically, until at the inflection point it exceeded the boiling temperature. From then on, the decomposition proceeded mainly as a vapor-catalyst interaction. The mechanism illustrated in Figure 49 was proposed, where the character **X** represents active sites on the catalyst surface and the dotted lines indicate electrons in motion.



**Figure 49:** Hydrazine decomposition reactions taking place at the surface of a catalyst.

The rate of hydrazine decomposition can be expressed as a function of all the kinetic rates of equilibrium reactions indicated by arrows in this scheme. Diazene is assumed to be an intermediate in the decomposition of hydrazine. However, the decomposition mechanism through N–N bond splitting proposed by the French authors is not supported by isotope studies (see preceding discussion).

The rate-determining step for hydrazine decomposition in the vapor phase is proposed to be the desorption of product ammonia. The desorption of ammonia and ni-

trogen from the surface is symbolically indicated by the upward-pointing arrow  $\uparrow$  in Figure 49.

The effect of initial CNESRO catalyst and hydrazine temperature on ignition delay could be accurately measured in this setup [1586]. At ambient pressure, ignition delay decreased linearly from 280 to 410 K. When the catalyst was above 360 K to start with, variation of the hydrazine temperature had little effect. When the catalyst was kept at 323 K to start with, warming of the incoming hydrazine from 283 to 313 K helped to shorten the ignition delay slightly (from 20 to 13 ms). Of particular interest for gas generator applications in a plenum system with possible catalyst self-poisoning by back-diffusion of product gases during cooldown is a study on the effect of gas composition and temperature on ignition delay. The catalyst was exposed at 293–413 K to gas mixtures representing ammonia dissociations from 0 to 0.9. At 293 K, the ammonia-rich mixture increased the ignition delay to 40 ms, whereas ammonia-lean mixtures increased the delay only slightly. Above 313 K, the effect was no longer noticeable.

Another microreactor that was operated with single injections of 40  $\mu$ L hydrazine onto alumina or rhodium-platinum as support or catalyst and was instrumented to measure the temperature of the catalyst and temperature and composition of the decomposition products by GC had been used by the same group of investigators in France to study the mechanism of hydrazine decomposition on catalysts [1587, 1588]. A similar investigation in the same type of apparatus used a zeolite 5A thermal bed without active metal deposition to study the thermal decomposition of hydrazine at temperatures from 573 to 963 K [1589, 1590]. The products of decomposition were analyzed by GC and the ammonia dissociation fraction plotted as a function of the initial bed temperature. Additional thermal bed materials tested in the same reactor included Pt/Rh wire mesh, CRES spheres (1 mm), Mo spheres (0.7 mm), alumina spheres (0.7 mm), and mol sieve 5A or 13X in the shape of 1.6-mm cylindrical pellets [1572, 1591]. The initial surface area of the alumina was on the order of 100 m<sup>2</sup>/g.

Iridium, rhodium, cobalt, and cobalt/platinum catalysts were prepared by repeated impregnation of  $\gamma$ -alumina and reduction under hydrogen for a nominal active metal content of 9–10% by weight [1592]. Some granules would fracture by the violence of the reaction with hydrazine if they were not properly restrained. To avoid further damage, granular catalysts were then tightly packed between two porous, sintered glass, fritted discs in an evacuated tube. A slug of hydrazine was admitted swiftly by injection with a hypodermic syringe through a rubber septum near the catalyst, and the pressure rise in the adjacent vacuum train was monitored as an indication of catalyst activity. Both the Ir and the Rh catalysts were the most active, with times to equilibration as short as 5 s, but became deactivated after only 10 consecutive tests. Other catalysts were sluggish initially but maintained their low activity for more than 10 tests. Catalyst activity increased with the reduction temperature (reduced at 693, 743, or 793 K under H<sub>2</sub>).

Six different catalysts containing 10% by weight of the six platinum group metals were tested by adding 5 mL anhydrous hydrazine to 0.5 g of catalyst contained in a test

tube with a thermocouple [1593]. Osmium, platinum, rhodium, and palladium had very little activity at room temperature, and the temperature rose only very slowly, until above a threshold temperature the reaction was rapidly self-accelerating. Iridium and ruthenium catalysts were more active and caused intense gas evolution at room temperature. A mixed catalyst containing both ruthenium and rhodium is said to be advantageous for the decomposition of hydrazine blends containing up to 40% water.

In searching for other intermediate species involved in catalytic hydrazine decomposition, a series of ESR experiments were carried out in a flow system, but no free radicals were involved in the reaction, or they were short lived (<10 ms) or remained too close to the catalyst surface [1480]. Furthermore, the catalytic decomposition of hydrazine was not affected by radical scavengers, such as *cis*-1,2,3,6-tetrahydrophthalic acid.

The following mechanism has been proposed by Sayer: the hydrazine molecule exists predominantly in the *gauche* form (Section 2.3), and the two lone electron pairs extend to the same side (e.g., toward the catalyst surface). The lone pairs establish a bond to the catalyst surface by interacting with the unfilled *d* orbitals of the active metal. Hydrazine molecules in the solution may then approach the adsorbed molecule and abstract two hydrogen atoms to form two molecules of ammonia and an adsorbed diazene on the surface. Under the conditions of formation, the *cis*-diazene is formed. The *cis*-diazene can then decompose either by reaction with a neighboring diazene, forming nitrogen that then desorbs or, if it cannot find an adjacent diazene, the diazene decomposes directly to nitrogen and hydrogen.

Active metals deposited on one and the same alumina carrier were compared with regard to their hydrazine decomposition activity in a liquid-phase reactor [1543]. Typical metal loadings were 20% by weight. The relative ranking of the supported catalysts was



and was like that obtained using bulk metal powders instead of supported catalysts. It was suggested that the metal crystal lattice constant of hydrazine decomposition catalysts should be on the order of  $2.6$  to  $2.7 \times 10^{-10}$  m. Compare this to  $2.65 \times 10^{-10}$  m for ruthenium and  $2.71 \times 10^{-10}$  m for iridium. Osmium, despite having the correct geometry ( $2.69 \times 10^{-10}$  m), does not make a good catalyst. Catalysts tested contained 5, 10, and 20 or 30% Ir, 5, 10, and 20% Ru, or 5 and 20% Rh. Catalysts that contained less than 4.5% Ir on  $\text{Al}_2\text{O}_3$  lacked activity for hydrazine decomposition. This was explained by suggesting that at low coverages a large fraction of the metal combines in ionic form with alumina. Iridium was three times more active than ruthenium. In a liquid/solid stirred reactor, 30% hydrazine gave maximum decomposition because the gas bubbles had time to move out of the way and did not surround the particles with a sheath of gas. At higher hydrazine concentrations, the tests became less reproducible. Activation energies for hydrazine (hydrate) decomposition on 11 supported catalysts were derived by repeating the tests at different temperatures. As expected, the addition of ammonia

slowed the rate of hydrazine decomposition. This was most pronounced for the first 1%  $\text{NH}_3$  added to the hydrazine: The rate dropped by 25%. Additional ammonia addition (up to 25% by mass) did not have that much of an effect. Under the conditions of the liquid-phase test, ammonia resulting from hydrazine decomposition accumulated in the propellant and caused the same effect as the initial addition.

With iridium identified as the most active metal, the next question was how to achieve the optimum dispersion of metal on the carrier [1594]. Dispersion is determined by the initial available active surface area of the carrier and the percent of active metal loading. The parameter for evaluating the benefits of dispersion is called *specific catalytic activity* and defined as mol hydrazine decomposed per surface area per unit time and measured in units of  $\text{mol cm}^{-2} \text{s}^{-1}$ . The rate of gas evolution was determined in a stirred reactor at 288 K. In this study, the surface area of alumina was varied from 13 to  $300 \text{ m}^2/\text{g}$ , and the active metal loading was varied from 1.2 to 42% Ir in the finished catalyst. One of the important parameters in this study is the crystallite size. It was assumed that the metal is in the form of equal sized cubes with side length  $d$ , with one face in contact with the support surface

$$d = \frac{5 \times 10^3}{\rho S_{\text{Ir}}}$$

where  $d$  is the side length (cm),  $\rho$  is the density of iridium ( $22.121 \text{ g/cm}^3$ ), and  $S_{\text{Ir}}$  is the active metal surface area as determined from hydrogen chemisorption. The theoretically maximum hydrogen chemisorption, in the case of atomic dispersion of Ir, is  $253 \text{ m}^2/\text{g Ir}$ . In the catalysts prepared here, the specific hydrogen chemisorption decreased from 230 to  $50 \text{ m}^2/\text{g Ir}$  for catalysts containing from 5 to 40 mass-% Ir. The decrease was due to growing crystallite sizes and to crowding of particles. The specific activity of hydrazine decomposition and the active surface area (expressed as  $\text{m}^2/\text{g}$  catalyst) increased initially with the crystallite size  $d$  (1–3 nm). This effect partially compensates for the loss of metal dispersion during the early hours of use of iridium/alumina catalysts at 1300 K in a rocket engine, maintaining the overall activity within acceptable levels. The specific surface area went through a maximum at 33% Ir, confirming the wisdom of early investigators in selecting the active metal loading of Shell 405 catalyst. The results obtained with supported catalysts were then compared to results obtained with iridium black sintered to different crystallite sizes and resulted in similar relationships. This shows that there is no electron transfer between the active metal and the carrier for this type of catalyst.

On the other hand, attempts have been made to explain the increased activity of alumina-supported iridium as not just a physical structural support but instead assuming that electrons exchange between the support and the metal and thus give a more stable quasi-chemical bond. UV spectroscopy, photoelectron XPS and Ir dissolution in acetylacetone were used to determine the nature of the adsorption sites and the state of Ir on supported Ir catalysts [1595]. The catalyst contained 36 mass-% Ir impregnated on  $\gamma\text{-Al}_2\text{O}_3$ . Catalyst attack with acetylacetone allows for the observation of

the dissolution of supported Ir, giving Ir acetylacetonate, which indicates the presence of Ir with a 3+ valence. UV spectroscopy showed that a part of hexachloroiridic acid is reduced during the impregnation of  $\text{Al}_2\text{O}_3$ , giving a chlorinated complex of Ir(III), and the structure of this Ir(III) complex is not destroyed by hydrogen reduction at 673 K (400 °C). The chemical shifts measured in photoelectron XPS spectra confirmed the presence of complexed Ir and demonstrated an electronic interaction between uncomplexed Ir and  $\text{Al}_2\text{O}_3$ .

The kinetics of dilute hydrazine (hydrate) decomposition on catalysts in aqueous solution are like those of hydrogen peroxide decomposition in solution [1596]. Both solutions are sometimes used in fuel cells. In either case, the reaction rate is sometimes diffusion limited.

Although not reversible, hydrazine hydrate is under evaluation as a hydrogen storage medium. Various types of supported metal catalysts for the decomposition of hydrazine hydrate under relatively mild conditions as a source of hydrogen gas were evaluated [1597–1601]. It was not reported how the ammonia in the initially resulting gas mixture was ultimately also decomposed to yield more hydrogen. The complete decomposition of ammonia requires additional energy. Some of these catalysts may be useful for rocket applications.

#### 4.13.2.3 Catalytic Decomposition of Liquid Hydrazine on Metal Oxides and Nitrides

Copper nitride and chromium nitride were tested as decomposition catalysts for hydrazine [58]. Some metal oxides act as catalysts for the decomposition of hydrazine. At higher temperatures, some metal oxides become reduced to the metals. Manganese(IV) oxide is a catalyst for the decomposition of hydrogen peroxide as well as hydrazine. If 100- to 200-mesh manganese dioxide particles are dispersed in dilute aqueous hydrazine solutions at 293–313 K, hydrazine decomposes by heterogeneous reaction [1602]. The kinetic rate can be measured by collecting the nitrogen formed in the reaction. The rate is proportional to the temperature and inversely proportional to the particle size of the manganese dioxide. The overall reaction is of second order. The mechanism seems to be a bimolecular reaction between active sites on the manganese oxide crystals and the hydrazine in solution.

Under most operating conditions in a hydrazine decomposition reactor, nickel oxide would quickly become reduced to a porous nickel structure, but it may last long enough for short rocket propulsion missions. Attempts have been made to alter the catalytic properties of NiO by doping with other oxides [1603].

Macroporous niobium oxynitride was prepared with a specific surface area of  $41\text{ m}^2/\text{g}$  and total pore volume of  $0.43\text{ cm}^3/\text{g}$  and compared to other catalysts in laboratory tests and in a 2-N monopropellant thruster [1604]. The activity of niobium oxynitride in hydrazine decomposition at laboratory scale was lower than that of previously tested tungsten oxynitride. The performance in a 2-N thruster was inferior to that of tungsten oxynitride and Shell 405.

A series of iron nitride catalysts was prepared by a temperature-programmed reaction method and evaluated in a microreactor for hydrazine decomposition [1605]. The catalytic activity of iron nitride was higher than that of iron oxide. The noble-metal-like characteristics of the nitrides might be responsible for the high catalytic activity. The iron nitrides with larger surface areas and smaller particle sizes had higher catalytic activities and  $H_2$  selectivities at high temperatures.

#### 4.14 Combustion of Hydrazine in Air and Oxygen

Even though hydrazine is not a common fuel and is not (yet?) being used to drive combustion engines on Earth at this time, the combustion of hydrazine in air or in combination with other oxidizers constitutes an important chapter in hydrazine chemistry. Many combustion studies have been performed in conjunction with decomposition studies, because hydrazine decomposition constitutes a key step in the reaction preceding combustion. Frequently, the same apparatus is used for both types of experiments [525, 1606].

This section is devoted mainly to the kinetics and mechanism of combustion and the speed with which it proceeds. The gas composition required for flame propagation (the limits of flammability) and the required initiation energy and other safety properties are discussed in Section 8, especially Section 8.3.1. Sometimes the combustion of a hydrazine mixture gets out of hand and results in a detonation. Such detonations are discussed in Section 8.4.2.

This section on combustion is also restricted to the combustion of liquid or vaporized hydrazines requiring an oxidizer. Sometimes the autodecomposition and strand burning of pressed or molten hydrazinium salts is also called “combustion,” but these reactions are discussed elsewhere in *Encyclopedia of Oxidizers*, in the chapter on hydrazinium salts, specifically on the stability of hydrazinium salts.

The same methods described in Section 4.9.1 for measuring decomposition flame speeds can also be used to measure flame speeds in oxidizer-supported combustion flames. Unfortunately, more studies have been performed on hydrazine combustion in oxygen than on the potentially more important combustion of hydrazine in air. Instead of actually measuring flame speeds, some publications discuss just the kinetics of the reaction between oxygen and hydrazine, which may precede the actual combustion. The combustion of hydrazine with other oxidizers is discussed in Section 4.15 following the current section on combustion in air and oxygen. Combustion with other oxidizers, mainly nitrogen oxides, is of practical interest for the use of hydrazine and its derivatives as rocket propellants in bipropellant combinations.

The results obtained during hydrazine combustion in an adiabatic flow reactor with nitrogen dioxide, nitric oxide, and oxygen as oxidizer demonstrated that combustion can occur both with and without prior decomposition of hydrazine, depending on the degree of reactivity of the oxidizer [525].

#### 4.14.1 Combustion in Flow Systems

A thorough investigation of stabilized hydrazine combustion flames in oxygen was conducted in combination with an investigation of hydrazine decomposition flames [1210]. Flames were studied over a wide range of stoichiometric ratios with hydrazine and hydrazine/water mixtures (60.9–97.2%  $\text{N}_2\text{H}_4$  at 423 K). The maxima of flame speeds (570 cm/s for 97.3%  $\text{N}_2\text{H}_4$  and 270 cm/s for 60.9%  $\text{N}_2\text{H}_4$ ) seemed to occur on the oxygen-rich side of the stoichiometric ratio. For comparison, a combustible mixture corresponding to hydrazine decomposition products ( $2\text{NH}_3 + \text{N}_2 + \text{H}_2$ ) was measured at 298 K. Its flame speed was quite low, 160 cm/s, near the stoichiometric ratio. The flame speed of stoichiometric ammonia/oxygen mixtures was even lower (120 cm/s). The difference in flame speeds of hydrazine/oxygen and ammonia/hydrogen/nitrogen/oxygen of identical gross composition must be due to the higher enthalpy of the hydrazine mixture. The data are not inconsistent with a two-stage process in the combustion of hydrazine where decomposition could precede combustion.

The technique used to determine flame speeds was to stabilize the flame on a circular orifice, photograph it, and measure the outline of the reaction cone. The hydrazine had to be pre-vaporized in a 1.2-cm-diameter  $\times$  60-cm-long Pyrex tube heated to 423–443 K. This is usually a very dangerous undertaking, but no flashbacks occurred under carefully controlled experimental conditions. In a 1.4-mm-orifice burner, Reynolds numbers were calculated to obtain an indication as to whether laminar flow could still be possible. In the absence of more accurate data, it was assumed that hydrazine vapor had the same viscosity as oxygen at 423 K ( $2.76 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1} = 2.76 \times 10^{-5} \text{ N s m}^{-2}$ ). With the use of the approximate value, Reynolds numbers of 1450 and 1950 were obtained for hydrazine decomposition and hydrazine plus oxygen combustion flames, respectively. Both flow conditions were thus below 2000, generally considered the transition from laminar to turbulent flow. The flames appeared to be stable to visual observers. As was later shown in closed-vessel combustion studies, the turbulent flame speed is significantly higher than the laminar flame speed.

When comparing calculated flame temperatures and measured flame speeds, the results were found not to be always proportional to each other, as would be predicted from the Zeldovich and Frank-Kamenetskii equation [1382, 1607]. Thus, the temperature plot of hydrazine hydrate/oxygen mixtures falls well below that of ammonia/oxygen mixtures, but the flame speed of 60.9% hydrazine/39.1% water plus oxygen lies well above that of ammonia-oxygen. The discrepancy is believed to be due to thermal conductivity effects. The thermal conductivity of the zone between the hydrazine decomposition front and the combustion front is thought to be increased as a result of hydrogen formed in the decomposition of hydrazine. Measurements of flame propagation, temperature, and flame front thickness in premixed, laminar hydrazine/oxygen/argon flames were correlated with a flame model based on activation energy and chain branching and chain propagation mechanisms and showed good agreement [1389].

Premixed oxygen-hydrazine flames stabilized on a 28-mm burner were found to burn at a flame speed of 2.36 m/s [620, 621].

#### 4.14.2 Combustion in Closed Vessels

The combustion of hydrazine in oxygen or air in a closed vessel may occur with explosive force, and proper precautions must be taken when conducting these experiments. The pressure limits of combustion of hydrazine in closed vessels and in the explosive combustion of hydrazine in oxygen were studied in two cylindrical Pyrex vessels, 4.6 and 2.6 cm in diameter [1608, 1609]. The premixed hydrazine vapor and oxygen were admitted to the preheated (643–813 K) reaction chamber until explosion occurred, and the pressure prior to explosion was recorded. Oxygen-rich mixtures were somewhat more readily ignited than stoichiometric ones. At 809 K and 40% hydrazine, explosions occurred at all pressures above 16 mm Hg total pressure. In the 4.6-cm-diameter vessel, spontaneous explosions would occur at lower pressures than in the 2.6-cm-diameter tube. Argon or nitrogen dilution seemed to lower the pressure limit and aid explosion, whereas helium dilution made it more difficult to ignite the mixtures. An unusual phenomenon was observed in the borderline regime. In mixtures containing more oxygen than the stoichiometric proportions at pressures below the limit for rapid explosion, a yellowish glow appeared after 5–10 s. The delayed ignition could not be found in mixtures containing more than 50% hydrazine. The regime for delayed ignition is restricted by an upper and a lower pressure limit. Various synthetic mixtures representing partially decomposed-combusted hydrazine mixtures were prepared in an effort to explain the delayed reaction. It is believed that the delayed ignition involves the combustion of hydrogen formed by decomposition of hydrazine. In a separate experiment, hydrazine was shown to inhibit the hydrogen + oxygen reaction. Ammonia does not exhibit such inhibition activity. For equimolar mixtures of oxygen and hydrazine, the boundary between slow reaction and explosion in a pressure vs. temperature plot is a straight line, dropping from 693 K/3.2 kPa (420 °C/23 mm Hg) to 761 K/1.6 kPa (488 °C/12 mm Hg) in a Pyrex sphere with 67 mm ID.

Using the same closed vessel and Schlieren photographic technique previously used to study hydrazine vapor decomposition flames, flame speeds in oxygen/hydrazine mixtures at 5.3 kPa (40 mm Hg) and 335 K (144 °F) were measured [1606]. The highest flame speed (4020 cm/s) was observed at a stoichiometric mixture ratio. Above that ratio, it decreased again and approached that of pure hydrazine vapor (1270 cm/s). In hydrazine-rich mixtures no undecomposed hydrazine remained after the combustion. Any hydrazine in excess over the stoichiometric ratio decomposed.

After further refinement of measurement techniques, additional experiments were conducted in a 1-L (61-in.<sup>3</sup>) spherical vessel over the temperature range 690–770 K [1610]. The spontaneous ignition of gaseous mixtures of oxygen and hydrazine was investigated, and emphasis was placed on the direct detection of pre-explosive self-heating in the reacting gas. Very fine thermocouples (made from



0.025 mm Pt and Pt-Rh wires) were used to follow temperature changes and to map temperature-position profiles during oxidation. Unusually among gas-phase oxidations, this spontaneous ignition was clearly thermal in character. Strong self-heating was always observed. In accordance with a conductive theory of heat losses, temperatures were not uniform throughout the reactant but depended on the distance from the vessel center, being greatest at the center and least at the walls. These experiments were aimed at the determination of the boundary line between slow reaction and explosion of equimolar mixtures of hydrazine and oxygen. Between 693 and 763 K these mixtures exploded above 3.2–1.6 kPa (24–12 mm Hg). The rate of temperature increase was measured with ultra-sensitive, fast-response thermocouples. With this technique it was possible to reveal the self-heating that precedes a thermal explosion. The platinum-rhodium thermocouples had to be coated with silica to reduce their catalytic activity. If the logarithm of  $P_{\text{crit}}/T^2$  was plotted against the reciprocal temperature, a straight line was obtained. From the slope of this line an activation energy of  $104 \pm 5 \text{ kJ/mol}$  ( $24.8 \pm 1.2 \text{ kcal/mol}$ ) was calculated for the oxidation of hydrazine.

In similar tests where a low-pressure  $\text{O}_2$ /hydrazine vapor mixture was admitted to a cylindrical quartz chamber (42 mm ID, 165 mm long), a distinct dependence of the autoignition vs. pressure curve on the wall material was noted [1611]. With the clean quartz tube alone, ignition occurred at 2–5 kPa at 830–700 K. Coating the wall with MgO caused the minimum ignition pressure to increase by a factor of 2.5. Coating the wall with  $\text{K}_2\text{B}_4\text{O}_7$  lowered the curve just a little. Admixing 1% dibromotetrafluoroethane, a flame retardant, prior to ignition increased the pressure required for ignition, most likely because the bromine compound traps free radicals (this is why it is used as a fire-extinguishing agent). These three observations were taken as indirect evidence that a branched-chain mechanism is responsible for the ignition of  $\text{O}_2$ /hydrazine mixtures. In addition, the presence of atomic hydrogen in the flame front was proven directly by operating an oxygen/hydrazine burned in the resonator cavity of an EPR spectrometer. The concentration of H atoms was  $5 \times 10^{14} \text{ cm}^{-3}$ , which is much higher than that expected from equilibrium calculations.

#### 4.14.3 Droplet Combustion in Oxygen or Air

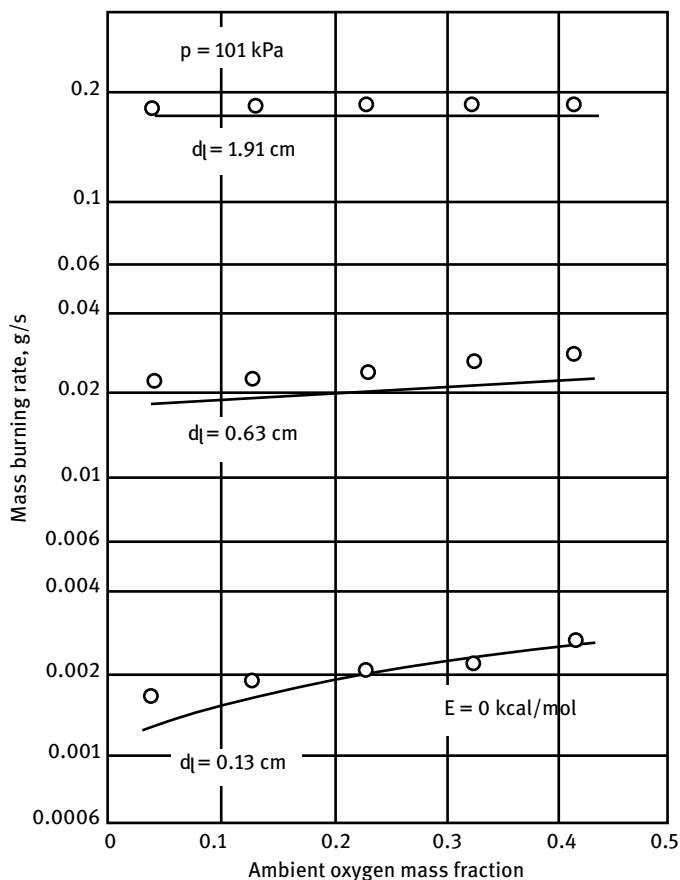
Because of the unique exothermic reactions preceding the combustion of hydrazine, the droplet combustion behavior of hydrazine in air differs from that of other fuels, for example, hydrocarbons. A non-linear droplet ignition model has been proposed [1612] that is distinguished from other models by the fact that it exhibits a discontinuity at the ignition temperature. Surprisingly, the air temperature required for ignition increased with decreasing droplet size. Small droplets were said to remain in the evaporative- or kinetic-controlled mode, whereas large droplets were subject to diffusion-controlled combustion. No experimental data exist for hydrazine to support this theory. For hydrocarbons, the dimensionless fuel mass burning rate  $a = (\text{burning velocity}) \times (\text{ra-}$

dus)/diffusivity vs. air temperature curve is S-shaped. For hydrazine, the overall rate of oxidation leading to ignition is assumed to be controlled by a radical-forming hydrazine decomposition reaction.

The droplet combustion of hydrazine alone and in oxygen/nitrogen mixtures with 5.9–21% oxygen was studied [1428–1430]. In addition to experimental work, a complex mathematical model was developed to predict burning rate and flame diameter as a function of droplet diameter and pressure.

Droplet combustion of hydrazine in air and in oxygen was studied in comparison to UDMH and kerosene RP-1 [1439]. Fuel droplets were suspended from a fiber in a quiescent atmosphere of air or oxygen and ignited. Then the combustion was filmed and the droplet size (surface area) measured from the film recordings. The order of increasing burning constant and decreasing droplet lifetime was RP-1, UDMH, and  $N_2H_4$ . The burning rates of all three fuels in oxygen were higher than in air. In a previous study, plots of  $d_2$  versus time gave straight lines for all three fuels, but some deviations were noted for hydrazine. The data resulting from these tests could only be used for a qualitative comparison, and it was very difficult to assign quantitative significance. The results of droplet combustion studies were very difficult to reproduce in other laboratories, and some discrepancies in the literature remained unexplained.

A very thorough study was conducted on the droplet combustion of hydrazine, MMH, and UDMH both in decomposition flames and when burning in an oxidizing environment that provided important new insights into droplet combustion mechanisms [1433, 1434, 1452, 1613]. The major objective of this work was to investigate the combustion characteristics of the hydrazine fuels in the form of liquid drops at atmospheric pressure. Emphasis was placed on high ambient temperature conditions representative of rocket chambers. The mass burning rates (g/s) of hydrazine, MMH, and UDMH as a function of drop diameter, ambient temperature, and ambient oxygen concentration were obtained. Aerozine-50 was also tested. However, a stable burning condition could not be achieved with Aerozine-50 for any test condition [1435, 1455]. The test environment included ambient oxygen concentrations of 0–42 mass-% and ambient gas temperatures of 1660–2530 K. This environment was generated by a flat flame burner fed with mixtures of nitrogen, hydrogen, carbon monoxide, and oxygen. The fuel droplets were then suspended from a quartz fiber, or larger droplets were simulated with porous spheres. The same apparatus was used for decomposition flame studies without oxygen supply (Section 4.15.1.2) and combustion flame studies. In the oxidation studies, all three fuels showed a flame with two distinct zones of luminosity. Because decomposition flames were non-luminous, it has been suggested that both zones were the result of oxidation reactions. A hybrid combustion model was formulated as opposed to a bipropellant combustion model, which assumes simple evaporation in a diffusion-limited environment. In the hybrid mode, the monopropellant decomposition of the fuel prior to combustion is taken into consideration. The results indicated that fuels capable of hybrid combustion showed increasing burning rate with increasing ambient oxygen concentration (Figure 50), diameter (Figure 51), and

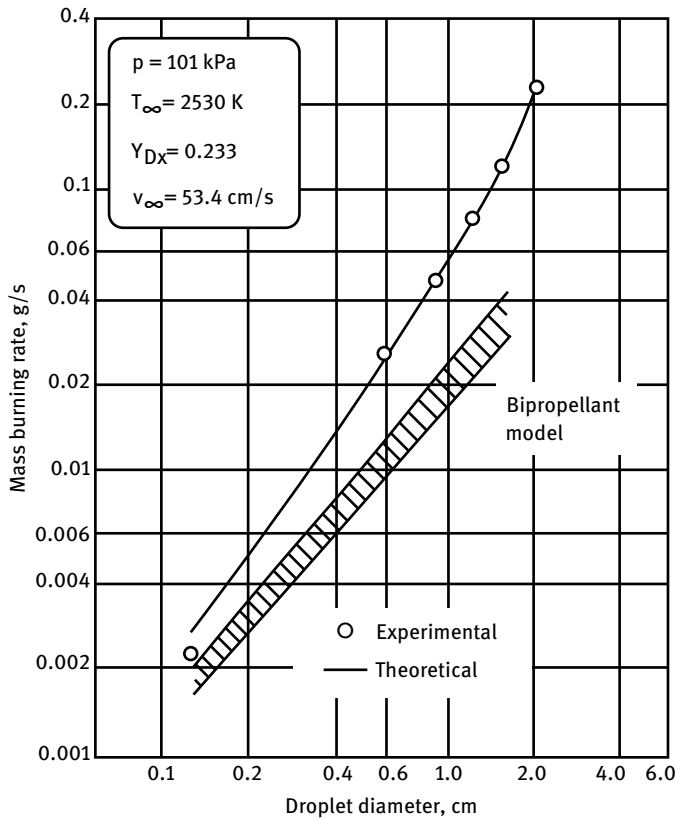


**Figure 50:** Hydrazine droplet burning rates at various ambient oxygen concentrations. (Reproduced and modified from [1613].)

ambient temperature. Similar graphs for MMH instead of hydrazine will be shown in the chapter on methylhydrazine.

As the effect of the monopropellant decomposition zone became more important (e.g., in the sequence UDMH, MMH, hydrazine), the burning rate was less sensitive to variations in ambient conditions. In the presence of monopropellant behavior, the burning rate was found to be proportional to the square of the droplet diameter. Of the three fuels tested, hydrazine exhibited most distinctly hybrid combustion with all droplet sizes, whereas MMH and UDMH showed this behavior only with very large droplets.

Comparison of the mass burning rate curves of hydrazine and MMH depending on oxygen concentration reveals that the hydrazine curves (Figure 50) are much flatter



**Figure 51:** Hydrazine droplet burning rate in an oxidizing atmosphere. (Reproduced and modified from [1613].)

(less dependent on oxygen) than the MMH curves (Figure 32 in the chapter “Methylhydrazine”). Droplet life studies are useful for designing injectors for bipropellant rocket engines, in particular those employing hypergolic oxidizers. Additional droplet combustion studies of hydrazine and methylhydrazine combustion in hypergolic oxidizer atmospheres are discussed in Section 4.15.1.2.

A two-step combustion process, consisting of monopropellant burning followed by bipropellant (i.e., two-reactant) burning, was modeled and burning-rate variations for reactions with large activation energies were predicted [1614]. The original reactant, vapor from a liquid droplet, decomposes into a fuel that burns with oxidant in the surrounding oxidizer-rich atmosphere. Complete responses of the evaporation rate of the droplet to the Damköhler numbers  $D_1$ ,  $D_2$  of the two reactions were determined within the limit of large activation energies. Conditions under which the re-

sponse was monotonic or multi-valued (thereby exhibiting auto-ignition and auto-extinction) were identified. The efficacy of activation-energy asymptotics in dealing with the strongly non-linear Arrhenius term of reactive fluid mechanics was thus demonstrated.

#### 4.14.4 Liquid Strand/Open Pool Burning of Hydrazine in Oxidizing Atmospheres

The strand burning technique as applied to monopropellant decomposition of hydrazine in the absence of an oxidizing atmosphere was already discussed in Section 4.10.1. The same tests repeated in air or oxygen would typically give higher regression rates and would allow one to observe the dual flame zones that were discovered previously for droplet combustion. Whereas strands with  $L/D$  larger than 1 are typically used for laboratory studies of combustion kinetics, open-air burning tests in pits or pans with  $L/D$  smaller than 1 are typically done to assess the fire hazard of burning fuel spills and to test methods for extinguishing burning propellant spills.

The addition of ethanol to hydrazine reduced the strand burning rate of hydrazine in air [1615]. In a 0.99-cm-diameter tube, the addition of 2, 8, or 14.4% ethanol decreased the burning rate from 0.032 g/s to 0.022, 0.020, or 0.012 g/s, respectively. The burning rate of hydrazine depends on the tube diameter, the flame consuming 0.026, 0.032, 0.052, or 0.083 g/s in 0.75-, 0.99-, 1.37-, or 1.81-cm-diameter tubes, respectively. The diameter dependence of the burning rate was in agreement with Spalding's formula. In an  $N_2O_4/NO_2$  atmosphere, hydrazine burned even faster, 0.083 g/s in a 1.37-cm-diameter tube. Measurements of the horizontal and vertical flame temperature profile of flames in air showed maximum temperatures near 1400 K, much hotter than ethanol flames.

If the hydrazine liquid is gelled prior to forming it into a strand, convection in the liquid is suppressed, and slightly different strand burning rates, such as those in gaseous oxygen, are obtained [1616]. The results indicated that the decomposition rate is a function of the heat transfer from the flame to the liquid surface. The limiting burning rate of hydrazine gel was roughly proportional to the pressure in the combustion bomb. If the oxygen was blown over the sample, such as in a hybrid rocket, the burning rate was also proportional to the injection velocity of the oxidizer.

#### 4.15 Combustion of Hydrazine with Other Oxidizers

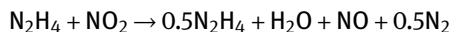
While the combustion reactions of hydrazine(s) with oxygen or ozone have been thoroughly studied, they may not necessarily be the practically most important combustion reactions. Other oxidizers, such as NTO, are more frequently used in combination with hydrazine fuels in rocket engines. Therefore, it is important to investigate reactions of nitrogen dioxide and NTO with hydrazines.

#### 4.15.1 Combustion of Hydrazine with Nitrogen Dioxide

The combustion of hydrazine with nitrogen dioxide (or, depending on the initial temperature, NTO) has undergone thorough investigation because of its practical importance as a hypergolic rocket propellant combination. Actually, NTO was not used with undiluted hydrazine in any bipropellant rockets for a long time because the cooling could initially not be managed safely. Because of the limitations in the use of pure hydrazine for regenerative cooling, a 50:50 mixture of hydrazine and UDMH called Aerozine-50 (Ae-50) had been used in all of the APOLLO and GEMINI missions and numerous other launch vehicles and upper stages. In this mixture, the interaction between nitrogen dioxide and hydrazine constitutes a key reaction leading to the desired hypergolic ignition. This reaction is considerably more vigorous than that of nitrogen dioxide with methylhydrazines. As a matter of fact, the reaction is so vigorous that it is difficult to obtain a reaction between liquid propellants. At the moment of first contact between NTO and hydrazine the reaction at the interface of the droplets is so fast and so vigorous that the droplets are driven apart, thus preventing further reaction going to completeness (reactive stream separation.) Numerous investigations deal with this problem and try to identify intermediates. Some of the kinetics and theories regarding possible intermediates in  $\text{N}_2\text{O}_4 + \text{N}_2\text{H}_4$  reactions were discussed in Section 3.1.7 (wet reactions in solution and vapor reactions) and rocket engine studies will be described in a future *Encyclopedia of Hypergolic Bipropellant Combinations*, in the chapter “Hypergolic Combinations with Nitrogen Oxides.”

##### 4.15.1.1 Vapor-Phase Reaction Kinetics of $\text{N}_2\text{O}_4/\text{NO}_2/\text{N}_2\text{H}_4$ Reactions

The reaction of nitrogen dioxide and hydrazine exhibited two distinct steps of greatly different rates [525, 1617]. The first step took place very rapidly and consisted of a reduction of the nitrogen dioxide to nitric oxide. This reaction was then followed by a second, slower one, the reduction of nitric oxide to nitrogen. Each of these steps involved several interconnected reactions. The kinetic study was conducted in an adiabatic flow reactor, like the one used for hydrazine decomposition. Rapid mixing of the highly diluted ( $10^{-7}$  mol/cm<sup>3</sup>) reactants was achieved in the inlet portion. The temperature profile along the 120-cm (4-ft)-long reaction zone was then measured as a function of initial parameters. The reaction of nitrogen dioxide and hydrazine produced a stepwise temperature profile with two reactions separated by a plateau of nearly constant temperature. The two steps are used to subdivide Table 64. The step I reaction



proceeded at a rate greater than, and an overall activation energy less than, that for hydrazine decomposition. It was concluded that this reaction occurred without dependence on hydrazine decomposition or breaking of the N—N bond (the activation energy for which would have been 251 kJ/mol = 60 kcal/mol) [525].

**Table 64:** Summary of postulated reaction mechanisms.

| $\text{N}_2\text{H}_4 + \text{NO}_2$ (Step I)                                                | $\text{N}_2\text{H}_4 + \text{NO}_2$ and<br>$\text{N}_2\text{H}_4 + \text{NO}$ (Step II)        | $\text{N}_2\text{H}_4 + \text{O}_2$                                                          |
|----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|
| <i>Initiation</i>                                                                            |                                                                                                 |                                                                                              |
| $\text{N}_2\text{H}_4 + \text{NO}_2 \rightarrow \text{N}_2\text{H}_3 + \text{HONO}$ (1)      | $\text{N}_2\text{H}_4 \rightarrow \text{M}^a \rightarrow \text{NH}_2 + \text{NH}_2$ (9)         | $\text{N}_2\text{H}_4 \rightarrow \text{M} \rightarrow \text{NH}_2 + \text{NH}_2$ (9)        |
| <i>Branching</i>                                                                             |                                                                                                 |                                                                                              |
|                                                                                              | $\text{N}_2\text{H}_3 \rightarrow \text{M} \rightarrow \text{NH}_2 + \text{NH}$ (10)            | $\text{N}_2\text{H}_3 \rightarrow \text{M} \rightarrow \text{NH}_2 + \text{NH}$ (10)         |
| <i>Propagation</i>                                                                           |                                                                                                 |                                                                                              |
| $\text{N}_2\text{H}_4 + \text{OH} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2\text{O}$ (2) | $\text{N}_2\text{H}_4 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_3 + \text{NH}_3$ (11)        | $\text{NH}_2 + \text{O}_2 \rightarrow \text{HNO} + \text{OH}$ (19)                           |
| $\text{N}_2\text{H}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{H}_2 + \text{HONO}$ (3)      | $\text{N}_2\text{H}_3 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_2 + \text{NH}_3$ (12)        | $\text{N}_2\text{H}_3 + \text{O}_2 \rightarrow \text{NH}_2\text{NO} + \text{OH}$ (20)        |
| $\text{N}_2\text{H}_3 + \text{OH} \rightarrow \text{N}_2\text{H}_2 + \text{H}_2\text{O}$ (4) | $\text{NO} + \text{NH}_2 \rightarrow \text{NH}_2\text{NO}$ (13)                                 | $\text{N}_2\text{H}_4 + \text{OH} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2\text{O}$ (2) |
| $\text{HONO} \rightarrow \text{OH} + \text{NO}$ (5)                                          | $\text{NO} + \text{NH} \rightarrow \text{N}_2 + \text{OH}$ (14)                                 | $\text{N}_2\text{H}_3 + \text{OH} \rightarrow \text{N}_2\text{H}_2 + \text{H}_2\text{O}$ (4) |
| $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ (6)                       | $\text{N}_2\text{H}_4 + \text{OH} \rightarrow \text{N}_2\text{H}_3 + \text{H}_2\text{O}$ (2)    | $\text{N}_2\text{H}_4 + \text{NH}_2 \rightarrow \text{N}_2\text{H}_3 + \text{NH}_3$ (11)     |
| $\text{NO}_2 + \text{H} \rightarrow \text{HONO}$ (7)                                         | $\text{N}_2\text{H}_3 \rightarrow \text{M} \rightarrow \text{N}_2 + \text{H}_2 + \text{H}$ (15) |                                                                                              |
|                                                                                              | $\text{NH}_2\text{NO} \rightarrow \text{HN}_2 + \text{OH}$ (16)                                 |                                                                                              |
|                                                                                              | $\text{HN}_2 \rightarrow \text{N}_2 + \text{H}$ (17)                                            |                                                                                              |
| <i>Termination</i>                                                                           |                                                                                                 |                                                                                              |
| $\text{N}_2\text{H}_2 \rightarrow \text{N}_2 + \text{H}_2$ (8)                               | $\text{N}_2\text{H}_2 \rightarrow \text{N}_2 + \text{H}_2$ (8)                                  |                                                                                              |
|                                                                                              | $\text{NH}_2\text{NO} \rightarrow \text{H}_2\text{O} + \text{N}_2$ (18)                         | $\text{NH}_2\text{NO} \rightarrow \text{H}_2\text{O} + \text{N}_2$ (18)                      |
|                                                                                              |                                                                                                 | $\text{OH} + \text{NO} \rightarrow \text{HONO}$ (21)                                         |
|                                                                                              |                                                                                                 | $\text{HNO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}$ (22)                     |

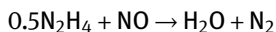
<sup>a</sup> **M** symbolizes the wall of the reaction vessel acting as third body.

Data source: [525]

The global rate constant for step I can be expressed as

$$k = 10^{15.83 \pm 0.58} e^{-\frac{26700 \pm 1100}{RT}}$$

The second step of the reaction of nitrogen dioxide and hydrazine



proceeded at a rate comparable to the reaction of hydrazine and nitric oxide. Under these conditions, approximately 15% of the hydrazine decomposed before it reacted with NO, and the decomposition products hydrogen and ammonia did not react with NO under the conditions of the adiabatic reactor. The rate constant for step II is

$$k = 10^{10.17 \pm 0.55} e^{-\frac{39600 \pm 2600}{RT}}$$

compared to that for the  $\text{NO} + \text{N}_2\text{H}_4$  reaction

$$k = 10^{11.48 \pm 0.32} e^{-\frac{45400 \pm 1500}{RT}}$$

The Arrhenius parameters were compared assuming a first-order dependency on the hydrazine concentration in both cases. Actually, the rate of hydrazine consumption in

mixture with NO in the adiabatic flow reactor was found to be proportional to only the 0.75<sup>th</sup> power of the hydrazine concentration. Table 64 gives a summary of the postulated reaction mechanism, in which the abstraction of hydrogen by nitrogen dioxide and hydroxyl radicals plays a key role.

One of the suspected explosive intermediates in the reaction of  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{H}_4$  is hydrogen azide and its hydrazinium salt. Hydrogen azide was detected in the gas phase when  $\text{N}_2\text{O}_4$  vapor was passed over condensed  $\text{N}_2\text{H}_4$  and analyzed by mass spectrometer as indicated by peaks at  $m/e = 43$  and  $42$  [613]. In a different test, the reactants were diluted in tetrachloromethane and then poured together. Azide also forms in aqueous solutions of hydrazine and nitrate ions, during storage of aqueous hydrazinium nitrate solutions, and solutions of hydrazinium nitrate in hydrazine.

The conservation equations in the boundary layer form have been solved for coaxial flowing and reacting streams of hydrazine and nitrogen dioxide [1618]. The model for the hypothetical burner was patterned after the Burke-Schumann approach, for axially symmetric flow in cylinder coordinates, but the new model included substantially more computing power. The oxidizer was assumed to be introduced in the core and surrounded by an excess of fuel vapor. Detailed chemical kinetics and transport equations were used in the simulation, which included 22 species and 151 reactions. Reaction intermediates receiving special attention were nitrous acid HONO, hyponitrous acid HNO, and hydrogen peroxide. A gradual buildup of peroxide in the low-temperature fuel-rich region of the flame is thought to play an important role in the overall mechanism.

To construct a  $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$  combustion model that is useful for bipropellant thruster simulation, the literature concerned with elementary  $\text{N}_2\text{O}_4/\text{N}_2\text{H}_4$  reactions was surveyed in detail [1619]. A total of 245 reactions were found in 16 available studies that needed a common denominator for future use in a computer model.

A hydrazine and NTO combustion model that is useful for bipropellant thruster CFD simulation was developed by extracting appropriate elementary reactions from a detailed kinetic reaction model developed by Ohminami and Ogawa [1619]. The reduced hydrazine and NTO combustion model was composed of 61 extracted reactions with 23 chemical species and was coincident with the original detailed kinetic reaction model in terms of combustion gas temperatures and ignition delay times over the oxidizer and fuel mass ratio (O/F) range from 0.82 to 1.84 [1620]. The simulated combustion gas temperatures agreed with the adiabatic flame temperatures, and the simulated ignition delay time at  $\text{O/F} = 1.2$  was consistent with the literature value.

Hydrazine and nitrogen dioxide co-flowing plane jets and coaxial jets were simulated to explore the double flame structures in hypergolic  $\text{N}_2\text{O}_4 + \text{N}_2\text{H}_4$  bipropellant thrusters [1621]. The Navier-Stokes equations with a detailed chemical kinetics mechanism were solved in a manner of direct numerical simulation to reveal the interaction between fluid dynamics and the distinct chemical reaction, i.e., hydrogen abstraction by  $\text{NO}_2$  and the thermal decomposition of  $\text{N}_2\text{H}_4$ . The flames are uniquely composed of two types of flame, a diffusion flame and a decomposition flame. The diffusion flame



came from the oxidation by  $\text{NO}_2$ . The decomposition flame was caused by the heat transfer from the diffusion flame and a high rate of heat release from the thermal decomposition of  $\text{N}_2\text{H}_4$ .

#### 4.15.1.2 Hydrazine Droplet Combustion in an $\text{N}_2\text{O}_4$ Atmosphere

The combination of NTO and hydrazine(s) constitutes a very powerful rocket propellant. Because  $\text{N}_2\text{O}_4$  vaporizes at a lower temperature than fuel, the condition near the injector of an  $\text{N}_2\text{O}_4$ /hydrazine fuel rocket is usually that of hydrazine (or MMH or UDMH) droplets burning in an  $\text{N}_2\text{O}_4$  or  $\text{NO}_2$  gas atmosphere. Many experimental and theoretical studies have been conducted to study the hydrazine droplet combustion and unsteady phenomena associated therewith.

In a study on hydrazine droplets suspended from a thermocouple and burning in  $\text{N}_2\text{O}_4$  vapor, it was found that the hydrazine droplet temperature remained at the boiling point during steady-state burning [1622–1624].

The effect of additives on the burning rate of hydrazine droplets burning in dinitrogen tetroxide vapor was measured and an attempt was made to relate these effects to rocket engine (in)stability [1625–1628]. This depended on a basic understanding of the hydrazine/dinitrogen tetroxide flame structure, using this knowledge to select effective additives, and then measuring the effectiveness of these additives in changing the hydrazine burning rate. The application of this work to stability control then involved the computation of additive distillation and inclusion of this effect in a steady-state combustion computer program. The resulting combustion profiles with and without additives were compared, and stability changes were identified.

It was also found that (in analogy to hydrazine combustion in oxygen) hydrazine droplets burned in two distinctly different flame regions: an inner decomposition flame and an outer oxidation flame [1629]. Hydrazine burned much faster in  $\text{N}_2\text{O}_4$  than in any other oxidizer. Ignition of the hydrazine droplets was preceded by the formation of a milky film on the droplet (ammonium nitrate?), followed by the initiation of a vapor-phase reaction. Occasionally droplet shattering was observed, but this occurred at random and could not be correlated to any test parameter.

The theoretical monopropellant decomposition unit area burning rate for hydrazine itself was calculated as  $140 \text{ g m}^{-2} \text{ s}^{-1}$  ( $2.86 \times 10^{-2} \text{ lb ft}^{-2} \text{ s}^{-1}$ ). This value agrees within 2% of that reported based on experimental data [1431, 1432]. When plotting the unit area burning rate as a function of oxidizer ( $\text{N}_2\text{O}_4$ ) concentration  $O_x$ , the intercept at  $O_x = 0$  corresponded to the monopropellant burning rate.

The effect of additives on the droplet burning rate of hydrazine in  $\text{N}_2\text{O}_4$  vapor was studied [1626]. Ammonium nitrate was tested as an additive [1628]. It was found that some of the additives would cause hydrazine droplets to break up, thereby leading to increased rates of vaporization and possibly shorter characteristic lengths in rocket engines.

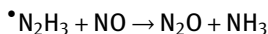
A mathematical model representing two phases, liquid and gas, was developed for the steady-state combustion of a single hydrazine droplet in an NTO atmo-

sphere [1630]. The spherically symmetric model generates a two-point boundary value problem in one dimension (the spherical coordinate), which was solved by Newton's method with an adaptive gridding technique. The burning rate of the droplet was obtained as an eigenvalue to eliminate the uncertainty or complexity of evaporation and condensation rate laws. The resulting temperature profile exhibited a two-zone flame structure, which was like that observed in an experiment reported in the literature.

#### 4.15.2 Combustion of Hydrazine with Nitric Oxide or Nitrous Oxide

One proposed reaction mechanism for the reaction of nitric oxide with hydrazine was already shown in Table 64. In this mechanism as well as in the oxidation with nitrogen dioxide or oxygen, nitrosamine  $\text{H}_2\text{NNO}$  is believed to take part as an intermediate in most of the reactions. However, there has been no attempt to identify it in the reacting mixture by drawing samples into a mass spectrometer. This was achieved only in a later study on the elementary steps for the formation and consumption of nitric oxide in the H/N/O system [543]. In the  $\text{NO}/\text{O}_2/\text{N}_2\text{H}_4$  system,  $\text{NO}_2$  formation took place in two steps: The first rapid reaction of NO and  $\text{N}_2\text{H}_4$  proceeded in the presence of  $\text{O}_2$  and yielded a relatively stable (yet unidentified) species. This reaction was followed by a slower reaction, which produced  $\text{NO}_2$  [1631].

In one of the earliest studies on hydrazine decomposition and combustion flames, the formation of  $\text{N}_2$  in the reaction of hydrazine with nitric oxide was observed [1228]. Lacking additional information and modern instrumentation, it was postulated that hydrazyl radicals participate in hydrazine decomposition:



This assumption was later assailed [1200], but all data available now indicate that Bamford was indeed right with his early prediction. The only question is whether  $\bullet\text{N}_2\text{H}_3$  is involved in the rate-determining step.

The temperature-pressure-composition limits for the initiation of thermal explosions in nitric oxide/hydrazine mixtures have been determined in a silica vessel between 613 and 923 K [1632]. In general, nitric oxide is not as active an oxidizer in combustion systems (hydrocarbons,  $\text{H}_2$ , CO) like oxygen itself. However, with ammonia or hydrazine as fuel this relation is reversed. Nitric oxide/hydrazine mixtures exploded somewhat more readily than the corresponding oxygen/hydrazine mixtures. The minimum ignition temperature for stoichiometric oxygen, nitric oxide, or nitrous oxide mixtures with hydrazine at 6.6 kPa (50 mm Hg) total pressure were 608, 673, or 943 K, respectively. Surprisingly, nitrous oxide ( $\text{N}_2\text{O}$ ) acted more like a diluent than an oxidizer, but once the reaction was started, it was consumed in the combustion. One way to compare the action of the two gases is to plot the hydrazine partial pressure in the total pressure/composition diagram. Whereas it underwent a minimum and then increased with hydrazine concentration (indicating reaction) in the  $\text{NO}/\text{N}_2\text{H}_4$  system,

the graph with  $\text{N}_2\text{O}$  showed the hydrazine partial pressure to be a straight line parallel to the abscissa, indicating a mere dilution effect of  $\text{N}_2\text{O}$ .

Although both nitric oxide and nitrous oxide have positive heats of formation (as does hydrazine), the flame speed in mixtures of hydrazine vapor with these oxidizers did not exceed that of oxygen/hydrazine mixtures [1606]. At 5.3 kPa (40 mm Hg) pressure and 335 K, the maximum flame speed with NO was 31.5 cm/s and 24 m/s with  $\text{N}_2\text{O}$  at a stoichiometric mixture ratio.

In addition to the flame speeds and flammability limits of the binary nitric oxide/hydrazine and nitrous oxide/hydrazine mixtures, ternary nitric oxide/nitrous oxide/hydrazine mixtures have also been investigated at sub-atmospheric pressures [1633]. The maximum burning velocity was that of a fuel-rich binary NO/ $\text{N}_2\text{H}_4$  mixture with no  $\text{N}_2\text{O}$  present. This is different from the behavior in the NO/ $\text{N}_2\text{O}$ / $\text{NH}_3$  system, where the flame speeds of ternary mixtures were faster than those of either binary system. With hydrazine as a fuel, nitric oxide supported combustion better than did nitrous oxide. With the use of hydrogen gas as a fuel, the relative activity of the two oxides was reversed. Nitric oxide in the hydrogen flame tended to act both as an inhibitor and as an oxidant. A flame speed of 3600 cm/s was measured in a fuel-rich (50%  $\text{N}_2\text{H}_4$ ) mixture with NO from which  $\text{N}_2\text{O}$  was absent. In lean ternary mixtures, the two oxidizers enhanced each other's activity.

## 5 Materials of Construction for Hydrazine

Many summaries and survey papers on material compatibility with hydrazine have been published, of which the following few may serve as starting points for further study: [1634–1638]. Many of these summaries, in particular [1639, 1640], are already obsolete and now only of historical value to the spacecraft designer. Some of these summaries deal not only with hydrazine itself, but also with some of its methyl derivatives.

An excellent design handbook, but only for privileged readers eligible to obtain copies, is [1641]. It contains information on hydrazine liquid and hot decomposition product materials' compatibility and the effects of temperature, hydrazine purity, and passivation techniques on compatibility. Because a complete compilation of all material compatibility data with hydrazine fuels would easily fill another book equal in size to this one, a compromise format had to be sought in presenting material compatibility data here.

Even after published data are located, there are often serious questions about the reliability of these data and their applicability to the current material selection question at hand. The results obtained by different researchers vary with the method and the purity of the hydrazine used. Often materials that are acceptable for use in bipropellant rocket tanks may not be acceptable for monopropellant systems with their increased purity requirements. It is very regrettable that many of the early publications

on hydrazine material compatibility dating to the 1950s and 1960s have simply copied data (often unreliable data) indiscriminately from each other, thus propagating misinformation, and these publications should be ignored. An example is [1642]. Many of these reports, such as [1643], are concerned only with bipropellant use of hydrazines. This Battelle DMIC report is one of the most frequently misquoted summary reports in this category, and its conclusions need to be carefully scrutinized and verified before designing any system, in particular a monopropellant system. Many of the materials listed in this Battelle DMIC report were later shown to be unacceptable for hydrazine monopropellant systems.

Another design guidebook on material compatibility with space storable propellants was [1644]. It contained sections on hydrazine, MMH, and a hydrazine/hydrazinium nitrate blend. In addition, it contained material compatibility information on other liquid rocket propellants (diborane, NTO, liquid fluorine, oxygen difluoride, FLOX). The hydrazine section of this design guidebook was reprinted as an appendix to a JPL report published in the same year [1635], but most of the information therein needs updating.

The present book unfortunately is no exception in relying on data obtained by other sources because it is only a summary (albeit a critical summary) of data published by other principal investigators. Data on material compatibility research with hydrazines generated by the author during the author's experimental chemistry career in the US aerospace industry remain company-proprietary data and have not been released for general distribution.

**Sources of Information.** The most methodical way to organize the vast amount of data on material compatibility with hydrazine(s) would be in a database with cross-referencing, possibly distributed to interested parties on a CD-ROM disc or available for online search. Initial modest attempts have been made at various places in this direction, but only for company internal use and not intended for general distribution. Most of the references retrievable by public services prior to 1994 were already incorporated into the second edition of the hydrazine book for the convenience of the reader. References to the other online databases may help readers in updating their files and obtaining even more recent information, although the URLs or the public availability of databases may change from time to time between the date of publication of this book and the date when the reader is logging on the Internet. It has been common practice to annotate each URL listing with the note "accessed on ... (date)," but this has not been done consistently for the current book.

From time to time, entire conferences have been devoted to the topic of propellant and hydrazine material compatibility. Proceedings from such conferences are a good source of information. For several years in a row, a Working Group for Materials Compatibility of Storable Propellants convened in conjunction with other JANNAF meetings and was a very useful forum for exchange of information. It is regrettable that no comparable organization exists at this time. There should be at least a bulletin board on the Internet where compatibility issues and contamination incidents caused by in-

compatibility could be posted and incompatible materials can be red flagged. Material compatibility issues with rocket propellants are often discussed at JANNAF Propellant Development and Characterization meetings, but the proceedings are not available to the general public. Additional information used to be available from the manufacturers of hydrazines, sometimes in the form of product data sheets for hydrazine [1645], but this is no longer the case. Product information published on company web sites is sparse and rarely goes beyond the most fundamental physical properties like freezing point and boiling point.

**Rating Systems.** For the most common materials of construction, compatibility ratings are often given only in qualitative terms. There exists no standardized rating system for the compatibility of materials. Trying to obtain a material compatibility rating for a material of construction is not like consulting your personal stockbroker and financial advisor for a Moody's bond rating system (e.g., AAA, BB+) that is widely accepted in the financial community. At the other end of the compatibility spectrum, some flagrant cases of material incompatibility and the resulting system malfunctions are cited here as warning examples of the lack of reliability of information found in the literature. It is difficult to give a general stamp of approval for materials of construction without knowing the exact circumstances of the intended application. In many cases, a certain material compatibility test will have to be performed under simulated conditions to make sure that the questionable material is suitable for the intended conditions of hydrazine service (temperature, duration). Many materials have been rated for hydrazine hydrate solution use, but exposing them to anhydrous hydrazine is a totally different corrosive and more reactive environment.

Some chemical suppliers have posted material compatibility data banks on the Internet, but these can only provide crude and often erroneous compatibility information. One example with misleading information is the Cole Parmer databank, which erroneously lists polyacetal resins (Delrin) as compatible ("Good") with hydrazine. Delrin dissolves in anhydrous hydrazine. Another blatant mistake is the rating of Kynar 460 as "Excellent" when it actually catalyzes thermal decomposition of hydrazine between 388 and 413 K and in one instance caused the destruction of a test apparatus [1646].

## 5.1 Compatibility with Liquid Hydrazines

A major concern to the designer of hydrazine systems is the compatibility of wetted components with hydrazines in the liquid phase during storage and transfer. In other applications, such as in the design of distillation columns for the production of anhydrous hydrazine, compatibility with hydrazine vapors must also be known.

For structural applications in tanks, lines, valves, or surface tension propellant management devices the metals most commonly selected are the alloys of titanium or stainless steels. Such alloys have been used in many flight systems with anhydrous

hydrazine such as the MARINER, VOYAGER, VIKING, CASSINI, and NEW HORIZONS space probes and many satellites in Earth's orbit. Fairly complete compatibility data are available for the following alloys in anhydrous hydrazine for periods of 4 years and beyond: titanium 6Al-4V, aluminum Al-6061, Al-2014, and Al-2219, and the stainless steels CRES-301, CRES-304, CRES-304L, and CRES-321. All these metals when immersed in hydrazine showed corrosion rates much lower than  $25\mu\text{m}/\text{year}$ . There is no evidence from published data that any of these metals in contact with propellant-grade hydrazine are subject to stress-corrosion cracking (SCC), intergranular corrosion, embrittlement, or shock sensitivity. Individual sections will discuss titanium alloys, stainless steels, and aluminum alloys on the following pages.

**Material Compatibility Quantified.** To compare the suitability of candidate materials of construction for a given application, it would be best to have a figure of merit that includes all possible parameters. Depending on the application, each of the properties will receive a different weighting factor if one wants to evaluate different candidate materials for a given application and perform a systematic evaluation matrix.

One of the many variables is the purity of the hydrazine. When a special high-purity hydrazine was developed for the VIKING mission to Mars, initially there was concern that removal of trace contaminants might change the corrosion behavior of propellant-grade hydrazine. Aniline that was removed from the VIKING-grade hydrazine might have acted as a corrosion inhibitor, just like it inhibits the activity of some catalysts. The purified material turned out to be less corrosive than the propellant-grade material, but the difference was only minor [110, 241]. At higher temperature (343 K), the differences between the three metals were less pronounced, and the rate exponents were very similar.

**History of Hydrazine Material Compatibility Testing.** One of the leading organizations in hydrazine material compatibility research is the Jet Propulsion Laboratory managed by the California Institute of Technology in Pasadena, CA. A Phase I program was intended only as a screening program and involved 51 samples in hydrazine, a 76% hydrazine/24% hydrazinium nitrate blend, and a 50:50 hydrazine/UDMH blend [1647]. A very comprehensive material compatibility program followed in 1970. Initially more than 700 test ampoules (including some with MMH or NTO) were placed in long-term storage testing at 316 K (110 °F). Intermediate results after up to 5 years in storage at 316 K (110 °F), based on the opening of 108 ampoules containing hydrazine, 12 ampoules containing a hydrazine/hydrazinium nitrate blend, and 4 ampoules containing MMH, were reported [1638]. At that time (1976), 578 specimen capsules remained in active test, and some were scheduled to remain in testing for a full 10 years.

In preparation for the tests, the glass ampoules were cleaned, loaded with a specimen, filled with propellant, cooled in liquid nitrogen, evacuated, and hermetically sealed with a blow torch. Most test specimens were in the shape of flat rectangular coupons, typically 1.27 cm wide, 7.62 cm long, and 0.076 cm thick. They were typically half submerged in the liquid propellant. The top half was exposed

to vapor and condensate only. Each constant temperature test bay was equipped with a circular rotatable storage rack (a lazy susan type of a carousel arrangement) with a capability to hold over 900 test capsules. The internal ampoule pressure was intended to be measured by externally mounted strain gauges forming part of a Wheatstone bridge. Unfortunately, nearly all strain gauges failed after only a few years of testing. Subsequent measurements of the amount of hydrazine decomposition thus had to rely on collecting the gases by remotely opening the capsule after it was removed from the constant-temperature test bay. This gave only one terminal data point for gas evolution. The decomposition gases were analyzed by GC for  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , MMH, and UDMH. Aniline was determined by UV absorption. Metals leached from the specimens were analyzed by atomic absorption. Chloride, fluoride, and carbon dioxide were also analyzed on selected samples. Unfortunately, many samples had residual CFC-113 (Freon-TF) from a cleaning process included with the hydrazine at the moment the ampoules were sealed, resulting in high chloride and fluoride concentrations in the off-loaded hydrazine and accelerated corrosion of many metal specimens. This invalidated many of these test results. Even titanium samples were coated with a layer of corrosion products. It is still possible to derive some useful information from the JPL data despite the unfortunate halide contamination. When tabulating results from JPL tests, one should sort the database by the halide concentration and eliminate all those with higher than MIL-SPEC levels of chloride (counting all fluoride as chloride).

Besides MIL-SPEC monopropellant-grade hydrazine, VIKING-grade hydrazine, MMH, and a 24% hydrazinium nitrate/hydrazine mixture have been used for many material compatibility tests at JPL. The effect of carbon dioxide contamination on CRES-303, CRES-304L, and CRES-347 corrosion in hydrazine after 15, 30, 45, and 91 d was the subject of a special series of tests. Hydrazine spiked with 27, 52, 90, and 230 ppm  $\text{CO}_2$  suffered progressively worse decomposition with increasing  $\text{CO}_2$  content. The amount of iron leached from the steel also increased drastically, up to 40 ppm Fe leached from CRES-303 within 91 d in hydrazine doped with 230 ppm  $\text{CO}_2$ . The lowest level of hydrazine decomposition was caused by CRES-304L, whereas CRES-347 caused the worst. CRES-303 was much more susceptible to iron leaching than CRES-347, and CRES-347 was more susceptible than CRES-304L. The JPL authors concluded that a  $\text{CO}_2$  content below 50 ppm would be acceptable for long-term contact with all three metals (less than 0.5% decomposition per year) [1638]. This compares to a MIL-SPEC limit of 30 ppm  $\text{CO}_2$  in high-purity-grade hydrazine as of 1999. Post-test examination of specimens under a scanning electron microscope revealed the formation of thin oxide films on aluminum, CRES, and titanium, which after drying tended to shrink and flake off the specimen surface when the film thickness exceeded 1 or 2  $\mu\text{m}$ . Short of applying a numerical rating scheme, the results were summarized by ranking the materials as acceptable or not acceptable with the qualifying terms “incomplete” or “restricted” attached. The term “incomplete” indicated in 1983 that not all the 10-year data were in. “Restricted” materials may be used for shorter

missions or in non-wetted parts of a system. In MIL-SPEC monopropellant-grade hydrazine, Al-2219-T86, Al-6061-T6, CRES-302, CRES-303, CRES-304, CRES-304L, CRES-316, CRES-321, and CRES-347 were considered acceptable, although the steels had a “restricted” qualifier. Stainless steels of types 350, 355, 416, 446, 17-4PH, and 17-7PH were rated acceptable despite pitting and surface discoloration. The best material identified after 10 years of testing was Ti-6Al-4V, although the data were incomplete.

The 10-year compatibility results milestone report was published in [1160, 1161]. It contained the results of the opening and examination of 36 ampoules containing hydrazine (8 of these containing the VIKING-grade hydrazine) and 8 with MMH. After 10 years, 164 specimens plus 28 hydrazine controls remained in storage. Another 59 ampoules contained samples in VIKING-grade hydrazine. Only 16 samples (Al, Ti, and controls) remained in the hydrazine/hydrazinium nitrate test, since all steel samples were found to be incompatible with this fuel and had to be terminated after only a few months of testing. Eight surviving samples and several controls were finally removed in 1984, and the results were presented in an interim publication [1648].

Interim results on 40 more hydrazine samples were reported in 1990 [1649]. These were the only long-term hydrazine samples opened between 1982 and 1989. As of 1990, the plan was to open the remaining several hundred samples that were approaching 20 years of storage at the rate of 50 samples per year. Unfortunately, funding limitations prevented a systematic completion of this well-planned test schedule. Several samples were taken out and temporarily put into a freezer, which would halt all further corrosion, awaiting their disposition and opening or disposal. Unfortunately, under the pressure of an environmental pollution cleanup campaign, all samples were hastily terminated in 1995 without gas pressure readings being taken and without analysis of the off-loaded hydrazine for leached metals and propellant deterioration. Owing to the shortsightedness of some government agencies, large amounts of valuable data were lost, which would take at least 20 years to obtain otherwise. This was a loss to the space propulsion community (government and industry) at large and a waste of taxpayer money. A hydrazine manufacturer had offered to analyze the off-loaded hydrazine samples for free, but the samples were hastily destroyed instead.

The JPL long-term storage test facility was also used in the 1980s for shorter (from half a year to 2 years’ duration) tests devoted to special objectives, such as tank components for a hydrazine actuation system [1162] or the effect of included air and carbon dioxide on the corrosion of stainless steel [1650]. Unfortunately, not all data obtained from the JPL program could be included here in this book because it would take up too much space. It would have been worthwhile to assemble all JPL data in spreadsheet format and post them on a web site so they could be readily accessed and searched by material type and propellant type. Valuable data might have been lost because they were never published.

**Material Compatibility Databases.** In the past, material compatibility data exchange between rocket propulsion engineers was mostly by way of conferences [1651,



1652], workshops, and information printed in hard copy [1634]. With the advent of personal computers and the Internet, the most efficient way to prevent future incompatibility problems with hydrazines and other rocket propellants would be by posting material compatibility test results and sharing them with other hydrazine users. Unfortunately, much of the material compatibility information rests in the archives of aerospace companies is considered proprietary information. Other material compatibility data were outright classified as confidential or “NOFORN, DoD use only” and could not be published here.

When it comes to priority in funding, material compatibility testing should be on an equal level of importance as toxicity testing in support of safety and hazard evaluation of propulsion systems, in particular for piloted missions. However, historically speaking, over the past five decades, a disparately large amount of funding has been devoted to toxicity testing and only a handful of thorough material compatibility studies has been published. Whatever little material compatibility information we have, it is scattered over many different publications. A few embarrassing material incompatibility incidents occurred in the aerospace community, but these are usually swept under the rug, as they say, and not widely published. Nobody has taken the time to assemble a so-called lessons-learned database to prevent the repetition of some of these expensive mistakes. What the spacecraft designer needs is a user-friendly database, either as a CD-ROM or as a periodically updated web site accessible to qualified users in the aerospace propulsion community. A plea was issued for the creation of a hydrazine material compatibility database [1653], but it has been left unanswered. What is needed is a material compatibility database that summarizes all material compatibility data of various metallic and non-metallic construction materials in contact with hydrazine propellants. In addition to the results of systematic material compatibility immersion tests, the database should contain a chapter on lessons learned from incidents caused by material incompatibility.

The extended-life capability of other spacecraft components (solar panels, traveling wave tubes) and future refueling capability generate an ongoing need for reliable long-term (longer-term) compatibility data. Problems caused by hidden material incompatibilities can be mission-threatening and pose a potential hazard to ground test personnel and astronauts, much more so than accidental inhalation of propellant vapors or splashes of propellants on unprotected skin. A failed mission would be much more costly than a hospital stay of an injured propellant handler.

The NASA Materials and Processes Technical Information System II (MAPTIS-II) was put into operation in 2003 (<https://maptis.nasa.gov>; accessed 9-Mar-2022). MAPTIS-II is a product of the NASA MSFC Engineering Directorate, Materials, Processes and Manufacturing Department, and Project Engineering Group. MAPTIS-II is a single-point source for physical, mechanical, and environmental properties for metallic and non-metallic materials for NASA and NASA-associated contractors and organizations and includes only limited corrosion data for propellants like hydrazine. Access is limited to users registered with US government agencies.

## 5.2 Methods of Compatibility Testing

The test methods described here for material compatibility testing with hydrazine can be equally well applied to other propellants, such as hydrogen peroxide or HAN-based monopropellants. Criteria used in selecting construction materials and determining material compatibility include pressure buildup in closed vessels by hydrazine decomposition, loss of structural strength of the material as a result of corrosion by hydrazine, and contamination of hydrazine by leached corrosion products. If a material that meets only one of these criteria is selected, the system may still fail because the other property requirements may not be met, which is sure to cause some unexpected problems. The test procedures used by many laboratories to determine compatibility differ significantly (as do the results). There is no standard ASTM or DIN method for determining compatibility of materials with hydrazine fuels. Many of the methods were adapted from other test methods for rocket propellants and corrosive materials. For the sake of being able to compare compatibility data from different sources on different materials and different propellants, it would be desirable if a standard compatibility test method could be agreed upon. This would be a task for one of the ASTM or AIAA standardization committees. It is widely recognized that different types of apparatus will be needed for ambient-, high-, and very high-temperature ( $>340\text{ K}$ ) testing, one for each temperature regime.

The various methods for material compatibility testing are summarized here for their applicability to hydrazine material compatibility, but the methods might be applicable to any other corrosive fluid as well. It is just that only a few corrosive liquids are so unforgiving when errors in material selection are made. Hydrazine is not only a corrosive, but also an energetic liquid. If anhydrous hydrazine is accidentally stored in containers made of materials of dubious compatibility, a catastrophe is sure to ensue.

Another question where no general agreement exists between material compatibility experts is whether the sample should be completely immersed in the liquid or only partially immersed, with part of it sticking out of the liquid and being exposed to the vapor phase. Total immersion is likely to give more reproducible results but may not be representative for real-life situations. There are many cases where observed corrosion was worst at the liquid-vapor interface. The cause may be that condensate refluxes from the vapor phase and washes contaminants and corrosion products down to the interface where they accumulate and accelerate the attack (in a stagnant system without forced convection). In other cases, the gas phase may contain trace oxygen or trace carbon dioxide, which makes corrosion by hydrazine worse at the interface, an effect that would be overlooked with total immersion. Table 65 gives a summary of partial/total immersion practices at different organizations. Some organizations conduct compatibility tests with partial immersion, while others specify total immersion.

**Table 65:** Hydrazine material compatibility – total vs. partial immersion

| Organization | Degree of immersion | References |
|--------------|---------------------|------------|
| SRI for JPL  | Two-thirds to total | [1647]     |
| JPL          | Half                | [1638]     |
| JPL          | Total               | [1161]     |
| PERME        | Total               | [1158]     |
| MIL-R-83412A | Total               |            |

### 5.2.1 Short-Term Exposure Tests

Before starting long-term material compatibility tests, a quick screening test will be useful to eliminate materials that are obviously incompatible. Such open-air, visual observation tests in a Petri dish will also need to be performed on materials that are not necessarily wetted with hydrazine by design but may be exposed to hydrazine in case of an accidental propellant spill during fueling or a leak. A procedure for casual exposure of materials to hypergolic fluids has been developed [1654]. A so-called casual exposure is assumed to last less than 240 min. Fabric and splash shield and goggle materials intended for use as personnel protective equipment will need to be subjected to more rigorous tests.

#### 5.2.1.1 Methods for Material Compatibility Evaluation

Methods for material compatibility evaluation include gas evolution measurements [1159, 1655–1658], differential pressure measurements [110, 241, 1158, 1659–1666], external strain gauges on sealed glass vials [1160–1162, 1638], Bourdon gauges [1647, 1667, 1668], microcalorimetry [1174, 1669], electrochemical impedance spectroscopy [1650, 1670–1677], dimensional and mass change measurements, sub-scale pressure vessels made from materials under test [1678–1680], and full-scale flight tanks made from materials under test. The last method is the most realistic, but it is also the most expensive method used in material compatibility testing for long-term missions. Only rarely is there enough time to conduct this type of test in real time prior to actual launch of a mission or fielding a weapons system. For some militarily strategic or tactical missile systems, it may be possible to go back in and do a post-storage disassembly and inspection (D&I) after the systems are decommissioned and demilitarized. Some tank storage tests are summarized in Section 6.8, where different tank designs are compared. The most expensive mode of tank storage testing is where the propellant is fed from the tank into rocket thrusters replicating a complete mission duty cycle on the ground. This may be part of a system development test, a system qualification test, or an after-the-fact troubleshooting exercise.

Gas evolution during hydrazine storage and material compatibility tests is often shown in graphical form of pressure rise plots. These graphs are of limited value or no value at all if the sample wetted surface area and the ullage volume of the apparatus

are not given. What can be learned from the shape of the curves alone is whether the sample passivates (slope is decreasing with time) or whether a protective coating is eaten away or leached contaminants result in progressive homogeneous decomposition throughout the liquid propellant sample (slope is increasing with time). Because pressure rise curves are hardly ever a linear straight line, one must average over an arbitrary time interval to determine gas evolution rates. Sometimes the first 60 d of a long-term test are ignored, and the rate is determined as if the experiment had only started on day 61. This is a better approximation of a linear slope for the prediction of pressures in the distant future.

Typical gas evolution data for two metals in hydrazine of three different purity grades at two different temperatures are summarized in Table 66. As can be seen, gas evolution on stainless steel is higher than on titanium, and removal of impurities reduces the gas evolution rate. This effect was more pronounced for the sample stored at room temperature.

**Table 66:** Gas evolution rate of metals in hydrazine.

| Metal     | Temperature, K   | Hydrazine purity grade | Years in test | Micromols of gas/cm <sup>2</sup> | Pressure rise factor, psia in. <sup>3</sup> in. <sup>-2</sup> year <sup>-1</sup> |
|-----------|------------------|------------------------|---------------|----------------------------------|----------------------------------------------------------------------------------|
| Ti-6Al-4V | 295              | Monopropellant         | 10.9          | 11.10                            | 0.14                                                                             |
| Ti-6Al-4V | 295              | Distilled              | 10.9          | 5.12                             | 0.06                                                                             |
| Ti-6Al-4V | 295              | BaO Treated            | 10.5          | 6.71                             | 0.09                                                                             |
| Ti-6Al-4V | 313 <sup>a</sup> | Monopropellant         | 12.1          | 15.51                            | 0.17                                                                             |
| Ti-6Al-4V | 313              | Distilled              | 10.6          | 12.17                            | 0.15                                                                             |
| Ti-6Al-4V | 313              | BaO Treated            | 10.6          | 12.68                            | 0.15                                                                             |
| CRES-304L | 295              | Monopropellant         | 10.9          | 24.64                            | 0.31                                                                             |
| CRES-304L | 295              | Monopropellant         | 10.5          | 21.92                            | 0.28                                                                             |
| CRES-304L | 313              | Monopropellant         | 10.9          | 45.78                            | 0.58                                                                             |
| CRES-304L | 313              | Monopropellant         | 10.6          | 52.74                            | 0.69                                                                             |

<sup>a</sup> Sample spent only 1426 d at 313 K, stored at room temperature for remainder of test  
Data source: [1159]

Assuming that the gases in the low-pressure glass apparatus behave the same as in a pressurized flight tank and neglecting homogeneous decomposition, the pressure rise in tanks of given volume, wetted surface area, and ullage can be predicted from

$$P = \frac{KA t}{U}$$

where  $P$  is the pressure rise (psia),  $K$  is the pressure rise factor (psia in.<sup>3</sup> in.<sup>-2</sup> year<sup>-1</sup>; see Table 66),  $A$  is the surface area (in.<sup>2</sup>),  $U$  is the ullage (in.<sup>3</sup>), and  $t$  is the time (years). The pressure measured is the sum of the vapor pressure of hydrazine, dissolved ammonia, and permanent gases such as nitrogen and (formed to a much lesser extent) hydrogen.

Quite often the main reason for measuring the rate of gas evolution is to determine how much ullage must be left in the tank for a long-term space mission so as not to overpressurize the tank during the cruise and idle period. The concern for overpressure is caused by the permanent gases. At pressures approaching the proof and burst pressure of space flight tanks, all ammonia is in solution and it is only a minor contributor to the pressure in the vapor phase. In those cases where separate data on ammonia evolution and permanent gas evolution are available, only the permanent gases are used for pressure rise predictions.

The partial pressure of ammonia over hydrazine-ammonia solutions can be calculated from

$$P \cong \frac{N/m}{K}$$

where  $P$  is the partial pressure of ammonia (atm),  $N$  the mols of ammonia in the system,  $m$  the mols of hydrazine in the system, and  $K$  the equilibrium constant (0.0455 at 316 K) [1638]. If the test measures the effect of catalytic metal surfaces, the rate of gas evolution can be normalized by the wetted surface area of the metal coupon. If a galvanic couple is tested, the surface area by which the gas evolution is normalized is the sum of both coupons (although only one of them may be the culprit). If the vial does not contain a sample coupon and gas evolution occurs as a homogeneous hydrazine decomposition reaction (ignoring contribution from the glass), then the rate of gas evolution can be normalized by the volume of hydrazine in the test. The contribution of vapor-phase or homogeneous decomposition to the overall decomposition can be isolated by repeating identical tests with varying degrees of filling the test vessel. Tests conducted in a 32-L titanium tank filled to 12, 30, and 90% of its capacity with liquid hydrazine showed that the straight line did not intercept the origin of the axes at zero but had a positive intercept for the tank with zero percent liquid hydrazine [1158]. The surface of the vapor-phase titanium was never truly dry but was wet with condensate most of the time, and the surface-normalized rate of decomposition was independent of the degree of filling.

It is important that all hydrazine material compatibility tests be done with concurrent controls with vials that contain only hydrazine and no coupon. Sometimes the rate of gas evolution of the control is deducted from that of a test coupon before the gas evolution is normalized by the wetted surface area.

#### 5.2.1.2 Identification of Evolved Gases

Theoretically, the products of hydrazine decomposition that are responsible for unwanted pressure buildup during storage are nitrogen, ammonia, and hydrogen. Under the conditions of slow decomposition in the liquid phase (Section 4.4), mainly nitrogen and ammonia and only a trace of hydrogen are formed. At room temperature and sea-level pressures, most of the ammonia will stay in solution in the hydrazine and not contribute to the pressure in the ullage. One would have to evacuate the sample

and pump off the ammonia to obtain a complete ammonia analysis. Gas evolution rates reported by different authors often differ because the ammonia partial pressure is included or omitted, depending on the operating conditions of the test. Tests that start out at vacuum will include the ammonia in the gas evolution calculation. Other tests that start out at 1 bar and increase in pressure from there will leave most of the ammonia dissolved in the liquid. The composition of the evolved gas after terminating long-term compatibility tests has been analyzed by several investigators, but such an analysis is not routinely performed.

In one series of 51 material compatibility tests with hydrazine, the mol ratio of nitrogen to hydrogen in the non-condensable portion of the gas phase was analyzed by mass spectrometry and ranged from 12 to 57 [1647]. In a similar test with 76%  $\text{N}_2\text{H}_4$ /24%  $\text{N}_2\text{H}_5\text{NO}_3$ , the ratio ranged from 5 to 28. Mixtures of hydrazine or water with hydrazinium nitrate may also evolve hydrogen azide.

Sometimes one can make an approximate statement about the likely composition of the gas evolved at the end of the experiment by cooling the sample in increments to 273, 240, and 80 K (fractional condensation, gradually condensing ammonia, then nitrogen) and measuring the pressure at each temperature.

Only 1% by volume hydrogen was found in the vapor space of hydrazine material compatibility tests using different test setups [1158]. As shown in Appendix A of that paper, the pressure increase measured in samples starting at atmospheric pressure can be corrected for the dissolved ammonia.

### 5.3 Compatibility of Hydrazine with Structural Metals

As already mentioned, it has become difficult to quickly qualify materials for use with hydrazine during long-term deep-space missions lasting up to 10 or 20 years. Besides accelerating corrosion rates by superimposed electric potentials as described in one of the preceding sections, one can also extrapolate from short-term data obtained by radioisotope tracer methods [1681–1685]. So far, both methods have been applied to metals only. Using radioactive Type 304 corrosion-resistant steel and liquid hydrazine yielded data about the metal uptake by hydrazine that heretofore had never been generated. The data showed a continual increase in the concentrations of iron and chromium as a function of time over a period of 7 months. The concentrations of these metals as a function of surface area at constant time were not as expected, however.

A summary of literature references dealing with metal compatibility tests with hydrazine, arranged by type of metal and type of test, is available in [1686]. It is very difficult to condense this much information into a single table. Individual metals are discussed in subsequent paragraphs in alphabetical order, not necessarily in the sequence of preference for tankage or valve materials. Many of the reports referenced here deal with more than one propellant in addition to hydrazine. Sometimes the same

report contains valuable information on methylhydrazines, which constitute less of a metallic material compatibility problem than hydrazine itself.

Incompatibility of metals with hydrazine can be caused by either catalytic decomposition of hydrazine on the metal surface or by chemical reaction of hydrazine with the metal. Chemical reactions will leave the metal pockmarked with corrosion pits, oxide films may form on the surface and subsequently flake off, and leached metals will contaminate the hydrazine.

Besides the planned duration of a mission, the wetted surface area also determines whether or not a metal will be acceptable. The rate of gas evolution in hydrazine is generally proportional to the wetted surface area, indicating a mechanism of heterogeneous catalysis as opposed to homogeneous catalysis (often the result of dissolved contaminants), in which case the gas evolution would be proportional to the volume of liquid in the tank. If a component that has to be made of a metal of marginal compatibility is only exposing a small surface area, such as in the ram of a pyro valve or the valve seat of a hard seat valve, the material may be acceptable in spite of a high rate of gas evolution when immersed in hydrazine at elevated temperatures. If the wetted surface area is as large as the tank wall surface or even the wire mesh in a surface tension propellant management device (PMD) or a micron-rated filter, then extreme demands are made for low rates of gas evolution. One and the same metal may be acceptable in one location but not in another.

Low rates of gas formation are important in designing a hydrazine system. Besides concern about overpressurizing the tank or slugs of liquid trapped between two valves, there is also concern about bubbles trapped in the propellant line, which may be hot spots when compressed adiabatically. Thrusters firing in pairs might throw the spacecraft into a wild spin if only one of the two ingests a bubble and the other does not. Bubbles passing through the gas generator of hydrazine arcjets may cause the arc to extinguish. For these reasons, the rate of gas evolution must be kept at a minimum by selecting only materials that are fully compatible with hydrazine.

Quite often data may be available for one of the three propellant hydrazines, but not for the hydrazine of interest. To a limited extent, it is possible to extrapolate metal compatibility data from one hydrazine to another. For metallic materials, the extrapolation is easier than for non-metals. Metals found to be compatible with hydrazine will most likely also be compatible with MMH and UDMH. Similarly, metals found to be compatible with MMH will most likely also be compatible with UDMH. Polymeric materials are more likely to swell in UDMH than in MMH or hydrazine.

### 5.3.1 Compatibility of Aluminum Alloys with Hydrazine

Aluminum will frequently be preferred for the design of spacecraft and service with hydrazine because it is economical to obtain and easy to machine. Unfortunately, several aluminum alloys are incompatible with anhydrous hydrazine, and *none* of the aluminum alloys can be used with hydrazine hydrate. The addition of water to alu-

minum samples in hydrazine or the use of impure hydrazine results in rapid loss of the protective oxide layer, and gassing ensues [1687]. When water was accidentally allowed to enter drums with aluminized drums, the drums exploded. Threads on aluminum drum closure plugs that are wetted by hydrazine on one side and exposed to ambient atmospheric moisture on the other side will gradually corrode. There was a short period in the last century when hydrazine was shipped in aluminum drums, but this practice was soon discontinued.

Aluminum bomblets made from Al-1100 and Al-6061-T6 had to be prematurely removed from a material compatibility test with MIL-SPEC hydrazine at 408 K (275 °F) [1678, 1679]. The pressure in the Al-1100 bomblet exceeded 1.4 MPa (200 psig) in less than 64 h, and the gas evolution rate was  $4 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2}$ . The Al-6061-T6 bomblet fared only slightly better and had to be removed after two 64-h heating cycles. The gas evolution rate of aluminum in contact with hydrazine is an order of magnitude higher than that of titanium. All aluminum alloys showed evidence of corrosion. Hydrazine off-loaded from the bomblet was visibly contaminated by a white gelatinous precipitate. Despite obvious signs of corrosion, the tensile strength of the two aluminum alloys was not affected after the relatively short duration of the test.

Aluminum cylinders containing 3.5–5.5 L of MIL-SPEC standard-grade hydrazine and made of Al-2014-T6 or Al-6061-T6 were used during a 2-month storage test [1688]. Different cleaning procedures (chem-milled, liquid-honed) did not affect the rate of pressure buildup. A slow pressure increase was noticeable only during the first half of the test. Although the appearance of the inside of the tanks had changed where it was exposed to liquid hydrazine, the relatively short tests revealed no gross incompatibility. Based on results from a 10-year compatibility test, aluminum alloys Al-6061-T6 and Al-2014-T6 were rated as acceptable but were restricted because of moderate corrosion and the formation of a surface film that flaked off. The film did not appear to catalyze propellant decomposition. If it flakes off, it may plug filters and valves. Following the small-scale tests, a flight-weight 1.48-m<sup>3</sup> (55-cu.ft.) aluminum tank made from Al-2014 was filled with 1169 kg (2580 lb) hydrazine and stored in a desert climate for 3.5 years. Several hydrazine samples were taken and analyzed during the storage tests. At the end of the storage test, the off-loaded hydrazine was test fired in an uncooled bipropellant rocket engine with NTO as the oxidizer.

The following aluminum alloys were rated acceptable for brief general service based on 7- to 90-d immersion tests [1636]: 2S, 2SO, 2SH, 3S, 3SH, 24ST, 52ST, 61ST, and 75ST. Other aluminum alloys can be used only for limited service: 40E, 43, and 716. The same rating was given for hydrazine hydrate service, which is somewhat surprising and very doubtful because most aluminum alloys react with all alkaline solutions, including hydrazine hydrate solutions. Aluminum alloys that contain zinc are most certainly not recommended in contact with hydrazine.

It is interesting to note that for a short period in the 1960s, Rocky Mountain Arsenal shipped anhydrous hydrazine in aluminum drums. It is not known why the use of aluminum drums for the transport and storage of hydrazine was discontinued. One



source commented that closure plug diameters of the aluminum drums were different from those in CRES drums. This difference required propellant transfer personnel to keep two sets of eductor tools, one for CRES drums and one for aluminum drums, which made it more difficult and made the aluminum drums less popular. Anhydrous hydrazine offered by the People's Republic of China in the late 1980s was to be shipped in aluminum drums holding 100 kg hydrazine.

As part of a composite overwrapped aluminum-lined propellant tank with aluminum PMD development effort, long-term compatibility and wettability testing with hydrazine was performed on Al-6061 and Al-2219 coupons fabricated and cleaned by conventional processes [1689, 1690]. Long-term compatibility was confirmed. However, the wettability of the conventionally cleaned aluminum as measured by contact angle produced higher than desired angles ( $> 30^\circ$ ) with excessive scatter. A cleaning or treatment process was developed to produce consistently low contact angles, i.e., good wettability.

### 5.3.2 Compatibility of Stainless Steels with Hydrazine

Stainless steels are usually subdivided into martensitic (e.g., CRES-440), ferritic (e.g., CRES-430F), and austenitic (e.g., CRES-304) steels. Sometimes the same numbers are carried with an AISI designation. The austenitic group is non-magnetic; the martensitic and ferritic groups (CRES-400 and 4000 series) are magnetic and therefore often used for armatures in solenoid valves, where they are also wetted by hydrazine. The 300-series stainless steels show in general good compatibility with hydrazine but often lack the strength for lightweight, flight-weight, thin-walled tanks that need to be pressurized. Precipitation-hardened age-hardenable (PH) steels have the strength and hardness required for many container applications but are not very compatible with hydrazine, mainly due to their molybdenum content. Despite this disadvantage, small components with only small wetted surface areas in valves have been made from PH steels. When in contact with air and moist hydrazine, these steels often rust and that makes things even worse.

Materials used in the construction of hydrazine hydrate manufacturing plants are mainly stainless steel. The first large plant constructed in the 1940s in Gersthofen, Germany, used V2A steel in most of the distillation columns. V4A steel was used in the salt separator and the lower portion of the concentrating distillation column.

In compatibility tests with bomblets manufactured from CRES-321 simulating a spacecraft sterilization process by six heating cycles to 408 K (275 °F) for 64 h each, the CRES-321 bomblet had to be removed after only three heating cycles because the pressure exceeded 1.37 MPa (200 psig) [1678, 1679]. The pressure rise data from the test indicated that 3% ullage volume at 408 K (275 °F) was enough to prevent excessive pressure buildup if titanium tanks are used. The gas evolution rates of CRES-321 were more than four times higher than those of Ti-6Al-4V, namely,  $2.1 \times 10^{-6}$  compared to  $3.5 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2}$ .

Based on the results of 10-year storage tests at 316 K (110 °F), CRES-302 and CRES-303 caused excessive pressure buildup. CRES-304L, CRES-308, and A-286 were thoroughly tested as tank materials for a long-term storage missile application [1159, 1691, 1692].

In high-temperature storage tests, three explosions were encountered with hydrazine in CRES-347 and PH15-7Mo stainless-steel tanks above 416 K (290 °F) [1693]. After 16 h of continued heating at 416 K (290 °F), an explosion occurred with  $N_2H_4$  in a CRES-347 stainless-steel tank, demolishing the oven and part of the building. Prior to this event, the pressure rise rate had been 179 kPa/h (26 psig/h). Subsequent investigation pointed to decomposition of  $N_2H_4$  in stainless-steel tank No. 2, which shattered, sending shrapnel at the other seven tanks, causing tank Nos. 1 and 4, which also contained hydrazine, to rupture. Other than slight decomposition, no such problems were encountered with UDMH in identical tanks at temperatures up to 422 K (300 °F). This would indicate that hydrazine is more reactive and less forgiving than UDMH.

CRES-303 was found to exhibit a high rate of gas evolution and iron leaching after 12 years in hydrazine at 316 K [1649]. In the same test series, CRES 17-7PH had a very high rate of gas evolution, and a welded bimetallic CRES-301/CRES-304 sample with a high rate of gas evolution was suspicious due to possible contaminants in the weld bead.

The rate of corrosion of CRES-304 and all other steels increases dramatically if hydrazine becomes contaminated by absorbed carbon dioxide. As long as the carbon dioxide pickup is carefully controlled (i.e., minimized), anhydrous hydrazine can be stored in CRES tanks in tactical or strategic rocket propulsion applications for more than 10 years (Section 6.8).

Cast iron, whether gray cast or ductile or nodular, and all AISI 1000-series carbon steels cannot be used for anhydrous hydrazine or hydrazine solutions.

CRES-304 does not normally contain molybdenum. CFR49 § 173.276(a) (4) and (6) prohibits the transportation of hydrazine in a tank car made of steel that contains more than 0.5% Mo. The rationale for this restriction is not well documented. Although alloys like AM350 (3.25% Mo, 5% Ni, 17% Cr) and AM355 (3.25% Mo, 5% Ni, 16% Cr) would never be used to make tank cars, they have been used for components in hydrazine systems. CRES-316 with 3% Mo is widely used for valve components and has been used in ground support equipment (fuel carts, 4BW cylinders) without any undue effects. CRES-A286 has 1.25% Mo and is considered compatible with hydrazine [1162]. The adverse effect of molybdenum on hydrazine compatibility of steels may have been overestimated. Lawton, Moran and DiStefano [1650] stated that “*The presence of molybdenum in stainless steels to the 3% level is not necessarily deleterious, contrary to published reports,*” and continues, “*Alloys containing up to 3% Mo can be compatible with hydrazine for at least 13 years.*” Of course, it depends on which component of a propellant feed system is under consideration and how much surface area is wetted.

### 5.3.3 Compatibility of Titanium Alloys with Hydrazine

Titanium alloys combine good strength:weight ratios with nearly infinite duration compatibility with hydrazine, making them the preferred material for all long-term mission hydrazine tanks. Examination of titanium tanks after numerous extended storage tests with hydrazine has not revealed any signs of corrosive attack [1694–1697].

Chemically pure titanium may show good material compatibility but lacks the strength of alloys like Ti-6Al-4V. Different grades of so-called chemically pure titanium differ by the amount of iron allowed (which has a pronounced effect on hydrazine compatibility). Chemically pure titanium may be used in locations where maximum strength is not required or where malleability is desired, as in crimped joints of PMDs or in crushable seals.

One of the very early material compatibility reports erred in its conclusion that Ti-6Al-4V was not compatible with hydrazine [1647]. It is not known what caused a Ti-6Al-4V sample coated with Apiezon-L to behave poorly. The early SRI program may have had unrecognized amounts of residual halogenated cleaning solvents included in the sealed ampoules.

Unaged welds in Ti-6Al-4V of normal interstitial content are extremely susceptible to sustained-load crack growth (SLCG), in particular in the presence of chloride contamination [1698–1700]. Aging both the weld itself and the heat-affected zone for 4 h at 783 K reduces susceptibility to SLCG. Fracture mechanics design curves of crack growth threshold stress intensity vs. temperature are generated from 313 to 344 K (40 to 71 °C).

Titanium-6Al-4V is not sufficiently ductile to be drawn. The machining of tank hemispheres to final shape is a very costly operation. As opposed to Ti-6Al-4V,  $\beta$ -titanium has excellent formability, and conventional hydroform equipment can be used to make deep-drawn tank shells to near net shape. A more ductile alloy, Ti-15V-3Cr-3Al-3Sn, became available in the 1970s and now offers a significant cost and weight reduction in flight-weight titanium tanks for hydrazine or MMH because it can be drawn [1701–1703].

A large amount of information exists on the attack of methanol on titanium under various conditions that may cause hydrogen embrittlement. Care must be taken in selecting cleaning agents for titanium to make sure that they do not contain methanol. Hydrazine is not likely to contain methanol as a contaminant, and hydrazine/methanol blends have rarely been used as propellants. See also [1704].

### 5.3.4 Bimetallic Specimen Corrosion in Hydrazine

The potential problems of galvanic corrosion in a good electrolyte such as hydrazine have frequently been overlooked. The JPL studies are particularly valuable because they included many bimetallic specimens either in isolated juxtaposition or in electrical contact with each other [1161, 1638, 1705]. Several of the bimetallic contact speci-

mens had to be pulled from the test chamber early because of excessive pressure rise, indicating the importance of this corrosion mechanism.

Weld beads of CRES-308 filler on CRES-301 tanks had a higher rate of gas evolution than the metals by themselves [1659, 1660]. Joints between titanium and stainless steel showed relatively high rates of pressure buildup [241]. The pressure buildup rates were higher by a factor of 20 than those of the metals by themselves. The use of bimetallic joints in propulsion systems performing long-duration missions was judged undesirable. Despite this controversy, the VOYAGER (MJS 77) propulsion systems did include transition tubes from the Ti-6Al-4V tank to CRES-304 tubing, apparently without ill effects on system performance. Such transition joints are now in routine use on many other spacecraft.

Aluminum Voi-Shan or similar soft seals are not suitable for sealing stainless-steel fittings for hydrazine service. Disassembly of threaded fittings revealed severe corrosion of aluminum seals in contact with stainless steel [1635]. Some of the damage may have occurred after most of the hydrazine was flushed out with water and the fittings were wet with alkaline water. Aluminum and stainless steel in hydrazine or Aerozine-50 form a galvanic element with accelerated corrosion [1706].

### 5.3.5 Metals Leaching into Hydrazine

Data on metals leached from 304 stainless steel into 15 mL MIL-SPEC propellant (standard) grade hydrazine at a surface : volume ratio of  $0.394 \text{ cm}^{-1}$  and (presumably) ambient temperature showed a linear relationship on a double-log graph (metal concentration vs. time). The amount of iron and chromium leached from a specimen of CRES-304 was determined by a radioactive tracer technique. The metal ion concentration increased from 0.05 ppm after 1 d to 30–60 ppm after 120 d [1635]. In the presence of carbazic acid in hydrazine, this rate can be many times higher [1638].

### 5.3.6 Stress Corrosion of Metals in Hydrazine

Most metal compatibility tests with hydrazines so far have been conducted with unstressed coupons under static conditions in stagnant fluids. Stress corrosion was not observed in pure hydrazine, and a few stress-corrosion-type failures that did occur have been blamed on contaminants. Stress corrosion cracking (SCC) is an insidious phenomenon difficult to detect in its incipient state. It is often caused in an innocuous environment by stresses derived from applied loads. Residual stresses from heat treatment, forming, extruding, rolling, and welding may aggravate the situation. Cracks in titanium alloys can propagate either between or across grain boundaries.

A more detailed investigation has shown that some metals are indeed susceptible to stress-corrosion crack growth in liquid hydrazines. Stainless steel 410, used as a tankage material in the DELTA 89 vehicle, showed stress-corrosion susceptibility with Aerozine-50 that was most likely contaminated with carbazic acid by the absorp-

tion of atmospheric carbon dioxide. In tests with the alloy AISI 4130, a high-strength, low-alloy material that was selected as a test material because it is known to be highly susceptible to stress corrosion in several fluids, hydrazine was the more active fluid causing stress corrosion [1707]. Although AISI 4130 is generally not recommended for anhydrous hydrazine service because it rusts too easily, it is compatible with MMH and UDMH, based on static compatibility test results. In addition to 4130, for which stress corrosion in contaminated hydrazines was not unexpected, several other alloys, stainless steel 410, titanium-6Al-4V, aluminum-6061-T6, and Inconel 718, were also tested for stress-corrosion susceptibility. These alloys find more frequent use in components where they are wetted by hydrazine. The metal specimens were pre-cracked by fatiguing, and then a tapered plug was inserted to load the stressed area. The plug was not immersed in the liquid. The liquid level reached only to and above the pre-cracked area. With AISI 4130 no crack extension occurred in UDMH up to at least 2000 h, whereas MMH caused growth after 500 h and hydrazine, after about 60 h. Hydrazine was more active in causing stress corrosion than was MMH or UDMH. Methylhydrazine, in turn, was more active than UDMH. The aforementioned alloys can be ranked in the following order of decreasing susceptibility to stress corrosion: 4130 steel, CRES-410, Inconel 718, Ti-6Al-4V, and Al-6061-T6. Steel AISI 4130 failed after 60 and 20 h when propellant-grade hydrazine was spiked with 0.2 and 1% CO<sub>2</sub>, respectively, whereas it sustained the maximum stress intensity without failure for the entire duration of the 4000-h test if the hydrazine was pre-treated with barium oxide to remove carbazic acid. Similarly, water addition (5 or 30%) shortened the time to beginning failure from 50 to 40 and 10 h, respectively. The action of carbazic acid on stress propagation is very rapid. If a stressed sample is kept in BaO purified hydrazine where no crack propagation can be observed and the purified hydrazine is replaced with untreated hydrazine, crack growth will commence within a short period. No crack growth was observed with Ti-6Al-4V, but other investigators using different sample geometries have observed SCC of this material in Aerozine-50 [1708, 1709].

SLCG studies are closely related to SCC. In studies with Ti-6Al-4V coupons in hydrazine, using uniaxially loaded fracture mechanics specimens containing part-through cracks, an electric-discharge-machined notch was used to start the crack [1698–1700]. Pre-cracking before sustained-load testing was done by cyclically loading the notch in bending. Then three specimens were loaded in tandem in a standard creep testing machine. The applied stress intensity during sustained loading was varied by changing the width of the three simultaneously loaded specimens. The hydrazine was pressure-forced into the crack, and the samples were stressed and exposed for 24 h at 333, 339, and 344 K (140, 150, and 160 °F). Following hydrazine exposure, the samples were cleaned, dried, and marked, and the fracture was completed in air. The appearance of a crack formed in air was different from that of a crack formed while wet with hydrazine. The fracture surface was studied under a scanning electron microscope to identify the contribution of hydrazine exposure to crack growth. In this test, unaged weld metal in Ti-6Al-4V of

normal interstitial content was very susceptible to SLCG. One specimen was tested in helium, and only very little crack growth occurred. SLCG in a similar unaged weld sample in hydrazine under otherwise identical conditions occurred under much lower loads, showing that SLCG was actually caused by the hydrazine. Aging of both metal and heat-affected zone at 783 K for 4 h after welding removed this susceptibility completely. Unaged weld metal and heat-affected zones were less susceptible to crack growth in VIKING-grade hydrazine than in MIL-SPEC hydrazine, indicating a possible contribution by the trace contaminants usually found in commercial anhydrous hydrazine prior to 2004.

As a continuation of these studies, the same technique was used to study the effect of cleaning fluids, residual cleaning fluids, and chloride contamination in hydrazine on SLCG in Ti-6Al-4V [1699]. In this study, a forged titanium tank was cut into slabs, solution-treated at 1227 K for 1 h, water quenched, and then aged at 783 K for 4 h. Panels of aged forging material were welded together. Some of the welded specimens were aged in argon at 783 K for 4 h, but most of them were tested in the “as-welded” condition because actual flight tanks cannot be subjected to aging treatment without distortion. Monopropellant-grade hydrazine per MIL-26536C Amendment 1 was used for these tests. In one series, the hydrazine was deliberately contaminated with 90 ppm hydrogen chloride. The effect of chloride on SLCG is believed to be limited to Ti-6Al-4V sheet. Ti-6Al-4V was more susceptible to SLCG in isopropyl alcohol than in any of the hydrazine propellants. In addition to concern about SLCG in liquid hydrazines, there is also concern over SLCG in hydrazine decomposition products, such as moist ammonia.

#### **5.3.6.1 Effects of Acidic Contaminants**

Acidic impurities derived from nitric acid, carbon dioxide, or halogenated solvents in hydrazine and hydrazine fuels are said to cause material failure by hydrogen embrittlement. For instance, welds in type 410 steel failed in 3–10 d under load when exposed to contaminated Aerozine-50 but did not fail even after 30 d in much more corrosive nitrogen tetroxide. The addition of potassium hydroxide to hydrazine and hydrazine fuels is claimed to neutralize acidic contaminants and prevent hydrogen embrittlement [1698–1700].

#### **5.3.6.2 Effects of Carbon Dioxide/Carbazic Acid**

During a study of the kinetics of CRES-304L corrosion by hydrazine, it became apparent that the amount of carbazate/carbazic acid in the system has a pronounced effect on the rate of corrosion [1682–1685]. The CRES-304L coupons used for the tests were cut from the same manufacturing lot number as those used in JPL’s long-term storage test to allow some correlation between the two methods. First, CRES-304L coupons were immersed in a static test into hydrazine at 316.5 or 344.5 K with varying amounts of carbon dioxide added. The hydrazine contained less than 3 ppm CO<sub>2</sub> to start with and was doped with 13, 50, and 86 ppm CO<sub>2</sub> during the test. The hydrazine contained

1318 ppb Fe, 65 ppb Cr, 4 ppb Mn, and 161 ppb Ni at the beginning of the test. The increase in iron as measured by atomic absorption spectroscopy (AAS) was the most sensitive indicator of ongoing steel corrosion. For the first 30 d, the rate of iron buildup was roughly linear and independent of the amount of CO<sub>2</sub> added. After 30 d the rate of corrosion suddenly increased. The acceleration was proportional to the CO<sub>2</sub> content. It appears that during the first 30 d the steel was partially protected by an oxide layer. Once the passivation layer was removed, corrosion chemistry could act directly on the fresh metal surface. The leached metal content increase eventually leveled off after 160 d because the carbazic acid was depleted. It appeared that the CO<sub>2</sub> was not regenerated in this process. In some instances, at the highest CO<sub>2</sub> levels tested, leached iron concentrations approached 25 ppm and precipitates of iron carbazates formed in the hydrazine. Such precipitates would be devastating in a flight system where they might clog filters, valves, and capillary injector tubes and cause flow blockage of hydrazine propellant to the thrusters.

It would be desirable to develop a rate expression that provides the hydrazine user with a predictive tool with which the rate of pressure rise and metals leaching can be predicted as a function of CO<sub>2</sub> content, temperature, pre-treatment of the metal surface, ullage fraction, and surface: volume ratio. Due to the many variables involved, no such generally valid equation exists at this time. A first attempt resulted in a two-part rate expression, one for the first 30 d and one for days 31 through 160 [1684].

In an effort to minimize pressure buildup in CRES-304L tanks for a post-boost control system application, the effect of CO<sub>2</sub> contamination on pressure rise rate was subjected to a very thorough examination [1692]. A group of propellant storage assemblies (PSAs) was loaded with hydrazine doped with known amounts of CO<sub>2</sub> in a range of 30 to 200 ppm CO<sub>2</sub>. A good correlation between the pressure rise rate and the CO<sub>2</sub> concentration was demonstrated. The MIL-SPEC limit of 50 ppm CO<sub>2</sub> was deemed too high to achieve 10-year storability in CRES-304L.

Hydrazine decomposition in a 1.348-L CRES-304L stainless-steel tank with 11% ullage was strongly affected by the amount of carbon dioxide (carbazic acid) contained in or added to the hydrazine [1178, 1179]. Addition of up to 229 ppm CO<sub>2</sub> increased the gas evolution rate from 0.6 to 15.9 cm<sup>3</sup> STP/d at 333 K (60 °C). Five different CO<sub>2</sub> concentrations were tested, and the rate of gas evolution increased linearly with the amount of CO<sub>2</sub> added, but at least 20 ppm were required to obtain a noticeable effect. The amount of iron leached from the tank wall also increased from 1 to 18 ppm in the off-loaded hydrazine. The concentration of nickel or chromium leached at the same time increased also but reached only 2 ppm at the most. A distinction was made between labile and non-labile carbon dioxide, where the non-labile is complexed in metal carbazate salts and is no longer corrosive. It is important to re-emphasize that it is not the carbazate ion or its complexes that make hydrazine more corrosive toward metals, but the hydrazinium ion. The carbazate ion only provides a mechanism for instant removal of free metal ions by complexation, which is a driving force for additional metal removal and conversion to metal ions. This is explained by the law of

mass action as an equilibrium that is constantly shifted in one direction by the removal of one reactant (free metal ions).

In the early 1970s it was stated that “*Unless further specific data is available, it should be concluded that material compatibility ratings are not improved by using purified hydrazine*” [1635]. Surprising as this may be, this is probably still true, since materials that are not compatible with mono-grade hydrazine will most likely not be compatible with high-purity hydrazine either. This raises the question as to why one goes through the expense of using high-purity hydrazine for material compatibility testing when some answers can be obtained more economically with mono-grade hydrazine. The relative ranking of candidate metals remains the same, but if one wants to predict the pressure rise after 10 or 20 years in space, then the test will have to be done with high-purity hydrazine, and no lower-grade substitutes can be accepted.

During a thorough examination of the effect of doping hydrazine with 190 ppm CO<sub>2</sub> on the corrosion of Ti-6Al-4V in two heat treatment states, AM-350 and AM-355, at two different temperatures, 316 and 333 K, samples were withdrawn after 139, 182, 293, and 328 d of testing [1650]. Within experimental error, the two microcrystalline forms of Ti-6Al-4V behaved the same at both temperatures and regardless of whether or not the hydrazine was doped with CO<sub>2</sub>. The addition of CO<sub>2</sub> accelerated the decomposition of the hydrazine, but it did the same in the blanks, which did not contain any metal coupons. With AM-350 and AM-355, there was a pronounced effect of heat treatment on hydrazine compatibility as measured by gas evolution. AM-355 was subjected to the heat and chill treatment recommended by Carpenter Technology Corp. for maximum resistance to halide corrosion. In the case of hydrazine, the heat treatment made the AM-355 metal more susceptible than the as-received, untreated alloy. Either of the two AM alloys caused significantly more hydrazine decomposition and iron leaching if the hydrazine was doped with 190 ppm CO<sub>2</sub>. SEM examination of the metal surface after the test revealed pronounced attack at the grain boundaries. SEM-EDAX spot images showed possible depletion of Mo, Si, and O at the grain boundaries and pits.

In the search for clogging materials causing flow decay, the flow properties of hydrazine doped with CO<sub>2</sub>, ammonia, or water were measured by flowing hydrazine through a 0.127-mm (0.005-in.) capillary test section using an extrusion rheometer [1710]. The extrusion rheometer used during a previous program was modified to improve heat transfer characteristics. Although flow blockage occurred in two runs and flow decay occurred in another two runs, the cause was not identified, and no gelatinous material was observed.

### 5.3.6.3 Effects of Halogen-Containing Contaminants

In many cases it is not the chloride or fluoride ion as such, but the acidity accompanying it in the form of N<sub>2</sub>H<sub>5</sub>Cl or N<sub>2</sub>H<sub>5</sub>F that can cause severe corrosion of hydrazine systems. The results will differ if chloride is added as NaCl or N<sub>2</sub>H<sub>5</sub>Cl. Hydrazine that has become contaminated by Freon-TF (a cleaning solvent) or Freon-13B1 (used as a pressurant) will attack stainless steels and braze alloys [1711]. Freon-13B1 was



at one time used as a pressurant fluid to expel hydrazine from a positive expulsion tank with a stainless-steel diaphragm, but the metal diaphragm may have leaked, resulting in hydrazine contamination. In another case, Freon-13B1 was considered as a pressurant for hydrazine in an AF-E-332 bladder tank, but the Freon had high permeability through the elastomer and would have saturated the propellant with Freon. The effects of Freon-13B1 on catalyst survival were not tested. It is assumed that the halogenide contamination would have been disastrous on the catalyst activity and durability. Freon-TF is a more deleterious contaminant than Freon-13B1. Freon-TF, even in trace amounts of contamination in hydrazine, increased the rate of gas evolution from hydrazine in contact with CRES-304L at 298 K by a factor of six. Contamination by 0.033 mass-% Freon-13B1 increased the rate of gas evolution of CRES-304L at 298 K by a factor of eight based on 100 h of exposure and by a factor of 5.5 based on 500 h of exposure. The corresponding factors for CRES-308 were 55 and 25.6, and for the bimetallic braze joint they were 734 and 199. Both CRES-304 and Au-Ni braze resisted the Freon-contaminated hydrazine better than did CRES-308 and Cu braze.

Chloride and fluoride resulting from residual CFC-113 (Freon-TF from a cleaning process) that was accidentally not removed when the ampoules were loaded with hydrazine accelerated the corrosion of many metal specimens tested at JPL [1160, 1638, 1649] and rendered some of the test results useless or dubious. It is possible to study the effect of halides on metals corrosion in hydrazine by sorting the results by halide concentration and plotting the halide concentration against parameters of corrosion (metals leaching, gas evolution, hydrazine decomposition).

The effect chloride ion at up to 100 ppm has on SCC tests of Al-2014-T6, CRES-304L, and Ti-6Al-4V in UDMH will be discussed in the chapter "Dimethylhydrazines." Many titanium alloys in other fluids are sensitive to chloride contaminations on the order of 1 ppm.

### 5.3.7 Compatibility of Metals with Hydrazine Solutions

It may be difficult enough to find structural metals that are compatible with hydrazine and hydrazine mixtures, but the problem becomes much more difficult if one must find materials for hydrazine solutions, such as hydrazinium nitrate (HN) in hydrazine.

**Binary Blends.** Based on the Brønsted acid theory, a solution of HN in hydrazine is tantamount to a solution of nitric acid in water, and the corrosion problems are accordingly aggravating. Early compatibility tests with three hydrazine/HN/water mixtures (and hydrazine as a baseline) showed very rapidly that wrought iron, cast iron, Armco iron, brass, copper, monel, cobalt, molybdenum, manganese, stainless steel 18-8, lead, zinc, nickel, and magnesium are not suitable for HN service [242]. Aluminum and titanium showed no apparent reaction.

For a 24% HN/1% H<sub>2</sub>O/75% N<sub>2</sub>H<sub>4</sub> propellant, stainless steels are not acceptable because of rapid corrosion and gas evolution. Some of the glass sample ampoules con-

**Table 67:** Gas evolution rates of metals in HPB-2400 propellant at 313 K.

| Specimen No                           | Days | Material name             | Configuration   | Gassing rate normalized, $\text{cm}^3 \text{d}^{-1} \text{cm}^{-2}$ | $\text{N}_2 + \text{H}_2$ gas rate, $\text{cm}^3 \text{d}^{-1} \text{cm}^{-2}$ |
|---------------------------------------|------|---------------------------|-----------------|---------------------------------------------------------------------|--------------------------------------------------------------------------------|
| 0218                                  | 949  | Ti-5Al-2.5Sn-ELI          | 1/4" × 3" rod   | $2.08 \times 10^3$                                                  |                                                                                |
| 0209                                  | 949  | Ti-6Al-4V-ELI             | 1/4" × 3" rod   | $2.35 \times 10^3$                                                  |                                                                                |
| 0213B                                 | 949  | Al-6061-T6/Ti-6Al-4V      | 1/4" × 3" rods  | $2.54 \times 10^3$                                                  |                                                                                |
| 0221                                  | 949  | Ti-6Al-6V-2Sn<br>annealed | 1/4" × 3" rod   | $2.85 \times 10^3$                                                  |                                                                                |
| 0212                                  | 949  | Ti-6Al-4V                 | 1/4" × 3" rod   | $4.22 \times 10^3$                                                  |                                                                                |
| 0042                                  | 1550 | Al-6061-T6                | 1/4" × 3" rod   | $6.11 \times 10^3$                                                  |                                                                                |
| 0215                                  | 949  | Ti-5Al-2.5Sn              | 1/4" × 3" rod   | $7.44 \times 10^3$                                                  |                                                                                |
| 1961                                  | 5286 | Ti-6Al-4V                 | Slug, stressed  |                                                                     | $2.32 \times 10^5$                                                             |
| 2007                                  | 5286 | Al-6061                   | Weld            |                                                                     | $2.64 \times 10^5$                                                             |
| 2011                                  | 5286 | Ti-6Al-4V                 | Weld            |                                                                     | $4.42 \times 10^5$                                                             |
| 1953                                  | 5286 | Al-6061                   | Slug, stressed  |                                                                     | $5.51 \times 10^4$                                                             |
| 1963                                  | 5286 | Ti-6Al-4V                 | Slug, stressed  |                                                                     | $1.28 \times 10^3$                                                             |
| 1871                                  | 4513 | Ti-6Al-4V                 | Slug            |                                                                     | $2.10 \times 10^3$                                                             |
| For comparison: Hydrazine, Mono Grade |      |                           |                 |                                                                     |                                                                                |
| 4004                                  | 807  | CRES-304L                 | ACS Diaphragm   | $1.70 \times 10^4$                                                  | $2.48 \times 10^5$                                                             |
| 4071                                  | 308  | CRES-17-4PH               | Valve, TIG weld | $3.53 \times 10^4$                                                  | $3.53 \times 10^5$                                                             |
| 4075                                  | 245  | CRES- 347                 | Bar Stock       | $8.00 \times 10^4$                                                  | $2.05 \times 10^4$                                                             |
| 4046                                  | 245  | CRES-A286                 | Tank Shell      | $1.60 \times 10^3$                                                  | $7.07 \times 10^4$                                                             |

<sup>a</sup> Data source: [1648]

taining stainless steels ruptured during the first few months of the test, whereas other ampoules with titanium and aluminum alloys remained in test for up to 14.5 years at 316 K [1648]. Aluminum-6061-T6 is considered only marginally acceptable. Even if the pressure rise with aluminum alloys can be tolerated, the formation of aluminum oxide flakes and sludge may clog surface tension screens and filters or cause valves to leak **internally** if it prevents complete closure of the valve. Titanium-6Al-4V was rated provisionally acceptable [1160, 1638] but is still the best choice of all other candidate metals [1648]. This test series is very valuable because it systematically examined galvanic couples of dissimilar metals. Gas evolution rates measured on a few samples are summarized in Table 67 in comparison to those observed with hydrazine by itself.

For many published samples the final pressure in the ampoules is not available because they may have ruptured before a final measurement could be taken. In these cases, the short duration of the test, often less than 100 d, was an indication of incompatibility. In other cases, a pronounced weight loss (up to 9%) of the sample caused by corrosion and metal leaching is proof of incompatibility. The data in Table 67 above were extracted from a spreadsheet of 71 samples with HPB-2400 or HPB-2401. There are two columns of gas evolution rates normalized by the wetted surface area: The first

was calculated from the pressure reading and the known ullage volume, the second is based on actual measurement of nitrogen and hydrogen gas volume collected in a vacuum system when opening the ampoule and is considered more accurate. Data in the first column for 22 samples opened after 949 to 1550 d all ranged from  $1.3 \times 10^{-3}$  to  $9.7 \times 10^{-3} \text{ cm}^3 \text{ d}^{-1} \text{ cm}^{-2}$ , and only 7 of those are included here. Some of the pressure data were corrected for the vapor pressure of the propellant.

Another freezing-point depressant evaluated for hydrazine was hydrazinium azide. Rapid discoloration and pressure buildup were observed with hydrazine/hydrazinium azide mixtures in any type of steel, stainless or not. Moderate rates of gas evolution were measured for three such mixtures in aluminum-6061-T6 or titanium-6Al-4V [141, 142], although the rates were still higher than for neat hydrazine. Hydrazinium azide was also an ingredient in MHF-8. MHF-8 consisted of 72%  $\text{N}_2\text{H}_4$ , 19%  $\text{N}_5\text{H}_5$ , and approximately 9%  $\text{NH}_3$  [1712]. When MHF-8 was in contact with stainless steel, the solution turned pink within 8 h, which is an indication of leached metals. The rate of gas evolution of stainless-steel coupons in MHF-8 was also prohibitively high. Passivating treatments of CRES and protective treatments did not give the desired results.

**Ternary Blends.** It is difficult enough to find compatible materials for binary hydrazine propellants such as HPB-2400, but the task becomes even more difficult when metals that are resistant to ternary hydrazine/hydrazinium nitrate/water blends must be identified. Based on coupon and tank tests, it was found that Ti-6Al-4V and Ti-15V-3Al-3Cr-3Sn are suitable for such low-freezing propellant blends. Electropolished Al-1100 is marginally usable, but dissimilar Al alloys in contact, such as Al-1100/Al-2219, cannot be used [1680]. Tests at four different temperatures were used to derive an activation energy of the gas evolution process. This allows one to extrapolate to other propellant storage temperatures.

#### 5.3.7.1 Hydrogen Embrittlement of Metals in Hydrazine

Many metals, in particular refractory metals such as tantalum and zirconium, are susceptible to hydrogen embrittlement. Hydrazine is a reducing medium and likely to give off hydrogen under various conditions. Slow decomposition of liquid hydrazine during storage does not produce much hydrogen, but the small amount may be enough to embrittle metal [1713]. When excess hydrazine is used as a boiler feedwater additive for the removal of oxygen, it may decompose at the high temperatures and under the influence of radiation in the boiler, forming hydrogen gas and embrittling metals in the heat exchanger system, in particular in nuclear power plants.

#### 5.3.7.2 Compatibility of Hydrazine with Welding and Brazing Materials

Whenever possible, joints in tanks, lines, and components are electron beam welded or argon arc welded to avoid introducing additional dissimilar metals from welding rods. Frequently the size of the assembly or the delicacy of adjacent components does not allow welding.

Final assembly of hydrazine tanks, lines, valves, and thrusters in the spacecraft is then achieved by brazing, where a connection can be heated very rapidly by induction coils. Although only a small area is exposed to hydrazine where the braze compound wicks into the joint, compatibility of braze alloys must be assured before selecting such materials for hydrazine service.

Hydrazine decomposition caused by brazing alloys and their constituents was measured by capturing and analyzing the ammonia formed [1714]. The compatibility of hydrazine or Aerozine-50 with either the 82Au-18Ni alloy or the pure metals (Au or Ni) was equally poor as soon as the temperature exceeded 430 K. The amount of ammonia evolved was taken as the indication of hydrazine decomposition at 330 K. It would have been better to use the amount of nitrogen formed because some of the ammonia may remain dissolved in the propellant. A gold-nickel brazing alloy was blamed for a high rate of gas evolution observed with a 308L stiffening wire brazed to a CRES-304L diaphragm liner [1162]. Exposure of gold-based brazing alloys to Aerozine-50 at 339 K (150 °F) for 48 h did not result in leaching of excessive amounts of gold, nickel, or palladium [1715]. Pressure rise in a manometric vessel was not excessive, even in samples deliberately contaminated with 0.5 mass-% chloride ion or 0.5% ammonia.

The rate of gas evolution (normalized by the wetted surface area) from a Nioro (82Au/18Ni) braze joint in hydrazine at 322 K (120 °F) was two to three orders of magnitude higher than the rate from CRES-304 [1659, 1660]. If hydrazine, MMH, or UDMH becomes accidentally contaminated with halocarbons, the corrosion of braze joints and the resulting rate of gas evolution will be extremely bad [1060, 1711].

Sometimes the design requires very dissimilar metals to be joined by brazing. Inconel 600 has been vacuum-brazed to Ti-6Al-4V using a Ag-9Ga-9Pd braze alloy intended for a hydrazine pump [1716].

It should be noted that while nowadays one would be concerned about bringing hydrazine or hydrazine hydrate into contact with silver solder, the discoverer of hydrazine, Th. Curtius, was successful in distilling hydrazine hydrate in an apparatus where the retort and the condenser were made entirely of silver [1717].

## 5.4 Compatibility of Non-Metals with Hydrazine

Just as hydrazine and hydrazine derivatives may attack metals, hydrazines may also alter chemical bonds and mechanical properties of organic polymers. Non-metallic materials are needed as gaskets, seals, containment bladders, diaphragms, and lubricants. In addition, attempts have been made to replace metals with lighter-weight engineering thermoplastics in support structures and tank walls where they would be in constant contact with the hydrazines. It has been very difficult to find totally compatible materials for each of these applications. A summary of literature references dealing with non-metallic material compatibility tests with hydrazine, arranged by type of material and type of test, is available in [1718].

Quite often material compatibility data may be available for one of the three propellant hydrazines, but not for the hydrazine of interest. To a limited extent, it is possible to extrapolate from compatibility data for one hydrazine to another. For organic materials, the extrapolation is more difficult than for metals. Polymers found to be compatible with UDMH will most likely also be compatible with MMH and hydrazine; similarly, polymers found to be compatible with MMH will most likely also be compatible with hydrazine, but polymers known to be compatible with hydrazine may dissolve or swell in either MMH or UDMH. All polymers have some permeability for hydrazine(s). Hydrazine that had diffused into polymers and decomposed before exiting on the other side may cause the polymer to blister by forming nitrogen bubbles. See also [1719, 1720].

### 5.4.1 Gasket and Seal Materials for Hydrazine Service

#### 5.4.1.1 O-Rings

It may be difficult enough to find elastomers that satisfy requirements for hydrazine service at ambient temperatures. However, if the entire spacecraft is to be heat sterilized prior being loaded with hydrazine and sent off to another planet, material selection becomes a formidable problem [1678, 1679]. For repeated cycles at 408 K (275 °F), FEP Teflon with 20% glass filler and TFE Teflon O-ring seals have performed satisfactorily. Plasticized Kel-F has been specifically prohibited for use with hydrazine tank cars (MIL-R-87992, 29 Nov 1989).

One of the most widely used O-ring material is Parker Compound EPR 515-8 (or, as it is now called, E515-80). Besides carbon filler, it also contains zinc oxide and sulfur compounds. This material maintains its lubricity in hydrazine. However, because carbon was used in formulating this rubber, the rate of gas evolution was high [1162]. In most cases the O-rings do not contribute much surface area to the overall system and the gassing contribution is negligible. The O-rings are usually lubricated with Apiezon-L, a hydrocarbon grease, to avoid gouging them while they are slipped over valve nipples and adapters. In a 14-d immersion test evaluating four different O-ring materials in hydrazine at room temperature, Parker EPR XE2773-01 showed the least weight change and swelling and maintained its Duro hardness throughout the test. Parker EPR E515-80 O-rings were a close second. Parker Silicone S604-70 was swollen and did not meet acceptance criteria. E515-8 O-rings in hydrazine were tested at 333 and 353 K, and samples were taken after 69, 113, and 161 d [1721]. Changes in mechanical properties were evident at and above 353 K.

Viton O-rings in the oil seal cavity of the Space Shuttle Space Transportation System (STS) auxiliary power unit (APU) became embrittled when hydrazine leaked into the cavity. To correct this problem, they were replaced by Kalrez 1050 O-rings. Kalrez 1050 is a perfluoroelastomer and contains carbon black filler. A carbon-free variety called Kalrez 1045 is available and used for N<sub>2</sub>O<sub>4</sub> oxidizer systems. Kalrez 1045 O-rings caused exothermic reactions when in contact with hydrazine [1722]. Kalrez is often

used for MMH in bipropellant systems but is not suitable for hydrazine in monopropellant systems. See also [1723, 1724].

#### 5.4.1.2 Soft Valve Seats

Stillman rubber SR721-P80 and SR724-90, candidates for valve seat materials, were alternately exposed to hydrazine and air, water, or carbon dioxide [1725, 1726]. Earlier studies had shown that bladder elastomers after long immersion in hydrazine and drying would appear to become wet again on standing in air overnight, even though the specimens had been wiped dry the previous day. IR analysis proved the presence of carbazic acid in “sweat” droplets. During the repeated immersion/air exposure cycles with the two rubber samples, it was shown that the weight gain of SR724 leveled off at 3% by weight while SR721 continued to gain weight, up to 26% after 40 cycles. It is therefore undesirable to expose flight hardware to hydrazine and then to air prior to the actual launch. Similar observations were made with expulsion diaphragms for hydrazine tanks [1727].

A new rubber compound intended primarily for use as hydrazine thruster valve seats but adaptable to other engineering requirements was based on ethylene/propylene rubber reinforced with HYSTL pre-polymer resins and co-cured with peroxide [1728]. Compatibility tests in elevated-temperature hydrazine were used at the beginning of the program to identify compounding ingredients that did not react significantly with the propellant. Ingredients identified as hydrazine-compatible were then prepared in about 40 formulations and evaluated competitively in laboratory tests against a state-of-the-art hydrazine thruster seat compound in use on military and commercial satellites in the 1960s. These laboratory screening tests included measurements of swelling, compression set, and retention of properties following exposure to the propellant and to isopropyl alcohol valve cleaning fluid. At the conclusion of the program, the best compound was selected and designated AF-E-102.

Soft valve seat elastomers like AF-E-332 and AF-E-411 can absorb hydrazine, which is not totally removed from valve seats following an acceptance test procedure (ATP) firing at the thruster manufacturer. Subsequent exposure to air and carbon dioxide allows carbazates to form in and on the valve seat, where they will corrode adjacent metals. The time elapsed between breaking the vacuum in a vacuum tank after the ATP firing and flushing the valve with water in a clean room should be limited and controlled by process specification and inspection points. Some test specifications limit this time interval of air exposure to less than 30 min.

A variety of elastomers intended as valve seat materials for a new design Space Shuttle SRB APU Gas Generator Valve Module (GGVM) were tested, including polyether ether ketone (PEEK), Tefzel HT2004, various grades of IM Ryton (A, B, R-7, R-10), CM-X (hexafluoroisobutylene and vinylidene fluoride copolymer), IPC GR 5304, and TR-88 (the latter two are PPS and PTFE blends). Compressive creep/deformation tests in air and in hydrazine at room temperature and 366 K showed that hydrazine did not degrade the compression strength properties of Ryton. Ryton is

a polyphenylene sulfide (PPS) material. The GGVM valve used compression molded Tefzel HT2004 reinforced with 25% short glass fiber for a long time, but it cold flows. One grade of Tefzel was shown to catalyze the decomposition of hydrazine at 366 K [1722].

In the 1960s and early 1970s, some valves used a valve seat material called AF-E-102, until a better valve seat material became available in the form of AF-E-411. The development of AF-E-411 was a major breakthrough in the development of hydrazine-compatible elastomers. It was initially intended as an O-ring material but now has found its main application as a soft valve seat material. Its predecessor was AF-E-102, which had been developed under a NASA contract. The development of elastomers for soft valve seats often went hand in hand with the development of elastomers for propellant expulsion bladders and diaphragms [1729, 1730].

AF-E-102 had flown in O-rings and valves on a small number of satellites [1731–1733], before it was made obsolete by the improved AF-E-411 [1728, 1734]. AF-E-411 is a polymerized peroxide-cured ethylene propylene diene terpolymer (EPDM).

In parallel, valve seat and gasket materials were developed for use in NTO and Aerozine-50. One of the materials developed for this oxidizer application was AF-E-124D [1734]. AF-E-124D is a terpolymer of tetrafluoroethylene, perfluoromethyl vinyl ether, and perfluorophenyl vinyl ether, but it is not typically used for hydrazine.

AF-E-411 has been tested for compatibility with hydrazine at temperatures up to 477 K (400 °F) in a liquid-phase exothermicity test [1735, 1736]. This study was prompted by concern about the reactivity of AF-E-411 in the Space Shuttle Auxiliary Power Unit Gas Generator (APUGG) GGVM under hot restart conditions. Compatibility was tested in a liquid-phase exothermicity test like the one described in Section 5.2.1. A static immersion test was used to determine changes in tensile strength, elongation, hardness, weight, and dimensions. Samples of EPDM AF-E-411 were immersed in hydrazine for 30 d at 339 and 422 K (150 and 300 °F). There was no significant change in tensile strength, but increases in elongation at ultimate tension of 20–22% were measured. Hardness decreased 2% after the 339-K exposure and increased 11% after the 422-K exposure. Weight or dimensions changed less than 2%. The thickness increased by 1% in one dimension. When measuring 1% unidimensional expansion, volume swelling must be at least on the order of 3% (see the following discussion on swelling).

A compression-deflection set of AFE-411 seals in thrust chamber valves (TCVs) on 20-N thrusters may have caused internal leakage during long-life tests. It was believed that the compression-deflection set was caused by long-term fatigue. Dry compression-deflection tests were performed for 90 d on seal pucks made of AF-E-411, held in a simulated plunger and orifice that tied down the seal pucks like those used in the 20-N TCVs [1737]. The plunger press force was simulated by two weights: one for simulating the plunger spring force only and another for the maximum upper side pressure of the propellant valve.

#### 5.4.1.3 Swelling of Valve Seat Materials

Elastomers that are to be used as seat materials for soft seat valves must meet reproducible (preferably low or zero) swelling requirements and demonstrate dimensional stability. If the material swells too much after being exposed to hydrazine, it may close off the flow passage and restrict the travel of the valve poppet. However, AF-E-411 seems to have satisfactory dimensional stability in hydrazine and has been widely used for valve seats. Development tests have shown that the swelling of AF-E-411 in hydrazine is nominally less than 3% by volume. Despite the minor swelling, some valves with AF-E-411 may have different gas leakage rates depending on the history of exposure of the soft seal to liquids. If it was recently exposed to IPA or hydrazine, the valve would not leak any gas. If the seal is allowed to dry out prior to flight, it may leak gas [1738]. Gas leakage tests on valves that are already installed in a plumbed system may give misleading results, rejecting valves for gas leakage that would work perfectly fine in hydrazine.

Immersion of AF-E-411 in Freon-TF or trichloroethylene for 14 d at room temperature followed by air drying for 7 d causes permanent damage and permanent swelling [1734]. Distilled water caused no swelling, and IPA caused only minor swelling (after air drying). It is important to know the swelling of AF-E-411 in water or IPA in the *wet* state. Some reports show swelling data for Aerozine-50, but not for neat hydrazine. In the Aerozine-50 propellant, the elastomer had swollen 2.9% on removal from the liquid, and dimensional change remained at +1.9% even after drying in air for 7 d.

One case of gross material incompatibility was observed when a soft seat valve seat made from ethylene propylene rubber (EPR) (Parker Compound E-515-8) swelled so badly as to prevent any flow through the valve when the armature was actuated [1739]. Other materials tested in valve seats include Teflon, AF-E-102, and tungsten carbide.

It is sometimes difficult to correlate gas leakage measured on the dry valve prior to the test and the liquid hydrazine leakage during the test. Attempts have been made to establish a correlation between liquid hydrazine and gaseous nitrogen leakage rates of solenoid latching valves [1738, 1740]. It is believed that AF-E-411 swells just a little in the presence of liquid hydrazine, IPA, or water and then contracts again during drying. There is some hysteresis such that the elastomer may not return to its original dimensions after a swelling/drying cycle. Valves that flow correctly during short-term exposure to hydrazine (as during an ATP firing) may not flow correctly after extended soaking in hydrazine because the valve seat has more time to swell and the clearance between the poppet and the seat has diminished. Less clearance allows less propellant flow. Because the AF-E-411 disk (“hockey puck”) is typically pushed into a cavity (with only a small hole to allow escape of air), swelling can occur in only one direction, toward the opposing metal cone-shaped opening. In the dry state, the valve may leak gas. In the wet state, it may flow less than a nominal amount of liquid after it has



swollen. It is suspected that insufficient understanding of swelling phenomena has resulted in

- Unnecessary rejection of as-received valves, based on dry gas leakage tests, which would have performed perfectly well for liquid service after the initial wetting period
- Valves built to much tighter tolerances to meet unrealistic gas leakage requirements, which are more likely to swell shut accidentally while in liquid hydrazine service

It was necessary to obtain more accurate dilatometric data on AF-E-411 during exposure to hydrazine. Initial data of this type were generated when AF-E-411 and AF-E-332 were first developed [1741], but no additional systematic dilatometric studies were performed (or at least they were not published). MIL-R-83412A (30 Jun 1977) specifies three types of elastomers for seals, bladders, and valve seats for hydrazine service. The specification limits compression set but does not specify maximum swelling tolerated. The formulation shown in MIL-R-83412A for Type III valve seat material does not include Teflon powder, but according to other sources, AF-E-411 does contain 5% Teflon. Table 70 lists nominal compositions of the most frequently used elastomers AF-E-332 and AF-E-411. Questions have been raised about the upper temperature limit to which Teflon in hydrazine can be heated without splitting off fluoride ions and causing corrosion of adjacent metal parts. The hydrazinolysis of perfluoro polymers like Teflon requires additional study.

#### **5.4.1.4 Decontamination of Valves Following Hydrazine Service**

There is a question about the amount of hydrazine retained in AF-E-411 seats if flight thrusters with their flight valves attached as one unit are acceptance tested and subsequently decontaminated. Small amounts of hydrazine may diffuse into the elastomer and may not be completely removed during the typical post-ATP decontamination. Although AF-E-411 swells less in hydrazine than any other valve soft seat material developed so far, the elastomer may swell sufficiently during ATP to cause different valve gas leakage response after the ATP test. Valves may pass the gas leakage test immediately after ATP but fail it after the valve seat has completely dried out and shrunk back to its original shape.

There is concern that hydrazine cannot be completely removed from valve seats in TCVs following ATP. Exposure to air will cause carbazate formation and zinc and calcium leaching similar to the problem observed with pre-tested hydrazine-soaked propellant expulsion diaphragms on some satellite reaction control system (RCS) tanks [1727].

#### **5.4.1.5 Other Problems and Precautions with Valve Seat Materials**

As-manufactured AF-E-411 may have oil oozing out of it that may cause valves to stick if they are not used soon after purchase. Attempts have been made to extract the oil

with a solvent. The elastomer expands in hydrocarbon solvents to twice its original size but returns to the original size after all solvent is removed.

AF-E-411 should not be exposed to hot dry air. This is a concern if solenoid valves, in particular latch valves, are inadvertently activated in the dry state prior to launch of a spacecraft. It was once common practice to check out the electric circuitry in assembled spacecraft by dry-cycling the valves. (This is a bad practice; in addition to the risk of overheating, some metal-to-metal sliding surfaces might gall in the dry state.) Some latch valves could reach 444 K in orbit if one coil is energized, or they might even heat to 533 K if both coils are inadvertently energized (if no propellant is flowing or this branch of the system is isolated). AF-E-411 should not be heated in air to above 344 K or in nitrogen above 380 K.

There is concern that heating Teflon-containing elastomers in hydrazine to above 422 K (300 °F) may hydrazinolyze the Teflon and result in the local formation of hydrofluoric acid and hydrazinium fluoride, which in turn would attack any steel (stainless or not) in the vicinity of the valve seat. Several fluorinated elastomers tested per NHB 8060.1C Test 15 showed significant increases of fluoride in the off-loaded hydrazine [1663, 1664].

#### 5.4.1.6 Graphite as Seal Material

The STS APU hydrazine and lubricant pumps used a graphite rotary seal. The seal part was machined to achieve ultimate dimensions only after exposure to hydrazine because it swells during hydrazine exposure [1742–1745]. Hydrazine was dropped to the fuel pump usually a few days prior to launch to allow the seal to achieve its proper dimensions before the unit was pressurized.

### 5.4.2 Polymers for Structural Components in Satellites

By way of elimination, materials known to be incompatible with hydrazines should also be listed here. Polyester polymers are *not* compatible with hydrazine. In fact, carboxyl groups in polyethyleneglycol terephthalate are routinely analyzed by hydrazinolysis because the reaction goes to completion quantitatively. Hydrazine has been patented as a solvent for removal and etching of polyimide films, which are otherwise very inert to all common solvents and thermally extremely resistant. Hydrazine hydrate reacts with polyvinyl chloride (PVC). The reaction products of hydrazine and PVC oxidize when exposed to air. Cellulose acetate, Nylon, Mylar, Saran, Silastic LS-53, Epon, and Tygon were listed among non-compatible elastomers for valves [1637]. Polyvinyl alcohol or Kel-F 500 dissolved in hydrazine in less than 2 h.

Cellulose acetate, polyester, polystyrene, polyvinylalcohol, or Saran are *not* compatible with hydrazine [1636]. Epoxy, ethyl cellulose, furan resin, Hycar, Kel-F, Lucite, melamine formaldehyde, Nylon, phenolic, Silastic, or Tygon are said to be only conditionally (short-term) compatible with hydrazine or hydrazine hydrate by some

sources, but who would believe them? Anyone who has seen Nylon dissolve in anhydrous hydrazine knows that it is not compatible in any conditions.

A two-volume report lists hydrazine compatibility data of 39 polymer samples at 313, 333, and 353 K [1746, 1747]. Terylene dissolved in hydrazine within a few minutes. Kapton polyimide film dissolved just as quickly. The following polymers were found to be incompatible with hydrazine: Nylon cloth embrittled after 30 d. Viton (polyhexafluoropropylene/vinylidene fluoride) expanded to twice the original size and blistered within less than a day. PVC turned yellow and brown within 6 d. After 29 d the hydrazine had become syrupy and contained large transparent crystals. Different grades of neoprene blistered and became embrittled. Acrylonitrile-butadiene (Hycar nitrile rubber) did not show immediate visual changes but became badly embrittled after 344 d. Likewise, styrene/butadiene rubber (SBR) had lost both tensile strength and elongation after 344 d; CNR nitroso rubber disintegrated within 4 d. Fluorel LCS 2160 (Dowty 2055) disintegrated within 10 min. Several silicone rubbers, including RTV 731 and Silastoseal B, did not survive hydrazine exposure. On all these materials, weight changes were recorded during the entire exposure (up to 130 d). Initially many materials gained weight from hydrazine absorption and swelled. After some time, the samples lost weight again as they began to disintegrate and dissolve in hydrazine. The following polymers were classified as compatible, and extensive mechanical data were gathered after hydrazine exposure for up to 1130 d: Parker EPR 515, EPR Dowty IM 1333, and silica filled-butyl rubber. Polyethylene and polypropylene are only conditionally acceptable. Polyethylene totally immersed in hydrazine did not change much over several years, but hydrazine stored in polyethylene bottles caused the plastic to blister.

A Mylar (polyethylene terephthalate) sensor disc was used as a leak detection device in a double-walled hydrazine tank. If the internal shell of a hydrazine tank had leaked, the Mylar would have dissolved and allowed movement of a spring-loaded magnet, which would have triggered a Reed switch on the outside of the tank and triggered an alarm.

The mechanical properties of polyethylene were unaffected by immersion in 64%  $\text{N}_2\text{H}_4$  (= HH100) for up to 90 d at up to 333 K [1748]. The hydrazine assay was unchanged, and there was no residue buildup in the hydrazine hydrate. Polypropylene was just as compatible, but PVC and nylon were attacked by hydrazine hydrate. However, 64%  $\text{N}_2\text{H}_4$  (= HH100) sold and shipped in polyethylene bottles in cardboard boxes was found to permeate the polymer and destroy the cardboard after years of storage on the shelf in an industrial building, narrowly avoiding ignition. HDPE (plastic bottles) will form blisters because hydrazine permeates into it, but gas does not diffuse out.

Occasionally hydrazine or MMH is spilled on the outside of a spacecraft during a fueling mishap. Material immersion/impingement tests for such short-term exposure have been conducted for many materials that ordinarily would not be exposed to hydrazine.

Molded parts made from thermoplastic resins can be manufactured in the near-net shape ultimate dimensions, which require no further machining, thus leading to cost savings. The trouble was that until recently, very little was known about the compatibility of thermoplastic resins with rocket propellants because many of these materials have become available only within the past four decades. Ten engineering thermoplastics were tested in anhydrous hydrazine for suitability in an Aerozine-50 application, as summarized in Table 68.

Polycyanurates formed by heating bisphenol-A monomers containing cyanate ( $-\text{OCN}$ ) groups are a new class of thermosetting polymers that can be worked into high-strength composites. These have higher toughness, reduced moisture absorption, and improved dimensional stability compared to conventional epoxy resins. They are now used for primary bus structures, tubes, struts, solar-array panels, and many other structural components in satellites such as MILSATCOM, AXAF, and CLEMENTINE. Spill tests with exposure times of 2 min. to 24 h indicated that polycyanurate resins and composites exposed to hydrazine will lose strength rapidly and become partially dissolved [1750]. The polycyanurate resins did not fare any better than a conventional epoxy resin that was also exposed to hydrazine for comparison. Epoxy/carbon composites seemed to offer better resistance to hydrazine and polycyanurate/carbon composites were more resistant to NTO oxidizer.

### 5.4.3 Lubricants for Hydrazine Service

Several lubricants were tested as reported in in the chapter “Methylhydrazine,” for exothermic reactions with hydrazine or MMH. Exothermic reactions would indicate incompatibility of these materials with hydrazine(s) and advise against their use.

#### 5.4.3.1 Lubricant Oils and Greases

Hydrazine itself is a very poor lubricant, and many metal-to-metal rotary seals or sliding seals in pumps, flow meters, or valves for hydrazine service have failed for this reason. The problem appears to be less severe with MMH or UDMH. A low-load, short-duration ball bearing test failed in hydrazine due to lack of lubrication [1637]. Most wet lubricants are either washed off or attacked by hydrazine. A perfluoropolyether grease made by DuPont, Krytox 240, appears to be compatible with hydrazine and MMH based on gas evolution measurements and lack of corrosion of the lubricated metals. Krytox greases contain a polymer of tetrafluoroethylene and perfluoroalkylpolyethers of the general formula  $\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}_2\text{CF}_3$ .

Eight different metal samples coated with Krytox 240AC were included in a 10-year storage test with hydrazine [1160, 1161]. Another type of Krytox tested was Krytox 143AB [1638]. However, earlier recommendations of Krytox ignored the danger of hydrazinolysis at higher temperatures (when Krytox droplets are swept into the catalyst bed with hydrazine) and subsequently fluoride killing the catalyst just as Freon did (see *Encyclopedia of Monopropellants*, in the chapter “Hydrazine Monopropellants”).

**Table 68:** Results of hydrazine immersion tests of engineering thermoplastics.

| Thermoplastic        | Type of polymer                     | Yield strength, MPa, before | Yield strength, MPa, after | Yield strength change, % | Ultimate tensile strength, MPa, before | Ultimate tensile strength, MPa, after | Ultimate tensile strength change, % | Weight change, % (estimated) |
|----------------------|-------------------------------------|-----------------------------|----------------------------|--------------------------|----------------------------------------|---------------------------------------|-------------------------------------|------------------------------|
| Kadel E1000          | Polyketone                          | 64.8                        | 61.4                       | -5                       | 100.0                                  | 96.5                                  | -4                                  | -0.14                        |
| Kadel EP 3140        | Polyketone                          | 122.0                       | 124.1                      | 2                        | 144.8                                  | 142.0                                 | -2                                  | -0.14                        |
| Kadel E 1140         | Polyketone                          | 131.0                       | 131.0                      | 0                        | 168.9                                  | 159.3                                 | -6                                  | -0.14                        |
| Kadel 1230           | Polyketone                          | 203.4                       | 191.0                      | -6                       | 222.0                                  | 218.6                                 | -2                                  | -0.14                        |
| Radel AG 230         | Polyarylsulfone                     | 82.7                        | 66.2                       | -20                      | 107.6                                  | 86.2                                  | -20                                 | 1.2                          |
| Udel GF 130          | Polysulfone                         | 73.8                        | 63.4                       | -14                      | 92.4                                   | 80.7                                  | -13                                 | 0.7                          |
| Ryton BR 90 A        | Polyphenylene sulfide               | 154.4                       | 129.6                      | -16                      | 169.6                                  | 148.9                                 | -12                                 | —                            |
| Ryton R 402          | Polyphenylene sulfide sulfone       | 137.9                       | 135.1                      | -2                       | 141.3                                  | 142.7                                 | 1                                   | —                            |
| Verton PPS OF-700-07 | Polyphenylene sulfide               | —                           | 86.2                       | —                        | 109.6                                  | 89.6                                  | -18                                 | 0.15                         |
| Victrex PEEK 450 G   | Polyether etherketone               | 60.7                        | 54.5                       | -10                      | 88.9                                   | 87.6                                  | -1                                  | 0.25                         |
| Victrex PES 4100G    | Polyethersulfone                    | 39.3                        | 26.2                       | -33                      | 79.3                                   | 52.4                                  | -34                                 | 2.0                          |
| Verton PP MFX 7008   | Polypropylene                       | 72.4                        | 62.7                       | -13                      | 78.6                                   | 67.6                                  | -14                                 | 0.4                          |
| Tefzel 2004          | Poly(ethylene tetrafluoro ethylene) | 35.9                        | 34.5                       | -4                       | 68.9                                   | 67.6                                  | -2                                  | 0.1                          |

Data source: [1749]. 12-d immersion, immersion temperature not defined.

Krytox 240AC was widely used for servicing the Space Shuttle Orbital Maneuvering System (OMS)/RCS bipropellant systems and does not interfere with the combustion process in a bipropellant engine. Occasionally, more than generously applied Krytox 240AC is swept away and accidentally also finds its way into monopropellant hydrazine systems for which Krytox is not recommended. Excess Krytox 240AC is not soluble in hydrazine but may wash off in flowing hydrazine and gets carried along as floating globs of grease. There is concern that the fluoride formed by reductive pyrolysis in the monopropellant reactor may result in corrosion of metals in the injector or deactivation of Shell 405 catalyst. A coupon of CRES-304L coated with Krytox 240 AC and subjected to Test 15 of NASA 8060.1C in hydrazine (48 h at 344 K) showed higher gas evolution on the coated sample when an uncoated piece of CRES-304L was the reference coupon. The off-loaded hydrazine from the Krytox samples should have been analyzed for fluoride like fluorinated elastomers tested earlier per NHB 8060.1C Test 15, which showed significant increases of fluoride in the off-loaded hydrazine [1663, 1664]. Dow Corning Silicone Oil 710 was used to disperse hydrazine droplets at freezing temperatures, apparently without adverse reactions [114].

The space shuttle APU turbine and gear box was lubricated with Mobil Jet II per MIL-L-23699, a phosphate ester, which was not intended to come in contact with hydrazine. The hydrazine fuel pump and the lubrication oil pump were on the same drive shaft, and the two fluids were separated only by a pair of rotating seals. Early designs did not prevent hydrazine from leaking across the rotating seal and contaminating the lube oil, forming a wax-like precipitate (pentaerythritol) by hydrazinolysis of the phosphate ester in the synthetic oil, clogging the oil filter, and forcing the bypass relief valve open. This happened on STS-2 and again on STS-4, causing launch aborts [1742]. At one time, it was considered to add hydrazine-scavenging additives to the oil [1744]. Later, the two seals, which used to drain into a common cavity, were changed to have separate seal drain cavities and collection bottles in which eventual leakage was collected separately and removed after each flight. The pressure in the drain bottles was measured. A similar incompatibility occurred early during the development of the STS APU with ammonia exhaust gas from the turbine housing leaking into the hydraulic fluid. Ammonia reacted with an additive in the hydraulic fluid and formed a silt, which clogged the hydraulic fluid filters. The hydraulic fluid specification is MIL-H-83282, which is a synthetic hydrocarbon (to reduce fire hazards).

A thin film of Apiezon-L is often used to lubricate O-rings prior to sliding them over valve stems or hydrazine engines. Apiezon-L is a hydrocarbon-based, halogen-free lubricant.

#### 5.4.3.2 Dry Lubricants

Most dry lubricants are attacked and removed by hydrazine. Electrofilm 1000G and Lubeco 2029-3 were said to be partially compatible, but wear life was reduced once the unit was exposed to hydrazine [1637]. The rams in pyro valves (e.g., Siebel Air P/N 55-02462-5) were at one time lubricated with dry lubricants such as molybdenum

disulfide to facilitate movement of the ram. Unfortunately, molybdenum disulfide is highly reactive with hydrazine, resulting in a rapid rate of gas evolution by hydrazine decomposition and possible poisoning of the iridium catalyst by sulfide released in catalytic thrusters. In a ground test simulating a 2-month hold on the launch pad, pyro valves with MoS<sub>2</sub> dry lubricant were filled with hydrazine and tested in the unfired or fired state, and in both cases the closed-off section rapidly overpressurized and the hydrazine turned black. Molybdenum disulfide may also have been used by some manufacturers as a lubricant in extruding titanium wire and become embedded in the surface of the wire, resulting in high rates of gas evolution when mesh woven from the contaminated wire came in contact with hydrazine. Such wire may have been used inadvertently in surface tension propellant management devices for MMH, hydrazine, and NTO.

Two greases and two dry lubricants were tested for compatibility with hydrazine for 48 h at 416 K when coated on a 17-7PH coupon. Apiezon-L (a petrolatum hydrocarbon grease) and Microseal-100-1 (graphite) were deemed acceptable, but Braycote 3L38RP grease and Microseal-200-1 (MoS<sub>2</sub>) dry lubricant were not acceptable.

Insufficient information is available on graphite as a dry lubricant. One would hesitate to allow all brands of dry lubricants with graphite to be used on hydrazine systems. It is known that hydrazine may cause graphite to swell because it can intercalate between the layers of carbon atoms. Graphite seals on the STS APU fuel pump had to be wetted with hydrazine several days ahead of a flight so they would swell to the intended dimensions and provide a tight seal.

#### 5.4.4 Propellant Expulsion Diaphragms and Bladders

For a propellant expulsion bladder or diaphragm it is important that the material be strong and flexible, remain flexible under conditions of propellant exposure and radiation exposure, have low permeability to propellant liquid, propellant vapors, and pressurant gases, and not leach any contaminants into the propellant. A summary of contamination incidents caused by contaminant leaching from diaphragms is given in Section 5.4.4.2. The chemistry and manufacturing engineering of expulsion diaphragm and bladder production have made enormous progress over the past six decades, allowing hydrazine to be used in many launch vehicle and satellite applications.

##### 5.4.4.1 General Elastomer Mechanical Properties and Gas Evolution

In the early days of hydrazine flight system development, hydrazine stability in elastomer expulsion devices was measured only in weeks [1751, 1752]. For instance, a butyl rubber expulsion bladder was used on the RANGER 3 spacecraft, where storability was asserted to be better than 9–13 weeks. Although EPR-5 showed no measurable Ae-50 permeation, Butyl-7 allowed 0.7% of the propellant to escape after 7 d. Among six candidate formulations based on *cis*-1,3-polybutadiene, Butyl-218, Hydropol, or EPR, the

latter showed the lowest swelling (16%) after immersion in Ae-50 at 344 K (160 °F) for 30 d. Other rubber formulations swelled 40%. Hydrazine immersion tests with 12 different elastomers showed that E515-8 and butyl rubbers FR-6-60-26 and SR-722-70 were among the worst for gas evolution but at the time were the only ones with sufficient manufacturing background that could be formed into bladders and diaphragms to meet launch dates. Despite considerable concern about pressure rise, FR-6-60-26 was chosen for the MARINER missions.

The carbon-black filler material in EPR-132 was found to be responsible for the high rate of gas evolution when EPR-132 samples were immersed in hydrazine [1655, 1656]. The rate of gas evolution with a sample that did not contain carbon black was much lower than with the standard grade of EPR-132 (100 parts Enjay 404, 50 parts carbon black, 10 parts Di-cup 40C [= 40% dicumyl peroxide and 60%  $\text{CaCO}_3$ ]). The rate of gas evolution for several EPR samples tested was  $0.011\text{--}0.094\text{ cm}^3\text{ cm}^{-2}\text{ day}^{-1}$  ( $0.0044\text{--}0.037\text{ in.}^3\text{ d}^{-1}\text{ in.}^{-2}$ ).

Standard Teflon/aluminum laminate bladders employed as NTO and MMH zero-g propellant management devices on the MARINER Mars 71 space probe failed because of cracks and tears near an aluminum seal ring which formed the mouth of the bladder [1753]. These failures occurred during flight-acceptance tests with inert solvents (Freon-TF and isopropanol) used as simulant fluids. It was found that one of the laminate polymers, FEP 120, was particularly solvent-sensitive, and it was then eliminated from future laminates for expulsion bladders.

Over the past six decades, substantial effort has gone into the development of hydrazine-compatible elastomers for expulsion bladders and diaphragms. It is only after reviewing all that literature generated during the 1960s that one begins to appreciate the availability and properties of AF-E-332, which was the mainstay diaphragm material for hydrazine for several decades after first being introduced on the market. Compounding studies directed at improving the compatibility and permeability of EPR [1754] and EPT rubbers evaluated 10 new formulations [1755]; EPR-132 was run along as a baseline. Non-carbon fillers (clay, fumed silica Silene-D) gave lower tensile strengths. Terpolymer formulations were less resilient than copolymer formulations. Bladders for MARINER 69 were produced from Butyl Compound FR-6-60-26. In addition, bladders were also produced from Compound 10, a forerunner of EPT-10. It was during this development effort that passivation by presoak in hydrazine, then discarding the hydrazine used in the presoak, was first recommended (a practice followed for several years, but which later led to other complications).

A material called HYSTL offered attractive processing characteristics and showed good compatibility with hydrazine and hydrazine-type fuels. Co-curing HYSTL and EPDM gave elastomers of superior mechanical and hydrazine compatibility properties suitable for diaphragms as well as valve seats and gaskets [1730].

Continued efforts resulted in the development of ethylene-propylene-terpolymer (= EPT-10) bladders that were used on numerous flight vehicles. Polymers filled with higher silicon dioxide levels exhibited better hydrazine compatibility. Forty-three



other rubber formulations, including butyl rubber, were tested, but EPT-10 performed best [1756]. Typically, EPT showed a 13% loss in tensile strength, 70% increase in elongation, 30% loss in modulus, and 20% swelling after exposure to hydrazine. After a few years, most flight applications had switched to AF-E-332, which was superior to EPT-10 in terms of physical properties [1757]. AF-E-332 was developed by the Applied Chemistry Department of TRW Systems Group under contract from the Air Force Materials Laboratory [1758–1760]. Elastomers developed for service with hydrazine included AF-E-332 (EPDM rubber) for hydrazine positive expulsion devices, AF-E-411 (EPDM rubber) for hydrazine valve seals, and AF-E-124D (perfluorinated polymer) for both hydrazine and NTO seals and positive expulsion devices. Tests ranged from simple laboratory screening to complete design verification testing of a full-size AF-E-332 positive expulsion bladder. The initial version AF-E-332-6 demonstrated the concept of co-reacting elastomers with low-molecular-weight 1,2-polybutadiene resin. An advanced version AF-E-332-11 later became the mainstay of expulsion elastomer production for propellant tanks for several decades. The original formulation of AF-E-332 was based on the use of DuPont Nordel 1040, an ethylene-propylene-diene-modified (EPDM) terpolymer (EPT) but had problems with low-molecular-weight oligomers extracting into the hydrazine and contaminating and plugging small thrusters. To overcome this problem, the APT was first extracted with boiling methanol, then 2-butanone. DuPont later produced a Nordel 1035 that did not have the low-molecular-weight oligomers, and it was the main polymer for many years until DuPont ceased manufacturing Nordel 1035. Based on lengthy development tests, a 50 : 50 mixture of Nordel 1440 and Nordel 2744 gave an elastomer identical to that obtained in earlier years with Nordel 1635. This history of AF-E-332 modifications and ingredient substitutions may be important when comparing contaminant-leaching properties of AF-E-332 measured at different organizations over a span of several decades. Contaminant leaching may depend on the quality of the binder that is holding the filler particles together. Side-by-side 11-year storage tests of hydrazine in a titanium/EPT-10 and a CRES/AF-E-332 tank showed that both elastomers suffered a reduction in tensile strength of 15–30% [1761].

EPDM elastomer formulations like AF-E-332, but without the calcium oxide and zinc oxide fillers, have been developed in other countries, but improvements over AF-E-332 have not been demonstrated [1762]. The specific gas generation rate of these materials dropped off very sharply during the 670 h of an immersion test at 343 K. Fluor-elastomers were expected to be resistant to hydrazine as well as NTO, but permeability problems persisted [1763].

#### **5.4.4.2 Contaminants Leached from Diaphragms and Bladders**

Both EPT-10 and AF-E-332 have had their share of contaminant-leaching problems. The most troublesome contaminants leached were zinc and silica (and other silicon compounds). It was observed that when EPT-10 elastomer was immersed in hydrazine, some of the Silene-D silica was shed from the rubber and was visible as white particu-

late matter floating in the liquid [1635]. This observation led to a pre-flight pre-soak for 168 h of EPT-10 diaphragms in hydrazine in order to remove some of the leachable silica (and sulfur?) prior to flight. In some applications, the pre-flight soak was combined with the measurement of the pressure rise rate as an indication of cleanliness of the diaphragm. The pressure rise rate was expressed as a diaphragm activity index (DAI). Unfortunately, hydrazine was retained in the elastomer, and some diaphragms and tanks were subsequently exposed to air and they absorbed carbon dioxide, making the zinc-leaching problem even worse [1727].

Six EPT-10 diaphragms representing two different methods of post-DAI decontamination and two controls were immersed in pure hydrazine, and leached contaminants were analyzed. It was shown that the DAI method that only vacuum dried at room temperature and  $10^{-5}$  mm Hg for 24 h resulted in the highest zinc leaching, whereas diaphragms baked for 12 to 36 h at 310 K in air caused less zinc leaching. All diaphragms had seen air exposure of several months between DAI and the leaching test. During this period, they must have picked up significant amounts of  $\text{CO}_2$  and formed zinc carbazate. Based on parallel coupon tests under controlled conditions, AF-E-332 and Parker EPR-515-8 were less susceptible to zinc leaching than EPT-10. Noticeable amounts of zinc could be leached from Parker EPR-515-8.

AF-E-332 normally caused little propellant contamination (NVR) when immersed in hydrazine. Shortly after AF-E-332 became first available, nine 22-in. diaphragms were molded from two different AF-E-332 compositions and subjected to soak tests and expulsion cycles in heavy-duty bolt-up tanks. After three of the diaphragms were subjected to a 50-d soak in hydrazine, the propellant remained virtually unchanged in NVR [1757]. Very little zinc and calcium was leached, in contrast to EPT-10, where the NVR (mostly Zn and Ca) could reach 140 ppm in a very short time. When studying hydrazine contamination caused by materials leached from AF-E-332 bladders, it was noted that large amounts of silicon were leached [1764]. Other trace contaminants analyzed included zinc, magnesium, calcium, and aluminum. The amount of silicon leached is proportional to the surface : volume ratio, the soak temperature, and the immersion time. Dynamic testing at less than 100000 expulsion cycles also increased the rate of silicon transfer. The amount of silica leached at different temperatures seemed to fit into an Arrhenius rate chart when the logarithm of the rate was plotted versus reciprocal absolute temperature. The source of silicon is most likely a hydrophobic grade of fumed silica used as filler for the elastomer. The silanization of particulate silica forms a protective coating that inhibits wetting (and extraction) by hydrazine. It is not known whether or not ester-like  $-\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_2-\text{O}-$  and  $-\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3$  groups protruding from the surface are subject to hydrazinolysis or hydrolysis in the presence of hydrazine. If they are, some of the leached silicon may be in the form of volatile silicon organic compounds. Silicon analysis in hydrazine is a difficult task because unknown amounts of silicon may be leached from glassware commonly used for analytical work. Side-by-side comparison of analyses done in glassware versus Teflon labware showed that the blank sample handled in glass had 3.7 ppm Si versus 1.0 ppm in Teflon. Three

different analytical methods for Si analysis were compared: colorimetry, atomic absorption inhibition titrimetry, and atomic absorption with a nitrous oxide/acetylene flame [1764]. Based on a round-robin with three participating laboratories, agreement among the different laboratories was good once the samples had been transferred to aqueous solutions. There was more scatter among samples doped with colloidal silica compared to samples doped with sodium silicate. The main differences were caused by sample concentration methods while removing the hydrazine and digesting the residue. Calculations of the volume occupied by silica residues left in the injector of a rocket engine after each pulse showed that even very small silica concentrations are enough to block injector passages in a monopropellant thruster. See also Section 6.1.5.

Analysis of hydrazine off-loaded after side-by-side 11-year storage tests of hydrazine in a titanium/EPT-10 and a CRES/AF-E-332 tank showed that the silica content in the AF-E-332 tank had increased to 10.9 ppm, whereas silica concentration in the propellant from the EPT-10 tank remained below the detection limit of 1 ppm [1761]. However, the non-volatile residue in the EPT-10 tank increased to 100 ppm, significantly above the specification limit.

Hydrazine sampled during a FLTSATCOM flight tank storage test showed a gradual increase in leached Zn, Ca, Si, and NVR as summarized in Table 69. Fluctuations may be caused by a different mode of agitation of the tank before taking a sample.

**Table 69:** Contaminant leaching from AF-E-332 at 322 K (120 °F).

| Time, weeks    | 0      | 7      | 15   | 31   |
|----------------|--------|--------|------|------|
| NVR, mg/100 mL | 3.1    | 3.1    | 38.7 | 41.5 |
| Zn, ppm        | < 0.08 | < 0.08 | 0.11 | 0.19 |
| Ca, ppm        | 0.18   | 0.18   | 0.21 | 0.40 |
| Si, ppm        | 0.64   | 0.30   | —    | 1.92 |

Data source: [1765]

There has been continued concern about silica and other particles shed from AF-E-332 during immersion in hydrazine. Several in-orbit anomalies of European satellites of the ECS, TELECOM, and OTS series have been blamed on silica leaching. The failure mechanism, feed tube clogging or catalyst deactivation, has been reproduced in ground testing. As the result of various silica problems, several organizations had started development of silica-free elastomers for hydrazine expulsion tanks. Silica can be replaced by alumina as the filler. The nominal compositions of AF-E-332 and AF-E-411 are compared in Table 70.

To be accurate, the complete designation of AF-E-332 in the early days was AF-E-332-11, where the -11 indicated the variation of curing agents and compounds used in making the elastomer. The -11 was the most successful compound in replacing EPT-10 and was used exclusively from then on. The -12 variant did not contain any zinc oxide

**Table 70:** Nominal composition of AF-E-332 and AF-E-411 elastomers.

| AF-E-332 Type B    |              |              | AF-E-411-1         |               |              |
|--------------------|--------------|--------------|--------------------|---------------|--------------|
| Ingredient         | Manufacturer | Parts by wt. | Ingredient         | Manufacturer  | Parts by wt. |
| Nordel 1635        | DuPont       | 100          | Nordel 1635        | DuPont        | 100          |
| Aerosil R972       | Degussa      | 30           | Cab-O-Sil M5       | Cabot         | 25           |
| B-3000 Resin       | HYSTL Dev.   | 20           | B-3000 Resin       | Dynachem      | 25           |
| Teflon Powder T-8a | DuPont       | 10           | Teflon Powder T-8a | DuPont        | 5            |
| Zinc oxide         | Baker        | 5            | Zinc oxide         | Baker         | 5            |
| Calcium oxide      | Baker        | 5            | Calcium oxide      | Baker         | 5            |
| Lupersol 101       | Lucidol      | 0.9          | Vinyl silane A-172 | Union Carbide | 1            |
|                    |              |              | Di-Cup R           | Hercules      | 2            |

(which was responsible for some of the problems observed with flight systems). It was suspected that air exposure of AF-E-332 would also enhance silica shedding. There is no indication that air exposure aggravates subsequent silica shedding on first-time exposure of the elastomer to hydrazine.

A hydrazine propellant blend called HPB-2012 and consisting of 20% HN, 12% water, and 68% hydrazine is not compatible with AF-E-332, and it is suspected that it will dissolve metal oxide fillers [1766]. The mechanical properties of AF-E-332 exposed to HPB-2012 or MMH for 2 months at room temperature degraded to the point where some samples broke when a static load of 75% of the breaking strength of an unexposed control was applied to the post-test dried samples. Hydrazine or UDMH did not damage the elastomer to the same extent. This loss of strength has been blamed on the leaching of fillers like CaO or ZnO. Unfilled EPDM was weaker than AF-E-332 to start with, but its mechanical properties were not affected by the HPB-2012 propellant exposure.

#### 5.4.4.3 Multi-Cycle Applications of Diaphragms and Bladders

Typical space flight tanks get filled with hydrazine only once and go through only one reversal cycle. An exception were the three Space Shuttle Orbiter APU hydrazine tanks, which were qualified for at least 20 missions. A program was conducted predicting useful lifetimes of elastomer diaphragms with multiple reversions in hydrazine tanks [1767, 1768]. Previous space applications of diaphragm tanks required only a limited number of diaphragm reversals and filling-draining cycles; however, the Space Shuttle APU tanks had to withstand numerous flexing cycles. Therefore, emphasis has been placed on dynamic testing of materials for hydrazine diaphragms [1769–1771].

When AF-E-332 was first selected for STS APUGG, NASA contractors were concerned about silica shedding from AF-E-332. There were insufficient data available at that time to assess the effects of silica shedding on the APU. It has become apparent in the meantime that the wear products from the teeth of the gear pump outweigh any

other particulate contamination that may be in the fuel entering the APUGG, and the concern about silica contamination on Space Shuttle has gone away.

#### 5.4.4.4 Gas and Propellant Permeability Through Elastomers

Positive expulsion PMDs, such as tank bladders or diaphragms, must maintain the propellant side of the tank free of pressurant gas either dissolved or in a bubble gas phase in order to function properly. The pressurant gas, which surrounds the bladder and provides the pressure necessary to force the liquid propellant from the tank, may diffuse through the bladder or diaphragm wall and, in time, will saturate the propellant. This results in poor engine performance depending on the level of contamination and the disposition of the gas, i.e., dissolved or in the form of bubbles, on the liquid side of the PMD. In addition, propellant vapor can diffuse in the opposite direction through the polymer into the pressurant gas space. Not all components on the gas side may be compatible with propellant vapors. Laminated (“sandwiched”) Teflon-metal foil-Teflon composite bladder structure had been used during the early years of hydrazine applications in space propulsion until improved and compatible polymers became available. Without the thin metal foil sandwiched between the Teflon layers, the diffusion rate of propellant and pressurant would be excessive for long-term space missions. With a perfect (no holes) metal foil barrier, the diffusion rate should be essentially zero. However, small pin holes in the foil resulting from handling of the bladder or imperfect manufacture of the sandwich structure may be expected to occur in assembled expulsion bladder systems. The permeation rates of pressurant gases, hydrazine, or NTO were measured [1772, 1773]. The pressurant gas solubility and rate of diffusion of gases in liquid propellants were measured and entered into a model for propellant saturation.

In a scaled-down propellant tank, permeability of AF-E-332 toward hydrazine was measured during 130-d storage tests to simulate actual conditions as closely as possible. At 308 K, less than 0.002% of the propellant permeated, whereas at 358 K, approximately 0.02% permeated through the bladder [1774].

Out of 22 plastic materials tested for compatibility with hydrazine/HN/water mixtures, only Teflon, Kel-F, and polyethylene showed negligible weight change [242]. Polyvinylidene fluoride (PVF, Kynar) suffered some embrittlement on long contact with hydrazine [1775]. For short-term missions, PVF bladders may be acceptable if permeability is not an important factor. In the NHB 8060.1C Test 15, Kynar 460 had a low rate of gas evolution, but increased the fluoride content of the off-loaded hydrazine to 2400 ppm (!) [1661–1663]. It may also cause problems in MMH in contact with steel [1776]. In the same test, Kel-F 81 had a low rate of gas evolution but also increased the fluoride content to 213 ppm, which makes it unacceptable for hydrazine monopropellant use. Rulon J changed color, and the hydrazine turned brown during a 48-h test at 344 K [1662]. Seamless Teflon positive expulsion bladders were used for MMH and Aerozine-50 propellants on APOLLO Command Module, Service Module, Lunar Descent Module, and even on the S-IVB upper stage [1777].

One of the applications for which Teflon and other polymers were evaluated was the advanced liquid propulsion system (ALPS) developed by JPL, although it has never seen flight use. Teflon had been evaluated extensively as a bladder and diaphragm material in the early days of hydrazine rocket propulsion, but it was found to cold flow in the bead holding it in place; it was too stiff and had high permeability for hydrazine [1778].

Long-term tank storage tests have often found hydrazine on the pressurant side (the “wrong” side) of positive expulsion diaphragms [1761]. The situation becomes more serious if operational spacecraft are flying with hydrazine on the “wrong” side of the diaphragm because the pressurant gas lines are usually not heated and hydrazine may freeze if the pressurant gas line temperature drops below 270 K. One of the hydrazine APU tanks removed from the shuttle OV 102 (Columbia) had substantial quantities of liquid hydrazine on the nitrogen side of the tank [1769–1771]. The hydrazine was analyzed and contained 2.6% water and 300 ppm isopropanol.

Hydrazine vapor permeating through the propellant tank diaphragms was suspected of diffusing through the pressurant gas system of a Defense Meteorological Satellite Program (DMSP) satellite and may have come into contact with components that were not compatible with hydrazine [1779].

Nitrogen permeation through EPT-10 and hydrazine propellant saturation with  $\text{GN}_2$  was suspected as the cause for a 5-psi pressure drop in the freshly fueled RCS of the SCATHA satellite during a 2-d thermostatted pre-launch hold and observation period [1780]. It is surprising that propellant saturation should occur in such a short period despite the barrier of the elastomer diaphragm.

There are at least two areas in aerospace technology where hydrazine permeation through elastomers is of practical interest: the permeation of positive expulsion bladders and diaphragms discussed earlier and permeation through protective clothing discussed in Section 7.6.2. There are two methods for permeability testing, a transient method in which the time to breakthrough is measured, or a steady-state method in which the permeation rate is allowed to stabilize and the permeate is measured over a constant time interval. In Europe, a test method for permeation through elastomers (DIN 53580) has been proposed for propellant permeation testing of new diaphragm materials. This method was used to test perfluoro polymer TFM-PFA-TFM-PFA laminates (PFA facing the fluid side) with MON-1, MMH, and hydrazine [1781]. PFA is an abbreviation for perfluoroalkoxy polymers. TFM and PFA are PTFE co-polymers using perfluoropropylene-vinyl-ether (PPVE) as co-monomer. TFM is a copolymer with about 0.1% PPVE and PFA is a copolymer with 3–15% PPVE. TFM is similar to PTFE but with higher porosity and elongation and with a high degree of weldability. PFA is a melt-processable thermoplastic with chemical resistance like PTFE. It has much lower porosity and is translucent. The emphasis in this ESA-sponsored program was to develop silica-free expulsion diaphragms for satellite tanks. Test methods were supported by mathematical modeling of gas and propellant permeation.

## 5.5 Hydrazine Vapor Compatibility at Ambient Pressure

The gas evolution of hydrazine vapor at low partial pressures (below saturation pressure) decomposing on the internal surface of propellant tanks intended for liquid hydrazine service has been used as a method for determining the cleanliness of tanks without inserting a fiber optic probe and without cutting the tanks open [1500, 1501]. This is a useful non-destructive examination technique that could be used for the inspection of new tanks on the assembly line or for trouble shooting of tanks and completely assembled systems suspect of harboring contamination (e.g., rust, weld scale, Freon solvent reaction/decomposition products). The difficulty is to make sure that all the hydrazine is removed after the test so that the residual hydrazine does not cause corrosion problems beyond those suspected prior to performing the test.

Hydrazine vapor inhibited the rate of crack growth during fatigue testing of pre-cracked Al-7075-T6, an aircraft alloy [1782]. Although the control sample (60% RH air) failed (2-in. crack formation) after only 33000 cycles, the same sample in hydrazine vapor managed to survive 60000 cycles. Crack growth seems to be accelerated by moisture. If the control test was conducted in dry air, it failed after 44250 cycles.

## 5.6 Hydrazine Compatibility with Non-Metallic Tank Materials

Composite overwrapped pressure vessel (COPV) tanks with a thin metal shell allowed considerable mass savings in spacecraft design. Initially COPV tanks were used only for pressurant gases, but later these tanks were used for both pressurant gases and liquid propellants. If propellant is accidentally spilled on the outside of the tank or it leaks through a pinhole in the shell, the integrity of the composite overwrap may be jeopardized, and the tank may burst [1783, 1784].

## 5.7 Liquid Hydrazine Impingement in Vacuum

Occasionally hydrazine leaks are suspected to have occurred in flight systems, and it was suspected that leaked hydrazine ice and hydrazine vapor may have destroyed adjacent electronic components. Several liquid/frozen hydrazine spray impingement tests and vapor exposure tests under simulated space conditions have been conducted for many materials that would ordinarily not be exposed to hydrazine. The main concern was that hydrazine (vapor, liquid, or frozen) might jeopardize the insulating qualities of electric cable insulations and cause electric shorts.

Other situations where hydrazine impingement is potentially fatal include where it impinges on and dissolves space suits worn by astronauts during extravehicular activity (EVA) and propellant transfer operations in space. Material compatibility tests have been conducted with space suit materials to make sure that the materials are

compatible with a wide range of corrosive propellants [1785, 1786]. When sprayed onto space suits in vacuum, hydrazine will freeze, and it sublimates only slowly [111].

## 6 Selection of System Components for Hydrazine Service

The selection of system components for monopropellant and bipropellant flight propulsion systems is a carefully guarded trade secret with most of the hydrazine propulsion system suppliers. The rationale in selecting compatible system components (valves, filters, tanks) may determine the success or failure of a flight mission. Little useful information can be learned from published reports. In addition, because the availability of components changes so rapidly, recommendations for specific types and models of valves and filters have only limited time value. Some materials may no longer be produced, and new materials are becoming available all the time; the same is true of components made from these materials.

### 6.1 Examples of Component Incompatibility Problems and Propellant Contamination Incidents

Despite extensive laboratory testing with test coupons and efforts to eliminate incompatible materials before including them in hydrazine system assemblies, several instances of compatibility problems on the systems level have unfortunately occurred. The following paragraphs attempt to give a summary of published events to serve as a warning and prevent recurrence of the same problems. There is reason to believe that an equal or even larger number of incidents went unreported and many were swept under the rug, so to speak. However, those hydrazine users who are not willing to learn from the mistakes of the past are condemned to repeat them.

Some of the events listed in the following summary may not necessarily be the cause of incompatible materials but may rather be the result of negligent handling procedures. However, some materials are more forgiving to contamination and corrosion by hydrazine than others. There may be no foolproof material, or it may be prohibitively expensive.

#### 6.1.1 Residual Cleaning Solvents

When degreasing glass capsules with titanium specimens in preparation for hydrazine compatibility tests, Freon-TF (1,1,2-trichloro-1,2,2-trifluoroethane) vapor was inadvertently left in the glass capsules [1787]. The hydrazine turned greenish black and contained 0.78 to 0.99% insoluble black solids (Al and Ti compounds) and 1.1 to 2.9% soluble solids (containing approx. 30% chloride and 8 to 19% carbon). The pressure rise was excessive, and the Ti-6Al-4V coupons appeared mottled where they had been exposed to the liquid. The titanium became so embrittled that the coupons



could be broken by hand. The chloride content of the off-loaded hydrazine NVR was near 30%. This contamination-corrosion mechanism could be reproduced by spiking pure hydrazine with known amounts of Freon-TF and submersing Ti-6Al-4V, Ti, Al, and V in it. It was shown that vanadium reacts with Freon-TF in hydrazine, forming green corrosion products. Corrosion of stainless steel and braze joints in hydrazines is accelerated by residual Freon [1060, 1788].

### 6.1.2 Pressurant Leakage Through Diaphragms

If hydrazine becomes accidentally contaminated with halocarbons (chlorofluorocarbon cleaning fluids, evaporating liquid tank pressurant and lubricants), the corrosion of braze joints and the resulting rate of gas evolution is extremely bad [1711]. Freon-13B1 was at one time used as a pressurant fluid to expel hydrazine from a positive expulsion tank with a stainless-steel diaphragm, but the metal diaphragm may have leaked, resulting in contamination of the hydrazine. Trace amounts of bromotrifluoromethane (Freon-13B1) had been found in hydrazine in a metal diaphragm tank that was pressurized by the evaporating liquid. The metal diaphragm leaked pressurant gas into the hydrazine propellant. The compatibility of hydrazine containing various amounts of Freon-13B1 and Freon-TF with 304L and 308 stainless steels that had been joined with Au-Ni braze and Cu braze was investigated in detail. The results were presented in various tables and graphs. 304L stainless steel and Au-Ni braze were the most compatible of the combinations of materials, and Freon-TF was a more deleterious contaminant in hydrazine than Freon-13B1.

### 6.1.3 Valve Leakage

Injector clogging and valve leakage were observed during a vacuum start study of catalytic hydrazine reactors using dry ice (solid carbon dioxide) for temperature conditioning [1789, 1790]. Contaminant crystals collected on a filter were analyzed and found to be a carbazic acid derivative. A white residue was observed after vacuum evaporation of hydrazine from a simulated flight hardware tank. The residue showed an IR spectrum like that of ammonium bicarbonate. It was most likely hydrazinium carbazate formed by reaction of hydrazine with carbon dioxide. Carbon dioxide from the cooling system or ambient air must have found its way into the propellant and caused this problem. In a few instances on INTELSAT III, valves became clogged by corrosion products, brown crystalline salts from atmospheric carbon dioxide interaction, probably caused by a similar problem.

It used to be common practice to “passivate” EPT-10 diaphragms of propellant expulsion tanks in anhydrous hydrazine prior to flight applications and to measure the gas evolution rate as an indication of acceptability of diaphragms, which varied substantially from batch to batch (diaphragm activity index = DAI). However, EPT-10 swelled and absorbed large amounts of hydrazine during this pre-treatment. For a long time, the users were not aware that the hydrazine could not be completely removed by

water flushing. Subsequent exposure of the diaphragms to air (containing 0.03% CO<sub>2</sub>) allowed carbazic acid to form that slowly attacked the zinc oxide filler in the EPT-10 and converted it to a soluble salt. This salt contaminated the next load of hydrazine propellant with dissolved zinc [1727, 1791]. The zinc leached from the diaphragm, dissolved in the hydrazine as carbazate, and deposited as zinc residue on valve seats. The residue caused the valves to leak during preflight engine tests on the ground with flight tanks that had gone through DAI. Coupons cut from diaphragms removed from other post-DAI tanks showed that the post-DAI samples leached more zinc into clean hydrazine during a 51-d soak test than samples that had not gone through DAI. Subsequently, the DAI pre-treatment of EPT-10 was abandoned, and hardly any zinc was subsequently extracted from the diaphragms. In laboratory tests, it was shown that the amount of leachable zinc from new diaphragms was proportional to the added carbazic acid content of carbazic acid solutions in hydrazine [1727].

Hard-seat valves using Kennametal K-96 showed gas leakage if they were not decontaminated promptly after ATP firing. Exposure of hydrazine-wet valve surfaces to air and carbon dioxide allows carbazates to form in and on the valve seat, where they will corrode adjacent metals. In laboratory tests, the interaction of hydrazine, moisture, air, and carbon dioxide on the cobalt-bonded tungsten-carbide hard seat material was reproduced, and crystals of  $\text{N}_2\text{H}_5[\text{Co}(\text{N}_2\text{H}_3\text{COO})_3] \cdot \text{H}_2\text{O}$  formed on the surface of the metal were identified by chemical analysis. The cobalt is preferentially leached from the material, leaving loose tungsten carbide particles behind.

The Hughes INTELSAT IV HE-54 22-N thruster used a Hydraulic Research dual-seat torque tube valve with tungsten carbide seats and poppets [1792]. The valve, like many other hydrazine valves, was reported to be very sensitive to contamination and had to be thoroughly cleansed of any residual hydrazine before it could be exposed to air (and carbon dioxide therein). If the valve still contained residual hydrazine and was exposed to atmospheric carbon dioxide, carbazic acid would attack the metal parts, and the removal of corrosion products was very difficult. Carbazic acid could cause pitting of smoothly polished surfaces, which may erode further in high-speed flow, preventing a reliable and tight metal-to-metal seal.

The flight-ready ATS-F propulsion subsystem was fueled and subjected to a ground propulsion system test in a large vacuum chamber prior to launch, which was very unusual, and a test procedure heavily recommended against by most other organizations [1793]. Unfortunately, it was very difficult to remove all residual hydrazine after the all-up ground test and before actually launching the satellite. Atmospheric interaction with wet valves caused valve corrosion and valve leakage before the satellite could be launched, but the damage was recognized only later [1794]. Reddish deposits were found on the valve seat area of dissected valves removed from the spacecraft. These deposits prevented complete closure of the valve and caused gas leakage and would have caused liquid leakage if they had remained on the prototype flight vehicle. The light tan to deep red deposits were insoluble in hot water or isopropanol but would slowly dissolve in hot hydrazine.

Chloride-containing corrosion products found were attributed to hydrazinolysis of Freon-TF that might have soaked into the Teflon seats during valve manufacture and valve cleaning. Attempts to reproduce the stainless-steel valve corrosion with carbazic-acid-doped hydrazine in the laboratory resulted initially in water-soluble crystals, which hydrolyzed in moist air, converting to rust-brown crusts, and became gradually water-insoluble. The ATS-6 satellite suffered several valve/thruster failures in orbit, which were blamed on alternating exposure of the entire system to hydrazine and air during ground operations prior to launch [1795].

#### **6.1.4 Injector Clogging**

The clogging of capillary feed tubes in injectors in small hydrazine monopropellant thrusters has been an industry-wide problem. The clogging material could be the non-volatile residue that is always found in hydrazine and has most likely been leached from the distillation towers during manufacturing or from the stainless-steel drums during storage and transport. There are few thorough investigations of capillary feed tube clogging, but they are usually not published.

#### **6.1.5 Silica Shedding**

In a number of cases, injector clogging and catalyst bed fouling were caused by silica shedding from AF-E-332 diaphragms in positive expulsion tanks. Sometimes injector clogging and catalyst bed fouling were observed separately but in parallel in the same type of thrusters fed from the same tank, the only difference being the duty cycle at which the thrusters were operating.

Numerous silica leaching/shedding investigations have been conducted with AF-E-332 and its precursor elastomer, EPT-10. These involved ground tests as part of pre-flight development and qualification programs as well as after-the-fact problem investigations in which silica shedding was one of the prime suspect mechanisms contributing to the failure of propulsion sub-systems in satellites in orbit. They included tests where the hydrazine was exposed to AF-E-332 and subsequently passed through monopropellant thrusters to study the clogging potential of leached contaminants.

OTS-2 was launched on May 11, 1978, on a DELTA-3914, and its BOL mass was 865 kg. OTS-2 and subsequent European Communications Satellites (ECS-1 through ECS-5 = EUTELSAT1 F1 through F5) using similar AF-E-332 diaphragm tanks have all experienced erratic steady-state thrust performance that could not be explained by bubbles entrapped in the feed line [1796]. ERNO replicated the OTS-2 on-orbit behavior in tests on the ground using duplicate flight hardware including tank, lines, valves, and thrusters. This test was often referred to as the ECS long-term test (LTT). Testing was done with 313 K (40 °C) fuel and extended over 1 year. The 0.5-N REA had a capillary feed tube injector. Tests had shown that the OTS-2 problem is a poisoning (fouling, coating of active sites with an inert, unreactive layer) of the catalyst, not injector tube clogging as occasionally observed with long-life gas generator feed tubes

in electrothermal thrusters. For the ground test, 27.5 kg of high-purity-grade hydrazine was loaded and during the third test sequence after 9 months, 23 kg propellant consumption, and less than 30 h cumulative run time, the thruster washed out, as evidenced by solid hydrazine emerging from the nozzle in a vacuum chamber environment. Post-test cold gas flow of the thruster was 22% below nominal, indicating some clogging. Disassembly showed the clogging to be in the catalyst bed and not in the feed tube. The catalyst granules were coated with a glassy layer, which was rich in silicon, as shown by SEM-EDAX. Later testing with two different grades of hydrazine showed that the silica leaching occurred with both grades of hydrazine. The 0.5-N thruster suffered major performance degradation after passing 18–21 kg of propellant, and the 2-N thruster degraded after 25 kg of propellant [1797]. The engineering analysis, partially based on an analysis of telemetry data from satellites still operating in orbit, indicated that 28 to 31 mg of silica deposited in the catalyst bed or on the injector screens of thrusters on board ECS-1, ECS-2, or TELECOM-1A was sufficient to cause thrust degradation. The initial interpretation by European investigators was that the silica came from a mold release powder that was allegedly used in the manufacturing of the diaphragms, not from the diaphragm rubber itself. This representation was disputed by tank manufacturers. The OTS and ECS diaphragms with cylindrical midsections were manufactured in the mid-1970s, and the manufacturing methods may have changed since.

The EURECA retrievable carrier platform did not experience any thrust decay problems while in orbit but is a valuable data point in assessing the rate of silica leaching from diaphragms. It offered a rare opportunity to inspect a satellite propulsion sub-system after it had flown in space for almost 1 year. EURECA-1 was launched on STS-46 and retrieved by STS-57 after 10 months in orbit. It had thrusters of three different thrust levels, including 2-N, 5-N, and 20-N REAs with shower head-type injectors. It carried 660 kg hydrazine in six tanks of equal size, enough to maintain orbital elements for twice the intended 9- to 10-month mission duration, and close to the nominal maximum full load of 670 kg liquid propellant. After its retrieval, EURECA-1 offered a unique opportunity to physically “hands-on” examine thrusters that had actually operated in space and were fed from tanks with AF-E-332 diaphragms. There are thousands of thrusters like them in orbit, but they are usually inaccessible for post-flight examination. EURECA-1 thrusters that have flown once were initially earmarked for another EURECA flight (EURECA-2) and were not available for D&I. The reflight opportunity was canceled, and the fate of the thrusters remains unknown. Apparently only one of the thrusters was taken off the platform and ATP test fired on the ground, providing performance identical to its first ATP. The thruster was then reinstalled on the platform and was destined to fly again until the reflight was canceled.

Hydrazine off-loaded from EURECA-1 following the flight had a silicon content identical to that found in a similar tank during ground testing. The propellant had spent 450 d in the tanks. The results are summarized in Table 71.

**Table 71:** Summary of silicon analysis in hydrazine off-loaded from EURECA-1.

| Tank No. | Residual propellant, L | Silicon concentration, mg Si/L | Mean surface: volume ratio | Silicon generation rate, ng Si cm <sup>-2</sup> d <sup>-1</sup> |
|----------|------------------------|--------------------------------|----------------------------|-----------------------------------------------------------------|
| 1        | 56                     | 0.44                           | 0.0647                     | 15.1                                                            |
| 2        | 80.7                   | 0.42                           | 0.0581                     | 16.1                                                            |
| 3        | 110.3                  | 0.38                           | 0.0551                     | 15.3                                                            |
| 4        | 35.5                   | 0.52                           | 0.0920                     | 12.6                                                            |
| 5        | 20.3                   | 0.46                           | 0.2493                     | 4.10                                                            |
| 6        | 42.9                   | 0.50                           | 0.1284                     | 8.65                                                            |

Data source: [1798]

As one can see from Table 71, the silicon concentration in all tanks was substantially (by one order of magnitude) above the maximum silicon concentration tolerated for electrothermal hydrazine thruster testing. ESA assumed an average silicon generation rate of 12 ng Si cm<sup>-2</sup> d<sup>-1</sup>. This is below the rate reported by ERNO in earlier OTS/ECS LTT tests. The lower numbers during the first months of leaching in hydrazine may be due to the system-level checkout of the entire flight system on the ground prior to launch using water as an inert hydrazine simulant [1798]. Some silica may already have leached into the water. The off-loaded water was not analyzed for colloidal SiO<sub>2</sub>.

If one plots the amount of silicon found in the off-loaded propellant versus the mean surface: volume ratio, it appears that there is an almost linear, very steep relationship for tanks 1 through 4. However, tanks 5 and 6, which were emptied early in the mission, do not fit this relationship. Tanks 1 through 4 were emptied late in the mission. This would indicate that much of the silica was shed early in the exposure sequence, and the high *A/V* ratio for the remainder of the mission has not resulted in higher silicon concentrations. ESA calculated the maximum amount of hydrazine passed through a single 20-N thruster during the EURECA-A mission and concluded that the maximum consumption of a single thruster was 92 kg, which is substantially less than the 175 kg/thruster for which the system was qualified. Therefore, they concluded that the thrusters returned from space are good for another mission.

It would be of interest to obtain hydrazine analysis results from the Japanese Space Flier Unit, which was also retrieved by the Space Shuttle and returned to Earth. It is not known what type of tank was installed on this reusable spacecraft. If it was an AF-E-332 tank, the hydrazine should be subjected to a thorough analysis for leached contaminants. Likewise, if the thrusters are not needed for another mission, they should also be examined for contaminant deposition.

Matra Marconi Aerospace conducted ground tests with the ERNO 5-N and 20-N thrusters qualified for EURECA and intended for SOHO with propellant taken from a tank that contained an AF-E-332 diaphragm like the flight unit [1799, 1800]. They found that silica deposition occurred predominantly in the injector area, not in the

catalyst as with the smaller 0.5- and 2-N thrusters. Silica deposition in the catalyst bed was measurable but did not disable the thruster. It was concentrated axially in the core of the catalyst bed. MATRA developed a mathematical model to predict silica concentrations in hydrazine as a function of surface: volume ratio, time, and temperature. Another opportunity to examine hydrazine tanks and thrusters returned from space would have been with the Atmospheric Reentry Demonstrator, although the wetted time was only relatively short.

There are several postulated mechanisms for thruster degradation by silica deposition:

1. High-pulse-number missions where the injector holdup volume/dribble volume vaporizes after each pulse, leaving a layer of NVR, often uniformly distributed over the entire length of the capillary injector tube;
2. Long steady-state firings with lots of heat soak-back, where thermal margin is lost and film boiling starts at a point somewhere between the valve outlet and the injector face, depending on heat conductance and presence or absence of thermal shunts;
3. Gross catalyst coating with NVR deposits and fouling of the catalyst bed;
4. Platinum screens form a low-melting alloy with silicon and degrade prematurely.

In the case of catalyst coating (item 3), silica in the presence of other metal oxides, in particular sodium oxide, forms low-melting glasses that wick into the catalyst pore structure and effectively seal it off from hydrazine flow. Pure  $\text{SiO}_2$  melts at temperatures above thruster operating temperatures and deposits appeared to be coalesced like glass, but one should not expect the deposit to be pure  $\text{SiO}_2$ . Any other oxide, predominantly sodium oxide, will lower the melting point and form a glass.

In addition to the concern about injector clogging and catalyst fouling, there is concern about elemental silicon (formed by reduction of silica by hot hydrazine) in contact with platinum (item 4 above). Some injectors use platinum or rhodium/platinum screens as dispersion elements. In the presence of very small percentages (% by weight = equivalent to larger percent by atom population) of silicon, the melting point of platinum is lowered to below the operating temperature of a hydrazine reactor and the screens fail. There is some silica already in the alumina from which Shell 405 is made, but additional silicon carried in with the propellant or diffused from adjacent L-605 alloy makes things worse. Platinum/rhodium screens appear to be less susceptible to silicon damage than pure platinum screens.

Many questions remain open as to the nature of the silicon-containing compound leached from AF-E-332. It could be a physical suspension or a chemical solution. Depending on the particle size, a physical suspension should make it possible to filter out the silica particles. Silica cannot be filtered out mechanically. It is either colloidal or it is in dissolved form. Propellant sampling for particulate matter becomes very difficult because the tanks should be agitated and stirred each time before taking a sample. Otherwise it would be impossible to obtain reproducible particulate results, and one

is more likely to obtain high readings toward the end of the test when the “dredges” remaining in the tank bottom are used up.

The silicon problem was not evident with EPT-10, which used Silene-D silica that was not made hydrophobic. Some investigators maintain the position that silica leaching was overshadowed by problems with zinc leaching with this precursor polymer. Also, engine lifetimes and mission durations in the days of EPT-10 were short in comparison to the 10- to 15-year useful life requirements of today’s satellites. EPT-10 contains 65 parts  $\text{SiO}_2$  per 100 parts polymer, whereas AF-E-332 contains only 30 parts  $\text{SiO}_2$  per 100 parts polymer. AF-E-332 contains less  $\text{SiO}_2$  but, oddly enough, has a worse  $\text{SiO}_2$  shedding problem. There must be some contributing factor other than the gross  $\text{SiO}_2$  concentration in the rubber. One of the differences is that Silene-D was not made hydrophobic by silane treatment. Free hydroxyl (silanol) groups in Aerosil R-972 are converted to dimethylsilylether linkages by reaction with dimethyldichlorosilane. Approximately 70% of all silanol groups are converted by reaction with the dimethylsilane, resulting in the disappearance of the —OH stretching bond in the IR spectrum of the material. Hydrazine can hydrazinolyze the ether/ester linkages and form silylhydrazines, which are totally soluble in hydrazine, but would decompose under injector and reactor conditions to  $\text{SiO}_2$ .

Two flight tanks were tested side by side for storability and contaminant leaching [1761]. One tank was a CTS tank with an EPT-10 diaphragm made by PSI; the other was a Block 5D tank with AF-E-332 made by TRW. The testing covered the period from 1974 to 1985 for a total of 11 years. In the EPT-10 tank, silicon (silica?) ranged from <0.6 to <3.3 ppm with a final value of <1 ppm, whereas in the AF-E-332 tank, silicon content ranged from <1.5 to 15.5 ppm with a final value of 10.9 ppm Si. Despite the high silicon level, investigators concluded that this is *not considered sufficient to cause deterioration of the bladder or pose a potential valve leakage problem*. They did not address feed tube clogging or catalyst fouling. They also test fired 0.2-lb<sub>f</sub> thrusters with hydrazine off-loaded from tanks in which AF-E-332 had been soaked and did not observe any untoward effects. Hydrazine that was stored in contact with AF-E-332 for 200 d at 344 K (160 °F) and later used for engine tests showed a significant increase in silicon content (up to 45 ppm) [1801]. Elastomer EPT-10 was also tested in the same series, as well as in a GPS flight tank for 5 years. The silicon increase in EPT-10 diaphragms was only moderate (from less than 1.5 to 2.25 ppm). The zinc content in hydrazine exposed to EPT-10 remained low because the carbon dioxide content was also carefully controlled, and the hydrazine-soaked diaphragm was never exposed to ambient air. The exposed hydrazine was analyzed not only for silicon and zinc, but also for seven other metals and eight other constituents. After the test sequence with contaminated fuel, the thruster had accumulated 22348 pulses, whereas an ordinary GPS mission at that time required only 1000 pulses. Even with contamination that far exceeds MIL-SPEC limits, the thruster was expected to deliver the total impulse as under normal conditions.

In a tank qualification test program for FLTSATCOM, most of this effort was concerned with mechanical properties and expulsion efficiency [1765]. A propellant sample collected from the tank after 31 weeks contained 1.92 ppm Si, and a control kept in a glass bottle had 0.64 ppm Si. The difference was less than the stated accuracy of the analysis method used. A mission life test with the MRE-0.2 lb<sub>f</sub> thruster was conducted with propellant supplied directly from a flight tank containing an AF-E-332 diaphragm after 6 months' storage at 344 K (160 °F) [674]. Post-test performance compared favorably with identical tests on other thrusters fired from facility tankage, indicating no measurable effects of the AF-E-332 diaphragm on thruster operation.

When normalizing the results obtained at different organizations by the surface:volume ratio and correcting for temperature, consistent silica concentrations were obtained per unit area. The silicon content was normalized to  $A/V = 0.05 \text{ cm}^{-1}$  and 297 K (75 °F). However, correlation as a function of immersion time was not good [1061, 1764].

Another comparison of leaching study results also included data on Dowty D11, a European replacement material for AF-E-332. Its silica shedding rate was worse than that of AF-E-332. The rate entered for EURECA-A was close to  $12 \text{ ng cm}^{-2} \text{ d}^{-1}$ , and it is assumed that this is silica, not silicon. Some reports are not specific if the reported numbers are silica (molecular weight 60.8) or silicon (atomic weight 28.09). In summary, after several silica-induced problems were published, the rocket propulsion industry is now generally aware of the limitations of current technology elastomer materials, and corrective action has been taken by both the suppliers and the end-users.

### 6.1.6 Other Material Compatibility Problems in Components

In some rare instances, materials became corroded when hydrazine leaked onto external parts in the presence of air and moisture. This problem is caused primarily by the external leakage (which was not supposed to happen), but if the leakage cannot be prevented, one may need to rethink the materials selection and include an answer to the "What if ...?" question. In the case of the gear drive for a hydrazine fuel pump (which is on the same shaft as the turbine lubricant pump), which was made from M-2 tool steel, the primary selection criterion was the hardness of the material. M-2, in particular rusted M-2, is more reactive toward hydrazine than any other metals once found in the STS APU. Rusted M-2 can initiate an exothermic reaction at 335 K (62 °C). Unfortunately, the graphite ring bearing in the fuel pump does not provide a perfect seal (it shrinks when it dries out), and hydrazine was often found in the fuel drain cavity (now separated from the lubricant drain cavity). Hydrazine in the fuel drain cavity was a potential hazard if it ignited on the M-2 tool steel dust. The NHB 1060.1c Test 15, ARC, and a thermal runaway temperature (TRT) test, like the liquid-phase exothermicity test (LPET), were used to determine the potential ignition hazard [1802]. It was concluded that oxygen should be excluded from the fuel drain cavity to lower the risk of ignition. Coating the gear with Apiezon-L provided only limited protection.



## 6.2 Cleaning and Passivation Methods

Because hydrazine is so sensitive to contaminants introduced with a freshly forged, welded, spun, drawn, or machined surface, cleaning and passivating methods have been recommended prior to filling a propellant tank with hydrazine and launching a spacecraft. These methods are applicable mainly to anhydrous hydrazine. There seem to be fewer corrosion and compatibility problems with flight systems using methylhydrazines as bipropellant fuels.

### 6.2.1 Cleaning Methods

The cleaning methods for stainless steel, aluminum, or titanium alloys are usually very well established in the industry. The objective is to remove oxide coatings left over from extruding, deep drawing, or spinning the metals while in the hot state. Welded specimens must be cleaned to remove weld fluxes, weld spatter, and oxide layers. Removal of greasy contaminants from cutting fluids or lubricants used during the machining process is usually done with organic solvents. CFC-113 (Freon-TF) was widely used on the parts level until it was banned for environmental reasons along with other ozone-depleting chlorofluorocarbons. Trichloroethane (methylchloroform) and trichloroethylene were also widely used at one point. The problem is that if these halogenated solvents are not completely removed from the assembled units, subsequent aggravated corrosion in hydrazine may lead to system failures. All components for a  $\text{ClF}_5/\text{N}_2\text{H}_4$  rocket engine test stand were meticulously cleaned using a method that avoided the use of chlorofluorocarbon cleaning solvents [1803].

#### 6.2.1.1 Contamination Incidents with 2-Propanol

Isopropyl alcohol (IPA) (isopropanol, 2-propanol) is usually used for removing other organic contaminants, and sometimes it is used to replace and flush out water from complete flight systems following spin tests, center-of-gravity determinations, or acoustic tests with water in the propellant tanks simulating the actual propellant. IPA is easier to remove from a system by hot nitrogen purge and/or evacuation than water. IPA is compatible with most materials that hydrazine is also compatible with and it is miscible over the entire range of mixture ratios with water and/or hydrazine. The only problem with IPA is that it may contain up to several percent acetone as a result of selecting a crude solvent grade to start with or as a result of inadvertent autoxidation of high-purity IPA during storage in partially filled drums when a nitrogen blanket is not maintained. The procurement specification for IPA for hydrazine service should limit the amount of acetone tolerated. Residual IPA in a flight system will become partially autoxidized to acetone while the fuel system is sitting idle waiting for fueling. If acetone-containing IPA residues in the system mix with hydrazine, a brown polymeric mass ("mess") of hydrazones/azines forms that may clog filter screens and cannot be removed by either IPA or water. This was the cause of a satellite propellant loading ground-service cart contamination incident.

The only solvent that will remove the brown goo is hydrazine. Hydrazine is the best known solvent for cleaning out brown polymeric residue.

A fuel cart intended for ATS-F had to be totally disassembled and rebuilt after it became clogged from reaction products of bad IPA and hydrazine. A propellant loading cart built by another contractor in 1972 experienced similar contamination problems. There have been several incidents where the hydrazine loaded from a drum into the propellant cart was perfectly clean, but the propellant cart contaminated the hydrazine, in particular when it was used for the first time or if it was left unattended and partially filled between launches.

IPA may ignite on iridium catalysts in air and its oxidation products may poison the catalyst. It is not recommended to flush IPA through monopropellant thrusters intended for flight use, although this had been done at some locations, apparently without undue effects. It should be mentioned that IPA in prolonged contact with air may form explosive peroxides that are likely to explode when attempting to distill aged and recycled IPA for purification.

#### **6.2.1.2 Contamination Incidents with Alkaline Cleaners**

In an effort to use more environmentally friendly cleaning methods, avoiding all halogenated solvents, water-based cleaning agents are now widely adopted as substitutes. This is not without problems, as illustrated by the Space Shuttle boosters where SRB motor liners did not bond properly after the manufacturer had switched to a so-called “green” cleaning agent, delaying the return of a frustrated lady astronaut from Mir in 1996.

One of the water-based cleaning agents used to clean CRES-304L tubing is Turco 3878, which contains diethylene glycol butyl ether, detergents, silicates, and hydroxides. If it is used in excessive concentration and with insufficient water rinse, the glass-hard silicate residues formed after drying or on contact with hydrazine will be impossible to remove with chemical solvents.

#### **6.2.1.3 Contamination Incidents with Halogenated Solvents**

Residual Freon solvent in a propellant system causes hydrazine or MMH to become more corrosive, attacking the titanium [1787] or stainless-steel screen [1060, 1804] in the PMD in surface tension tanks. All hydrazine users should examine the assembly/servicing procedures and make sure that Freon-TF or other halogenated solvents are no longer used. Trichloroethane (methyl chloroform) or trichloroethylene causes similar problems. Sometimes halogenated solvents have been used to clean only a pressurant gas system, which ordinarily would never be exposed to hydrazine, but pressurant gas carried residual solvent vapors into the propellant tank, where it reacted with MMH. In reproducing the problem in the laboratory, MMH was doped with 0.25 to 2.5% Freon-TF, and 96Sn/4Ag solder, Ti-6Al-4V, iridized aluminum 6061-T6, and stainless-steel samples were immersed in the adulterated propellant for 63 d [1060, 1804]. Freon is less soluble in hydrazine than in MMH. In similar tests

with hydrazine, initial Freon solubility was limited to 0.5%. Yellow discoloration of the propellant was usually observed within a few days. The iron concentration leached from CRES increased to several hundred ppm. In tests where hydrazine was doped with fluoride, it was shown that hydrogen fluoride doping accelerated the corrosion of metals (except aluminum) so that the corrosion and blackening of the samples were evident within hours, but potassium fluoride addition did not corrode the metals. It is thus the hydrazinium  $[\text{N}_2\text{H}_5^+]$  cation in the presence of fluoride or chloride that is the corroding agent. The halide ion may aid in complexing metal ions once the metal is dissolved, for instance by forming  $[\text{FeF}_6]^{4-}$  complex ions. An electrochemical method was used to analyze trace fluoride in hydrazine [1804].

There was a problem when the decomposition of residual Freon-TF vapors, most likely present during the brazing of pressure transducers, caused subsequent rust formation on the 15-5PH metal braze stub of an unused pressure transducer while it was sitting in a plastic bag in ambient air on a shelf. The rust would constitute a potential problem for an identical pressure transducer that was already installed in a kick stage being readied for launch at the time the rust was discovered in its unused twin. In a laboratory test in glassware, it was shown that gas evolution from the rusted part immersed in hydrazine was much faster than from a clean braze stub of the same metal undergoing a parallel test for comparison. Despite the faster gas evolution from the rusted part, the projected overall gas evolution and pressure increase in the blowdown tank was not significant enough to warrant a “last-minute” recall of the kick stage for a space probe a few weeks prior to launch. This was confirmed by measuring the tank pressure for several weeks after loading the propellant and just prior to launch.

Liquid Freon-13B1 was used as a pressurant gas in a hydrazine expulsion system with metal bellows. Since the evaporation of Freon maintains a constant (although temperature-dependent) feed pressure (near 1300 kPa = 190 psi), this results in more reproducible rocket engine thrust than blowdown from a compressed gas source without a regulator. Unfortunately, metal bellows can be cycled only one to five times. Elastomer (AF-E-332) bladders or diaphragms would be superior to metal bellows since they can be cycled many times. However, Freon permeability through rubber prevents direct replacement of metal bellows with elastomer bladders [1805].

#### 6.2.1.4 Reactivity with Cleaning Agents

The reactivities of several selected halogenated precision cleaning solvents with hypergolic propellants was determined by analysis of the rates of formation of halide ion decomposition products [1806]. The solvents tested were Asahiklin AK 225, Asahiklin AK 225 AES, HFE 7100, HFE 7100 DE, Vertrel XF, Vertrel MCA, Vertrel MCA, Plus, 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), and trans-1,2-dichloroethylene (DCE). The propellants tested were hydrazine, MMH, and mixed oxides of nitrogen (MON-3). The Vertrel solvents showed significant reactivity with hydrazine. All the solvents except DCE exhibited significant reactivity with MMH, particularly HFE 7100 DE and CFC-113.

### 6.2.2 Passivating Methods

Some investigators recommend passivating fuel tanks and lines by filling the system with full-strength hydrazine, allowing the system to sit idle for some time, off-loading, and refueling with fresh fuel immediately prior to flight. Other schools of thought recommend keeping the entire system dry until fueling immediately prior to launch. This approach is frequently dictated by the fact that it is very difficult if not impossible to decontaminate a system of residual hydrazine between the passivation exercise and the actual launch.

A wide variety of passivation procedures are practiced by contractors working on hydrazine systems, but no standard technique has emerged. The basic process generally includes wetting all critical internal surfaces with hydrazine or hydrazine/water mixtures. In some cases, a dilute hydrazine solution is used first, followed by anhydrous hydrazine. Some procedures recommend heating the system to accelerate the passivation process. The passivating fluids are left in the system for 2–48 h and then discarded. Success criteria are not always applied to gauge the results of the treatment. In some cases, the rate of pressure buildup during passivation is monitored, or a particle count is taken on the off-loaded fluids. In a survey of the propulsion industry in the 1970s, it was noted that there was a “wide diversity of procedures, all somewhat lacking in credibility,” and there was “no basic agreement about necessity or value of conditioning at all” [1659, 1660]. When attempts were made to establish a correlation between pressure rise rates observed on freshly fueled all-up systems and gas evolution rates obtained in the laboratory on individual components, rates of gas evolution at 322 K (120 °F) were measured on CRES-301, CRES-304L, CRES-308L, and a 82Au/18Ni braze alloy in addition to Al-2021 and Ti-6Al-4V. It took more than 800 h for the gas evolution rate to level off, a sign of removal of the initial consumable layer on stainless steels. Calculations assuming additive contributions from each wetted component for a system at a fill rate of 60% (40% ullage) agreed only moderately well with the measured pressure rise rate during the pre-launch hold period.

Tanks (37.6 L = 10 gal volume) made of stainless steels (A-286, AM-350, and 17-7PH) and Ti-6Al-4V were passivated by the manufacturer with a mixture of 40% hydrazine and 60% water for 24 h at 361 K (190 °F) [1807]. Stainless-steel tanks showed a distinct pressure rise during passivation, but titanium tanks did not. Aluminum tanks were passivated with MIL-SPEC-grade anhydrous hydrazine for 24 h at 325 K (125 °F).

Only a few investigators reporting the results of material compatibility tests with hydrazines disclose the cleaning and passivation techniques used during their study to prepare metal coupons for tests. References [1638] and [1647] are an exception because they are some of the few that listed the cleaning and passivation to which coupons were subjected prior to immersion in hydrazine.

Sometimes flight tanks or entire flight systems are filled with hydrazine, and pressure rise is observed during the pre-launch hold period to see whether any inadvertently introduced, catalytically acting contaminants cause a higher than normal pressure rise rate. For instance, the complete propulsion sub-system on Intelsat IV was

vacuum filled to capacity with anhydrous hydrazine and connected to a small ullage volume (approx. 160 mL = 10 cu. in.) and heated to 350 K (170 °F) [1808]. After temperature stabilization, the system's pressure was monitored for 24 h.

## 6.3 Flow Controls for Hydrazine Systems

Precision impulse bits delivered from hydrazine propulsion systems depend on accurate metering of the hydrazine flow to the thrusters. A wide variety of hydrazine flow control components are on the market and the list of available components changes daily.

### 6.3.1 Solenoid and Torque Motor Valves

Valves are the most important components in hydrazine monopropellant flight systems, and the selection of the correct valve is a science in its own right. The marketplace of valve suppliers is changing frequently and requires constant attention by a component engineer. Many space flight missions have been cut short by valve failures. Failure modes can be a failure to open, failure to close, or slow leakage in the closed position. Leakage can be internal leakage or external leakage. The word *valve* will likely evoke an immediate association with valve leakage. One of the more dramatic bipropellant valve failures occurred on GEMINI 8 when bipropellant roll control thruster valves got stuck open and accelerated the space capsule to a whirlwind roll. Shortly after the GEMINI and the AGENA docked, the craft began spinning out of control. Armstrong jettisoned the AGENA, thinking the problem was there, but the tumbling worsened. Armstrong shut down the GEMINI's reaction control system and manually brought the craft under control using a second set of 16 thrusters intended only for use on re-entry during a later phase of the mission.

The discussion here is restricted to valve materials and does not extend to valve designs. Several publications discussing hydrazine thruster designs will often also provide useful information on valves. For instance, sometimes the only difference between a manufacturer's thruster model designation like HE-54 or HE-55 is the valve. The most sensitive part of a valve is the sealing surface, the point of contact between the seat and the poppet. We differentiate between soft seat valves and hard seat valves.

Hydrazine is a very poor lubricant, and metal-on-metal sliding fit valves are susceptible to damage of the sealing surface even when operating in the wet state. Basic data were acquired on the sliding characteristics of metal surfaces under hydrazine to gain an understanding of the phenomena of wear and friction inside these valves [1809]. Sliding fit valves should never be operated in the dry state.

Measurements in a friction tribometer that simulates the sliding parts in thruster valves showed that the tribological properties heavily depend on the lubricating ability of the applicable fluid. Hydrazine is a very poor lubricant. In the case of hydrazine,

the typical phenomena were galling due to the strong reducing property and chemical change of the sliding surface [1810].

#### 6.3.1.1 Materials of Construction for Solenoid Valves

A wide range of valve materials was surveyed as part of the advanced valve technology program [1637]. The survey included 15 aluminum alloys, 14 steels, 18 miscellaneous metals, and 15 non-metals.

Valve seat (AF-E-411 and AF-E-102), armature (CRES-430 and CRES-430F), spring (CRES-302 and 17-7PH), and housing samples (CRES-304L, CRES-347) representative of the MJS77 (VOYAGER) systems were tested in JPL long-term storage tests [1160, 1638].

One of the most important and most complex components of the Space Shuttle APU was the gas generator valve module (GGVM), which was a block containing several valves. Until the late 1990s, it used a hard seat (tungsten carbide/Co seat, tungsten carbide/Co poppet) and was qualified for 450000 operating cycles. During each typical Space Shuttle orbiter mission (start *and* landing), the valve would have to cycle 6300–7500 times to control flow of hydrazine to the gas generator and control the spin rate of the turbine wheel and the hydraulic fluid pump delivering hydraulic fluid to the main engine swivel actuators, rudders, and elevons, as well as to the landing gear and air brake during landing. A similar but different valve was used on the solid rocket booster hydraulic power units. The metal-to-metal seal on the orbiter was very susceptible to particulate contamination and corrosion at the hydrazine-air interface. Slow leakage during idle periods would cause corrosion of injector stems and injector panels, partially through hydrazine and ammonia that became oxidized to nitrate ion on the Shell 405 catalyst in the presence of traces of oxygen. It would be difficult to replace the metal-to-metal seal by a metal-to-elastomer seal because this part of the system gets very hot despite thermal shunts and (occasionally) active water spray cooling. In an effort to replace the metal-to-metal seal, NASA initiated a program to evaluate other valve seat materials and sponsored development and testing of a new GGVM [1811]. The operating pressure at the valve inlet was 11 MPa (1600 psi), requiring an extra-rigid construction of the housing and connectors. The corrosive chemistry environment at the outlet region of the valve made it more difficult to select alternative materials. Most valves used for hydrazine in satellites are welded constructions and cannot be opened without destroying the valve. Design constraints for the Space Shuttle included a non-welded fluid mechanical portion of the valve to permit disassembly and refurbishment of the valve module as required. Spring-cushioned seat designs were employed to reduce peak impact loads on the sealing surfaces during valve operation to achieve the high cycle life performance required while maintaining acceptable leakage performance. The spring-supported seats not only cushioned the dynamic impact during valve operation but also provided a degree of angular compliance, which facilitated the matching of the sealing surfaces between the valve poppet and the seat. Flat-faced metal-to-metal sealing surfaces have been shown to provide adequate sealing performance for three of the four seats, while PTFE against metal

has performed successfully for the one seat that has the zero liquid leakage sealing requirement but a relatively low 60000 cycle life capability.

#### **6.3.1.2 Valve Failure Investigations**

Thermal management of temperature in spacecraft hydrazine valves and lines is critical. Quite frequently valves and lines have heaters attached to keep the hydrazine from freezing. In at least one case, hydrazine freezing in a valve has caused loss of a satellite [1812]. In another instance, Kel-F valve stem packings in a fill valve disintegrated during six sterilization cycles at 408 K (275 °F), allowing much of the pressurized hydrazine to leak out [1813].

One of the most thorough valve leakage investigations was the one conducted on ATS-F [1794]. It illustrates the wide range of tools available to the component engineer to examine valves that are not operating properly and to determine the cause of the problem. The cause of the problem was incomplete removal of hydrazine from a flight unit following a ground test where it was filled with hydrazine and test fired in a vacuum chamber several months before it was launched into space. None of the satellites launched later was subjected to complete propulsion sub-system hot fire testing in a vacuum chamber on the ground prior to launch.

During early Space Shuttle flights, a few GGVMs suffered leakage and limited life due to wear and breakage of the tungsten carbide valve seat [1744]. Considerable effort was invested in redesign of the seat and in improving manufacturing techniques. This resulted in a seat design with concentric, dual-sealing surfaces and re-designed internal flow passages. The seat was honed with a diamond paste to remove a re-cast layer left after EDM machining. The re-cast layer was the cause of stress risers and seat cracking. It was learned that the tungsten carbide/cobalt material was sensitive to many solvents. Leaching of the cobalt binder can significantly reduce strength. Stress concentrations were avoided by rounding corners. Eventually, the valve armature on the coil side of the flex tube was filled with damping oil to reduce impact speed and valve chatter (rebound).

#### **6.3.1.3 Ground Service Equipment Valves**

On September 30, 2005, at WSTF TC 844B during a low-pressure test, a 0.5-in. manual valve bonnet (B-nut) failed catastrophically under a moderate pressure of only 345 kPa (50 psia). The failure caused the valve bonnet and stem to be ejected from the assembly, thus spilling approximately 74 gal of liquid  $N_2H_4$  into the test cell [1814]. The failure began as an intergranular crack in the nickel-plated, aluminum bronze bonnet threads. It was believed that the crack began as a result of the ethylene propylene rubber and Teflon soft seals allowing corrosive agents to slowly leak into the thread region where they reacted with  $CO_2$  in the air. Contributing causes of the bonnet failure were that material compatibility for non-wetted components was not considered during valve procurement, and the bonnet may have been overtightened (excessive torque when assembling) [1815].

#### 6.3.1.4 Correlation between Gas and Liquid Leakage

The objectives of a hydrazine valve leakage evaluation program were to demonstrate simple, reliable measurement techniques for valve seat leakage, to investigate pressure, temperature, and cycling effects on valve seat leakage, and to establish a correlation between liquid hydrazine leakage and gaseous nitrogen leakage [1740]. The results indicated that, whereas gas leakage is a strong function of inlet pressure, liquid hydrazine leakage is not strongly affected by inlet pressure. The amount of leakage is inversely proportional to the temperature (probably a viscosity function). Two satellite thruster valves were tested for leakage at temperatures up to 394 K (250 °F). Attempts to correlate hydrazine and nitrogen leakage were hindered by the significant liquid leakage variation with time, that is, random leakage variations with each valve actuation. In some cases, liquid hydrazine leakage will decrease with valve exposure time to propellant. This could be caused by particles in the hydrazine that become trapped in the leaking passage and clog some of the paths entirely. Swelling of soft valve seat elastomers with continuing hydrazine immersion has often been ignored and was not too well characterized.

Attempts have been made to establish a correlation between liquid hydrazine and gaseous nitrogen leakage rates of solenoid latching valves [1160]. It was shown that AF-E-411 swelled in the presence of liquid hydrazine, IPA, or water, and then contracted again in the dry state. There is some hysteresis such that the elastomer may not return to its original dimensions after a swelling/drying cycle. Valves that flow correctly during short-term exposure to hydrazine (as during an ATP firing) may not flow correctly after extended soaking in hydrazine because the valve seat has swollen and the clearance between the poppet seal and the seat in the valve open condition has diminished. Less clearance allows less propellant flow.

Six normally closed thrust chamber valves and two latching solenoid valves were tested for hydrazine service simulating a deep-space mission (VOYAGER-Jupiter-Saturn) including 100000 cycles [1739]. Valves included hard seat (metal-metal) and soft seat (metal-elastomer) valves. One case of gross material incompatibility was observed where a soft seat valve seat made from EPR (Parker Compound EPR E-515-8) swelled so badly as to prevent any flow through the valve when the armature was actuated. Other materials tested in valve seats included Teflon, AF-E-102, and tungsten carbide. It is sometimes difficult to correlate gas leakage measured on the dry valve prior to a test and the liquid hydrazine leakage during the test.

Valve leakage can be measured by enclosing and pressurizing a volume of hydrazine upstream of the valve seat. A flexible membrane forms part of a chamber holding a volume of hydrazine. Hydrazine leaking away causes a deformation of this membrane that can be measured [1816]. Special care must be exercised to remove all gas bubbles before loading the hydrazine to achieve maximum system hardness. The compressibility of hydrazine must be known for data reduction.



#### 6.3.1.5 Special Valve Applications

The Strategic Defense Initiative of the 1980s posed a previous unmatched challenge to the missile designer: The entire kinetic kill vehicle was to weigh only 2 kg, including IR seeker, control electronics, battery pack, attitude control thrusters, divert propulsion thrusters, propellant, and propellant tanks and feed system. This challenge resumed at the turn of the millennium with work continuing on a US national missile defense system. In pushing miniaturization to an extreme, coaxial monopropellant solenoid valves as light as 6 g were developed and tested [1817]. Cold gas thrusters weighed only 2.3 g. Warm gas thrusters providing 90 N thrust and operating on hot hydrazine decomposition products from a plenum weighed only 22 g. A miniature pilot-operated valve for divert engines was designed and developed in response to the need for high-flow capacity valves that exhibit the fast response times and weights typically associated with valves providing much lower flow rates [1818]. Hard seat valves with metal-to-metal seals are capable of withstanding higher operating temperatures, as well as in bipropellant thrusters, but are more susceptible to leakage than soft seat valves [1819].

Valves for small thrusters used in missile post boost propulsion systems must satisfy long-term storage requirements, but valves intended for the upper stages of satellite launchers or satellites are usually flown soon after they are installed in the propulsion sub-system. Very rarely is there a procurement specification requiring a demonstrated dry shelf life of a valve before it ever gets to see hydrazine. The ACSs for the Transtage upper stage on the TITAN III satellite launcher were procured in quantities sufficient to satisfy the launch requirements for several years. When concerns arose about the dry shelf life of the propellant TCVs, nine valves were set aside and tested periodically over a period of 5 years [1820–1823]. No changes in dry valve performance were noted.

#### 6.3.2 Latching Valves

Latching valves have the advantage over pyro valves that they can be operated repeatedly and do not require electrical power to hold them in one or another position. They are bistable valves, and the armatures are usually held in place by permanent magnets. In addition, latching valves can also act as relief valves and are designed to allow backward leakage if the pressure in the downstream section exceeds that of the upstream section (e.g., by thermal expansion of a trapped liquid volume). Such situations would be destructive if a pyro valve were used to close off a trapped volume of liquid and the liquid expanded. A low-cost all-titanium latching valve was developed that improved on the performance of existing latch valves [1824].

Sometimes it is possible to upgrade valves that had previously been used only as isolation or pressurization valves to more responsible positions in the fuel system. For instance, isolation latching valves of the same type as those that had already flown on VOYAGER were modified by replacing the EPT seat material with Teflon and using a dual-seat instead of a single-seat design. Thus modified, the valves met the reliability

requirements for RCS/ $\Delta V$  propulsion of satellite payloads to be launched by the Space Shuttle, as well as in bipropellant systems such as INSAT, LEASAT, or SAL [1825]. They could even be used as thrust chamber valves for thrusters with long burn times.

In January 1976, the Canadian CTS satellite experienced an anomaly when a latch valve was opened to fill an evacuated line [1826]. The latching valve vibrated (“fluttered”) and high-amplitude vibrations of 100 to 300 Hz with peak pressures of 8.9 to 13 MPa (1300 to 1900 psia) damaged a pressure transducer on the upstream side, causing it to short out against its casing. The downstream line did not fill completely within the allocated 3 s time after which the current was removed from the latching valve. When an attempt was made to energize the latching valve open again, it operated normally since this time there was not much  $\Delta p$  between the upstream and downstream portion of the line.

If propellant becomes trapped between two valves and experiences an increase in temperature, thermal expansion can cause a devastating increase in pressure [194]. Latching valves must be designed with the ability of backpressure relief.

### 6.3.3 Check Valves

The purpose of check valves is to prevent fluids from backing up during brief pressure spikes downstream of a check valve location. This is the main task of check valves in hydrazine systems. Check valves can be placed either on the gaseous pressurant side or the liquid propellant side of hydrazine propulsion systems. Commercial suppliers offer a wide range of check valves for hydrazine service. Check valves for pressurant gas service must still be compatible with hydrazine since vapor and condensate may accumulate next to the check valve during idle periods or negative accelerations and in temperature gradients. It is important to keep hydrazine vapors out of pressurant lines since these are usually not heated, and hydrazine condensate might freeze in the lines on the shaded side of spacecraft.

### 6.3.4 Burst Discs

Burst discs are the most reliable permanent seal of propellant passages. They are designed to burst once the propellant tank is pressurized. Since burst discs are permanently wetted on at least one side, corrosion of the thin metal may alter their designed burst pressure.

### 6.3.5 Pyrotechnic Valves

The designation “pyrotechnic valve” is usually abbreviated as “pyro valve.” In many flight applications, a valve must be actuated only once, typically a normally closed enable valve (isolation valve) that is opened at the beginning of the mission. Sometimes propulsion system branches (e.g., the apogee insertion engine branch) are shut off by firing a normally open pyro valve to avoid future trouble in case of leakage after

that initial part of the mission is completed. The lines are closed by firing a normally open pyro valve. For such applications, it is easiest and usually quite reliable to use a pyrotechnic actuator to open or close a shuttle valve, which is then rammed permanently into its new position. In most cases the high pressure generated by the pyrotechnic charge allows a fast traveling ram to shear a metal barrier to open a flow passage or to seat a plug in the flow passage to shut it off for good. The metal-to-metal seal is achieved under high pressure and friction, and often the rapidly deformed metal heats to near the melting point. Pyrotechnic valves come in two types: normally closed (NC) and normally open (NO); many satellites carry both types. NO valves may be used to isolate thrusters that have developed problems or to isolate a loop A and a bank of thrusters at the end of its useful lifetime while a redundant loop B takes over the active duty.

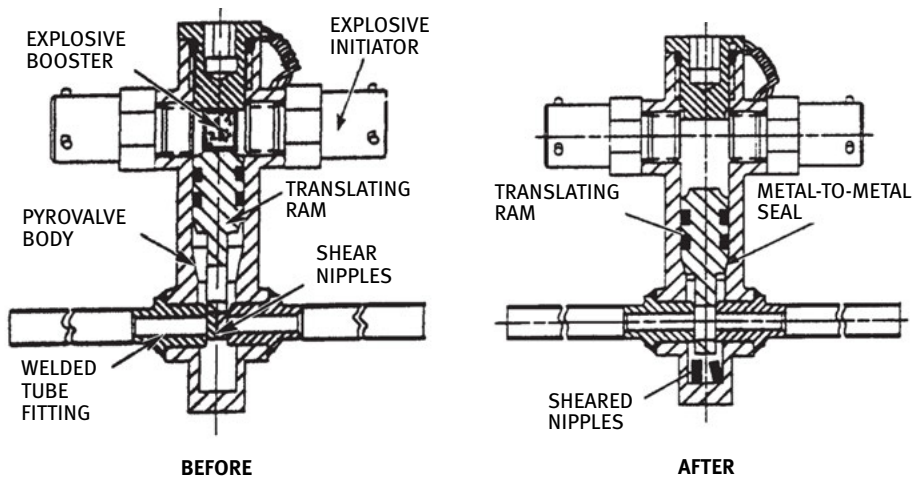
Some pyro valves have dual actuators or dual bridge wire initiators for increased reliability by redundancy. The initiator can have enough gas output by itself, or sometimes pellets of a gas-generating booster composition are added for additional gas output. The NASA standard initiator uses a potassium perchlorate/zirconium mixture, and the booster pellets are made from potassium perchlorate/titanium hydride, which has a higher gas output. If by mistake the driving charge is too energetic, the initiator may be ejected and become a projectile hazard to neighboring spacecraft components. This has happened in ground tests of some pyro valves.

In the early 1990s, after a string of satellite and space probe failures attributed to pyro valve explosive interaction with the hydrazine propellants, a flurry of studies was conducted on all conditions under which hydrazine propellants can be initiated to accidental explosions by activating a pyro valve. The National Oceanic and Atmospheric Administration (NOAA) published a news release on October 3, 1995, that identified a ruptured manifold as the most likely cause of the loss of LANDSAT F shortly after stage separation from the TITAN II launch vehicle in October 1993. LANDSAT F, an Earth-resources satellite, was launched aboard a TITAN II space launch vehicle from Vandenberg Air Force Base in California on October 5, 1993. Initial indications were that the spacecraft separated from the booster at the appropriate time and location but did not achieve orbit. The NOAA review board confirmed this and attributed the failure to a ruptured hydrazine manifold. The ruptured manifold rendered the satellite's reaction engine assemblies useless because fuel could not reach the engines. Consequently, there was a failure to maintain attitude control during the apogee kick motor (AKM) burn. This failure caused the spacecraft to tumble during the AKM burn and not accumulate enough energy to attain orbit.

A few months thereafter, a similar failure occurred in a communications satellite when the second of two parallel pyro valves was fired with a programmed delay sequence into a manifold that at the time was partially filled with helium and hydrazine froth. Blow-by of hot gases from the second pyro valve past a leaking ram piston is thought to have initiated a thermal runaway reaction in the hydrazine that ruptured

the tubing. This most likely sequence of events was reproduced in ground tests after the flight anomalies had occurred.

The results of industry-wide workshops were documented in a series of workshop proceedings [1827–1830], and new and improved pyro valve designs emerged in the mid-1990s. Cross sections of typical pyro valves before and after actuation are shown in Figure 52.



**Figure 52:** Typical pyro valves before and after actuation. (Republished from [1828] with permission of ©1996 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

The effectiveness of O-rings in pyro valves has been questioned. There are numerous accounts where post-test inspection reported the condition of the O-rings as sheared and shredded. Testing has shown that blow-by occurred regardless of whether O-rings were installed or accidentally omitted.

The Mars OBSERVER failure in August 1993, which involved NTO and MMH instead of monopropellant hydrazine, had a slightly different failure scenario, but nevertheless pyro valves installed in Mars OBSERVER received a thorough examination as part of that failure investigation [1829, 1831, 1832]. Ground testing of flight-type pyro valves and heavy-duty, reusable pyro valve simulators with hydrazine and MMH allowed the analysis and quantification of blow-by and its effect on initiation of hydrazine explosions. Pyro valves manufactured by two suppliers, OEA and Conax, were tested, and it was found that the Conax pyro valves had less blow-by. Valves come with different bore diameters to be used in 0.25-, 0.375-, and 0.5-in. O.D. tubing systems. One pyro valve simulator was sized to represent the OEA 1420-7 stainless-steel configura-

tion. Another used a titanium alloy body. The travel speed of the ram piston could be measured with a laser Doppler interferometer. Blow-by gases were analyzed by GC and residual gas analyzer mass spectrometers. Particulates were collected and examined microscopically and counted on a Millipore filter. Another test setup simulated the geometries of TELSTAR 402 and LANDSAT F, both of which experienced in-flight failures at the moment when the second pyro valve was initiated. For the ground tests, the first pyro valve was replaced with a mechanical ball valve since the delay time between filling the manifold and firing the second pyro valve was on the order of minutes and the first valve did not need to be a fast-acting valve. The clearance between the pyro valve simulator housing and the ram could be varied by choosing pistons of different geometries. The clearance had a pronounced effect on the amount of blow-by. In one test with a 0.14-mm (0.0055-in.) clearance, there was only a mild hydrazine reaction and the peak pressure was 2200 kPa (320 psia). One test with a 0.17-mm (0.00685-in.) clearance caused a hydrazine explosion that destroyed the system and developed many fragments. The fragmentation pattern suggested that this was neither a gas-phase nor a liquid-phase detonation. It was suspected that it was related to a low-velocity detonation in a two-phase system (hydrazine froth or hydrazine with many gas bubbles). In another test, only a burst disc ruptured, but the tubing remained intact. A fourth test produced a pressure spike of 13.76 MPa (2000 psia). As a sequel to these tests, the setup was modified to reduce the hazard potential of the reaction propagating into the hydrazine supply tank and a high-speed camera was added to film the events [1833].

#### 6.4 Propellant Filters

Propellant filters have the potential to cause major operating problems with hydrazine flight systems. They may become clogged with particulate debris, increasing the pressure drop and decreasing the flow rate of hydrazines to the engines. They may act as bubble traps, accumulating small gas bubbles and then allowing a large bubble to be displaced, which may cause momentary thrust imbalance if a pair of thrusters is firing simultaneously on either side of the spacecraft. In the case of arcjets, a bubble may cause the arc to extinguish, requiring a restart, which shortens the life of the electrodes. When tabulating the wetted surface area of components suspected of contributing to gas evolution or metal leaching, the filters are the leading contributors because of the large surface area of the fine-mesh filter screen they contain. The wire mesh is often accordion-pleated to increase the particle-retention capacity. Filter screen and housing samples from CRES-304L representative of the MARINER MVM73 and CRES-304L, CRES-321, and CRES-347 representative for the MJS77 (VOYAGER) systems were tested in the JPL long-term storage tests [1160, 1161, 1638].

The most troublesome property of micrometer-sized filter screens that is often not recognized by system engineers is the tendency of liquids (cleaning agents, solvents,

water, residual hydrazine) to become trapped behind filters when one is attempting to evacuate the system in order to dry it out prior to launch or after flight use. Numerous contamination incidents have been caused by residual fluids in the propellant system. In some cases, water or hydrazine may actually freeze on the filter and evaporate/sublime only very slowly even with the best vacuum in the world applied to the suction side.

The inlets to propellant valves are usually protected by filters to retain particles that might get lodged on the valve seat and cause the valve to leak when it is commanded shut. The screen material on the filters must be compatible with the propellant, which in the case of hydrazines is not as difficult a task as with oxidizers. The corrosion product (carbazate, carbonate) film growing on the thin metal wires might cause a narrowing of the passages and increase the pressure drop or embrittle the wires. A similar wire mesh is used in surface tension propellant management devices in propellant tanks for zero-*g* operation. The long-term effects of propellant immersion on fine micronic stainless-steel wire cloth were studied for hydrazine, MMH, UDMH, and six other propellants [1834]. Immersion time histories reported in the literature ranged from 3 months to 7 years.

## 6.5 Propellant Pumps

Hydrazine is a very poor lubricant, and it is not easy to design pumps where the metal-to-metal contact surfaces do not gall after some time. The problem seems to be less pronounced with the alkylhydrazines. There is not much information on pumps used in hydrazine manufacturing plants and tank farms. Whenever possible, anhydrous hydrazine transfer is achieved by pressurization instead of with mechanical pumps. It is a lot easier to just clean out a dip tube than to clean out a pump after the transfer is completed. The new hydrazine transportation and storage 4BW cylinders introduced in the early 1990s are designed to be pressurized (the 55-gal drums were not) and the dip tube is permanently installed.

Because of the poor lubricity of hydrazine, galling of fuel pump gears during the development of the APU for the Space Shuttle was an early problem that significantly limited gear pump life [1744]. Galling problems could be reduced by decreasing the pitch velocity, by designing gear teeth to minimize sliding contact, and by selecting a very hard gear material like M2 tool steel. A fuel filter immediately behind the gear pump was installed to collect some of the abrasion products before they had a chance to plug valve and injector orifices. Despite this precaution, catalyst in post-flight APU gas generators collected sufficient iron to become magnetic.

The largest hydrazine pumps flown were those in the TITAN II, III, and IV pumping Aerozine-50 and those in ARIANE IV pumping UH-25. These pumps were driven by exhaust gases from gas generators burning fuel-rich main propellants or stoichiometric

oxidizer/fuel combinations with water coolant injection. It has always been desirable to operate propellant pumps on propellants that are already on board in order to avoid having to carry separate pump drive fluid (hydrogen peroxide) tanks, as was done on the A-4 (V-2) or the VIKING, the first planned US satellite launch vehicle, and is still in practice with the Russian SOYUZ launch vehicle.

Small missiles must rely on heavy pressurant tanks or can use hot hydrazine decomposition products from a gas generator to drive a piston pump or a set of piston pumps to feed hydrazine to the thrusters and gas generators. These propellant feed systems are best used in high-performance rocket propulsion systems with short mission durations that must operate in a thrust-on-demand mode such as for divert propulsion, evasive maneuvers, and terminal homing exercises of interceptors [1835–1837]. The exhaust from the reciprocating piston-driven piston pumps can be vented overboard or collected in a plenum for attitude control in warm gas thrusters. Flight-weight pumps with a displacement of  $106\text{ cm}^3$  ( $6.5\text{ in.}^3$ ) have a mass of under 100 g and can deliver flow rates equivalent to their own weight in hydrazine per second. Additional weight savings arise from using a lightweight, thin-walled aluminum tank instead of a tank that must withstand thousands of psi feed pressure. Using piloted solenoid valves, development units could be operated on hot gas near 1023 K ( $1400^\circ\text{F}$ ) [1838–1840]. If a pair of alternating pumps is used, a continuous stream of propellant can be delivered since one pump is expelling liquid as the other is being filled with fresh propellant. Flight-weight units use automatic warm gas pneumatic valve controls instead of solenoid valves [1841]. The same principle can also be applied to reciprocating pumps for bipropellant propulsion systems [1842]. This requires a total of four pumps, but they can share some of the controls and operate in synchrony. Small hydrazine pumps on satellites as an alternative to pressure-fed systems would allow lightweight propellant tanks and would not require as much pressurant gas as a blowdown or regulated pressure system [1843].

The ground-service equipment (GSE) fueling system for the EURECA reusable platform used a novel concept with nitrogen-driven PTFE diaphragm pumps supplying propellant directly from the shipping drums [1798].

Electrokinetic pumping offers a method to precisely meter liquid propellants under purely electrical control at pressures and flow rates well suited for microthruster applications. Electrokinetic pumping can be applied to very small microthrusters [1844]. After exploring a variety of materials and surface treatments for the electrokinetic pumping media, electrokinetic pumping of anhydrous hydrazine using both packed-capillary and larger sintered-monolith pump designs were demonstrated [1845]. Specific impulses up to 190 s have been shown for hydrazine in non-optimized capillary thrusters at a mass flow rate of  $1.5\text{ mg/s}$ . Controlled thrust pulses with a maximum continuous thrust of  $1.5\text{ mN}$ , minimum impulse bit of  $7\mu\text{N}\cdot\text{s}$ , and average specific impulse of 110 s have been demonstrated with an electrokinetically pumped microthruster assembly.

## 6.6 Pressurant Gas Selection

Obviously pressurant gases for hydrazine monopropellant and bipropellant propulsion systems must be compatible with hydrazine, which narrows the choice to nitrogen, helium, and argon. Nitrogen is often chosen because it has lower leak rates than helium. Helium has the advantage of being lighter weight where total system weight is critical, such as in lunar and planetary probes. Some of the pressurant gas selection and pressurization system design considerations described for hydrazine here apply just as well to other liquid propellants.

Pressurant gas selection depends on the type of barrier between the pressurant gas and liquid propellant. If contact times are short, as in a missile with a sealed pressurant tank during storage, less stringent purity requirements may be tolerated than in a 15-year satellite. Piston tanks may suffer from blow-by of gas, and some liquid may adhere to the walls and not get wiped off by the O-ring seals of the piston, causing adverse interaction of propellant and pressurant gas. Elastomers have some gas and liquid permeability; therefore, one must anticipate some pressurant gas/propellant interaction, although it will be slow. Oxygen contamination of the pressurant gas must be avoided because in extreme cases hydrazine will autoignite and explode with air or oxygen under pressure. Cryogenic oxygen and propellant hydrazine systems should not share a helium supply. Metal diaphragms are impermeable to either gas or liquid and allow a wider choice of pressurant gases but can be reversed only once or a few times at best before the metal fatigues.

The design of blowdown tanks or storage tanks in which the pressurant gas sits in the same tank as the liquid must allow for thermal expansion of the liquid if the tank is stored at high temperature. These considerations apply even to storage cylinders to determine the minimum size of the ullage required to accommodate the thermal expansion of the liquid and the pad pressure that is typically maintained to prevent intrusion of air during storage and shipment. Cylinders must not be overfilled with liquid hydrazine before shipment. As the liquid expands, the ullage gas bubble is compressed, and the elevated pressure allows some gas to be dissolved in the liquid propellant. It is also unusual for gas solubility in hydrazine to increase with temperature, whereas that in most other liquids decreases with temperature (see information on gas solubility in Section 2.1.12). The calculation of the necessary tank size to accept and hold a given mass of hydrazine at elevated temperature without exceeding the safe operating pressure rating of the tank is a frequent design problem facing system designers. The following variables enter this calculation: thermal expansion of the liquid, thermal expansion of the pressurant gas, thermal expansion of the tank, and solubility of the gas in the liquid [1846].

Another consideration in selecting pressurant gases is potential bubble release when the propellant is expanded to lower pressure on its way into the rocket engine. Gas bubbles may cause irreproducible impulse bits and cause arcjets to extinguish.



Gas bubbles may sensitize hydrazine to explosive decomposition upon rapid (adiabatic) compression. Dissolved gases may cavitate at the inlet of pumps unless the necessary net positive suction head is maintained [1847]. For this reason, it may be desirable to choose a gas that has very little solubility in hydrazine(s).

If propellant is rapidly withdrawn from a blowdown tank without diaphragms or pistons separating the liquid and gas phase, it will take some time before the phase equilibrium adjusts and dissolved gas is released from the liquid to restore equilibrium. This is the inverse problem of tank pressurization and propellant saturation with pressurant gas prior to launch (Section 7.5.2).

One-shot systems such as in tactical missiles using storable liquid propellants can be pressurized by warm gas from solid gas generant cartridges. It is important that the temperature at the pressurant-liquid interface not exceed the thermal stability limits of the hydrazine fuel. In some cases, the interface is formed by a metal bellows or a piston, such that the hot gases and the propellant are not in direct contact.

A significant amount of effort has been devoted to vaporizing liquid pressurants for the expulsion of hydrazine propellants [1848]. In this case, the pressurant and the propellant must be separated by metallic diaphragms or the pressurant has to be totally compatible and immiscible with hydrazine and the catalyst. Many vaporizing liquid pressurants are available. Their physical properties have been tabulated and some have been tested in ground test expulsion systems. The problem with vaporizing liquid pressurants is that the feed pressure (i.e., the vapor pressure of the liquid) is dependent on the temperature of the pressurant tank. However, as soon as propellant is withdrawn, the vaporizing liquid cools the residual liquid and the vapor pressure drops. The vaporizing liquid reservoir must be a high-heat-capacity massive tank, or one could surround it with heat-storage phase change materials to maintain the temperature a little longer and soak up heat during idle periods.

Many of the vaporizing liquids studied are fluorochlorohydrocarbons often used as refrigerants and aerosol propellants. Unfortunately, most of those react with hydrazine or poison the catalyst.

## 6.7 Flow Meters

Turbine and Micro Motion flow meters are routinely used for all three types of propellant hydrazines to meter propellant into rocket engines during ground testing and to calculate delivered specific impulse. Flow meters do not fly with rockets or satellites.

For ground testing of the liquid apogee kick stage engine for the Japanese ETS-4 satellite, a flow meter accuracy of  $<\pm 0.25\%$  was desirable to verify specific impulse accuracy of  $\pm 1$  s. To achieve this narrow level of uncertainty, an in-place, end-to-end turbine flow meter calibration system became an integral part of the thrust stand [1849], combined with digital data processing [1850]. Flow meters, valves, and pressure trans-

ducers for the TITAN II missile were endurance-tested and calibrated in a closed-loop propellant pumping system containing two 22.7-m<sup>3</sup> (6000-gal) tanks and two 984-L/min (260 gal/min) pumps for NTO and Ae-50 [1851].

## 6.8 Flight Tanks and Propellant Management Devices

A large branch of the aerospace industry has specialized in supplying pressurant and propellant tanks to the propulsion subsystem contractors and the prime contractors and commercial companies who build their own propulsion subsystems and integrate them with the payload. It is not possible to provide a complete overview of all tanks that at one time or another have been used with hydrazines or may at some time in the future be used with hydrazines. A snapshot in time of tanks that were available as of 1984 or 2001 was provided in the two earlier editions of the hydrazine book [11, 22]. It has not been possible to keep such a compilation up to date. Historical surveys of flight-weight propellant tanks have been published earlier and quickly became obsolete [1852–1854], because these survey reports unfortunately go out of date as soon as the ink dries. Just as with the valve industry, changes in product availability are occurring daily, and it is very difficult to maintain a complete and current list of flight tanks qualified for hydrazines. The only way to keep up to date with what is available in real time would be to post a tank availability list on the Internet and update it periodically. Candidate propellant tanks for hydrazine(s) include composite overwrapped tanks, tanks without PMDs, elastomer diaphragm and bladder tanks, reversible metal diaphragm and metal bellows tanks, piston tanks, and surface tension PMD tanks. The summary of flight tanks for hydrazine and MMH use that was published in 2001 in [22] has not been updated because many of the same space-qualified tanks are still in use [1855].

Surface tension and contact angles of liquid propellants must be known for the design of surface tension tanks for use in a zero-g environment in space. Surface tension tanks have fine-mesh screens in the form of chimneys, vanes, and galleries to collect and hold propellants in position near the tank outlets even in a zero-g environment, such that only liquid and no pressurant gas can enter the engines [1856–1858].

The Air Force Rocket Propulsion Laboratory (AFRPL) has conducted an extended propellant tank ground storage program that has been under way for several decades. The items included in this program can be divided into three categories: **(1)** small containers, **(2)** full-size flight-system representative tankage, and **(3)** tankage systems with associated expulsion devices. It included flight test articles as well as laboratory test tanks made from various materials (but without PMDs inserted), including five tanks each made from steels AM-350, 17-7PH, and A-286 and aluminums 2014-T6, 2021-T6, 2219-T8, and titanium-6Al-4V [1696, 1697]. In addition, some tanks, such as MARINER space probe tanks containing AF-E-332 bladders, were also included in the

test. Table 72 gives a list of reference numbers, report number, and date of publication. This table should help in keeping this very useful source of information organized (this is only useful for those readers eligible to obtain reports that may have limited distribution status). Many of these storage tests also included tanks filled with MMH or NTO instead of anhydrous hydrazine.

**Table 72:** Summary of tank storage test reports from AFRPL Edwards AFB.

| AFRPL-TR Report No. | Accession No. | Report date | References |
|---------------------|---------------|-------------|------------|
| 69-082              | AD-857561     | Apr 1969    | [1859]     |
| 70-043              | AD-875081     | May 1970    | [1694]     |
| 71-020              | AD-882232     | Mar 1971    | [1860]     |
| 71-113              | AD-735288     | Nov 1971    | [1696]     |
| 72-126              | AD-755383     | Dec 1972    | [1697]     |

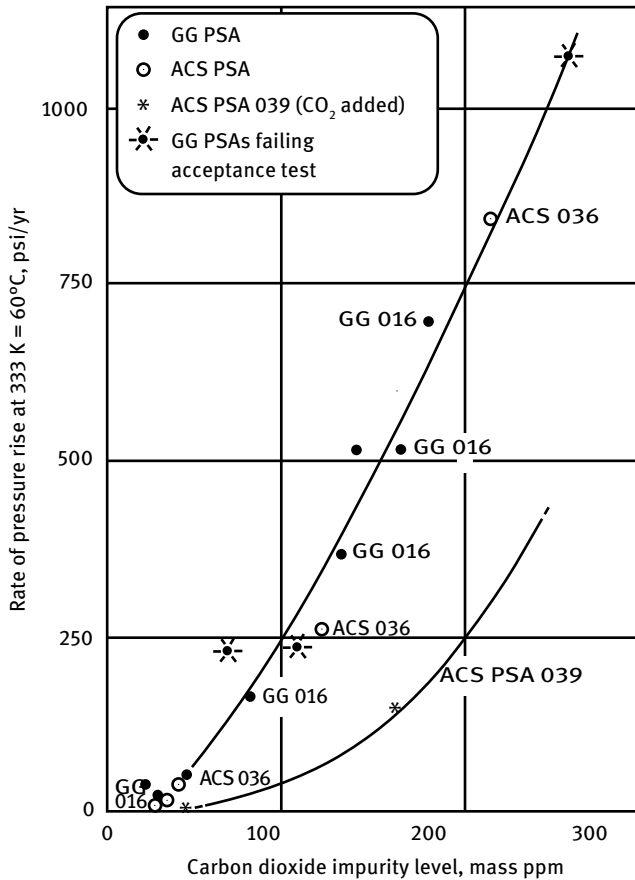
Storage tests with tanks filled with hydrazine are frequently conducted under desert conditions at elevated temperatures to check for pressure buildup by hydrazine decomposition on metal surfaces with which it is not compatible. Initially tanks made from 17-7PH and AM-350 stainless steels experienced some rapid pressure rise. However, when the AFRPL storage program was interrupted after 10 months and the hydrazine replaced with a fresh load of hydrazine, the rate of pressure rise was much lower [1696, 1697, 1861].

It appeared that some passivation had taken place, and most contaminants were leached from the tank surface by the first propellant load. Similar results were obtained at Bell Aerospace, where 17-7PH and AM-350 tanks were exposed to hydrazine initially at nominal 301 K (83 °F) for 1 year with numerous temperature excursions as a result of controller failure and accompanying hydrazine decomposition, which required venting of the tanks to prevent overpressurization [1862]. After the hydrazine was replaced and the temperature was held steady at 322 K (120 °F) for 3.5 years, the pressure rise from hydrazine decomposition was minimal. It is advisable to inspect test articles for possible corrosion immediately after termination of the exposure test and not let exposed tanks sit around in air until a metallurgist happens to have some time to examine them. Residual hydrazine and air (CO<sub>2</sub>) may cause additional corrosion if the test articles are not thoroughly decontaminated.

A flight-weight Al-2014 tank containing 1170 kg (2580 lb) of anhydrous hydrazine was stored in a desert climate for 46 months [1688]. At the end of that test, the tank was found to be slightly corroded. Subsequent firing tests showed the fuel to be satisfactory for combustion with NTO, but it is very doubtful whether it would have been clean enough for monopropellant use. The hydrazine content of the fuel decreased from 98.1 to 96.5% N<sub>2</sub>H<sub>4</sub>, probably by decomposition and ammonia dilution.

Storage of post-boost propulsion systems on missiles in submarines requires careful cleaning and filling procedures of the propellant tanks [1863]. In a series of controlled on-shore storage tests, it was observed that the pressure rise rate decreased with time by a factor that varied from 1.1 to 3.0 [1864, 1865]. The reasons for this wide variation were not fully understood. Removal of active material from the tank surfaces seemed to reduce the heterogeneous rate and simultaneously enhance the homogeneous rate. The predicted tank lives of 189 units tested based on the 72-h/60 °C acceptance test ranged from 10 (minimum acceptable) to 189 years. Even identical tanks filled side by side from the same drum of hydrazine varied significantly. One of the variables suspected of causing variations in the rate of hydrazine decomposition and pressure buildup was the microscopic surface roughness of the steel, in particular after pickling. It was suspected that multiple pickling operations with nitric/hydrofluoric acid (tanks recycled because they were not visually clean after the first pickling exercise) may result in increased surface roughness and increased rate of gas evolution. The nominal duration of pickling was 50 min. SEM surface analysis of CRES-304L treated in this manner showed a very rough surface and signs of severe etching and crystallographic pitting with some signs of intergranular attack. The number of allowable pickling operations should be limited in the procurement specification for CRES-304L tanks for long-term storage applications. Conversely, based on coupon testing, it was shown that electropolishing would reduce the rate of gas evolution by an order of magnitude. Another variable was drum-to-drum variation of the quality of hydrazine used.

A group of stainless-steel propellant storage assemblies (PSAs) was loaded with different batches of hydrazine that had been intentionally doped with controlled levels of CO<sub>2</sub> in the range of 30–200 ppm [1692]. The specification limit for MIL-P-26536 in effect at that time was 30 ppm CO<sub>2</sub>. Figure 53 shows the observed decomposition rates and demonstrates the distinct correlation that exists between CO<sub>2</sub> contamination and the rate of gas evolution. The rates of gas evolution were normalized for 10% ullage. The serial numbers of the PSAs (016, 036, 039) are for reference only. The design of the PSAs was essentially similar, with reversible metal diaphragms for zero-g propellant management, with spherical 1.5-L tanks serving as the source of propellant for gas generators for the expulsion of the bipropellant (GG PSA) and ellipsoid 6-L tanks serving as the source of propellant for the attitude control system (ACS PSA). The significance of these data is that it implies that the influence of CO<sub>2</sub> is associated with the heterogeneous decomposition of the hydrazine on the surface of the steel rather than homogeneous decomposition in the liquid. During a 10-year storage test at 302K (29 °C) with 15 PSAs sampled at random from a production line, the pressure in the ullage in a typical stainless-steel PSA with clean hydrazine rose from 117 to 220 kPa (17 to 32 psia).



**Figure 53:** Gas evolution rates in propellant storage tanks as a function of carbon dioxide contamination. (Reproduced and modified from [1692].)

## 6.9 Propellant Couplings and Hoses

This section on fluid connectors for hydrazine service can give only a preliminary overview of this component selection area. It is difficult to maintain a current file because the list of available components and list of potential suppliers change so frequently.

### 6.9.1 Fittings, Couplings, and Quick Disconnects

With increasing demands on the lifetime of satellites, refueling of unmanned satellites in orbit is the next major step in space operations (Section 7.5.3). Refueling is routinely done with bipropellants on the International Space Station using the Russian propulsion module. These in-orbit refueling operations require quick disconnect couplings

with a minimum of liquid leakage when making and breaking a connection. The same requirement begins to be imposed on Earth-based hydrazine transfer operations for reasons of toxicity and minimizing worker exposure. Quick disconnects initially intended for space operation will see ground-based use as well. Quick disconnect couplings described here are used not only for hydrazine but can also be used for other liquid propellants, maybe even cryogenic propellants.

Several connector companies have been active in the development of quick disconnects for hydrazine and hydrazine-based fuels. All these systems require a thorough understanding of material compatibility with hydrazine, in particular on the sliding fits of the moving parts that achieve the connection of mated parts and the hermetical sealing of demated parts against the full operating pressure on one side and vacuum on the other side. Some of the couplings were developed for automated, robotically controlled docking and mating of resupply vehicle and propellant-consuming spacecraft; other quick disconnects were designed with astronaut safety in mind, in particular with regard to residual propellant inadvertently leaking onto the surface of a space suit and dragged into the living quarters of the manned space station or shuttle following the EVA. NASA attempted to standardize the couplings such that an entire fleet of satellites could be serviced by the same tanker [1866–1868] or propellants could be transferred between satellites (peer-to-peer transfer). At least three flow inhibitors had to be installed on each side of the couplings. One of these couplings has been installed on the GRO satellite in anticipation that it might be possible to refuel it at some future time. With a standard, current technology quick disconnect, astronauts have very limited knowledge about the condition between the coupling halves at the moment they are about to break the connection. This potential problem has been solved with so-called smart disconnects, which contain additional sensors and safeguards against liquid spillage [1869]. Older connectors used since the APOLLO program and once used with hydrazine on the STS APU had a history of leakage and spills. The F-16 EPU uses a more advanced quick disconnect for the H-70 fuel.

## **6.9.2 Transfer Lines and Hoses for Hydrazine**

### **6.9.2.1 Transfer Lines for Liquid Hydrazine**

USAF safety inspectors insisted at one time that contractor use electrically conductive, carbon-filled, Teflon-lined, stainless-steel-braided flex hoses for the fueling of satellites because they were worried about the buildup of electrostatic charges in flowing liquids. Unfortunately, insufficient material compatibility testing was done before putting graphite-filled, Teflon-lined, electrically conductive hoses into service. A spacecraft may have been launched with “black” hydrazine because it was noticed too late that carbon was shed from the new hoses into the fuel. NASA has noted the blistering of similar flex hoses used for MMH service. Apparently, some agencies had been using them to avoid a perceived ESD hazard during fueling operations, but they caused worse problems than those they were trying to avoid.

### 6.9.2.2 Sampling Hoses for Hydrazine Vapors

Tubing for remote sampling by drawing air samples from outlying work areas to a centrally located analyzer should be non-reactive, non-absorptive, and impermeable to hydrazine, MMH, or UDMH vapors [1870, 1871]. There was a case where for many years animal exposure cages were overdosed accidentally because the hydrazine arriving at a central monitoring station after traveling through very long tubing was only a fraction of what was in the exposure chambers of the animals. Most of the hydrazine had absorbed into or diffused through the tubing, and some became oxidized. The published animal exposure toxicity data obtained with this faulty analysis technique should have been invalidated. Hydrazine decay during transfer in the sampling lines was not measured.

## 6.10 Propellant Gauging (Gaging)

Sight glasses, floats, or other liquid-level gauging methods that are commonly used on the ground are no longer working in space in a zero-*g* or low-*g* environment. Commercial satellite operations are a multi-billion-dollar industry whose revenue is often dependent on the accuracy of predicting the remaining life of a satellite as it nears its end of life. This information is needed in planning satellite replacements, in transponder leasing contracts, and in squeezing maximum revenue out of existing space assets. In crowded geostationary orbits with a limited number of orbital slots, enough propellant must be reserved for moving the exhausted satellite to a graveyard orbit or de-orbit it altogether. Incorrect propellant gauging information may result in bubble ingestion, loss of pressurant gas, or uneven thrusting and spacecraft tumbling out of control when thrusters need to operate in pairs and one of them is starved of propellant. Considering how important this information can be, it is surprising how few propellant gauging systems have been tested or even flown. The propellant gauging methods described here for hydrazine work equally well for NTO and MMH. Many possible gauging techniques that might work in zero-*g* are quite susceptible to low-*g* disturbances [1872]. Problems are caused by ambiguous liquid orientation, bubble entrapment, sensor wetting, and reduced convection. Techniques evaluated in sub-orbital parabolic KC-135 flights include (1) an ultrasonic point sensor system, (2) a nucleonic gauging system, (3) an ultrasonic torsional wave guide, and (4) an ultrasonic flow meter [1873]. Other gauging methods suggested were (5) IR-absorption trace gas, (6) integrating flow meters [1874], or (7) detection of resonant acoustic mode shifts due to changes in the tank's effective mass [1875]. Despite all these efforts, there remains an uncertainty about the accuracy of propellant gauging systems for spacecraft in orbit [1876].

Accurate temperature and pressure telemetry may enable ground controllers to calculate the amount of remaining propellant in a blowdown tank from PVT equa-

tions [1877]. This method would be applicable to any liquid propellant, not just hydrazine.

Every drop of hydrazine in orbit is worth more than its weight in gold. For communication satellites, just 1 lb hydrazine more or less can translate into about \$2.5 million in revenue difference by extending the useful life of a satellite.

Short of having actual liquid level telemetry data (it is not known whether any of the satellites currently using hydrazines have this capability), the filling level of tanks can sometimes be implied from the telemetry of tank temperature increases after the satellite enters sunlight or after tank heaters have been turned on. This was the method used in G-STAR III as it approached its end of life in orbit after the station keeping propellant was exhausted early. An estimate of remaining propellant was needed to rescue it and move it from a faulty transfer orbit to 24-h GEO [1878]. Temperature variations between the two pairs of tanks cause unequal helium expansion, leading to thermal pumping of the hydrazine between tanks on a daily basis. This thermal pumping had the potential of depleting all the hydrazine from one tank and pressurant gas entering the propellant lines leading to the thrusters, resulting in loss of pressurant and loss of impulse reproducibility. By selectively turning tank heaters on and off, the flight controllers had a limited method of distributing the propellant evenly to keep this from happening too soon. One group of hydrazine monopropellant tanks in the Indian Remote Sensing (IRS) satellite emptied much earlier than expected [1879]. Temperature differences in the tanks were blamed for this anomaly, and after-the-event calculations showed how much propellant imbalance would have to be expected for a given  $\Delta T$ .

Using tank temperature and tank heater energy input telemetry, it is now possible to fairly accurately predict the amount of residual propellant in surface tension PMD tanks in satellites in orbit, allowing extension of useful mission duration and leaving just enough propellant to do the controlled graveyard orbit decommissioning burn [1880–1882].

Even in spin-stabilized satellites such as the HS-376, where the whereabouts of the propellant should be well known (as opposed to three-axis stabilized satellites), propellant gauging has not always been an easy task [1883]. Using tank pressure (PVT method) measurements during the blowdown of four conospheroid tanks in combination with thrusting bookkeeping for cumulative propellant consumption derived from  $\Delta V$  and known  $I_{sp}$  performance of the 5-lb<sub>f</sub> thrusters, it was possible to obtain remaining propellant measurements with satisfactory accuracy. Hughes had the rare opportunity to verify their propellant gauging method based on telemetry data when two wayward satellites were plucked from orbit by daring Space Shuttle astronauts and brought back to the surface, where the off-loaded propellant was weighed and compared to the bookkeeping by PVT methods and found to agree within a few percent accuracy. Much improved accuracy was achieved by Hughes Space and Communications Co. in its large HS-601 geostationary bipropellant satellites using high-resolution pressure transducers and brief pulsing of the pressurant valves between existing



pressurant tanks and propellant tanks [1884]. Momentary opening of the interconnect valve results in periodic re-pressurization of the propellant tanks. Measurements of pressures in the propellant tanks before and after re-pressurization make it possible to determine the gas volume in the propellant tank, which translates into propellant volume and propellant mass knowing the total volume of the tank and the density of the propellant. The re-pressurization capability offers the additional advantage of closely controlling the oxidizer : fuel ratio for maximum delivered  $I_{sp}$ .

### 6.11 Other Components

It is unfortunate that the freezing point of hydrazine is relatively high, close to that of water. A system designed to operate in outer space, including Earth's shadow, must be designed to keep hydrazine above freezing. The thermal design of spacecraft is a science by itself. All the way from the propellant tanks to the thruster inlet, temperature must be maintained by a series of tank heaters, line heaters, valve heaters, and catalyst bed heaters. These components along with their controls and power distribution lines add to the complexity of hydrazine propulsion systems. Some of the upper stages of launch vehicles, such as the Inertial Upper Stage (IUS), had to operate as the upper stage of expendable launch vehicles (TITAN) as well as in the payload bay of the Shuttle STS. For TITAN launches, the mission was completed in a few hours, but if carried to low Earth orbit by the STS, the IUS may spend several days in the payload bay before it can be launched. For those situations, electric heaters are used to protect the hydrazine system from freezing, and multi-layer insulation (MLI) blankets are used to reduce the heat loss from the solid rocket motors. In addition, the payload satellite or space probe may also contain hydrazine that has to be kept in the liquid state. Sub-system and system vacuum chamber tests were conducted to confirm the thermal design and analysis of the hydrazine system under these conditions [1885].

The concern about inadvertently freezing hydrazine lines in satellites and upper stages has led to the development of self-regulating line heaters such as the Raychem Thermolimit heater tape used on the CENTAUR upper stage [1886]. Since the main propellants of this upper stage are cryogenic oxygen and cryogenic hydrogen, some parts of the stage may get very cold, cold enough to freeze hydrazine used in the RCS. The operating principle of the Thermolimit tape is based on the observation that the resistance of a conductive polymer (Kynar) increases with temperature, but so does its specific volume, reducing the cross section across which current can flow. It should be mentioned that Kynar is not compatible with hydrazine. It is important to avoid spills of hydrazine propellant on Kynar heater tapes.

If the temperature controller of line heaters fails closed, the lines may inadvertently become overheated. The worst-case scenario of overheated propellant lines was simulated in dynamic and static ground tests [1173].

## 7 Handling of Hydrazine

Because of the toxic and corrosive properties of hydrazines, these compounds should not be handled in the literal sense of the word, that is, with bare hands or in close contact with the skin. The toxic and corrosive properties of hydrazines make it mandatory that precautions necessary for safe handling be sufficiently understood. Once the proper precautions for storage and transfer of hydrazines have been taken, hydrazines can be handled as safely as any other hazardous chemicals. It is the objective of this section to provide the hydrazine user with at least the most important information to get the job done safely and successfully. This chapter is the chapter for anhydrous hydrazine, but many of the considerations for safe handling of hydrazine are the same as those for methylhydrazines, which are discussed in other chapters of *Encyclopedia of Liquid Fuels*.

One of the main applications for hydrazines is in space propulsion. Space propulsion system hazards for hydrazines and other rocket propellants are summarized in the *Space Propulsion Hazards Manual*, a three-volume series useful for planning of ground service equipment (GSE) and fueling operations [1887–1889]. Storage and transport of large quantities of hydrazines constitute a potential corrosion, flammability, and toxicity hazard and must be carefully planned to avoid uncontrolled release of hydrazines in either liquid or vapor form. First sources of information on handling and storage of hydrazines are the manufacturer's product data sheets [1645, 1890], safety data sheets, and publications by the US federal government.

Disposal and spill cleanup of hydrazine fuels has been practiced for many decades, and there exists a good database on available methods for safe handling of this fuel, for instance Chapter 2 in [1891].

### 7.1 Design of Storage Facilities

Hydrazine storage facilities are needed at the point of production, as a method of government stockpiling of strategically important fuels, at the point of consumption to assure against interruptions of supply, and, finally, for the storage of waste propellant waiting to be reprocessed or destroyed.

One of the largest storage and mixing facilities for propellant hydrazines during the 1960s was the Rocky Mountain Arsenal near Denver, CO. This facility could store hundreds of thousands of gallons of various hydrazines and was also in charge of mixing Aerozine-50 from its ingredients. The Rocky Mountain Arsenal storage and mixing facility was closed in the late 1970s amid accusations of improper housekeeping procedures and environmental pollution (Section 7.12). In 1988, Olin Chemicals opened a new hydrazine storage and mixing facility in McIntosh, AL, which was mostly devoted to blending and storing Aerozine-50 but also had limited storage capacity for some MMH.

**Storage Compatibility Requirements and Setback Requirements for Liquid Propellants.** Quantity-distance regulations for liquid propellants and explosives were once set forth in two US Army safety manuals [1892, 1893]. The first manual, in Section 15, pages 15–1 through 15–27, contains a section on quantity-distance storage criteria for liquid propellants and categorized all propellants into four hazard groups, I through IV, then designated six storage compatibility groups, A through F. Hydrazine, MMH, UDMH, Ae-50, and mixed amine fuels have been classified in Hazard Group III and Storage Compatibility Group C. A 200-kg (440-lb) drum of anhydrous hydrazine in unprotected storage requires a setback of 180 m (600 ft) from inhabited buildings, public traffic routes, and other storage structures containing incompatible propellants. If the drum is in a protected bunker, the setback requirement is reduced to 39 m (130 ft). For 10 drums of hydrazine, the unprotected setback is still the same, 180 m, but the protected setback is increased to 63 m (210 ft). Additional quantity-distance regulations for explosives (most are much more hazardous than liquid hydrazine) are described in the Department of Defense (DoD) *Contractor's Safety Manual for Ammunition and Explosives* [1894] and the Department of Energy (DoE) *Explosives Safety Manual* [1895–1897]. These manuals are not always directly applicable to hydrazine and are listed here only as examples of how quantity-distance requirements were derived. The standards applicable to energetic liquids have been reviewed [1898] and need to be updated periodically.

## 7.2 Applicable Storage and Transportation Regulations and Recommendations

This section constitutes only an incomplete summary of regulations and recommendations affecting the storage and transfer of hydrazines. Regulations change daily, and the hazardous materials coordinator for a chemical company or rocket test site will need to follow updates on a day-to-day basis. This is a full-time job.

### 7.2.1 Applicable Government Regulations

The transportation of hydrazines in interstate commerce must comply with the Code of Federal Regulations CFR 49, § 172.101. According to the 1987 revision of that document, anhydrous hydrazine was then classified as a **Flammable Liquid** and **Poison**. The shipping classification of anhydrous hydrazine has changed several times during the past 50 years. At one time, anhydrous hydrazine carried only a **Corrosive Liquid** label. Now the segregation requirements from other cargo are still the same as for Corrosive Liquid. Prior to 1987, hydrazine hydrate required only the **Corrosive Material** label. Because regulations change frequently, it is advisable to check the most recent revision for the applicable requirements before shipping hydrazines. Hydrazine, MMH, and UDMH are or were shipped in containers of the types listed in Table 73.

Normally, the Department of Transportation (DOT) requires all rail cars or tanker trailers to be hydrostatically tested every 5–10 years. However, because of the age of

**Table 73:** Transportation containers for hydrazine fuels.

| Fuel                                                                 | Type of container          | DOT specification                     | Metal                                  | Safe volume capacity (at 10% ullage) |                   | Load capacity |       | Tare mass |         | Max. allowed differential press. inside – outside |                                         | Safe to apply vacuum to container? |
|----------------------------------------------------------------------|----------------------------|---------------------------------------|----------------------------------------|--------------------------------------|-------------------|---------------|-------|-----------|---------|---------------------------------------------------|-----------------------------------------|------------------------------------|
|                                                                      |                            |                                       |                                        | L                                    | gallons           | kg            | lb    | kg        | lb      | kPa                                               | psig                                    |                                    |
| N <sub>2</sub> H <sub>4</sub>                                        | Trailer                    | MC 311                                | CRES-304                               | —                                    | —                 | 18160         | 40000 | —         | —       | —                                                 | —                                       | no                                 |
| N <sub>2</sub> H <sub>4</sub>                                        | Rail car                   | 103AALW                               | Al                                     | —                                    | —                 | 22700         | 50000 | —         | —       | —                                                 | —                                       | no                                 |
| MMH                                                                  | Trailer                    | MC312                                 | CRES-304                               | —                                    | —                 | 18160         | 40000 | —         | —       | —                                                 | —                                       | no                                 |
| MMH                                                                  | Rail car                   | 103CW                                 | AlSi-430                               | —                                    | —                 | 31780         | 70000 | —         | —       | —                                                 | —                                       | no                                 |
| UDMH                                                                 | Trailer                    | MC311                                 | CRES-304                               | —                                    | —                 | 18160         | 40000 | —         | —       | —                                                 | —                                       | no                                 |
| UDMH                                                                 | Rail car                   | 105A300W                              | Carbon steel                           | —                                    | —                 | 30870         | 68000 | —         | —       | —                                                 | —                                       | no                                 |
| UDMH                                                                 | Drums                      | 17C                                   | Carbon steel                           | —                                    | —                 | 152           | 335   | —         | —       | —                                                 | —                                       | no                                 |
| All hydrazines                                                       | 30-gal cylinder            | UN1A1                                 | CRES-304L                              | 102                                  | 27                | —             | —     | 66        | 146     | 688                                               | 100                                     | yes                                |
| Mono grade and high-purity grade N <sub>2</sub> H <sub>4</sub> , MMH | GPTU                       | DOT51                                 | CRES-304L                              | 1893                                 | 500               | —             | —     | 2600      | 5760    | 2064                                              | 300                                     | yes                                |
| NTO, MMH                                                             | Pallet-mounted             | Hughes DOT110A500W                    | CRES-304L                              | 950                                  | 250               | —             | —     | —         | —       | —                                                 | —                                       | yes                                |
| Hydrazine, UDMH or any hydrazine-UDMH blend                          | Rail car                   | DOT105J500W MIL-R-87992 (29 Nov 1989) | CRES-304L (with CRES-347 for fittings) | 37800                                | 10000 (3% ullage) | —             | —     | —         | <263000 | 3440                                              | 500 proof, relief valve set at 225 psig | no                                 |
| Hydrazine                                                            | Arch Propellant Serv. Unit | DOT4BW                                | CRES-304L                              | —                                    | —                 | 362           | 800   | —         | —       | 3440                                              | 500                                     | yes                                |

Data sources: [1899–1901]

some of the aluminum tank cars still in use in the late 1990s, the testing requirement was increased to annually.

As one example of the continual changes being made to transportation regulations, which make it very difficult to maintain an up-to-date file, one can refer to the announcement in FR **63**, No. 132, pp. 37453–63 announcing changes made to the requirements that tank cars for hydrazine, MMH, or UDMH have pressure relief valves. Special Provision B7 was added for the entries “Dimethylhydrazine, unsymmetrical,” “Hydrazine, anhydrous or Hydrazine aqueous solutions with more than 64% hydrazine, by mass,” and “Methylhydrazine.” DOT exemptions, DOT-E 11200 and DOT-E 11490, authorize the shipment of hydrazine materials in multi-unit tank car tanks *without* pressure relief devices. A hydrazine manufacturer also sponsored a risk analysis that focused on the transportation of propellants that are toxic and the risks associated with those materials when transported in multi-unit tank car tanks equipped with or without safety relief devices. The results of the analysis determined that there was an increased likelihood of the release of toxic materials when a pressure relief device is present.

A new class of mobile equipment has been designed for the dedicated transport of NTO ( $\text{N}_2\text{O}_4$ ) and MMH liquid rocket propellants [1902]. The existing equipment, operated under special permit, became obsolete in the late 1980s as a result of new DOT regulations. New regulations focus on increasing public safety and reducing the risk of environmental impact. The design and construction of a prototype vehicle was completed concurrently with the development of new DOT rules and specifications. The basis of the new design was a 2.06-MPa (300-psig) ASME pressure vessel, packaged as a semi-trailer with several noteworthy safety features. It was designed to withstand a frontal collision, lateral impact, rollover, and external fire without breaching the pressure integrity of the lading vessel.

### 7.2.2 Reportable Quantities of Hydrazines under SARA Title III

The presence of Extremely Hazardous Substances (EHSs) in quantities in excess of the Threshold Planning Quantity (TPQ) requires certain emergency planning activities to be conducted. A consolidated chemical list including chemicals subject to reporting requirements under Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA), also known as the Emergency Planning and Community Right-to-Know Act (EPCRA), and chemicals listed under Section 112(r) of Title III of the Clean Air Act (CAA) of 1990 was posted on an EPA web site for distribution and downloading in November 1998. This so-called mother of all lists was prepared to help firms handling chemicals determine whether they need to submit reports under Sections 302, 304, and 313 of SARA Title III (EPCRA) and, for a specific chemical, what reports may need to be submitted. Accidental releases of Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA) hazardous substances, in quantities equal to or greater than their reportable quantity (RQ), are subject to reporting to the National Response Center

under CERCLA. Such releases are also subject to state and local reporting under section 304 of SARA Title III (EPCRA). The provisions of the act are found at 40 CFR Parts 350 through 372. SARA Title III has two distinct goals: (1) to encourage and support emergency planning for responding to chemical accidents and (2) provide local governments and the public with information about possible chemical hazards in their communities. The TPOs for various hydrazines are summarized in Table 74. As of March 2022, this information was available at <https://www.gpo.gov/fdsys/pkg/CFR-2016-title40-vol30/pdf/CFR-2016-title40-vol30-part355-appA.pdf>.

**Table 74:** SARA Title III List of Lists, Consolidated list of chemicals subject to Emergency Planning and Community Right-To-Know Act (EPCRA) and Section 112(R) of Clean Air Act (CAA), as amended November 1998.

| CAS No.   | Chemical name         | Sec. 302<br>(EHS) Thresh-<br>old Planning<br>Quantity, lb | EHS<br>reportable<br>quantity,<br>lb | CERCLA<br>reportable<br>quantity,<br>lb | CAA 112(r)<br>total<br>quantity,<br>lb | RCRA<br>waste<br>code |
|-----------|-----------------------|-----------------------------------------------------------|--------------------------------------|-----------------------------------------|----------------------------------------|-----------------------|
| 302-01-2  | Hydrazine             | 1000                                                      | 1                                    | 1                                       | 15000                                  | U133                  |
| 57-14-7   | 1,1-Dimethylhydrazine | 1000                                                      | 10                                   | 10                                      | 15000                                  | U098                  |
| 60-34-4   | Methylhydrazine       | 500                                                       | 10                                   | 10                                      | 15000                                  | P068                  |
| 540-73-8  | 1,2-Dimethylhydrazine |                                                           |                                      | 1                                       |                                        | U099                  |
| 1615-80-1 | 1,2-Diethylhydrazine  |                                                           |                                      | 10                                      |                                        | U086                  |

Data source: 40 CFR Parts 302 and 355

EPA tries to keep track of the path of hazardous chemicals as they wend their way through chemical processing into other chemicals or end uses. The Toxics Release Inventory (TRI), published by the US EPA, is a valuable source of information about toxic chemicals that are being used, manufactured, treated, transported, or released into the environment. Hydrazine, MMH, and UDMH and some of their production waste products are on this list. It was estimated that discharges of hydrazine into surface water (presumably in the form of boiler condensates and blowdown) had decreased from 12600–9000 kg (28000–20000 lb) in 1987–1988, though it is unclear whether this reduction was a result of more efficient effluent cleanup methods or a decrease in overall usage. Even with the reductions there may still be concern for aquatic toxicity. However, the concern for air releases was not mitigated by the apparent decrease in water releases. Because EPA is concerned with large air releases of hydrazine, it was suggested in 1990 that it would be placed on the Risk Reduction Candidate List until more data were made available. In addition, hydrazine will be added to the Master Testing Candidate List for developmental toxicity. It is not known why hydrazine was singled out among 479 chemicals on the EPA CAA Section 112 list in 1998 to be one of the 33 high-priority chemicals suspected of posing the “greatest potential threat to public health in the largest number of urban areas” [1903, 1904].

### 7.3 Hydrazine Ground Service Equipment

Hydrazine storage and hydrazine transfer into the satellite or upper stage were once separate functions. The transfer equipment, propellant loading carts, were part of the ground service equipment (GSE). Fueling tasks were simplified when the two functions could be combined.

The Generic Propellant Transfer Unit (GPTU) is a top-loading, top-unloading, vertically oriented DOT Code 51 cylinder designed primarily for storage and transfer at launch sites, but it also has DOT approval to transport propellants on public highways [1905–1908]. This unit serves double duty as a storage and transfer tank from the manufacturer to the launch site storage area and then to the space vehicle without the need for intermediate transfer and without the risk of inadvertent contamination during intermediate transfers. Of course, the 500-gal unit is only suitable for very large spacecraft. The tank is nested in an insulated crash protection jacket, which itself is pressurized with inert gas. The valving is configured to allow propellant circulation for thermal conditioning. Overall, the tank is 1.62 m (5.33 ft) in diameter and stands 2.4 m (8 ft) tall. The GPTUs are normally provided on their own dedicated trailers. The tanks sit on feet equipped with load cells and readout units to indicate the weight of the unit accurately to within a pound. Both single- and double-tank trailers are in use, and both versions have permanently mounted access platforms; the double-tank trailer has a control panel that integrates both tanks into a single piping system. The units have lift points where they can be lifted by a forklift from below or a crane from above. As of 1993, the GPTU was qualified for use with monopropellant-grade hydrazine, high-purity-grade hydrazine, MMH, and NTO/MON.

Prior to the introduction of the GPTU and pressure-resistant 4BW cylinders, there had been a multitude of propellant fueling carts in a fleet of GSE, each one designed for only one specific satellite program, lacking commonalty and interchangeability. Each cart required its own operating team, and carts often needed to be off-loaded, rinsed, and decontaminated between launches, creating large volumes of wastewater. However, while the fueling carts were equipped to transfer hydrazine *and* pressurize the tanks on the satellite with helium or nitrogen pressurant gas, a GPTU could do only the hydrazine transfer and flight tank pressurization still had to be provided from a separate GSE unit.

Looking back at the history of the 55-gal barrel replacement, the 250-gal DOT110A500W cylinder was first qualified by Hughes Space & Communications Group and is now widely used by other satellite and launch companies. The same design was initially qualified for use with NTO and MMH. It can now be used for anhydrous hydrazine, hydrazine solutions, and UDMH as well.

The NASA KSC web site maintained by the Liquid Propellants and Fluids Management Office lists a range of cylinders that can now be used to dispense, store, and transport anhydrous hydrazine and MMH [1909–1911]. A summary of these cylinder tanks is presented in Table 75.

**Table 75:** Hydrazine fuel cylinders in use at NASA KSC.

|                                                              | Nominal cylinder size, gal  |                             |                             |                             |                             |
|--------------------------------------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                                                              | 5                           | 30                          | 34                          | 55                          | 120                         |
| Dimensions, in.                                              | 24.5 L × 12 D               | 43.5 L × 18 D               | 38.5 L × 22 D               | 48.5 L × 22 D               | 48.5 L × 36 D               |
| Tare mass, lb                                                | 44                          | 135                         | 240                         | 300                         | 780                         |
| Gross mass when filled w/N <sub>2</sub> H <sub>4</sub> , lbm | 82                          | 362                         | 498                         | 720                         | 1687                        |
| DOT specification                                            | DOT4BW<br>w/DOT-E-<br>11378 | DOT4BW<br>w/DOT-E-<br>11378 | DOT4BW<br>w/DOT-E-<br>11580 | DOT4BW<br>w/DOT-E-<br>11173 | DOT4BW<br>w/DOT-E-<br>11173 |
| Net capacity, gallons, at 10% ullage                         | 4.5                         | 27                          | 31                          | 50                          | 108                         |

A 30-gal cylinder is a top-loading, vertically oriented cylinder. Allowing 3-gal ullage for thermal expansion, it will hold 27 gal of liquid. It has a 46-cm (18-in.) diameter and stands 1.12m (44 in.) tall. The 30-gal container was sized specifically such that it could be manhandled by self-contained air-breathing protection ensemble (SCAPE)-suited personnel. It fits very well on a hand truck for moving it around the storage yard or into position for fueling of small spacecraft.

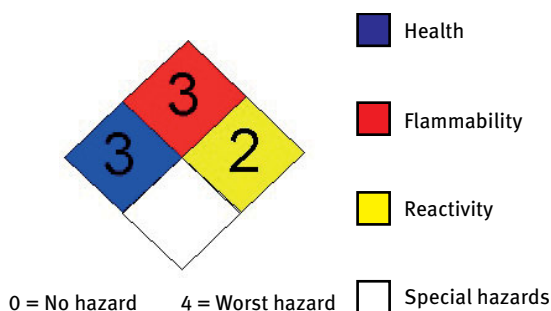
There are four different sizes of DOT4BW cylinders available at KSC/CCAS that can be used for hydrazine, MMH, or UDMH [1908]. All share a common heritage with the original NASA-designed 30-gal version. “DOT4BW” refers to the Department of Transportation design specification. There are various exemptions to existing DOT specifications primarily due to being constructed of 304L stainless steel, which was not always recognized as an “authorized” material for this classification of containers. All cylinders have a built-in dip leg (standpipe). A sight glass is not required because normally the cylinders are placed on a scale to determine their content. Their operating pressure ranges from full vacuum to 688 kPa (100 psig), and the maximum allowed working pressure is 1548 kPa (225 psig), except for the 128-L (34-gal) cylinder, where the maximum allowable working pressure is 2064 kPa (300 psig). The connections have a 0.5-in. KC male thread. The advantage of the cylinders is that they allow pre-saturation of propellants with pressurant gases during storage. Pre-saturation is a time-consuming operation that often had to be carried out in dedicated separate GSE equipment at launch sites, but now pre-saturation can be achieved while the cylinders are in transfer or in storage. The cylinders do not have a pressure relief valve or a burst disc. The GSE compressed gas control panels from which the cylinders are pressurized for propellant transfer must still carry relief valves and burst discs.

A small 5-gal “model A” cylinder (which actually holds 4.5 gal of liquid) is essentially a scaled-down version of the 30-gal cylinder, suitable for small experimental users. As of 1993, an additional overpack was still required to ship MMH in either a 30- or 5-gal cylinder.



Government regulations can be the inadvertent cause of safety hazards in situations where the initial intent was to avoid hazards. For instance, 49 CFR § 173.276(a)(2) prescribed the shipping of hydrazine in glass bottles (not exceeding 1 gal capacity each) in vermiculite in a metal can in vermiculite in a wooden outer box. There have been incidents where hydrazine leaking into vermiculite autoignited in air because vermiculite has a large surface area and contains traces of transition elements that act as catalysts. The ignition and the fire add to the toxicity hazard of a leak. Alternative packaging materials should be evaluated to replace the vermiculite in the government regulations. Several regulations, e.g. 49 CFR § 173.276(a)(1) Specification 1D or 1M, also referenced in [1912], p. 4–19, allowed the use of bottles packed in expanded polystyrene packaging materials. That does not seem to be a good choice for anhydrous hydrazine either!

Safety tests used for the classification of transportation hazards of anhydrous hydrazine in France were very similar to those used in the United States [1913]. The Standard Transportation Commodity Code for anhydrous hydrazine is 4906225, and for aqueous solutions of hydrazine hydrate it is 4935030. The United Nations identifier for anhydrous hydrazine is UN2029, for aqueous solutions of hydrazine hydrate containing less than 64%  $\text{N}_2\text{H}_4$  it is UN2030, and UDMH and MMH go under the UN Identification numbers UN1163 and UN1244, respectively. The Hazardous Materials Diamond described in NFPA Nos. 49 and 704 for anhydrous hydrazine is shown in Figure 54.



**Figure 54:** Hazardous materials diamond for hydrazine in accordance with NFPA704 [1914]

The Hazardous Materials Diamond ranks hazard properties on a scale from zero (no hazard) to 4 (worst hazard). For anhydrous hydrazine, most MSDSs have a 3 for flammability (red), a 3 for health hazard (blue), and a 2 for reactivity (yellow), where a 3 in the Health field describes a chemical “extremely hazardous to health,” a 3 in the Flammability field describes a “liquid that can be ignited under almost all normal temperature conditions,” and a 3 in the Reactivity field describes “materials which in themselves are capable of detonation or of explosive decomposition or of explosive reaction but which require a strong initiating source or which must

be heated before initiation.” A 2 in the Reactivity field describes “materials which in themselves are normally unstable and readily undergo violent chemical change but do not detonate.” Some safety-related web sites show the Hazardous Materials Diamond for hydrazine with a 3 rating in all three top fields of the diamond.

## 7.4 Recommendations for Safe Storage of Hydrazine

Hydrazine can be handled safely as long as the personnel doing the fueling work are properly trained and obey the safety regulations and the equipment is in perfect working order. There exists a long history of safe handling and storage in the industry [1915] and with organizations that routinely transfer hydrazine at launch sites [1916].

In addition to government-issued regulations, some industrial organizations have issued recommendations for the safe storage of hydrazines. Among those are recommendations from hydrazine manufacturers who undoubtedly have the best experience in the safe handling of the material. These recommendations are shown on the product data sheets and MSDSs. Product data sheets and MSDSs must be updated periodically. Hydrazine users must maintain a set of the most recent versions of these sources of information in their records. Links to web sites where this information can be downloaded must be updated periodically. In addition, Factory Mutual Research has issued and periodically updates a Loss Prevention Data Sheet on hydrazines that provides recommendations on spacing of outdoor storage tanks in a tank farm and the type of water sprinklers that should be used to protect tanks from a spreading fire [1917].

## 7.5 Hydrazine Transfer Procedures

### 7.5.1 Transfer from Surface Transport Containers

In the 1970s and 1980s an average of about 5700 metric tons (5.2 million lb) of hydrazine fuels were moved over about 322000 km (200000 mi) of public highway in the United States each year, so there was a remote possibility of spillage along these routes. So far, no major anhydrous hydrazine spill has occurred en route. The track record of anhydrous hydrazine transportation has been clean [1900, 1918]. There is one case where a storage area was inadvertently flooded by a sprinkler that went off without a fire alarm and a storage tank was floated and some of the contents spilled.

Estimated annual movements of hydrazines in the United States in 1977 were as follows:

- 1430 metric tons (1.3 million lb) hydrazine
- 550 metric tons (0.5 million lb) MMH
- 1542 metric tons (1.4 million lb) UDMH
- 2203 metric tons (2.0 million lb) Aerozine-50 mix

Not all of this consisted of new hydrazine fuels. Some of it may have been waste fuel being moved to disposal sites. Sometimes propellant is moved between government installations because it is no longer needed when a program is canceled. As of 1977, all six hazardous materials incident reports involving hydrazines were caused by leaking 55-gal drums. In the late 1990s, all US government-owned drums were retired and replaced by cylinders. The 55-gal cylinders have now replaced the old 55-gal DOT5C/UN1A1 drums (which are no longer available at NASA KSC/CCAS Controlled Storage).

In 1995, NASA KSC requested that NASA WSTF provide 2500 gal hydrazine to support Space Shuttle operations. A KSC tanker loaded the propellant for transportation to KSC and the transfer was completed safely. The propellant was originally stored at WSTF to conduct Space Station Freedom propulsion module testing but was no longer needed there when NASA decided to use a Russian propulsion module instead. A brief description of Air Force practices for the transport of hydrazine is published at [1919].

Tank cars usually have a standpipe through which liquid can be withdrawn. Before unloading is done, the drums and other equipment should be electrically grounded. Before a drum is discarded, it must be filled and flushed with water. Manufacturers of hydrazines recommend storing the propellants under a slightly positive pressure of a blanketing gas (nitrogen) to prevent intrusion of atmospheric carbon dioxide by “breathing” of the tank during storage temperature fluctuations.

In terms of total tonnage, much more hydrazine is transported in the form of hydrazine hydrate and hydrazine solutions than in anhydrous form. In view of the wide distribution network and the many forms of transport, it is not surprising that occasionally transportation incidents with hydrazine solutions happen despite all precautions taken in transporting hazardous chemicals. One isolated incident was caused by the derailment of a train, causing a spill of hydrazine hydrate from 16 punctured steel drums in a railroad accident near Sea Cliff, CA, on July 28, 1991. No major environmental damage occurred since the spill site was quickly surrounded by a dam and leaked hydrazine hydrate was destroyed with hypochlorite solution.

Regardless of whether small or large quantities of hydrazine must be transferred, it is imperative to avoid exposure of anhydrous hydrazine to ambient air. Otherwise, serious contamination and system failure may result from the absorption of atmospheric contaminants. The surprisingly fast take-up of water and carbon dioxide was demonstrated by exposing a 25-mL sample of anhydrous hydrazine in a beaker (16.3 cm<sup>2</sup> surface, 1.5 cm deep) to air at 829 mbar (630 mm Hg) and approximately 30% ambient RH [110]. The low ambient pressure of the high-elevation test site should have had little effect on the rate of contaminant absorption, and similar results can be expected at sea-level atmospheric pressures of 1 bar. The water content of the sample increased within 24 h to 38% and began to level off near 50% after 4 d, whereas the carbon dioxide concentration showed a steady climb throughout the 4-d test period to 33% CO<sub>2</sub>. The average rate of increase was 50 ppm CO<sub>2</sub> per minute.

In terms of total weight of hydrazine consumed, the transfer of hydrazine solutions to boiler feedwater treatment facilities exceeds the amount of anhydrous hydrazine fueled into space vehicles. Consequently, in view of tightening occupational exposure limits and concern about the potential carcinogenicity of hydrazine solutions, the electric power industry and steam plant operators in cooperation with hydrazine suppliers have overhauled and upgraded the handling and transfer procedures for hydrazine solutions in power plants, established safe handling practices for hydrazine solutions, and provided equipment that allows closed-system transfer of solutions with a minimum of vapor formation.

### 7.5.2 Launch Site Ground Service Equipment and Propellant Carts

Propellant service carts are used to load an accurately measured amount of hydrazine into a satellite or spacecraft. Because this is done as one of the last operations immediately prior to launch, the fuel must be metered from the cart because it would not be accurate enough to weigh the launch vehicle plus payload before and after loading the hydrazine. Most satellites are loaded with hydrazine before they are stacked on top of the launch vehicle, so it would be possible to weigh the receiving unit. Both volumetric and gravimetric metering has been used by various propellant servicing carts built for Intelsat III, Pioneer, Atmospheric Explorer, or RCA Satcom with hydrazine loads ranging from 18 to 1711 kg (40 to 3770 lb), but that is now history [1920]. The carts also supplied compressed helium or nitrogen at 2.7–4.1 MPa (400–600 psia) to pressurize the fuel tanks.

Until 1992, the monopropellant RCS system in the CENTAUR upper stage flown on TITAN or ATLAS was fueled directly from 55-gal drums. The CENTAUR contains two tanks that must be fueled with 77 kg (170 lb) of hydrazine each. Because the shipping drums could not be pressurized sufficiently (actually the shipping drums were not intended to be pressurized!), this was a very slow procedure. The procedure could be accelerated by designing and building a Hydrazine Automated Loading System (HALS) propellant cart with an ASME-code-compliant pressure tank capable of pressurized transfer of 300 L (80 gal) of hydrazine at 930 kPa gauge (135 psig) [1921]. Two redundant flow meters measured and integrated the mass flow. The cart also carried 37 L (10 gal) each of demineralized water and IPA. The water was used to displace the residual hydrazine from the manifold and hoses after the fueling. The IPA was used to displace the water and allow for easy drying by evacuation.

Temperature conditioning of propellants about to be metered by flow meters is important to obtain the accurate density. Pressurant gas saturation of propellant to be transferred is also important. If the propellant is oversaturated, bubbles will be released during transfer and the metering becomes inaccurate. If the propellant is insufficiently saturated, it will take too long to achieve equilibrium while it is stagnant and sitting on the launch pad before the pressure of blowdown systems can be topped off. It is interesting to compare pressure histories of tanks during the prelaunch period.

Pressure changes occur due to pressurant gas absorption and temperature fluctuations/temperature gradients in the payload shroud [1922, 1923]. Many payload shrouds are actively temperature conditioned with forced air (gas) convection during launch preparations to make sure that propellant loads are balanced between communicating tanks. Because numerous launch sites are in hot climates (Florida, Guayana), temperature conditioning of the shroud is not always easy.

One of the approaches to simplify fueling transfer operations led to the development of the Olin Propellant Servicing Unit (PSU) for either grade of monopropellant or high-purity-grade hydrazine and directly applicable to methylhydrazines and their blends [1924, 1925]. The Olin PSU replaced conventional propellant servicing carts but can deliver propellant at much higher pressures (up to 3440 kPa = 500 psig) and with a minimum of SCAPE suit operations. Conventional propellant carts such as those used for Delta Star, Brilliant Pebbles, or ERBS shown for comparison were much more complex and required substantial on-site support for decontamination and propellant quality control. In contrast, the Olin PSU requires only a minimum of support at the launch site. The only facility support needed is the vapor scrubber for the hydrazine vapor-saturated pressurant  $\text{GN}_2$  bled after completing the propellant transfer. The Olin PSU is filled at the manufacturer with a pre-weighed accurate amount of hydrazine to exactly meet the requirements of one satellite load. The load is drained into the spacecraft “to the last drop,” similar to a bag of intravenous fluid administered to a hospital patient by prescription of the doctor. All connections on the emptied unit are then capped and the unit is returned to Olin for refilling. One of the first applications of the Olin PSU was for fueling the Atmospheric Composition Explorer (ACE) satellite launched in August 1997. This particular satellite was a “spinner” and did not contain diaphragms. That made it possible to fill the system through the same fill and drain valve that was used to apply tank pressurization.

For satellites where the manifold is filled with hydrazine prior to launch, such as SPOT 4, it is common practice to deliberately leave a helium bubble gas cushion at the thruster end of the line to accommodate thermal expansion of the liquid as a result of ambient temperature fluctuations. For some large satellites, such as the Polar Platform Propulsion Subsystem used for ENVISAT, the propellant lines between the tanks and the thrusters can be up to 13 m long, leaving a disproportionately large gas bubble at the end of the line and introducing uncertainties about the location of the gas bubble. An analysis was conducted by the designers of ENVISAT to determine the adiabatic compression hazard potential upon sudden filling of the manifold and the compression of gas bubbles at the end of a long run of tubing and to select an acceptable bubble size [1926]. One may not assume that the gas is evenly distributed among the eight thrusters, and gas bubbles will be of varying sizes, requiring different valve opening times to expel gas bubbles once the satellite is launched. It was difficult to predict impulse delivered if the first slug of propellant was a mixture of hydrazine and gas. The line volume in one half-system of ENVISAT was 761 mL compared to only 180 mL for a SPOT 4 system (from which ENVISAT was derived). As a result of this larger volume,

the manifold filling and gas priming procedure had to be changed from that practiced for several launches of SPOT satellites. As a result of the computer analysis and inert fluid testing, a different propellant loading strategy was developed.

A hydrazine transfer vehicle intended to fuel a hydrazine auxiliary power system on a large military aircraft was designed to hold up to 1040 kg (2300 lb<sub>m</sub>) of hydrazine in a single tank with 10% ullage, capable of transferring the hydrazine by pressurization with GN<sub>2</sub> to 342 kPa (35 psig) into the aircraft [1927]. The tank had three top penetrations, but none at the bottom. The top penetrations carried a dip tube, a pressure relief valve set at 410 kPa (45 psig), and a GN<sub>2</sub> connection for inert gas blanketing and pressurized transfer. The design of hypergolic propellant GSE for fueling launch vehicles and satellites at NASA KSC is outlined in [1928].

Pre-packaged gas generators for a submarine emergency deballasting system are routinely filled on shore with hydrazine in an operation very similar to fueling a satellite or an upper stage [1929].

### 7.5.3 In-Orbit Refueling with Hydrazine

In the near future it may be possible to routinely transfer hydrazines between tanker vehicles and unmanned US spacecraft. It has been predicted that within 10 years, in-orbit servicing will become so common that satellites will be designed for towing, repairs, or refueling.

The Multimission Modular Spacecraft (MMS) would have had extended mission life capability by on-orbit servicing and refueling with monopropellant hydrazine [1930]. The larger MMS spacecraft, Mark II, would have required the transfer of 2265 kg (5000 lb) of hydrazine. Various tank configurations have been studied in an effort to identify existing tank designs that would utilize the space available in the Space Shuttle cargo bay most effectively. Some of the existing tanks would have had to be converted from MMH service to N<sub>2</sub>H<sub>4</sub> service to fit this application. Another basic consideration was if the tanks and their mounting were sturdy enough to withstand re-entry and landing shock in the STS payload bay if a rendezvous cannot be achieved or propellant transfer cannot be completed. Shuttles on extended duration missions could have carried OMS kits in the cargo bay and would have had the option to dump unused fuel prior to re-entry. Similar provisions would have had to be made if large hydrazine tanks for refueling missions had been flown in the cargo bay.

Refueling capability will be needed for monopropellant hydrazine as well as bipropellant NTO/MMH. Orbital fluid re-supply can significantly increase the cost-effectiveness and operational flexibility of satellites and orbiting platforms. For the sake of simplicity, the refueling of monopropellant hydrazine would be practiced first.

The Orbital Refueling System was an experiment flown on Shuttle Mission STS 41-G in October 1984. Liquid hydrazine fuel was transferred back and forth from one

spherical bladder tank to another using pressurized nitrogen as the driving force, which required EVA work of two astronauts making a fluid connection to a simulated Landsat interface [1931]. The system used existing flight-qualified STS APU tanks and a Fairchild quick disconnect [1932, 1933]. There was concern that excessively rapid (adiabatic) compression of the ullage in the receiving tank might cause exothermic decomposition of the hydrazine vapor if any hydrazine had inadvertently leaked across the diaphragm. Six back-and-forth transfers were achieved between the two diaphragm tanks without any incident. An analysis of the ullage heat transfer and comparison with actual flight data showed that the compression was much closer to an isothermal than an adiabatic process [1934, 1935].

Propellant transfer between tanks can be achieved by pumping or by pressurization. A particular concern is the venting of the propellant vapor-saturated pressurant gas from emptied tanks after a pressurized transfer is accomplished. The venting could result in undesirable reaction forces on the space station or the tanker vehicle. This can be minimized by using a pair of thrust-neutral nozzles. The corrosive propellant fumes contained in the vented pressurant gas might contaminate the solar panels or electronics. Special sorbent canisters have been considered for  $N_2O_4$  and MMH venting [1936]. In the case of hydrazine, the gas/vapor mix was passed through a catalyst bed identical to that used in hydrazine monopropellant thrusters. It would be ideal if the gas displaced by liquid in the tank being filled could be compressed and returned to the tank being drained (like vapor return hoses now seen at many Earth-based gas stations for automobiles to minimize air pollution). Analysis and modeling of no-vent transfers showed promising possibilities for larger satellites [1936]. Earlier experiments flown on STS used inert fluids and surface tension PMD tanks to study the behavior of liquids during transfer in surface tension PMD tanks. It would be easiest to transfer liquids only between diaphragm or bladder or piston tanks. However, diaphragm or bladder tanks are only available in small sizes. Eventually, the transfer of liquids between surface tension PMD tanks must be mastered so that transfers can be achieved between larger tanks.

Part of the propellant transfer operation in space involves the draining of propellant-filled hoses and line sections after the transfer is complete. On Earth's surface one would flush the lines with water and IPA, a luxury one does not have in space. Because manifold lines are not temperature-controlled and otherwise might freeze and rupture, it is best to empty them out at the end of the transfer operation. The complete evaporation of hydrazine from a manifold in vacuum is a very slow process, even with very carefully applied heat (possible by pointing that part of the spacecraft to the sun). It is difficult to verify how much hydrazine will remain after venting. It may not be acceptable to vent undecomposed hydrazine in the vicinity of delicate optics and electronic parts. If the hydrazine vapors must pass through a catalyst bed to decompose them to nitrogen, hydrogen, and ammonia, the process of emptying the lines will be even slower, and it is not known how complete the decomposition is at very low reactor operating pressures.

A computer model was developed to study the dynamics of propellant transfer during refueling of GRO satellite in orbit [1937]. The design goal was to transfer 387 kg hydrazine in less than 6 h, assuming that the tank still contained 169 kg residual hydrazine. It was concluded that the transfer would have to be extremely slow if helium was used as the pressurant due to adiabatic warming if one limits the maximum allowable ullage temperature to 338.7 K (150 °F) for safety reasons and fear of hydrazine vapor explosions. To be able to transfer the propellant within less than 6 h, nitrogen instead of helium was recommended as the pressurant gas. Nitrogen has a lower adiabatic coefficient  $\gamma = c_p/c_v$  than helium.

Military satellites are more vulnerable if they remain in the same predictable orbits all the time and would benefit from greater maneuverability and on-orbit propellant resupply. The US Defense Advanced Research Projects Agency (DARPA) conducted the Orbital Express mission, a two-satellite demonstration of propellant transfer launched in 2007. The system consisted of two spacecraft: the Autonomous Space Transport Robotic Operations (ASTRO) servicing satellite and a prototype modular next-generation serviceable satellite, NEXTSat [1938]. The ASTRO satellite successfully rendezvoused with and pumped hydrazine into its NEXTSat partner, the first in a series of increasingly challenging tests. In the first Orbital Express demonstration, ASTRO transferred just under 14 kg (32 lb) of hydrazine to the NEXTSat client, and then followed up by transferring an additional 8.6 kg (19 lb) of propellant to NEXTSat a day later. NEXTSat would then return propellant to ASTRO sometime later. After several back-and-forth propellant transfers, adding up to 15 transfer operations in the end, the 2 satellites separated, ASTRO vented its hydrazine propellant and was deactivated in July 2007 [1939–1941]. See also [1942].

Refueling of the SALYUT or MIR or International Space Station by unmanned PROGRESS tankers has already become a routine operation in the Russian space program.

## 7.6 Personnel Protection Equipment for Hydrazine Transfer Operations

Protective clothing to be worn by personnel in the vicinity of a pressurized hydrazine system depends on the type of operation to be performed [1943].

### 7.6.1 Gloves, Boots, and Aprons

One of the main concerns in selecting materials for gloves, boots, and aprons is the permeability in case of a liquid hydrazine spill on the protective equipment. In addition, there is concern over vapor permeability. Hydrazine permeation tests with various glove materials are summarized in the following section. Quite often one will want to reuse gloves after they have been contaminated with hydrazine. Effective decontamination methods should be tested before one decides to reuse those stained gloves. In



hypergolic propellant spill tests at NASA WSTF, it was determined that under adverse conditions the exterior of protective equipment may be exposed to vapor concentrations as high as 800 ppm MMH or 2%  $\text{N}_2\text{O}_4$ . These numbers were then used for permeation testing of different protective clothing materials [1944, 1945]. In these tests, four suit materials and one glove material were exposed to liquid splashes or heavy vapor concentrations of MMH or NTO under controlled conditions [1946]. The simple water wash and air dry sequence was not effective in removing residual propellants from the materials. Additional tests showed that an 8-h oven bake at 311 K (100 °F) or, even better, vacuum oven bake would more effectively remove MMH from the fabric. Arch Chemicals, a hydrazine manufacturer, recommends the use of Tychem<sup>®</sup> suits, aprons, and gloves. Tychem<sup>®</sup> is made by DuPont and is a PVC/polyvinylidene copolymer.

### 7.6.2 Hydrazine Permeation Tests

Commercially available protective gloves were tested for chemical resistance to H-70 hydrazine blend and subjectively evaluated for dexterity/flexibility [1947]. The gloves were considered alternatives to the bulky rocket fuel handler gloves used in maintenance and support of the F-16 EPU. A number of gloves (Edmont-Wilson 37-165; Surety 10-136R, 10-156R, and 10-166R; and Norton NSN: 8415-00-753-6550 through 6555) showed no detectable permeation of H-70 over a 6-h exposure at 293 K (20 °C) and were found suitable for one-time use during spill cleanup operations. These same gloves are considered adequate for repeated use during routine maintenance tasks; however, if liquid H-70 contact is experienced, the gloves should not be reused. Gloves should be decontaminated with 5% sodium hypochlorite bleach before disposal. Nitrile gloves of the same thickness, but from different manufacturers, gave breakthrough times of greater than 6 h versus less than 10 min. at 293 K (20 °C). Unfortunately, glove manufacturers change elastomers and manufacturing procedures based on economic conditions and market demand, and gloves evaluated 10 years ago may behave differently from ones bought today under the same brand name. It appears that the most important specification to ensure adequate chemical resistance from a glove is to have representative glove samples of various styles and construction from each manufacturer pass a chemical resistance test for the specific chemical of interest.

Several materials for gloves, boots, aprons, and splash shields were evaluated in permeation tests with hydrazine, UDMH, and IRFNA [1948–1950]. A group of 28 glove materials, 9 suit materials, and 3 other materials were tested for permeability to hydrazine, MMH or NTO following exposure to these propellants for 90 min. [1951, 1952]. Breakthrough times were determined and correlated with static permeation rates. Of the 28 glove materials, 9 had breakthrough times for hydrazine of less than 90 min. (2 of these shorter than 10 min.), 1 was marginal, 3 had barely detectable permeation, and 15 resisted permeation for at least 90 min. The comparable numbers for MMH were 19, 5, 1, 1, and 7 min. This indicated that it is more difficult to find good gloves for MMH protection than for hydrazine protection.

### 7.6.3 Full-Body Protection Suits

NASA developed the SCAPE suit as an alternative to industrially available personnel protection ensembles (PPEs). The NASA suits are fully encapsulated butyl-rubber-based suits and provide breathing air via either backpack or air hose [1916].

Eight different full-body protection suit materials were tested for permeability to hydrazine, MMH, or NTO during controlled exposure to these propellants. No hydrazine or MMH was detectable after 5 min of exposure [1952].

SCAPE suits used at NASA launch sites are made from a chlorobutyl coated Nomex fabric. The fabric and its coating are subjected to wear and tear, and its integrity needs to be monitored daily [1953]. In addition to corrosive chemicals from the outside, the inside of the suit is exposed to sweat and condensation [1954]. While every effort is made to keep astronauts in space suits during EVAs comfortable and safe, the design technology of SCAPE suits for ground-service crews lags behind. The amount of time a technician can safely spend suited up is typically less than 4 h, often shorter in the hot climates of Florida and Guyana.

Permeation resistance was determined by measuring the breakthrough time and time-averaged vapor transmission rate of MMH through two types of personal protective equipment [1955]. The two types of suits evaluated were the totally encapsulating ILC Dover Chemtursion Model 1212 chemical protective suit and the FabOhio PVC splash garment. The simulated exposure was (1) a saturated vapor exposure for 2 h or (2) a brief MMH splash followed by a 2-h saturated vapor exposure. Results showed that the totally encapsulating suit provided adequate protection at the new 10 ppb TLV-TWA. The permeation resistance of the PVC splash garment to MMH was poorer than any of the totally encapsulating suit materials tested because breakthrough occurred soon after initial vapor or splash exposure.

Several decontamination procedures for personal protective suit materials in use at NASA WSTF, including Chloropel (a chlorinated polyethylene [CPE]), were tested after the material was exposed to NTO or MMH [1956]. Each exposure sequence was followed by a simple room temperature water-wash decontamination sequence. Two versions of heated decontamination sequences were used: (1) a simple purged heated sequence and (2) a heated evacuation sequence. After the second water decontamination sequence these two versions of heated decontamination sequences were used to further reduce the concentration of residual fuel trapped in the material.

The permeation resistance of CPE used in chemical protective clothing for protection against hydrazine, MMH, or UDMH was determined by measuring breakthrough times and time-averaged vapor transmission rates using an ASTM F739 permeation cell [1957, 1958]. Two exposure scenarios were simulated: (1) a 2-h fuel vapor exposure and (2) a liquid fuel “splash” followed by a 2-h vapor exposure. To simulate internal suit pressure during operation, a positive differential pressure of 0.3 in. water (75 Pa) on the collection side of the permeation apparatus was used. Breakthrough was observed after exposure to liquid MMH and vapor or liquid UDMH. No breakthrough was observed after exposure to vapor or liquid hydrazine or vapor MMH.

Calculations showed that the maximum allowable permeation rates of hydrazine fuels through CPE were on the order of  $0.05$  to  $0.08 \text{ ng cm}^{-2} \text{ min}^{-1}$  for encapsulating suits with low breathing air flow rates (on the order of  $5 \text{ scfm}$  or  $140 \text{ L/min.}$ ) [1958].

The need to wear SCAPE suits and keep a second crew on standby ready to suit up if needed has a considerable impact on the cost and time required to fuel satellites and upper stages. There may be more economical and equally safe alternative ways to load propellants into satellites and upper stages [1959].

#### 7.6.4 Space Suits

Refueling of spacecraft in orbit may require EVA by astronauts to make connections of fuel hoses and operate valves. Propellant leaks may splash on the space suit and jeopardize the integrity of the fabric. Splashes on the visor of the space helmet may turn the plastic opaque and the astronaut may become disoriented if he/she cannot see the surroundings.

Fifteen different space suit materials in either the vertical or horizontal position were exposed to hydrazine spray from a spray nozzle in a vacuum chamber [1960]. Hydrazine, in the form of an approximately  $1.5\text{-mL}$  shot, was fed from a supply tank pressurized to  $207 \text{ kPa}$  ( $30 \text{ psig}$ ) through a spray nozzle. The samples were exposed to the splash for  $\sim 5 \text{ min}$  while their behavior was observed with a TV camera. Hydrazine splashed on the sample materials froze and evaporated (sublimed) only very slowly. The materials tested included Ortho fabric (a double layer of Teflon and Nomex used in the outermost layer of space suits), aluminized Mylar, Chemglaze A276 (white paint on helmet), buffed aluminum, RTV-630 silicone on aluminum or Dacron, Lexan polycarbonate (coated and uncoated), polysulfone (coated and uncoated, used for visor), Xenoy, composite of all suit materials, polyurethane glove internal bladder, and glove composite of all layers. Ortho fabric exhibited staining and soak-through as evidenced by staining on the reverse side of the fabric. Staining appeared on both Chemglaze A276 and RTV-630. Lexan polycarbonate crazed and became opaque, partially dissolved, and produced a gummy, sticky substance on the surface of the sample. Such a propellant splash on a helmet visor would cause astronauts to lose the view of their surroundings. Polysulfone in either a coated or uncoated condition did not suffer the same crazing as polycarbonate.

Splash evaporation tests of propellants spilled on space suit materials at three different initial sample temperatures showed that most propellant spills freeze almost immediately in vacuum [1785, 1786]. Hydrazine supercooled to  $355 \text{ K}$  and then froze to ice, which was near the triple-point temperature. The force needed to scrape frozen hydrazine from the material sample by scraping and the time needed to sublime frozen hydrazine under one solar flux (simulated with a heat lamp) was measured. MMH did not freeze but evaporated before much ice could form. MMH was the only propellant that visually damaged the suit material. Aluminized Mylar layers were found to be dissolved in the area where the propellant had impinged on the fabric. Supercooled

MMH dissolved the aluminized Mylar layers of the suit ensemble, and both hydrazine and MMH caused cracking in the polycarbonate helmet visor, but not in the helmet material alone.

### 7.6.5 Gas Masks

Air Force Occupational Safety and Health (AFOSH) Standard 48-137 (November 1, 1998) implements Occupational Safety and Health Administration (OSHA) Standard 29 CFR 1910.134, Respiratory Protection, for Air Force installations. That OSHA standard provides guidelines in the safe use of gas masks and determines when supplied air respirators or self-contained breathing apparatus should be used. It is interesting to note that AFOSH Standard 48-8 on page 35 of Attachment 8 states that “The end-of-life indicator on the rocket propellant gas mask does not adequately respond to hydrazine. The maximum use time is 8 hours; supervisors will enforce procedures to replace the canisters before the canisters have been exposed for 8 hours, without regard to whether the mask is being worn.”

The MSA Rocket Propellant Mask 92372GM-SSW canister and, to a lesser extent, the M9 mask with the M11A1 charcoal canister provided effective protection against hydrazine and UDMH vapors when tested under actual field conditions [711, 712]. Whereas outside concentrations were as high as 2 ppm hydrazine or 3 ppm UDMH, no hydrazines could be detected inside the M9 mask. Only during one test with 4.6 ppm UDMH outside was a trace (0.03 ppm) of UDMH detected inside the mask. This isolated incident was blamed on an inadequate mask-to-face seal. Other cartridges for removing hydrazine from air consisted of a two-layer bed, one a charcoal, silica gel, alumina, or molecular sieve sorbent and the other a solid oxidizer on a solid support [1961].

## 7.7 Detection of Hydrazine Leaks

A space vacuum leak-detection concept was able to generate distinctive leak characteristic temperature curves by evaporative cooling for each leak rate assuming hydrazine was leaking into the APU compartment of the Space Shuttle [1962]. Although exact quantification of a leak would not be possible, qualitative determination of the leak amount and location appeared achievable. The tests demonstrated potential for use of an evaporative cooling sensor in a vacuum environment where conventional leak sensors do not work effectively. A leak-detection concept was based on evaporative cooling as a result of an instantaneous reduction of the fluid surface pressure when an on-orbit leak occurs. The effect of the surface evaporative cooling produces a characteristic temperature drop as a result of heat removal by conduction.

## 7.8 Controlled Spill Tests with Hydrazine and Hydrazine Blends

Hydrazine leaking into vacuum is going to cool by evaporation down to the triple-point temperature, and liquid droplets in a hydrazine spray will soon freeze and turn into hydrazine snow. This condition was simulated by spraying liquid hydrazine into a vacuum chamber with visual (video camera) observation [1963]. Hydrazine leaking into vacuum will quickly freeze and assume triple-point conditions. The rate of hydrazine sublimation may be very low, depending on available sources of heat. Hydrazine spilled on a space suit during EVA activities may not evaporate quickly enough and could be dragged into the space station after the astronauts re-enter the air lock [111].

### 7.8.1 Spill Decontamination and Disposal

Despite all the precautions taken in planning and conducting storage and transfer of hydrazines, occasional spills may occur. Transfer personnel should be well trained in the containment and neutralization of hydrazine spills. Several mathematical models have been developed for spill hazard assessment by hazardous materials response teams. These will be discussed in the following paragraph.

Hazardous material (HazMat) teams are specifically trained on how to deal with propellant spills, either off site or on site. A computer program can assess the type of response needed to bring the situation under control, depending on the type and quantity of propellant spilled, the proximity to populated areas, and geographical conditions [1964].

### 7.8.2 Hydrazine Spill Hazard Evaluation and Mitigation

Hazardous chemical spill response training has become an important part of the transportation industry and local accident response teams.

### 7.8.3 Atmospheric Dispersion Models of Hydrazine Vapor (without Reaction)

A vapor cloud caused by either the vaporization or reaction of hydrazine, UDMH, MMH, and NTO, as it was used on the APOLLO spacecraft, was analyzed to determine the generation and concentration of toxic products and the safe toxic distances in case of a spill [1965]. It was predicted that the process of vaporization of propellant without reaction would create the largest quantity of toxic products. Assuming that the total quantity of fuel or oxidizer aboard the APOLLO spacecraft would be spilled in sand and vaporized during unfavorable atmospheric conditions, it would have resulted in a maximum safe toxic distance of 5.5 km (3.4 miles). This safe toxic distance was considered to be the worst case because the cooling effects of vaporization tend to reduce the actual rate of vaporization. Reaction of hydrazine, UDMH, and MMH with NTO will produce a smaller quantity of toxic product, thereby reducing the toxicity hazard.

These hot products, when formed, being above ambient temperature and buoyant, will rise and expand, creating a faster rate of product dispersion and dilution.

Evaporation studies with simulated 10 g hydrazine and H-70 spills in 9-cm-diameter Petri dishes showed that although all samples lost hydrazine, some gained weight by moisture and carbon dioxide absorption from the air [723, 1966, 1967]. With pure hydrazine, 6–9 g evaporated within 3 h under Florida outdoor conditions. Similar loss rates (7.6 g/3 h) were obtained in a hood in a laboratory with an air speed of 0.6 m/s at 294 K. The evaporation rate slowed down significantly after 20 h. The remaining hydrazine was very viscous from carbazate formation. In a separate test where pure CO<sub>2</sub> was bubbled through H-70 fuel to constant weight, 50 g of H-70 fuel absorbed 30 g of CO<sub>2</sub>, and carbazate precipitated. Carbon dioxide suppressed hydrazine evaporation. No hydrazine evaporated when CO<sub>2</sub> was passed over the sample, and CO<sub>2</sub>-free nitrogen caused more rapid evaporation than ambient air.

Fuel evaporation rates were determined under controlled laboratory conditions in glass dishes of various sizes (11.6, 63.6, and 177 cm<sup>2</sup>) [1968]. Air velocity over the evaporating fuel was 132 cm/s, and the temperature was controlled to within  $\pm 2^\circ\text{C}$ . The evaporation rates in a 177-cm<sup>2</sup> dish were 0.49 mg cm<sup>-2</sup> min.<sup>-1</sup> for hydrazine, 1.7 mg cm<sup>-2</sup> min.<sup>-1</sup> for MMH, and 13 mg cm<sup>-2</sup> min.<sup>-1</sup> for UDMH.

The determination of a hazard corridor following a hydrazine spill involves two separate calculations [1969, 1970]. First, an estimate of the evaporation rate (source strength) must be made [1971]. Then an atmospheric diffusion model must be employed to predict the downwind distance required to dilute that source strength to a concentration that is considered tolerable. Sample calculations for a 20-m<sup>3</sup> trailer spill on a 36-m<sup>2</sup> area assumed a short-term public limit (STPL) of 7 mg/m<sup>3</sup>. For a spill depth of 2.5 cm and a wind speed of 3 m/s, the hazard corridor would extend 360 m downwind. Computer models are available that will predict the concentration-time profile of the vapor plume as a function of 10 input parameters. Constants that are part of the equations have been determined for hydrazine, H-70, MMH, and UDMH. A 30-min public exposure limit (PEL) for hydrazine of 20 ppm (26 mg/m<sup>3</sup>) was assumed for these calculations.

A computerized evaporation algorithm predicts the rate of evaporation as a function of soil temperature, solar insolation, air temperature, wind velocity, and spill dimension [1972, 1973]. A single-source Gaussian dispersion formula calculates the downwind, ground-level centerline concentration based on dispersion coefficients available in current EPA models. The dispersion algorithm also calculates the crosswind dimension of a hazard corridor in which the STPL is exceeded. The model allows for the absorption of water and carbon dioxide from the atmosphere into the liquid puddle, which would slow the rate of evaporation. It will also provide a calculation of the amount of water required to dilute a spill below hazardous concentrations. In some instances, such as in the massive TITAN III or TITAN IV launch failures, the toxic vapor/toxic aerosol plume is a mixture of solid propellant combustion products containing hydrogen chloride and aluminum oxide with

the unreacted NTO and hydrazines from the liquid stages. Modeling atmospheric diffusion of plumes of this nature is a very complex task [1974, 1975]. Some reactions continue to occur on the aluminum oxide particles while they disperse and descend.

Sample calculations for 200-L (drum), 20000-L (trailer), and 36000-L (rail car)  $N_2H_4$ , MMH, and UDMH spills at three different ambient temperatures (273, 288, and 303 K) showed that in the case of a 36000-L spill, the hazard corridor would reach 480 m downwind for hydrazine, 1380 m for MMH, and 680 m for UDMH. The rate of evaporation from a liquid pool is

$$\dot{m} = k_m \frac{P_v M A}{R T_p}$$

where  $\dot{m}$  is the mass flow (kg/h),  $k_m$  the mass transfer coefficient (m/h),  $P_v$  the vapor pressure (kPa),  $A$  the spill area ( $m^2$ ),  $R$  the universal gas constant ( $8.314 \text{ kPa m}^3 \text{ kg}^{-1} \text{ mol}^{-1} \text{ K}^{-1}$ ),  $M$  the molecular weight, and  $T_p$  the pool temperature of pool (K). Allowances were made for composition changes in the remaining pool due to preferential evaporation of a more volatile constituent of a mixture, absorption of water from the atmosphere, and both absorption of and reaction with carbon dioxide from the atmosphere. The evaporation rates of UDMH and MMH for similar meteorological and spill conditions are 11 and 3 times that of hydrazine, respectively. Comparison of predicted and experimentally observed evaporation rates showed good agreement for the first hour of the experiment.

None of the atmospheric dispersion models published so far accounts for the decay of hydrazine vapor as a result of autoxidation or photolysis. These need to be factored in because the half-life of hydrazine vapors may be of the same order as the time required to diffuse from the location of the source to the area of concern.

An empirical diffusion equation was used to calculate the downwind hazard distance in case of accidental spills of toxic chemicals [1976]. The width of the toxic corridor, specified in angular degrees centered along the mean wind direction, was based upon the variability of the wind direction. Estimating toxic corridor evacuation areas on the scene of an accident was facilitated through four different methods using tables, monograms, or a programmable calculator and procedures for determining meteorological inputs and evaporation source strength, as well as other items. See also [1977].

The Atmospheric Release Advisory Capability (ARAC) suite of three-dimensional transport and diffusion codes MATHEW/ADPIC was used to assess the consequences of severe, hypothetical accident scenarios [1978]. One set of calculations developed the integrated dose and surface deposition patterns for a non-nuclear, high-explosive detonation and dispersal of material. A second set of calculations depicted the time-integrated dose and instantaneous concentration patterns for a substantial, continuous leak of the missile oxidizer converted to nitrogen dioxide ( $NO_2$ ). The downwind areas affected and some of the implications for emergency response management can be predicted by this model.

The launch abort problem, for instance for a TITAN III or TITAN IV launch mishap, is especially difficult because there are separate initial clouds of fuel and oxidizer, with regions of mixing between them. An attempt was made to deal with this problem using a so-called multi-bin approach, which treated the fuel and oxidizer and an interface as separate bins but kept the computation tractable [1979]. The computer program was based on SURFACE CHEMKIN, a standard chemical kinetic sub-routine package [1980]. The model results showed that the outcome was highly dependent on initial conditions. For instance, a likely scenario for a Titan IV accident will result in 24% of the initial oxidizer remaining, of which at least half is transformed into nitric acid, and 2% of the initial fuel remaining.

Concentrations and dispersion of toxic vapor clouds formed by non-burning propellant that splashed onto the ground and evaporated and diffused after a launch failure of a liquid propellant launch vehicle can be predicted by an analytical model, depending on the launch site environment and weather conditions [1981, 1982].

Predictions from a theoretical model of liquid rocket propellant vaporization rate for the source strength were compared to experimental results of the evaporation rate of spilled propellants in a natural environment [1983].

#### 7.8.4 Spill Immobilization

During the testing of materials to permanently destroy spilled hydrazines, various concepts were tested that would temporarily immobilize the hydrazine spill until more permanent corrective action could be taken. Such immobilization methods include gelling, sponges, wipes, and foaming. Dry powder gelling agents were tested as treatment for 96%  $N_2H_4$  by dumping 5 g of solid onto 5 g of fuel [1984]. The most effective solid was a gellant, CMC Type 7HS cellulose gum, that permitted only 0.03% of the spill to escape overhead as vapors. The second best was a hydroxyethyl cellulose gellant. Unfortunately, gelled hydrazine is more difficult to neutralize later than a clear aqueous solution. Another method to minimize hydrazine evaporation until more permanent control methods can be instituted is to cover the hydrazine up with high-expansion aqueous foam for firefighting. Three types of foam were tested, and all three were equally effective as a vaporization barrier. In another study, several types of foaming agents were tested to reduce the evaporation of hydrazine and keep the hydrazine concentration in the vicinity of the spill below 0.5 ppm [1985]. The following foaming agents were tested: aqueous film forming foam (AFFF), National AeroFoam protein foam 6% regular, National XL 6% fluoroprotein foam, National Aero-O-Water 6% fluorocarbon foam, and MSA Ultrafoam V surfactant. AFFF can make high-expansion foam, but it drains very fast. Protein base foams were not very compatible with hydrazine. A fluorocarbon-based polar solvent foam made by 3M was compatible with hydrazine and provided good protection. Ideally, a foaming agent was sought that would leave a polymer skin on the liquid puddle even after the foam had collapsed. An acrylic modified foam that gels when it comes in contact with ammonia (recommended as treatment of liquid ammonia spills) was also tested for its efficacy against



hydrazine evaporation. A Type 95 foam reduced hydrazine vapor concentration above the spill to a few ppm, but its supplier was not identified.

Passing carbon dioxide snow (e.g., from a CO<sub>2</sub> fire extinguisher) over hydrazine spills will reduce the rate of hydrazine evaporation. Dumping liquid nitrogen or dry ice or water ice on the spill was another method tested to reduce hydrazine evaporation and to gain time until other control methods could be implemented [1986].

Laboratory screening tests were conducted to evaluate a variety of foam systems for hydrazine and/or N<sub>2</sub>O<sub>4</sub> vapor mitigation and minimizing the release of toxic hypergolic propellant vapors from spills [1987]. Two of the systems demonstrated the feasibility of maintaining a cover atop the propellant spill over an extended time by periodic reapplications of fresh foam. The vapor suppressant properties of these foam systems had been sufficiently demonstrated so that they could be incorporated into the arsenal of emergency response equipment for hypergolic propellant spills. The evaporation of hydrazine (and ammonia) from hydrazine spills can be retarded by adding a surface-active agent (surfactant) to the flushing water. Additives that have been patented for this purpose are long-chain amines of the general formula RNH<sub>2</sub>, where R is an alkyl group containing at least 12 carbon atoms and generally in the range of 12–26 carbon atoms [1988]. The mechanism by which the surfactant inhibits the volatilization of ammonia or hydrazine is not completely understood. Absorbent pads or pillows have been evaluated that can be applied to spills as a first step measure [1989].

#### 7.8.5 Spill Decontamination

Chemicals used to decontaminate hydrazine in water are generally oxidizers that permanently destroy and oxidize hydrazine to nitrogen and water, hopefully without the formation of nitrogen oxides or hydrogen azide as byproducts. Methods discussed here for spill decontamination that must be portable (so the decontamination unit can quickly move to the location of the spill) may work equally well in stationary installations but may not be the most economical solution to a stationary, continuous disposal problem. The same chemical may serve both applications, or different chemicals would be used for accidental (rarely occurring) spills and continuous, planned disposal of hydrazine. Olin Chemicals, once a major hydrazine manufacturer, recommended an aqueous solution of calcium hypochlorite (Olin trade name HTH<sup>®</sup>) for the decontamination of hydrazine spills. In the as-purchased form, Olin HTH is a white granular powder that is easily stored in sealed containers and must be dissolved in water prior to application. HTH is mainly used for swimming-pool disinfection and is generally available from swimming pool supply stores. Liquid decontaminants such as chlorine bleach (sodium hypochlorite, NaOCl, household bleach) or hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, are not as safe to store and may decompose during storage. During the disposal of hydrazine itself with NaOCl or H<sub>2</sub>O<sub>2</sub>, none of the toxic *N*-chloroamines or nitrosamines form that are occasionally observed with MMH or UDMH oxidation reac-

tions. With all decontaminating agents acting on any of the three hydrazines, nitrogen will be evolved that may lead to the buildup of high pressure in a closed system. Thus, provisions for venting gases and aerosol mists must be made while decontamination is in progress. The gas may also carry away some unreacted hydrazine vapor and nose-irritating mists. Reaction of hydrazine with hydrogen peroxide under incorrect pH conditions may form hydrazoic acid (hydrogen azide), which is even more poisonous and explosive than hydrazine itself.

None of the hydrazine spill decontamination agents can be applied to undiluted spills of anhydrous hydrazine or MMH or UDMH directly. It is important to dissolve HTH in water first, forming a dilute solution; otherwise the spilled hydrazine may ignite and aggravate the problem at hand. As a general rule, the spill must be diluted with water first and flushed into a holding tank. Decontamination can then take place in the holding tank. If any of the decontaminating agents, such as concentrated sodium hypochlorite solution or HTH powder, is poured directly on undiluted concentrated hydrazines, the heat of reaction will most likely lead to ignition of the spill.

Polypropylene felt wipes were evaluated and are now recommended by NASA and USAF for cleaning up small hydrazine or H-70 spills on smooth surfaces. The felt is less efficient in mopping up spills on porous surfaces, such as concrete. The procedure there would be to mop up as much of the spill as possible, dilute with water, and then treat the wet spot in the concrete pad with hypochlorite (diluted household bleach or HTH).

During a series of hazard classification tests, both above-ground and in-silo configuration spill tests were undertaken with hydrazine, Aerozine-50, and NTO for the TITAN II program, with up to 815 kg (1800 lb) of propellants spilled at a time [1990, 1991]. This was done in order to assess the potential hazard during cleanup. A total of 92 small-scale tests were performed using propellant quantities not exceeding 2.26 kg (5 lb) in weight. Propellant weights used on the nine large-scale tests ranged from 61 to 815 kg (135 to 1800 lb) of total propellant.

In one of the first thorough studies on hydrazine (and UDMH) spill decontamination, 94 different chemicals were reviewed for their suitability as spill control agents [1984]. One percent sodium hypochlorite solution was most efficient in minimizing hydrazine vapor emissions while the neutralization was in progress. One percent potassium permanganate solution reacted faster than hypochlorite but allowed more unreacted hydrazine to escape during neutralization. Eight solids were tested as decontaminants for 96%  $N_2H_4$  by dumping 5 g of solid onto 5 g of fuel. In the case of dry calcium hypochlorite, the mixture promptly ignited.

Spill decontamination methods were developed for hydrazine-based propellant mixtures such as MHF-3, MHF-5, alumizine, and beryllizine [1992]. Spill neutralization and disposal of the gelled, metallized propellants is more difficult because of the presence of metal powders and gelling agents. On the other hand, spills of gelled propellants remain localized, which is a substantial safety advantage of gelled propellants. Alumizine may exotherm if it is diluted with insufficient water and the hydro-

gen gas evolved may become a secondary explosion hazard. Neutralizing agents (hydrogen peroxide, sodium hypochlorite, potassium permanganate, potassium dichromate) were applied as 5% solutions and with a 50:1 mass ratio. The gel of alumizine was broken down by several neutralizing agents, which facilitated further cleanup. Three percent NaOCl solution was judged too reactive since it would spatter reactants around. Three percent  $\text{H}_2\text{O}_2$  solution was the preferred agent for the neutralization of metallized propellants, since it was the only agent that showed satisfactory neutralization effectiveness with no undesirable side reactions.

As an alternative to hypochlorite, copper-catalyzed hydrogen peroxide has also been evaluated, but the report fails to mention the potential of hydrogen azide and copper(II) azide formation under these conditions if the pH is not correctly adjusted. The use of calcium hypochlorite (e.g., HTH) is the most economical way to neutralize hydrazine spills, water runoff from such spills, and water extracts from felt squares used to mop up such spills, but the remaining calcium salts are sometimes hard to remove from surfaces, and a lime slush may settle at the bottom of the neutralization vessel. Hypochlorite should be added (5 kg HTH dissolved in water for every liter of H-70 = 42 lb/gal or 100 volumes of 5% household chlorine bleach for each volume of H-70 spilled) until an excess of free hypochlorite can be detected with 0.1% orthotolidine in 8% HCl aqueous solution indicator. A catch treatment container of approximately 30-gal capacity should be on hand to treat the contents of one F-16 EPU tank holding 6.5 gal of H-70 mix.

Solid sorbents/neutralizing agents would be preferred over liquid reagents because they do not constitute a spill/leak hazard of their own. Various transition metal oxides and sulfates were tested at very low pressures for the speed of reaction with hydrazine vapor (their so-called reducibility) using changes in the oxide-oxygen XPS peak as an indicator. Hydrazine vapors adsorb reversibly on silica-alumina evaluated as a sorbent [1993]. Copper(II) oxide was the most reactive and iron(III) oxide was the least reactive of nine oxides tested. Copper(II) oxide becomes reduced to metallic copper in the process. The copper(II) oxide is preferably deposited on an inert porous clay material to prevent excessively fast and hot reactions [1994]. Some of these agents may cause spilled hydrazine to ignite, which would make the situation even worse. If the hydrazine spill is diluted below its flash point, the agent may react only very slowly.

One of the more promising spill control materials was 10.5% copper(II) oxide supported on silica or Microcell-E foam. NASA WSTF evaluated these two materials by applying them to a simulated spill consisting of 1 L of 1% hydrazine solution [1995, 1996]. The materials were applied as loose powders or contained in a polypropylene fabric pillow. The temperature increased by up to 25 °C during the neutralization reaction, which did not aggravate the disposal hazard. The hydrazine decomposition reaction reached 75% completion within 3–15 h for all spill-control materials. The general reaction stoichiometry was 2 mols copper(II) oxide to 1 mol hydrazine.

An acetate-acetic acid buffer with a gelling agent was tested as a spill control medium against small spills of Aerozine-50 or NTO [1997]. See also [1998–2002].

USAF Armstrong Laboratories (Brooks AFB) have evaluated the *in situ* biological remediation of hydrazine spills in the soil using gel-encapsulated enzymes. This would be a very slow process.

#### **7.8.6 Accidental Hydrazine (Hydrate) Spill Case Histories**

There was an isolated incident caused by derailment of a train, causing a spill of hydrazine hydrate from 16 punctured steel drums in a railroad accident near Sea Cliff, CA, on July 28, 1991. No major environmental damage occurred since the spill site was quickly surrounded by a dam and leaked hydrazine hydrate was destroyed with hypochlorite.

In July 1992, three people suffered minor injuries when a box containing anhydrous hydrazine leaked in the Air France/Continental Airlines cargo area at O'Hare International Airport.

In November 2003, a leaking tractor trailer released nearly 20 gal hydrazine hydrate onto Interstate 190 near West Boylston, MA, causing a 4-mile stretch of the southbound lanes to be closed for about 9 h. As the truck was pulling into the breakdown lane, it shot out a thick cloud of chemical that covered all the southbound lanes. The truck was transporting 43600 pounds of hydrazine hydrate. The leak was probably caused by a pressure release valve that functions when the inside pressure of a tank becomes too high.

### **7.9 Disposal of Hydrazine**

Before one undertakes the task of disposing of surplus hydrazine and hydrazine wastes, one should investigate salvage and reuse of the waste hydrazine. There may be methods of reprocessing contaminated hydrazine into a useful product, the manufacturer may agree to take aged and out-of-spec product back for reprocessing, or one may find other applications for the waste hydrazine. For instance, in a large industrial operation that also has chrome plating finishing operations and chromate-containing wastewaters, the use of hydrazine to convert hazardous chromate to the precipitable chromium(III) would be a way to kill two birds with one stone, so to speak. In other instances, precipitation of hydrazine from hydrazine waste solutions as sparsely soluble hydrazinium(2+) sulfate may lead to a saleable solid waste product that may find other uses. Hydrazinium(2+) sulfate is easily stored as a solid and does not have a noticeable vapor pressure.

### **7.10 Disposal of Concentrated Hydrazine**

Hydrazines that must be disposed of for some reason (contamination, surplus, demilitarization) can be destroyed by burning, autoxidation, or chemical oxidation. The de-

struction of hydrazine itself is the easiest task compared to the effort required for the disposal of methylhydrazines. Several of the methods described here for hydrazine may work equally well on methylhydrazines. Some of the methods for the disposal and decontamination of hydrazine(s) will be discussed here and again in the accompanying chapters on alkylhydrazines.

### 7.10.1 Open-Pan Burning

One quick method of disposing of surplus hydrazine, although frowned on by some regulatory agencies, is to burn it in open pans. Because the only products of combustion are nitrogen and water, this should be an environmentally benign and ecologically acceptable method of disposal. For instance, 25 mL anhydrous hydrazine in a 18 × 28-cm steel pan burned and disappeared within 17 s [2003]. Only 0.3–0.7% of the total hydrazine was found unburned when the pan was rinsed with water after the fire. Neat hydrazine burned rapidly, leaving little residual hydrazine, but ignition of aqueous solutions became progressively more difficult as the water concentration increased. Ambient air concentration during the fire ranged from less than 0.1 to 11.5 mg/m<sup>3</sup>. While anhydrous hydrazine burned quite readily, disposal of the 70/30 hydrazine/water mixture by burning did not go as smoothly. Three to eight percent of the hydrazine was left unburned, and the ambient hydrazine concentration was up to 75 mg/m<sup>3</sup>. The mixture burned much more slowly than did 100% N<sub>2</sub>H<sub>4</sub>, and it took 88 s to consume 25 mL fuel.

Hydrazine solutions containing less than 50% by weight N<sub>2</sub>H<sub>4</sub> could not be burned in open pans unless some supplementary fuel was added [1966]. Adding 1:1 volume parts of methanol to an otherwise incombustible 50% N<sub>2</sub>H<sub>4</sub>/50% H<sub>2</sub>O solution rendered the mixture again flammable, and it burned with 92% efficiency (8% of the hydrazine was left unburned in the pan). Adding JP-4 instead of methanol achieved even more efficient hydrazine destruction; only 2% of the hydrazine was left unburnt after burning a 1:1 (by volume) JP-4/50% N<sub>2</sub>H<sub>4</sub> mixture. This method is not suitable for dilute solutions but is restricted to concentrated hydrazines.

### 7.10.2 Incinerator Burning

The two-stage combustion of hypergolic rocket propellants (N<sub>2</sub>O<sub>4</sub> and the three hydrazine fuels) in an optimized burner was expected to lead to a minimum discharge of NO<sub>x</sub> into the environment [2004]. The first stage of combustion allowed the fuel or oxidizer to react in a respectively lean or rich flame, yielding a mixture of products including the inevitable NO<sub>x</sub>. The second stage of combustion was supposed to achieve the reduction of NO<sub>x</sub> as the result of addition of NH<sub>3</sub> or H<sub>2</sub> (Thermal DeNO<sub>x</sub>) or cyanuric acid. The objective was to understand and control the turbulent combustion of these propellants through the application of fluid dynamics and kinetics modeling, in conjunction with optical and mass-spectrometer-based flame diagnostics.

Several incinerator burner designs were qualified and certified for the destruction of chemical warfare agents, and they should work just as well for the less toxic and

more reactive hydrazines. A toxic waste burner has been built and evaluated for burning of hydrazine or UDMH with a hot gas (pre-burner) and additional air [2005]. The goal was to reduce  $\text{NO}_x$  emission in the exhaust gases down to less than 165 ppm. Initially, hydrazine and UDMH were tested in an existing air-cooled liquid incinerator with natural gas used for ignition (and in some cases necessary to sustain combustion). Air was used as the oxidizer. Hydrazine and UDMH could be destroyed by incineration down to a level below 2 ppm residual hydrazines with  $\text{NO}_x$  emissions in the discharged gas in concentrations well below 165 ppm. Incinerator dwell times were on the order of 0.1 s.

Another burner developed for the disposal of liquid propellants disposed of over 453 kg/h (1000 lb<sub>m</sub>/h) of liquid propellants including hydrazine by burning it in air to produce exhaust gases in the 977 K (1300 °F) range, which contained only acceptably low levels of nitrogen oxides [2006].

## 7.11 Entrapment and Disposal of Hydrazine Vapors

### 7.11.1 Hydrazine Vapor Scrubbers for Absorption from Vented Pressurant Gases

Several methods have been considered for the disposal of hydrazine vapors such as those emanating from tanks (stationary tanks, tank cars, drums) to be filled with hydrazines or those from pressurized tanks that are vented to ambient pressure after the completion of transfer operations. Because hydrazine concentration and flow rate can vary over a wide range, it is difficult to design a system that suits all conditions equally well.

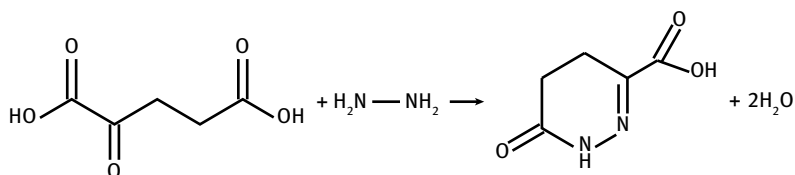
In most cases, for stationary test operations on the ground, the hydrazine vapors are passed through a counter-current liquid scrubber. This does not actually solve the pollution problem; it only converts it from an air pollution problem to a water pollution problem. The advantage of the liquid wastes generated from a scrubber is that they can be accumulated in a holding pond and then treated at a slower rate of reaction than would be necessary for the rapidly venting gases. As a first approach, one might use just plain water (no acid) as the scrubber liquid. In this case, the efficiency of the scrubber is limited by the volatility of hydrazine(s) from dilute aqueous solutions. The vapor-liquid equilibrium is governed by Henry's law. The Henry's law constants (Section 2.1.9.4) must be known to design a scrubber and determine how many stages are required to achieve satisfactory absorption of hydrazine vapors contained in the pressurant gas of propellant tanks [2007]. These constants were determined for aqueous solutions containing 0.1 to 1% of hydrazine or MMH in buffered (pH = 7) and unbuffered solutions. The effect of salinity on hydrazine volatility was also tested. Instead of using just plain water as the scrubber liquid, for all practical purposes it is more efficient to use acidic solutions as scrubber liquids.

During the early 1980s NASA KSC initially used bubble-cap scrubbers 0.5 m wide and 6 m high with 18 plates to absorb propellant vapors from gases vented from hydrazine servicing equipment into recirculating water [2008]. Each plate carried 16

bubble caps, typical for chemical industry absorption towers. The propellant vapor was washed with water, and the hydrazine-laden water was subsequently treated with hypochlorite in a separate installation. The scrubber was tested with gases containing 100 ppm hydrazine, 150 ppm MMH or 45000 ppm MMH, or 110000 ppm UDMH, and the effectiveness of the scrubber was verified by sampling the off-gas with Dräger tubes. The scrubber system was later converted to operate on citric acid solutions instead of plain water. The bubble cap scrubber was later replaced by a portable, skid-mounted  $1.8 \times 1.8 \times 3$ -m system containing four vertical columns packed with Raschig rings. The four columns drained by gravity into a common 2800-L scrubber liquor tank located beneath the towers. The gas flowed through each of the four towers in series.

Hypergolic fuels and oxidizer pressurant gases were vented during fueling and de-servicing Space Shuttle and other spacecraft and cleansed of toxic propellant vapors before allowed to be vented to the environment. The scrubbers are not 100% efficient and traces of propellant vapors pass through the apparatus. Scrubber emissions are difficult to measure due to the intermittent purge flow and due to the presence of suspended scrubber liquor droplets. An alternative method for emissions monitoring and estimating was introduced [2009, 2010]. It was suggested that emissions could be determined from field scrubbers without the direct measurement of vent flow rates and escaped hypergol vapor concentrations. This alternative approach was based on the scrubber efficiency, which was previously measured during normal steady-state operations, and on the accumulated weight of hypergol captured in the scrubber liquor, which is part of the routine monitoring data of scrubber liquors. The emissions from scrubbers can be calculated by measuring the buildup of hypergol propellant in the liquor, and then using the appropriate efficiency to calculate the fugitive emissions. An estimate of the total emissions from 16 scrubbers at NASA KSC over a period of 3 years indicated that only 0.3 kg/year of fuel (MMH and hydrazine) and 234 kg/year of nitrogen dioxide were emitted [2011, 2012].

$\alpha$ -Ketoglutaric acid [= 2-ketoglutaric acid, AKGA,  $\text{HOOCCH}_2\text{CH}_2\text{C(O)COOH}$ ], a water-soluble solid, has been proposed for hydrazine or MMH vapor absorption from air or for the decontamination of wastewater from rinsing hydrazine- or MMH-contaminated rocket propulsion systems [2013–2015]. The reaction of  $\alpha$ -ketoglutaric acid with hydrazine or MMH forms a non-volatile, non-toxic (less toxic) heterocyclic pyridazine compound.



Alpha-ketoglutaric acid and ethyl acetoacetate were examined as potential alternatives to the hydrazine-family fuel vapor scrubber neutralization techniques used at

NASA KSC. Both reagents react with hydrazine-family fuels to form non-volatile hydrazone derivatives. Each of these reactions was characterized with an emphasis on applicability for implementation in so-called real-world processing scenarios such as the decontamination of flight hardware and ground support equipment or as drop-in replacements for the current scrubber liquor used in typical KSC four-tower vapor scrubbers. Preliminary testing was performed by the reaction of reactant solutions with hydrazine fuels in both liquid and vapor phases. A one-tenth-scale scrubber was built to demonstrate this technology. Specific properties examined included reaction efficiency and comparison to the current citric acid scrubber reagent, product solubility, and undesirable precipitate saturation points.

$\alpha$ -Ketoglutaric acid adsorbed onto a solid silica-based substrate was examined as a vapor scrubber medium, a potential alternative to the hydrazine-family hypergolic fuel absorption/neutralization techniques currently used at NASA/KSC [2016]. Hydrazine-absorbent fabric or metal screen saturated with solutions of dicarbonyl compounds like  $\alpha$ -ketoglutaric acid or acetylacetone or ethyl acetylacetate can be used to absorb hydrazine vapors from air or can be used as a sorbent pad to immobilize small hydrazine spills [2017].

A critical review of patent claims and preliminary laboratory test results with  $\alpha$ -ketoglutaric acid for hydrazine or MMH vapor absorption or decontamination of hydrazine- or MMH-contaminated rocket propulsion systems concluded that the uncertainties of the completeness of the reaction and lack of complete identification of all reaction products prevented the practical application of this chemical under real-life rocket launch site GSE conditions [2018]. When reacting 0.73-M AKGA solutions in benchtop lab tests, a solid formed with hydrazine but not with MMH. In more dilute 0.2-M AKGA solutions, no precipitate formed with either hydrazine or MMH. Another di-keto compound tested in hydrazine or MMH scrubber liquids was ethyl acetoacetate  $\text{H}_3\text{C}-\text{C}(\text{O})-\text{CH}_2-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}_3$ , but its reaction with hydrazine or MMH produced a gummy, sticky substance (a carbinolamine intermediate converting to 3-methylpyrazol-5-one) that clung to the walls and was difficult to remove.

NMR reaction kinetic studies verified that the  $\text{N}_2\text{H}_4/\text{AKGA}$  reaction proceeds at a rate sufficient for industrial wastewater treatment uses even in the presence of other compounds found in industrial waste streams [2019]. Toxicity studies determined that the products of the reactions were not toxic to crustaceans and fish. Therefore, waste streams produced from these reactions can be metered into a municipal wastewater facility for final disposal. NMR identified byproducts produced by the reaction of  $\text{N}_2\text{H}_4/\text{AKGA}$  and MMH/AKGA as being only 6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (PCA) and 1-methyl-6-oxo-1,4,5,6-tetrahydro-pyridazine-3-carboxylic acid (mPCA), respectively. Biodegradation NMR studies with  $^{13}\text{C}$ -labeled PCA and mPCA were made to compare the labeled material before and after exposure to microbial populations obtained from a wastewater treatment plant. PCA (up to 5000 ppm) degraded almost completely forming  $\text{CO}_2$ , but mPCA did not show significant biodegradation in a period of 28 d.



Rainwater collecting on the pad surrounding a scrubber may contain some residual hydrazine and must be treated as hazardous waste if the hydrazine concentration is above 200 ppb [2020]. Most likely the hydrazine would slowly deteriorate on its own under the influence of air and sunshine.

Because of the intense flashback hazard, it is not easy to dispose of hydrazine vapors by feeding them directly into an incinerator. There is concern about vapor detonations when attempting to destroy hydrazine vapors without prior absorption in water. Vapor detonations can propagate from the hot reactor through very narrow tubing into the reservoir of the hydrazine vapors that are to be destroyed, but this can be done only slowly in high dilution and in a controlled manner.

There may be concern over the flashback of flames into gas streams undergoing treatment if hydrazine concentrations exceed safe limits, but some intrepid investigators nevertheless recommend the use of hydrazine decomposition catalysts to remove hydrazine vapors from gas streams vented during depressurization of rocket propellant tanks. Another concern would be that during an inadvertent reversal of gas flow toward the end of depressurization (e.g., caused by brief non-destructive deflagration puffs), catalyst fines could be blown back into the propellant tank. One such patented catalyst contains mainly manganese(IV) dioxide plus mixed oxides of lanthanide rare earth metals [1548]. Another proposed catalyst contains rare earth/transition metal oxide mixtures and is said to be capable of treating hydrazine concentrations of 4000 to 5000 mg/L at space velocities of  $10000\text{ h}^{-1}$  at 287 K [1547]. The claimed concentrations are most likely an error that occurred in translation, because this would be a flammable and explosive vapor mixture. Even at  $5000\text{ }\mu\text{g/L}$  in air and even in nitrogen instead of air, this is a potentially hazardous operation. Flashback is most likely to occur toward the end of the blowdown operation when the flow rate drops to near zero. It would be necessary to dilute the vented gas with inert gas to below detonable concentrations (partial pressures below  $1.07\text{ kPa} = 8\text{ mm Hg}$ ).

At NASA KSC, the handling of propellants is confined to a few select areas operated by well-trained personnel. In contrast, H-70 powered EPU in F-16 fighter maintenance is done at many air bases around the world. Pressurant gas from spent F-16 EPUs containing H-70 blend is usually vented through a 7.5-L (2-gal) stainless-steel bucket containing 3.8 L (1 gal) of ordinary chlorine bleach (5% NaOCl). As an alternative, a transparent cartridge containing a dry chemical (100 g alumina granules impregnated with potassium permanganate  $\text{KMnO}_4$ ) has been tested [2021]. The  $\text{KMnO}_4$  undergoes a highly visible color change from purple to brown as a result of hydrazine absorption. Venting of a single F-16 EPU discolors approximately half the contents. Sixty percent of the hydrazine in the vent gases is destroyed by reaction with the dry chemical, while 40% remain adsorbed on the exhausted portion of the dry chemical. The cartridge would require secondary treatment before it may be disposed of safely. One of the cleanest methods for hydrazine disposal is the reaction with oxygen or ozone, as was discussed earlier in Section 3.1.1.1 (“Oxidation of Hydrazine”).

### 7.11.2 Cryogenic Cold Trap Scrubbers

A LN<sub>2</sub>-cooled cryogenic cold trap has been evaluated for the removal of MMH vapor from vented pressurant gases; presumably the same method would work for trapping hydrazine vapors from vented pressurant gases [2022].

## 7.12 Hydrazine Wastewater Decontamination

### 7.12.1 Neutralization and Disposal of Diluted Rinse Waters and Scrubber Solutions

There are many situations during the use of hydrazine(s) in the aerospace and electric power industries where dilute hydrazine-containing rinse waters must be disposed of:

1. Rinse waters accumulate after system-level tests (expulsion tests, vibration tests, spin tests, acoustical tests) with hydrazine tanks in missiles and satellites.
2. Transfer hoses must be rinsed before storage and reuse.
3. Hydrazine and MMH or UDMH rail and road tank cars must be hydrotested once every year and are rinsed clear of propellant prior to the test with water (periodic pressure tests are required by DOT).
4. Unreacted hypergolic propellants dissolve in cooling water on flame deflector chutes during ground testing or launch of NTO/UDMH or NTO/Ae-50 engines, where they form NDMA.
5. Condensate and blowdown from steam power plants where hydrazine hydrate was added for boiler feedwater deoxygenation.

Wastewater at rocket test sites would result from rinsing containers that contained hydrazine and from rinsing hardware that has gone through development, qualification, or quality control acceptance test firings. Wastewater also is produced by vapor scrubbers, although that water also contains scrubber chemicals like citric acid or ketoglutaric acid.

Launch operations at NASA KSC and CCAFB generate large volumes of hydrazine-laden wastewater for disposal. Some of this waste is contained and shipped out for subsequent disposal by incineration, which makes it a very expensive operation. Alternative remediation methods evaluated by NASA and contractors include oxidative and reductive pathways as well as biodegradation in fixed film reactors.

Hydrazine and hydrazine-type fuels that are contained in wastewater constitute a more diffuse source of contamination than undiluted propellants. This problem arises with wastewaters discharged from fuel-blending facilities [2023], rocket test/launch sites, and fossil-fired or nuclear steam power plants. Comparison of the various hydrazines and their resistance to autoxidation (Section 3.1.1.1) reveals that the alkylhydrazines are generally more difficult to dispose of than hydrazine itself. Occasionally, hydrazine-containing boiler feedwater must be discharged if the boiler is shut down for repair. Depending on the location of the power plant, it may not be permissible to dump this water without pre-treatment and removal of the

**Table 76:** Wastewater generation as a result of propellant handling operations.

| Propellant           | Propellant, L | Wastewater, L              |
|----------------------|---------------|----------------------------|
| <b>Fuel</b>          |               |                            |
| MMH                  | 58000         | All three combined: 718000 |
| Aerozine-50          | 77000         |                            |
| Hydrazine            | 14300         |                            |
| <b>Oxidizer</b>      |               |                            |
| Dinitrogen tetroxide | 164000        | 132000                     |
| Total                | 313300        | 850000                     |

Data source: [2024]

hydrazine. Power plant effluents also contain organic amines like cyclohexylamine or morpholine for pH adjustment in addition to hydrazine.

It is of interest to compare the volume of wastewater generated in relation to the amount of rocket propellants handled for a typical rocket launch site such as NASA KSC for a typical year, based on data collected in 1985. As shown in Table 76, the amount of wastewater generated is a multiple of the volume of rocket fuels used.

The safe and environmentally acceptable disposal of all that wastewater is indeed a difficult task. The amount of oxidizer waste is less and is shown here only for comparison. What is not shown behind these numbers is that the waste treatment requirements and government environmental regulations have created a shadow army of inspectors and waste processors that significantly contributes to the overall expense of getting payloads into orbit. It would be interesting to plot the growth of environmental and safety jobs at launch sites as a function of time since the creation of EPA and OSHA.

**7.12.1.1 Neutralization of Hydrazine Rinse Solutions**

In some cases, it is beneficial to neutralize (adjust the pH and thus minimize evaporation) hydrazine solutions before they are subjected to destructive disposal. It has been suggested to use dilute solutions of glycolic acid (hydroxyacetic acid) as rinse water for cleaning of hydrazine components, e.g., Ae-50 flow meters after calibration with actual propellants [2025]. Glycolic acid is only a weak acid and not likely to cause damage to the hardware being cleaned, as long as all residual acid is flushed out with water. Wetting agents and antifoaming agents may be added to the cleaning solution as necessary. The odor of glycolic acid is not as objectionable as that of acetic acid, which could be used for the same purpose. Glycolic acid is biodegradable.

**7.12.1.2 Hydrazine Wastewater Decontamination by Autoxidation by Aeration with Air**

Although most of the methods described here were developed for the removal of hydrazine hydrate from power plant wastewater, they can be just as well applied to the

removal of hydrazine from other wastewater streams, such as those that may originate in hydrazine manufacturing plants, rocket test stands, or rinse waters from freshly reduced polymers. The easiest way to remove hydrazine from wastewater is to aerate the water in the presence of activated charcoal that acts as a catalyst [2026–2028]. The number of periodical publications is dwarfed by the number of patents issued for this procedure. The tightening requirements for the removal of hydrazine from blowdown in power plants before releasing the contaminated blowdown and condensate into surface waters has brought about a decade-long flurry of patenting activity, mostly in Japan, of different methods for removal of hydrazine from dilute aqueous solutions. The most widely practiced method is the aeration of hydrazine solutions over packed beds or in a trickle bed of activated charcoal [2029–2031]. However, activated charcoal may become inactive with extended use. In this case, it can be regenerated by treatment with 1% hydrogen peroxide solution and then returned to active hydrazine service [2032]. Thus, aerating 0.05 to 0.5% activated charcoal powder or granules slurried in 100 to 1000 ppm  $\text{N}_2\text{H}_4$  in  $\text{H}_2\text{O}$  will rapidly reduce the concentration to less than 1 ppm [2033]. Adding 100–1000 ppm  $\text{Fe}^{3+}$  to the solution at a  $\text{pH} > 8$  ( $\text{pH} 10$  preferred) will speed up the process. This is a batch process where the treated material must sit in a settling pond for a while to allow the charcoal and hydroxide sludge to settle. The sludge can be reused. The destruction of hydrazine can be completed by sodium hypochlorite. An eventual excess of active chlorine can be removed by passing the solution once more over activated charcoal. In one design example using activated charcoal in a six-stage fluidized system with 1 h retention time, bubbling  $23 \text{ m}^3/\text{h}$  air, containing 48 kg charcoal per stage, the hydrazine concentration at the entrance to the system and successive exits from the six stages was 400, 260, 165, 95, 50, 15, and, finally, 0 ppm [2034]. Aeration in the presence of copper turnings or copper salts reduced the hydrazine content of wastewater from 163 to 3 ppm after only 1 h [2035, 2036]. A similar patent proposes aeration with copper turnings first, followed by cation exchange [2035]. Aeration with the addition of copper(II) sulfate, copper(II) chloride, or copper(II)oxide as catalysts will quickly remove unwanted hydrazine [2037]. A USSS No. 10 to 24 size Raney copper catalyst containing 9.6% Al was packed into an aerated column and used for treating a hydrazine solution containing 250 ppm [2038], thereby reducing the hydrazine concentration to 0.02 ppm. Aeration in the presence of a manganese(IV) dioxide granular catalyst removed most of the hydrazine, and remaining traces of hydrazine could be removed with sodium hypochlorite or hypochlorous acid  $\text{HOCl}$  [2039]. The manganese(IV) dioxide catalyst can be coated on a fabric of synthetic polymer fibers through which the solution flows [2040]. Aeration in the presence of a granular nickel peroxide catalyst is equally effective [2041]. Another variant of this process treats the waste solution in the presence of a nickel oxide or nickel peroxide slurry and adds hydrogen peroxide or sodium hypochlorite to the stirred slurry to regenerate the catalyst [2042, 2043]. Yet another variant of this process mixes the hydrazine with hydrogen peroxide first, then passes the mixed solutions over a bed of nickel peroxide pellets [2044].

The nickel peroxide pellets can be formed and extruded with the aid of a cement binder [2045]. It is known that iridium is a good catalyst for the decomposition of anhydrous hydrazine in rocket engines, but it may be prohibitively expensive to use iridium (<20% Ir) on activated charcoal as catalysts for autoxidation of hydrazine wastewater solutions [2046, 2047].

Palladium is not as expensive as iridium and may serve the same purpose equally well. Palladium catalysts catalyze the autoxidation of hydrazine solutions in air, also in combination of air with hydrogen peroxide [2048–2050]. Concentrations of 200 ppm  $\text{N}_2\text{H}_4$  and more in wastewater can be removed by the addition of hydrogen peroxide and additional aeration in the presence of a palladium catalyst [2051]. Residual hydrazine concentrations after 3.5 h were less than 1 ppm.

Palladium-coated wire mesh catalysts used for hydrazine removal, as well as from effluents of ketazine hydrazine production plants, can be regenerated by treatment with sodium hydroxide at  $\text{pH} > 13$  or 0.1% hydrogen peroxide solutions [2052–2055]. Palladium catalysts with aeration allow the removal and destruction of hydrazine at  $\text{pH}$  8.6–11 from the regeneration effluent of ion-exchange resins used for the demineralization of recycled boiler condensate [2056]. Using oxygen-enriched air diminished the necessary contact time to  $1/2$  to  $1/3$  of that required with normal air [2057].

Catalysts proposed for the removal and autoxidation of excess hydrazine in the condensate that leaves steam power plants as wastewater include cobalt(III) complexes such as sodium hexanitritocobaltate(III) or cobalt(III) hexammino chloride [2058]. Wastewater containing small hydrazine concentration can be purified more rapidly by aerating it in the presence of UV light [2059].

### 7.12.1.3 Hydrazine Wastewater Decontamination by Ozone Treatment

Ozonization (synonym: ozonation, ozonolysis) in combination with UV illumination has been used in drinking water sterilization with good success. Commercial ozonation units are available from several vendors to destroy dissolved organic contaminants present in groundwater and wastewater with low levels of suspended solids [2060]. The system uses a combination of UV radiation, ozone, and hydrogen peroxide to effectively oxidize most contaminants.

One of the most complex tasks in the disposal of hydrazine-contaminated rinse waters was faced by the cleanup contractors for the Hydrazine Blending and Storage Facility at Rocky Mountain Arsenal near Denver, CO in the 1980s. Several cleanup contractors surveyed the site, continued to take air, soil, and groundwater samples and proposed remedial action for the 300000 gal of contaminated rinse water still stored at the site. Since in 1982 there was no demonstrated proven technology for the total decontamination of UDMH/NDMA-contaminated rinse water, a survey of available and proposed wastewater decontamination technologies was started. Several techniques were evaluated in bench- and pilot-scale setups, including UV/ozonation and UV/hydrogen peroxide treatment [2061], or adsorption on activated charcoal [2062]. As one of several interim response actions being conducted at Rocky Mountain Ar-

senal under Superfund legislation, UV/chemical oxidation was chosen as the best process for the treatment of approximately  $1130\text{ m}^3$  (300000 gal) of hydrazine- and NDMA-contaminated rinse water [2063]. Because the project action level for NDMA was 1.4 pg/L (1.4 ppt) and because the hydrazine fuels decompose before NDMA is destroyed to the action level, 1.4 pg/L of NDMA was targeted as the goal for treated effluent. The UV/chemical oxidation process typically can treat hydrazine compounds in 16 h, while 35 h are required to decrease the NDMA concentration to approximately 1 to 2 ppb ( $\mu\text{g/L}$ ), which still does not meet the treatment goal of 1.4 pg/L. Investigating a possible secondary treatment that could reduce NDMA concentrations even further, Rocky Mountain Arsenal and the US Army Engineer Waterways Experiment Station attempted to achieve a lower effluent level without costly additional UV/chemical oxidation treatment. Three adsorption processes, granular activated carbon (GAC), organic-based ion-exchange resins, and activated alumina, were evaluated, but the results were not satisfactory [2062]. Three different vendors offered equipment for this task, including ozone/UV and hydrogen peroxide/UV treatment. These were first tested in pilot-scale operations at the 3780 L/batch level. All techniques had the potential for generating NDMA from UDMH as an undesirable intermediate of the disposal process. Thus, if the hydrazine wastewater disposal process had to be interrupted for an unforeseen reason, one would be stuck with an even larger quantity of NDMA-containing wastes. The capacity of the system was selected such that two parallel systems could treat  $1130\text{ m}^3$  (300000 gal) of wastewater over a 7-month period or 18900 L/week/system (5000 gal/week/system). The target post-treatment tolerable concentration of NDMA was established as 1.4 ppt (parts per trillion), or the lowest achievable certified reporting limit. NDMA concentration in the untreated wastes stored on site ranged from 2.9 to  $360\text{ }\mu\text{g/L}$ . In addition to new treatment techniques, analytical methods for analysis of NDMA in wastewater in the presence of unreacted hydrazines had to be developed and certified to meet government requirements.

In addition to treating waste that had been stored above ground in tanks, groundwater collected at various intercept points to prevent it from flowing off-site had to be treated [2064]. Two activated granular charcoal systems were not effective in removing NDMA from groundwater. Analysis of inflow and effluent streams indicated that NDMA may merely be recirculated through the system without appreciative removal. NDMA concentrations between 0.04 and  $5\text{ }\mu\text{g/L}$  have been recorded at these locations. Use of an ozone/UV technique would require treatment times in excess of 50 h to achieve the desired removal to the non-detectable level. In addition, alternative adsorption methods were evaluated.

Ozone instead of air as a decontaminating agent (without enhancement by UV radiation) is useful for unsubstituted hydrazine only [2065]. Ozonation products of wastewater containing hydrazine and hydrazine-related rocket fuels were characterized [575, 2066]. Minor amounts of nitrate were produced from the ozonation of hydrazine, MMH, and UDMH. This was probably a result of ammonia or nitrosamine oxidation.

The rates of oxidative destruction of hydrazine, MMH, and UDMH were investigated using ozone alone or ozone activated with UV [2067]. All three hydrazines were oxidized rapidly with ozone or ozone/UV. The ozone was consumed as rapidly as it was introduced as long as any hydrazine was present. The limited solubility of ozone in water is one of the rate-limiting factors. Metal catalysts accelerated the destruction of hydrazines and NDMA [2068, 2069]. Operation at pH 9.1 for destruction of hydrazines was recommended for optimum results. The rate at which the three hydrazine fuels were destroyed was about six times slower at pH 2.5 than at 9.5. Three different methods for treatment of hydrazine wastewaters were tested at IITRI: ozone as the primary oxidizing agent, UV light as a catalyst for the reaction between NDMA and ozone, and, finally, chlorine as a final “polishing” agent following the treatment with either of the two aforementioned methods [2070]. Three different reactors were used in the study: a tubular reactor containing a liquid column and a gas dispersion (sparging) element at the bottom, a UV spray chamber with two different quartz lamps (high-pressure and low-pressure mercury lamps), and a commercial UV water purifier consisting of a CRES-316 tube with a coaxial quartz tube holding the UV lamp. Chlorination was not pursued any further because halocarbons are not permitted in the effluent of the treatment plant. The combination of ozone and UV was able to reduce the NDMA concentrations to below 20 ppt.

Modeling of the kinetics of hydrazine ozonolysis showed that fuel destruction rates were limited by the rate of ozone input [573]. Using a stopped-flow technique, it was shown that while the overall, global destruction was rapid, observed “rate constants” were five to six orders of magnitude lower than the true kinetic rate constants ( $10^7$  to  $10^9$  L mol<sup>-1</sup> min<sup>-1</sup>). Initial mol ratios of fuel to ozone consumption were about two to five, and this ratio decreased to less than unity or even less than unity as the ozonolysis proceeded. The same UV-ozonolysis installation that was originally developed for hydrazine wastes can also be used for the destruction of other industrial organic wastes generated during routine operations [2071, 2072].

NASA WSTF acquired an ozone generator capable of producing 2.75% ozone in oxygen and installed it in a pilot-scale reactor [2073–2075]. It was important to feed the ozone generator with dry oxygen and maintain its temperature below 287 K to optimize the ozone yield. The UV ozonator reactor was a rectangular chamber with six spray nozzles capable of flowing 3.8 L/min and atomizing the liquid into a fine spray. The residence time of the droplets during each passage was ~14 s. Twenty-three low-pressure UV lamps rated at an average output of 6.6 W of UV light were mounted through the sides of the chamber. The power consumption of the UV lamps was 152 W. Experiments with hydrazine lasted 78 h, MMH 180 h, and UDMH 334 h. Ozone dissolves in cold water better than in hot water.

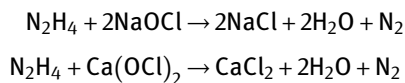
NASA WSTF then fabricated and tested a full-scale 85.2-m<sup>3</sup> (2250-gal) hydrazine wastewater treatment system [2076]. The system was based on an IITRI design featuring the use of ozone and UV to destroy the hydrazines and NDMA. A series of 21

tests evaluated the performance of the system using synthetic mixtures of hydrazine, MMH, and UDMH at 100- and 3900-ppm concentration levels. In addition, one of these tests was performed on actual wastewater obtained from a Vandenberg Air Force Base launch site sump. The tests demonstrated that the UV ozonation system would satisfactorily reduce the hydrazine concentration to less than 5 ppb and the NDMA concentration to less than 100 ppt. Hydrazine-containing wastewater can be decontaminated by treatment with ozone at pH > 7.0 and in the presence of bromide [2077, 2078].

NASA conducted a pilot-scale study to evaluate the efficiency of UV radiation and ozonation technology of an Ultrox UV ozonation system for the on-site destruction of propellant (hydrazine) wastewater generated at NASA KSC [2079]. The Ultrox Model P-75 was a skid-mounted unit containing separate modules that were integrated as a single unit, including a UV radiation and oxidation reactor module, an ozone generator module, a hydrogen peroxide feed system, and a catalytic ozone decomposer. The study demonstrated the capability to effectively destroy all three hydrazine propellants tested, their associated impurities, and toxic oxidation products such as NDMA. The Ultrox system achieved removal efficiencies exceeding 99% for different waste types and waste matrices such as hypergolic fuel in citric acid solution, hypergolic fuel in a combined wastewater, and organic solvents in an oil/grease wastewater. Hydrogen peroxide has been observed as an intermediate in the reaction of ozone with solutions of hydrazinium salts [574].

#### 7.12.1.4 Hydrazine Wastewater Decontamination by Chlorine, Hypochlorite, and UV Chlorinolysis

In solutions that contain only hydrazine and no alkylhydrazines, oxidation by hypochlorite is the standard and most effective method of hydrazine destruction [2080, 2081]. Hypochlorites are most economically available as sodium hypochlorite solution (chlorine bleach, often used as a disinfectant and laundry additive) and as calcium hypochlorite, a solid (commercially available as HTH<sup>®</sup>), often used as a swimming pool disinfectant. Commercial sodium hypochlorite solution typically contains 5.2 mass-% NaOCl, corresponding to 2.5% active chlorine. Commercial HTH<sup>®</sup> typically contains 68% active chlorine in the form of its active ingredient calcium hypochlorite Ca(OCl)<sub>2</sub>. The hydrazine neutralization reactions proceed according to



The reactions are exothermic, and the large amount of nitrogen gas evolving may carry unreacted ingredients as an aerosol out of the system. Assuming an NaOCl content of 5.24 mass-% in the commercial sodium hypochlorite solution, 59 kg of bleach would be required for each kg of HH100 (100% hydrazine hydrate = 64 mass-% N<sub>2</sub>H<sub>4</sub> in water). The hydrazine solutions should be diluted to below 35% N<sub>2</sub>H<sub>4</sub> before attempting



to neutralize them. Sodium hypochlorite solutions decompose during storage and lose active chlorine due to disproportionation to chloride and chlorate. Better storage stability and higher storage density can be achieved with calcium hypochlorite. It can be stored as a dry powder and must be dissolved in water to form solutions containing no more than 10 mass-% HTH before attempting to neutralize hydrazine solutions containing no more than 35%  $\text{N}_2\text{H}_4$ . 45 kg of a solution containing 4.5 kg HTH is required for the disposal of 1 kg of HH100.

The following section initially deals with the disposal of all three propellant hydrazines, but there are specific sections for MMH and UDMH disposal contained in the chapters “Methylhydrazine” and “Dimethylhydrazines.” Chlorinolysis of hydrazine at pH 4 was found to be an effective method for the destruction of hydrazine in the absence of MMH or UDMH without the formation of detectable annoying byproducts [2082, 2083].

The chemistry and kinetics of chlorinolysis activated by UV light as a means of disposal and neutralization of dilute aqueous hydrazine, MMH, and/or UDMH solutions were investigated in the laboratory and with a 113-L (30-gal) pilot reactor. On the basis of these results, a process to treat a minimum of  $7.5\text{ m}^3$  (2000 gal) of contaminated wastewater per day was developed [2084].

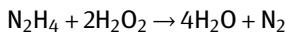
One of the studies [2003] illustrated the hazards of trying to decontaminate hydrazine spills with dry calcium hypochlorite (HTH) powder: The mixture ignited instantaneously. Even household bleach can cause pooled undiluted H-70 fuel to ignite. The worst instructions for the disposal of hydrazine were found in a government manual and are quoted here as an example of poorly written safety instructions: “*Hydrazine can be neutralized by mixing 7–10 pounds of calcium hypochlorite (HTH) with one pound of hydrazine.*” This is most certainly asking for trouble and is quoted here only as an example of how **not** to do it. Again, for safe operation, hydrazine should be diluted with water to less than 35%  $\text{N}_2\text{H}_4$  first, and the HTH powder needs to be dissolved in water first and then added as an aqueous solution with a maximum of 6% active chlorine.

Using more advanced GC/MS and GC/FTIR instrumentation, later investigators [2085–2087] found a mixture of 90 to 100 compounds resulting from the reaction of UDMH with sodium hypochlorite, not all of which could be identified. Aniline, which was known to be present in propellant-grade hydrazine in concentrations up to 0.5%, became oxidized only after all hydrazine was consumed and the gas evolution had ceased. As a result of its aniline content, the solution turned pale yellow immediately after all hydrazine was consumed. No unreacted aniline was found, but the colored reaction products were not yet identified. The concern about aniline as a contaminant in anhydrous hydrazine is now a thing of the past because it is no longer used.

#### 7.12.1.5 Hydrazine Wastewater Decontamination by Hydrogen Peroxide

Hydrogen peroxide is used for the decontamination of many industrial wastewater streams, in particular in pulp mills. Ideally, the reaction of hydrogen peroxide with

hydrazine would lead to only nitrogen and water, innocuous reaction products that can be released to the environment:



However, under certain pH conditions, the reaction can also lead to hydrogen azide, which is toxic and explosive. The presence of traces of copper ion is essential to avoid azide formation and achieve oxidation to water and nitrogen.

For the decontamination of wastewater from rocket test and launch sites, of course, it is always cheaper to use air instead of hydrogen peroxide as an oxidant. However, in special situations it may be advantageous to use hydrogen peroxide as an oxidant instead because the reaction is faster and goes to completion within the confines of the apparatus. In either case, air or hydrogen peroxide oxidant, the destruction of hydrazine is accelerated if the solution is passed through a tower packed with activated charcoal catalyst [2088] or if the reaction is carried out in the presence of copper salts [2089].

A mixture of hydrogen peroxide with iron(II) salt solutions is a strong oxidizing agent (Fenton reagent) with free hydroxyl radicals. This oxidant is capable to convert many organic contaminants to carbon dioxide. The complete conversion of organics to  $\text{CO}_2$  is also called mineralization.

A mobile apparatus was described that destroys hydrazine with hydrogen peroxide with a Pd-coated anion exchanger as catalyst [2090]. Low hydrazine hydrate concentrations in the blowdown condensate water from power plants can be neutralized with hydrogen peroxide in the presence of Cu(II) ions as catalysts, enhanced by bubbling air through the solution [588, 2091]. The oxidation of hydrazine in aqueous solutions at substantial rates takes place only in an alkaline medium and in the presence of catalysts, such as the ions of transition metals. The catalytic activity of the metal ions in the solution increases in the sequence  $\text{Fe} < \text{Co} \ll \text{Cu}$ . Hydrazine in the cooling water of primary and secondary water loops of nuclear power plants would decompose by radiolysis while near the core of the reactor, and the decomposition by radiolysis was compared to the destruction by hydrogen peroxide, the technique used for decontamination of hydrazine hydrate containing condensates in steam power plants before the water can be released to surface waters [592, 2092]. The rate of hydrazine disappearance during hydrogen peroxide treatment was measured as a function of copper ion concentration, pH, and temperature. Hydrazine destruction by reaction with hydrogen peroxide with a trace of copper ion was very slow at  $\text{pH} < 3$  but complete at  $\text{pH} = 5$ .

Neutralization and detoxification of wastewater from the production of hydrazine hydrate is more difficult due to the high salinity of the wastewater from Raschig processes and the presence of organics from the ketazine and PCUK processes [2093]. Hydrazine-containing wastewater can be treated with hydrogen peroxide in the presence of freshly precipitated, finely divided, suspended copper hydroxide as a catalyst [2094].

#### 7.12.1.6 Hydrazine Wastewater Decontamination by Bioremediation

The disposal of wastewater containing hypergolic propellants (including MMH rinse waters) by keeping them in an open holding pond with bioregeneration through water hyacinths has been tested in Florida [1891, 2095]. Similar methods will work for wastewater containing just hydrazine and no MMH. Active contributions by sunlight-induced oxidation reactions may accelerate the biological digestion process.

Although the use of biological mechanisms has been successfully applied to the cleanup of numerous chemical contaminants, the concentrations of hydrazine at a spill would prove toxic to conventional microbes. It was concluded that research conducted in the period 1975–1995 has had little success in providing a hydrazine-tolerant microbe [2096]. This 1996 conclusion contradicts other findings that some soil bacteria thrive on dilute hydrazine and can digest it [2097, 2098]. It appears that those investigators were mostly looking for immediate, swift treatment methods for undiluted H-70 spills [2096], but failed to include downstream bioremediation of more dilute spills and rinse waters or hydrazine rinse water that had already soaked into soil.

Hydrazine concentration levels typically associated with hydrazine wastewater from rocket test sites would require a dilution of at least 100 to 1 for effective biological degradation. At low concentrations of hydrazine, the presence of bacteria doubled the rate of hydrazine oxidation. This increase of oxidation was attributed to cellular metabolism. The results of the toxicity studies showed that hydrazine was least toxic to *Nitrosomonas*. Because *Nitrosomonas* had the ability to survive at doses toxic to other bacteria, it was chosen for further study. Because hydrazine seriously affects the natural bacterial balance in the aquatic environment, the researchers [2099] concluded that hydrazine contamination in a natural aquatic environment can be expected to seriously disrupt bacterial populations.

Wastewater with any or all of the three propellant hydrazines can be decontaminated in a holding pond stocked with aquatic plants (common water hyacinth, *Eichhornia crassipes*, water cabbage *Pistia stratiotes*) [2100].

#### 7.12.1.7 Hydrazine Wastewater Decontamination in Active Sludge Processes

Active sludge processes are conducted in closed digesters for the treatment of municipal sewage. Pulsed and continuous loads of hydrazine at concentrations up to 10 g/L did not affect the methane-forming capability of an active sludge sewage treatment process, and the hydronitrogen was digested as a welcome nutrient for bacteria growth [2101]. Apparently, some of the sewage treatment plant bacteria are not only tolerant of hydrazines (up to certain limits) but will also digest them and thrive on them. At concentrations of <5 mg  $\text{N}_2\text{H}_4/\text{L}$ , wastewater can be treated directly in aeration tanks. At >5 mg  $\text{N}_2\text{H}_4/\text{L}$ , the waste is treated with excess activated sludge in pre-aeration tanks, followed by aeration treatment [2102]. Complete removal can be achieved at process parameters typical for conventional biochemical treatment plants. Based on this information, hy-

drazine in small concentrations could possibly be mixed in with fecal wastes and the treatment plant would not even notice its presence.

Hydrazine in wastewater can be degraded by effective microorganisms added to sewage that contains hydrazine. The changes in hydrazine concentration under different conditions, such as microorganism content, pH, temperature, and hydrazine concentration, were analyzed [2103]. Under the conditions with a temperature of 303 K (30 °C), pH of 8.0, and a microorganism content of 5%, the microorganisms proliferated in the complex culture medium within 3.5 d and had a high hydrazine degradation rate. It was demonstrated that under the laboratory conditions, hydrazine can be degraded effectively by microorganisms.

#### **7.12.1.8 Hydrazine Wastewater Decontamination by Electrolytic Oxidation**

The environmentally most friendly method of removing excess hydrazine from dilute aqueous solutions (in the absence of other reductants) is electrolytic oxidation, which does not introduce any additional chemicals and does not increase the salinity of the wastewater [2104]. The electrodes used for the removal of hydrazine from water and other electrolytes can also be purged and depolarized with air as in a fuel cell [2105–2107].

Hydrazine and/or UDMH in wastewater in the concentration range 100 to 800 ppm can be destroyed by direct electrolysis with a stainless-steel cathode and a carbon, lead, or nickel anode [2108]. Disodium hydrogen phosphate was added to increase conductivity and pH was adjusted with phosphoric acid.

Electrolytic oxidation has also been evaluated for the removal of UDMH [2109]. Another technique considered is electrodeionization [2110]. These methods will also work for the removal of hydrazine.

Instead of using electrical energy for electrooxidation of hydrazine in wastewater, deoxygenated hydrazine wastewater streams with the correct hydrazine concentration can be fed to a fuel cell with air used for depolarization of the opposing cathode, thereby generating electrical power instead of consuming it for waste detoxification [2111]. The cell includes a solid polymer electrolyte sandwiched between electrodes that have three-dimensionally complex, high-surface-area structures and contain appropriate electrocatalysts. The solid polymer electrolyte separates the anodic compartment from the cathodic compartment. Thus, there is no mixing of rinse-water-containing hydrazine with any oxidant, and therefore the undesirable formation of nitrogen oxides, nitrite, or nitrate is prevented. The system can easily be automated, requires little maintenance, and can be operated without much training. The cell can be operated in an electrolyzer or fuel-cell mode: if the concentration of hydrazine is sufficiently high, the cell can be operated as a fuel cell; otherwise, the cell can be operated as an electrolyzer. If the concentration of hydrazine is enough to enable operation in the fuel-cell mode, then the power generated by the system could offset some or all of the cost of treatment.

#### 7.12.1.9 Hydrazine Wastewater Decontamination by Photocatalytic Oxidation

A variety of  $\text{TiO}_2$  suspensions,  $\text{TiO}_2$ -coated glass films, and  $\text{TiO}_2$ -coated foils have been used to destroy UDMH in water by photocatalytic oxidation (chapter “Dimethylhydrazines,” Section 1.6.6.16) and the same methods should be usable for the destruction of hydrazine, generally a simpler chemical reaction. Photocatalytic degradation of hydrazine in aqueous solution was studied under ambient conditions using UV radiation and nano-sized anatase titania ( $\alpha\text{-TiO}_2$ ) synthesized by an anhydrous sol-gel route [2112]. Degradation of hydrazine was followed by a complexometric spectrophotometric procedure to derive the kinetics of degradation.

#### 7.12.1.10 Hydrazine Wastewater Decontamination by Reversible Adsorption

Hydrazine can be reversibly adsorbed from dilute aqueous solutions onto zeolite [2113]. After the zeolite is saturated, it is air dried at 383 K, then heated to 673 K to burn off the hydrazine; it can be recycled for the same use repeatedly. Sorbents made from aluminum triphosphates  $\text{H}_2\text{AlP}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  or chromium(III) triphosphates  $\text{H}_2\text{CrP}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$  were patented for the removal of the last traces of hydrazine from waste streams [2114].

#### 7.12.1.11 Hydrazine Wastewater Decontamination by Irreversible Absorption

Hydrazine and alkylhydrazines may be absorbed onto crosslinked polyvinylpyrrolidone that is added to the contaminated water in the form of a latex suspension. The hydrazine-loaded latex will precipitate and can be filtered off [2115].

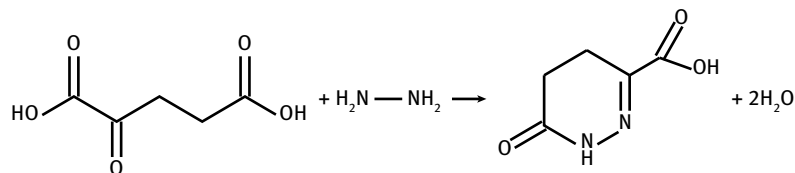
#### 7.12.1.12 Hydrazine Wastewater Decontamination by Sonolysis

Intense ultrasound in a resonating cavity in water will cause cavitating bubbles that allow accelerated interaction with dissolved air or added hydrogen peroxide. The degradation of 0.1 and 1.0 mmol/L hydrazine in water was investigated as a function of pH under stirring and ultrasonic irradiation (200 kHz, 200 W) conditions [2116, 2117]. It was found that the hydrazine degradation depended greatly upon pH under ultrasonic irradiation condition, while it did not take place over the whole pH range (0.8–9) under the stirring condition. The hydrazine degradation may be achieved by OH radicals. A suspension of coal ash aids the degradation of hydrazine but inhibits the formation of OH radicals [2118, 2119].

#### 7.12.1.13 Hydrazine Wastewater Treatment by Reaction with $\alpha$ -Ketoglutaric Acid

$\alpha$ -Ketoglutaric acid (= 2-ketoglutaric acid, AKGA,  $\text{HOOCCH}_2\text{CH}_2\text{C(O)COOH}$ ), a water-soluble solid, has been proposed for hydrazine or MMH vapor absorption from air (Section 7.11.1) or for the decontamination of wastewater from rinsing hydrazine- or MMH-contaminated rocket propulsion systems [2014, 2015, 2120]. Hydrazine and MMH wastewater neutralization by reaction with alpha-ketoglutaric acid (AKGA) to form the stabilized pyridazine derivatives PCA and mPCA has been explored. Similar

reactions with alpha-ketoglutaric acid for the removal of hydrazine vapors from vented pressurization gases were already discussed earlier in Section 7.11.1.



Questions remain concerning the completeness of the reaction, 100% scavenging of hydrazines to be removed, and potential hydrolysis of pyridazines in wastewater ponds, releasing the hydrazines again. Pyridazines are not very soluble in water and are likely to clog process equipment.

A critical review of the patent claims and preliminary laboratory tests with  $\alpha$ -ketoglutaric acid for the decontamination of vapor scrubber effluents or rinse water from hydrazine- or MMH-contaminated rocket propulsion systems concluded that the uncertainties of the completeness of the reaction and lack of complete identification of all reaction products prevented the practical application of this chemical under real-life rocket launch site GSE conditions [2018]. When reacting 0.73-M AKGA solutions in benchtop lab tests, a solid formed with hydrazine but not with MMH. In more dilute 0.2-M AKGA solutions, no precipitate formed with either hydrazine or MMH. Another keto compound tested in hydrazine or MMH scrubber liquids was ethyl acetoacetate  $\text{H}_3\text{C}-\text{C}(\text{O})-\text{CH}_2-\text{C}(\text{O})-\text{O}-\text{CH}_2\text{CH}_3$ , but its reaction with hydrazine or MMH produced a gummy, sticky substance (a carbinolamine intermediate converting to 3-methylpyrazol-5-one) that clung to the walls and was difficult to remove.

### 7.12.2 Disposal of Hydrazine Production Process Wastes

Some of the methods used for the removal of hydrazine from hydrazine production waste streams can also be used for the decontamination of wastewater streams from rocket test and launch sites. Hydrazine and acetone contained in the saline wastewater effluent from production plants using the Bayer ketazine process can be cleaned by bacterial treatment using salt-resistant bacteria scooped from the Great Salt Lake [2121]. After stripping the volatile ketazine, residual hydrazine in Bayer-process plant effluents can be removed by chlorination [2122–2124].

### 7.13 Off-Loading of Hydrazine from Spacecraft

Occasionally it becomes necessary to off-load (de-tank) propellants from a fueled satellite or space probe because the launch date has been postponed or because

repair work on a damaged spacecraft cannot be conducted in proximity to loaded propellants.

In the past, propellant off-loading has become necessary for GALILEO (MMH and NTO), ARTEMIS (MMH), ROSETTA (MMH) [2125], and MEASAT-B (anhydrous hydrazine and NTO) [2126]. All spacecraft in this category used bipropellant systems and tanks with surface tension PMDs. In most cases only the fuel was removed, and the oxidizer was left in the tanks, because its removal or depressurization might introduce gas bubbles into the capillary gallery or the bubble traps and cause loss of NO from MON. Also, the evaporation of NTO or MON leaves behind a thin film of nitric acid, which would make the corrosion environment even worse than in NTO. There are no generally accepted guidelines for off-loading of propellants from spacecraft, so the personnel in charge of the operations had to develop their own procedures. Some spacecraft do not even have a drain at the lowest point in the system to allow all liquid to be drained by gravity. Other line-plumbing systems may have check valves that allow liquid to flow in only one direction, into the tank, and not out of the tank. Most plumbing schematics have dead-ended passages where propellants will pool and cannot be removed by flushing.

#### **7.14 Inerting of Decommissioned Satellites and Upper Stages in Orbit**

The fragmentation of a PEGASUS HAPS upper stage on June 3, 1996, stands as one of the worst accidental satellite breakups on record in terms of cataloged orbital debris scattered. Orbital debris constitutes a hazard for other satellites in similar or intersecting orbits. Following the fragmentation of a PEGASUS HAPS kick stage and scattering of orbital debris after separation from the payload [2127], it became necessary to make provisions to dump unused propellants at the end of a mission and inert the tanks by exposing them to vacuum. In the case of hydrazine this cannot be done by simply exposing the tank to vacuum because residual hydrazine would freeze and greatly delay the time required to achieve a totally inert stage. Supersaturated hydrazine would help to clear the lines, because the released dissolved pressurant gas will eject the slug of liquid ahead of it like champagne from a suddenly opened bottle that had not been sufficiently cooled.

The geostationary orbit is crowded, and satellites are now spaced closer and closer to each other. A satellite breakup in geostationary orbit would cause significant damage to neighboring satellites and must be avoided by controlled passivation after end-of-life satellites have been moved to a graveyard orbit [320, 2128].

The ACS of the European heavy launcher ARIANE 5 is a hydrazine monopropellant system including two or more bladder tanks pressurized by nitrogen. Depending on the mission, a residual pressure of some 10 to 20 bar with several kg of hydrazine may remain at the end of the mission in the second stage adapter. To avoid any orbital debris generation, the tanks should be vented to space before the stage re-enters [2129].

The slow rate of evaporation and the formation of frozen hydrazine plugs in the plumbing may delay the inerting of tanks in space once they are exposed to vacuum at the end of a mission [2130].

For upper stages, after having delivered their payload to orbit, venting of unused propellant while still in orbit prior to re-entry into the atmosphere would alleviate some of the concerns about propellant toxicity and tank fragmentation [2131]. This process yields a rarefied vapor and droplet field around the final-stage rocket. This computational method was applied to three-dimensional rarefied vapor and droplet plumes arising from discharging in orbit the residual UDMH fuel of a Chinese CZ-4B final-stage rocket and can probably be applied to other propellants as well.

### 7.15 Firefighting Methods

The extinction of hydrazine fires is easy compared to firefighting of other commonly used fuels (gasoline, kerosene) because hydrazine and its derivatives are miscible with water and after enough water is applied, the puddle of liquid becomes non-flammable. In the event of a fire, the area is best flushed with copious amounts of water until the hydrazine is diluted below the fire point concentration (60% hydrazine) (Section 8.3). Open-air burning tests with hydrazine in open pans of 28-, 315-, and 2100-cm<sup>2</sup> surface area showed that 4.7 L of water was consumed per liter of hydrazine to extinguish a hydrazine fire [2132–2136].

Two parts by weight of water per part of Ae-50 will inert an Ae-50 spill against ignition in air [2137]. In a burning Ae-50 pool, the fuel evaporation rate is approximately 49 g s<sup>-1</sup> m<sup>-2</sup>. A well-dispersed flow of water at 100 g s<sup>-1</sup> m<sup>-2</sup> is enough for extinguishing a fire. A tenfold excess of water (10 kg water per kilogram of fuel) is required to inert an Ae-50 spill against hypergolic ignition with NTO. Bromotrifluoromethane (Halon 1301) can be used to inert vapor spaces or to extinguish small fires, but very high BrCF<sub>3</sub> concentrations are required (>7% by volume), and the protection is not long-lasting.

A series of 38 vapor suppression tests with acrylic-modified foam was conducted on spilled hydrazine, MMH, Aerozine-50, and N<sub>2</sub>O<sub>4</sub> in a remote test site in 1985 and 1986 [2138]. The residues of some of the inerting/fire suppression tests were later ignited on purpose (after the foam had collapsed) as a means of hydrazine disposal. An aqueous acetate-acetic acid buffer solution with a gelling agent was tested as a spill control and fire extinguishing agent against small spills or fires of Aerozine-50 and/or NTO [1997]. Firefighting foams can be used for spill containment and ignition prevention of spilled hypergolic propellants.

The problem with approaching and attempting to extinguish a multi-container hydrazine fire is that hydrazine in adjacent containers may become overheated and explode before the first fire can be extinguished [2139]. In the case of a fire burning around hydrazine drums with varying degrees of fullness in a storage shed, the drums were observed to explode one after the other, ejecting the drum tops, but remaining



standing upright. This behavior would speak for storing drums standing upright on their flat ends, rather than storing them sideways. Some storage yard operators prefer storing drums on their sides because it is easier to roll them around and a hand truck is not needed to move them. It may not be advisable to try to extinguish a hydrazine fire if re-ignition must be feared because the extinguished pool of burning liquid cannot be immediately diluted below the flash point. Emphasis should be on cooling and protecting adjacent containers and structures while allowing the one burning drum to burn out if only one drum is on fire. It is easier to clean up a burnt-out drum than to have to treat hydrazine-contaminated water that floods the fire scene. Additional information on the fighting of hydrazine fires is in the chapter “Dimethylhydrazines.”

## 8 Safety Properties of Hydrazine

Handling safety properties of hydrazine, besides toxicity (which is discussed in detail at the end of this chapter), which must be observed and respected, are predominantly flammability and detonability. This section deals with the safety properties of hydrazine and its mixtures. The safety properties of solid hydrazinium salts were already summarized in *Encyclopedia of Oxidizers*, in the chapter “Hydrazinium Salt Oxidizers.” This current section at hand is restricted to conditions that induce the (inadvertent) vapor decomposition or combustion, whereas the more academic discussions of decomposition or combustion mechanism and kinetics under controlled conditions are discussed in Section 4. For detonability, only the limits of detonability and required modes of initiation of hydrazine by itself are discussed here.

Useful summaries of the hazard properties of hydrazines and other rocket propellants have been published by several organizations. The Air Force *Space Propulsion Hazards Manual* is a three-volume series useful for the design of GSE and planning of fueling operations [1887–1889]. Another very useful three-volume series is the *Hazards of Chemical Rockets and Propellants* handbook published by CPIA. Volume 1 deals with safety, health, and the environment [2140], Volume 2 is on solid propellants, and Volume 3 addresses liquid propellants [2141]. NASA WSTF has put together three very practical handbooks, *Ignition and Thermal Hazards of Selected Aerospace Fluids* (including hydrazine, MMH, UDMH, and Ae-50) [2142], *Fire, Explosion, Compatibility, and Safety Hazards of Hydrazine* [1912], and a similar handbook on MMH [2143]. These handbooks were originally published in loose-leaf format in a ring binder and could be updated periodically. Two of them were later also published by AIAA under the aerospace specification series. These handbooks and survey papers, like the comparison study of explosion hazards of hydrazine and MMH in aerospace launch vehicle environments [2144], cite numerous WSTF test reports as references, but most of these cited reports have unfortunately never been deposited with NTIS and are not available to the general public. Hydrazine manufacturers have published summaries of the safety properties of hydrazine [2145].

A good summary of safety considerations for the use of hydrazine and aqueous hydrazine solutions in the chemical process industry where hydrazine is used as an intermediate and reducing agent is provided in [2146]. This publication provides a summary of the hazards of hydrazine and its aqueous solutions and promotes an understanding of the important role dilution plays in increasing the inherent safety of aqueous hydrazine solutions. It is often difficult to determine whether hydrazine is safe and acceptable for a given application, in particular if the process is scaled up, and if so, what concentration range in aqueous solutions may provide an acceptable safety margin and not constitute an environmental risk.

## 8.1 Flammability of Hydrazine

The limits of flammability of combustibles depend on composition, temperature, pressure, mode of initiation, geometry of vapor space, availability of oxygen, and the direction of flame propagation [1607]. It is impossible to discuss all these parameters in detail, mainly because they have not yet been determined in detail for hydrazine and its derivatives. Most of the hydrazine work was done on the limits of flammability in air, but some information is also available for other oxidizing atmospheres (oxygen, nitric oxide, nitrogen dioxide) or in dilution with inerting compounds (nitrogen, heptane, water). Some work has been done on ammonia flammability that may be of interest to the evaluation of fire hazard of hydrazine/ammonia mixtures and of hydrazine decomposition products. For this reason, some of these data are included here. Because the methylhydrazines are more volatile than hydrazine, there is greater concern over forming flammable mixtures with these fuels than with hydrazine itself.

To evaluate the potential fire hazard of hydrazine and hydrazine fuels and compare it to that of better-known fluids already in use (e.g., gasoline, kerosene, hydraulic oil), the following properties are examined: limits of flammability, autoignition temperature, flash point, and minimum required ignition energy. A comparative hazard evaluation must be based on a consistent set of data, all obtained with the same method. The results of flammability or autoignition of the same compound will vary widely depending on the method and the apparatus used. It would be desirable for all investigators to use standardized flammability test methods. Unfortunately, only the flash-point procedure is covered by an ASTM standard (ASTM D98). For the other fire hazard properties, there exist no standard procedures applicable to hydrazine, and the results vary from investigator to investigator, depending on the method used, making a comparison very difficult.

Most data on flammability characteristics of combustible gases and vapors other than hydrazines were obtained by the US Bureau of Mines (USBM) using a setup that has become known as the USBM Flammability Tester. Results obtained with this apparatus are described in the following section.

### 8.1.1 Limits of Flammability of Hydrazine in Air

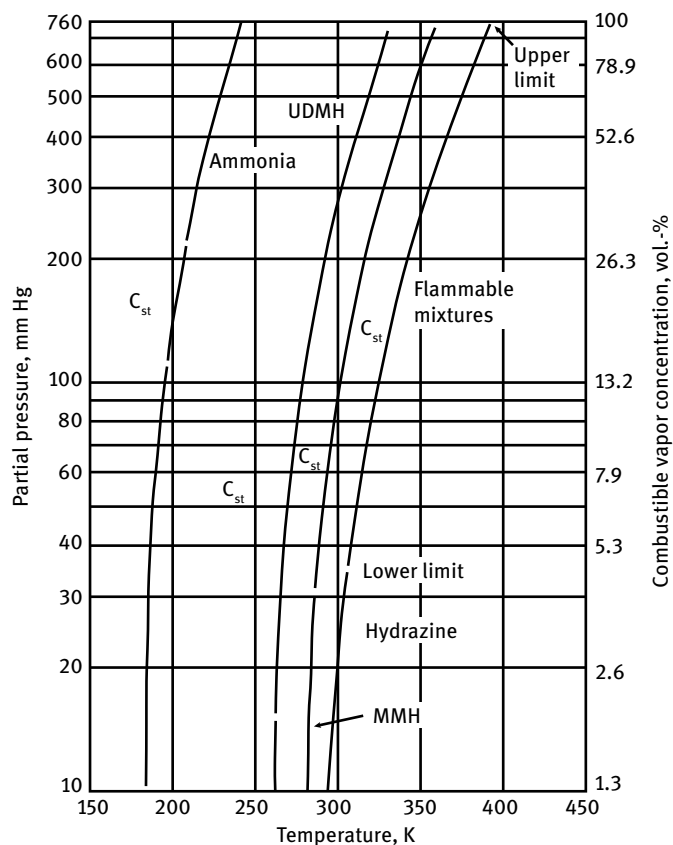
The apparatus used in early tests on hydrazine flammability was not the standard USBM flammability tester described in [2147] or [1607], but a small-scale modification of this apparatus that was previously used to determine the flammability limits of liquids of low volatility [1408]. Hydrazine has a low volatility and high boiling point compared with other more volatile liquids where flammability is a concern. The problem encountered by experimenters in the determination of flammability limits of high-boiling liquids was condensation. To prevent condensation, the entire system had to be submerged in a heated constant-temperature bath. Whereas a 50-mm-diameter tube 1.5 m long with upward propagation is used in the standard flammability tester, a smaller tube (25 mm in diameter by 0.25 m length) was used for the hydrazine tests. Ignition by a spark between two electrodes occurred at the bottom of the tube, and the flame propagated upward.

The lower limit of hydrazine flammability at 100.7 kPa (758 mm Hg) and 373 K in air was found to be 4.67% by volume [1408]. Unlike other combustibles (e.g., gasoline), hydrazine does not have an upper limit of flammability, and the flammable range extends all the way to 100%. This range can be narrowed by inerting additives, such as nitrogen, water, or heptane, with or by the removal of air. Strangely enough, heptane, itself a flammable vapor, is the most effective additive in narrowing the flammability range of hydrazine, as is discussed in what follows.

The practice of determining limits of flammability at constant temperatures well above the saturation point does not resolve all safety problems with regard to flammability of saturated mixtures in air. The data of interest to a safety engineer are the temperatures above which the saturated vapor in air becomes flammable. Unfortunately, no studies on flammability of hydrazine fuels have been carried out in this mode. In calculating the lower limit temperature, one must assume that the limits of flammability are independent of temperature and use the data obtained at higher temperature (above saturation) in conjunction with a vapor pressure chart. Within the temperature range considered, the limits are indeed almost independent of temperature. Thus the flammable ranges of hydrazine and its methyl derivatives shown in Figure 55 are superimposed on vapor pressure curves, even though the actual flammability testing was conducted at higher temperatures where all propellant was in the vapor state.

The ignition limits of hydrazine/air and MMH/air mixtures at reduced pressures were measured in a 15-cm-diameter 2-L CRES-304 chamber without provisions for stirring the gas-vapor mix [2148–2150]. A 750-mJ spark jumping a 3.2-mm gap was used to initiate the mixtures. As shown in Figure 56, the flammable range narrows as the pressure decreases, until below 4 kPa partial pressure no ignition occurs at any mixture ratio tested. The temperature scale (not a linear scale) on the top of the graph indicates a saturation temperature of pure hydrazine above which enough hydrazine is present in the vapor phase to form flammable mixtures.

Overpressure data from the closed vessel indicated that all mixtures deflagrated rather than detonated. The destruction potential of hydrazine-air explosions would

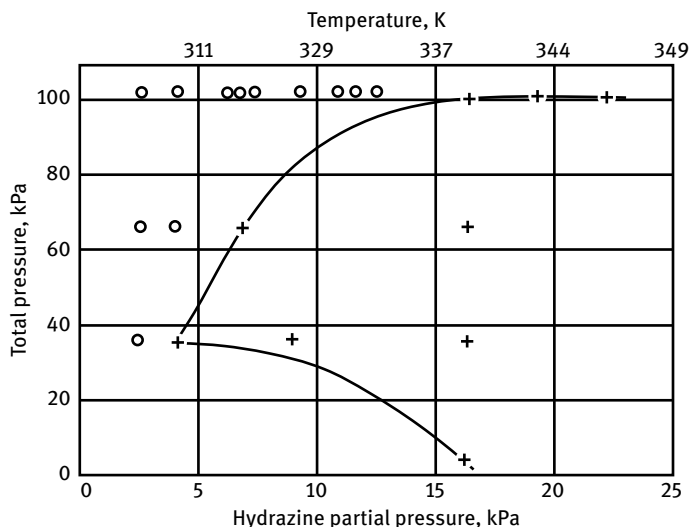


**Figure 55:** Limits of flammability of hydrazine, UDMH, MMH, and ammonia at atmospheric pressure in saturated and near-saturated vapor/air mixtures. (Reproduced and modified from [1607].)

be more severe if the geometry of the vessel and the mode of initiation allowed a detonation to develop. It is very likely that detonations would have occurred in much larger vessels with a shock-wave initiation from an adjacent detonation chamber filled with acetylene and oxygen.

Based on the NASA WSTF data, the lower limit of flammability of hydrazine in air at 101 kPa and 366.5 K is at 5% by volume [2149]. This compares to a value of 4.67% reported by Scott, Burns, and Lewis [1408]. The lower flammable limit at 311 K was observed to increase from 5.8% to 7.2% if the pressure was lowered from 50 to 6.2 kPa. The upper limit of flammability at 311 K remained at 100% down to a pressure of 2.2 kPa. Substitution of air with oxygen at 101 kPa had a negligible effect on the lower or upper limits of flammability.

Flash-point data by Olin Chemicals (now Lonza-Arch Chemicals-Arxada) indicate that mixtures down to 40%  $N_2H_4$ /60% water are flammable at room temperature.



**Figure 56:** Hydrazine flammability limit in air. (Reproduced and modified from [2148]).

Legend: + Positive Test; O Negative Test (No Ignition).

### 8.1.2 Effect of Partial Pressure on Decomposition Limits (Without Air)

As indicated in the previous section, the flammable range of hydrazine vapor extends all the way to 100% at ambient pressure. At lower pressures, a pressure limit exists below which hydrazine decomposition flames will not propagate. This pressure limit is dependent on the geometry of the test vessel. In a 2.7-cm-diameter, 118-mL-volume Pyrex tube with spark ignition, the lower pressure limit of hydrazine decomposition without air was determined to be 1.59 kPa (12 mm Hg) at 302 K [1408]. Previous authors [1228] had reported a limit at 4.65 kPa (35 mm Hg) in a 3-cm-diameter and 6.64 kPa (50 mm Hg) in a 1.5-cm-diameter tube. Sparks from an automotive ignition coil were used in the first study referenced earlier. It may be assumed that the energy per discharge was well in excess of 2.4 J. No systematic experimental studies have been conducted yet on the ignition energy required to initiate decomposition of hydrazine vapor (Section 8.3.1).

Three different test vessel geometries were used in the USBM study [1408] to determine the eventual participation of excess liquid hydrazine in the decomposition or explosion. A 2.54-cm-diameter tube with an attached mercury pressure gauge had a volume of 180 mL and the spark ignition electrodes could be placed either at the top or bottom. The largest test vessel was a 5-cm-diameter tube with a 7.5-cm base where the electrodes were located. The volume of this tube was approximately 775 mL, and electrodes were always located at the top. The amount of liquid hydrazine placed in the test vessel ranged from 1 mL in the smallest to 25 mL in the intermediate-size container. The 775-mL vessel was always charged with 10 mL liquid hydrazine. The hy-

hydrazine vapor pressure was adjusted by controlling the bath temperature between 300 and 388 K. The vapor pressure was increased after each test. A new tube and a fresh sample were used for each test in the 89-mL category. At 79.9 kPa (600 mm Hg) initial pressure, the entire apparatus and the oil bath were broken by the force of the explosion after the spark was energized. In the 180-mL tube, up to three consecutive tests were sometimes conducted on the same sample. It was not stated whether the decomposition products of the previous test were removed prior to a repetitive test on the same sample. It must be assumed that the vapor phase was diluted by the products of the preceding partial decomposition test. The results of these repetitive tests are thus not very meaningful and were omitted from the summary in Table 77.

**Table 77:** Hydrazine vapor-liquid decomposition tests.

| Test vessel<br>volume | Liquid<br>hydrazine | Initial hydrazine<br>pressure |       | Bath<br>temperature | Direction<br>of propa-<br>gation <sup>a</sup> | Result         |
|-----------------------|---------------------|-------------------------------|-------|---------------------|-----------------------------------------------|----------------|
| cm <sup>3</sup>       | cm <sup>3</sup>     | kPa                           | mm Hg | K                   |                                               |                |
| 89                    | 1                   | 9.7                           | 73    | 331.2               | U                                             | +              |
| 89                    | 1                   | 27.1                          | 203   | 351.7               | U                                             | +              |
| 89                    | 1                   | 53.3                          | 400   | 369.7               | U                                             | +              |
| 89                    | 1                   | 80.0                          | 600   | 380.2               | U                                             | + <sup>b</sup> |
| 180                   | 2                   | 73.3                          | 550   | 378.2               | D                                             | +              |
| 180                   | 5                   | 2.0                           | 15    | 298.2               | D                                             | —              |
| 180                   | 5                   | 23.5                          | 176   | 346.7               | D                                             | +              |
| 180                   | 10                  | 2.13                          | 16    | 299.7               | D                                             | —              |
| 180                   | 10                  | 23.6                          | 177   | 347.2               | U                                             | +              |
| 180                   | 10                  | 86.6                          | 650   | 381.7               | D                                             | +              |
| 180                   | 10                  | 101.9                         | 765   | 388.2               | D                                             | + <sup>b</sup> |
| 180                   | 25                  | 2.40                          | 18    | 303.2               | D                                             | +              |
| 180                   | 25                  | 5.9                           | 44    | 318.2               | U                                             | +              |
| 180                   | 25                  | 12.0                          | 90    | 332.2               | D                                             | +              |
| 775                   | 10                  | 30.0                          | 225   | 353.2               | D                                             | +              |
| 775                   | 10                  | 44.0                          | 330   | 363.2               | D                                             | +              |
| 775                   | 10                  | 89.3                          | 670   | 382.2               | D                                             | + <sup>b</sup> |

<sup>a</sup> U = upward, D = downward.

<sup>b</sup> Apparatus burst.

Data source: [1408]

As shown in Table 77, the lowest vapor pressure at which vapor decomposition was observed was 2.39 kPa (18 mm Hg) in downward propagation. There was no noticeable difference between tests initiated at the top or at the bottom. In none of the tests would the vapor decomposition initiate decomposition of excess liquid in the glass tube. However, in those tests at initial hydrazine pressures above 80 kPa (600 mm Hg) where the apparatus burst, no liquid hydrazine could be recovered.

The lower decomposition limit of hydrazine was found at 309 K, corresponding to a vapor pressure of 3.17 kPa (23.8 mm Hg) [1216]. However, in the diagram (Figure 57) it is very difficult to explain why, at a given temperature, the decomposition zone narrows with increasing temperature rather than widens as one would expect. The decrease in pressure changes the limits of flammability but does not seem to have a pronounced effect on the flame speed of the decomposition flame. Flame speed and other aspects of decomposition flames will be discussed in Section 4.9.

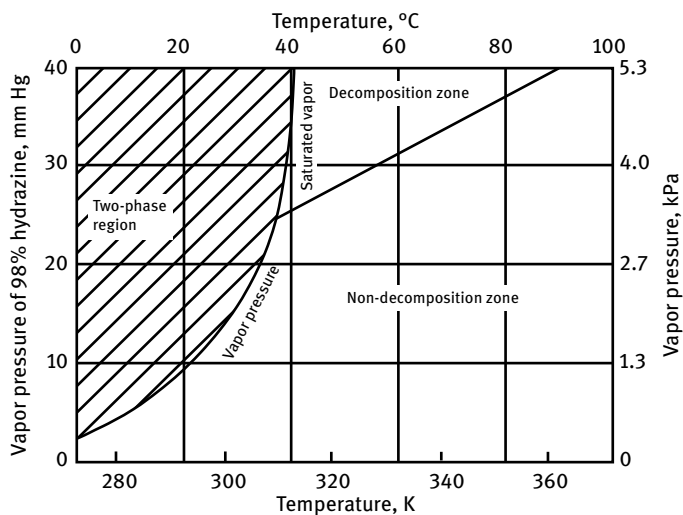


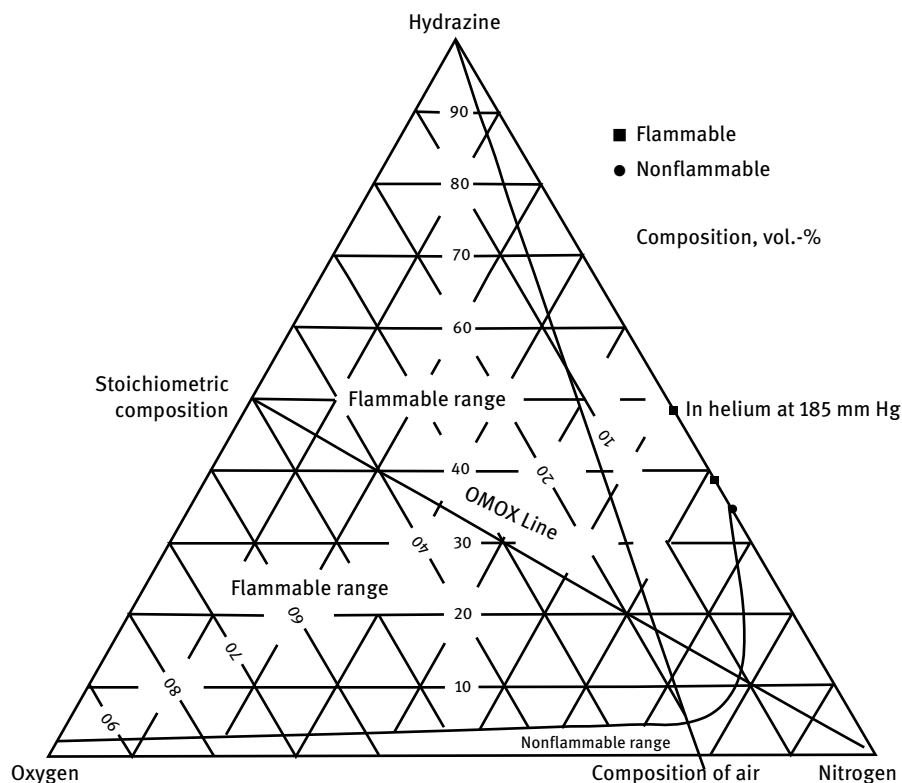
Figure 57: Decomposition of hydrazine vapor. (Reproduced and modified from [1216].)

### 8.1.3 Effect of Diluents on Decomposition Limits of Hydrazine (Without Air)

The upper limit of 100% hydrazine vapor flammability in the absence of air can be lowered by the addition of inert diluents. Inert diluents that have been tested include nitrogen [1216, 1228, 1408], helium [1408], water vapor [1408], argon [1216], hydrogen [1216], and ammonia [1228]. Ammonia was found to be more effective in suppressing hydrazine explosions than nitrogen [1228]. This section discusses the effect of such diluents on the flammable limits of hydrazine vapor decomposition without air. In a later section the effect of diluents on the limits of flammability of hydrazine in air will be discussed.

The hydrazine-nitrogen system has been investigated by several authors. This system is of practical importance over a wide range of pressures and temperatures because during the distillation of anhydrous hydrazine a blanket of nitrogen is often maintained for safety reasons. After the drums or tank cars are filled with hydrazine for shipment, a nitrogen “pad” is also used to fill the ullage space. In the USBM flammability tester in a spark-ignition tube with a 25-mm (1-in.) diameter, the lower limit of

flammability was 38% by volume hydrazine, 62% nitrogen at 383 K, and ambient pressure [1408]. Similar results were obtained with helium as a diluent (37% hydrazine, 63% helium). At lower pressure (total pressure = 24.7 kPa = 185 mm Hg) and lower temperature (373 K) in a 30-mm-diameter glass tube, the limit was found at 48.6% hydrazine [1228]. These limits are shown along the  $N_2$ - $N_2H_4$  side of the triangular chart in Figure 58.

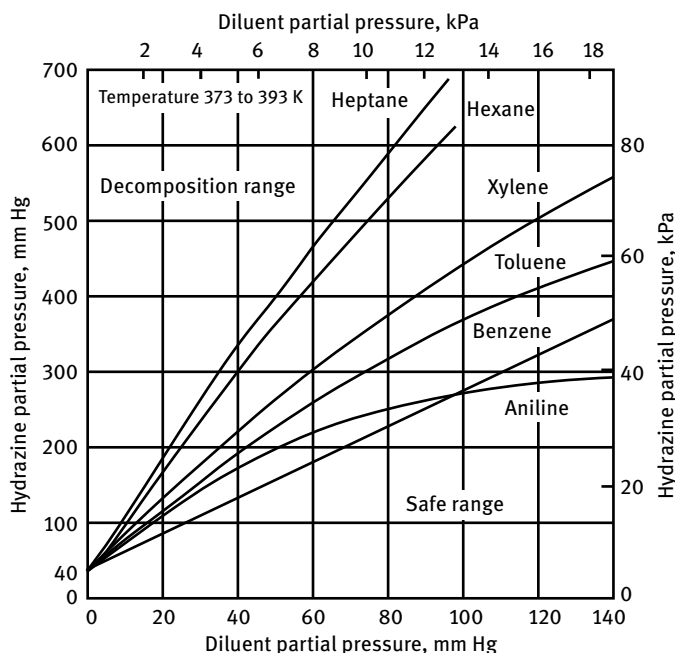


**Figure 58:** Flammability of hydrazine/oxygen/nitrogen mixtures. (Reproduced and modified from [1228] and [1408].)

The water-hydrazine system is also of interest because hydrazine hydrate is being distilled in large amounts in the chemical industry. Furthermore, hydrazine/water mixtures may be formed in the attempt to extinguish hydrazine fires with water. In the USBM tester the lower limit of hydrazine-steam flammability was found at 30.9% by volume (vapor) hydrazine = 44.3% by weight at ambient pressure and 408 K (275 °F). This indicated that under adverse conditions even the vapor of 100 or 85% hydrazine hydrate (64 or 54.4% hydrazine) can still explode (see Figure 61 discussed in the next section).



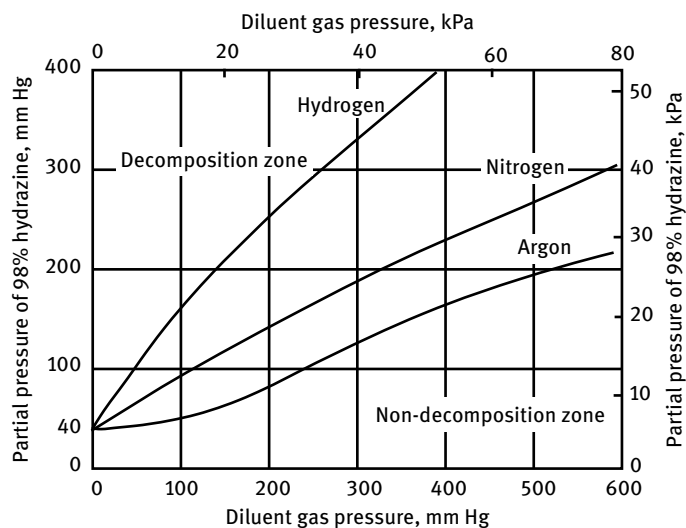
In a study of the effect of hydrocarbon or aniline vapor on the decomposition of hydrazine vapor initiated by an electric arc, in the absence of any other diluent or air, hydrazine vapor could be ignited at partial pressures above 5.33 kPa (40 mm Hg) [2151]. In the presence of diluents, the partial pressure of hydrazine could be increased above this level without forming flammable mixtures. Of the various compounds evaluated and illustrated in Figure 59, *n*-heptane was the most active inhibitor, whereas benzene and aniline had only a very small effect. These data were measured at 373–393 K in the absence of air.



**Figure 59:** Suppression of decomposition of hydrazine vapor by hydrocarbons or aniline. (Reproduced and modified from [2151].)

In a similar study, the effectiveness of hydrogen, nitrogen, or argon in suppressing the decomposition of hydrazine was studied at different pressures [1216]. Generally, the permanent gases were less effective than the organic compounds shown in Figure 60. The gas data could probably be superimposed on the same chart, but the available data extend to 66.7 kPa (500 mm Hg) instead of 18.7 kPa (140 mm Hg).

Ambient pressure of the mixture is reached as soon as the two partial pressures read from the axes add up to 760 mm Hg. Of the three gases evaluated, hydrogen was found to be the most active inhibitor, but it was not as active as the worst of the organic vapors evaluated in Figure 59.



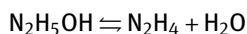
**Figure 60:** Suppression of hydrazine decomposition by hydrogen, nitrogen, or argon. (Reproduced and modified from [1216].)

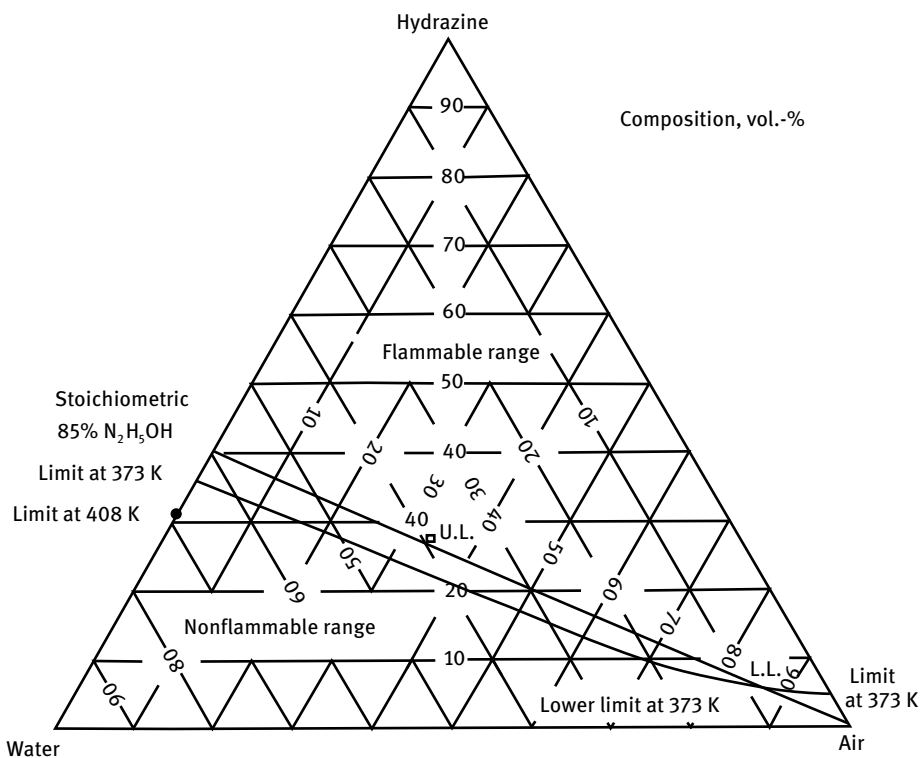
It is interesting to note that ignition near the limit in the hydrazine vapor/heptane vapor system at 388 K (239°F) depends on the ignition energy applied to the spark gap [1408]. When more than 7% by volume heptane vapor was mixed with hydrazine vapor, the mixture could not be ignited by the spark from an automotive ignition coil fed with 12-V, 60-cycle AC at 1.7 A. However, when a capacitor of 400  $\mu$ F was charged to 10 kV DC and discharged across the gap, the arc would ignite mixtures with up to 9.1% heptane. A discharge from a 7108- $\mu$ F capacitor array charged to 12 kV would even ignite mixtures containing 13% by volume heptane vapor.

#### 8.1.4 Effect of Diluents on Flammability of Hydrazine in Air

Some of the diluents tested to suppress the combustibility of hydrazine in air were already discussed in Section 8.1.3 with regard to their effectiveness to suppress the vapor-phase decomposition of hydrazine in the absence of air. The diluents tested there included water, nitrogen, and *n*-heptane.

Water is a diluent that may be admixed to the hydrazine itself and form hydrazine hydrate in the liquid state. *n*-Heptane is not miscible with liquid hydrazine, and mixtures exist in the vapor phase only. In addition to the limits of anhydrous hydrazine, the limits of 85% hydrazine hydrate (54.4% hydrazine in water) in air have been determined as well [1408]. At the time when those data were first reported, some uncertainty still existed as to the degree of dissociation of hydrazine hydrate vapor into its constituents:





**Figure 61:** Flammability of hydrazine/water/air mixtures. (Reproduced and modified from [1408].)

Because the hydrazine hydrate was admitted to the apparatus by weight and the air by volume, the flammability limits expressed in percent by volume will depend on the vapor density/dissociation of hydrazine hydrate. In the meantime, more detailed information has become available on the dissociation of hydrazine hydrate in the vapor phase [226] (Section 2.1.9.4). According to these data, hydrazine hydrate is completely dissociated above 350 K. The vapor composition (in percent by volume) at the lower limit of flammability at 373 K is thus 5.95% hydrazine, 8.66% water, and 85.39% air. This lower limit (LL) is shown along the dashed line in Figure 61 from [1408]. This figure shows the extrapolated flammability range in the hydrazine-air-water system.

Except for the data obtained with 85% hydrazine hydrate, no data are available to fill in the center of this ternary diagram. More accurate data are available for the limits in the binary systems hydrazine-water and hydrazine-air shown along the left and right side of the triangle. From these data the approximate course of the flammability borderline can be extrapolated (solid line). Its exact location is dependent on the initial temperature of the flammable mixture; the line shown is for 373 K. At higher

temperatures the flammability range is wider, as is evident from the location of the data point for hydrazine-water at 408 K.

One phenomenon that is not quite understood and also is not sufficiently discussed in the original publication is that of an alleged upper limit of flammability (UL in Figure 61) said to be encountered at 27.4% hydrazine, 39.8% water, and 32.8% air [1408]. It was previously stated that hydrazine itself does not have an upper limit, and the same seems to be true for 85% (by weight) hydrazine hydrate, equivalent to 40.16% by volume hydrazine in the vapor phase. This composition is within the flammable range of the hydrazine-water system in the absence of air. Apparently, mixtures between the upper limit and the air-free composition are only marginally flammable. A third limit has not yet been detected, and additional work in this system may be warranted to clarify the contradictions.

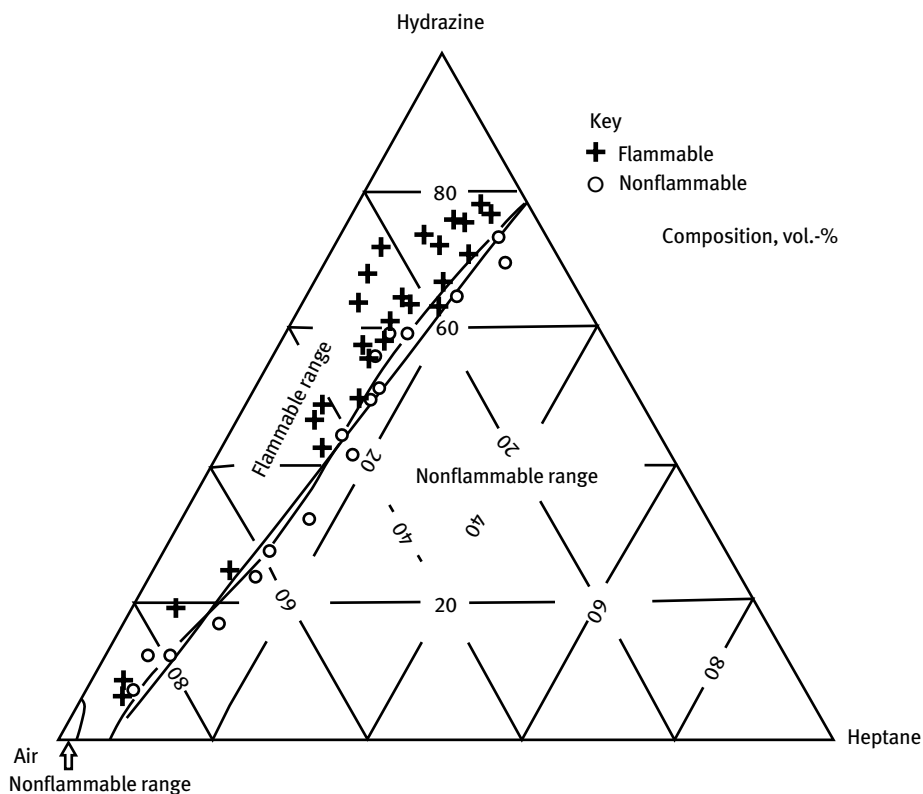
Unfortunately, no accurate data are available on the flammability of the ternary system hydrazine-nitrogen-oxygen. From the two data points available (38% hydrazine/62% nitrogen; 4.67% hydrazine, 75.3% nitrogen and argon, 20.0% oxygen), attempts have been made to extrapolate the borderline in the ternary chart in Figure 58. Until more experimental data become available, this curve should be used with caution.

The hydrazine-heptane-air system has been thoroughly investigated because of the unique ability of heptane vapor to suppress decomposition and combustion of hydrazine vapor. Tests in a 32-mm-diameter tube gave results essentially identical to those obtained with a 50-mm tube. For this reason, all tests were done with a 32-mm-diameter borosilicate glass tube. Of all hydrocarbons investigated, heptane was the most active diluent [2152, 2153]. Cumene, xylene, toluene, and benzene were found to be less active in this respect. Heptane has thus been suggested as a blanketing fluid during hydrazine distillation to prevent the formation of detonable mixtures. Figure 62 shows the flammability limits of the ternary system hydrazine/heptane/air at 398 K. The minimum heptane concentration for flammability suppression is 21% by volume, revised from an earlier questionable finding of 13%.

### 8.1.5 Limits of Flammability of Hydrazine in Other Atmospheres

The explosive decomposition of hydrazine vapor in the absence of oxidizers was first studied in the laboratory in 1939 [1228]. In 15-mm- and 30-mm-diameter quartz vessels with an arc across tungsten electrodes for ignition, the lower limits of explosion were found at 6.66 and 4.66 kPa (50 and 35 mm Hg), respectively.

In the presence of oxidizers, mixtures of hydrazine vapor and other atmospheres may autoignite above a threshold temperature. In other cases, even liquid hydrazine may ignite. Nitrogen dioxide and hydrazine are hypergolic. The autoignition flammability characteristics of hydrazine fuels in dilute NO<sub>2</sub> atmospheres was investigated [2154, 2155]. The technique used was to inject small amounts (70 μL) of fuel into



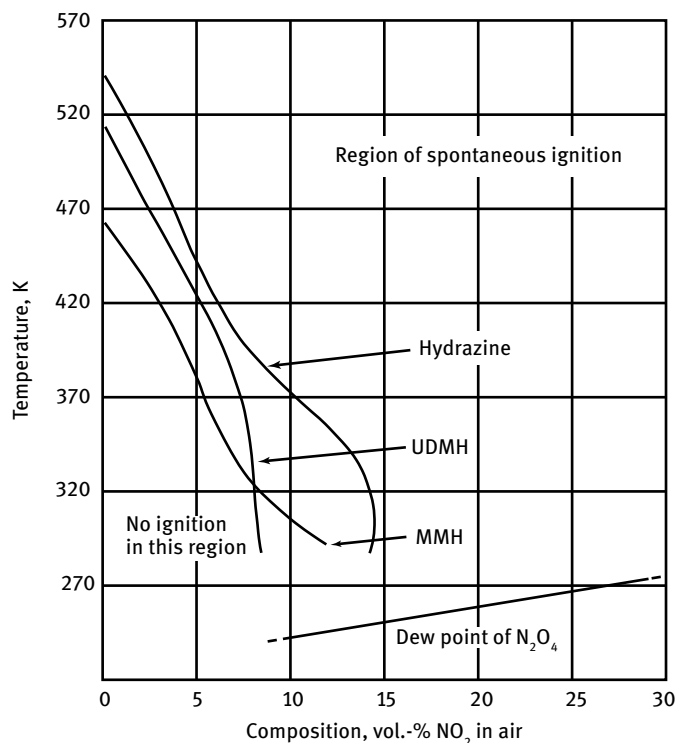
**Figure 62:** Flammable mixture compositions of hydrazine/heptane/air system at 398 K and atmospheric pressure. (Reproduced and modified from [2153].)

a uniformly heated 250-cm<sup>3</sup> borosilicate glass Erlenmeyer flask containing air and NO<sub>2</sub>. The results for ambient temperature are shown in Figure 63 as a function of NO<sub>2</sub> concentration. Under these conditions, hydrazine itself was more difficult to ignite than methylhydrazines.

With increasing ambient temperature, ignition occurred at lower and lower NO<sub>2</sub> concentrations, as shown in Figure 64 for hydrazine. A similar graph is available for MMH (chapter “Methylhydrazine”). Helium dilution narrows the autoignition range, and pressure increase widens it.

## 8.2 Autoignition Temperature of Hydrazine

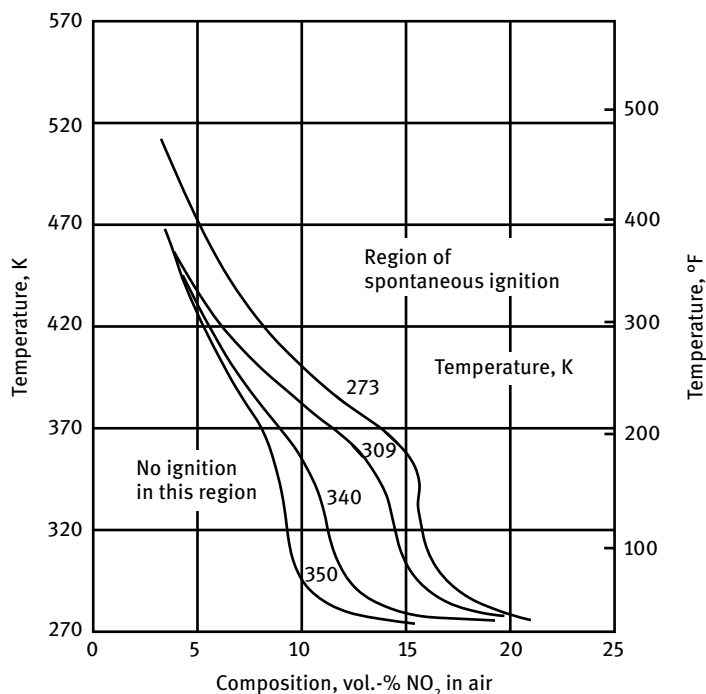
The autoignition temperature of a fluid is the minimum temperature at which a combustible fluid with or without an oxidizer (usually air) will spontaneously



**Figure 63:** Minimum spontaneous ignition temperatures of liquid hydrazine, MMH, and UDMH in contact with NO<sub>2</sub>/air mixtures. (Reproduced and modified from [1607].)

ignite and produce a flame. Autoignition temperature depends on the composition and pressure of the combustible vapor and on the type of hot surface present. It also depends on the amount of confinement, whether or not the vessel is vented. Upward propagation in a gravity field will aid ignition. Generally, autoignition tests are conducted at atmospheric pressure and with stoichiometric mixtures.

Because there are many different experimental setups in use, it is very difficult to compare autoignition data from different sources. ASTM methods exist for measurement flash points where a pilot flame is moved over a supply of vapors, but autoignition is a different situation without the use of a pilot flame. The instructions for ASTM E659-78 state, "This method is not designed for evaluating materials which are capable of exothermic decomposition." Hydrazine is capable of exothermic decomposition, and therefore Method E659 is not suitable for determining the autoignition temperature of hydrazine in air. Another method used for determining the self-ignition temperatures of combustible fluids uses the Setchkin apparatus.



**Figure 64:** Minimum spontaneous ignition of liquid hydrazine at various initial temperatures in NO<sub>2</sub>/air mixtures. (Reproduced and modified from [1607].)

### 8.2.1 Autoignition Temperature of Hydrazine in the Presence of Air

In the literature there exist many conflicting data on the autoignition of hydrazine in air. Autoignition temperatures between 438 and 673 K have been reported using glass vessels. Using a Setchkin apparatus and a modified borosilicate glass apparatus, and scanning a temperature range of 448 to 538 K in 10-K increments, the lowest statistically significant (4 ignitions out of 25 tests) ignition occurred at 498 K [2149]. All tests were repeated at least 25 times. The percent ignitions did not increase systematically with the test temperature, as expected.

There was a low incidence of ignitions at an intermediate temperature and a total “outlier” of an isolated ignition event at the lowest temperature tested. These observations cast a shadow of doubt on the accuracy of the data and the adequacy of the method used. One cannot give an exact autoignition temperature for hydrazine in air. At best, one can give a range of temperatures over which ignitions have been observed. A very comprehensive summary of autoignition temperatures of combustible gases and vapors is given in the US Bureau of Mines Bulletin 627 [1607] and other publications by that same organization [2154, 2156]. The dimensions of the uniformly heated apparatus were chosen to be large in relation to the quenching diameter to minimize

wall effects. USBM used two different size vessels for testing, a 0.2-L borosilicate glass flask and a 4.9-L cylindrical steel vessel. The glass flask and the test method used for it were patterned after ASTM-D-2155-63T. The vessel and the oxidizing atmosphere in it were brought to test temperature first, and the test fluid (at room temperature) was injected with a hypodermic syringe. Ignition was determined through a sudden pressure rise recorded by a pressure transducer. At the lower test temperatures, ignition delays could extend to 10 s. The results are summarized in Table 78.

**Table 78:** Autoignition temperatures of hydrazines in air and oxygen at atmospheric pressure.

| Oxidizer<br>Fuel/Vessel | Air         |             | Oxygen      |             |
|-------------------------|-------------|-------------|-------------|-------------|
|                         | Glass 0.2 L | Steel 4.9 L | Glass 0.2 L | Steel 4.9 L |
| Hydrazine               | 543         | 451         | 423         | 371         |
| MMH                     | 457         | 423         | —           | 345         |
| UDMH                    | 525         | 499         | 497         | 457         |

Data source: [2154], all temperatures in K

In addition to data for air and oxygen, intermediate data were obtained for oxygen enriched air with 50 and 70% oxygen. The effect of oxygen enrichment is more pronounced for hydrazine than UDMH. The same two vessels were used to measure the effect of initial pressure on autoignition temperature. The results are summarized in Table 79.

**Table 79:** Autoignition temperatures of hydrazine in air and oxygen as a function of initial pressure (in comparison to those of MMH and UDMH).

| Fuel      | Oxidant | Vessel, L | Lowest observed AIT, K |     |     |     |     |
|-----------|---------|-----------|------------------------|-----|-----|-----|-----|
|           |         |           | 740                    | 400 | 100 | 50  | 25  |
| Hydrazine | Air     | 0.2       | 543                    | 518 | —   | —   | —   |
| Hydrazine | Air     | 4.9       | 451                    | 518 | 705 | 747 | —   |
| Hydrazine | Oxygen  | 0.2       | 423                    | 489 | 575 | 623 | 723 |
| Hydrazine | Oxygen  | 4.9       | 371                    | 383 | 603 | 663 | 697 |
| MMH       | Air     | 4.9       | 423                    | 463 | 571 | 619 | 671 |
| MMH       | Oxygen  | 4.9       | 345                    | 358 | 441 | 541 | 617 |
| UDMH      | Air     | 0.2       | 525                    | 527 | —   | —   | —   |
| UDMH      | Air     | 4.9       | 499                    | 518 | 537 | 573 | —   |
| UDMH      | Oxygen  | 0.2       | 497                    | 503 | 531 | 573 | 627 |
| UDMH      | Oxygen  | 4.9       | 457                    | 478 | 523 | 533 | 543 |

All temperatures in K; data in *italics* are interpolated.

Data source: [2154].



If the logarithm of the test pressure was plotted against the reciprocal absolute temperature of autoignition, a straight linear (Arrhenius-type) relationship could be observed, suitable for data interpolation.

If oxidizer and fuel are pre-mixed first and then heated, the difficulty frequently encountered with autoignition temperature testing is raising of the test temperature uniformly and quickly without triggering premature slow reactions in the gas phase. Some ignition reactions also show an inhibition induction period, causing a delayed ignition only a long time after the test temperature has been reached. This has also been observed with hydrazine or UDMH in closed vessels at low pressures.

The autoignition temperature of hydrazine in air was determined in Pyrex and stainless-steel vessels [1408]. In Pyrex glass the autoignition temperature was 543 K (518 °F) in air and 477 K (397 °F) in oxygen. In stainless steel it was considerably lower, 429 K (312 °F) in air. A catalytic effect of the metal surface cannot be excluded. In the presence of rust or platinum, hydrazine may even ignite at room temperature. When a black iron pipe threaded cap was substituted for the Pyrex flask, ignition occurred at much lower temperatures, 405 K (270 °F) in air. In the presence of Shell 405 catalyst, hydrazine vapors and hydrazine decomposition products in air may ignite at room temperature [2157].

Early ignition tests at NASA WSTF were patterned after ASTM D2155-66 but did not give the desired information about the catalytic contributions of incompatible materials of construction of space vehicle propulsion systems [2158]. The ASTM apparatus was modified and additional instrumentation and a sample holder added to the borosilicate Erlenmeyer flask. At temperatures above the minimum reaction temperature many materials continued to heat up as long as they were exposed to a fresh air supply and repeated injections of hydrazine. The thermal regeneration temperature was defined as the minimum initial specimen temperature, which continually increased when hydrazine was injected into the test flask at a rate of 50  $\mu$ L in 30-s intervals. The lower the thermal regeneration temperature, the less compatible the material was rated for hydrazine service.

A 15.7-cm-diameter and 14.7-cm-high CRES-304 chamber was used to study the pressure dependence of the autoignition temperature of hydrazine in air at 20–100 kPa [2159]. The chamber pressure was adjusted to the desired pressure by evacuation. The chamber was heated prior to injection of the fuel sample. The fuel sample was temperature conditioned to 322 K prior to injection. Photocells, thermocouples, and pressure transducers were used to sense the reaction. The test sequence was such that hydrazine was injected into the test chamber, which had been pre-conditioned. If autoignition occurred, then the same quantity of fuel was injected for a subsequent test at a temperature that was 10 °F lower than before. The process was repeated until the lowest autoignition level for temperature, pressure, and amount of hydrazine injected was verified. In two test series with hydrazines in air at four different pressures, this required 529 individual tests for hydrazine. The ignition delay of hydrazine in air varied from 0.5 to 27 s. The autoignition temperature

of hydrazine decreased from 488 to 400 K when the pressure was increased from 20 to 100 kPa. In most cases, measured overpressure agreed closely with that predicted for a deflagration and was far lower than what would have to be expected if a detonation had occurred. No ignitions were observed at pressures below 6.5 kPa.

The autoignition temperature of 0.03-mL droplets of hydrazine squirted on heated material samples in air showed a marked dependence on the type of materials exposed. Some materials showed more catalytic activity than others. Even the same material gave different autoignition temperatures, depending on the degree of corrosion or other contaminants present [2160]. The materials tested were those that could possibly be exposed in the movable nozzle section of the solid rocket booster of the Space Shuttle. A hydrazine-powered gas generator and gas turbine provided power for a hydraulic pump that pivoted the nozzle for thrust vector control. A hydrazine leak in the vicinity of hot surfaces could theoretically lead to a fire hazard. The following materials caused ignition on contact of liquid hydrazine with the material at  $403 \pm 5$  K: stainless steel 301 corroded in salt spray, stainless steel 301 contaminated with WD-40 lubricants, and D6AC steel corroded by 24-h immersion in seawater. At  $573 \pm 5$  K, ignition occurred on Hastelloy B contaminated with WD-40; at  $503 \pm 5$  K, ignition occurred on Inconel 600 and Pyrex glass. Ignition on Inconel 602 occurred only at much higher temperatures. The following materials were tested at  $403 \pm 5$  K with hydrazine in air, but ignition followed by explosion of vapor did *not* occur: CRES-301, CRES-302, CRES-304L, CRES-316, CRES-321, Ti-3Al-3.5V, Ti-6Al-4V, Inconel 600, Inconel 718, 17-4PH Steel, Al-6061-T6, Al-2219-T87, Al-7075-T73, and glass. Five more materials were tested at 473 K with no ignition: D6AC Steel, Al-2124-T85, PR-1422 Sealant, DC-93-076 Sealant, and Hastelloy B. Materials that caused hydrazine ignition in air were retested in a nitrogen atmosphere, but the nitrogen environment prevented ignition in all the cases where it previously occurred in air. Tests in a carbon dioxide atmosphere were complicated by the premature reaction between hydrazine and  $\text{CO}_2$ , but no explosions occurred.

The autoignition temperatures of many hydrazine mixtures are not known. As expected, the autoignition temperature of 85% hydrazine hydrate was considerably higher than that of anhydrous hydrazine, namely, 565 K (557°F) in air and 491 K (424°F) in oxygen when the Pyrex flask was used [1408].

### 8.2.2 Autoignition Temperature of Hydrazine in Oxidizer-Enriched Air

Hydrazine, MMH, and UDMH have found widespread use as bipropellant fuels with NTO as an oxidizer. These combinations are the most important storable fuels and have been used throughout the GEMINI, APOLLO, and Space Shuttle programs. The Space Shuttle used NTO/MMH for the OMS and the reaction control system. In evaluating the safety of these fuels for manned space flight operations, the minimum spontaneous ignition temperatures in pure air as well as  $\text{NO}_2$ -contaminated air were of interest. Because the composition of the oxidizing atmosphere varies with

temperature and pressure as a result of the  $\text{N}_2\text{O}_4$  dissociation equilibrium, “ $\text{NO}_2$ ” is frequently used to describe the  $\text{NO}_2/\text{N}_2\text{O}_4$  equilibrium mixture. Flammable and self-igniting hydrazine/ $\text{NO}_2$  mixtures in air could result from simultaneous leaks of both the oxidizer and the fuel system.

### 8.2.3 Autodecomposition Temperature of Hydrazine in the Absence of Air

A widely used method for determining the thermal stability of monopropellants and explosives was the ICRPG (later JANNAF) Liquid Propellant Test Method No. 6, which is now an antique [2161]. It used a 2.5-mL bomblet holding a 0.5-mL sample immersed in a molten metal bath (Wood’s metal) pre-heated to 460 K. The bath temperature and the differential temperature between the bath and the propellant sample were recorded in order to detect the onset of exotherms. The results of ICRPG thermal stability tests with hydrazine are summarized in Table 80. Similar data are available for MMH, MHF-5, and MHF-7 (*Encyclopedia of Liquid Fuels*, chapter “Methylhydrazine”).

**Table 80:** ICRPG thermal stability test results for hydrazine (sorted by material name).

| Material    | Exotherm |     | Disk rupture |                 |
|-------------|----------|-----|--------------|-----------------|
|             | K        | °F  | K            | °F              |
| 17-7PH      | 514      | 465 | 553          | 535             |
| Al-1100-0   | —        | —   | 533          | 500, detonation |
| Al-2014-T6  | 500      | 440 | 547          | 525             |
| Al-6061-T6  | 483      | 410 | 534          | 502             |
| CRES-304L   | 505      | 450 | 544          | 520             |
| CRES-316    | 478      | 400 | 572          | 570             |
| CRES-321    | 525      | 485 | 550          | 530             |
| CRES-347    | 511      | 460 | 550          | 530             |
| Hastelloy X | 469      | 385 | 539          | 510             |
| Haynes-25   | 525      | 485 | 550          | 530             |
| Inconel X   | 511      | 490 | 553          | 535             |

Source: [2161]

Only the lowest temperature at which exotherms occurred or burst disks ruptured are listed. (The original source showed a range of temperatures.) There was a distinct dependence of the exotherm and disk rupture temperatures on the material from which the bomblets were made. The heating rate was 5.5 K/min. With hydrazines, most of the exotherms began at 505 K and the burst disk ruptured above 533 K. The stability was best in Inconel X or CRES-321 and worst in aluminum. With MMH, the stability was best in Hastelloy X and worst in aluminum. In comparative tests where hydrazine or MMH vapors only were contained in the bomblets, the burst disks ruptured at lower temperatures than in the liquid tests. Rupture occurred at temperatures 55 K below

those measured in the liquid tests. MHF-5 was much less stable than any of the other propellants.

The autodeonation-autodeflagration potential of liquid hydrazine or hydrazine vapor above liquid at saturation temperature was tested in a liquid-phase exothermicity test (LPET) at NASA WSTF [2148, 2162]. The LPET was conducted in a 100-mL CRES-304 chamber with 112 to 116 cm<sup>2</sup> of wetted surface area [2163]. The test chamber was approximately 5 cm in diameter with a wall thickness of 0.5 mm and had fittings on each end to accommodate sample loading, fill and vent lines, and thermocouple instrumentation. The test chamber had a tested burst strength of 11.7 MPa. Air was carefully excluded from these LPETs. The sample container was connected to a helium-pressurized accumulator to maintain quasiisobaric conditions prior to ignition. The accumulator was located above and connected to the test chamber through a 6-mm-O.D. capillary bore steel tubing. Helium was chosen because it has a lower density than hydrazine and would prevent hydrazine vapor from entering the accumulator. The temperature of the sample was raised at the rate of 3 K/min until decomposition or evaporation occurred. The results are summarized in Table 81.

**Table 81:** Hydrazine autodecomposition temperature.

| Pressure                                                              |      | Vaporization temperature | Number of positive tests per total number of tests | Mean explosion temperature |
|-----------------------------------------------------------------------|------|--------------------------|----------------------------------------------------|----------------------------|
| kPa                                                                   | psig | K                        |                                                    | K                          |
| <b>HF/HNO<sub>3</sub>-pickled, HNO<sub>3</sub>-passivated chamber</b> |      |                          |                                                    |                            |
| 690                                                                   | 100  | 457.6                    | 0/5                                                | —                          |
| 2416                                                                  | 350  | 521.7                    | 2/13                                               | 506 ± 4.9                  |
| 6900                                                                  | 1000 | max.                     | 5/9                                                | 533 ± 12.8                 |
| <b>Same as above, hydrazine-conditioned</b>                           |      |                          |                                                    |                            |
| 2416                                                                  | 350  | 520                      | 1/11                                               | 516.4 ± 0                  |
| 4140                                                                  | 600  | 548.7                    | 2/3                                                | 533 ± 15.6                 |
| 6900                                                                  | 1000 | max.                     | 4/4                                                | 528.7 ± 28.9               |

Data source: [2148]

Allowing the chamber to become conditioned in hydrazine for 16 h at 394 K raised the decomposition temperature threshold slightly, and there was also more scatter in the data compared to the non-passivated chamber. In another series, various materials of interest to the Space Shuttle program were added to the test chamber prior to testing. Of the 13 materials tested, CRES-304, chromium plating, anodized aluminum, K96 tungsten carbide, Graphitar 86, and pure graphite (658 RC) did not catalyze decomposition sufficiently to result in a catastrophic explosion under the conditions of the test. Tests with Rene 41 nickel and M2 tool steel resulted in high-order reactions, but it

could not be determined whether the reaction started in the vapor phase and whether it involved any liquid.

A vapor-phase exothermicity test (VPET) and an LPET were used at NASA WSTF to test the compatibility of hydrazine vapor or liquid with construction materials at elevated temperature in inert atmospheres [2144, 2164]. The VPET apparatus itself, a 500-mL Pyrex test chamber, was inert to hydrazine at 473 K. An amount of 0.02 mL hydrazine was squirted on flat panel test samples in the chamber, and eventual temperature rises were recorded. After the hydrazine had evaporated and eventually reacted with the sample, the vapor space was purged and the remaining hydrazine amount analyzed. If the metal sample was incompatible with hydrazine, as indicated by an exothermic event, only very little undecomposed hydrazine was remaining.

The LPET consisted of a smaller, 100-mL stainless-steel chamber. The chamber was made from CRES-304L. The liquid level was adjusted such that 112 cm<sup>2</sup> of wall was wetted in each test. The bomb was then pressurized with helium or nitrogen to 2760 kPa (400 psig) to prevent the liquid from evaporating. It appears that early tests [2148, 2163, 2164] used helium, but later tests [1912] used nitrogen. The system could be operated in the adiabatic (well-insulated) mode or with a heat sink attached to maintain isothermal conditions.

The parameter reported in the LPET is the exothermic threshold temperature in the presence of the material under test, the initial temperature at which a runaway decomposition is first seen to occur. This temperature gives an indication of the relative catalytic activity/incompatibility and needs to be compared to the temperature at which the empty chamber by itself would cause hydrazine(s) to decompose. The absolute value of the LPET exotherm temperature is highly system dependent and should not be taken as applicable to all situations. In many cases a temperature range instead of a specific temperature number is given to emphasize the inaccuracy of the data.

Initially, the different types of response of hydrazine or MMH liquid in contact with the material specimens at 473 K were classified into three groups [2148, 2163]:

Type 1 materials showed no detectable reaction. No material in this category could be distinguished from the background heat release rate ( $0.6 \text{ kJ}/1.8 \text{ ks} = 0.33 \text{ J/s}$ ) of the stainless-steel system.

Type 2 materials showed detectable reaction, but passivated, and the rate decreased with time.

Type 3 materials showed a progressive increase in heat release rate, such that the heat release rate would exceed the cooling capacity of the heat sink, and a runaway reaction would result.

Some Type 3 materials were then retested at lower temperature to see how low a temperature would be required to move them to a Type 2 or Type 1 category. In one test series looking at various STS APU materials, 18 materials exhibited no detectable exothermicity, 1 material was marginal, and 13 materials exhibited enough catalytic activity to result in thermal runaway conditions [2163]. The difference between CRES-304 and CRES-304L in columns 1 and 3 of Table 82 is hard to explain.

**Table 82:** LPET results for materials in contact with hydrazine in nitrogen.

| Reference                                | Exothermic threshold temperature, K |         |
|------------------------------------------|-------------------------------------|---------|
|                                          | [2144]                              | [1912]  |
| Kynar 460                                | 366                                 | 367     |
| Tungsten carbide K96 sheet               | —                                   | 396     |
| Microseal 100-1, AMS2525 dry lubricant   | 407                                 | 408     |
| Tefzel                                   | 422                                 | —       |
| Teflon FEP                               | 422                                 | 422     |
| Silver plating TY2                       | 427                                 | —       |
| M2 Tool steel CEVM                       | 429–443                             | 429–443 |
| AFE-411                                  | 430–480                             | 430–480 |
| Al-2024-T4, anodized Type 1              | 431–457                             | —       |
| Kalrez 1045                              | 436                                 | 422     |
| Teflon ETFE film                         | —                                   | 422–450 |
| Hastelloy X                              | 469–489                             | —       |
| Pure graphite (658)                      | 473                                 | —       |
| Graphitar 86                             | 473                                 | 470     |
| CRES-316                                 | 477–489                             | —       |
| Stainless steel 17-7 PH precip. hardened | 478                                 | 478     |
| Teflon PFA                               | 478                                 | —       |
| Inconel 718                              | 478                                 | —       |
| Tungsten carbide KZ96 rod                | —                                   | 427–450 |
| CRES-304                                 | 479                                 | 480     |
| EPR Rubber E515-80                       | 479                                 | 429–478 |
| Ti-6Al-4V                                | —                                   | 479     |
| Chromium plating on CRES-304             | —                                   | 479     |
| Apiezon L grease                         | —                                   | 479     |
| Stainless steel 15-5 PH precip. hardened | —                                   | 481     |
| Al-2024-T4                               | —                                   | 481     |
| Al-6061-T6                               | 483                                 | —       |
| Al-2014-T6                               | 500                                 | —       |
| CRES-304L                                | 505–511                             | 480     |
| CRES-347                                 | 511                                 | 480     |
| Haynes-25                                | 525                                 | —       |
| CRES-321                                 | 525–530                             | 505     |
| Inconel X750                             | 527–530                             | 430     |

(sorted by threshold temperature  $N_2H_4$  in first column)

The presence of a trace amount of carbon should not catalyze the decomposition of hydrazine. It is more likely that the two samples had different surface finishes or different passivation treatments. Later data in column 2 show better agreement. The data in the second column of Table 82 for  $N_2H_4$  are those temperatures where the rate of heat evolution exceeded the detectable threshold of  $55 J s^{-1} m^{-2}$  and the surface: volume ratio was typically  $1.25 cm^{-1}$ . Similar LPET data are available for MMH (chapter “Methylhydrazine”).

For some of the materials in Table 82 additional data obtained with an ARC have become available. For such tests, the activation energy can be measured and the heat generation per unit surface area can be calculated as a function of temperature and presented in graph form, as has been done in the NASA report [1912]. In many instances the acceptability of materials may also depend on the degree of dispersion. Thus, metal samples may be acceptable when tested in bulk, but, ground to a fine powder (e.g., abrasion from sprockets of gear pump) and accumulated in an in-line filter, the same metal may be the cause of instant autodecomposition and gas evolution. When tests with M-2 tool steel (one of the least compatible samples tested) were repeated at higher pressure (6.9 MPa instead of 2.76 MPa), the time to runaway reaction was shortened. This disproves earlier suggestions that one would only have to keep the hydrazine from evaporating to prevent explosions.

The thermal hazard test consisted of a 100-mL CRES-304 chamber installed in an expendable thermally insulated chamber [2164] and eventually evolved into the LPET. Material samples with 112-cm<sup>2</sup> surface area were mounted in the chamber, submersed in 90 mL hydrazine, and heated to 500 K while simultaneously recording pressure and temperature. This setup was very similar to an accelerating rate calorimeter. Several thermal runaway reactions in the chamber resulted in an explosion. With hydrazine alone, an exothermic reaction occurred at 450 K, which produced an initial heat release rate of 1.8 J/s. Raising the temperature to 478 K increased the rate to 5.3 J/s. The apparatus can only detect incompatibilities with materials that are less compatible than CRES-304, the container material. The thermally most unstable material in this test series was A-FM silicon core iron. Anodized aluminum was not much different from the background rate of decomposition. In a group of seven non-metallic materials tested, AF-E-411 and EPT were the most compatible, Kynar was the least compatible polymer. An exothermic reaction between hydrazine and Kynar 460 started between 388 and 413 K and in some instances caused destruction of the test apparatus [1646]. Kalrez 1045, two grades of Tefzel, and FEP Teflon were subsequently evaluated as replacements for Kynar 460 [1722]. With Kalrez 1045, an exothermic reaction was observed as low as 422 K and exothermicity with a sample of dyed Tefzel began even lower at 366 K. It is not known what function the dye had in the polymer. An undyed sample was a little more compatible. It was surprising that Teflon FEP, which is considered to be compatible with hydrazine under most conditions, did also begin to react at 422 K. Microseal 100-1 AMS255 and tungsten carbide were the most reactive seal and valve seat materials.

In most satellites, propellant lines are wrapped with electrical strip heaters to keep the hydrazine from freezing. Malfunction of the temperature controller for the strip heaters leads to a failure mode where the heaters receive full power all the time and overheat the lines and the hydrazine therein. This worst-case condition was simulated in two tests, one using a 23-cm section of heated CRES-321 line with an active thruster connected to its end to study the effects of hot propellant on thruster operation [1173]. Twenty-six tests were conducted with the thruster in different duty cycles

and pre-test soak temperatures from 450 to 538 K (350 to 510 °F). At the higher temperatures, the heated section of the line would dry out and the thruster had to ingest bubbles before it developed full thrust. The hot section of the line slowly filled with decomposition product gases, and the liquid/vapor front recedes to cooler zones. Thruster operation at feed line temperatures up to 538 K was demonstrated without any damage to the thruster or the feed system. The second test, a static test, simulated 53 cm of heated CRES-321 propellant feed line complete with Au/Ni brazed unions. Six test specimens with this L-shaped geometry were two-thirds filled with liquid hydrazine, pressurized with nitrogen (1.03 to 1.37 MPa = 150 to 200 psia), heated for 4 weeks to 394, 463, or 505 K (250, 375, or 450 °F) while the pressure was monitored. The pressure rise rate seemed to obey an Arrhenius-type temperature dependence. Hydrazine and gas space were analyzed at the end of the test. One of the six tubes exploded during the heat-up transient, possibly due to tube contamination. Aside from this event, it is amazing to see that hydrazine can tolerate such abuse and not explode. One would not want to design for this condition, but up to a certain point hydrazine may be forgiving, as long as one stays with small line diameters (<5 mm) and as long as the thruster valve is kept cool by heat-sinking it to a mounting plate with large heat capacity.

Concern about the possible effects of a suspected hydrazine fuel line leak in a satellite prompted a study of the autodecomposition temperature of hydrazine sprayed onto a hot (1200 K = 1700 °F) Hastelloy X plate in a vacuum chamber in the absence of air [2165]. Injection of 6-mL slugs of hydrazine onto the plate in a 2.5-m<sup>3</sup> vacuum chamber evacuated to an initial pressure of 4–8 μm Hg caused the hydrazine to instantly turn into a cloud of snow of hydrazine crystals that slowly sublimed and filled the chamber with hydrazine vapor. The distance between the injector and the plate was initially 10 cm but was decreased to 2.5 cm in later tests. A total of 29 tests were reported. In two tests, the volume of injected liquid was decreased to 5 mL, then to 4 mL hydrazine, with essentially identical results. The spray cooled the hot plate, and, based on ultimate pressure readings in the chamber, it was suggested that hydrazine did not decompose because the ultimate pressure in the vacuum chamber was equal only to that expected for hydrazine vapor. No gas analysis was conducted to prove that theory. If any hydrazine decomposition had occurred, the pressure in the chamber would have had to be higher than that observed. For comparison, the same amount of hydrazine was passed through a catalytic thruster in the vacuum chamber. The resultant vacuum chamber pressure was much higher (12 mm Hg) than after the impingement tests.

Slightly different results were obtained by injecting 4-mL slugs of hydrazine onto a metal plate heated to 1043 to 1073 K in a 128-L vacuum chamber evacuated to 10<sup>-5</sup> mm Hg [2166]. In that test, the injection valve opening time could be varied from 12 to 126 ms, the delay until opening an evacuated sample tank valve varied from 5 to 230 ms, and the sampling valve could be kept open for 100 to 1260 ms. Typically, the sampling valve was kept open for 1000 ms. The gases were analyzed by mass spectrometer, showing ammonia, nitrogen, and hydrogen, but no undecomposed



hydrazine. Hydrazine may have adsorbed to the tank walls or hung up in the sampling system. The pressure rise in the vacuum chamber (with vacuum pumps still running) was 1.3 to 8 mm Hg. Complete vaporization of all hydrazine in a closed system should have increased the pressure to 20 mm Hg and complete decomposition would cause the pressure to go to 40 mm Hg.

Until the 1980s, exothermicity tests had to be conducted in large experimental setups to obtain measurable heat flows. Such large tests could not be conducted in a normal chemistry laboratory and had to be relegated to remotely located hazardous test facilities with concrete walls. This situation changed when the first differential scanning calorimeters and then accelerating rate calorimeters and microcalorimeters became commercially available. These instruments are now found in most energetic materials laboratories and enable investigators to safely conduct rocket propellant exothermicity tests in the comfort of a laboratory. Differential scanning calorimeters and accelerating rate calorimeters have also been used to measure the thermal stability of hydrazinium salts, discussed in *Encyclopedia of Oxidizers*, chapter “Hydrazinium Salt Oxidizers.” The current section deals mostly with the thermal stability of liquids as they affect their safety and hazard properties. The kinetics of hydrazine decomposition reactions are discussed in Section 4. More hazardous, uncontrolled decomposition reactions are those occurring in cook-off and bonfire tests (Section 8.12). Before elaborating to set up an expensive and potentially catastrophic cook-off test, it would be advisable to totally characterize the propellant with DSC and ARC tests. These tests can be conducted in the laboratory and consume less sample. They are standardized by the ASTM E-698-79 *Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials*.

Prior to using ARC, an attempt was made to obtain thermal stability, kinetic rate, and activation energy data by testing hydrazine or MMH in a differential scanning calorimeter [2167]. The difficulty encountered with all testing of liquid samples in a differential scanning calorimeter is the pressure buildup first due to evaporation and then by decomposition products, which causes conventional sample holders (crimped metal pans, glass vials, capillaries, sometimes called crucibles, although they are no longer crucible-shaped) to bulge, leak, and rupture. ASTM Methods E557 (DTA) and E698 (Arrhenius kinetics) deal with these problems insufficiently, and little progress has been made on the DSC of hydrazine or other monopropellants like those based on hydroxylamine. The internal pressure in the crucibles can be compensated by enclosing the sample and the reference cell in a pressurized enclosure and/or using pressure-resistant crucibles. The increased thermal mass of heavier walls of pressure-resistant crucibles reduces the sensitivity of the method. The first exotherm of hydrazine in a CRES-304 sample holder at a heating rate of 10 K/min. seemed to occur at 370 K

The accelerating rate calorimeter used at NASA WSTF for studying the acceleration of hydrazine decomposition reactions by various materials of construction consisted of a 25-mm-diameter spherical sample holder vessel made of pure titanium weighing approximately 8 g by itself and 30 g with the adapter attached, similar to

an accelerating rate calorimeter. The sample holder was mounted in an insulated heater chamber approximately  $25 \times 25$  cm in size surrounding the sample holder [1574, 1576, 2168]. The heater chamber in turn was enclosed in a heavy-duty steel tank with a flanged lid to contain any shrapnel in case the sample holder exploded. Cartridge heaters increase the chamber temperature incrementally and the thermocouple instrumentation on the sample holder looks for signs of an exothermic reaction. If none is found, the temperature is increased another increment and held at that level isothermally for typically 20 min., after which waiting period the whole heat-wait-heat cycle repeats itself until an exothermic reaction is detected. Once an exothermic reaction is detected, the electric heaters provide just enough heat to maintain a zero temperature difference between the reaction vessel and the walls of the heating jacket. The system is then essentially adiabatic. The minimum detectable exotherm was 0.02 K/min. A pressure transducer can be connected to the neck of the spherical vessel to obtain both temperature and pressure readings of the events in the sample holder. Gas that evolves causing pressure buildup can be analyzed for residual hydrazine and decomposition products after each run. Blank runs were done with hydrazine alone, followed by tests with materials samples and hydrazine. With hydrazine alone, the onset of exotherms was usually near 468 K [1574, 1575]. The metals in powder form were weighed in the sample holder and 0.5 mL hydrazine added in a glove box under nitrogen. With CRES-304L, the heat release rate for the sample holder vessel was proportional to the surface area of the stainless-steel powder added. The heat release rate (expressed as  $\text{J s}^{-1} \text{m}^{-2}$ , where  $\text{m}^{-2}$  is the surface of the sample holder) was proportional to the surface area of the metal sample, when nickel powder, nickel turnings, and nickel foil were inserted into the titanium sphere. Surprisingly, chromium, aluminum, CRES-410L, and CRES-316L had very low catalytic activity, which could not be discerned from the background effect caused by the titanium vessel alone. The catalytic effect of CRES-304L was distinct, but low. When normalized by the surface area, CRES-304L, iron, molybdenum, nickel, and cobalt had increasing catalytic activity in that order (increasing from left to right). Cobalt was the most active metal tested in this series at 353 K. The relative ranking of these metals may depend on surface pretreatment (cleaning, passivating) of the samples. As-received metal powder samples are likely to have substantial oxide coatings which may have catalytic activity.

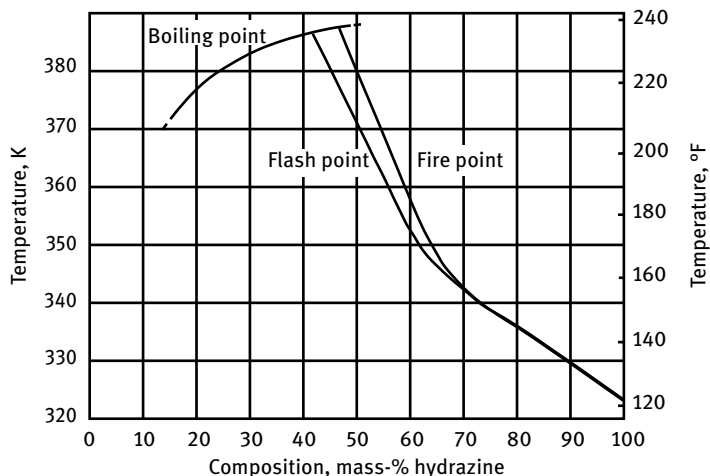
#### 8.2.4 Autoignition of Hydrazine Solutions

The autodecomposition temperature of liquid hydrazine in the ICRPG test in stainless-steel bombs ( $0.5\text{-cm}^3$  sample heated at  $10^\circ\text{C/min}$ ) was lowered from  $519 \pm 2\text{ K}$  ( $475 \pm 5^\circ\text{F}$ ) to  $402 \pm 4\text{ K}$  ( $265 \pm 10^\circ\text{F}$ ) by the addition of 21.8% hydrazinium azide. The addition of 24.6 or 27.6% hydrazinium azide lowered the autodecomposition temperature of hydrazine to  $408 \pm 2\text{ K}$  ( $275 \pm 5^\circ\text{F}$ ) [141, 142]. In every case the exothermic reactions caused rupture of the burst diaphragm, which was rated for 32.3 MPa (4700 psi) at room temperature.

Mixtures containing 19, 20, or 27% ammonium perchlorate in hydrazine detonated when heated to 437, 433, or 432 K in an ICRPG/JANNAF thermal stability bomb made from stainless steel [2169]. The heating rate was greater than 10 K/min. Propellant-grade hydrazine (without ammonium perchlorate) could be heated to 493 K before the aluminum burst disk ruptured. The hydrazine disk was only bulged and cracked, whereas the perchlorate disks were strongly sheared.

### 8.3 Flash Point of Hydrazine

The “ignitability” or, scientifically more accurately, flash point is determined by heating the liquid in an open cup while moving a pilot flame back and forth over the surface. This test using brass cups is extensively used for the characterization of petroleum products. The Cleveland open-cup method is described in ASTM Method D92-85 and the Tag closed-cup method is described in ASTM Method D56-82. Another Tag open-cup flash point test is described in ASTM Method D1310-86. Because hot hydrazine reacts with brass, a glass insert must be used for hydrazine tests. Occasional puffs of ignition are observed below the flash-point temperature when the pilot flame is moved across the surface, but sustained combustion may or may not occur. The temperature above which sustained combustion occurs is called the fire point. For pure hydrazine, flash point and fire point are identical (324 K = 124 °F), but for hydrazine/water mixtures the fire point may be up to 10 K (18 °F) higher than the flash point (Figure 65).



**Figure 65:** Open-cup flash and fire points for aqueous hydrazine solutions using ASTM-D92 Cleveland open-cup method. (Reproduced and modified from [1645].)

The lowest reported closed-cup flash point for hydrazine in air at 101.3 kPa is 311 K. The open-cup flash point is 324 K [2144]. The TAG closed cup flash point of hydrazine solutions decreased only gently from 359 K at 64% to 352 K at 90%  $\text{N}_2\text{H}_4$ . The flash point of hydrazine is high compared to common combustible liquids such as gasoline (230 K =  $-40^\circ\text{F}$ ) or kerosene JP-4 (259 K =  $7^\circ\text{F}$ ). Despite this, hazardous material transportation regulations (49 CFR 172.101) currently classify anhydrous hydrazine as a flammable liquid (red label). The Cleveland open-cup flash point of hydrazine itself is significantly higher than that of its methyl derivatives, MMH (294 K =  $70^\circ\text{F}$ ) or UDMH (274.2 K =  $34^\circ\text{F}$ ). Both MMH and UDMH are classified as flammable liquids.

The flash point of hydrazine is increased by the addition of water (Figure 65) until above 58% by weight water (below 42% by weight or 40% by volume hydrazine) the mixture can no longer be ignited under any open air conditions, not even with a very hot ignition source. This limit is only a few percent hydrazine above the limit of propagation in an oxygen-free hydrazine-water system.

Temperatures above which ignition can occur in the open-cup test do not agree with those calculated from flammability tests and vapor-pressure curves. The main difference is that the open-cup method is a dynamic method where the liquid is constantly evaporating and mixing with air. In the USBM flammability test apparatus the gases are premixed and static. Furthermore, the vapor in the USBM test must be heated above the boiling point of the liquid to prevent condensation and is thus hotter to start with. Fire extinguishing tests have confirmed that dilution of anhydrous hydrazine with water below 40% by volume hydrazine renders the mixture non-flammable [2132, 2134, 2135].

### 8.3.1 Minimum Required Ignition Energy of Hydrazine

This section covers the energy required to initiate the combustion of hydrazine. A recommended method to measure minimum ignition energies and quenching distances is described in ASTM Method E582-76. Of equal interest as the limits of flammability is the energy required to ignite a flammable mixture of hydrazine and air as a function of composition, temperature, and pressure. Unfortunately, no accurate data are available for any of the hydrazines in air.

The most convenient way to determine ignition energy is by using electric ignition. A high-voltage 60-cycle AC arc from an automotive ignition coil was used for some ignition tests [1408]. Only four tests were conducted with a DC capacitance discharge, for example, a 400- $\mu\text{F}$  or 7.1-mF capacitor charged to 10 or 12 kV, respectively.

Equally few data are available on the minimum ignition energy of hydrazine vapor in the absence of oxygen. Calculated minimum ignition energies for hydrazine vapor decomposition flames showed that for hydrazine vapor at 1 atm pressure and 423 K, the absolute minimum ignition energy lies between 71 and 85 nJ (assuming a prolate ellipsoidal hot pocket with  $a/b = 2$  and a volume equivalent to a sphere radius of 0.033 mm) [1394, 2170]. The computer program in [1394, 2170] allows predictions regardless of

whether an initiation will propagate, depending on electrode gap and vapor temperature. At 345 K, extending the gap from 2 to 4 mm will allow the ignition energy to drop from 1 mJ to below 0.1 mJ. However, at 338 K, extending the gap will only dilute the energy density of the hot pocket, and more energy is required to achieve initiation. At this temperature the minimum ignition energy is 0.9 mJ at an electrode gap of 2 mm.

### 8.3.2 Flammability of Hydrazine Decomposition Products

In addition to the flammability of hydrazine itself, the flammability of its decomposition products in air is of practical interest because sometimes rocket engine or gas generator testing is done at sea-level pressure in closed buildings (test hangars) or the exhaust from vacuum pumps has to be vented to an area free from sources of ignition. The exhaust gas from Space Shuttle APUs was vented to the air during launch and re-entry. The flammability of hydrazine decomposition products depends to a large extent on the degree of ammonia decomposition, that is, on the operating conditions of a hydrazine reactor. No comprehensive study exists on the flammability of these mixtures in air. The simplest case would be  $X = 0$ , with no ammonia decomposition and consequently no hydrogen present. This case can be treated as ammonia flammability with nitrogen diluent. Since ammonia/air mixtures have a narrow range of flammable compositions and are difficult to ignite, the nitrogen dilution will make ignition even less likely. However, with beginning ammonia dissociation and hydrogen formation, mixtures become more flammable and easier to ignite. The limits of flammability and flame speeds in the ternary system hydrogen/ammonia/oxygen have been determined at low pressures, 9.33 kPa = 70 mm Hg and ambient temperature (293 K) [2171]. Similar data are needed for air/hydrogen/ammonia mixtures. If the effects of nitrogen dilution can be quantitatively assessed, some data on combustion in air can be extrapolated from these results. The effect of nitrogen dilution may be like that of lowering the total pressure. The rich limits for the two binary mixtures were at 87.4%  $H_2$  and 70.5%  $NH_3$ , respectively. The lean limits occurred at 4%  $H_2$  and 16.5%  $NH_3$ . At lower pressure (6.66 kPa = 50 mm Hg) the flammable range was a little narrower, for example, lowering the hydrogen upper limit to 81%. The borderlines of flammability followed essentially the lines connecting the pairs of upper or lower binary limits in a ternary diagram, obeying Le Chatelier's mixing rule. The actual flammable range was slightly wider than that predicted by the Le Chatelier rule.

The flame speeds in the ternary diagram showed a decrease from hydrogen to ammonia. The fastest flame ( $S_B = 41.80$  m/s) occurred in a slightly lean 63%  $H_2$ /37%  $O_2$  mixture. With ammonia/oxygen mixtures, the fastest flame speed ( $S_B = 12.50$  m/s) also occurred in a lean mixture (53%  $NH_3$ ). For ternary mixtures, flame speeds fell off on either side of the line joining the two maxima. This line was also running parallel to the stoichiometric line. These flammability and flame speed data are of practical interest where ammonia, dissociated ammonia, or hydrazine exhaust products are mixed with air as oxidizer and used to drive an internal combustion engine or combusted in an afterburner of a ramjet.

## 8.4 Explosive Properties of Hydrazine

The mechanisms that enable the rapid and often very destructive propagation of explosions in energetic substances differ for vapors and condensed (liquid or solid) phases. Therefore, hydrazine explosions in the vapor and condensed state are discussed in separate sections.

This chapter on hydrazine contains two sections dealing with hydrazine detonations. The current section in Section 8.4 deals with detonations of both vapor and liquid hydrazine from a standpoint of safety property evaluation and accident prevention. The other section in Section 4.5.1 deals only with detonations of hydrazine vapor in shock tubes from a more academic point of interest where shock tubes are a useful tool to study kinetics of hydrazine vapor decomposition.

This section on the safety properties of hydrazine deals only with the thresholds and margins under which a detonation may be initiated on purpose. These threshold conditions must be avoided in the design and operation of hydrazine systems in order to prevent accidents.

### 8.4.1 Definition of Deflagration, Explosion, and Detonation

Quite often it is difficult to reconstruct from the remnants of an accident scene whether the cause was a “simple” deflagration or even a detonation. The term *detonation* is reserved for those reactions that obey the Chapman-Jouguet (C-J) equation, in particular high-velocity detonations (HVDs). There is a transitional regime in condensed-phase (mostly liquid) explosives where detonations propagate at lower than maximal velocity, called low-velocity detonation (LVDs). Propagation of LVDs is often aided by inhomogeneities in the detonating medium (bubbles, cavitation, inert granules, micro balloons). An explosion can be caused by either a detonation or a deflagration. Quite often, deflagration-to-detonation transitions (DDT) can be observed in condensed phases or in the gas phase, depending on the geometry of the sample and the amount of confinement.

A deflagration is a flame moving through a flammable mixture at the velocity of a subsonic wave (subsonic with respect to the unburnt mixture). A flame front moves through a mixture confined in a pipe and the pressure rises behind the flame front because combustion products cannot move out of the way fast enough. The increasing pressure behind the flame front will accelerate the propagation from a few meters per second to near sonic velocity in the unburnt mix. Obstacles or constrictions in the path of the flame may cause distortion or dilution with combustion products and cause the flame to slow down or quench altogether. Flame arrestors in ventilation ducts serve this purpose. If the pressure behind a flame front increases rapidly, a deflagration-to-detonation transition can occur. Detonations can also be initiated by a strong source, such as a blasting cap, an electric spark, or a detonation wave of known strength from an adjacent chamber (donor section, a more reproducible method). In a true detona-

tion wave, the chemical reaction coupled to a shock wave travels through the detonable mixture at supersonic speed (relative to the unburned mixture). Since detonations move at supersonic speeds, pressure-sensing devices cannot warn of their coming, and pressure relief valves are too sluggish to respond. In most cases, detonations are quite destructive if the apparatus is not properly designed to confine them.

#### 8.4.2 Vapor-Phase Explosions and Detonations of Hydrazine

The detonation velocity of hydrazine vapor was determined in 20-mm-diameter glass tubes of 3.65-m length at pressures 1.9–101 kPa (14–760 mm Hg) and saturation temperatures from 296 to 387 K (73–236 °F) [2172, 2173]. The glass tubes were held in a steel jacket with observation slots and thermostatted heating mantles. The propagation of the luminescent detonation wave was filmed with a streak camera. Attempts to initiate controlled detonations with a glow plug failed. At 101 kPa only a pale, not very luminescent flame propagating at low speed (50–100 m/s) was observed. Transitions from such a deflagration to detonation occurred only very rarely but are possible. To initiate hydrazine vapor detonations reproducibly, a tube with premixed oxygen-acetylene was attached as a donor section. The detonation velocity at 101 kPa and 387 K was 2360 m/s. At lower pressures it decreased from 2360 to 2270 m/s at 17.7 kPa and 341 K, to 2230 m/s at 7 kPa and 321 K, and eventually to 1980 m/s at 1.9 kPa and 296 K. Below 53 kPa (400 mm Hg) the detonation always propagated as spin detonation. Below 3.3 kPa (25 mm Hg) the spin detonation became unstable and oscillated and pulsed between two different detonation velocities. The spin frequencies also altered abruptly. Such changes were observed to occur approximately every 50–70 cm. The distance between the shock front and beginning luminescence of the reaction front was 6 mm at the lowest pressure and slowest propagation but was much less (below the resolving power of the apparatus) at higher pressures. In some cases, below 3.3 kPa (25 mm Hg) the detonation would simply revert to a deflagration wave.

NASA WSTF in cooperation with McGill University in Montreal, Quebec, Canada, conducted a study of hydrazine vapor detonations in a stainless-steel pipe of 150 mm ID, 7 mm wall thickness, and 1.75 m length [1258]. Detonations of hydrazine vapor were observed at pressures from 120 kPa all the way down to the lowest initial test pressure of 0.5 kPa. The results of these tests and efforts to shore up the experiments with a theory of detonation wave propagation are discussed in detail in Section 4.5.1. For a safety engineer, the most significant and surprising finding is the very low pressure down to which hydrazine vapor continues to be a detonation hazard.

In continuation of the vapor-phase detonation tests at NASA WSTF, detonation cell size, pressure, and velocity for hydrazine vapor and diluent gas mixtures were determined as a function of pressure and hydrazine and diluent concentrations (expressed as vol.-%) [2174]. Tests were conducted in the same horizontal detonation tube heated to 400 K. Hydrazine vapor and diluent gas mixtures and air mixtures were tested at initial pressures of 100, 50, and 10 kPa (14.5, 7.25, and 1.45 psia). Five diluents

were studied: nitrogen, helium, hydrogen, ammonia, and butane. All the diluents, except for helium and butane, are decomposition products of hydrazine and are expected to be present in most decomposing hydrazine systems. Helium, which is used as a pressurant or purge gas in some propulsion systems, could be present in in-flight systems. While the earlier tests used an oxygen/acetylene donor section, mixtures were now initiated using a commercially available blasting cap with an energy output of approximately 1735 J. Detonation velocities and pressures were measured using high-speed piezoelectric pressure transducers. Detonation cells were measured using the smoked-foil technique described earlier. It was concluded that the relative ranking of diluents correlates to the ratio of specific heats ( $C_p/C_v = \gamma$ ). Diluents with a high  $\gamma$  such as helium required a much higher concentration to prevent a detonation of the hydrazine vapor than diluents with a low  $\gamma$  such as butane. For instance, hydrazine vapors required dilution with at least 80% helium to become non-detonable, but only 10% butane would do the same job. The go-no go boundaries were bracketed by obtaining at least three positive and three negative tests on either side of the boundary. The detonation tube was 150 mm (6 in.) diameter and 2.4 m (6 ft) long. Excessive air-hydrazine interaction prior to firing a detonator made the air/hydrazine results very questionable. By the time the temperature had equilibrated in the chamber, most of the oxygen had already been consumed and the air boundaries were very similar to the nitrogen boundaries.

The detonation characteristics of hydrazine vapor have been compared to those of oxygen/hydrazine, oxygen/hydrogen, and other combustible mixtures [1259]. Hydrazine vapor detonations had the lowest cell diameter, along with oxygen/ethylene mixtures. Hydrazine vapor/ammonia mixtures containing less than 74% hydrazine could not be detonated [2175].

The hazard potential associated with hydrazine vapor has prevented thorough studies of the critical diameter of detonation propagation, and minimum ignition energy up to this time. Likewise, data on the effect of water addition on the vapor-phase detonation velocity and pressure-temperature threshold of detonability could not be found.

Hydrazine vapors are explosive even in mixtures with water and residual acetone. Bare steam coils at 533 K can initiate a hydrazine vapor decomposition explosion in a distillation column [1917]. The resulting decomposition dislodged all trays in the column but did no damage to the shell.

#### 8.4.3 Condensed-Phase Explosions and Detonations with Hydrazine

Many of the proposed and actual uses of hydrazines are in immediate proximity to explosive actuators for explosion-operated valves or for separation of rocket stages. As with any energetic fluid or solid, the energy content of hydrazine blends can be increased only up to a certain limit. If that limit is exceeded, the material becomes detonable. This is vividly illustrated by the change in detonability resulting from the addi-



tion of HN to hydrazine. Quite frequently the scale effect is overlooked in determining the detonability of energetic compounds and mixtures. For instance, a hydrazine/hydrazinium nitrate mixture may not be detonable in a 25-mm tube but may become detonable when stored in bulk quantities in 55-gal barrels.

#### 8.4.3.1 Detonability of Liquid or Frozen Hydrazine

The kinetics and fluid dynamics of reactions enabling the propagation of a detonation wave in hydrazine vapor or hydrazine liquid have been summarized in Section 4.5 along with other modes of decomposition of hydrazine. There is some overlap between these two sections. If the publications referenced here have the words *compression* or *adiabatic* in the title, they may be cited in both locations. If the publications deal with the propagation of shock waves in detonable media, they have been referenced in Section 4.4, including references such as [1266–1270].

Attempts at USBM to determine the detonability of liquid hydrazine by means of the Mettengang recorder were not successful because the material is not detonable [1408]. One test in ambient conditions in a steel tube, one test in ambient conditions in a polystyrene tube, and two tests in steel tubes at 378 K were all negative. A comparison test was made in a steel tube filled with water instead of hydrazine. The amount of damage by the army special blasting caps (a significantly stronger detonator than the standard No. 8 cap) to the steel tube was identical for water and hydrazine. The tube geometry was 18.5 cm (7.25 in.) long with a diameter of 2.2 cm (0.87 in.). The wall thickness of the stainless-steel tubes was 1.6 mm (0.0625 in.), but the ends of the tubes were not sealed hermetically. It may be that hot liquid hydrazine when initiated in confinement would exhibit more destructive force than in the unconfined stoppered tube test conducted at USBM.

The USBM liquid-phase detonability tests were repeated by other investigators with essentially identical results [2176]. Liquid hydrazine contained in a 15-mm-diameter, 0.3-mm-wall-thickness aluminum tube could not be detonated by an ordinary (“Briska”) detonator. Another sample in a 16-mm-diameter, 2-mm-wall steel tube would not even detonate if it was boosted by 20 g of NPMn95/5 (a mixture of 95% PETN and 5% mononitronaphthalene).

When liquid hydrazine was passed through heated tube sections to determine the maximum heat flux before burnout, frequent explosions were observed [283]. Based on high-speed cinematography, the tube would fail within less than 5 ms. It has been suspected that liquid hydrazine may have participated in these explosions, but no conclusive proof could be offered. The detonation of the vapor bubble in the boiling film may have been sufficiently powerful to rupture the tube.

Other tests of detonability of hot hydrazine, MMH, and MHF-5 in 20-cm (8-in.) × 2.2-cm (0.9-in.)-ID tubes showed that none of the three fuels will propagate a detonation [2161]. Testing was done in tubes made from CRES-304, -316, -347, Inconel X, Haynes-25, and Hastelloy X to study the contributions of container materials to detonability at 422–477 K (300–400 °F). There was no dependence of

detonability on container material because all tests were negative. Initiation was with a 50-g pentolite booster. In one test with hydrazine in CRES-304L at 477 K, the tube fragmented into large pieces. The test was then repeated with a longer, 76-cm (30-in.) tube, but no propagation occurred. In another case, a hydrazine-filled CRES-304 tube exploded at 490 K (422 °F) before the detonator could be activated. In total, 16 tests with hydrazine, 7 with MHF-5, and 4 with MMH at elevated temperatures were all negative. In a subsequent test series, liquid preheated hydrazine was pushed into an even hotter dead-ended tube simulating the hot restart of a hydrazine engine. In this case, a dependence of sensitivity on the material of construction was noted. It has been shown that 373 K (212 °F) hot hydrazine pushed into CRES-304L tubes will explode if the tube is hotter than 560 K (550 °F). In 17-7PH, hydrazine will begin to explode even at 500 K (442 °F).

Some of the early experimenters may have used poor-quality hydrazine in their detonability tests. Water and aniline as diluents and inhibitors might desensitize hydrazine. There was concern that the high-purity hydrazine used as monopropellant in most spacecraft may be more sensitive than the water-containing hydrazine used by early experimenters. In earlier tests [2177], the hydrazine contained 4% water. Hydrazine used by USBM was only 98% with the composition of the remaining 2% unknown [1408]. It marked an improvement in hydrazine quality control when MIL-P-26536D monopropellant-grade hydrazine was used for liquid hydrazine detonability tests at NASA WSTF [2178]. That specification at the time of these tests allowed up to 1% water. Two series of detonability tests were conducted, one in CRES-304 tubing with 13-mm (0.5-in.) OD and 0.89-mm (0.035-in.) wall thickness in lengths of 25.4, 50.8, and 76.2 cm (10, 20, and 30 in.), the other in a modified card-gap apparatus using 300-series steel tubes (5.08 cm [2.0 in.] ID, 0.55 cm [0.218 in.] wall thickness, 30.48 cm [12 in.] length) welded to a 0.95-cm (0.375-in.)-thick witness plate. In the 13-mm-diameter tube test, the donor charge was taped to the bottom of the tube, separated from the hydrazine by a Teflon foil. In the modified card gap test, the donor charge consisting of 223 g of C-4 was inserted on top of the hydrazine sample. In none of the tests, neither in the 13-mm nor in the 6-cm-OD tube, was there any indication of hydrazine undergoing a detonation. The amount of damage to the tubes was like that observed in control tests with water [2179]. Sensitized liquid hydrazine detonation studies where hydrazine was mixed with gas bubbles and micro balloons did not result in any condensed-phase detonations either [2180].

There are several hydrodynamic codes used for the prediction of detonation properties of explosives. One of the most frequently computer programs is that based on the BKW EOS described by Mader [2181]. The program was available on a CD-ROM disc attached to one of the editions of his book. Mader used hydrazine and HN as textbook examples and sample cases to demonstrate the capabilities of this program. This program was used to calculate detonation and shock Hugoniot wave properties of liquid hydrazine [1266–1268].

An attempt was made to calculate the parameters of the shock compression of liquid hydrazine within the framework of schemes developed for describing the compression of organic liquids and liquefied gases. In cases where the mass velocities behind shock fronts do not exceed  $3.1 \text{ mm}/\mu\text{s}$ , it may be implemented under the assumption of brief retention of the initial compound (hydrazine, in our case) behind a shock front [1274]. The detonation velocities of hydrazine solutions spiked with such explosives as nitromethane and hydrazine nitrate correspond to the destruction of hydrazine up to ammonia and nitrogen, which is accompanied by a noticeable energy release. The estimates performed demonstrated the possibility of the detonation of liquid hydrazine with a velocity of  $8 \text{ mm}/\mu\text{s}$ , during which the heating of the substance behind a shock front (approximately 2000 K) is comparable to those observed behind a shock front during the detonation of liquid explosives [1272, 1273]. The detonation of hydrazine solutions with added explosives (nitromethane or HN) transforms the hydrazine to ammonia and nitrogen with the release of a significant amount of energy [1271]. It is possible to detonate liquid hydrazine at a velocity of  $8 \text{ mm}/\mu\text{s}$  by heating the substance behind the shock wave to  $\sim 2000 \text{ K}$ . The activation energy of hydrazine decomposition is  $222.6 \text{ kJ/mol}$  ( $53.2 \text{ kcal/mol}$ ) (which is a factor of 1.4 higher than the activation energy of other liquid explosives) with large critical diameters ( $>1 \text{ m}$ ) of detonation.

NASA WSTF simulated conditions suspected to lead to the failure of an ATLAS-CENTAUR upper stage which uses liquid oxygen and liquid hydrogen as its main propellants and hydrazine for roll control and propellant settling maneuvers [2182, 2183]. It was suspected that frozen oxygen or frozen hydrazine had formed in a groove adjacent to the interstage adapter ring and was initiated to detonation by firing the adjacent flexible linear shaped charge which is done for stage separation. Tests were conducted with frozen oxygen or frozen hydrazine in a vacuum chamber at 20 Pa and the energy release was measured with a ballistic pendulum. Hydrazine froze readily and formed stalagmites in the catch basin below the leak. Some augmentation was noted with frozen oxygen or but only slight augmentation with frozen hydrazine. A mixture of frozen oxygen and frozen hydrazine was not tested.

#### 8.4.3.2 Detonability of Hydrazine Mixtures

There are many hydrazine mixtures besides the well-studied hydrazinium nitrate/hydrazine/water system that are detonable. Many of these have been considered or patented or actually commercially used as liquid explosives.

### 8.5 Drop-Weight and Bullet Impact Sensitivity of Hydrazine

The sensitivity of energetic compounds can be determined by dropping a weight on it, dropping the entire container from a predetermined height (typically  $12.16 \text{ m} = 40 \text{ ft}$ ), or by impacting it with a projectile.

### 8.5.1 Drop Weight Impact Sensitivity of Hydrazine

In 10 consecutive identical trials where a 5-kg weight was dropped from 1 m onto a one-drop sample of anhydrous hydrazine or 85% hydrazine hydrate, no explosions could be observed [1408]. The USBM drop-weight tester was modified, and no brass cups were used in this test. Instead, the sample was held in a depression in the anvil. Five negative tests out of five with a 5-kg weight from 3 m and one droplet of liquid hydrazine contained in a Bourges capsule showed that the material is not impact shock sensitive [2176].

### 8.5.2 Bullet Impact Sensitivity of Hydrazine

In rifle bullet impact tests, *n*-propyl nitrate, which was tested as a baseline material for comparison, exploded with all three types of ammunition used (20 mm incendiary, 20 mm high-explosive incendiary, and .30 caliber rifle) [2184]. In contrast, hydrazine and alkylhydrazine/24 HN/10 H<sub>2</sub>O monopropellant in 25% or 95% filled 3.78-L (1-gal) aluminum containers were exploded by high-explosive ammunition only, but not by the incendiary type or the .30 caliber rifle bullets. *n*-Propyl nitrate (and presumably also IPN) would be more hazardous as a propellant in a military battlefield situation where bullet impact must be anticipated. In other projectile impact tests, hydrazine and UDMH were shot at while stored in aluminum, stainless-steel, or titanium tanks [2185]. The stainless-steel tank was made from 89-mm (3.5-in.)-diameter tubing by welding on end caps and a similar aluminum tank was made from 102-mm (4-in.)-diameter tubing. The thickness of the end caps where the impact occurred was 0.8 mm (0.031 in.) for both tests. Steel spheres (5.6 mm = 0.219 in.) were accelerated to 1763 m/s and aimed at the end caps. No reaction was observed between the hydrazines and the tank wall in any of the tests, in contrast to liquid oxygen, which started a violent reaction in all materials tested and perforated by bullets.

### 8.5.3 Hypervelocity Projectile Impact Sensitivity of Hydrazine

The HAPS fragmentation event demonstrated the importance of passivating spacecraft and upper stages at the end of missions by draining all propellants from the tanks [2186, 2187]. It is not certain what caused the breakup of the tank after 25 months in orbit, but the impact of a piece of orbital debris is one explanation for the catastrophic event [2127]. After this event, federal authorities at the Federal Aviation Administration temporarily suspended the launch license for PEGASUS XL until OSC agreed that spent HAPS stages should be de-orbited or operated to full exhaustion of all propellant.

The ACS of the European heavy launcher ARIANE 5 is a hydrazine monopropellant system that includes two or more bladder tanks pressurized by nitrogen. Depending on the mission, a residual pressure of some 10 to 20 bar with several kilograms of hydrazine may remain at the end of the mission in the second stage adapter. In order to avoid any orbital debris generation, the explosion threshold pressure was determined

theoretically, then demonstrated experimentally [2129]. This pressure is defined by the behavior of the tank under the impact of a micrometeoroid or a piece of space debris: for pressures above it, the tank explodes; otherwise, it is simply punctured. A theoretical analysis based on fracture mechanics showed that the crack propagation would become divergent for pressures in the range of 20 to 25 bar. A worst case was determined, and a test was performed with a tank pressurized at 18 bar. The impacting particle was a 1-mm-diameter aluminum sphere, launched at a velocity of 9 km/s. The tank did not explode, and the size of the resulting hole was close to the one predicted (3.2 mm in diameter vs. 3 to 3.5 predicted).

Reactive molecular dynamics was used to estimate the risk of detonation in a liquid hydrazine layer. This calculation used the ReaxFF force field and the MD-solver LAMMPS to follow shock compression and decomposition of liquid hydrazine. The force field was initially developed for nitramine explosives but has been successfully applied to hydrazine [1373]. Simulations of a 3.5-mm aluminum spherical debris particle at a velocity of 14 km/s relative to a hydrazine tank showed that the degree of damage was strongly dependent on tank temperature and, hence, on the satellite thermal configuration at its end of life. The sample case was calculated for a typical hydrazine monopropellant propulsion system with a 50-cm-diameter titanium diaphragm tank and typical end of life residuals stored at 5 bar and 293 K (20 °C), including hydrazine vapor detonation initiated by the penetrating projectile.

A computational model for estimating the effect of hypervelocity impact from orbital debris particles on non-shielded propellant and pressurant tanks was based on Eulerian hydrocode and developed to model, first, penetration and shock wave formation in the propellant and, second, subsequent detonation wave propagation and interaction with the tank wall [2188].

## 8.6 Cap Sensitivity and Card Gap Sensitivity of Hydrazine

Card gap tests of hydrazine, hydrazine hydrate, or UDMH in heavy-walled (13-mm = 0.52-in. wall) stainless-steel tubes using two 50-g tetryl pellets as booster were negative, even at pre-test temperatures only a few degrees apart from the boiling points of the liquids [2189].

The results of zero-attenuation detonability tests in the  $\text{N}_2\text{H}_4/\text{HN}/\text{H}_2\text{O}$  system by Dwiggins and Larrick [2177] were confirmed in later tests [244]. The objective of these tests was to look for the possibility of LVD propagation in  $\text{N}_2\text{H}_4/\text{HN}/\text{H}_2\text{O}$  mixtures, which was considered an added hazard when handling bulk quantities of such propellants. Under the conditions tested at SRI, none of the mixtures containing up to 26% HN exhibited LVD. In addition to the standard 50-g tetryl charge for card gap tests, several shots were conducted with doubled booster charges of 100 g tetryl. Some tests were also done at elevated temperature and/or pressure. The results are summarized in Tables 83 and 84.

**Table 83:** Gap test results at 297 K (24 °C) on hydrazine/hydrazinium nitrate/water mixtures.

| Mixture<br>H/HN/H <sub>2</sub> O | HVD Tests          |                |        |                    |                |        | LVD Tests          |                |        |
|----------------------------------|--------------------|----------------|--------|--------------------|----------------|--------|--------------------|----------------|--------|
|                                  | 50-g Tetryl        |                |        | 100-g Tetryl       |                |        | 100-g Tetryl       |                |        |
|                                  | Tube I.D.<br>(in.) | Gap<br>(Cards) | Result | Tube I.D.<br>(in.) | Gap<br>(Cards) | Result | Tube I.D.<br>(in.) | Gap<br>(Cards) | Result |
| 74/26/0                          | 1                  | 0              | Go     | 0.5                | 25             | No go  | 0.5                | 25             | No go  |
| 74/26/0                          | 1                  | 5              | Go     | 0.5                | 1              | No go  | No evidence of LVD |                |        |
| 74/26/0                          | 1                  | 7              | Go     | 1                  | 0              | Go     | —                  | —              | —      |
| 76/24/0                          | 1                  | 1              | No go  | 0.5                | 25             | No go  | 0.5                | 25             | No go  |
| 76/24/0                          | 1                  | 4              | No go  | 0.5                | 1              | No go  | No evidence of LVD |                |        |
| 76/24/0                          | 1                  | 7              | No go  | 1                  | 0              | No go  | —                  | —              | —      |
| 78/22/0                          | —                  | —              | —      | 1                  | 0              | No go  | No evidence of LVD |                |        |
| 69/26/5                          | 1                  | 0              | Go     | 0.5                | 1              | No go  | 0.5                | 15             | No go  |
| 69/26/5                          | 1                  | 5              | No go  | —                  | —              | —      | No evidence of LVD |                |        |
| 71/24/5                          | 1                  | 1              | No go  | 0.5                | 1              | No go  | No evidence of LVD |                |        |
| 71/24/5                          | —                  | —              | —      | 1                  | 1              | Go     | —                  | —              | —      |
| 73/22/5                          | —                  | —              | —      | 1                  | 0              | No go  | No evidence of LVD |                |        |

I.D. = inner diameter

Data source: [244]

**Table 84:** Hydrazine/hydrazinium nitrate/water mixtures gap test results at elevated temperatures and pressures.

| Mixture<br>H/HN/H <sub>2</sub> O | Gap,<br>cards | Card<br>material      | Temperature |    | Pressure |      | Tube        | Tetryl | Test<br>type | Result        |
|----------------------------------|---------------|-----------------------|-------------|----|----------|------|-------------|--------|--------------|---------------|
|                                  |               |                       | K           | °C | kPa      | psia | I.D.<br>in. | g      |              |               |
| 76/24/0                          | 3             | Polyacryl-<br>acetate | 322         | 49 | 103      | 15   | 1           | 50     | HVD          | No detonation |
| 76/24/0                          | 25            | Polyacryl-<br>acetate | 322         | 49 | 103      | 15   | 0.5         | 100    | LVD          | No detonation |
| 76/24/0                          | 3             | Steel                 | 322         | 49 | 3447     | 500  | 1           | 50     | HVD          | No detonation |
| 76/24/0                          | 3             | Steel                 | 296         | 23 | 3447     | 500  | 1           | 50     | HVD          | No detonation |
| 76/24/0                          | 3             | Steel                 | 322         | 49 | 3447     | 500  | 1           | 100    | HVD,<br>LVD  | No detonation |
| 76/24/0                          | 3             | Steel                 | 296         | 23 | 3447     | 500  | 1           | 100    | HVD,<br>LVD  | No detonation |
| 71/24/5                          | 3             | Polyacryl-<br>acetate | 322         | 49 | 103      | 15   | 1           | 50     | HVD          | No detonation |
| 71/24/5                          | 25            | Polyacryl-<br>acetate | 322         | 49 | 103      | 15   | 0.5         | 100    | LVD          | No detonation |

I.D. = inner diameter

Data source: [244]

HVD tests were conducted in 2.54-cm (1-in.)-diameter, 7.5 cm (3 in.) long tubes, whereas LVD tests used narrower (1.27-cm = 0.5-in.) and longer (10-cm = 4-in.) tubes with thinner witness plates. In agreement with earlier reports [2177], the 24% HN mixture at one card was negative, whereas the 26% HN mixture at zero cards was positive with the standard JANNAF booster size. However, when the booster size was doubled, even the 24% HN mixture was made to go at zero cards in the wider tube but failed to propagate in the narrower tube. The same was true of the  $71\text{N}_2\text{H}_4/24\text{HN}/5\text{H}_2\text{O}$  mixture. In steel confinement and pressurized to 3.44 MPa (500 psig), the  $24\text{HN}/76\text{N}_2\text{H}_4$  mixture did not detonate with either the 50-g or the 100-g tetryl booster, not even at higher temperature (322 K).

In summary, only the mixtures containing 26% HN were initiated to HVD and then only with a gap of less than 10 cards. Nitromethane, a liquid considered relatively insensitive and at one time shipped in tank cars (prior to several severe LVD accidents), has a card sensitivity of positive at 19 cards under these same conditions. Mixtures with more than 26% HN may well exhibit LVD, but this regime was not retested. The SRI tests essentially confirmed the validity of the boundary line as drawn in *Encyclopedia of Oxidizers*, in the chapter “Hydrazinium Salt Oxidizers,” Figure 14.

When evaluating initially non-detonable  $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3/\text{H}_2\text{O}$  mixtures as rocket or gas generator propellants, one must keep in mind that under adverse conditions of a spill or leak at high ambient temperatures and low ambient relative humidity the residue may become more concentrated in HN and reach detonable concentrations [2190]. The mixture may also absorb water from atmospheric moisture and carbon dioxide and neutralize itself. Even if the HN concentration in the residue should rise to the detonable level (25 to 30%), there must be a very energetic source of ignition (e.g., detonator with 50-g tetryl booster) before a detonation hazard exists. The booster itself would already cause a significant amount of damage without HN present. At concentrations beyond 40% HN, the mixture becomes shock sensitive to impact. The concern about inadvertent enrichment of HN by evaporative loss of one of the propellant components is more prevalent with ternary propellants of the MHF-5 type, which contain MMH, HN, and hydrazine. MMH is more volatile than hydrazine, and the composition of MHF-5 monopropellant is more likely to change than that of ternary propellants of the HPB-1808 or HPB-2107 type.

## 8.7 Explosive Yield Tests with Hydrazine

Several methods exist for measuring the explosive yield of explosives. The most popular test is the Trauzl block test, where a sample of explosive is detonated in a cavity in a lead block and the enlargement of the cavity is measured by filling it with water before and after the test. Other methods, widely used by the military in measuring the yield of weapons, measure the overpressure of a shock wave propagating through air

at a safe (safe for the pressure gauge, not for the human observer) distance from the event.

The Trauzl block (= lead block) test is not a sensitivity test, but a performance test. Lead block tests of explosives and suspected explosives with PETN or picric acid as booster showed that the utilization coefficient was 69–84 for liquid hydrazine compared to 94 for TNT [2176]. Ballistic mortar tests gave only very scattered results. Medard concluded that some hydrazine decomposed in these tests, but it did not detonate.

The explosive yield as measured by the increase of cavity volumes in lead blocks depends on the mixture ratio of hydrazinium(1+) nitrate (HN) oxidizer and hydrazine fuel. The heat of explosion increases with increasing HN content. The explosive yield as the product of heat of explosion and the amount of gas produced thus remains constant over a wide range of compositions [2191]. The lead block volume as a function of composition maximum is wider than what is commonly observed with carbon/oxidizer-based explosives. Maximum Trauzl block indentations were obtained with  $\text{N}_2\text{H}_4/\text{N}_2\text{H}_5\text{NO}_3$  mixtures away from the stoichiometric composition. The cavity volume increased from 370 to a maximum of  $430\text{ cm}^3$  by increasing the HN content from 40 to 60%. Beyond 60% HN, the lead block cavity volume dropped back to  $340\text{ cm}^3$  at 100% HN. Similar mixtures with hydrazinium(1+) perchlorate achieved higher maximum indentations,  $470\text{ cm}^3$  instead of  $430\text{ cm}^3$ .

In another test series, using 2-mL samples in a lead block made from a 6-mm (0.25-in.) hole drilled into a cylinder 90 mm (3.5 in.) in diameter by 178 mm (7 in.) in length, Trauzl block indentations were measured for 16 hydrazine/hydrazinium nitrate/water mixtures with 15–50% HN and 3–10% water [242]. Initiation was achieved with a Hercules Mark 35 Mod 1 blasting cap. For comparison, the data in Table 85 also show results obtained with 0.5 and 1 g of TNT as a baseline.

## 8.8 Rapid (Adiabatic) Compression Sensitivity of Hydrazine

Most other monopropellants, organic nitro compounds and nitrate esters, are known to be sensitive to adiabatic compression. With those compounds, the sudden temperature increase in a collapsing bubble is enough to initiate detonation and, at the same time, provides a mechanism for propagation of low-velocity detonation (LVD) throughout the sample. A monopropellant of that type that has not been thoroughly degassed or is even filled with bubbles from transportation vibrations/sloshing or transfer from one container to another will propagate LVD once a source of initiation is present. In contrast, liquid bubble-free bulk hydrazine could not be initiated to detonation by rapid or adiabatic compression. However, hydrazine vapor (inevitably present above the liquid phase during high-temperature tests) may detonate when compressed at high rates. Under most practical conditions it will be difficult to elim-



**Table 85:** Trauzl block test data.

| Test No. | Material or solution <sup>b</sup> No. | Composition, Mass-%           |                                               |                  | Volume of cavity, mL | Volume increase, mL | Volume increase due to test material, % |
|----------|---------------------------------------|-------------------------------|-----------------------------------------------|------------------|----------------------|---------------------|-----------------------------------------|
|          |                                       | N <sub>2</sub> H <sub>4</sub> | N <sub>2</sub> H <sub>5</sub> NO <sub>3</sub> | H <sub>2</sub> O |                      |                     |                                         |
| 1        | Blasting Cap <sup>a</sup>             | —                             | —                                             | —                | 41.3                 | 36                  | —                                       |
| 2        | Cap + 0.5-g TNT                       | —                             | —                                             | —                | 55.1                 | 50                  | 14                                      |
| 3        | Cap + 1.0-g TNT                       | —                             | —                                             | —                | 118.5                | 96                  | 60                                      |
| 4        | 31                                    | 81.9                          | 15.0                                          | 3.11             | 52.1                 | 47.1                | 11.1                                    |
| 5        | 32                                    | 76.8                          | 15.3                                          | 7.86             | 59.9                 | 54.9                | 18.9                                    |
| 6        | 33                                    | 77.6                          | 19.4                                          | 3.05             | 54.5                 | 49.5                | 13.5                                    |
| 7        | 34                                    | 76.6                          | 19.0                                          | 6.96             | 52.2                 | 47.2                | 11.2                                    |
| 8        | 35                                    | 72.7                          | 24.3                                          | 2.99             | 83.0                 | 78.0                | 42.0                                    |
| 9        | 36                                    | 64.8                          | 24.7                                          | 10.6             | 49.0                 | 44.0                | 8.0                                     |
| 10       | 37                                    | 68.2                          | 28.8                                          | 2.94             | 62.0                 | 57.0                | 21.0                                    |
| 11       | 38                                    | 65.2                          | 28.2                                          | 6.66             | 53.2                 | 48.0                | 12.0                                    |
| 12       | 39                                    | 63.9                          | 33.8                                          | 2.88             | 93.5                 | 88.5                | 52.5                                    |
| 13       | 40                                    | 57.8                          | 35.1                                          | 7.11             | 80.5                 | 75.5                | 39.5                                    |
| 14       | 41                                    | 59.2                          | 38.0                                          | 2.83             | 140.0                | 135.0               | 99.0                                    |
| 15       | 42                                    | 53.2                          | 41.4                                          | 5.37             | 91.0                 | 86.0                | 50.0                                    |
| 16       | 43                                    | 53.9                          | 43.4                                          | 2.76             | 134.0                | 129.0               | 93.0                                    |
| 17       | 44                                    | 44.8                          | 44.8                                          | 10.4             | 114.0                | 109.0               | 73.0                                    |
| 18       | 45                                    | 48.7                          | 48.6                                          | 2.69             | 157.0                | 152.0               | 116.0                                   |
| 19       | 46                                    | 40.4                          | 49.9                                          | 9.69             | 99.3                 | 94.3                | 58.3                                    |

<sup>a</sup> Hercules Mark 35 Mod 1 blasting cap<sup>b</sup> In each case, 2 mL solution was used

Data source: [242]

inate contributions by hydrazine vapor bubbles when hydrazine is compressed suddenly, in particular in two-phase systems.

Rapid pressurization may occur when hydrazine flows (is dropped into) into initially empty, evacuated propellant distribution lines. Rapid pressurization may also occur in a two-phase system when the flow of liquid hydrazine is suddenly stopped by closing a valve, but the momentum of the flowing liquid continues to compress the liquid/vapor/gas mixture (“water hammer”). There have been incidents where rapid pressurization of hydrazine has caused rupturing of injector passages in STS APU gas generators and rupturing of system manifold lines in ground tests of satellite flight systems. This phenomenon was at one time called adiabatic compression detonation, but in recognition of the fact that substantial amounts of heat are lost to the walls of the apparatus and that the test methods are really non-adiabatic, other investigators called it rapid compression detonation. Some investigators question whether a full-blown detonation can develop in narrow tubes and refer to it as rapid compression deflagration or rapid compression thermal runaway reaction. Regardless of what it is

called, the end result can be very destructive. The problem has been thoroughly researched (mostly by NASA WSTF), and there are many reports on rapid compression of hydrazine. Occasionally the same equipment used for hydrazine rapid compression tests was also used for MMH tests, and there is sporadic mention of MMH in the context of rapid compression and vapor detonations. What is lacking is a computer model that, once provided with the geometry of the propellant manifold, the operating conditions (temperature, manifold fill gas, manifold fill pressure, feed pressure) will predict whether or not rapid compression deflagration of hydrazine is likely to occur. Several hydrodynamic computer models will predict water hammer or surge pressure, but none will raise a red flag if the conditions approach pressurization rates and bubble temperatures/froth conditions under which explosions have been observed. These computer models have been verified using water as the test fluid. Water hammer pressures can create sudden pressure spikes even in water that are sufficiently energetic to rupture burst discs, filters, or damage valve seats and pressure transducer membranes. This can happen, as the name implies, even with non-reactive fluids like water. Because hydrazine has a lower compressibility than water, water hammer or, rather, “hydrazine hammer” pressure spikes are more severe than those observed in model tests with water. In addition to purely hydraulic damage, hydrazine froth can decompose under adverse conditions and cause additional, sometimes destructive, pressure spikes.

This problem is not unique to hydrazine monopropellant systems and would occur regardless of whether a monopropellant or bipropellant thruster was connected to the exit end of the propellant supply line. Because this problem is not unique to monopropellant systems, and because we did not want to repeat the discussion of this topic in future sets of *Encyclopedia of Rocket Propellants*, the effects of surge flow and water hammer pressure spikes are summarized here in *Encyclopedia of Liquid Fuels*.

Many publications do not make a sharp distinction between water hammer and surge flow. A water hammer would compress bubbles in recessed areas as a flowing column of liquid comes to a sudden stop (e.g., by abruptly closing a valve in a system that is already mostly filled with hydrazine). Surge flow occurs when an initially empty or gas-filled manifold is filled with propellant for the first time and the liquid column runs into a dead-ended cavity, compressing the contents of the cavity ahead of it. Either situation can cause very high-pressure spikes because the compressibility of hydrazine is only half that of water.

The rapid compression sensitivity of monopropellants has often been called adiabatic or isentropic compression sensitivity. Truly adiabatic conditions can only be achieved in theoretical model calculations. Under real-world conditions, the walls of the apparatus in which the rapid compression experiment is conducted will absorb part of the energy, and then it is no longer truly adiabatic. In recognition of the adiabatic losses, which depend on the surface:volume ratio and the materials of construction of the apparatus, this property is more accurately called rapid compression sensitivity.

### 8.8.1 Rapid (Adiabatic) Compression Test Methods

The results of rapid compression testing with hydrazine differ substantially depending on the test apparatus used. Several test techniques have evolved over the course of years, and there is no generally accepted test method that serves all foreseeable hazard conditions equally well. The following sections and data in Table 86 are a brief summary of test methods that have been used for rapid compression testing of hydrazine propellants and other energetic liquids at one time or another. Unfortunately, the results from these different tests do not correlate very well, and in some cases the only way to obtain a definitive answer is to test a replica of the actual satellite manifold underground conditions, in particular if additional energy inputs have to be considered such as blow-by of hot gases from pyrotechnic valves.

**Hydrazine Rapid (“Adiabatic”) Compression Sensitivity Fundamentals.** The phenomenon of hydrazine rapid (“adiabatic”) compression sensitivity is still not quite understood despite all the effort that has gone into understanding it over a period of 25 years. Many publications on hydrazine rapid (“adiabatic”) compression sensitivity have been released by various authors, but nobody has ever attempted to arrange the sometimes conflicting test results in a systematic fashion. The difficulty arises from the different experimental techniques used at different times and at different organizations. Even the atmospheric pressure at the test site can influence the results, with experiments at high-altitude locations giving different results from those conducted at sea level. Standardization (using an ASTM standard test method) was once attempted, but without success.

The difficulty in arriving at a clear yes or no answer when applying the experience database to a given spacecraft design and manifold filling procedure is due to the large number of variables that can affect rapid compression initiation thresholds with hydrazine. The results of rapid compression tests with hydrazine may be influenced by the following factors:

- Compression ratio
- Rate of pressurization
- Initial downstream system (= “cavity”) pressure
- Propellant feed pressure
- Feed system line diameter
- Cavity diameter
- Wall thickness of cavity
- Pre-test separation between hydrazine and cavity (none, ball valve, pyro valve, burst disk, Teflon foil)
- Initial cavity fill gas or vacuum
- Presence of condensable vapors (water, cleaning solvents) in cavity
- Initial propellant temperature
- Initial hardware temperature
- Degree of gas saturation of propellant
- Type of gas propellant is saturated with

**Table 86:** Rapid (adiabatic) compression test methods.

| Test Method                              | Organization                | Propellants tested                                | Tube diameters, I.D./O.D., in. | Pressurization rate, psi/s | Remarks                                      | Reference   |
|------------------------------------------|-----------------------------|---------------------------------------------------|--------------------------------|----------------------------|----------------------------------------------|-------------|
| Adiabatic compression (piston apparatus) | ICRPG – JANAF               | N <sub>2</sub> H <sub>4</sub> , UDMH              |                                |                            | Obsolete                                     | [2192]      |
| U-Tube                                   | Aerojet                     | N <sub>2</sub> H <sub>4</sub> , MMH, MHF-5, MHF-7 | 0.18/0.25                      | 300000                     | Effect of materials, 10 metals tested        | [2161]      |
| U-Tube                                   | Sundstrand-Hazards Research | N <sub>2</sub> H <sub>4</sub>                     | 0.18/0.25                      | 25000, 50000               | STS-APUGG, 11 metals tested                  | [2193–2195] |
| U-Tube                                   | Sundstrand-Hazards Research | N <sub>2</sub> H <sub>4</sub>                     | 0.18/0.25                      | 40000 to 360000            | CRES-304L, 131 tests, He vs. GN <sub>2</sub> | [2196]      |
| Diaphragm separator                      | Sundstrand-WSTF             | N <sub>2</sub> H <sub>4</sub>                     | 0.63/0.75                      | up to 12500000             | CRES-304L                                    | [2197]      |
| Diaphragm separator – straight tube      | NASA WSTF                   | N <sub>2</sub> H <sub>4</sub>                     | 0.63/0.75                      | up to 17000000             | CRES-304L                                    | [2198]      |
| Straight tube                            | NASA WSTF                   | N <sub>2</sub> H <sub>4</sub>                     | 0.25, 0.375 and 0.5 O.D.       |                            | CRES-304L                                    | [2199]      |
| Piston apparatus                         | NASA JSC                    | N <sub>2</sub> H <sub>4</sub>                     | 0.25 and 0.5 O.D.              |                            | CRES-304L                                    |             |

- Surface : volume ratio at dead end of cavity
- Number of flow obstacles (orifices, tees, ells, viscojets, filters, valves, reducing nipples) in feed lines
- Number of flow obstacles (orifices, tees, ells, viscojets, filters, valves, reducing nipples) in cavity
- Purity of hydrazine propellant (aniline, water)
- Resonant effects of pressure oscillations
- Colliding countercurrent pressure waves

The largest source of data are the test records of NASA WSTF. Some of these have been published in a number of presentations and handbooks [1912, 2198, 2199], but it appears that there is a large amount of unpublished data that should be critically reviewed for their relevance in the design of spacecraft propellant manifolds.

In describing the rapid compression test equipment, it should be mentioned up front that the liquid sample attachment for the Olin Technoproducts drop-weight sensitivity tester is essentially already a bubble rapid compression technique. The sample holder is filled with the liquid sample only halfway, and a bubble (usually an air bubble) is left above the liquid level before inserting the burst disc and carefully torqueing down the lid. The correct torque and use of the correct O-ring will assure that the bubble always has the same size. Failing to apply the correct torque (most often caused by excessive friction in rusted threads) will result in scattered results. Hydrazine cannot be initiated under these conditions (Section 8.5.1) at the limit of hydraulic rupture of the burst disc, whereas isopropyl nitrate is so sensitive that it is often used to calibrate the apparatus.

ICRPG and JANAF (precursor of today's JANNAF) at one time issued a test procedure for adiabatic compression testing with a piston apparatus, but the apparatus was very complex, had too many parts that needed to be machined to close tolerances, and has rarely been used [2192].

Most rapid compression tests were conducted in laboratory settings with single tubes, one tube at a time being filled with hydrazine (see following Section 8.8.1.1). This is not always the case with real-life systems that are filled with hydrazine where rapid compression explosions are feared. These systems may have a multitude of L-bends and T- and cross-shaped-branches leading in different directions and with gradually decreasing diameters. System-level surge flow and rapid compression tests are discussed in Section 8.8.1.2.

#### **8.8.1.1 Single-Tube Rapid (Adiabatic) Compression Tests with Hydrazine**

**Early Model Piston Apparatus.** Hydrazine could not be detonated at the maximum rating ( $144 \text{ kg cm mL}^{-1}$ ) of an adiabatic compression sensitivity apparatus consisting of a gas-driven piston compressing a gas bubble in contact with the liquid propellant [2192]. The energy input was calculated as  $115 \text{ kg cm}$  work applied to a  $0.8\text{-mL}$  air bubble. Nitromethane and alkyl nitrates would detonate at much lower adiabatic

compression stimuli in the same apparatus. It was noted that the pressure rise in the sample chamber was preceded and accompanied by system-induced pressure oscillations. The rate of pressure rise in the first oscillation could be as high as 68 GPa/s ( $10^7$  psi/s). A similar piston apparatus was considered as the standard ASTM test, but it was later rejected.

**U-Tube Apparatus.** An adiabatic compression sensitivity study conducted at Aerojet measured four fuels (hydrazine, MMH, MHF-5, and MHF-7) in contact with 11 metallic materials of construction [2161]. The U-tube apparatus used for these experiments was subsequently adapted for safety investigations by several other research groups. It consisted of a 6.35-mm (0.25-in.)-OD tube bent to the shape of a U 152 mm (6 in.) high and closed on one end by a plug. The propellant sample (3 mL) filled only the lower one tenth of the nitrogen-filled tube. The entire assembly could be lowered by remote control into a temperature-controlled bath prior to the test. The upstream end could be pressurized with nitrogen using a fast-acting valve and a burst disk at a rate of 2064 MPa/s (300000 psi/s). Positive tests were indicated by burst tubes. Propellant-material interaction was apparent in the U-tube adiabatic compression tests. The sensitivity threshold temperature was lower for those metals with catalytic activity (nickel) and known reactivity with hydrazine (aluminum). The metals could be arranged in three hazard groups based on the results. Under adiabatic compression conditions, the threshold temperature limit for explosive decomposition of hydrazine was 377–363 K (217–195 °F) in CRES-321, Hastelloy X, Haynes-25, CRES-316, -347, or -304L (decreasing threshold temperature in this order). In the intermediate group, Inconel X and 17-7PH steel would allow adiabatic reaction at 327 K (130 °F). In aluminum-2014-T6 and 6061-T6, the threshold surprisingly dropped to less than 310 K (100 °F). Neither MMH nor MHF-7 was sensitive to adiabatic compression up to temperatures of 533 K (500 °F). Hydrazine vapor was the most sensitive compound tested; MMH vapor was able to desensitize hydrazine vapor. Whereas hydrazine by itself in CRES-304L would explode on adiabatic compression at temperatures above 366 K (200 °F), the addition of 2.5% MMH raised the threshold temperature to 477 K (400 °F). It was noted that MHF-5 was thermally unstable, and the liquid would sometimes explode during heat-up in a hot bath before the adiabatic compression test could be completed, but MMH contained in MHF-5 stabilized the vapor phase such that vapor-phase adiabatic explosions could not be initiated below 477 K (400 °F). Since the completion of the Aerojet study, there have been fewer investigations on the effect of materials of construction on the threshold of rapid compression deflagrations. It is now assumed that other than through physical properties, such as thermal diffusivity, surface roughness, and yield strength, the wall material has little effect on the rapidly occurring events in the froth zone.

In addition to U-tube tests in which the dead-ended cavity at the end of the tube was at the same temperature as the liquid, Aerojet also conducted several so-called confirmatory tests in which the slug of hydrazine was at 338, 358, or 373 K and it was

pushed into a 7.5-cm-long cavity preheated to 461 to 634 K [2161]. In the case of CRES-304, explosions occurred at 561 and 634 K, but in the case of 17-7PH, explosions occurred at lower temperatures (500, 515, and 555 K). The confirmatory tests were intended to demonstrate that the material of construction is an important factor in adiabatic compression events.

At lower compression ratios and slower compression rates than in the Aerojet tests, no hydrazine detonations were observed in U-tubes [2193–2195]. These tests were conducted to simulate the rapid pressure fluctuations and heat soakback that could be expected for the hydrazine feed system in the Space Shuttle APU. The Hazards Research/Sundstrand test method, also a U-tube adiabatic compression test, was patterned after the Aerojet tests, and the materials tested were those present in the space shuttle fuel system, in particular the fuel pump and the gas generator valve. The Space Shuttle fuel pump was expected to create compression ratios of up to 19:1 and compression rates of approximately 206 MPa/s (30000 psi/s). During previous tests, soakback temperatures of 408 K (275 °F) had been measured in the GGVM valve and near the pump, which might cause a possibly hazardous situation when compressing a hot gas bubble saturated with hydrazine vapor during hot restart.

For the initial Space Shuttle simulation tests, two test conditions were selected, first start and hot restart conditions. The initial start conditions allowed some air in the system. Samples were conditioned at 300 K and were compressed to 3.03 MPa at a rate of 172 MPa/s (25000 psi/s). The gas in the hot restart simulation was nitrogen, the U tube with hydrazine in it was conditioned to 408 K (275 °F), the compression ratio was 20:1, and the compression rate was 345 MPa/s (50000 psi/s). The U tubes were 6.3-mm (0.25-in.) OD, 0.89-mm (0.035-in.)-wall stainless steel. Because not all materials were readily obtained in tube form, some were inserted into the dead-end section of the U tube in the form of sleeves made from approximately 19-mm (0.75-in.)-diameter bar stock into which an axial hole was drilled with a diameter equal to that of the connecting stainless-steel tube. None of the 11 materials tested [CRES-304, CRES-304L, Steel 15-5PH, Steel 17-7PH, Tool Steel M-2(QQ-T-590), Al-2024, Al-355, Greek Ascaloy AMS5616, Ti AMS 4967, Graphitar 86, and tungsten carbide] caused or catalyzed adiabatic compression detonations with anhydrous hydrazine under any of the conditions tested. The apparatus should have been tested with a liquid known to be susceptible to adiabatic compression initiation, such as 2-propyl nitrate or ethyl nitrate, before starting the tests with hydrazine. It is always valuable to have tests with a referee fluid known to be sensitive to make sure that the apparatus works properly and to give other investigators who copied the same apparatus a chance to calibrate their system.

In the continuation of the rapid compression tests for STS APUGG, it was noted that the U tube quite often ruptured upstream of the liquid sample in the U tube, and the reproducibility of the tests was very poor [2196]. This series involved 124 U-tube tests and concentrated on just CRES-304L metal tubes but kept the geometry and test conditions of the first series. Only 1 out of a total of 42 explosions occurred on the downstream side of the sample where one would expect it. As the result of this

observation, the U-tube method was abandoned. One important finding was that helium sensitized hydrazine to rapid compression. Tube rupturing was less likely with nitrogen as the gas in the cavity. This can be explained by the different adiabatic coefficients of the monatomic gas helium ( $\gamma = 1.67$ ) versus a diatomic gas like nitrogen ( $\gamma = 1.40$ ). As a result of these tests, the pressurant gas for STS APU was changed from helium to nitrogen. It is common practice to show the boundary between safe and unsafe in a plot of pressurization rate vs. initial sample temperature. Unfortunately, rarely could enough tests be conducted to exactly pinpoint the location of a fiftieth-percentile curve such as is often done in drop-weight sensitivity tests in a probit plot. When comparing the nitrogen curve demonstrating the go/no go boundary in a compression rate vs. temperature plot to the helium curve, it was noted that the helium curve had the expected L shape near hyperbolic shape, but the nitrogen curve was U-shaped. It was difficult to explain why the system became less sensitive as the temperature was increased from 443 to 457 K (275 to 300 °F). It was suspected that under hot conditions the higher vapor pressure of hydrazine diminished the compression ratio. This U shape of the curve was no longer observed when testing moved to a different apparatus with straight tubes instead of U tubes.

Although the investigators concluded in 1978 that adiabatic compression did not appear to be a problem, occasional feed system explosions have occurred during “bench” testing of APUs on the ground under hot soakback conditions. Such hot restart maneuvers were later avoided during in-flight use of the APUs. As a temporary fix to a problem, an active cooling system had to be installed to lower the soakback temperatures in the injector and valve by squirting water on them from the outside. Concern about inadvertent inclusion of bubbles in the propellant continues for three reasons [2197]:

- (1) Bubbles might be introduced into the liquid side of the diaphragm tank during negligent servicing and refueling.
- (2) The propellant is often saturated with nitrogen at higher pressures, and bubbles are released much like opening a bottle of soda water when the pressure drops during expansion downstream of the pump.
- (3) The slow, ongoing decomposition of hydrazine during storage forms gaseous nitrogen.

**Diaphragm-Straight Tube Apparatus.** NASA WSTF modified the U-tube apparatus by keeping the gas feed system the same but replacing the U-tube test section with a sturdy U tube, which would ordinarily never see hydrazine prior to actuation, on the top of which was placed a flanged test chamber in which 1 mL hydrazine was separated from the pressurant gas by a flexible CRES-304L diaphragm and thin Teflon foil [2197, 2198]. The hydrazine was forced downward into a straight dead-ended 10.5-cm (4.25-in.)-long cavity that could be pre-filled with different gases and could be lined with different metals. A positive event was defined as an event that would rupture the sample tube. There were many experiments where the tube did not rupture, but merely



deformed and bulged. The fail/safe boundary of rapid compressions was mapped as a function of temperature and pressurization rate. In general, this apparatus required pressurization rates several orders of magnitude higher than the U-tube apparatus for tube rupture to occur, but the tests were somewhat more reproducible than with U tubes. Pressurization rates up to 11.7 GPa/s (1700000 psi/s) and temperatures up to 477 K (400 °F) were tested. In trying to identify some inconsistencies suspected of being caused by using hydrazine from different sources with minor variations of contaminants (but still within MIL-SPEC limits), the effect of additives on rapid compression sensitivity was tested. It is interesting to note that small additions of water or aniline (0.1 to 0.5%) sufficed to make hydrazine noticeably less sensitive to rapid compression deflagrations. Early adiabatic compression tests, carried out 20 to 30 years ago, may have been done with hydrazine of dubious purity and should be repeated with high-purity hydrazine.

It was also observed that liquid column movement and dispersal are essential for explosions to occur. If a gas space on top of a stationary hydrazine sample was compressed with the same rate of compression and same pressure ratio as that used to accelerate and explode a slug of hydrazine, no explosions took place. That mode of testing would be like the stagnant liquid sample in a drop-weight tester liquid sample holder consisting of a steel cup, an O-ring, and a burst disc under a plunger with a central bore for venting.

**WSTF Straight-Tube Apparatus.** Very reproducible operation was achieved with a straight-tube setup at WSTF in which neither the liquid nor the push gas had to flow around corners, minimizing turbulence and maintaining cylindrical plug flow as well as possible [2199]. A 10-L Hoke cylinder served as push gas (compressed nitrogen) accumulator. The test results may vary significantly with the type and speed of fast-acting valves used to pressurize the slug of hydrazine with the push gas. Initially, the 10.2-cm/10.2-cm (4-in./4-in.) apparatus used dual metal burst discs to obtain rapid pressurization on the upstream side of the slug of liquid. There was concern that hot metal fragments from the sheared burst discs might initiate reactions, and the burst discs were replaced with fast-acting valves, which allowed faster turnaround between tests and did not add to the cost of consumable items like burst discs that had to be replaced after each test. Later tests used fast-acting gas valves, first a 1-in. Marotta poppet solenoid valve (which did not open very fast in the low-pressure regime but can open within 8 ms at higher pressure), then a pneumatically actuated 12-mm (1/2-in.) Whitey ball valve. The problem with gas valves is that they may leak while the push pressure is adjusted to the desired level and the Teflon foil holding the hydrazine may bulge or rupture prematurely. It is good practice to attach a short-coupled pressure transducer in place of the hydrazine test section and check for gas leakage immediately prior to attaching the test section.

One of the initial setups used multiple 10-cm (4-in.)-long sections of tubing (identical diameters) separated by 2-mil (50  $\mu$ m)-thick Teflon foil to hold the hydrazine in place prior to the test. The 10-cm (4-in.) test sections were like those placed on top

of the earlier flanged diaphragm apparatus. One lower section was the gas cavity; the other served as the hydrazine reservoir. The two sections were flared on both ends and connected via an AN union. Instead of the flanged diaphragm that allowed only limited travel, the Teflon foil held the hydrazine in place with the intent of maintaining plug flow as much as possible, so the hydrazine would act as a ram piston in compressing the trapped gas at the dead-ended cavity. The Teflon foil would rupture and release the hydrazine as soon as the push pressure was applied. The Teflon foil remnants stayed in place and were not swept downstream with the hydrazine. Initial tests were performed with this arrangement with upward or downward travel of hydrazine. Most of the later tests were performed with downward travel only (gravity effects were not considered significant in comparison to the push pressures of several hundred psig).

In one test series with a push pressure of 13.8 MPa (2000 psig) and 0.5-in.-O.D. tubes, a 10-cm (4-in.) slug of hydrazine at 366 K was pushed into **(A)** a 10-cm (4-in.)-long cavity section filled with dry nitrogen, **(B)** a 20-cm (8-in.) section already filled with 4 in. of hydrazine, and **(C)** a 40.6-cm (16-in.) section already containing 30.5 cm (12 in.) of hydrazine. In case **(A)** (Test Nos. 31, 32, and 33), the tube ruptured at the dead head. In case **(B)**, the tube always ruptured at the bottom of the lower hydrazine column, not at the interface between the two impacting slugs of hydrazine where the gas bubble was compressed. This was surprising and is difficult to explain. In case **(C)**, no line ruptures were observed, but the line bulged at the bottom of the lower hydrazine column (like identical tests with water). The predicted burst pressure of 12.6-mm (0.5-in.)-O.D. CRES-304L tubing with a 1.24-mm (0.049-in.) wall was 17.9 MPa (26000 psi). A hydrotested sample ruptured at 100 MPa (15000 psi) [2199].

Experimentation with different lengths of hydrazine slugs and different lengths of gas cavities showed that ruptures occurred most often with a hydrazine slug of 20.3 cm (8 in.) rammed into a gas cavity of 38.1 cm (15 in.). This was then chosen as the standard geometry, and push pressure, cavity gas, cavity pressure, and hydrazine composition were varied to identify the most important variables.

Results obtained at NASA WSTF with the straight-tube apparatus (20.3-cm = 8-in. slug of hydrazine accelerated into a 38.1-cm = 15-in. cavity, hydrazine held by Teflon foil) are summarized in Table 87. These tests were aimed at determining the minimum push pressure that might cause line ruptures, and each hydrazine test was repeated at least three times under identical conditions.

In the NASA WSTF tests summarized in Table 87, none of the identical tests with water instead of hydrazine produced any line ruptures. Several tests were conducted with rapid response pressure transducers in various sections of the cavity, most notably at the dead-end cavity. It appeared that the rapid compression explosive event in the 20-cm hydrazine/38-cm cavity geometry occurs within 40  $\mu$ s from the beginning of the pressurization. Impact velocities of the slug at the dead-head were on the order of 50 m/s with a push pressure of 1.37 MPa (200 psig) and 90 m/s with a push pressure of 3.44 MPa (500 psig). One author of a design guide for hydrazine flight systems

**Table 87:** Experimental rapid compression test results with straight tubes at 298 K.

| Test facility       | Tube diameter, in. | Push pressure, psig | Cavity pressure, psia <sup>a</sup> | Hydrazine grade |           | Reference     |
|---------------------|--------------------|---------------------|------------------------------------|-----------------|-----------|---------------|
|                     |                    |                     |                                    | MIL-Mono        | Hi-Purity |               |
| NASA WSTF           | 1/4                | 200                 | 12.4                               | –               |           | [2200]        |
| NASA WSTF           | 1/4                | 500                 | 12.4                               | +++             |           | [2200], p. 38 |
| NASA WSTF           | 3/8                | 200                 | 12.4                               | +++             |           | [2200], p. 37 |
| Other organizations | 3/8                | 500                 | 14.7                               | -----           | -----     |               |
| NASA WSTF           | 1/2                | 200                 | 12.4                               | +++             |           | [2200], p. 36 |

Note: Each + or – sign indicates the positive (tube rupture) or negative result of a single test

<sup>a</sup> Prevailing atmospheric pressure at test site

suggested that the limiting criterion used to raise a red flag should be the hydrazine impact velocity rather than pressurization rates or compression ratios.

All tests in Table 88 were performed with the cavity filled with nitrogen gas at ambient pressure at WSTF. Since WSTF is located 1520 m (5000 ft) high, the normal atmospheric ambient pressure at that high desert location is only 85.6 kPa (12.4 psia). It appears that already minor fluctuations in cavity pressure, such as that caused by the test site elevation, may affect the outcome of the tests. Other organizations located at lower elevations and attempting to reproduce the WSTF results were not able to do so until the ambient pressure at White Sands was simulated by lowering the cavity pressure prior to each test.

In a test similar to an earlier test (0.5 tube diameter, 366 K, 2000 psia push pressure, 8 in./8 in.), but with water instead of hydrazine, the cavity tube end bulged only slightly from surge flow due to water hammer.

**Effect of Cavity Length on Surge Pressure.** The data summarized in Table 88 contain 8 tests where the cavity length (“bottom section”) was varied while all other variables were kept constant. It appears that the longer liquid slugs encounter flow resistance and eventually reach a constant speed not fast enough to cause hydrazine deflagration or hydrodynamic surge pressures high enough to cause the tubing to yield. With the longest tube, the surge pressures of hydrazine were only slightly higher than those of water and the difference could be explained hydrodynamically by different compressibilities.

**Effect of Flow Restrictions on Rapid Compression.** When a 1.3-mm (0.05-in.) or 2.5-mm (0.1-in.) orifice was inserted between the top and bottom chambers and tests repeated at room temperature, no line ruptures occurred in any of the tubes under conditions where the tubes would have ruptured without orifices. Most monopropellant hydrazine flight systems have orifices in the manifold, either in the form of enable and latch valves, cavitating venturi, or trim orifices to match pairs of thrusters. Rapid compression damage by hydrazine explosion is much less likely in the presence of ori-

**Table 88:** Summary of straight-tube test results with hydrazine at WSTF.

| Tube OD<br>diameter | Temperature | Push pressure |      | Top<br>section | Bottom<br>section | Result         | References |
|---------------------|-------------|---------------|------|----------------|-------------------|----------------|------------|
| in.                 | K           | MPa           | psia | in.            | in.               |                |            |
| 0.5                 | up to 421   | 13.9          | 2000 | 8              | 2                 | —              | [2200]     |
| 0.5                 | 298         | 13.9          | 2000 | 8              | 4                 | —              | [2200]     |
| 0.5                 | 366         | 13.9          | 2000 | 8              | 4                 | +              | [2200]     |
| 0.5                 | 298         | 13.9          | 2000 | 8              | 6                 | +              | [2200]     |
| 0.5                 | 298         | 13.9          | 2000 | 8              | 8                 | +              | [2200]     |
| 0.5                 | 366         | 13.9          | 2000 | 8              | 8                 | +              | [2200]     |
| 0.5                 | 298         | 13.9          | 2000 | 8              | 10                | +              | [2200]     |
| 0.5                 | 298         | 13.9          | 2000 | 8              | 15                | +              | [2200]     |
| 0.5                 | 298         | 2.07          | 300  | 8              | 5                 | — <sup>a</sup> | [2199]     |
| 0.5                 | 298         | 2.07          | 300  | 8              | 10                | +              | [2199]     |
| 0.5                 | 298         | 2.07          | 300  | 8              | 15                | +              | [2199]     |
| 0.5                 | 298         | 2.07          | 300  | 8              | 20                | +              | [2199]     |
| 0.5                 | 298         | 2.07          | 300  | 8              | 25                | +              | [2199]     |
| 0.5                 | 298         | 2.07          | 300  | 8              | 30                | +              | [2199]     |
| 0.5                 | 298         | 2.07          | 300  | 8              | 35                | — <sup>b</sup> | [2199]     |
| 0.5                 | 298         | 2.07          | 300  | 8              | 40                | — <sup>c</sup> | [2199]     |

<sup>a</sup> Cavity yielded, 230 MPa surge pressure<sup>b</sup> Cavity yielded, 96 MPa surge pressure<sup>c</sup> 38 MPa surge pressure

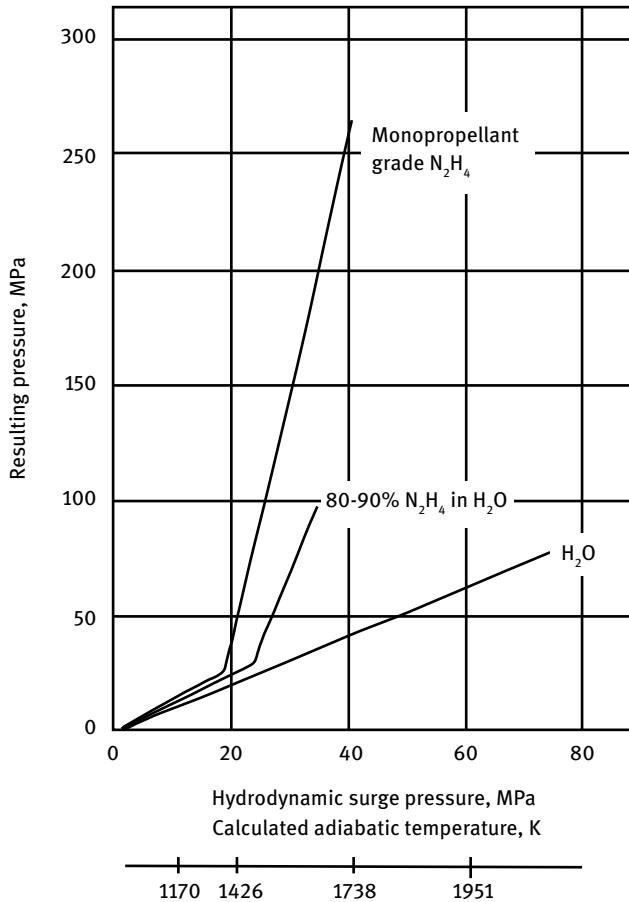
Data source: [2199]

fices, and this may explain why damage in hydrazine flight systems so far was limited to pressure surges that could be explained by hydrodynamics alone.

**Effect of Contamination by Residual Water on Rapid Compression.** When a trace of water was inadvertently left in the cavity, the tubes would not rupture under conditions where dry tubes would have ruptured. Adding 30% of water to the hydrazine (such as in the H-70 fuel blend) essentially suppressed all rapid compression sensitivity even under the most severe conditions tested at WSTF.

In a graph (Figure 66) where the surge pressure for water, hydrazine, and hydrazine/water blends is plotted versus the surge pressure observed for water in the same apparatus, the water data are represented by a straight line.

Tests with hydrazine, 90% hydrazine, and 80% hydrazine showed that for surge pressures below 17 MPa (2500 psi), the three curves stay close together and agree with data for hydrodynamic surge. At surge pressures above 17 MPa, the monopropellant-grade hydrazine showed a large deviation and surge pressures above 34 MPa ruptured the tubes. The deviation for 80 and 90% hydrazine became apparent only at surge pressures above 24 MPa. These deviations are the result of chemical reactions and not simply a hydrodynamic effect caused by different compressibility.



**Figure 66:** Resulting pressures and calculated adiabatic temperatures at various peak hydrodynamic pressures. (Reproduced and modified from [2201], with permission from ©1991 American Institute of Aeronautics and Astronautics 7-Jul-2021.)

**Effect of Increasing Top Chamber Diameter.** Although most of the WSTF tests were conducted with top and bottom chambers of identical diameters, a few tests were conducted with a wider top hydrazine reservoir (2.54 cm = 1 in. OD) than the bottom cavity (1.27 cm = 0.5 in. OD). Both top and bottom chambers were 10 cm (4 in.) in length. Both tests with push pressures of 3.5 MPa (500 psig) and 6.9 MPa (1000 psig) resulted in ruptures not only of both lower and upper chambers, but also rupture of the 19-mm (0.75-in.) line carrying the pressurant gas, overall major destruction.

**Conditions in Liquid Front Rushing into Cavity.** It appears that conditions in the slug of liquid, in particular at the front of the liquid column, as it is rushing into the gas cavity will determine whether or not an explosion will take place. For very short

slugs ( $<10$  cm), gas pressure may break through as core flow and squeeze the liquid on the wall, leaving it behind, not leading to an explosive event. If the slug is too long, flow resistance will increase with the length of the liquid column and the slug will slow down before it bottoms out. An intermediate length of liquid columns is susceptible to rapid compression. Tests with an inert X-ray opaque contrast fluid and X-ray photography during the test were not very helpful. A series of high-speed film frames was obtained with a see-through glass tube instead of a stainless-steel tube, showing a froth of an intimate mixture of liquid and gas bubbles [2199, 2201]. The high-speed photography was very informative as to the nature of the liquid front entering the gas cavity. Discussions centered around the source of the bubbles, if they were released as dissolved gas from the hydrazine or if they were entrained bubbles. The initiation mechanism of the explosive hydrazine decomposition was shown to be dependent on the formation of a froth with subsequent rapid temperature and pressure increase by ram effects. The general interpretation was that the froth is formed by entrained bubbles. Taylor instabilities at the liquid-gas interface and Helmholtz mixing result in an intimate mixture of hydrazine, hydrazine vapor, and gas bubbles in the rapidly moving mixture of the three. Based on the tests at NASA WSTF, it is now concluded that the rapid compression of hydrazine froth does not initiate a detonation (as was the case with nitromethane under similar test conditions [2192]), but the heat from the compressed bubbles is rapidly transferred to thin membranes of liquid hydrazine, creating a thermal runaway situation, which is as destructive as an explosion.

**Effect of Temperature on Rapid Compression Sensitivity.** The importance of the initial system temperature on the susceptibility of hydrazine to rapid compression became painfully apparent during the Space Shuttle APU hot restart tests. It was obvious that raising the initial temperature of the hydrazine would reduce the additional energy required to bring hydrazine/gas bubble mixtures to the threshold of explosion. For satellite manifold applications it is generally assumed that propellant and system are at the same temperature. There do not seem to be any tests where the propellant reservoir and the cavity were temperature conditioned at different temperatures.

**Effect of Cavity Pressure on Rapid Compression Sensitivity.** A series of tests was performed at WSTF in which a 20-cm (8-in.) column of hydrazine or water was accelerated into a 38-cm (15-in.) cavity chamber filled with nitrogen at pressures ranging from near vacuum to 141 kPa (20.4 psia) [2199]. The results are summarized in Table 89 and illustrated in Figure 67.

It is significant to note that based on the WSTF tests, there is only a narrow range of cavity pressures within which rapid compression explosions were observed for these particular geometric and operating push pressure conditions. At the high-pressure end, it is easy to explain that the gas in the cavity acts as a spring and shock absorber, slowing down the incoming slug of liquid (which will eventually rebound). This concept of a high pad pressure was used with advantage by several flight systems (e.g., IUS) to protect against unwanted rapid compression/water hammer events

**Table 89:** Effects of gas cavity pressure on surge pressure and hydrazine decomposition.

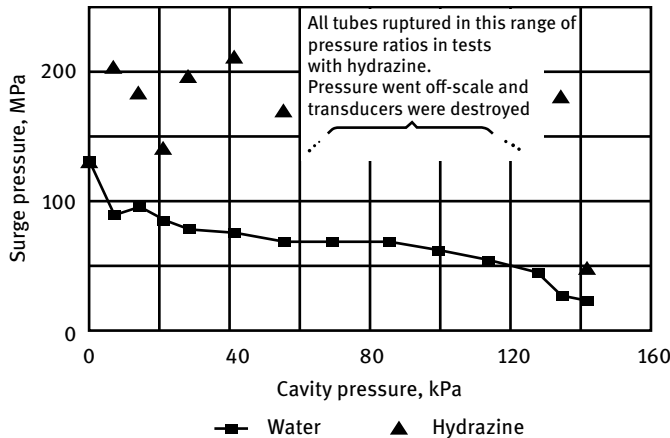
| Cavity pressure |         |         | Surge pressure, MPa |                  | Remarks               |
|-----------------|---------|---------|---------------------|------------------|-----------------------|
| kPa             | mm Hg   | psia    | Water               | Hydrazine        |                       |
| ≤ 0.005         | ≤ 0.038 | ≤ 0.001 | 131                 | 131 <sup>a</sup> |                       |
| 7               | 53      | 1       | 90 <sup>a</sup>     | 203 <sup>a</sup> |                       |
| 14              | 105     | 2       | 96 <sup>a</sup>     | 183 <sup>a</sup> |                       |
| 21              | 158     | 3.1     | 86 <sup>a</sup>     | 141 <sup>a</sup> |                       |
| 28              | 211     | 4.1     | 79 <sup>a</sup>     | 196 <sup>a</sup> |                       |
| 41              | 309     | 6.0     | 76                  | 210 <sup>a</sup> |                       |
| 55              | 414     | 8.0     | 69                  | 169 <sup>a</sup> |                       |
| 69              | 519     | 10.0    | 69                  | <sup>b</sup>     |                       |
| 85              | 640     | 12.4    | 69                  | <sup>b</sup>     | WSTF ambient pressure |
| 99              | 745     | 14.4    | 62                  | <sup>b</sup>     |                       |
| 113             | 850     | 16.4    | 55                  | <sup>b</sup>     |                       |
| 127             | 956     | 18.5    | 45                  | <sup>b</sup>     |                       |
| 134             | 1008    | 19.5    | 28                  | 179 <sup>a</sup> |                       |
| 141             | 1061    | 20.5    | 24                  | 48               |                       |

All data in 12.6-mm (0.5-in.) tubes.

<sup>a</sup> Cavity tube yielded, no rupture

<sup>b</sup> Cavity tube ruptured, pressure >276 MPa

Data sources: [2199, 2201]



**Figure 67:** Effects of cavity pressure on surge pressure and hydrazine decomposition. (Image created by Schmidt 2020 based on data from WSTF.)

when a manifold is first filled with hydrazine. It is more difficult to explain why no explosions occur with vacuum and at very low pressures, although the compression ratio is significantly higher. It is assumed that at the low-pressure end of the pressure regime there is not enough gas to entrain and form hot spots. Surge pressures for water and hydrazine were similar at the lowest cavity pressure tested [2199].

**Effect of Type of Cavity Gas on Rapid Compression Sensitivity.** One of the first significant findings of the WSTF tests, confirmed by testing in different apparatus and test tube geometries, was that helium rendered hydrazine more sensitive to adiabatic compression than nitrogen. Subsequently, hydrazine pre-pressurization on the Space Shuttle APU was changed from helium to nitrogen, although the Space Shuttle APU used a diaphragm tank and hydrazine was not in direct contact with the pressurant gas. Enough pressurant gas may permeate through the diaphragm during year-long storage and form trapped bubbles in the hydrazine. Hydrazine in the Space Shuttle APU tanks was only primed to a feed pressure of 2752 kPa (400 psia), and this was subsequently boosted in a gear pump for actual APU operation at 9.63 MPa (1400 psia). Bubbles were compressed as they passed through the pump and during pulse-mode operation of the control valve.

The sensitivity of pressurant-gas-saturated hydrazine depends on the type of gas contained in the cavity and in the bubbles. The difference in sensitivity to rapid (“adiabatic”) compression explosions can be explained by the difference in the adiabatic coefficient  $\gamma = C_p/C_v$  of nitrogen (a diatomic gas) and helium (a monatomic gas). The gamma of nitrogen is  $\gamma = 1.4$ , whereas for helium it is  $\gamma = 1.66$ , resulting in higher adiabatic compression temperatures in accordance with

$$T_2 = T_1 \left( \frac{p_2}{p_1} \right)^{\left( \frac{\gamma-1}{\gamma} \right)}$$

All nominal tests were conducted with nitrogen as the push gas and nitrogen in the cavity. In a rare test with helium as the push gas and nitrogen in the cavity, a 0.25-in.-O.D. tube ruptured with a push pressure of only 2.06 MPa (300 psig) instead of 3.44 MPa (500 psig) as with nitrogen push gas. This indicates that helium is more effective as push gas than nitrogen (which is why it is used in light gas guns).

Although the straight-tube test arrangement yielded a large amount of useful data, one question has never been completely answered: What effect do the hydrazine vapors diffused through the Teflon foil have on the results observed in the WSTF straight-tube tests? Since the cavities are hermetically sealed and not purged while the tube is waiting to be tested, hydrazine may diffuse through the thin foil and evaporate into the cavity fill gas. Although the tubes are usually tested immediately after the hydrazine is loaded, there is usually a delay of up to several hours while the test setup is tightened, leak tested, and the instrumentation hooked up. Some tests take several hours to reach the desired test temperature. Tests have shown that the breakthrough time for hydrazine through the same type of Teflon foil as was used at WSTF is less than 1 h and the rate of permeation is  $2.5 \times 10^{-7} \text{ g cm}^{-2} \text{ h}^{-1}$ .



NASA WSTF performed an additional series of rapid compression tests, initially with water and instrumented with numerous pressure transducers [2202, 2203], then with live hydrazine in support of the RCS/ACS system intended for the Space Station Freedom. In these tests, all hydrazine was contained in a larger reservoir, such that longer manifold sections (all 12.5-mm [0.5-in.] O.D.) with branch passages could be entirely filled with liquid. The problem with hydrazine permeation through the Teflon foil was avoided since the Teflon foil was replaced with a Carlton Controls poppet valve, capable of opening full bore within 10–20 ms. Feed pressure was nominally 2.75 MPa (400 psig), and none of the test sections with hydrazine ruptured under those feed pressure conditions. For much higher feed pressures and a 38-cm (15-in.) straight section, as used in earlier tests, feed pressures of 17.2 MPa (2500 psig) may result in the rupture of nitrogen-filled cavities, but only 10.3 MPa (1500 psig) may rupture cavities filled with helium or argon.

The French space agency also sponsored research on the study of the decomposition of hydrazine by rapid compression and its application to explosion hazard evaluation [1192, 1257, 2204].

#### **8.8.1.2 Rapid Compression Hazards in Flight System Manifolds**

There was concern that the sudden compression of hydrazine rushing into an evacuated propellant manifold on actuation of tank isolation valves in the IUS might cause explosions resulting from adiabatic compression and decomposition of hydrazine [2205]. Another damage mechanism would be pressure surges by the water hammer effect, which is a strictly physical phenomenon involving no chemistry but is aggravated by the low compressibility of hydrazine in comparison to that of water. In evacuated manifolds, hydrazine pressure surges of up to 49 MPa (7200 psi) with 0.4-ms duration were measured. Several methods were evaluated to suppress the surge, and pre-pressurization of the manifold with nitrogen was shown to dampen the water hammer effect. Similar pre-pressurization studies were conducted for other flight systems. It is difficult to ensure that the gas pad stays there until propellant is dropped into the manifold. Launch vibrations may unseat the thruster valves and allow some of the gas to leak out. Launch delays may require re-pressurization of the manifold prior to the next launch attempt.

The large pressure transients observed when hydrazine is released into an evacuated dead-ended tube are related to the low elastic compressibility (i.e., high velocity of sound) of hydrazine. This effect is more pronounced with hydrazine than with water because the velocity of sound in hydrazine is 1.4 times faster than in water.

**ISPM (Later ULYSSES) Manifold Filling Test.** The ISPM filling test was conducted at ERNO (later a division of MBB/DASA) in cooperation with British Aerospace to simulate the unlikely situation that the IUS/PAM-S-assisted launch from a Space Shuttle in orbit had to be abandoned and the spacecraft had to be brought back to Earth [2206]. The radioisotope thermal generator would have heated the entire space probe from the time the Space Shuttle payload bay doors were closed and the bump

on touchdown on the runway might have been severe enough to flip the latch valves open. The test series summarized in Table 90 was conducted to assess different “what if?” hazard conditions.

**Table 90:** ISPM manifold filling tests

| Test No. | Tubing temperature, K | Feed pressure, bar | Cavity pressure, bar | Hydrazine temperature, K | Filling condition                                       |
|----------|-----------------------|--------------------|----------------------|--------------------------|---------------------------------------------------------|
| 1        | 313                   | 26                 | 1                    | 313                      | 100% GN <sub>2</sub>                                    |
| 2        | 313                   | 26                 | 1                    | 313                      | 25% GN <sub>2</sub> , 75% N <sub>2</sub> H <sub>4</sub> |
| 3        | 313                   | 26                 | 1                    | 313                      | 10% GN <sub>2</sub> , 90% N <sub>2</sub> H <sub>4</sub> |
| 4        | 313                   | 26                 | 1                    | 313                      | 25% air, 75% N <sub>2</sub> H <sub>4</sub>              |
| 5        | 313                   | 26                 | 4                    | 313                      | 25% GN <sub>2</sub> , 75% N <sub>2</sub> H <sub>4</sub> |
| 6        | 313                   | 26                 | Vapor press.         | 313                      | Hydrazine vapor                                         |
| 7        | 351                   | 30                 | Vapor press.         | 363                      | Hydrazine vapor                                         |

Data source: [2206]

One of the options considered to minimize the pressure spike when first dropping pressurized propellant into the lines downstream of the latch valve was to pre-fill the lines partially with hydrazine and nitrogen at sea-level pressure. This option includes the risk that some of the unpressurized propellant will leak through the TCVs into the catalyst bed while the spacecraft is still in the Space Shuttle payload bay. Test Nos. 6 and 7 with hydrazine vapor in a dry line simulated a leaking latch valve. The line diameter for the tests was not given, but it was assumed it was close to 6 mm (1/4 in.). A manifold representing half of the symmetrical satellite propellant feed system was pre-heated to nominal 351 K = 78 °C = 172 °F. When hydrazine pre-heated to 363 K = 90 °C = 194 °F and pressurized at 30 bar (435 psia) was allowed to enter the manifold (filled with saturated hydrazine vapor at the vapor pressure at 351 K = 78 °C = 172 °F which is 42 kPa = 6 psia) through a latch valve, an explosion ensued after 361 ms which destroyed the line system and the filter. The last temperature recorded inside the manifold was 440 K = 167 °C = 333 °F due to the adiabatic compression of the bubble. The fragments of the remaining hardware gave the impression that explosions occurred in several places simultaneously. Post-event examination of the experimental setup concluded that the line sections had been inadvertently overheated locally to substantially above the nominal test temperature by crisscrossing and double-layering the heating tape in some areas, creating hot spots. The test was later repeated with a hot water bath at temperatures up to 363 K, providing more uniform temperature control, and no explosion was observed during the repeat test. For a while some critical voices out there in the propulsion community suggested that the water bath surrounding the tubing attenuated the shock wave propagating through the metal wall of the tubing and prevented the hydrazine from exploding as before. If the phenomenon is inter-

puted as an LVD, surrounding water might indeed attenuate the shock wave advancing through the stainless-steel tubing. Also, the ability of the cavity to expand and contract in multiple oscillations would be impeded by surrounding water. The pre-test temperatures in ground test inadvertent explosion events assumed to be due to hydrazine rapid compression were substantially above typical satellite manifold temperatures. The high temperature in each case sensitized the system to rapid compression explosions. On the other hand, line diameters were below the 9.5- and 12.2-mm (3/8- and 1/2-in.) O.D. lines now flown on many larger satellites. In many flight systems, a pad pressure ("gas cushion") is placed in the manifold before dropping hydrazine into it for the first time. One of the first systems to use this technique was IUS, and this practice was later adopted by many other systems (PAM-D, DELTA-II, ATLAS-II Roll Control Module). The preferred padding gas is nitrogen, but for unknown reasons, some satellite designers still prefer helium, although it may make rapid compression hazards worse (if only part of the gas cushion leaks out during launch vibrations) and it leaks out faster than any other gas. It is very likely that some of the pad gas leaks out during launch vibrations when the thrust chamber valve poppets start jumping up and down on the seats. It seems that nobody has proven that the pad gas is still there when the propellant is dropped into the manifold. It has been suggested that the propellant should be dropped as early as possible during the launch sequence.

Most Defense Support Program (DSP) satellites, except DSP-16, were launched on expendable launch vehicles and the manifold lines were filled with hydrazine prior to launch. STS payloads, on the other hand, require at least three inhibits to prevent leakage of propellants in the payload bay. To meet this requirement, DSP-16 was launched on STS-44 with dry manifold lines. Prior to launch, the potential for rapid compression-induced decomposition and detonation was investigated through analysis and test [2207]. Testing involved accelerating hydrazine into simulated line ullages for several ullage pressure conditions and dead-head cavity temperatures. These efforts demonstrated that the DSP plumbing system and fill procedure were not susceptible to adiabatic compression hazards of hydrazine. Operationally, a technique to manage a gas pad before and after propellant line priming was developed, and on-orbit activation of the propulsion subsystem went smoothly as expected.

Propellant manifolds on SPOT 4 satellites and precursors were usually filled with hydrazine prior to launch and a small (~1 mL) gas bubble was deliberately formed at the thruster end of the lines to allow for thermal expansion of the liquid. When scaling up the SPOT design for the Polar Platform Propulsion System (ENVISAT), a different approach was necessary because the lines were up to 13m long and the gas bubble would have been too big, and its location was unpredictable. Matra Marconi Space performed a very thorough mathematical analysis of propellant velocities during gas cushion discharge through the thrusters [1926]. Some of the equations derived there are also applicable to predicting rapid compression events caused by moving slugs of liquid. Since the pressure drop during gas cushion discharge through the thruster was low, propellant would be able to accelerate to high speeds, causing severe water ham-

mer spikes when the thruster valve was suddenly closed. Loading strategy alternatives of complete liquid fill or gas-only fill were not acceptable. The best solution was to introduce small bubbles of known size into each leg of the system by slowly filling it with propellant that was pre-saturated with helium at 3.53 MPa (35 bar). When this propellant expanded to sea-level pressure during filling of the manifold, a known amount of gas was released and would rise to the top of the vertical lines leading to the thrusters.

Hydrazine is not the only rocket propellant where explosions can be caused by rapid compression of propellant lines. Oxygen rushing into empty lines has been known to cause ignition of combustible materials, even inert polymers like PTFE. The mathematics, thermodynamics, and fluid dynamics of oxygen compression “adiabatic” heating in dead-ended tubes can be applied to the hazard prediction in hydrazine systems as well [2208].

### **8.8.2 Water (Fluid) Hammer and Surge Flow Conditions Conducive to Rapid Compression Events in Hydrazine**

As already discussed in earlier sections, water (fluid) hammer and surge flow with any liquid (reactive or not) can result in destructive pressure spikes. This is particularly true with hydrazine due to its low compressibility (compared to that of water). We list here some examples where such pressure spikes have caused hardware damage, but (as far as can be discerned from the information available) without participation of hydrazine decomposition reactions. Various observers have suspected that the rapid compression of hydrazine might have been the culprit for these events, but this has not been proven, and the explanation of a strictly physical, not chemical, phenomenon has generally been accepted. In what follows, the effects of surge flow (“priming”) into evacuated or low-pressure propellant manifolds are discussed first, and the effects of water (fluid) hammer, usually observed in completely filled lines, are discussed second. Some computer models may be capable to handle both types of compressible fluid flow. Not all models can handle multi-phase fluid flow. Experiments in replicas of actual flight plumbing systems are often conducted with water instead of hydrazine, and the results were extrapolated to hydrazine by adjusting for a different compressibility. But those extrapolation methods neglect the potential reactivity of hydrazine in two-phase flow situations.

#### **8.8.2.1 Surge Flow Conditions Conducive to Rapid Compression Events in Hydrazine**

Most satellite propulsion systems are activated in orbit by rapid opening of a pyro valve, dropping propellant into evacuated or partially gas-filled propellant lines. This is typically done after the last stage of the launch vehicle has completed its burn phase and the satellite has been injected into a low Earth orbit or a geostationary transfer orbit. The dropping of the hydrazine monopropellant into the manifold is delayed because launch vibrations might unseat some of the solenoid valves and allow propellant to leak if this downstream point of the system was wet and pressurized. This

process is also called “priming” or “dropping propellant.” The following discussion of hydrodynamics applies to all liquids and all propellants, but the conditions are most severe for hydrazine because of its small compressibility. If priming and water hammer problems occur with any rocket propellant, they will occur with hydrazine first. The severity of pressure spikes by surge flow into evacuated or low-pressure gas-filled lines could be limited if slow opening pyro valves were available. Unfortunately, most pyro valves available at this time open within milliseconds and send a surge of propellant into the manifold that needs to be filled with propellant. In all cases the solenoid valves at the end of these runs of line are closed at the moment the propellant is dropped into the manifold by firing the isolation valve or opening a latching valve. Many system designers specified a gas pad that will cushion the impact of the slug of liquid. However, the first series of pulses commanded to the thrusters will then be unpredictable until all the bubbles have been passed through the thrusters. Some trapped bubbles may linger around in filters and soften the hydraulics of the system and may move around unexpectedly at another time. Another method to slow the rapid advance of the propellant is to insert flow restrictors (orifices, cavitating venturi) upstream or downstream of the pyro valves. Most of the papers referenced here are valid for any fluid, not just hydrazine. The equations apply even to plain water, which is often used as a surrogate for hydrazine when testing new propellant distribution manifold designs. It is only the close relationship between surge flow pressure spikes and rapid compression explosions of hydrazine that is the justification for assembling all these papers and discussing them next to each other in the following section. Not all computer models described here are able to account for the release of dissolved gases while the column of liquid advances through the low-pressure section of the plumbing system. None can predict accurately when hydrazine will explode. Some of the models ignore the fact that the explosion may be triggered, not at the first impact pressure spike, but only after the first rebound and a reflected rarefaction wave that creates additional cavitation bubbles for the subsequent compression cycle as the system oscillates and gradually rings out. Additional bubbles create the two-phase medium that can propagate an LVD-like deflagration in hydrazine.

In January 1976, the Canadian CTS satellite experienced an anomaly when a latch valve was opened to fill an evacuated line [1826]. The latching valve vibrated (“fluttered”) and the downstream line did not fill completely within the allocated 3-s fill time. Critics suspected this could have been a rapid compression/adiabatic compression explosion event, but this was never proven.

A simplified model was derived to describe the flow of MMH (and NTO) into evacuated and pressurized straight lines, which allows for the prediction of peak pressures [2209]. This is described in the chapter on methylhydrazine. The model can be modified to be applied to hydrazine.

In the case of Compton Gamma Ray Observatory (CGRO), the concern about surge flow and water hammer damage to thruster valves was so dominant that it was considered to fly the propellant lines filled with hydrazine prior to launch

on the Space Shuttle. The propulsion subsystem had two independent branches called A-Side and B-Side. In April 1991, the GRO hydrazine propulsion system was accidentally subjected to high surge pressures during the on-orbit pressurization of the primary propellant manifold. Immediately upon opening one of the propellant tank isolation valves, the spacecraft telemetry indicated that two isolation latching valves had undergone uncommanded changes in the open/close position status (“flip-flopped”) and one of the pressure transducers indicated “over limit” pressure. A TRW analytical pressure transient model, which was correlated with test data as part of the CGRO surge pressure anomaly investigation, supported the following proposed mechanism for the high surge pressure: A relatively large volume of bubbles was inadvertently trapped in the thruster manifold downstream of the tank isolation valves. It had been introduced with supersaturated propellant during loading of the spacecraft on the ground. A sufficiently large pressure differential existed at the tank isolation valves (2.62 MPa = 380 psia propellant tank pressure; 0.101 MPa = 14.7 psia in the manifolds downstream of the tank isolation valves). A high surge pressure was initiated by the opening of the tank isolation valve and leaving it open instead of pulsing it. A NASA investigation determined that an oversight in a fuel loading procedure had left a significant volume of bubbles in the propellant lines [2210–2214]. A method to command the tank isolation valves in “pulse mode” (“fast cycling”) was successfully developed, characterized by testing, and applied to the CGRO redundant B-Side manifold when it was activated. In April–July 1993, this pulse-mode method was used to seep propellant from the propellant supply into the redundant B-Side thruster manifolds to gradually raise the downstream pressure prior to fully opening the valves for an orbit adjust maneuver. The priming of the B-Side Attitude Control Thrusters (ACTs) manifold required approximately 3500 cycles of the isolation valves. The priming of the B-Side Orbit Adjust Thrusters manifold required an additional 400 cycles. It was concluded that slow opening isolation valves need to be developed.

Several small satellite feed systems were tested on the ground for their surge flow and water hammer characteristics. Pressure drops across filters and latch valves were measured using water as a simulant fluid [2215].

The SeaStar Hydrazine Propulsion System was a blowdown monopropellant system used for orbit raising and maintenance and consisted of a single propellant tank with an expulsion diaphragm, a pyrotechnic isolation valve, four thrusters, two pressure transducers, and three service valves. Initial analysis of the system configuration indicated a potential failure mode due to adiabatic detonation of the propellant during system activation. To further understand the potential of high-pressure surges as a consequence of water hammer effects during activation, a test was performed with water as the surrogate fluid [2216].

In a more complex system, the surge flow of hydrazine into the evacuated or gas-filled propellant manifold of the hydrazine monopropellant propulsion subsystem of the planned Space Station Freedom was simulated with water flow tests and the pressure spike results were compared to predictions from a method-of-characteristics com-

puter model [2202, 2203]. Tests were conducted with straight-line sections, elbows, branch passages, and junctions. The feed pressure was 2750 kPa (400 psia) and the line diameter was 12.7 mm (0.5 in.), which is a wider diameter than typical satellite lines. The test results showed an increase of surge pressure with straight-line length from 25 to 50 and 75 cm. The pressure-time curve of the priming process could be closely matched with computer predictions. The experimental results were in between the theoretical predictions for an adiabatic and isothermal compression process.

Pressure transients during priming of a spacecraft propulsion subsystem have the potential to significantly affect on-orbit performance or can result in a catastrophic loss of spacecraft. A series of tests were performed to quantify the expected pressure transients experienced within a spacecraft propulsion system fuel manifold during on-orbit activation [2217]. Results have then been analytically correlated based on line travel distances and compared to recorded pressure values in order to establish a tool for predicting pressure surges at conditions outside the test envelope. Testing was designed to emulate priming of the propulsion system by pressurizing water to approximately 1.03 MPa (150 psia) and releasing it through the actuation of a solenoid valve into an evacuated tubing manifold representative of the Star-2 propulsion system. At this pressure, the fluid velocity attained was enough to generate a pressure surge once the flow was stopped suddenly by encountering a closed thruster valve in the system. Assumed design limitations were as follows: **(1)** a pressure spike in hydrazine fluid absolutely should not exceed 17.2 MPa (2500 psia) due to the risk of adiabatic compression explosion; and **(2)** component proof pressures should not be exceeded. Of the 26 test runs performed with and without water-hammer-suppression orifices, none resulted in surges exceeding or approximating the hazardous adiabatic compression explosion regime. Without suppression orifices, pressures as high as 13.4 MPa (1938 psia) were observed (correlated for hydrazine conditions) at the dead end having the greatest distance from the fluid release point. The installation of water-hammer-suppression orifices safely reduced the pressure surge values to non-hazardous levels of no more than 3.7 MPa (540 psia).

A computational method for analytical prediction of priming surge flow water hammer pressure has been developed and applied to the design and development of several spacecraft propulsion systems [2218]. The approach involved deriving and solving equations of motion for the fluid as it surges into a downstream manifold and impacts locations in the feed system. The technique has been validated using results of testing where actual measurements of water hammer were obtained. It offers improved accuracy over simpler calculation techniques and can provide sufficient accuracy in many cases without resorting to complex fluid codes. Results of these analyses have been used to confirm component and subsystem acceptability, determine the need for surge suppression, and guide the planning of verification experimental testing.

An experimental study was carried out with real propellants, such as hydrazine, MMH, and NTO, in comparison to water, and fluid hammer was measured into straight

pipe, bent pipe, elbow pipe, and tee pipe [2219]. Measurements have allowed us to obtain overpressure levels, to determine the sound velocity in the liquid propellant, and to define the speed of the flow by the transition time gas/liquid.

An experimental investigation of the water hammer phenomenon in a confined environment was carried out using a simplified setup with two inert fluids, ethanol and acetaldehyde, and an actual propellant, MMH [2220]. Numerous tests confirmed the excellent reproducibility of the results. The experiments showed that ethanol could be used as a surrogate fluid instead of toxic MMH for the water hammer amplitude measurements. The water hammer phenomenon produced in a pipe with a low initial pressure exhibited a complex evolution over time and slight differences in amplitude and features depending on the pipe geometry.

The classical surge flow water hammer taking place during priming involves multi-phase phenomena, such as cavitation and absorption/desorption of a non-condensable gas, which affects the pressure spikes produced in the lines. Even though this flow behavior is known, only a few studies model specific spacecraft hardware configurations, and a proper characterization of the two-phase flow is still missing. An experimental facility modeling a spacecraft propulsion system was built, where the physical phenomena taking place during priming can be reproduced and measured [2221–2223]. The influence of the driving pressure gas dissolved in the propellant was analyzed using either a saturated or a completely de-aerated test liquid. Two-phase flow was characterized by means of flow visualizations of the liquid front at the location where the fluid hammer is generated. For this purpose, an experimental study was carried out with inert fluids modeling a liquid propulsion system, where the gas saturation level of the test liquid was controlled, making it possible to run experiments under de-aerated and saturated conditions [2224, 2225]. An experimental investigation on the fluid hammer phenomenon taking place when filling a pipeline under vacuum conditions with a closed end was carried out in a facility allowing flow visualization, which was made possible by replacing the metal pipe closed end by a quartz cylinder drilled with the same tube inner diameter [2226]. In this way, the flow can be recorded with high-speed imaging at this location. The visualizations confirmed that the pressure evolution is accompanied by a complex multi-phase flow pattern. First of all, a foamy mixture of non-condensable gas, vapor, and liquid droplets precedes the liquid front arrival at the bottom end. During the fluid hammer compression wave, the vapor condensates and the non-condensable gas gets compressed. Afterwards, the arrival of an expansion wave induces the movement of the liquid column backwards, with the corresponding pressure drop that generates a gaseous bubble referred to as column separation. Finally, the collapse of this bubble is at the origin of the next pressure rise. A sequence of images showed a foamy mixture preceding the liquid front and the non-condensable gas compression when the front first impacts at the bottom end, the subsequent column separation with the creation of a multi-phase bubble, ending with a new impact of the separated liquid column against the bottom end. A higher release of desorbed



pressurant gas in the lines cushions the liquid front impact at the closed ends, inducing a lower pressure spike during fluid hammer occurrence. Ethanol or water were used as surrogate fluids for tests in a vertical tubing with downward flow [2227].

The commercial code CFD-ACE+ was used with a so-called full cavitation model, which considers the effect of absorption and desorption of a non-condensable gas, to clarify some issues of surge flow water hammer [2228]. A comparison between two different compressibility models made use of an inverse engineering technique, which allowed the tracking of the medium velocity of sound. A numerical reproduction of a valve opening leading to a sudden acceleration of the fluid and consequent vaporization of the liquid confirmed high sensitivity of the water hammer pressure spike depending on the amount of non-condensable gas present in the liquid.

From a physical point of view, the modeling of priming is a complex task because it involves transient multi-phase flow. As a first approach, an analytical model of the equations of motion was developed applying a rigid liquid column theory, considering only the inertial and frictional effects of the liquid treated as a slug [2229]. The friction plays an important role, in particular due to the unsteady conditions which increase its steady value. The cushion effect of an inert gas was also analyzed and the assumption of adiabatic vs. isothermal compression compared. Results indicated that a polytropic compression can better model the realistic gas behavior.

There has been a controversy in connection with establishing where the threshold for hydrazine detonability is, due to the high number of parameters affecting the results, the variability of the test conditions (e.g., test setups, initial conditions). An attempt was made to define the conditions where this phenomenon is triggered and a logic and methodology was proposed to resolve this problem [2230].

A network flow simulation software based on a finite volume method was used to predict pressure surges resulting from the sudden opening of a valve in a pipe that has entrapped air at one end of the pipe [2231]. The mathematical model was built by combining the flow equations in the liquid (water) zone and compressibility of the entrapped air. The numerical results were compared with experimental data available in the literature. The study was conducted for a range of reservoir feed pressures and for different amounts of initial air present in the pipe. The numerical results compared well (within reasonable accuracy, less than 8%) for a range of inlet-to-initial pressure ratios when the amount of air present was relatively high ( $\alpha \approx 0.45$ ). A fast Fourier transform was performed on the pressure oscillations to predict the various modal frequencies of the pressure wave.

The Global Precipitation Measurement satellite propulsion system was a blowdown monopropellant system with an initial hydrazine load of 545 kg in a composite-overwrapped propellant tank. At launch, the propulsion system contained hydrazine in the tank and manifold tubes upstream of the latch valves, with low-pressure helium in the manifold tube downstream of the latch valves. The system had a relatively high beginning-of-life feed pressure and long downstream manifold lines. These factors created conditions that were conducive to high surge

pressures, requiring surge mitigation in the propulsion system design and surge testing for verification [2232]. Based on the results of surge testing and pressure drop analyses, a configuration of cavitating venturis was chosen to mitigate surge while minimizing pressure losses during thruster maneuvers.

A study of fluid hammer and related multi-phase phenomena taking place in a confined environment, where pressurized liquid faces vacuum conditions after opening an isolation valve, described the experimental facility built for this purpose, the tests performed, and showed a comparison of laboratory test results with the numerical results obtained with a transient one-dimensional software based upon conservation equations [2233]. The leading edge of the liquid rushing into the low-pressure cavity was subdivided into several zones: boiling liquid front, foam (froth) front, vapor front, and gas pressure wave front. The results of the computations were presented in the form of two-dimensional color maps for each of the variables involved (e.g., pressure, temperature), where the history in time  $t$  and  $x$  coordinate along the different nodes can be followed. The  $x$ - $t$  diagrams allowed a simultaneous study in time and space for each of the magnitudes involved in the evolution of the fluid hammer. The tests showed the typical water hammer evolution as a succession of pressure peaks with decreasing amplitude. The multi-phase effect on the velocity of sound needs to be studied more in detail during experiments.

Experimental measurements in an instrumented test section simulating a satellite manifold, with water as the push fluid, were compared with predictions from calculations with the Flownex computer program [2234]. Flownex has the ability to solve the steady-state and dynamic flow simulations of systems in any combination of liquid systems, gas systems, mixtures of gases, two-phase systems with phase changes, and incondensable mixtures of two-phase fluids with gases coming out of the solution.

The phenomenon of priming involves complex two-phase flow: the liquid entering the evacuated pipe undergoes flash evaporation, creating a vapor cushion in front of the liquid that mixes with the residual inert gas, usually helium. Moreover, the dissolved pressurizing gas in the liquid will desorb making the priming process difficult to model numerically. For these reasons, priming and/or water hammer tests are always part of the qualification process of new propulsion subsystems of a satellite or spacecraft that uses storable propellants. Dissolved gases influence a step-plateau pressure trace shape observed in priming tests. To gain further insight into this aspect, a quartz pipe was installed at the dead end of a manifold, and high-speed imaging at framing rates up to 19200 frames/s was performed [2235]. The test section was 220 cm long, and the transparent clear quartz section was 20 cm long with an ID of 16 mm. The image analysis proved to give valuable information to better understand this complex transient phenomenon and a possible explanation of the first pressure peak profile was given based on these visual observations.

An overview of surge flow experiments and computational models for the study of multi-phase fluid-hammer effects in aerospace applications performed by a number of different organizations was given in [2236]. The accurate prediction of the peak pres-

sure transients that occur during the priming of a spacecraft propulsion system is vitally important because these transients can cause damage to components or even trigger the deflagration of hydrazine. Methods are needed for the accurate prediction of the pressure transients in a pipe due to the reflected pressure wave. During the priming of a spacecraft propulsion system, pressure transients occur from the rapid deceleration of propellant from a pressurized manifold to an evacuated manifold downstream of an isolation valve. When the isolation valve is opened, propellant will initially flow essentially unrestrained until the fluid column impacts an obstacle, such as a surge suppression device. In the case of a straight-edged orifice, this will cause cavitation that will slow down the fluid column. The propellant will continue to flow through the downstream piping until it hits a dead end. The initial impact of the fluid column with the dead end will cause a pressure spike. This transient is often referred to as a slug hammer. Once the line becomes filled with liquid, another pressure transient will occur that will cause a pressure wave to travel upstream through all wetted lines and eventually attenuate. This transient is often referred to as the reflected pressure wave. Surge suppression devices have the greatest effect on reducing the pressure spikes due to a slug hammer. Therefore, it is important to accurately predict the pressure transient due to the reflected pressure wave because this transient cannot be mitigated as effectively by simply adding additional margin. AFT Impulse, a surge/water hammer modeling software, was shown to accurately predict the peak pressure transient due to the reflected pressure wave despite some of its modeling limitations, as long as the peak pressure transient is due to the reflected pressure wave [2237].

An experimental research program was conducted to evaluate pressure transient levels in unrestricted liquid monopropellant propulsion system configurations and propellant manifolds generated by surge flow water hammer effects resulting from a priming event [2238]. In a water hammer experimental setup using distilled water as a propellant simulant for hydrazine, multiple test elements were evaluated using different internal diameters, line lengths, and flow control valves, at both atmospheric and sub-atmospheric pressure levels. Based upon experimental results, it was determined that the internal diameter, line length, valve flow coefficient, and valve opening response time all contributed to the pressure spike magnitude of the priming event. It was observed that water hammer pressure levels may be minimized and equally distributed throughout a propulsion system manifold using a ring layout, independent of line geometry, valve flow coefficient, and valve opening response time.

A replica of the manifold of the ExoMars lander retro-propulsion sub-system was built and various fill sequences were tested in the mockup, first with water and then with real hydrazine to prevent the re-occurrence of events such as those that doomed LANDSAT F and TELSTAR 402. A bypass line with an orifice flow restrictor was opened first to fill the manifold slowly before opening the main pyro valves [2239–2241].

The process of filling the downstream feedline can cause severe pressure spikes that could lead to structural failure or even to hydrazine adiabatic compression de-

flagration. For safety reasons the feedline is usually evacuated prior to launch. This causes the propellant to undergo flash boiling, generating a vapor front that mixes with the residual inert gas in the line, usually helium. This complex two-phase/two components flow is quite challenging to model due to a lack of understanding of the physical processes taking place. A dedicated test facility that allowed for fluid transient experiments under the same conditions as an operating space propulsion system was used for tests at different conditions (tank pressure, vacuum level, geometry of the feedline) with water or ethanol [2242, 2243]. To gain detailed insight into the complex flow pattern, a transparent clear quartz segment was installed at the end of the metal feedline and high-speed images were taken. The analysis of the images provided a comparison between de-aerated and saturated conditions of the fluid, making it possible to explain the complex profile of the pressure signal. In addition, a comparison between water and ethanol showed that the differences in the flow evolution of these two fluids can be related to their physical properties such as surface tension, density, and viscosity. This has important implications when testing with the real propellant is not possible and an inert surrogate replacement fluid must be used.

Pressure transients and time to system equilibrium in a pressure-regulated liquid propulsion system due to initial system activation were evaluated using a propulsion system experimental setup with gaseous nitrogen as the pressurant and distilled water as an inert propellant simulant for hydrazine [2244]. A common liquid reservoir was used as the propellant tank, and high-pressure gas was regulated to beginning-of-life conditions. A snubber orifice was installed upstream of the regulator to protect the regulator from high-pressure transients. Experiments were performed evaluating feed pressure, tank pressure, snubber orifice diameter, and system volume. Based upon experimental results, a mathematical model was created to predict activation time for regulated propulsion systems given initial conditions. Experiments with distilled water in an existing water hammer setup using numerous different internal diameters, manifold layouts, and flow control valves, under initial atmospheric and near-vacuum pressure levels, were conducted to determine the influence of restrictions in a propulsion system, as well as the propellant manifold design, in the mitigation of the surge event maximum pressure spike levels [2245].

A feedline system has been simplified to develop a mathematical model and experiments have been carried out to verify the model [2246]. The mathematical model was developed considering a pipe of uniform cross section and a moving liquid-gas interface. Experimental studies were done using water as working fluid instead of actual propellant. The studies showed that rate of pressurization plays a very critical role on the surge flow water hammer pressure spike amplitude. Sensitivity studies have also been carried out to study the effect of density, friction, and initial liquid column length on surge flow fluid hammer pressure spike amplitude. See also [2247].

During the start-up of the propulsion system of a satellite or spacecraft, the opening of the tank isolation valve will cause the pressurized propellant to flow into an

evacuated feedline and slam against a closed thruster valve. This filling process can cause severe pressure peaks that could lead to structural failure. A very detailed investigation was conducted that would apply to all liquid propellants but is of primary interest to priming flight systems with hydrazine [2248, 2249].

A study was performed to determine the pressure transient levels in unrestricted liquid monopropellant propulsion system configurations and propellant manifolds generated from surge events during system priming, using a commercial multi-physics system-level simulation software called GT-SUITE, which predicted the maximum peak priming event pressures in various liquid system configurations [2250]. Experimental data reported in earlier research efforts involving priming after the opening of a latch valve were evaluated using the numerical model to determine the accuracy of the results among various internal diameters, line lengths, manifold layouts, and flow control valves at different pre-test pressure levels in the system. Based on the results, it was determined that the numerical model was a promising tool to predict liquid system pressure transient levels. See also [2251].

A fixed flow restriction (an orifice) in the line would decrease the liquid impact velocity, thereby reducing the water hammer. The drawback to this approach is that the system will suffer from a pressure loss during normal flow usage. A different approach would be to install a flow limiter in the propellant line. Such a device would sense an abnormally high flow and quickly close a poppet so that the orifice size is reduced. This would temporarily limit the flow velocity, thereby reducing the pressure surge. The poppet would then return to its full open position during nominal flow, thus not producing any excess pressure drop during normal operation [2252].

An experimental study was conducted to evaluate pressure transient levels in unrestricted and restricted liquid monopropellant propulsion system configurations and propellant manifolds generated by surge flow pressure spikes during a priming event. This was accomplished through the development of a priming event experimental setup using distilled water as a propellant simulant for hydrazine [2253]. The data required subsequent corrections for the different compressibilities of the two fluids. Multiple test elements were evaluated using different internal diameters, line lengths, manifold layouts, and flow control valves at atmospheric, sub-atmospheric, and low-pressure pre-test pressure levels. The goals of these experiments were to determine the influence of restrictions in a liquid propellant flow system, as well as the propellant manifold design, in the mitigation of the priming event maximum pressure spikes. Based on experimental results, it was determined that the internal diameter, line length, valve flow coefficient, and pre-test pressure level all contributed to the pressure spike magnitude of the priming event. It was also observed that peak surge pressure spike levels might be significantly minimized and equally distributed throughout a propulsion system manifold using an inline cavitating venturi and a manifold layout promoting free flow of the fluid, which was independent of the line geometry, the valve flow coefficient, and the valve opening response time.

### 8.8.2.2 Water (Fluid) Hammer Effects in Propellant Feed Systems

This section deals with pressure spikes in propellant feed systems caused not by dropping propellant into evacuated lines (surge flow and “priming” discussed in the preceding section), but these spikes are caused in lines that are already completely filled with flowing propellant when the flow is brought to a sudden halt, usually by abrupt closing of a thrust chamber valve at the downstream end of the column of moving liquid. This phenomenon occurs with all propellants and all fluids, even with water, and can cause substantial damage. Water (fluid) hammer is a strictly mechanical phenomenon and there are no chemical reactions involved, but if there are hydrazine vapor bubbles in the system (multi-phase fluid hammer), they may explode when suddenly compressed by a water hammer pressure spike. Most of the papers listed here deal with pressure spike phenomena that can occur in any moving liquid, but the pressure spikes can be disastrous if hydrazine vapor bubbles are trapped near the end of the system. Similar problems can occur with liquid oxygen (LOX), NTO, or MMH, but we summarize this phenomenon here in the hydrazine chapter.

The hydrazine monopropellant system on converted TITAN II missiles (“Commercial TITAN”) used a complement of twelve 132-N thrusters, four of these for roll control and eight for  $\Delta V$ , pitch, and yaw control. The water hammer dynamics of this system were modeled to predict and avoid unwanted pressure spikes when several thruster valves close at the same time [2254]. Similar calculations were performed for the ARIANE V SCA [2255]. Most of the computer models described here are not unique for hydrazine and can be applied to describe the flow properties of other propellants as well.

A computer code called CEDRIC was used by Matra Marconi Space to calculate predicted water hammer pressure spikes and compare them to measurements in a replica of a satellite manifold for monopropellant hydrazine [2256]. This was a simple hydraulic network but used water as the reference fluid. The researchers studied the effect of the on/off duty cycle of the thrusters on the water hammer effects when closing several valves simultaneously. They also varied line diameters, line lengths, and the tubing wall material.

The ill-fated Mars Polar Lander '98 (MPL 98) used twelve 290-N thrusters to slow its descent and come in for what was supposed to be a soft landing. Thrust chamber valves in MPL 98 provided only on-off control and were not throttleable as they had been in VIKING. Special attention was devoted to the propellant manifold filling sequence in order to prevent problems encountered several years ago when firing pyro valves in other satellites in rapid sequence. Simultaneous closing of 2 or more of the 12 TCVs may cause pressure spikes, which may damage pressure transducers, filters, or valve seats. Thorough ground testing of the MPL '98 propulsion subsystem performed with water, hydrazine, and He-saturated hydrazine showed that water hammer pressure spikes as high as 6800 kPa (1000 psi) can be encountered if several valves close at the same time. Certain duty cycles had to be eliminated to keep pressure spikes below 5500 kPa (800 psia) at certain portions of the feed system. It was feared that higher-

pressure spikes might damage the in-line filters, valve-inlet filters, or valve seats. Also, the brief low pressure upstream of the thrust chamber valves following the reflection of the pressure wave might have allowed hot gas and catalyst fines to back up into the injector or even into the valve at the start of the next pulse [2257]. During launch and cruise, lines between pyro valves and thrusters were filled with 275 kPa (40 psia) helium to maintain the cleanliness of the lines, ensuring that contaminants from the ambient atmosphere do not leak into the system. Upon arrival on Mars, prior to filling the lines with hydrazine, the manifold lines were evacuated to space by opening TCVs for 30 s, per set of four TCVs. After closing the TCVs, a bypass pyro valve was fired first, allowing flow through a narrow orifice that acted as a flow restrictor. The narrow orifice in the bypass allowed hydrazine to slowly fill the manifold to avoid pressure spikes due to surge flow and to prevent hydrazine explosion by adiabatic compression. In ground experiments with a replica of the MPL 98 plumbing system, it took less than 30 s to fill the lines, leaving a 30-s safety margin for hydrazine froth to dissipate before the next pyro valve was fired. After 60 s, the first main pyro valve was opened. After 30 s, the second pyro valve was opened. A similar orificed design and manifold filling sequence had been used successfully on MAGELLAN.

The severity of water hammering in pipeline systems varies greatly because of differences in the number and the type of thrusters and the operating time of valves [2258–2260].

The ARES I upper stage would have used a reaction control system similar to that flown on CENTAUR upper stages. Water hammer effects were studied experimentally on a replica of the ARES I upper-stage monopropellant reaction control system consisting of 2 propellant tanks and 12 thruster locations [2261]. The effect of the pressure transducer side passage conduit on the water hammer process was computed and analyzed with an example of a liquid rocket engine as the engine is shut down [2262].

Similar fluid hammer experiments were conducted with MMH, NTO, or water in the propulsion laboratory of ONERA [2263]. The objective of one study was to generate an experimental database on the multi-phase fluid hammer occurring during the priming of evacuated propellant lines with non-cryogenic or cryogenic liquids in order to understand the physical phenomena and to benchmark the numerical code Ecosim-Pro [2264]. Two dedicated test facilities (non-cryogenic and cryogenic facilities) were built at the von Karman Institute. An extended test campaign was conducted on the non-cryogenic facility to analyze the effects of various parameters on the fluid hammer behavior such as the line configuration, the vacuum condition in the line, the liquid properties, and the saturated conditions of the liquid, leading to a better understanding of the influence of the desorbed gas on the pressure spike level and attenuation. The effect of the velocity of sound with dissolved gas and the friction model would need to be improved.

The priming of feedlines during start-up of an engine as well as the rapid closing of valves upon shutdown may lead to pressure spikes symptomatic of a water hammer pressure wave. Test benches used to conduct tests on development engines as well

as currently flying engines are sensitive to water hammer pressure waves traveling along their feedlines. Different plumbing configurations were investigated to study their influence on wave shape [2265]. The configurations included a coiled pipe setup with a support structure and without a mounting anchoring support structure. A beat phenomenon (the so-called Poisson-coupling beat) was observed. It was shown that the second water hammer peak can reach pressures a lot higher than the first peak by additive interference of the primary and reflected secondary water hammer wave.

### 8.8.2.3 Theory and Modeling of Adiabatic/Rapid Compression Initiation of Hydrazine

Several attempts have been made to explain the mechanism responsible for the adiabatic/rapid compression initiation of hydrazine deflagration. Several writers have called this a hydrazine “detonation,” but measurements did not indicate a true C-J detonation. High-speed photography images of a liquid front of hydrazine rushing into a transparent cavity were highly informative in visualizing the two-phase flow condition immediately prior to explosion of the tube. It is assumed that the liquid front rushing into a straight dead-ended tube will assume an arrowhead shape since friction along the walls causes the peripheral annulus to lag behind the core flow. If a Teflon foil is used to separate the liquid and the gas prior to the test, as was done in the NASA WSTF tests, it will stretch to rupture and its cone shape will also determine the shape of the liquid-gas interface as it rushes down the test section. Once the gas that is pushed ahead of the liquid “piston” is sufficiently compressed, it will be compressed against the rigid end plug by the momentum of the advancing liquid core. The momentum of the moving liquid keeps it moving faster than the gas, even as the gas pressure is building up. At the liquid-gas interface the differential velocity is sufficiently high to cause Taylor instabilities like a storm blowing over an ocean whipping up waves and whitecaps and carrying spray droplets with it. At a certain wave height, additional liquid spray droplets are ejected into the gas flow and more gas bubbles are entrained into the liquid flow. The front of the advancing liquid assumes a frothy appearance.

CNES conducted shock-tube tests of hydrazine vapor with and without diluents to explain the compression sensitivity of bubbly liquid hydrazine [1192, 1257]. While the study provided additional data on vapor decomposition kinetics, it only cursorily discussed bubble dynamics. It did, however, provide a brief comparison of hydrazine decomposition in compressed bubbles (at high pressures) as opposed to hydrazine vapor decomposition in reflected shock waves in shock tubes. It was stated that the shock-tube method does indeed have the ability to pressurize and heat a gas adiabatically at the precise temperature and pressure conditions encountered in rapidly compressed bubbles. The investigators cautioned that the heat and mass transfer at the gas-liquid interface of entrapped bubbles must not be neglected. The increase in pressure deforms bubbles, heats the medium, and leads to additional hydrazine vaporization. Hydrazine evaporation, though a slow process, cools the surface of bubbles. At the same time, hydrazine vapor in the bubble, which was saturated to start



with, is compressed to conditions beyond saturation and would be expected to condense in the form of a mist if the temperature did not increase very rapidly due to adiabatic compression. The rate of condensation may not be fast enough to avoid forming a supersaturated gas phase.

In a two-part study to determine hydrazine explosion conditions related to the presence of bubbles in a liquid, the first part was devoted to the kinetic modeling of the thermal decomposition of hydrazine in the gas phase in the presence of diluents [2204]. The reaction behind a reflected shock wave was analyzed by absorption spectrometry between 1100 and 1400 K for shock pressures between 200 and 1350 kPa. The influence of the nature of the diluent ( $N_2$ , He) and that of additives ( $H_2$ ,  $NH_3$ ) on the reaction rate made it possible to validate a detailed kinetic model comprising 48 steps and 11 species. The second part concerned the analysis of the behavior of a bubble, trapped in water as a model fluid and in contact with a wall, by rapid imaging (framing rate of 27000 frames/s). The bubble was subjected to a compression initiated by a shock wave reflected on a membrane separating the liquid from the impact tube. The gas consisted of a stoichiometric mixture of oxygen and ethylene, diluted in argon or nitrogen, whose thermodynamic properties and characteristic reaction times were close to those of hydrazine/diluent mixtures. The volume of the bubble was between 100 and 1000 mm<sup>3</sup>. The deformation of the bubble showed that the gas/liquid interface was preserved during the first compression phase and then gradually deteriorated in the expansion phase. Explosions were observed when the ignition delay was less than the time corresponding to the first phase of compression of the bubble.

When diluent gases are present and mixed with fuels, appropriate EOSs must be selected for the diluent gases to calculate the temperatures as a result of isentropic compression of mixtures of fuels and inert gases [2266]. Reliable engineering design and safety analysis for fuel diluent gas mixtures requires correct thermodynamic mixing rules for isentropic compression analysis. Simplifying approaches such as zero- and first-degree approximations are not adequate. The presence of multiple phases over the range of conditions examined suggests that additional work on multi-component, multi-phase systems is required. At pressure ratios above 100, estimating the isentropic compression temperature at ideal conditions gave temperatures approximately 5% greater than by estimating using the appropriate EOSs.

There are a few theoretical analytical studies of compression of reactive vapor/gas bubbles suspended in a non-reactive liquid. There are a few mathematical-analytical publications on reactive bubble compression and cavitation not specifically dealing with hydrazine [2267–2270]. Many of these studies relate to the propagation of LVD detonations in bubbly media. It would be worthwhile to combine this information with the experimental data on hydrazine and determine whether a correlation could be established. Liquid hydrazine (as opposed to hydrazine vapor) is assumed not to participate in rapid compression explosion events. It would be of interest to have an analytical method to predict the critical bubble: liquid volume ratio and compression pressure ratio beyond which hydrazine becomes explosive in the form of froth or foam.

The type of gas and the percentage of vapor entrapped in bubbles would be expected to influence the threshold. We would suspect that helium (frequently used pressurant or purge gas) would make the mixture more sensitive than nitrogen/ammonia (natural decomposition products). In some cases, the collapse of a bubble will be followed by expansion and an oscillatory mode that eventually attenuates and fizzles out. On a microscopic scale, cavitation of gas and vapor bubbles in an intense ultrasound field will cause decomposition (“sonolysis”) of hydrazine [2271]. This is the subject of a new field of study called sonochemistry. This mechanism can be used for the degradation of hydrazine for the decontamination of wastewater (Section 7.12.1.12).

## 8.9 Sensitivity of Hydrazine Exposed to Pyro Valve Blow-by Hot Gases

Several studies on the effects of hot gases from blow-by of pyrotechnic actuator charges in pyro valves on hydrazine and MMH have been conducted in the wake of the losses of MARS OBSERVER (August 21, 1993), LANDSAT F (October 5, 1993), and TELSTAR 402 (September 9, 1994).

In the early 1990s, after a string of satellite and space probe failures attributed to pyro valve explosive interaction with hydrazine propellants, there began a flurry of studies on all conditions under which hydrazine propellants can be initiated to accidental explosions by activating a pyro valve. The most likely cause for the loss of LANDSAT F shortly after stage separation from the TITAN II launch vehicle in October 1993 was a ruptured hydrazine manifold. The ruptured manifold rendered the satellite’s reaction engine assemblies useless because fuel could not reach the engines. Consequently, there was a failure to maintain attitude control during the apogee kick motor (AKM) burn. This failure caused the spacecraft to tumble during the AKM burn and not accumulate enough energy to attain orbit. A few months thereafter, a communication satellite failure occurred when the second of two parallel pyro valves was fired with a programmed delay sequence into a manifold that at that time was partially filled with helium and hydrazine froth. Blow-by of hot gases from the second pyro valve past a leaking ram piston may have initiated a thermal runaway reaction in the hydrazine that ruptured the tubing. This most likely sequence of events was reproduced in simulating ground tests after flight anomalies had occurred. The results of industry-wide workshops were documented in a series of workshop proceedings. Several of these publications deal with anhydrous hydrazine and MMH at the same time, so we need to reference them in more than one location in this book [1827–1833, 2272, 2273].

The effectiveness of O-rings in pyro valves in preventing blow-by of hot gases has been questioned. Numerous publications have been issued in which post-test inspections report that O-rings sheared and shredded. Testing had shown that with some valve designs blow-by occurred regardless of whether O-rings were installed properly or accidentally omitted. As a result of lessons learned, new and improved pyro valve

designs emerged in the mid-1990s, and the pyro valve problems have not re-occurred since then.

Theoretical calculations tried to support the experimental investigations. In one of the real gas (vapor) EOS studies for rapid compression of hydrazine vapors, an attempt was made to include typical pyro valve actuator pyrotechnic charge exhaust products in the calculations [209].

A theoretical kinetic study was conducted to investigate the effects of hydrogen presence in pyro valve actuator blow-by gases on hydrazine decomposition, with some representative calculations including the remaining gaseous species found to exist in blow-by gases [1371]. Since hydrogen is a normal product of hydrazine decomposition, all reactions necessary to evaluate its effect on hydrazine decomposition chemistry were in the original developed mechanism [1372]. However, the mechanism needed to be considerably expanded to include the reactions of other gaseous blow-by species with hydrazine, with all the intermediate species formed in its decomposition, and with each other. The expanded kinetic mechanism consists of 70 species interacting via a network of 452 reactions. Calculations indicated that  $H_2$  presence as an initial reactant in substantial amounts can dramatically impact the decomposition process for hydrazine. What was of particular interest, and somewhat surprising, was the extent to which molecular hydrogen in the initial mixture was predicted to accelerate the decomposition of hydrazine. The change in hydrazine half-life from the baseline case (i.e., no  $H_2$  initially present) to the case where a 1:1  $H_2:N_2H_4$  starting ratio exists was five orders of magnitude. Earlier studies on the effect of atomic hydrogen on hydrazine decomposition [2274] should have been referenced in that study. The other gaseous blow-by species [CO,  $CO_2$ ,  $H_2O$ , C(S),  $O_2$ , and  $N_2$ ] were found to have little effect compared to the inclusion of hydrogen itself as an initial reagent. This result was due, in part, to the fact that the blow-by gas used in one case consisted of 94.6%  $H_2$ . A more rigorous examination of the behavior of the fully detailed mechanism under a variety of conditions was not performed.

### 8.10 Electrostatic Discharge Sensitivity of Hydrazine

Both anhydrous liquid hydrazine and hydrazine hydrate have been tested for sensitivity to ESDs [1408]. No noticeable decomposition was noted in unconfined samples when a static charge of 12.5 J was discharged through the liquid. With partial confinement in a plastic tube, decomposition became apparent when the spark energy exceeded 2.6 J. Sparks of higher energy caused enough decomposition to break the plastic capsule. The potential applied to the electrodes was 5000 V, and the energy was varied by using all or only a portion of the capacitor bank.

Several liquid hydrazine mixtures containing up to 30% HN and up to 30% water were tested on the NOL electrostatic sensitivity apparatus [242]. No detonation or onset of burning was obtained with sparks from 150000-pF capacitors at 5.5 kV. In addition

to the solutions, some HN crystals (which may have contained a few percent of water) were also tested on the same machine, and no explosions were observed. Submerged electric discharge sparks have also been tested as a means of deliberately initiating the decomposition of HPB-3005 hydrazine/hydrazinium nitrate monopropellants in rocket thrusters or liquid propellant guns [2275, 2276].

The minimum spark ignition energy required to initiate decomposition or explosion of hydrazine vapor has never been measured. Likewise, the ignition energy of hydrazine-air mixtures is unknown. The energy available from an automotive ignition coil is more than enough to initiate the decomposition or combustion of hydrazine vapor [1408]. Designers for propellant storage and transfer facilities should adhere to the recommendations provided in [2277].

### 8.11 Friction Sensitivity of Hydrazine

Neither hydrazine nor the 85% hydrazine hydrate showed any sign of explosion, burning, or local crackling when 10 samples each were tested in the USBM pendulum friction test apparatus using a steel shoe and a stainless-steel anvil [1408]. Whereas hydrazine liquid is not friction sensitive, some of its solid and dry salts may be quite friction sensitive.

### 8.12 Bonfire Tests with Hydrazine

Another requirement of propellant classification for transport by common carrier is the bonfire test where a shipping container filled with the material is placed on a grate on top of a pile of wood and ignited. Wood-fired or oil-fired bonfire tests with the monopropellants hydrazine, 66% hydrazine/24% HN/10% H<sub>2</sub>O, *n*-propyl nitrate, and ethylene oxide in 1-gal aluminum containers showed that all four propellants caused container explosions regardless of the type of bonfire or the amount of liquid (95% full or 25% full) in the tank [2184]. It was recommended that storage drums have rupture disks that would allow pressure relief and evaporation of the liquid before explosion pressures are reached. With hydrazine, the 25%-full container would explode after approximately 1 min, whereas it took 2–19 min. for the 95%-full container to explode. In the case of the HN-containing mixture being cooked in a container, an explosion is inevitable even after (or particularly after) all liquid has evaporated.

Another method of testing propellant hazards is the open-pool burning. This test is of importance for propellants such as MHF-1, MHF-4, or MHF-5 that contain HN. If a container or a spill of these fuels caught fire, the volatile fuel (MMH) would burn away first, and HN would accumulate in the residue until the detonable limit is reached. Samples of 250 mL MHF fuels were burned in open dishes [2278]. The initial flame was yellow in color, later turning orange. After all the volatile liquid was

consumed, the flame changed to a tall, hissing columnar flame (“flare burning”), which consumed all the solid (molten) material. In only one out of hundred MHF-1 tests the flare burning was abruptly terminated by a detonation. This effect was not reproducible. By analyzing the nitrate content in residues from tests where the burning liquid was extinguished by a blast of nitrogen before flare burning started, it could be shown that hardly any HN is consumed during the luminous flame prior to flare burning. In other tests, with boiling off of the liquid constituents by external heat (without burning) and continued heating, the residue would typically explode. In all boil-off tests the temperature reached 564–592 K at the time of explosion.

An accident review published as CPIA Publication 661 [2279] makes reference to three events, including explosion of hydrazine storage drums or propellant tanks in fires with the violent explosion of pressure vessels (near field blast) but no mass sympathetic reaction to adjoining tanks, with minimal far-field fragment hazards.

## 9 Toxicity of Hydrazine

In arguments, the toxicity of hydrazine has been cited as the reason why industry-wide (not only the aerospace industry) use of hydrazine and hydrazine hydrate should be restricted. Some overly concerned, single-minded environmentalists have even discussed eliminating hydrazine (hydrate) altogether and have started working on so-called sunset legislation for the gradual elimination of hydrazine (hydrate) from the chemical inventory. Closer examination of some of the documents issued by some of the agencies, for instance a dossier issued by REACH in Europe [2280], reveals that the authors of those reports are poorly educated and have parroted unsubstantiated claims about the hazards of hydrazine. Worldwide recognized sources of information on hydrazines were omitted. No allowance was made for the reduced toxicity of hydrazine hydrate solutions compared to the toxicity of anhydrous hydrazine.

The world’s most complete reference publication on hydrazine(s), written by the same author as the rocket propellant book at hand, in its first [11] and second editions [22], contains a comprehensive list of references on toxicity. This should be the primary source of information and at this time there is very little that needs to be added to it. The current section on hydrazine toxicity presents a condensed review of more detailed sections available in the 2001 edition of the hydrazine book [22], which did not have to be repeated here. Frequent reference to that widely recognized source of information on hydrazines may suffice.

In attempting to organize a section on the toxicity of hydrazine, different approaches can be taken: The subject matter can be grouped by mode of administration (or inadvertent absorption), the body organ affected, or the symptoms observed. The initial main part of this section is arranged by body part affected by exposure to hydrazine. This material, collected from the literature, is then supplemented by several sub-sections discussing mutagenic, oncogenic, or teratogenic effects. This

section here is similar to sections on the toxicity of alkylhydrazines in the chapters on dimethylhydrazines and methylhydrazine, and there may be some overlap. Many publications deal with more than one hydrazine at a time, so these publications are referenced individually and repeatedly in several places in this book.

For a discussion of the possible adverse effects of hydrazine in an occupational environment, such as at rocket launch sites, two types of inadvertent exposure must be considered, vapor inhalation and liquid splashes. The first type of exposure would cause predominantly respiratory and systemic effects, whereas in the latter case effects on skin and eyes must be considered in addition to respiratory and systemic effects. Accidental oral ingestion has happened but is less likely and is readily diagnosed.

As Back et al. in their reviews on the occupational hazards of missile operations involving hydrazines already pointed out, “Chemists and materials engineers are spawning new chemicals and new uses for old chemicals faster than toxicologists, pharmacologists and occupational hygiene and industrial medicine personnel can cope with” [2281–2283]. The price of increased energy content in high-energy rocket propellants has been increased reactivity and biological activity. Recent decades have seen growing concern about environmental and occupational hygiene effects of hydrazines, requiring special attention and clarification.

## 9.1 Hydrazine Toxicity Literature

A detailed summary of the literature on the toxicity of hydrazine and hydrazine hydrate was published in the second edition of the book *Hydrazine and Its Derivatives* [22] on pages 895 through 1102, and there is very little to add to this readily available and exhaustively thorough source of information.

The first source of information on many hazardous chemicals is now the Material Safety Data Sheets (MSDSs), which usually accompany every shipment of chemicals. These MSDSs need to be updated from time to time. It is useless to copy an MSDS that does not have the latest date of revision printed on it. The most recent versions of MSDSs are often available on web sites of manufacturers, distributors, or government agencies. Most recently these documents are called just Safety Data Sheets and the word Material is omitted.

A thorough and ongoing search of the literature on the safety and performance of hydrazine as a rocket propellant and energy source has been performed by the author over the past 40 years. As is evident from the years of publication of many of the references cited in the list of references, hydrazine toxicity was very actively investigated during the 1970s and 1980s, leading to repeated lowering of the allowable TLVs in the air at workplaces. Very little relevant information on hydrazine is found in textbooks and standard reference books on occupational hygiene. It is deplorable that most of these books elaborate on anhydrous hydrazine toxicity, but very few data can be found

on the industrially much more important hydrazine hydrate and hydrazine hydrate solutions. At the point of absorption into the body, anhydrous hydrazine turns into hydrazine hydrate and hydrazinium ion, two chemical species different in chemical activity from their parent, anhydrous hydrazine.

*Patty's Industrial Hygiene* is now in its sixth edition and has grown to a multi-volume work consisting of Vol. 1, *Hazard Recognition*, Vol. 2, *Evaluation and Control*, Vol. 3, *Physical and Biological Agents*, Vol. 4, *Program Management and Specialty Areas of Practice*, but does not contain individual sections dealing with one specific chemical [2284].

*Sax's Dangerous Properties of Industrial Materials* is currently in its 12<sup>th</sup> edition consisting of five volumes [2285]. These two books are standard reference sources on the bookshelf of every industrial occupational hygiene and environmental protection expert.

The book *Hydrazines and Cancer* was published in 2000 [2286]. It is a very thorough review of carcinogenicity test data with both naturally occurring and artificial hydrazine chemicals. There are a few thorough review articles and summaries on hydrazine toxicity. The most notable ones in this category are those by Toth with 326 references [2287] and Moloney with 200 references [2288]. If we had better and up-to-date summaries like these examples, we would not have had to devote an entire section of this book to hydrazine toxicity.

As a group, these review summaries in combination with the selectively expanded toxicity section in this book provide a comprehensive list of references for further in-depth study of this subject. There have been no significant new additions to this list during the past 20 years.

Several authoritative research organizations and government agencies have published toxicity summaries on hydrazines. One of the most thorough studies is the *Environmental Health Criteria*, Vol. 68, published by the World Health Organization in 1987, containing 244 references [2289]. That study benefited from the availability of the 1984 first edition of the hydrazine book by the current author, which is included in the WHO list of references. This was supplemented by the *Hydrazine Health and Safety Guide*, a somewhat shorter summary [2290].

The *Criteria for a Recommended Standard: Occupational Exposure to Hydrazines*, published by NIOSH in 1978, is no longer up to date and requires a thorough revision [2291]. Forty years ago, it represented a good starting point because it contained 229 references. NIOSH Standard 78-172 *Hydrazine* is now available on-line as a series of nine files in .pdf format at <http://www.cdc.gov/niosh/78-172.html>. When that document was still in the review stage in December 1977, the USAF Office of the Surgeon General commented on the NIOSH draft, stating that no toxicology data existed at that time to support a NIOSH-proposed lowering of the 1977 American Conference of Governmental Industrial Hygienists (ACGIH) TLVs. It also explained that in view of restrictive handling procedures used by manufacturers and DoD operations, the po-

tential for routine chronic exposures was limited and the total number of potentially exposed personnel was small.

The US Environmental Protection Agency has published *Health and Environmental Effects Profiles* for hydrazine and hydrazinium sulfate [2292]. These represent useful summaries for someone just starting out in this field or someone trying to get a perspective on the history of hydrazine toxicity studies. An attempt was made to establish a carcinogenic potency factor for all three propellant hydrazines, hydrazine, MMH, and UDMH. Other toxicity data have been collected in a four-page hazard summary [2293].

A sub-committee of the German Society of Chemists (GDCh) has published a very detailed toxicity summary on hydrazine, hydrazine hydrate, and hydrazinium sulfates that contains several pages of references [2294].

A very comprehensive source of toxicity data for *all* chemicals (including hydrazines) is the Registry of Toxic Effects of Chemical Substances (RTECS) [2295–2298]. RTECS is a subscription-only database of toxicological information compiled, maintained, and updated by the National Institute for Occupational Safety and Health. Since 1971, the list has continuously grown and been updated. As of 2001, RTECS contained over 133000 chemicals as NIOSH strives to fulfill its mandate to list “all known toxic substances and the concentrations at which toxicity is known to occur.” RTECS provides identification of six types of toxicity data, including primary irritation, mutagenic effects, reproductive effects, tumorigenic effects, acute toxicity, and other multiple-dose toxicity. It includes specific numeric toxicity values such as LD<sub>50</sub>, LC<sub>50</sub>, TDLo, and TCLo.

More curious readers will appreciate references directing them to a few good starting points for more detailed studies. Many of these toxicity summaries are specifically on the use of rocket propellant hydrazines, which includes the methylhydrazines [2299–2303].

Several of the toxicity summaries were prepared by government agencies in trying to establish safe occupational exposure limits for hydrazines [2291, 2304], as well as for astronauts in closed environments, such as in spacecraft [2305].

When reviewing results from various experimental investigators, it was often very difficult to give a comprehensive survey that was free from contradictions. Even scientists who have studied toxicology their entire lives are often frustrated by the ambiguity and contradictions in many published reports describing the hazardous effects of chemicals [2306]. All carcinogenesis/epidemiological investigations in humans can be criticized because either too few patients were used or because the observation period was too short, since the latency of cancer could be 20, 30, or 40 years after exposure. It becomes apparent that toxicology is not an exact physical science, and statistical ground rules in experiment design and interpretation of data have not always been obeyed. This book can unfortunately offer only a mere juxtaposition of reported results, contradictory or not. The group consisting of hydrazine and its alkylated derivatives is often referred to in the plural case as *hydrazines*. In many instances,



hydrazine derivatives become hydrolyzed or oxidized in the body and hydrazine itself becomes an intermediate in their metabolism.

Until 1995, commercially available anhydrous hydrazine in the US usually contained 0.3 to 0.4% aniline. The initial aniline content was substantially higher when anhydrous hydrazine first became available in the late 1950s. It was noted that some toxicity investigators used commercially available anhydrous hydrazine and made dilutions from it to inject or feed to animals. Some investigators may not have known that the hydrazine contained aniline as an impurity. It is not known what effect the presence of aniline might have had on the results of animal tests conducted in the early years. On the other hand, if the toxicity test was performed to assess the hazard to propellant handlers at missile launch sites, it was appropriate to use the same fuel that the personnel might be exposed to. Aniline is less volatile than hydrazine, and its vapor concentration would not have been very high.

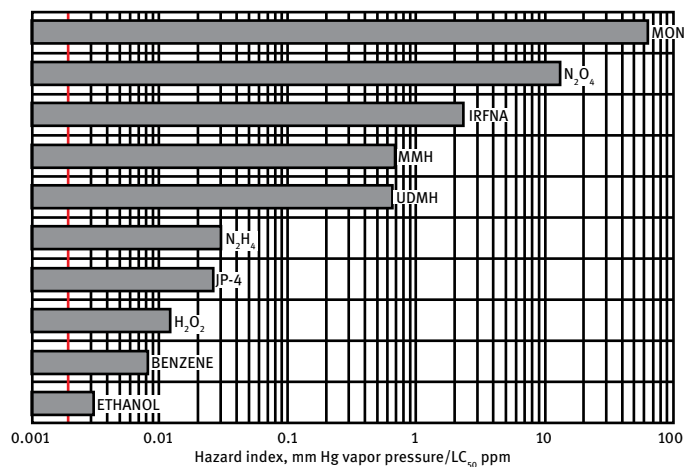
The USAF, as one of the main users of propellant hydrazines, has conducted a long series of toxicity studies and published the results in a series of reports that are summarized in a bibliography [2307]. Toxicity problems with hydrazines are minor compared to problems that would have to be anticipated with other, more energetic propellants like boranes and halogen fluorides that at one time were also considered rocket propellants [2308].

Hydrazine  $N_2H_4$  itself has the lowest vapor toxicity potential of the most frequently used hydrazine fuels. This is illustrated in Table 91 and Figure 68, which show a comparison of hazard indices for various rocket propellants and automobile fuels. More volatile liquids are more likely to cause accidents than less volatile liquids. The *hazard index* is often defined as the quotient of vapor pressure at ambient temperature and the  $LC_{50}$  (lethal concentration at which 50% of the test animals survive). The hazard index addresses only the most immediate acute toxicity hazard. In the format shown here for comparison only, it does not address chronic health hazards resulting from long-term exposures to even much lower concentrations. The

**Table 91:** Hazard indices of hydrazine and methylhydrazines.

| Compound                                | Formula         | Vapor pressure at 298 K<br>(25 °C = 77 °F), mm Hg | $LC_{50}$ , 4 h,<br>ppm | Hazard index,<br>mm Hg/ppm |
|-----------------------------------------|-----------------|---------------------------------------------------|-------------------------|----------------------------|
| Hydrazine                               | $N_2H_4$        | 14.4                                              | 570                     | 0.03                       |
| Methylhydrazine                         | $CH_3NHNH_2$    | 49.6                                              | 74                      | 0.67                       |
| Unsymmetrical<br>dimethylhydrazine      | $(CH_3)_2NNH_2$ | 156.8                                             | 252                     | 0.62                       |
| Symmetrical<br>dimethylhydrazine        | $CH_3NHNHCH_3$  | 69.9                                              | Avg. 340                | 0.21                       |
| For comparison:<br>Dinitrogen tetroxide | $N_2O_4$        | 875                                               | 67                      | 13                         |

Data source: [2309]



**Figure 68:** Hazard index of hydrazines in comparison to other propellants.

hazard index relates somewhat to the Immediately Dangerous to Health and Life concentrations defined in Section 9.11.5.

The toxicity of hydrazine and its derivatives is of interest from both a therapeutic (side effects of hydrazine-derived drugs), epidemiological (side effects of plant growth retardant residues in food for human consumption), and an occupational hygiene point of view. In recent decades, an increasing number of chemicals, even some of those encountered in daily use, have been identified as carcinogens and potential carcinogens. Accordingly, much work has been devoted to studying the carcinogenic (or oncogenic) potential of hydrazines (Section 9.7). See also [2310, 2311].

## 9.2 Observed Symptoms as a Result of Hydrazine Exposure

This section on symptoms observed as a result of hydrazine poisoning represents a summary and introduction that is intended mostly as a warning to someone who is trying to prevent (or a guideline to someone who is trying to explain) certain symptoms observed in humans and animals with a history of exposure to hydrazines. Obviously, most of the data compiled here were obtained on test animals. Few reports exist on symptoms observed in humans following accidental exposures. For the sake of brevity, the species in which the symptoms were observed, the mode of administration, the concentration of the toxicant, and the duration of the exposure details are not yet provided in this initial summary. Details on the exposure conditions can be found in the individual subsections following this introduction. These individual subsections are subdivided by the part of the body affected by exposure to hydrazine. As with many other toxic substances, the response may be species-dependent or even

strain-dependent. For instance, hydrazine may cause cancer in one species of test animal but not in another. Unfortunately, some of these disputes about contradictory results could not be resolved while this book and previous books were in preparation, and the reader may sometimes find a juxtaposition of contradictory data without a clear conclusion. The numbers in parentheses following the listed symptoms refer to the ensuing paragraphs in which these symptoms are discussed in more detail.

One of the prime target organs of poisoning by hydrazine and hydrazine derivatives is the liver [2312–2319]. Symptoms include fatty degeneration of liver tissue, centrilobular damage, changes in glycogen content, and loss of mitochondrial activity. In the blood, hydrazine hemolyzes red blood cells [2320]. Numerous enzymes are disturbed by the presence of hydrazines. The metabolic pathway of hydrazines can be traced by a number of experimental toxicokinetic techniques that help to explain the observed symptoms. Symptoms in the kidney and urinary tract that were caused by hydrazine(s) included changes in creatinine clearance and rate of glucose resorption [2321–2327]. Other symptoms caused by hydrazine include increased diuresis, salivation, hyperventilation, vomiting, diarrhea, and increased neuromuscular activity.

In summary, as depicted in Table 92, a variety of symptoms are observed as a result of hydrazine poisoning, but to a different degree depending on which hydrazine caused the problem. Some of the symptoms are not quite as severe with hydrazine itself as they are with methylhydrazines. The simple table tries to give an overview of symptoms observed with the four most commonly used hydrazine compounds. A single plus (+) sign marks cases where specific symptoms were observed. Two plus signs (++) identify conditions where these symptoms are always very strongly observed. A question mark (?) indicates that the information gathered was inconclusive. The table cannot be detailed enough to take into consideration the

**Table 92:** Summary of adverse effects of hydrazines.

| Adverse effects     | Symptoms observed                     | N <sub>2</sub> H <sub>4</sub> and N <sub>2</sub> H <sub>5</sub> OH | MMH | UDMH |
|---------------------|---------------------------------------|--------------------------------------------------------------------|-----|------|
| Respiratory effects | Nose and throat irritation            | +                                                                  | +   | +    |
| Respiratory effects | Tracheitis and bronchitis (secondary) | +                                                                  |     |      |
| Respiratory effects | Pulmonary edema                       |                                                                    | +   |      |
| Systemic effects    | Dizziness and nausea                  | +                                                                  | ++  | ++   |
| Systemic effects    | Anorexia                              | +                                                                  | +   | +    |
| Systemic effects    | Fatty degeneration of the liver       | ++                                                                 | +   | ?    |
| Systemic effects    | Degeneration of the kidneys           | +                                                                  |     |      |
| Systemic effects    | Methemoglobinemia                     |                                                                    | ++  | +    |
| Systemic effects    | Convulsions and stupor                | +                                                                  | ++  | ++   |
| Systemic effects    | Tumors                                | ?                                                                  | ?   | ?    |
| Skin effects        | Skin edema                            | +                                                                  |     |      |
| Skin effects        | Allergic dermatitis                   | +                                                                  |     |      |
| Eye effects         | Itching, burning, and swelling        | +                                                                  | +   | +    |
| Eye effects         | Cornea damage                         | ++                                                                 |     |      |

variation of species in which these symptoms were observed (e.g., mouse, rat, dog, monkey), nor does it differentiate between different durations or concentrations of exposure.

### 9.3 Metabolic Fate of Hydrazine

Many of the symptoms and effects caused by hydrazine discussed in this section are caused by the interference of hydrazine with metabolism in the various organs attacked. It is sometimes difficult in summarizing a large amount of data to separate the cause and effects of hydrazine on metabolism in some specific target organs. The more academic studies on the metabolic actions of hydrazine and the effects on certain target organs have already been summarized in other publications [22] and are not repeated here. Often the metabolic action of hydrazine is compared to the action of methylhydrazines, which are also used as rocket propellants.

Besides observing the adverse effects of hydrazine on various parts of the body, it is also of interest to determine which pathways hydrazine and its derivatives follow through the body and what fraction is excreted unchanged or as intermediate additive with other metabolites or totally metabolized to nitrogen and water [2328, 2329]. In addition, toxicokinetic studies have looked at the rate at which the poison is distributed throughout the body and at what rate it disappears through either metabolism or clearance in the unadulterated state.

Many of the early studies of metabolic pathways were done by identifying agents that could block a vital step of a metabolic cycle, then observing which metabolic substrates accumulated when the blocking agents were administered to living animals. Hydrazines and hydrazides were once studied in this way, until radioactive tracer techniques became available that allowed investigators to keep track of individual molecules as they moved through the body.

The reactions that hydrazine and its derivatives undergo in the human body can be grouped into non-enzymatic reactions, transferase reactions, hydrolase reactions, and redox reactions. The tracing of the metabolic pathways of hydrazines by the chemical analysis of body fluids and excrements is very difficult because hydrazines are so reactive. Important biotransformation reactions include hydrazone- or azine-forming reactions with carbonyl compounds, acetylation, hydrolysis, and oxidation. The biochemical pharmacology of hydrazine and hydrazine derivatives is a topic that has received extensive research attention in recent decades [2330, 2331]. Hydrazines can be bioactivated, leading to intermediates of increased reactivity [2332].

The metabolic fate of hydrazine(s) is independent of the mode of administration since blood acts as the transport vehicle in most cases. Resorption through the skin may be different from the other methods commonly used for administering experi-

mental drugs and poisons. The skin is a very inefficient barrier to hydrazine liquid splashes or hydrazine vapors, and hydrazine toxicokinetics after skin permeation are the same as if it were administered by other methods [2333].

Interspecies variation for hydrazine toxicity between rats and mice has been studied by administering hydrazinium(1+) chloride *po* to rats (30 mg/kg,  $n = 10$  and 90 mg/kg,  $n = 10$ ) and mice (100 mg/kg,  $n = 8$  and 250 mg/kg,  $n = 8$ ) [2334]. The direct biochemical effects of hydrazine in kidney, liver, and brain tissue were assessed in male Sprague-Dawley rats using NMR spectroscopy [2335]. Of special interest are reactions involving hydroxyl free radicals during the oxidative metabolism of hydrazine derivatives, since some of these compounds may lead to cancer.

Non-enzymatic reactions as part of hydrazine metabolism are those that are most easily reproduced *in vitro*. Hydrazines have a pronounced affinity to carbonyl groups in sugars and other compounds essential for living cells. The reaction of hydrazine with amides, whether singular amides or polymeric amides such as peptides, leads to the hydrazinolysis and breakage of the peptide chain. The hydrazine metabolism of microsomes (i.e., protoplasmic granules) is easily studied *in vitro*. It has been demonstrated that hydrazine is metabolized by rat liver enzymes located in the microsomal fraction.

Efforts to track the movement and location of hydrazine in body fluids are hampered by the reactivity of hydrazine and by the interference of biogenic amines in the analysis of trace hydrazine. Early studies on the excretion of hydrazines and metabolites used a gasometric method for determination of the sum of hydrazine and hydrazine derivatives in urine. The sample was reacted with potassium iodate in a Warburg apparatus or van Slyke apparatus, and the amount of nitrogen collected was measured.

Mass spectrometric analysis of exhaled air showed that 15% of a single dose of  $^{15}\text{N}_2\text{H}_4$  administered to rats was converted to  $^{15}\text{N}_2$  gas and exhaled within 30 min. after gavage. An additional 10% emerged within the subsequent 48 h [2336–2340]. Later studies [2341, 2342] eventually confirmed the presence of  $^{15}\text{NH}_3$  in urine.

When following the time dependence of tissue levels and excretion of hydrazine as measured by reaction with PDAB and spectrophotometry, hydrazine continued to appear in the urine of mice and rats for 20 h or more after a single injection [2343–2345]. Significantly high levels of all hydrazines and especially acetylhydrazine were detected in the kidney. The excretion of hydrazine and acetylhydrazine in the urine were dose dependent: The proportion of hydrazine and acetylhydrazine excreted declined with dose [2346, 2347].

A study of Japanese workers exposed to hydrazine (hydrate) vapors in an industrial setting, where the exposure level was  $\sim 0.1$  ppm  $\text{N}_2\text{H}_4$  in air, revealed that the workers excreted an average of  $2.7 \pm 2.0$  ppm ( $n = 8$ ) hydrazine in their urine [2348]. Humans differ in the rate at which acetylation occurs in their metabolism. Based on this study, occupational exposures are expected to produce urine excretions

greater than 1 ppm hydrazine and it may be possible to establish a biological activity index [2349]. Tracing the pathway of  $^{15}\text{N}_2\text{H}_4$  isotope-labeled hydrazine through rats by collecting urine specimens, lyophilizing, and analyzing them by NMR led to the identification of several new hydrazine metabolites [2342]. Ammonia and unchanged hydrazine were readily identified in the inorganic portion. Acetylhydrazine and diacetylhydrazine (known from previous studies) were readily confirmed. Carbazic acid, pyruvate hydrazone,  $^{15}\text{N}$ -enriched urea, and cyclic 2-oxoglutarate hydrazone had not been reported previously but were lately discovered and identified by their NMR spectra.

#### 9.4 Therapy and Prophylaxis of Hydrazine Poisoning

Although acute or chronic poisoning by hydrazines is quite rare, a significant amount of work has been devoted to the search for antidotes against accidental or experimental hydrazine poisoning. One objective in these studies was to alleviate undesirable side effects of hydrazine-derived drugs, such as INH. In many cases, the chemicals that were found to be effective antidotes also supported previous theories about the point of attack of hydrazine in metabolism. Some amino-type therapeutics may compete with hydrazine for a site or sites on cell membranes where an attack might otherwise occur. In other cases, makeup replacement is needed for carbonyl compounds that were tied up by hydrazone formation.

Handbooks on first-aid treatment for accidental poisonings in humans unfortunately do not adequately reflect the amount of study and the large amount of information available on the treatment of hydrazine poisonings, most of which has been summarized in the preceding sections. One handbook recommended chlorpromazin or barbiturates for the treatment of hydrazine-induced spasms in human patients [2350].

The USAF AFOSH Standard 161-13 (26 Dec 1979) on page 30 stated, "If convulsions occur, diazepam or a short-acting barbiturate with due regard for the CNS depressant effect of Hz. The use of pyridoxine in advanced CNS involvement is controversial. It does not appear to be helpful in prophylaxis of CNS symptoms." A more recent revision, when Std. 161-13 was incorporated into AFOSH Std. 48-8 (1 Sep 1997), omitted this section altogether.

Propellant handling personnel should undergo routine periodical health examinations and their medical records need to be reviewed for slow changes in body functions. Considerable information that is useful in evaluating the adequacy of control measures can be obtained by compiling and analyzing clinical laboratory results, physical findings, and subjective complaints. A detailed treatment procedure for victims of acute exposures to hypergolic fuels or oxidizers has been described [2351].

## 9.5 First Aid and Clinical Treatment of Hydrazine Poisoning

### 9.5.1 Human Accident and Treatment Histories of Hydrazine Exposures

Anyone reading about the results of various experimental animal studies dealing with prophylaxis and therapy of hydrazine poisoning using pyridoxine = vitamin B<sub>6</sub> may still have some doubt as to whether this chemical would help in human accident situations. Section 9.9.2 contains a summary of hydrazine accidents and several accounts of successful application of pyridoxine therapy of hydrazine poisonings. The reader should consult that section to obtain additional information on the circumstances of these accidents. A brief summary of the pyridoxine aspects follows here. There are two cases of acute accidental hydrazine/UDMH poisonings in rocket test technicians. In these cases, timely administration of pyridoxine•HCl brought about immediate improvement of the condition of the accident victims [2352]. After injecting 200 mg *iv* and 2 × 200 mg *im* pyridoxine hydrochloride, all nervous disorder symptoms except chest congestion vanished within 20 min. Another technician caught in the same leak had hyperactive reflexes, high respiration rate, and bilateral pulmonary edema. He also was given 200 mg *iv* plus 2 × 200 mg *im* pyridoxine•HCl. His dyspnea improved, and his other symptoms abated. Follow-up studies over subsequent days and weeks showed no permanent ill effects in any of the two patients. In another accident at the same test installation, four workers suffered severe nausea and vomiting, which possibly could have been prevented by the immediate use of pyridoxine. This drug was only later administered *iv* at the onset of vomiting, and the vomiting stopped in 20 min.

A 36-year-old man was admitted to a hospital 2 h after an industrial hydrazine explosion [2353]. Burns of second and third degree covered 22% of the body surface. Fourteen hours after the burn the patient became comatose and remained unresponsive for 60 h. A decision was then made to try 600 mg pyridoxine *im* and an additional 1.0 g pyridoxine as a continuous infusion over 3 h. Four hours after the initiation of therapy, the patient began to recover, and 12 h later he was alert. The patient was discharged after 38 d (after completion and healing of skin replacement graft surgery). This case suggests the more immediate use of pyridoxine in treatment of hydrazine poisonings. In another, though less severe, accident, a 24-year-old man accidentally swallowed a mouthful of hydrazine and immediately became confused, lethargic, and restless [2354]. Three days after admission to the hospital he remained confused, but stable, until his liver function degenerated. The patient was treated with a megadose of 10 g pyridoxine *iv* over a period of a few hours. Within 24 h, the patient's mental status improved, and liver function tests returned to normal within 5 d after therapy, when he was discharged from the hospital. The patient later returned with sensory neuropathy problems, which may have been caused by the megadose of pyridoxine.

Hydrazine sulfate caused severe encephalopathy in a patient after taking 180 mg hydrazine sulfate/day for 2 weeks followed by 360 mg/d. After receiving 5 g *iv* pyridoxine in the emergency room, the patient's encephalopathy resolved within 24 h after receiving pyridoxine. High-dose pyridoxine was shown to be an effective treatment

to reverse encephalopathy and hydrazine poisoning [2355]. Pyridoxine was also useful in treating human tuberculosis patients that had suffered adverse reactions to the hydrazine-derived anti-tuberculosis drug isoniazid.

Recommended best practices for emergency medical treatment of military personnel in cases of hydrazine exposure have been reviewed [2356]. Unfortunately, only NASA and hydrazine manufacturing facilities stock necessary amounts of *iv* pyridoxine in their first-aid dispensaries, and most military medical treatment facilities have no *iv* pyridoxine in stock.

### 9.5.2 Antidotes for Treatment of Hydrazine Poisoning Tested in Animals

Antidotes against hydrazine poisoning tested in laboratory animals at one time or another include mixtures of arginine glutamate,  $\alpha$ -ketoglutarate, and oxalylacetate [2357, 2358]; sodium  $\alpha$ -ketoglutarate [2359]; sodium pyruvate and sodium salt of  $\alpha$ -ketoglutaric acid as prophylacticum and therapeuticum [2360–2362]; arginine and ornithine [2363, 2364]; arginine enhanced by L-glutamate and L-alanine [2365] or  $\alpha$ -ketoglutarate and oxalacetate [2366]; fructose [2367]; and diphenylphenylenediamine [2368, 2369]. Sodium phenobarbital in sub-hypnotic amounts was found to increase the survival rate in mice poisoned by hydrazine [2370].

Only those amino acids that take part in the urea cycle and can decrease the amount of ammonia formed primarily from hydrazine are capable of providing protection against hydrazine toxicity [2357, 2358, 2371]. Citrulline exerted no protective action, while 1,3-diaminobutyric acid and 1,2-diaminopropionic acid and several diamines did.

Pyridoxine and phenobarbital were tested as a treatment of Aerozine-50 poisoning [2372, 2373] and all hydrazines as a group [2351, 2352]. See also [2353, 2354]. Arginine or L-glutamate or pyridoxine alone did not give any noticeable protection against the toxicity of Aerozine-50 [2374]. Pre-treatment of male mice with 6 mmol/kg of arginine given *ip* or *iv* at 30 min. or 18 h prior to hydrazine hydrate injections did not have the expected prophylactic effect against poisoning by hydrazine hydrate [2361].

Two-dimensional paper chromatography was used to study amino acid distribution in tissues of normal mice, mice treated with hydrazine, and mice pre-treated with protective amino acids prior to injection with hydrazine [2375, 2376]. Glucogenic amino acids were tested as a means to reduce chronic hepatic injury induced by hydrazinium sulfate when it was evaluated as a carcinostatic agent [2377].

Eighteen different compounds were tested for their therapeutic effect against hydrazine, MMH, or UDMH poisoning (*ip*, mice) [2363]. Of those found to be effective, arginine and ornithine provided clear-cut protection from death and convulsion caused by otherwise fatal hydrazine doses, but the two amino acids were ineffective against MMH or UDMH. Amino-oxyacetic acid or pyridoxine provided effective protection against MMH or UDMH poisoning but were ineffective against hydrazine.



Only partial protection against UDMH was offered by *p*-nitrobenzaldehyde or *p*-chlorobenzaldehyde.

In one study, 0.5 mM (3.65 g/kg) of  $\alpha$ -ketoglutaric acid as the sodium salt was administered orally to mice 30 min prior to an otherwise deadly oral dose of 100 mg hydrazine/kg, and this pre-treatment permitted 95% survival [2359, 2378]. The protective efficiency of pyridoxal and other forms of vitamin B<sub>6</sub> has been disputed and questioned [2362]. In tests with rats, these compounds either had no effect on the toxicity of hydrazine or even enhanced the seizure incidence over that found in animals receiving hydrazine alone. In rats, the *in vivo* formation of pyridoxal phosphate was impeded by hydrazine administration [2379]. It has been suspected that one of the modes of toxic action of hydrazine might be the displacement of the guanidino group of arginine by hydrazine. Therefore, if enough arginine is offered in excess of that altered by hydrazine, the toxicity of hydrazine might be reduced.

Hydrazine in mice *ip* at 3.5 mM/kg caused 100% mortality, and at 3.0 mM/kg the mortality rate was 75% within 60 min. [2362]. A dose-response curve was used to illustrate the protective effect of simultaneous administration of arginine at 6 mM/kg. Arginine significantly reduced mortality rate due to hydrazine toxicity in mice (from 75 to 20%) as well as rats. Administration of 50 mg nicotinoyl-D,L-methionine/kg reduced the hydrazine liver toxicity in rats given daily injections of 2  $\mu$ M/kg of a hydrazine salt [2380].

Vitamin E ( $\alpha$ -tocopherol acetate) and vitamin B<sub>6</sub>, especially in combination, were very effective in preventing liver dystrophy in rats exposed to hydrazine [2381–2383]. Combined administration of the vitamins increased the biliation and increased the rate of cholate synthesis and cholesterol and bilirubin excretion. There are numerous studies on the therapeutic effectiveness of pyridoxine or pyridoxal against consequences of hydrazine poisoning [2384–2391].

## 9.6 Acute Hydrazine Toxicity and Inhalation Toxicity

This section contains a summary of acute toxicity studies with experimental animals. Most of these studies were done for inhalation toxicity, which was expected to be the most likely mode of accidental entry for accidents with humans in places where hydrazines are manufactured and used.

### 9.6.1 Acute Hydrazine Inhalation Toxicity Studies

This section contains more diverse toxicity data than the heading indicates. The borderline between acute and sub-acute to chronic toxicity is not a fine line and is dependent on many variables. We decided to draw the line between acute (short-term) and chronic (long-term) exposure at 1 d. The assumption is that if accidental exposure occurs due to a leak, it should typically be detected after 1 d (at the latest) and corrective

action should have been taken to correct the intolerable situation. Of course, toxicity response is species dependent, and it may not always be justifiable to extrapolate from animal test results to predicted safe levels for human exposure [2392]. Since inhalation is the most likely pathway for hydrazines in accidental poisoning of humans, these data are discussed here first. Unfortunately, of all modes of administration, controlled inhalation concentration levels are the ones most difficult to maintain in an animal experiment because hydrazines are so reactive and may autoxidize in the air of the exposure chamber or may be absorbed by the fur of the animals or the bedding materials in the cage or by the food. In some instances, 96–99% of hydrazine metered into the air stream was decomposed or adsorbed after a single pass through the exposure chamber with or without dead or living animals. There is typically more scatter and less confidence in inhalation data than those obtained with other modes of administration, such as injection. The objective of these tests is to obtain a toxicity rating and to determine threshold levels below which no toxic symptoms can be observed. Because of the large variations in individual susceptibility, statistically large numbers of animals must be used in order to arrive at reliable numbers. The data are analyzed using statistical methods, typically a probit plot, in the dose-response relationship, from which then a lethal concentration 50 (LC<sub>50</sub>) or lethal dose 50 (LD<sub>50</sub>) can be derived [2392]. This number indicates the concentration or dose at which 50% of the animals in an exposed group will survive after a stated observation period. Quite often, investigators will report the duration of exposure but will fail to specify the post-exposure observation period within which fatalities were counted. Concentrations given in ppm are independent of the temperature, which makes it more convenient to use, since the temperature does not have to be listed all the time. Concentrations in mg m<sup>-3</sup> are temperature dependent. If the temperature is not listed, it is assumed that the data are for 298 K. It is more convenient to use mg/m<sup>3</sup> units if the toxic vapor arises from evaporation of a liquid and the amount of liquid that has evaporated can be weighed. To convert from ppm (by volume) to mg/m<sup>3</sup> at 298 K and vice versa, use the following equations:

$$\text{TLV (mg/m}^3\text{)} = \frac{(\text{TLV (ppm)})(\text{molecular mass (dalton)})}{24.45}$$

$$\text{TLV (ppm)} = \frac{(\text{TLV (mg/m}^3\text{)}) \times 24.45}{(\text{molecular mass (dalton)})}$$

A summary of hydrazine inhalation toxicity and acute toxicity data is available in [2393].

#### 9.6.1.1 Acute Hydrazine Inhalation Hazard Studies

**Hydrazine Vapors.** Because hydrazine vapor may be absorbed into the body not only by inhalation but also by skin permeation, early acute toxicity studies were not able to differentiate between the two pathways. Rodents often lick their fur. Quite often hydrazine would condense on the fur of rodents in the exposure chamber and provide

an additional pathway for intoxication, which would not be typical for workers who change work clothes and take showers more often. Another uncontrolled additional mode of ingestion is the hydrazine that condenses on the food or is absorbed from the atmosphere into the drinking water and then ingested by animals.

Test protocols are often inadequate to reconstruct how long food and water has been sitting in exposure chambers. Food sitting in a chamber becomes saturated with hydrazine(s). For instance, the Vernot and MacEwen study stated that **“Introduction of considerable excesses of hydrazine was required to attain the desired analytical concentrations.** Mean nominal concentrations of 21, 5.5, 3.1, and 1.9 ppm were generated to attain time-weighted average analyzed intended concentrations of 4.96, 1.00, 0.25, and 0.05 ppm, respectively” [2394]. Clearly, several loss mechanisms consumed hydrazine that was not being inhaled. Thus, for the 0.05-ppm case, **a 38-fold excess of hydrazine over and above the intended concentration was introduced.** It must be assumed that the difference between the hydrazine introduced and the hydrazine leaving the chamber in air samples was absorbed into the skin of animals and into the food in addition to the hydrazine that was intended to be incorporated through inhalation. The food and drinking water were not analyzed for adsorbed hydrazine in these tests. The test conditions used at the University of California, Irvine (UC Irvine) constitute overly severe exposure conditions for a true respiratory hazard evaluation. The conditions do not relate to the exposure of workers in the workplace under real-world conditions. It is difficult to set up the animals such that they breathe only adulterated air and eliminate all other routes of ingestion by way of skin absorption, licking their fur, and absorption of hydrazine into food and drinking water. Workers exposed to hydrazine vapors at work are unlikely to store and eat their sandwiches and leave beverages sitting open in the same atmosphere in which they work.

One of the worst-case scenarios is a test where groups of six rats each were exposed to saturated (!) hydrazine vapors at the saturation partial pressure (14.2 mm Hg) at 298 K in air, corresponding to approximately 18600 ppm [2395]. Exposure durations were 0.5, 1, 2, and 4 h, and mortalities were very high. Examination of nasal passages revealed acute catarrhal rhinitis. Autopsy showed pulmonary edema in addition to the destruction of bronchiolar mucosa. Backing off to more moderate concentrations of 300, 76, and 26 mg/m<sup>3</sup> for 6 h/d, 5 d/week for a total of 6 weeks simulating chronic exposure conditions still resulted in some deaths in each of the 3 groups of 20 rats each. Half of the animals had perished after 27, 50, and 144 h. Lungs, livers, spleen, and kidney showed pathological changes after less than 4 d of exposure.

It appears that some of the early investigators (Vernot et al.) used a single central hydrazine analyzer with excessively long plastic hose sampling lines leading to a gallery of many exposure chambers. Hydrazine decay, permeation, and adsorption on the surface of the sampling train were ignored, resulting in possibly excessively high(er) actual hydrazine concentrations at the point of exposure of the animals. A USAF-sponsored workshop in 1990/1991 attended by participants from NASA, USAF-SD, the Navy, and the Chemical Manufacturer's Association recommended

a re-evaluation of the hydrazine vapor generation system and the monitoring used in the Vernot studies, but results of the re-evaluation have never been published.

More than 50% of a group of rats exposed to the extremely high concentration of  $20 \text{ g/m}^3$  hydrazine vapor in air for 2–4 h died during the experiment [2396]. Periodic daily exposures to lower concentrations in air, 6 h/d for 6 weeks, caused porphyrinuria, 10–20% weight loss, and pulmonary edema. The lowest concentration at which damage was detected in rats was  $26 \text{ mg/m}^3$ . Dogs exposed to  $6 \text{ mg/m}^3$  hydrazine vapor in air for 6 months got used to the toxic challenge after initial weight loss and muscle tremors. The autopsy of dogs after the 6-month test showed necrotic destructions of liver and kidney and biliary engorgement.

One of the earliest inhalation studies in 1954 also initially used excessively high vapor concentrations ( $20000 \text{ mg/m}^3$ ) for exposure periods with rats from 0.5 to 4 h, but quickly retreated to less toxic concentrations to simulate more closely the potential exposure profile of soldiers accidentally exposed to rocket propellant fumes on the battlefield [2397]. Based on these crude tests, it was estimated that the maximum allowable concentration would be below  $6 \text{ mg/m}^3$  (5 ppm).

More recent inhalation toxicity studies with rodents therefore attempted to separate the two effects by either allowing the animals to breathe the hydrazine-laden air through a mask or by placing them in a hydrazine vapor exposure chamber but allowing them to breathe clean air through a mask. Such skin permeation effect studies are discussed in Section 9.6.4.1.

The oncogenic potential of hydrazine inhalation was examined after 1 (acute) or 10 (subchronic) 1-h weekly animal exposures, and a variety of acute toxicity problems were noted [2398]. The objective of this study was to investigate the relationships of acute and sub-chronic effects of hydrazine to nasal tumorigenesis. In Type 1 (acute and sub-chronic) and Type 2 (lifetime experiments), groups of male and female Fischer 344 rats and male Syrian golden hamsters were exposed by inhalation to 0, 75 (Type 2 only), or 750 ppm hydrazine for single (acute) or 10 (sub-chronic) 1-h weekly exposures. Groups of rodents were euthanized 24 h after exposure Nos. 1 and 10 and also 24 to 30 months after study initiation. Significant reductions in body weight were observed in hydrazine-treated rodents compared to controls during the exposure interval, but none of the animals died as a result of hydrazine-induced mortality. Histopathologic examination after the acute and subchronic exposures revealed degeneration and necrosis of transitional, respiratory, and olfactory epithelia in the anterior nose and, in rats exposed sub-chronically, squamous metaplasia of the transitional epithelium. Minimal to mild rhinitis resulted from hydrazine exposures. Apoptosis was observed in olfactory and squamous metaplastic transitional epithelium. Lesions occurred at sites having high air flow and generally appeared to be more severe in the anterior portion of the nose. By 24 months, the squamous metaplastic transitional epithelium had reverted back to normal-appearing transitional epithelium. After 24+ months, low incidences (sexes combined) of hyperplasia (5/194, 2.6%) and neoplasia (11/194, 5.7%) were detected, principally in the transitional epithelium of

the rats exposed to 750 ppm. A similar incidence of hyperplasia (2/94, 2%) and neoplasia (5/94, 5.3%) was detected in the high-exposure group of hamsters. The location and type of hydrazine-induced proliferative lesions were similar to those reported in a chronic hydrazine exposure study (5.0 ppm  $\times$  6 h/d  $\times$  5 d/week for 1 year) conducted in the same laboratory, but the chronic study had much higher incidences (rats, sexes combined: hyperplasia 15.5% vs. 2.6% and polypoid adenoma 44.6% vs. 5.2%). The product of concentration  $\times$  time was the same (750 ppm h) for the high-dose groups for both studies, but the duration of exposure was 150 times longer and the concentration was 150 times lower in the chronic study. The oncogenic (long-term) aspects of this experiment with rats and hamsters are discussed in more detail in Section 9.7.

Male and female Sprague-Dawley rats (five animals/sex/group) were exposed (nose only) for 1 h to an aerosol of hydrazine (64% aqueous solution, equivalent to 100% hydrazine hydrate, mass median aerodynamic diameter  $\pm$  geometric standard deviation of  $5.0 \pm 2.56$ ,  $1.1 \pm 3.56$ ,  $1.8 \pm 3.04$ , and  $2.4 \pm 2.40$  for the 0.65, 2.04, 4.98, and 3.24 mg/L exposure atmospheres, respectively) [2399]. The rats were observed throughout the exposure period (clinical signs recorded at the end of chamber equilibration period and at 0.25, 0.5, 0.75, and 1 h during exposure) and daily (or more frequently as necessary) for an additional 14 d. During the exposure, the rats exhibited exaggerated respiratory movements. During the post-exposure observation period, clinical signs included death (at the two highest concentration exposures only), exaggerated respiratory movements, noisy respiration, lethargy, secretions from the eyes, brown staining around the snout and jaws, and poorly groomed appearance. The lethality data are summarized in Table 93.

**Table 93:** Lethality in rats following 1-h nose-only exposures to 64% hydrazine aerosol.

| Exposure group, mg/L | Males | Females | Total |
|----------------------|-------|---------|-------|
| Control              | 0/5   | 0/5     | 0/10  |
| 0.65                 | 0/5   | 0/5     | 0/10  |
| 2.04                 | 0/5   | 0/5     | 0/10  |
| 4.98                 | 2/5   | 4/5     | 6/10  |
| 3.24                 | 1/5   | 3/5     | 4/10  |

Note: Except for one female in the 3.24 mg/L exposure group that died 3 d after exposure, all deaths occurred overnight following the exposure; there was a 14-d post-exposure observation period.

Data source: [2399]

Using a log probit method, LC<sub>50</sub> values for the 64% hydrazine atmosphere were estimated as 9.0, 5.3, and 6.5 mg/L, respectively, for males, females, and sexes combined (equivalent to 9000, 5300, and 6500 mg/m<sup>3</sup>). Based upon hydrazine content of the hydrazine hydrate solution alone, these respective estimates were 5.8, 3.4, and 4.2 mg/L

(equivalent to 5800, 3400, and 4200 mg/m<sup>3</sup>). Recovery from signs of exposure was observed on day 2 for the 0.65-mg/L groups, and on days 3 and 4 for the 2.04-mg/L groups. For some rats in the higher-exposure groups, exaggerated respiratory movements were observed throughout the post-exposure observation period. Malondialdehyde formation in lung and liver tissue of rats increased following 2-h exposures to hydrazine vapors at different concentrations [2400].

The toxicokinetics of hydrazine, MMH, and UDMH in rabbits during and following inhalation exposure were investigated by administering hydrazine, MMH, or UDMH to different groups of rabbits through *iv* injection and inhalation in different experiments [2401]. Blood, urine, and expired air samples were collected at regular intervals. Concentrations of N<sub>2</sub>H<sub>4</sub> in the samples were determined using colorimetric methods. From these data, the absorption kinetics of N<sub>2</sub>H<sub>4</sub> through respiratory system in rabbits were analyzed, and toxicokinetics parameters were derived. The exhalation rates of N<sub>2</sub>H<sub>4</sub> vapor in respiratory system were as high as 95%, which were not affected by the vapor concentration and ventilation volume. The N<sub>2</sub>H<sub>4</sub> left in the respiratory system could be rapidly and totally absorbed into the circulation system. The half-life of distribution and apparent distribution volume for N<sub>2</sub>H<sub>4</sub>, MMH, and UDMH in rabbits after intravenous injection were calculated to be 0.019–0.048 h and 1.32–1.48 L/kg, respectively. The half-life of elimination after all routes of administration were calculated to be 1.49–2.30 h for N<sub>2</sub>H<sub>4</sub>. The amount of N<sub>2</sub>H<sub>4</sub> excreted in urine was less than 50% of the total elimination. The absorption of N<sub>2</sub>H<sub>4</sub> through respiratory system in rabbits was nearly complete with an apparent zero-order rate. The distribution of the hydrazines in whole body was very quick. There are other elimination pathways of N<sub>2</sub>H<sub>4</sub> other than through the kidney. See also [2402].

Pulmonary toxicity in rats induced by a ternary hydrazine/HN/H<sub>2</sub>O propellant blend called DT-III, whose main component is hydrazine, was studied by intratracheal intubating 0, 5.5, 13.7, 27.5 mg/kg (based on hydrazine content in DT-III), respectively [2403]. Following exposure to DT-III by instillation once a day for 14 d, the rats were sacrificed, and the histopathology, oxidative damage, inflammatory factors, and DNA damage of lung tissue were examined. Results showed that DT-III can cause pulmonary inflammation and oxidative damage. With an increase of DT-III concentrations, the levels of TNF- $\alpha$  and IL-6 in lung tissue homogenate increased gradually. DT-III may induce DNA damage in pulmonary cells.

#### 9.6.1.2 Long-Term (Chronic) Hydrazine Inhalation Studies

In one of the first comprehensive long-term inhalation toxicity studies of hydrazine vapor at the Army Chemical Center, dogs and rats were exposed 6 h daily, 5 d/week at an average concentration of 5 ppm for six consecutive months [2397]. The dogs lost appetite intermittently during exposure. There was some weight loss and fatigue. Recovery could be noted after weekends when exposure was suspended. No deaths were noted in either dogs or rats. However, when the concentration was increased to 14 ppm, 2 out of 4 dogs, 23 out of 30 rats, 15 out of 20 mice, and 8 out of 10 guinea pigs

died during a 6-month test. In rats, an  $LC_{50}$  was determined to be 225 ppm after 4.5 d, 53 ppm after 8.6 d, 20 ppm after 23.5 d, and 14 ppm after 27 d of continuous exposure.

Following the early Army tests, series of long-term inhalation tests spanning several decades were sponsored by the Air Force Medical Research Laboratory and mostly conducted at the Toxic Hazards Research Unit (THRU) of the University of California at Irvine and Mantech Environmental Technology in Dayton, OH. The reports contain a large amount of data on the inhalation toxicity of hydrazines ( $N_2H_4$ , MMH, and UDMH, in addition to the toxicity of Otto Fuel II, diesel, and jet fuels and other chemicals in the military inventory) [2404–2416]. Not all of these reports may deal with hydrazine.

Six-month hydrazine inhalation exposures of mice, rats, dogs, and monkeys were carried out at 5 and 1 ppm intermittent (industrial type) exposure and 1.0 and 0.2 ppm continuous (space chamber) exposure [2417, 2418]. The results (hepatotoxicity in mice, weight loss, and anemia in dogs) indicated that the recommended TLV at that time (1973) was not a safe limit. A group of mice was kept for 1 year following the exposure. The increased frequency of occurrence of alveolargenic carcinomas was a first warning of potential oncogenic problems associated with chronic inhalation exposures to hydrazine.

Serious concern about the safety of previously established TLV limits for hydrazine arose in 1964 when it was found for the first time that continuous 90-d exposure of animals to hydrazine vapor at the then valid TLV (1 ppm) was lethal to 2 out of 10 monkeys, 48 out of 50 rats, and 98 out of 100 mice [2419]. Although a typical TLV load would be only 8 h/d and 40 h/week, this test demonstrated that there was not sufficient margin for safety if this concentration was applied around the clock lifelong. It took more than 10 years and additional testing before the TLV for hydrazine was lowered to 0.1 ppm. Another 10 years and a series of additional tests [2412, 2420, 2421] later, the TLV was eventually lowered further by another order of magnitude to 0.01 ppm.

In a more thorough chronic toxicity inhalation study with hydrazine vapors in air for 1-year exposures, mice, rats, hamsters, and dogs were exposed to concentrations of 0.05, 0.25, 1.0, and 5.0 ppm for 1 year [2394]. Rats were held and observed for 18 months post-exposure, mice 15 months, hamsters 12 months, and dogs 38 months. Male and female rats exhibited dose-dependent incidences of benign nasal adenomatous polyps and smaller numbers of malignant nasal epithelial tumors. Nasal tumors were often associated with chronic irritation and were most frequent in male rats. Hamsters exposed to  $\geq 0.25$  ppm showed pathologic changes indicating degenerative diseases, possibly amyloidosis. At the 5-ppm level, hamsters developed a 10% incidence of benign nasal polyps compared to 0.5% in controls. Also, small numbers of colon neoplasms and thyroid parafollicular cell adenomas were found in hamsters, but only at the highest concentration tested (5 ppm). Lung adenomas appeared to be marginally increased in mice exposed to 1 ppm hydrazine, the highest concentration tested in this species. Only hamsters suffered significant mortality during the exposure phase of the study,

but a mortality of 19% alone in the control group does not speak highly for the health of any of the animals tested. All groups of hamsters lost weight beginning at 12 months. While all these alarming observations were made in rodents, none of the effects could be observed in dogs at any of the concentrations tested, even with the much longer observation periods. Only one dog was diagnosed with liver problems, and pathological examination showed diffuse clusters of swollen hepatocytes. It appears that the nasal tract in rodents is much more sensitive because rodents in their natural habitat spend a large amount of time in the dark, sniffing rather than seeing their food. Under these conditions, the nasal tract is much more sensitive and susceptible to irritation than in non-rodent mammals. Several studies demonstrated that of all tissues tested, the nasal respiratory epithelia of rats and hamsters are extraordinarily sensitive to the tumorigenic action of hydrazine following long-term inhalation [2422]. This is similar to the action of formaldehyde, where also very poor correlation was found between rodent statistics and data obtained in other mammals.

### 9.6.2 Acute Non-Inhalation Toxicity of Hydrazine

Early studies of acute hydrazine toxicity were performed where hydrazine was introduced into the body of test animals by means other than inhalation or skin absorption [2423–2425]. The hydrazine was administered by intratracheal intubation, *iv* injection, *ip* injection, *sc* injection, or orally *po* with or without the use of a stomach tube, which is a more reproducible method than by inhalation or percutaneous absorption. In all cases hydrazine itself was more toxic than any of the methylhydrazines. This comparison is based on a weight basis (milligrams of toxicant administered per kilogram of body weight of animal). Under ordinary conditions of hydrazine usage, the primary concern should be respiratory toxicity, on which basis hydrazine is less hazardous because of its lower volatility. The experiments may not all have administered free hydrazines in solution. In many instances, the free bases were neutralized to pH 7 and dissolved in isotonic saline, in particular for *ip* or *iv* administration [2363, 2384, 2424, 2426–2430]. Repeated administration of subacute concentrations ( $<LD_{10}$ ) of hydrazinium sulfate to mice or rats decreased body weight but had no effect on blood indices. Hydrazinium sulfate increased the sensitivity of the animals to the toxic effects of ethanol or barbiturates.

Prior to 1963, little was known about the mechanism of toxic action of hydrazine. The possibility of interference with  $\gamma$ -aminobutyric acid formation and vitamin B<sub>6</sub>-dependent enzymes was just beginning to emerge. A better understanding of the mechanism has been gained only during the past 50 years. Descriptions of the symptoms of acute poisoning of rats by hydrazines suggested that hydrazine itself acts in a way different from MMH or UDMH [2384].

In a study on the acute toxicity of N<sub>2</sub>H<sub>4</sub>, MMH, UDMH, and SDMH administered (after buffering to pH 7) *ip* to mice, it was noted that the average time to first response with hydrazine was 16 min., UDMH 104 min., MMH 129 min., and SDMH 48–72 h [2363].



Additional animal exposure tests were done with guinea pigs by *iv* injection [2431], rats *po* with their drinking water [2432, 2433], rhesus monkeys by *ip* [2434, 2435], and rats *po* [2436].

### 9.6.3 Nervous System Effects of Hydrazine

The mechanism by which hydrazine acts on the nervous system is not yet completely understood. It is most likely closely related with blood effects and the ability of the blood to provide nerve and brain cells with enough oxygen [2437]. Laboratory studies of nervous system, brain, and cardiac effects of hydrazine are described in [22]. A boiler operator/water treatment technician in the steam plant of a hospital was exposed to hydrazine hydrate vapors for several years while transferring hydrazine solutions from drums into open buckets, from which it was dumped into the boiler feedwater metering tank [2438]. His mental state and attention span degenerated drastically, and he finally was referred for psychological testing. After quitting the boiler job and avoiding hydrazine exposures, he remained under observation for 5 years while undergoing a very slow, only partial recovery of mental capacity.

### 9.6.4 Skin Effects of Hydrazine

Most hydrazines are water soluble and can penetrate the skin barrier. They will also often form chemical bonds to carbonyl and acid groups in the skin material.

#### 9.6.4.1 Animal Studies of Skin Permeation and Absorption of Hydrazine

Hydrazine itself is a stronger skin irritant than any of the methylhydrazines. Skin exposure tests with dogs showed that hydrazine is absorbed through the skin at high rates [2439]. With a dose of 12mg/kg of hydrazine applied to the skin of rabbits (covered with a fiberglass screen and stainless-steel screen to minimize evaporation losses), 86% of all hydrazine applied was absorbed into the bloodstream [2440]. In similar tests with H-70, a 70% N<sub>2</sub>H<sub>4</sub>/30% H<sub>2</sub>O EPU fuel blend, only 55% of all the hydrazine was absorbed. The extent of percutaneous hydrazine absorption in the rabbit appears to be greater than in the dog. It is difficult to extrapolate from these results to human skin. The dermal LD<sub>50</sub> of hydrazine for the rabbit is 91 mg/kg, compared to 20 mg/kg by *iv* injection. The second part of this study exposed rabbits to hydrazine or H-70 for only 2, 6, or 12 min, simulating an accidental splash in a propellant handling situation, where corrective action is taken almost immediately [2333]. The exposure was terminated by rinsing with a dilute hydrochloric acid solution and then with water. For these short exposures, serum concentration of hydrazine peaked 30 to 60 min after the start of the experiment. The third part of the investigation used very dilute solutions of either 15% or 2% hydrazine. There was no damage to the epidermis from the dilute solutions, but permeation through the skin was just as fast as with the more concentrated solutions.

Sixty percent of all hydrazine absorbed at doses of 17.4 and 41.7 mg/kg through the skin of rabbits showed up in the blood within a very short time [2441]. The elimination from the blood occurred with half-life times from 1.49 to 3.8 h. Renal clearance was 37 to 47% of the total body clearance, so there must be other clearance or destruction pathways. In another series of tests, when applied directly to the skin of rabbits, hydrazine caused corrosive skin disintegration [2430].

In an effort to establish a maximum allowable hydrazine in air concentration for propellant handlers wearing only a fresh air mask instead of a SCAPE suit, an exposure chamber was designed in which the shaved skin of six rats was exposed to hydrazine vapor, but the rats were breathing fresh air through a mask [718, 719]. Rats were trained to wear a face mask prior to the exposure experiment. A cannula was implanted into the animals' jugular vein prior to the experiment, through which blood samples could be withdrawn from the outside of the exposure chamber. Parameters for a two-compartment pharmacokinetic model were determined from an *iv* exposure. A two-compartment computer model was used to calculate how much hydrazine was present in each of the two compartments and how much was eliminated. Hydrazine vapor concentrations in the chamber were set at 100 or 500 ppm, which is substantially higher than the TLV. Following a 2-h exposure at 500 ppm, the  $N_2H_4$  concentration in blood peaked at 0.5  $\mu\text{g/mL}$ . The results indicated that hydrazine vapor has very low permeability through skin (0.00006 cm/h), a value like that of water vapor, and much lower than that of lipophilic organic vapors. Exposure limits recommended for special skin-only conditions are summarized in Section 9.11.7. Most inhalation exposure limits are established for simultaneous inhalation and whole-body exposure. Calculations showed that the vapor concentration during a skin-only exposure would have to be at least 200 times higher than that during inhalation to cause the same level of poisoning. In the 1980s when the inhalation TLV for hydrazine was still 0.1 ppm and TLV for UDMH was 0.5 ppm, the equivalent skin absorption TLV concentrations were calculated as 48 ppm for hydrazine and 32 ppm for UDMH, assuming that propellant-handling personnel wears only fresh air masks and face shield, apron, gloves, and boots for protection. This would allow them much better mobility and communication than the bulky SCAPE suits. The skin-only limits for UDMH are lower because UDMH was shown to have a higher skin permeation rate than hydrazine.

#### 9.6.4.2 Adverse Skin Reactions to Hydrazine Exposure in Humans

Several cases of skin rashes caused by hydrazine solutions and hydrazinium salts have been reported in the literature [2442]. The investigators of most of these cases identified the cause by patch tests, a common practice in trying to identify the cause of skin allergies. Two cases of hydrazine hydrate dermatitis without systemic intoxication have been reported [2443]. One patient developed small vesicles on the palm and between the fingers within 1 d following exposure. The patient stated that this was the fourth time he had developed dermatitis after using hydrazine hydrate. During

recovery, he unwittingly came into contact with hydrazine again. Within 7 h, his fingers were irritated, and the rash reappeared. Another patient had repeated episodes of rash and blisters of the fingers. Both patients had been in contact with hydrazine in irregular intervals for about 5 months before developing a skin rash. A 1.5% alcoholic solution of picryl chloride was recommended as a reagent for hydrazine. With this reagent, hydrazine could still be detected in the skin of workers 1 d after the exposure despite normal washing in between. The persistence of hydrazine in the skin is surprising. Apparently, there are no readily reducible compounds in the epidermis that could react with hydrazine. Five cases of allergic skin reactions attributed to hydrazinium sulfate have been reported [2444]. Although the main product of the factory where the five were employed was hydrazinium sulfate, it must be assumed that hydrazine hydrate vapors contributed to the adverse reactions, in particular in the case of the fifth patient, who only walked through the factory on his way to and from his work station. The skin eczema appeared within 2–5 months after the individuals started working in the area. Patch tests with 2% hydrazinium sulfate solutions were positive in most patients. Many of them changed the place of employment and did not suffer from any other skin allergies thereafter. However, 13 more persons working in the same area and so far not complaining of skin afflictions did not react to a patch test with 2% hydrazinium sulfate solution.

Several adverse skin reactions were reported in workers who were exposed to hydrazine hydrate vapor in power plants during boiler feedwater treatment [2445, 2446]. A characteristic feature in hydrazine allergy seems to be cross-sensitization to hydrazine derivatives, especially drugs such as isoniazid or hydralazine. One report described two cases of contact dermatitis caused by hydrazine hydrate [2447]. One marine engineer with no previous skin complaints developed dermatitis of his hands within several months after being assigned to hydrazine hydrate (24%  $N_2H_4$ ) duty. After 4 months of continuous vesicular eruptions on his hands, he resigned and sought different employment. The eruptions cleared within a few weeks. Two years after first working with hydrazine hydrate, he returned to duty on the ship and resumed the handling of hydrazine. Almost immediately he developed a vesicular dermatitis and had to be discharged from the ship. The second fast reaction indicated that a latent sensitization persisted throughout his absence from the ship. A second case was very similar, also involving a marine engineer, and hydrazine was identified by patch tests as a likely cause. The patch test remained positive for several days. There are numerous other reported cases of dermatitis caused by hydrazine exposure at the workplace [2448].

A 22-year-old, active-duty, USAF, senior airperson was seen because of a 1-year history of a slowly enlarging mass on the volar aspect of her left thumb metacarpal-phalangeal joint region [2449]. The patient had worked refueling tactical jet aircraft for the past 4 years. Her duties included refueling F-16 aircraft with hydrazine fuels. She always wore her required personal protective equipment, which included a respirator, coveralls, and gauntlet gloves. She recalled four instances that hydrazine fuel spilled

over the top of her gloves, contaminating her left hand each time. Each time, she followed the prescribed decontamination routine. The patient underwent two operations, with the biopsy of the first tissue removed showing a distinct nodular arrangement of tumor cells. The second operation removed residual tumor cells and replaced the tissue with a skin graft.

There was the case of a 68-year-old man with multiple basal cell carcinomas covering his arms and face after having worked in a steam power plant with extensive exposure to hydrazine hydrate for a period of over 10 years [2450]. A German documentation of MAK values gave a summary of dermatology problems, skin sensitization, and allergies with hydrazine and hydrazinium salts [2451].

### 9.6.5 Eye Effects of Hydrazine Splashes

Ocular toxicity studies of hydrazine and methylhydrazines showed that anhydrous hydrazine splashed on eyes of animals caused permanent corneal damage, whereas methylhydrazines showed only transient effects for 2–7 d [2430].

## 9.7 Carcinogenic Effects of Hydrazine

Several hydrazines have been shown to be carcinogenic in animal tests. As part of the overall effort to understand the conditions leading to the development of cancer, and in order to find a cure of this very complex disease, the carcinogenic actions of hydrazines have been thoroughly studied. The carcinogenic action is most pronounced with SDMH and UDMH and its oxidation products. Though SDMH can induce cancer in a reproducible and predictable way, this is not the case with hydrazine  $N_2H_4$  itself. Many tests have been done with hydrazinium salts, but they may lead to different results. Hydrazine or hydrazine hydrate that is ingested would be quickly converted to hydrazinium chloride by stomach acid. Besides UDMH, autoxidation products such as dimethylnitrosamine (*N*-nitrosodimethylamine, NDMA) are listed among the most potent carcinogens known. NDMA used to be produced as an intermediate in the manufacture of UDMH. Because of increased concern about NDMA carcinogenicity, several UDMH production facilities in the United States were shut down since the plants could not be modified to assure zero emissions of NDMA. It is not known which UDMH production process has been used or is now used in Russia and the other former states of the USSR as well as in China and North Korea.

This section of the book on the carcinogenic effects of hydrazine is an abbreviated and updated version of chapters offered in previous books on hydrazine [2452]. It would require too much space to deal with that subject again here in detail. Readers who need more detailed information are referred to the aforementioned source.

A question that has been asked frequently but has not been answered conclusively is the correlation between animal test results and carcinogenic risks to humans. Hy-

drazines have been designated as “suspect human carcinogens.” But if one follows the several decades of wavering on-again, off-again designations for such a commonly used household item as saccharin sweetener, one really wonders how accurate such designations are.

The existence of many designated rodent carcinogens for which at least one epidemiological study found no evidence of human carcinogenicity has thrown doubt on the validity and poor predictivity of rodent bioassays [2453]. In a review of correlations between rodent bioassays and human epidemiological studies, for 18 of the 22 chemicals examined, the human evidence was consistent with predictions based on the rodent bioassay results. Hydrazine was included in the group of 18, but it seems that the correlation was misinterpreted. The number of deaths found to be attributable to exposure in the cited epidemiological study of hydrazine was 2 deaths observed vs. 1.25 expected, which is not a significant difference due to the small number of incidents.

Epidemiological and mortality studies on chemical industry workers who were exposed to hydrazine vapors for up to several decades at their workplace have not revealed an increased incidence of cancers [2454–2457] (Section 9.10).

A good way to stay informed on the latest developments on carcinogens and government regulations affecting potentially hazardous chemicals is to tap into the web sites of some toxicology research organizations, such as [2458–2461]. In 1997 the US Department of Health and Human Services published new criteria for determining whether substances can be listed as “reasonably anticipated to be a human carcinogen.” The new criteria allowed the determination to be made not solely on rodent research data, but on a broader scientific base that includes the known chemical structure of the substance and its effects at the cellular level. In the Biennial Report on Carcinogens, the National Toxicology Program (NTP) lists substances “known to be human carcinogens” as well as substances “reasonably anticipated to be human carcinogens.” Since 1981, when the report was first published, the “reasonably anticipated” list has been based on experiments in which rats and mice have been exposed to the substances in question, as well as limited human data. The new criteria will allow the listing to be based on broader and more sophisticated criteria. The new criteria were developed through a collaborative process involving cancer scientists as well as consumer and industry representatives.

In addition to the new scientific criteria, the NTP is also creating a new process that will accommodate continuing advances in the science and that will provide a more structured approach to listing and de-listing of substances. Under the new criteria, even though there may not be available direct evidence that a substance causes cancer in humans, or in traditional bioassays using rats and mice, the substance could still be listed as “reasonably anticipated to cause cancer in humans” if there is convincing information that it works in living cells in a similar manner as other known human carcinogens. Conversely, if a traditional 2-year study shows a substance to cause cancer in laboratory rodents, the substance would not be listed

if there were compelling data showing that the action or mechanism by which the cancer in laboratory animals occurred did not exist in humans. Most of the 180 substances listed in the Biennial Report, including hydrazine, hydrazinium(2+) sulfate, and UDMH, are listed as “reasonably anticipated” to be a human carcinogen and are listed based on studies performed in laboratory animals and linked to an increased incidence of malignant tumors in two or more species, or in two or more studies, or when there are particularly unusual cancers that do not normally occur in the animals studied. The criteria have been revised to state:

Conclusions regarding carcinogenicity in humans or experimental animals are based on scientific judgment with consideration given to all relevant information. Relevant information includes, but is not limited to, dose response, route of exposure, chemical structure, metabolism, pharmacokinetics, sensitive sub-populations, genetic effects or other data relating to mechanism of action, or factors that may be unique to a given substance. For example, there may be substances for which there is evidence of carcinogenicity in laboratory animals, but there are compelling data indicating that the agent acts through mechanisms which do not operate in humans and would, therefore, not reasonably be anticipated to cause cancer in humans. *Quoted from NTP Documentation*

The original criteria for listing a substance as a known human carcinogen remain unchanged: that “there is sufficient evidence of carcinogenicity from studies in humans which indicates a causal relationship between exposure to the agent substance or mixture and human cancer.” With regard to hydrazine and hydrazinium(2+) sulfate, the NTP listed both under the category “reasonably anticipated to be carcinogen” and stated (with our reference numbers substituted):

There is sufficient evidence for the carcinogenicity of hydrazine and hydrazine sulfate in experimental animals. When administered orally, hydrazine induced pulmonary adenomas and adenocarcinomas in mice (IARC). Intraperitoneal injection of hydrazine induced reticulum cell sarcomas of the mediastinum and myeloid leukemias in mice. When administered by inhalation, hydrazine induced alveolarogenic carcinomas, and lymphosarcomas of the spleen, in female mice [2418]. When administered orally, hydrazine sulfate induced pulmonary adenomas and adenocarcinomas, hepatomas, and hepatocarcinomas in mice of both sexes. When administered by stomach tube, hydrazine sulfate induced lung adenomas and adenocarcinomas in rats of both sexes and hepatic cell carcinomas and spindle cell sarcomas in male rats [2462]. There is inadequate evidence for the carcinogenicity of hydrazine and hydrazine sulfate in humans [2463]. *Quoted from NTP Documentation*

On the other hand, the 7<sup>th</sup> *Annual NTP Report on Carcinogens* (1997) listed no hydrazines as known carcinogens, but it did include 24 other chemicals like benzene and asbestos. Another valuable on-line source of information on carcinogenic potency of chemicals in comparison to that of hydrazines is the Carcinogenic Potency Database (CPDB) [2464]. The Carcinogenic Potency Database reports analyses of animal cancer tests on 1547 chemicals. This is a widely used resource on the results of chronic, long-term animal cancer tests. It provides a single, standardized, and easily

accessible database that includes enough information on each experiment to permit investigations into many research areas of carcinogenesis. Both qualitative and quantitative information on positive and negative experiments are given, including bioassays from the National Cancer Institute/National Toxicology Program (NCI/NTP) and results from the general literature that meet a set of inclusion criteria. As of 1997, analyses of 5152 experiments on 1298 chemicals were presented. For each experiment, information is included on the species, strain, and sex of test animal; features of experimental protocol such as route of administration, duration of dosing, dose level(s) in mg/kg body weight/d, and duration of experiment; histopathology and tumor incidence; carcinogenic potency ( $TD_{50}$ ) and its statistical significance; shape of the dose-response curve; author's opinion as to carcinogenicity; and literature citation. There is a printed version of the *Carcinogenic Potency Database* and user's guide which contains an index with chemicals listed by CAS registry number and allows cross referencing between the carcinogenicity and genotoxicity databases, making data easy to find [2465].

The US EPA has designated hydrazine as a probable human carcinogen, classified as weight-of-evidence Group B2 under the EPA Guidelines for Carcinogen Risk Assessment [2466]. Evidence on potential carcinogenicity from animal studies is "sufficient," and the evidence from human studies is "inadequate." The potency factor for hydrazine was estimated to be  $107 \text{ mg kg}^{-1} \text{ day}^{-1}$ , placing it in potency group 1 according to the CAG's methodology for evaluating potential carcinogens. Combining the weight-of-evidence group and the potency group, hydrazine was assigned a "HIGH" hazard ranking for the purposes of Reportable Quantity adjustment [2467].

The US government and several government agencies, including the armed services, in particular the USAF, have struggled with the mounting indications of animal carcinogenicity and attempted to establish policies under which the continued use of hydrazine propellants had to be justified and all necessary precautions taken to prevent exposure of propellant-handling personnel to propellant vapors [2301]. One of the first precautions was to lower the exposure limits for inhalation of hydrazines, but it was not possible to quantify the cost and benefits, i.e., the cost:benefit ratio of such an action (Section 9.11). At one time [2468] it was considered safe enough to lower the TLV from 1.0 to 0.1 ppm to protect the working population from hydrazine-induced cancer, but a few years later the TLV was lowered by another order of magnitude for an extra measure of safety. The working populations who lived through the several decades when the TLV was still 1 or 0.1 ppm showed no adverse effects that were clearly induced by exposure to only one chemical.

Special caution is recommended in extrapolating from animal data to toxicity and tumorigenesis in humans. The animal data are often inconsistent. Researchers sometimes do not always stick to the correct protocol for animal exposure and twist the data to yield the results they were hoping for. Depending on the mode of administration and the type or strain of test animal used, hydrazine itself produced a high rate of tumors in some animals. However, in other animals under otherwise identical

conditions, no tumors were found at all. Compilations of the carcinogenic risk of hydrazine chemicals to humans were published repeatedly by the International Agency for Research on Cancer (IARC) [2462]. The IARC *Monograph on the Evaluation of the Carcinogenic Risk of Chemicals to Humans* was updated in a supplement in 1987 and again updated in 1999 [2469]. In addition, interpretations of negative epidemiological evidence for the carcinogenicity of hydrazine have been discussed in another special scientific report published by IARC in 1985 [2455, 2470]. Hydrazine was considered by the IARC Monographs Working Group in 1973, 1987, and 1998 (published by IARC in 1974, 1987, 1999).

In February 2016, 24 experts from 8 countries met at the IARC in Lyon, France, to assess the carcinogenicity of 7 industrial chemicals [2471]. The experts concluded that there was limited evidence in humans for the carcinogenicity of hydrazine, that a positive association has been observed between exposure to hydrazine and cancer of the lung, and that there is sufficient evidence in experimental animals for the carcinogenicity of hydrazine. IARC classifies chemicals suspected of causing cancers in humans in five categories:

- Group 1: The agent is carcinogenic to humans.
- Group 2A: The agent is probably carcinogenic to humans.
- Group 2B: The agent is possibly carcinogenic to humans.
- Group 3: The agent is not classifiable as to its carcinogenicity to humans.
- Group 4: The agent is probably not carcinogenic to humans.

Hydrazine was evaluated previously as **possibly** carcinogenic to humans (Group 2B), but in its most recent 2018 edition, IARC classified hydrazine in Group 2A: “*The agent is **probably** carcinogenic to humans*” [2472]. This is a substantial change from their previous assessment of the risks associated with hydrazine exposure.

In reviewing dozens of animal studies, it becomes clear that a carcinogenic effect can only be demonstrated for hydrazine when it is administered for practically the whole life of the animals in toxic doses that do not reduce the life span very much. In many instances only the unambiguously toxic concentration after the longest possible period produced a weak carcinogenic effect. These lifelong conditions do not apply to human occupational exposure.

In laboratory test animals, hydrazines and related compounds may cause cancers of the colon [2473], lung [2474–2477], skin [2450], or nasal cavity [2468]. Even naturally occurring hydrazine compounds can induce colon cancer [2478]. To better understand chemically induced cancer in test animals and cancer of unknown causes in humans, it is of interest to compare the actions of known site-specific carcinogens on identical parts of the body (i.e., the colon) of humans and test animals.

The use of rodent whole-body exposure data to set TLVs for human exposure at the workplace has been criticized, but there are currently no other generally accepted methods to determine safety data. It has been argued that rodents often lick themselves and that they absorb more hydrazine by ingestion than inhalation. Their food



sits in the same atmosphere they are inhaling, and the food and drinking water become saturated with hydrazine. This would not be the case for humans in an occupational setting.

The use of rodents for hydrazine inhalation tests has been criticized, arguing that rodents spend most of their natural life (not talking about pampered test animals in a laboratory cage) in dark burrows, where they depend on the sense of smell to sniff their way around. The sense of smell is much more developed, the olfactory organs more sophisticated and more vital for rodents than they are for humans. Consequently, the nose (where some of the hydrazine-induced adenocarcinoma have developed) is a location of high cell turnover in rodents and more susceptible to chemical insults. The same argument arose about the use of formaldehyde toxicity data from animal tests. These data were needed after it was found that most plywood used in domestic construction (mostly mobile homes) emitted formaldehyde for a long time after it was laminated together.

## 9.8 Mutagenic and Teratogenic Effects of Hydrazine

A detailed summary of the mutagenic effects of hydrazine and methylhydrazines was provided in [2479], which has not yet been updated. Hydrazine and hydrazine derivatives have been shown to have mutagenic effects in plant and insect chromosomes and in bacteria [2480]. Hydrazine was mutagenic in a host-mediated assay [2481]. Hydrazine can cause mutations by reaction with DNA [2482]. In many cases hydrazine and hydrazine derivatives are outright cytotoxic, such that bacteria exposed to these chemicals do not even have a chance to multiply and mutate. Hydrazines may interfere with the metabolism of these bacteria [2099].

The *in vivo* genotoxicity of three hydrazines, SDMH, UDMH, and hydrazine  $N_2H_4$ , was tested in mouse liver, lung, kidney, brain, and bone marrow and in the mucosa of stomach, colon, and bladder [2483]. Hydrazine  $N_2H_4$  at 100 mg/kg yielded DNA damage in the stomach, liver, and lung when given *ip* and in the brain when given *po*. Thus, the administration route is important when evaluating organ-specific genotoxicity in multiple organs. A summary of the teratogenic effects of hydrazine and methylhydrazines appears in [2484], which has not yet been updated.

## 9.9 Hydrazine Use History and Accident History

### 9.9.1 Hydrazine Use History and Use Statistics

It has been estimated that as of 1987, 10528 workers in the US were potentially exposed to hydrazine (hydrate) part-time and 1156 workers were potentially exposed full-time [2465, 2485].

### 9.9.2 Hydrazine Accidental Exposure History

Several cases of accidental human exposure to hydrazine are described in the literature. All accidents were the result of gross neglect of standard safety procedures in handling hazardous chemicals [2353, 2354, 2486–2497]. There were several poisoning accidents in workers in steam power plants where hydrazine hydrate solutions were used for boiler feedwater deoxygenation [2438, 2498, 2499].

## 9.10 Epidemiological and Cohort Studies of Hydrazine Exposure

This section deals with long-term, chronic exposure studies and not with the consequences of occasional accidental exposure episodes. Epidemiological studies in this narrow context of workers in chemical factories and rocket test sites must be viewed against the ubiquitous presence of hydrazine derivatives in the environment, in food (mushrooms), and in pharmaceutical applications. It has been estimated that hundreds of millions of people all over the world are exposed to varying amounts of artificial and naturally occurring hydrazines, even before the space age (yet people continue to live) [2287].

A very detailed epidemiological evaluation of workers exposed to hydrazine (hydrate) has been carried out in Great Britain as a voluntary cooperative project of nine hydrazine hydrate producers [2500]. Five of the nine companies had started manufacturing hydrazine hydrate on dates ranging from 1940 to 1956. One company had records of all 53 men employed in hydrazine hydrate manufacture for more than 10 years between 1940 and 1974 (the date of the study). Another company operated a hydrazine hydrate manufacturing plant between 1945 and 1970 and had records of all 423 people who had worked at the plant during that period. When assembling data from both companies in categories by the level and duration of exposure, only a fraction (64%) of the people involved could be traced and their state of health ascertained. Several had died of natural causes not related to any suspected chemically induced cancer. Of those traced, 18 had died, and 2 of these from cancers. Mortality and frequency of cancers were not different from those of a group of workers of identical age calculated from statistical tables. The observed and expected number of deaths were similar. While the existing data were crude and incomplete, they indicated that these past occupational exposures to hydrazine did not result in any greatly increased risk of cancer.

This 1978 preliminary analysis of men working at a hydrazine plant did not reveal an excess risk of cancer associated with exposure to hydrazine. The follow-up was incomplete, however, and as mortality was not analyzed by cause, a fresh study was conducted using the same cohort. The cohort of 427 men from the larger of the 2 manufacturers was studied further and the results were reported in an IARC scientific publication on the *Interpretation of the Negative Epidemiological Evidence for Carcinogenicity* [2454, 2455]. The facility where the exposures had occurred was located

in the east Midlands of England. It had produced 700 tons of hydrazine in the form of hydrazine hydrate per year during the years from 1945 until 1971 when it was closed. The hydrazine hydrate was processed into derivatives on-site in open vats. This study involved a group of men who had worked at the site for at least 6 months during this period. The subjects were categorized by their severity of exposure, one group associated with the direct manufacture of hydrazine, a second group with incidental presence in the area of hydrazine hydrate production (e.g., pipe fitters, engineers), and a third group with no documented work assignments in the hydrazine hydrate plant. It was possible to trace 406 (95%) of the 427 men. No hydrazine in air measurements had been taken in the factory, but it was common practice to make hydrazine derivatives in open vats in a closed building with no enhanced ventilation to bring in fresh air. In those days, hydrazine hydrate vapor was considered a nuisance, just like ammonia. It is estimated that hydrazine in air concentrations in this part of the plant varied between 1 and 10 ppm with local spikes of 100 ppm. In the cohort of 427 men, as of July 1982, there were 49 deaths (61.47 expected) from all causes, including 5 deaths from lung cancer (6.65 expected). Two of the lung cancer deaths occurred in the group with the heaviest exposure, where only 1.61 were expected. One had worked in the high hazard area for 16 years, the other for only 2 months. None of the deaths involved nasal cancer. Realizing that the total number of exposed workers was statistically small, the preliminary results showed that there was no obvious hazard associated with hydrazine exposure, and continuation of the epidemiological study was highly recommended. The study was continued, and by the end of January 1992, a further 37 deaths had occurred [2456]. Again, the observed mortality for the total cohort was close to that expected for all causes and for lung cancer, cancers of the digestive system, other cancers, and all other causes, irrespective of the level of exposure. Men in the highest-exposure group did not seem to have significantly different mortalities for lung cancer, compared with other men in this study or compared with the population at large. The only category where the number of observed deaths exceeded statistical expectations was the high-exposure category for men with more than 6 months of exposure (3 observed vs. 2.43 expected). Cancers in the digestive system in the low to moderate exposure group was slightly elevated (8 vs. 6.54 expected).

It is fortunate that the study was continued, covering a 50-year period, and by the end of December 2012, 205 deaths had occurred [2457]. For men in the highest exposure category with greater than 2 years of exposure and after more than 10 years since the first exposure, the relative risks compared with national rates were 0.85 (95% confidence index (CI): 0.18–2.48) for lung cancer, 0.61 (95% CI: 0.07–2.21) for cancers of the digestive system, and 0.44 (95% CI: 0.05–1.57) for other cancers. The only categories in which the number of observed deaths exceeded expected deaths (but not significantly) were lung cancer in men in the high exposure category for 6 months or more (6 observed vs. 4.55 expected), cancers of the digestive system in men in the moderate or low exposure category (20 observed vs. 17.21 expected), and ischemic heart disease in men in the high exposure category for 6 months or more (16 observed vs. 14.56 ex-

pected). Half of the six deaths from lung cancer in men in the high exposure category were in men exposed in that category for less than 2 years. Two deaths from cancer of the digestive system occurred in men with exposure in the high exposure category compared to 3.27 expected. After 50 years of follow-up, the results provided no evidence of an increased risk of death from lung cancer or death from any other cause as a result of hydrazine vapor exposure. The strengths of this study are that it constitutes one of very few datasets available on exposure to hydrazine, and there is now 50 years of follow-up. We hope similar epidemiological studies will be carried out on hydrazine (hydrate) workers at other production and usage facilities.

A similar study in France of 140 men working at a plant producing hydrazine hydrate since 1962 reached similar conclusions (personal communication Cordier to Morris 1995). No significant excess in incidence of cancer was observed in the cohort of workers in comparison to the statistical numbers expected from local cancer incidence. However, an excess of digestive cancers was found in the low exposure group. No excess of respiratory cancers was observed in the French study.

A mortality study submitted in January 1979 on workers who had worked for at least 3 months in a hydrazine hydrate plant during the years between 1953 and 1978 showed an increased incidence of myocardial infarction (death and non-death). There were five cases of myocardial infarction vs. 1.2 cases expected statistically. The average duration of hydrazine work employment for the five men was 16 years. This higher incidence of heart attacks may be simply stress related and may not have been chemically induced. Additional data gathered during the observation period 1978–1985 revealed no increased myocardial infarction incidence among workers [2501]. It was concluded that the experienced cluster of incidents was a chance occurrence and did not represent a direct health hazard. Otherwise, the hydrazine exposed workers were no different from any of the other groups.

A Danish Air Force study involved medical surveillance on personnel working with EPU maintenance in F-16 fighters. Since the introduction of the F-16 system in Denmark, 41 male technicians had been routinely examined due to these regulations, and personnel potentially exposed to H-70 during three leakage incidents were examined, but no lasting effects were noted [2492].

One study suggested that workers most likely exposed to rocket fuel hydrazines and other chemicals at the Rocketdyne Santa Susana Field Laboratory in Simi Valley, CA, were more likely to have died of lung cancer and several other types of cancer than were co-workers not exposed to the chemicals [2502, 2503]. The purpose of the study was to estimate the effects of occupational exposures to selected chemicals on cancer mortality among nuclear and aerospace workers who were employed at Rocketdyne/Atomics International between 1950 and 1993. There was an excessive number of cancer deaths among workers in the high-exposure hydrazine group. The study, which examined 6107 men first employed at the Rocketdyne plant before 1980, found that workers presumed to have a high exposure to hydrazine or other chemicals in the workplace died from lung cancers and possibly cancers of the bladder, kidney, and

blood and lymphatic system about twice as often as other Rocketdyne workers who were not exposed to the chemical. One must realize that the workers were exposed at the workplace to many other chemicals in addition to hydrazine, so hydrazine cannot be singled out as the sole cause of the higher incidence of cancer mortality.

All three hydrazines, hydrazine itself, MMH, and UDMH were implicated in an epidemiologic, retrospective study of causes of death among former workers at a large aerospace company in California. The results of this retrospective cohort study suggested that exposure to hydrazine or other chemicals associated with the same jobs at rocket-engine test stands increased the risk of dying from lung cancer and possibly other cancers [2504, 2505]. However, the hydrazine chemicals were just a few of several other chemicals and other adverse conditions these workers might have been exposed to while working in various jobs in the defense and aerospace industries. Any one of these other chemicals could have caused the observed effects and hydrazine(s) cannot be singled out as the sole cause. There were no records of actual workplace concentrations of hazardous vapors in the air that could be correlated with the effects observed in sick people several decades later.

A similar retrospective cohort mortality study of 8372 Rocketdyne workers employed from 1948 to 1999 at the Santa Susana Field Laboratory came to a different conclusion [2506]. Non-significant associations were seen between lung cancer and hydrazines, and stomach cancer and years worked as a test stand mechanic. No trends over exposure categories were statistically significant. It was concluded that work at the rocket engine test facility or as a test stand mechanic was not associated with a significant increase in cancer mortality overall or for any specific cancer.

A statistical survey of frequency of prostate cancer in workers who were employed between 1950 and 1992 at a nuclear energy and rocket engine-testing facility in Southern California and had been exposed to a variety of solvents (including trichloroethylene, a popular degreaser solvent) and propellants (hydrazine) revealed that high levels of trichloroethylene exposure were associated with more frequent cases of prostate cancer among workers in this study population [2507, 2508]. This study was not specific for hydrazine, which was just one of several chemicals and possibly nuclear radiation these workers were possibly exposed to.

Despite the thousands of tons of hydrazine fuels handled by USAF personnel during the past decades, a review of exposure data published in 1976 indicated only six exposures, none of which proved to have significant consequences [2304]. The scarcity of exposure information is no doubt due to the careful approach that the armed forces have applied to the handling of the hydrazine fuels, sometimes involving the use of self-contained breathing apparatus. In a 1978 survey, it was stated that "there are no known cancer cases among hydrazine, MMH, and UDMH propellant manufacturing and handling personnel as of today" [2281–2283].

The F-16 air combat fighter, which entered service in the USAF in 1979, is the first production fighter aircraft to use a monopropellant hydrazine EPU. Although the quantity of hydrazine flown on each aircraft is small in comparison to the quantities

used in expendable launch vehicles, reusable space launchers, space stations, or ballistic missiles, the number of persons potentially exposed to a hydrazine-contaminated environment is large. Every effort was made by the USAF medical staff to provide for adequate protection of service personnel exposed to hydrazine hydrate during servicing of the EPU [705, 2301, 2509, 2510]. Part of this effort was an education and training program for flight-line personnel. For maintenance and repair on the F-16 EPU, a potentially large number of military service personnel and contractors could be exposed to hydrazine vapors in case of spills and violations of safety procedures. The USAF has established guidelines and test protocols to protect its personnel and to assess the toxicity of the chemicals used for power generation and propulsion [2511]. A survey conducted by USAF laboratories on the magnitude of potential hydrazine exposure during EPU maintenance during the development phase identified some deficiencies that were promptly corrected, and engineering changes to system hardware and support equipment were implemented. Although the USAF had considerable experience in the safe handling of hydrazines for space and missile applications, the introduction of H-70 to the flight line presented new and challenging problems to the USAF medical and aircraft maintenance communities. Flight-line servicing of a used EPU involves depressurization of the tank, expelling residual H-70 from the lines through the catalyst bed, and replacing the H-70 tank with quick-disconnect fittings. Hydrazine concentrations measured in the vicinity of maintenance operations ranged from 0.0001 to 0.007 mg/m<sup>3</sup> when calculated as a TWA spread over the 8-h work shift and were well below the TLV [2512]. The approach later taken as a joint effort between the USAF and industrial suppliers emphasized the importance of a closed system concept. Prior to introducing the F-16 to the flight line, an Air Force Occupational Safety & Health Standard 161-13 was developed for hydrazine to provide detailed surveillance. Because the records to be kept on the population at risk of exposure will be very accurate and detailed, further epidemiological studies will have a good database to work from. It was planned that for the first year of the F-16 program, occupational hygiene monitoring would be done on a quarterly basis. As of 1995, approximately 3600 F-16 fighter jets were flying in the armed forces of many countries worldwide. NATO countries that were adding F-16s to their arsenal in the early 1980s have also prepared themselves for the safe handling and disposal of H-70 in case of unexpected events [2513].

Although the concentrations are usually very small, residual hydrazine in the blowdown from steam power plants constitutes a potential hazard to workers and surrounding communities [2514], but in recent times precautions have been taken to remove residual hydrazine from the condensate before it is discharged to surface waters.

A review of chemical industry-wide epidemiological studies in the US and Western Europe selected the Morris 1995 study as one of 181 qualifying studies among 385 studies, and data were abstracted from the 181 studies representing the most recent report for a cohort, or the earlier study of the same cohort that provided relevant data according to stringent selection criteria [2515]. Of these, 156 reported only mor-

tality data, 10 reported only incidence data, and 15 reported both mortality and incidence data. Only 69% of the studies reporting mortality data received “satisfactory” quality scores, and the Morris 1995 study was among them. The Morris et al. 2015 50-year follow-up [2457] would also qualify. Overall, 10% fewer premature deaths were observed than expected.

Workplaces where hydrazine or hydrazine derivatives are handled must be monitored. Airborne concentrations need to be measured and recorded over several work shifts and on non-working days to determine the background contamination without manufacturing and testing activities in progress. In terms of the quantities of hydrazine(s) stored and transferred, the Rocky Mountain Arsenal near Denver, CO, was the leading propellant storage and mixing facility in the US in the 1960s and early 1970s. Unfortunately, it left a not-so-pleasant legacy of environmental contamination that took many years to clean up.

Air sampling during fuel transfer operation was done once in conjunction with the evaluation of respiratory protection (gas mask canisters) for workers at Rocky Mountain Arsenal. Measurements were on the order of 2 ppm hydrazine and 3 ppm or even up to 4.6 ppm UDMH. Air samples were taken in 1976 and 1977 during drum and truck/rail tanker filling operations [2516]. The sampling methods used were sulfuric-acid-coated silica gel tubes and impingers. Air samples were taken both outside and inside gas masks worn by propellant handlers. Outside air samples were typically on the order of 0.2 ppm for hydrazine and UDMH, with peak excursions of 1.66 ppm hydrazine or 1.98 ppm UDMH. Air inside the gas masks was clean. If there was any hydrazine or UDMH, it was close to the detection limit. The TLV in effect at the time was 1 ppm for hydrazine and 0.5 ppm for UDMH, but lowering to 0.1 ppm was imminent. The odor of hydrazine and UDMH was noted when walking past the storage area, outside the general work area proper. NDMA was detected in the air in the vicinity of UDMH storage tanks. Some of the operating procedures had been improved, and necessary repairs were made before the inspection team returned several months later. Shortly before the facility was shut down, air samples were taken and analyzed for NDMA in 1980 while railroad cars and tankers were cleaned and loaded [2517]. NDMA was found in the entire area using two different sorbent tube materials. Since there was no gas mask with proven effectiveness against NDMA, industrial hygiene staff recommended that compressed air respirators should be worn when working in the area. Another inspection 2 years later, after shutdown of operations, found no detectable hydrazine or UDMH in the air (D.L. of  $0.05 \mu\text{g}/\text{m}^3$   $\text{N}_2\text{H}_4$  or  $0.1 \mu\text{g}/\text{m}^3$  UDMH), but persistent NDMA levels of typically  $2 \mu\text{g}/\text{m}^3$  (D.L.  $0.05 \mu\text{g}/\text{m}^3$ ) with excursions of  $20 \mu\text{g}/\text{m}^3$  were noted [2518]. The silica sorbent for hydrazine analysis was replaced with fire brick for the later set of analyses. Air sampling at Rocky Mountain Arsenal Hydrazine Blending Facility continued for several more years while the cleanup was in progress [2519, 2520].

An industrial hygiene study including walk-through industrial hygiene surveys of several industrial and government sites was conducted by a contractor for NIOSH [2521, 2522]. As part of this study, the team assembled tables of job titles

of exposed workers and exposure levels, determined the significance of recurring and non-routine exposures, and assessed the reliability of exposure data gleaned from exposure records provided by the facilities visited. Walk-through and in-depth industrial hygiene surveys were conducted between February 1983 and February 1984 at eight facilities in the US where hydrazines were produced and/or used. The sites visited included three hydrazine and hydrazine-derivative manufacturers, one USAF base, an aircraft manufacturer, and three sites where space propulsion systems were tested. Many boiler operators were contacted, but none agreed to a site visit. Only one provided data gathered in boiler water treatment rooms at nine of its power plants. From the information gathered during the visits, the investigating team concluded that employees and employers were aware of the toxic effects of hydrazine(s) and the need to avoid exposure. The time-weighted averages (TWAs) reported and observed were well below the TLV (0.1 ppm) and recommended NIOSH limits (0.03 ppm) in effect at the time. The number of exposed workers was reported to be small; only a few workers were involved in hydrazine manufacture and the routine use of hydrazine(s) as propellants. Because many of the process plants were relatively new and because not too many years had passed since the introduction of the F-16 EPU, it was considered unlikely that suitable cohorts existed in 1985 for retrospective exposure studies. Only one of the eight facilities selected for walk-through inspection was revisited for more in-depth air sampling: An industrial hygiene survey of Olin's ketazine hydrazine production unit at Lake Charles, LA, was conducted by a contractor for NIOSH [2523]. Worker exposures to hydrazine vapor were determined by pumping air through solid sorbent (sulfuric acid on fire brick) tubes, which were later extracted, and the extract analyzed by PDAB spectrophotometry. Full-shift, time-averaged hydrazine exposure concentrations ranged from less than 0.002 to 0.27 ppm. Generally, concentrations were well below the TLV in effect at the time (0.1 ppm).

Another summary report on human exposure to hydrazine in the workplace lacked actual measurements [2524]. Instead, it relied entirely on measurements taken by other investigators and quotes 53 obsolete references from the literature.

A survey team from the USAF Occupational and Environmental Health Laboratory conducted an analysis of maintenance tasks associated with the F-16 EPU [2525]. This analysis involved the collection of personal and short-period air samples to define airborne exposure to hydrazine during maintenance tasks, such as nitrogen depressurization, catalyst purge, poppet valve replacement, and refilling. Measurements indicated compliance with a time-weighted-average value of 0.1 ppm hydrazine; however, potential peak exposures that ranged as high as 5 to 8 ppm occurred during some tasks. A technician would be unaware of many such exposures, since concentrations below the odor threshold of 3 to 5 ppm give no warning but are at least an order of magnitude above acceptable occupational exposure limits. Data collected during two on-site surveys of F-16 maintenance installations indicated that (prior to imposing stricter controls) hydrazine concentration in the vicinity of a piston tank being in-



stalled or depressurized on the aircraft was 0.03 ppm, and during on-the-ground (off-the-airplane) tank servicing it was 0.03–0.12 ppm, with possible short-time excursions of up to 6 ppm. After imposing stricter controls, the concentrations during piston tank servicing were brought down to below 0.01 ppm, one-tenth of the TLV-TWA in effect in the late 1970s [705, 2525].

Measurements at NASA KSC showed that occupational exposure of technicians to hydrazine and MMH vapors was well within tolerable limits even after the lowering of the TLV from 100 to 10 ppb in 1991 [2526]. Sampling methods were sensitive enough to measure exposure levels at or below the proposed ACGIH TLV of 10 ppb/8 h. The operations monitored included propellant transfer operations, flight hardware processing, and launch vehicle fueling operations that occurred at KSC or the adjacent CCAFS. A similar set of 128 air samples taken and analyzed for hydrazine, MMH, and UDMH at NASA WSTF in 1991 showed that hydrazine or MMH concentration in most work areas was below the proposed TLC of 10 ppb [2527]. The air samples were taken by aspirating air through glass tubes filled with USSS No. 30–60 granular sulfuric acid impregnated fire brick at a rate of 1 L/min for 10 min. The sorbent was then leached with buffer solution in an ultrasonic agitator and the solution analyzed by HPLC with electrochemical detection. Several samples were reported as “none detected,” but unfortunately, the detection limit was not stated (it is assumed to be below 2 ppb). Parallel tests showed the dubious value of conventional Interscan 4186 measurements that did not correlate with the absorption tube readings at all.

A workplace occupational hygiene survey was carried out on 172 male hydrazine-hydrate-exposed workers and 125 male unexposed reference workers at 5 factories in Japan [2528, 2529]. The biological half-lives of hydrazine hydrate after 1 h of exposure were determined in 12 workers, 4 workers in each of 3 NAT2 phenotypes. No hydrazine was detected in either the breathing zones or the urine of the reference workers. The mean hydrazine concentration in the breathing zones, hydrazine, and acetylhydrazine in urine, and the cumulative exposure levels were 0.0109 ppm, 0.8660 micromol/g, and 2.80 ppm-years, respectively. There was no difference and no dose-dependent change in the health examination items between hydrazine-hydrate-exposed and reference workers after adjusting confounding factors, nor in terms of the differences of NAT2 phenotypes. The half-life time of urinary hydrazine and acetylhydrazine on rapid, intermediate, and slow phenotypes was 1.68, 3.01, and 4.46 h, respectively. This information would be useful if a biological exposure index (BEI) for examination of post-work-shift workers could be found.

### 9.11 Established Exposure Limits for Hydrazine

Many different types of exposure limits are in use for establishing safe working and living conditions. There are many variables that must be taken into consideration when setting tolerable limits. This applies to the inhalation of air contaminants as well as

the tolerable concentrations of food additives or pesticides in food. The section here only deals with airborne contaminants, those that are primarily absorbed by inhalation, although some of these may also be absorbed by and permeate through the skin. The margin of safety is required to cover at least the average population (assume a 3 $\sigma$  distribution of resistance to chemical attack). In many cases the tightening of exposure limits comes at a substantial cost of enforcement or implementation of engineering controls. Typically, the guideline maximum limit for a toxic chemical is set at one to two orders of magnitude below levels demonstrated in animal experiments to be without adverse effect. For carcinogens, it is very difficult to demonstrate the no-effect concentration. Some toxicologists suggest that no level of exposure to carcinogens, no matter how small, is without potential for harm. Of course, they would like to outlaw cosmic radiation, as well as terrestrial radon radiation.

A careful balance is sought between the desire to reasonably protect all persons and the economic impact of tightening exposure limits. First of all, one must determine whether the limits are to be established for a workplace environment with exposures for a constant number of hours per day and a constant number of days per week, only for the working population, or for the rest of the population, possibly living downwind from a chemical manufacturing or rocket testing installation. The general population includes a wider age group and breathes potentially contaminated air around the clock, not only during the 8-h work shift. Statisticians will introduce risk factors at this point, like a risk of one cancer in 1000 to 10000 being considered an acceptable risk for an occupational setting versus a disputed tolerable risk of one in 100000 to 1000000 in the general public. EPA has classified hydrazine as a Group B2 probable human carcinogen. EPA uses mathematical models, based on human and animal studies, to estimate the probability that someone will develop cancer from breathing air containing a specified concentration of a chemical. EPA calculated an inhalation unit risk estimate of  $4.9 \times 10^{-3} \text{ (g/m}^3\text{)}^{-1}$ . EPA estimates that if an individual were to breathe air containing hydrazine at  $0.0002 \text{ g/m}^3$  over his or her entire lifetime, that person would theoretically have no more than a one-in-a-million increased chance of developing cancer as a direct result of breathing air containing this chemical. Similarly, EPA estimates that breathing air containing  $0.002 \mu\text{g/m}^3$  hydrazine would result in no greater than a one-in-a-hundred thousand increased chance of developing cancer, and air containing  $0.02 \mu\text{g/m}^3$  would result in no greater than a one-in-ten thousand increased chance of developing cancer. EPA's Office of Air Quality Planning and Standards, for a hazard ranking under Section 112(g) of the Clean Air Act Amendments, has ranked hydrazine in the non-threshold category. The  $1/\text{ED}_{10}$  value is  $10^7$  per  $(\text{mg/kg})/\text{d}$ , and this would place it in the high category under the Superfund ranking of carcinogenic hazards. Up-to-date information from EPA's Integrated Risk Information System can be downloaded from EPA's web site.

The problem in deciding which exposure limit applies to a certain exposure situation is that there are two to three times as many limits promulgated as there are federal, state, and professional organizations dealing with occupational hygiene, each

of them coming up with their own acronyms, resulting in a proliferation of abbreviations. It may be worthwhile to reference the definitions for each established limit to make sure that the discussion is based on the same set of data. Table 94 shows the exposure guidelines published by authoritative organizations for both groups of the population and for different durations of exposure. The abbreviation for the organization that establishes these limits is shown in parentheses.

**Table 94:** Occupational and general public exposure guidelines.

| Type of exposure         | Type of population    |                       |
|--------------------------|-----------------------|-----------------------|
|                          | Occupational exposure | General public        |
| Short term, emergency    | EEL/EEGL (NAS)        | PEL/SPEL/SPEGL (NAS)  |
| Short term, emergency    | IDLH (NIOSH)          | ERPG-1, -2, -3 (AIHA) |
| Non-emergency short term | STEL (ACGIH)          | STPL (NAS)            |
| Long-term, life-long     | TLV (ACGIH)           | NAAQS (EPA)           |

#### 9.11.1 Occupational Hydrazine Exposure Limits Established for Working Population

Permissible Exposure Limits (PELs) for places of employment are established by OSHA in the US, as published in 29 Code of Federal Regulations Part 1910.1000. Table Z1A of that standard lists several hundred controlled chemicals, including hydrazine, MMH, and UDMH. The first list published by OSHA in response to the Occupational Safety and Health Act of 1970 simply adopted the ACGIH TLVs from the 1968 booklet. The TLV for hydrazine in those days was 1 ppm. The PEL is an enforceable government-imposed limit, but the ACGIH TLV is a voluntary guideline recommended by a professional organization. The 1989 revision of the list in the Z1A table included 600 chemicals. For each chemical, it lists a transitional PEL, a TWA, STEL, and a ceiling limit C that may not be exceeded even if the exposure is compensated by exposure to zero contamination for the rest of the work shift. In addition, several chemicals, including all hydrazines, have a “skin” notation. The TWA is the employee’s average airborne exposure in any 8-h work shift of a 40-h work week that shall not be exceeded. A TWA is a calculation that combines exposure times and concentrations measured throughout the work shift into a single concentration, which is often compared to the TLV to verify one’s compliance. The short-term exposure limit (STEL) is the employee’s 15-min TWA exposure that shall not be exceeded at any time during a workday unless another time limit is specified in a parenthetical notation below the limit. PELs, TWAs, and STELs from the 1989 and most recent version of Table Z1A are summarized in Table 95. The most recent version of Table Z1 is available on the GPO web site [2530]. It is interesting that this table includes phenylhydrazine, which, of course, is eaten by the general population in tonnage quantities as a constituent of agaritine in brown cap mushrooms.

**Table 95:** Time-weighted average and short-term exposure limits.

|                 | Transitional PEL |                   | Skin | TWA |                   | STEL |                   | Ceiling |                   | Skin |
|-----------------|------------------|-------------------|------|-----|-------------------|------|-------------------|---------|-------------------|------|
|                 | ppm              | mg/m <sup>3</sup> |      | ppm | mg/m <sup>3</sup> | ppm  | mg/m <sup>3</sup> | ppm     | mg/m <sup>3</sup> |      |
| Hydrazine       | 1                | 1.3               | X    | 0.1 | 0.1               | —    | —                 | —       | —                 | X    |
| MMH             | C 0.2            | C 0.35            | X    | —   | —                 | —    | —                 | 0.2     | 0.35              | X    |
| UDMH            | 0.5              | 1                 | X    | 0.5 | 1                 | —    | —                 | —       | —                 | X    |
| Phenylhydrazine | 5                | 22                | X    | 5   | 20                | 10   | 45                | —       | —                 | X    |

<sup>a</sup> per 29CFR 1910.1000 Table Z1A Data, 1989 Revision

### 9.11.2 Long-Term Exposure Limits Established for the Working Population

The most widely accepted TLVs are those established by the ACGIH. The definition for TLV reads: “Threshold limit values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed to day after day 8 h/d, 40 h/wk without adverse effect.” Three series of ACGIH publications are particularly useful in establishing and maintaining safe working conditions at places of employment (regardless if the workplace contains hydrazines or not): The annually updated TLV booklet [2531], the less frequently updated and slightly more detailed *Guide to Occupational Exposure Values* [2532], and the most detailed loose-leaf issue of *Documentation of the Threshold Limit Values and Biological Exposure Indices*, a loose-leaf issue in five-ring binders that was, as of 2001, in its seventh edition [2533]. These are the standard reference sources in this field. In the sixth edition of the loose-leaf publication, hydrazine was covered on pp. 761–765, MMH on pp. 1009–1012, and UDMH on pp. 491–494. These loose-leaf summaries are the best way to get started on a hydrazine occupational hazards/toxicity study, and they provide a useful number of references. Most of these documents are available from ACGIH not only on paper, but also on CD-ROM or diskette in electronic, easily searchable format. ACGIH has a web site where some of the information can be downloaded. Because regulations change so frequently, some of them every year, this is the most efficient way to stay up to date. The TLV booklet, which for many years was small enough to fit into a shirt pocket as the indispensable *vade mecum* of an industrial occupational hygienist, has now grown to a spiral-bound book format that no longer fits into a shirt pocket. Maybe the database stored in a smartphone computer will eventually take its place. See also [2534].

It is of interest to follow the historical evolution and tightening of hydrazine occupational exposure limits in various industrialized countries of the world. It appears that as soon as one country lowered the exposure limit, other countries would follow suit. This is a direct result of close international cooperation, where many safety issues, e.g., transportation classifications, are now handled by international agencies like UNO or EEC. Other countries where publications dealing with hydrazine TLVs are on record include France [2535], UK [2536], and Germany. The German Committee for

Hazardous Substances at the Workplace (AgA) in 1982 established a recommended threshold limit concentration (TRK) for 14 proven or suspect carcinogens, including hydrazine. The recommended upper limit for hydrazine was 0.1 ppm [2537].

It has often been shown that occupational exposure limits (OELs) for the same substance can vary significantly between different standard setters. An attempt was made to identify the steps taken by various agencies in the often arbitrary process toward establishing an OEL and how variations in those processes could account for these differences [2538]. This study selected for further scrutiny substances for which the OELs varied by a factor of 100, focusing on 14 substances from 8 standard setters. Like the hydrazine data, several of the OELs studied were more than 20 years old and based on outdated knowledge. Furthermore, different standard setters sometimes based their OELs on different sets of data, and data availability alone could not explain all differences in the data selected by standard setters.

The case of hydrazine hydrate poisoning in Finland that led to the death of a boiler operator [2498] caused authorities in Finland to issue tighter regulations about chemical exposures in the workplace. Health authorities in other countries, such as Germany [2539, 2540], have followed suit and tightened their regulations on the use of hydrazine in boiler feedwater treatment installations in power plants. At the same time, hydrazine solution producers have provided shipping and transfer containers, which allow for the hermetically sealed transfer of solutions, minimizing operator exposure.

A publication by the International Labor Office compares established limits in 15 countries and gives examples of the different criteria adopted by different countries in establishing their domestic exposure limits. Another suspected reason for the continued tightening of long-term exposure limits is that in the past, previously available analytical methods were not capable to reliably and rapidly measure contaminant concentrations in air. It appears that as soon as a more sensitive analytical method became available, the tolerable level for that particular chemical was lowered, placing a new challenge on the sensitivity and accuracy of the analytical instrumentation. Detection limits and tolerable levels have been in a “leapfrogging” mode for several decades. Some governments have issued a rule stating that carcinogens should be kept below detectable levels, which makes the tolerable concentration a variable dependent on the analytical technique used. As of 1991, the maximum allowable concentrations (equivalent to our TLV) in other countries were as summarized in Table 96.

Table 2 on page 12 of the recommendation from the European Scientific Committee on Occupational Exposure Limits for hydrazine contains a summary of occupational exposure limits for many countries in the world [2542–2544]. A complete table listing the 8-h and short-term exposure limits in 24 countries is available online at the German Institute for Worker Protection, part of the federal workmen’s compensation accident insurance [2545], although that table does not indicate when it was last updated. So far, only Japan has issued specific limits for hydrazine hydrate, which should have

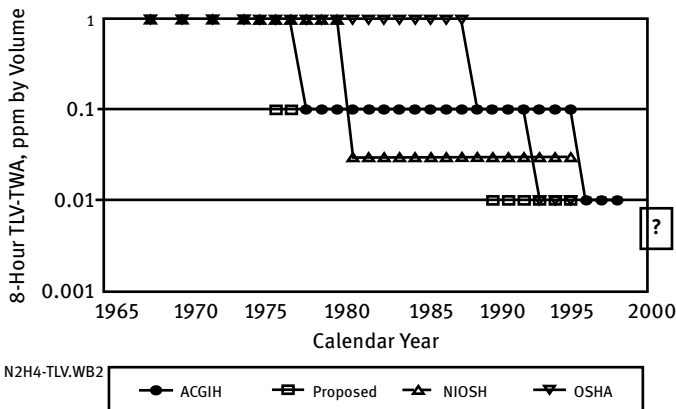
**Table 96:** Maximum allowable concentrations in other countries, ppm (equivalent to TLV).

| Country               | Hydrazine                                             | MMH                                                          | UDMH                                                                     |
|-----------------------|-------------------------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------------------|
| Germany (1991)        | 0.1, Group A2 <sup>a</sup> , skin, sensitizer; [2541] |                                                              | no MAK established, Group A2 <sup>a</sup> , skin, sensitizer             |
| Australia (1990)      | 0.1                                                   | 0.2 short term peak 15 min limitation, Category 3 carcinogen | 0.5 short term, Category 2 probable human carcinogen, skin, under review |
| Sweden (1989)         | 0.1 (short term 0.3)                                  |                                                              | 0.1; 15-min STEL 0.2 ppm, skin, carcinogenic (1984)                      |
| United Kingdom (1991) | 0.1 skin                                              |                                                              | no limit established, carcinogen                                         |

<sup>a</sup> A2 = unmistakably carcinogenic in animal experimentation only

been done by all countries because the hazard with anhydrous hydrazine inhalation would be different from that with hydrazine hydrate.

The American Conference of Governmental Industrial Hygienists (ACGIH) grades hydrazine as “A3 – confirmed animal carcinogen with unknown relevance to humans.” TLVs for hydrazines as established by ACGIH are summarized in Table 99. The 8-h/d, 40-h/week TLV for hydrazine was lowered in 1995 from 0.1 to 0.01 ppm. Figure 69 illustrates the historical evolution of TLVs for hydrazine in the US during the past several decades, lowering the TLVs by several orders of magnitude. The scientific rationale for lowering the TLV has been questioned, and the cost:benefit ratio fails to show a reasonable justification.

**Figure 69:** Historical evolution of hydrazine TLV.

Significant discussions were held among a worldwide group of hydrazine manufacturers (a so-called hydrazine coalition), hydrazine users, and governmental regulatory agencies during the early 1990s when it was proposed to lower the TLV from 0.1 to 0.01 ppm. An industry/government team of toxicologists met several times and reviewed the available evidence, which was quoted in support of a request to lower the TLV [2546]. The difficulty was that most of the data cited in making that decision were quite antiquated and typically 20 years old. There were insufficient funds to repeat the inhalation exposure tests with hundreds of animals and with more accurate measurement of the actual vapor concentrations in the exposure chambers.

The impetus for the ACGIH proposal to lower the TLV was based on an outdated 1985 report on animal exposures done during the preceding 10-year period, 1975–1985 [2394]. It reported a slightly elevated incidence of nasal tumors in rats exposed to *what was intended to be* 0.05 ppm hydrazine for 1 year (6 h/d, 5 d/week) and held for 1 year post-exposure as compared to unexposed controls. The words *what was intended to be* require explanation: There were obvious experimental errors in the vapor exposure techniques used several decades ago, foremost among them the use of very long sampling lines between the many external animal cages and a single, central vapor concentration measuring station. It was later shown that hydrazine and UDMH absorbed irreversibly, permeated, and decayed in sampling lines made of various materials [1870, 1871, 2547]. The introduction of a considerable excess of hydrazine into the animal exposure chambers was required to attain the desired vapor in air concentrations at the end of a long sampling line (see Section 9.6.1 “Acute Inhalation Hazard Studies” [2394]). The total intake by the animals was increased by hydrazine that had adsorbed on the food and because the animals often licked their hydrazine-soaked fur. Despite being aware of these metering errors, a government study group concluded in 1994 that “All procedures used in the study and the data regarding exposures of the animals were found to be valid and consistent with the technologies available at the time of the study in 1976.”

Considerations for a rational approach to arriving at a safe limits of occupational exposure of workers would differ from those applied for general public exposure [2548]. Experimental uncertainties about antiquated animal exposure data make it difficult to arrive at a decision that could have significant economic impact on the industry, yet the number of individuals at risk is relatively small.

The ACGIH TLV committee did not include a quantitative cancer risk assessment in setting the 1995 TLV at 0.01 ppm. The risk associated with the new TLV has been estimated to be on the order of 2 in 1000, which is consistent with the risk associated with other suspected human carcinogens regulated by OSHA [2548]. However, these risk levels are higher than the criteria used by OSHA to classify “insignificant” risk, which is 1/10000. If that acceptable risk were used, the hydrazine TWA would have to be 0.4 ppb.

Hydrazine is used in various industries in Poland, where as of 2011 approximately 2000 people were assumed to be exposed to hydrazine and its salts [2549]. Until

2015, in Poland, TWA of  $0.05\text{mg}/\text{m}^3$  and STEL of  $0.1\text{mg}/\text{m}^3$  were in effect. The European Union proposed a binding BOELV value of  $0.013\text{mg}/\text{m}^3$ . The LoAEL value is  $0.332\text{mg}/\text{m}^3$ . The derived limit value is  $0.014\text{mg}/\text{m}^3$  and the STEL value is  $0.042\text{mg}/\text{m}^3$  because of the irritant effects. After discussion and voting at the 77<sup>th</sup> meeting of the Interdepartmental Commission for Maximum Admissible Concentrations (MAC) and Maximum Admissible Intensities (MAI) (January 14, 2015), an exposure limit value TWA of  $0.013\text{mg}/\text{m}^3$  and a STEL value of  $0.039\text{mg}/\text{m}^3$  were accepted.

### 9.11.3 Biological Exposure Indices

Ideally, in addition to wearing dosimeters that indicate the cumulative exposure to hydrazines during a work shift, it would be desirable to have BEIs, for instance, hydrazine concentration in the urine or plasma of workers measured before and at the end of each work shift, which can be correlated with the exposure profile. However, most hydrazines are metabolized too fast to serve as an indicator. Sensitivity of analytical methods for hydrazine in urine or plasma is insufficient to serve as a routine analysis in place of a dosimeter or in addition to a dosimeter. If hydrazine or MMH or UDMH as measured using current instrumentation started showing up in the urine, one would already have a serious poisoning incident at hand. This approach to BEIs works only with less reactive chemicals, such as halogenated solvents or benzene.

### 9.11.4 Information Relevant for Occupational Health Standards

Government regulators depend on published information to establish limits. In a survey of information relevant to occupational health standards for hydrazines, several hundred references on hydrazine, MMH, and UDMH toxicity have been compiled [2304]. At that time, the main concern in this study was to gather evidence that would support or dispute the proposal by ACGIH to lower the TLV for hydrazine from 1.0 to 0.1 ppm and to place it and other methylhydrazines on the list of suspected carcinogens. In addition, the search was extended to *N*-nitrosodimethylamine (a one-time intermediate in the production of UDMH and a known carcinogen) and nitrosomethylurea and nitrosomethylurethane, intermediates of a proposed but never used alternative UDMH production process. A similar effort by NIOSH in 1978 resulted in a document titled *Criteria for a Recommended Standard* [2291] in which NIOSH recommended to lower the TLV for hydrazine from 0.1 to 0.03 ppm.

### 9.11.5 Emergency Exposure Limits for Hydrazine Exposure

Emergency exposure limits for hydrazines were established by the Committee on Toxicology, National Research Council, National Academy of Sciences (NAS-NRC); they were defined as follows: “The Emergency Exposure Limit for short-term exposure to



an airborne contaminant is a concentration which, when inhaled for a specified single brief period, rare in the lifetime of an individual, is believed not to result in a period of disability or interfere with the performance of his assigned task" [2550–2553].

The EEL was established for healthy young males under close medical supervision. Emergency exposure limit data are available only for a fraction of all those chemicals for which TLVs were established. Limited data are available for hydrazine and methylhydrazines [2554–2556]. EELs for hydrazines as recommended by the NAS-NRC are listed in Table 99 along with the TLVs. As can be seen from this table, the ratio between EEL (10 min) and TLV valid at that time varies from 200 to 30, depending on the fast-acting nature of the compound. Hydrazine as a fast-acting skin and mucous membrane irritant has been given a low EEL in comparison to UDMH, which is more a systemic poison (but UDMH has a higher vapor pressure!).

In addition to establishing an EEL, some agencies have begun to collect information and publish information on the immediately dangerous to life and health (IDLH) concentrations of fast-acting acute poisons [2557]. The IDLH documentation is also available in the form of a NIOSH Pocket Guide to Chemical Hazards [2558]. The criteria used by the commission in setting the IDLH limits are described in [2559].

The NIOSH/CDC home page has IDLH information posted for hydrazine and MMH. The recommended limits are summarized in Table 97 in comparison with several other commonly used hazardous chemicals.

**Table 97:** Immediately dangerous to life and health limits for hydrazines.

| Compound        | Original IDLH (SCP), ppm | Revised IDLH, ppm | Date posted     |
|-----------------|--------------------------|-------------------|-----------------|
| Hydrazine       | 80                       | 50                | August 16, 1996 |
| MMH             | 50                       | 20                | August 16, 1996 |
| For comparison: |                          |                   |                 |
| Ethanol         | 15000                    | —                 | August 16, 1996 |
| Ammonia         | 500                      | —                 | August 16, 1996 |

Data source: NIOSH Web Page at <http://www.cdc.gov/niosh>

Acute exposure threshold levels (AETLs) for the general population in Europe were developed in the context of the risks of major accidents from chemical sites such as the Seveso or Bhopal accidents [2560]. Twenty-one substances were selected to be used as preliminary case studies in the development and testing of the AETL methodology, and the development of a prioritization methodology to support initial substance selection for a possible further AETL program. In discussion with a critical review panel and ACUTEX experts, hydrazine was selected because it had appropriate data and was in relatively widespread use in the EU, but no specific numbers were given.

### 9.11.6 Hydrazine Exposure Limits Established for General Population

It is generally assumed that exposure of workers at their place of employment is at least partially voluntary, because workers can choose where to work. The general public does not have that choice and has the right to clean air even if they live downwind of a chemical installation. Quite often exposure limits are extrapolated from occupational TLVs to non-occupational exposure conditions without due consideration of the different populations involved. The need to protect the population at large from disastrous or chronic exposures gained legislative momentum as the result of EPCRA, enacted as Superfund Amendments and Reauthorization Act of 1986, which is SARA Title III, and CERCLA, also part of Superfund. SARA Title III requires local authorities to develop emergency response plans to deal with accidental release of extremely hazardous substances in their communities. This was partially prompted by Seveso- or Bhopal-type accidents in chemical plants that had severe impacts on the surrounding communities. “Extremely hazardous substances” are defined in 40 CFR Part 355 issued by EPA [2561]. That list contains more than 400 chemicals, including hydrazine, MMH, and UDMH. The reportable quantity of hydrazine is 1 lb (453 g). Oddly enough, the table does not include hydrazine hydrate and does not specify the type of dimethylhydrazine (1,1- or 1,2-). This indicates a poor understanding of chemistry on the part of the people assembling this table.

A STPL of 5.3 ppm (7 mg/m<sup>3</sup>) and a 30-min PEL of 20 ppm (20 mg/m<sup>3</sup>) were used as examples to determine the hazard corridor downwind from hydrazine spills [1969, 1970]. Additional STPL and PEL data are summarized in Tables 98 and 99. The AEGL limits (see below) are intended to replace the old SPEGL limits for hydrazines issued by the NRC on earlier occasions, which are now obsolete (from the NIOSH-CDC web page, like IDLH listings).

The National Advisory Committee on Acute Exposure Guideline Levels (AEGLs) was established to identify, review, and interpret relevant toxicological and other scientific data and develop AEGLs for high-priority, acutely toxic chemicals. AEGLs represent ceiling exposure values for the general public and are applicable to emergency exposure periods ranging from less than 1 to 8 h. Three AEGLs apply to each of four exposure periods (30 min, 1, 4, and 8 h) and are distinguished by varying degrees of severity of toxic effects. The three AEGLs have been defined as follows:

**AEGL-1** is the airborne concentration (expressed as ppm or mg/m<sup>3</sup>) of a substance at or above which it is predicted that the general population, including “susceptible” but excluding “hypersusceptible” individuals, could experience notable discomfort. Airborne concentrations below AEGL-1 represent exposure levels that could produce mild odor, taste, or other sensory irritations. Below AEGL-1, the criterion is detectability: a chemical can be perceived only by smell, taste, sight, or mild sensory irritation.

**AEGL-2** is the airborne concentration of a substance at or above which it is predicted that the general population, including “susceptible” but excluding “hypersusceptible” individuals, could experience irreversible or other serious, long-lasting effects or impaired ability to escape. Airborne concentrations below AEGL-2 but at or

above AEGL-1 represent exposure levels that may cause notable discomfort. Below AEGL-2, physical discomfort is the key factor; exposure does not impair escape, produce disablement or disorientation, or result in permanent or long-lasting effects.

**AEGL-3** is the airborne concentration of a substance at or above which it is predicted that the general population, including “susceptible” but excluding “hypersusceptible” individuals, could experience life-threatening effects or death. Airborne concentrations below AEGL-3 but at or above AEGL-2 represent exposure levels that may cause irreversible or other serious, long-lasting effects or impaired ability to escape. Disability can ensue, and external assistance is needed because people can become disabled and disoriented as a result of exposure or experience permanent or long-lasting residual effects. Above AEGL-3, life-threatening effects or death can occur either immediately or shortly after exposure.

Proposed AEGLs for hydrazine, MMH, and UDMH were published in 1997. The criteria document for hydrazine spans 56 pages and contains 49 references. AEGLs proposed for hydrazines are summarized in Table 98.

#### **9.11.7 Exposure Limits Established for Special Skin-Only Conditions**

Most inhalation exposure limits are established for simultaneous inhalation and whole-body exposure. Attempts have been made to replace the bulky SCAPE suits with supplied air respirators, providing clean air for breathing but leaving the skin exposed to potentially toxic vapors. Skin permeation of hydrazine and UDMH vapors has been measured (Section 9.6.4.1), and a pharmacokinetic model was used to calculate the vapor concentration to which propellant handlers with supplied air respirators may be exposed and still meet the TLV limitations for inhalation as far as the total body dose is concerned [2565, 2566]. The calculations showed that the vapor concentration during a skin-only exposure would have to be at least 200 times higher than that during inhalation to cause the same level of poisoning. For the old TLVs for hydrazine and UDMH of 0.1 and 0.5 ppm, the equivalent skin-only tolerable concentration would have been 48 ppm for hydrazine and 32 ppm for UDMH. For the new TLVs of 0.01 ppm, the equivalent skin-only TLVs would be 4.8 ppm for hydrazine and 0.64 ppm for UDMH.

#### **9.11.8 Effects of Long-Term Exposure to Hydrazine in Closed Environments**

The 8 h/d, 40 h/week exposure cycles are quite different from that of astronauts working and living in space stations or navy personnel in submarines. A different set of criteria must be generated for these conditions. Spacecraft Maximum Acceptable Concentrations (SMACs) are being established by NASA for potential contaminants in closed environments [2567]. A draft table of derived SMACs was submitted to the NRC Committee on Toxicology for review before implementing the new limits on all future space flights [2305, 2568, 2569]. Derived SMAC concentrations for hydrazine

**Table 98:** Proposed AEGL values for hydrazines (Proposed in 1997).

| Chemical  | Classification      | Limit | 30-min                              | 1-h                                 | 4-h                                 | 8-h                                 | Endpoint                                                                               | References   |
|-----------|---------------------|-------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|----------------------------------------------------------------------------------------|--------------|
| Hydrazine | AEGL-1 <sup>a</sup> |       | 0.1 ppm<br>(0.1 mg/m <sup>3</sup> ) | 0.1 ppm<br>(0.1 mg/m <sup>3</sup> ) | 0.1 ppm<br>(0.1 mg/m <sup>3</sup> ) | 0.1 ppm<br>(0.1 mg/m <sup>3</sup> ) | Eye and facial irritation in monkeys                                                   | [2562]       |
|           | AEGL-2              |       | 8 ppm<br>(10 mg/m <sup>3</sup> )    | 6 ppm<br>(8 mg/m <sup>3</sup> )     | 3 ppm<br>(4 mg/m <sup>3</sup> )     | 2 ppm<br>(3 mg/m <sup>3</sup> )     | Nasal lesions                                                                          | [2398]       |
|           | AEGL-3              |       | 47 ppm<br>(61 mg/m <sup>3</sup> )   | 33 ppm<br>(43 mg/m <sup>3</sup> )   | 17 ppm<br>(22 mg/m <sup>3</sup> )   | 12 ppm<br>(16 mg/m <sup>3</sup> )   | Lethality in rats                                                                      | [2399]       |
| MMH       | AEGL-1              |       | N/A                                 | N/A                                 | N/A                                 | N/A                                 | N/A <sup>b</sup>                                                                       |              |
|           | AEGL-2              |       | 2 ppm<br>(3.8 mg/m <sup>3</sup> )   | 1 ppm<br>(1.9 mg/m <sup>3</sup> )   | 0.2 ppm<br>(0.4 mg/m <sup>3</sup> ) | 0.1 ppm<br>(0.2 mg/m <sup>3</sup> ) | Three-fold reduction in AEGL-3                                                         |              |
|           | AEGL-3              |       | 6 ppm<br>(11.3 mg/m <sup>3</sup> )  | 3 ppm<br>(5.6 mg/m <sup>3</sup> )   | 0.7 ppm<br>(1.1 mg/m <sup>3</sup> ) | 0.3 ppm<br>(0.6 mg/m <sup>3</sup> ) | 1-h LC <sub>50</sub> of 82 ppm reduced 3-fold to estimate a lethality threshold        |              |
| UDMH      | AEGL-1              |       | N/A                                 | N/A                                 | N/A                                 | N/A                                 | N/A <sup>b</sup>                                                                       |              |
|           | AEGL-2              |       | 6 ppm<br>(14.7 mg/m <sup>3</sup> )  | 3 ppm<br>(7.4 mg/m <sup>3</sup> )   | 0.8 ppm<br>(2 mg/m <sup>3</sup> )   | 0.4 ppm<br>(1 mg/m <sup>3</sup> )   | Behavioral changes and muscle fasciculations in dogs exposed to 360 ppm for 15 minutes | [2563, 2564] |
|           | AEGL-3              |       | 22 ppm<br>(54 mg/m <sup>3</sup> )   | 11 ppm<br>(27 mg/m <sup>3</sup> )   | 3 ppm<br>(7.4 mg/m <sup>3</sup> )   | 1.5 ppm<br>(3.7 mg/m <sup>3</sup> ) | Lethality threshold of 327 ppm for 1 h estimated from 1-h LC <sub>50</sub> in dogs     | [2563, 2564] |

<sup>a</sup> Because the contact irritation response to the extremely reactive hydrazine is concentration dependent rather than time dependent, the AEGL-1 is the same for all time periods.

<sup>b</sup> Inappropriate because notable toxicity may occur at concentrations below the odor threshold (see text)

exposures for 1 h to 30 d were all above the new 1996 TLV of 0.01 ppm, which applies to NASA workers on the surface of the Earth. Only the proposed 180-d limit of 0.004 ppm was below the current TLV. For MMH, SMAC limits of 0.002 ppm were proposed for all exposure durations, because a different metabolic mechanism/target organ is involved. While one would intuitively expect that the toxicities of hydrazine and MMH would be similar, NASA toxicologists arrived at quite disparate SMAC values.

### 9.12 Olfactory Threshold of Hydrazine Vapors

There is a wide discrepancy in reported olfactory threshold values for hydrazine itself. Several sources agree that one should not rely on the odor of hydrazine as a warning for imminent acute or subacute exposure because it may cause olfactory fatigue. Also, the olfactory threshold is far above the established safe levels. Table 99 summarizes the reported olfactory threshold of hydrazines in comparison to former and current TLV and EEL TLVs.

It is interesting to compare odor thresholds for hydrazines and ammonia with those of 214 other industrial chemicals [2573]. Hydrazine is not easily identified by its odor. The olfactory threshold for hydrazine in air is 3.7 ppm, that for ammonia is 5.2 ppm, and that for MMH or UDMH is 1.7 ppm. Methylhydrazines have a more distinct fishy odor, although it would be difficult to differentiate them from methylamine or dimethylamine, common constituents of fish degradation products.

### 9.13 Medical Surveillance Protocols for Monitoring Hydrazine Propellant Handlers

Personnel anticipated to work routinely with hydrazines should undergo thorough entry medical exams. The following pre-existing medical conditions are contraindications for working with hydrazines and would aggravate the results of inadvertent exposure: pregnancy, anemia, hematological disorders, history of convulsive episodes and other neurological disorders, "slow acetylator" phenotype, glucose-6-phosphate dehydrogenase deficiency, 6-phosphogluconic dehydrogenase deficiency, glutathione reductase deficiency, therapeutic use of tranquilizers, and existence of any tumors, benign or not. For USAF personnel, Air Force Occupational Safety and Health (AFOSH) Standard 48-8, Attachment 8, [2574] reviews the considerations for occupational exposure to hydrazine in missile, aircraft, and spacecraft systems, specifies the selection criteria for personnel potentially exposed to hydrazine, and establishes a medical surveillance routine and record-keeping requirements [2575]. Industrial and academic organizations working with hydrazines may want to adopt similar plans.

Table 99: Olfactory threshold and exposure limits for hydrazines.

| Type of data <sup>a</sup> | Hydrazine      | References | MMH            | References   | UDMH           | References   |
|---------------------------|----------------|------------|----------------|--------------|----------------|--------------|
| Olfactory Threshold       | 69–83          | [2570]     | 1–3            | [2570, 2571] | 0.5–1.0        | [2572]       |
| Olfactory Threshold       | 3–4            | [2571]     |                |              | 6–14           | [2571]       |
| ACGIH-TLV (1981)          | 0.1 (skin)     | ACGIH      | C 0.2 (skin)   | ACGIH        | 0.5 (skin)     | ACGIH        |
| ACGIH-STEL (1981)         | —              | ACGIH      | —              | ACGIH        | 1              | ACGIH        |
| ACGIH-TLV (1998)          | 0.01 (skin) A3 | ACGIH      | 0.01 (skin) A3 | ACGIH        | 0.01 (skin) A3 | ACGIH        |
| NRC-EEL, 10 min           | 30             | [2551]     | 90             | [2551]       | 100            | [2550, 2551] |
| EEL, 10 min               |                |            | 10             | [2550]       | 200            | [2554]       |
| NRC-EEL, 30 min           | 20             | [2551]     | 30             | [2551]       | 50             | [2550, 2551] |
| EEL, 30 min               |                |            | 7              | [2550]       | 100            | [2554, 2555] |
| NRC-EEL, 60 min           | 10             | [2551]     | 15             | [2551]       | 30             | [2550, 2551] |
| EEL, 60 min               |                |            | 3              | [2550]       | 50             | [2554, 2555] |
| NRC-STPL, 10 min          | 15             | [2556]     | 9              | [2556]       | 50             | [2556]       |
| NRC-STPL, 30 min          | 10             |            | 3              |              | 25             |              |
| NRC-STPL, 60 min          | 5              |            | 1.5            |              | 15             |              |
| NRC-PEL, 10 min           | 30             |            | 90             |              | 100            |              |
| NRC-PEL, 20 min           | 20             |            | 30             |              | 50             |              |
| NRC-PEL, 30 min           | 10             |            | 15             |              | 30             |              |

<sup>a</sup> All data in ppm by volume.

### 9.14 Toxicity of Hydrazine Mixtures

Many hydrazine mixtures have been used as rocket propellants, foremost among them is Aerozine-50, the 50 : 50 mixture of hydrazine and UDMH. Since the inhalation toxicity of this mixture is mostly dominated by that of the more volatile UDMH, the toxicity of this mixture is discussed in *Encyclopedia of Liquid Fuels* in the chapter “Dimethylhydrazines.”

One of the first hydrazine mixtures to be used as a rocket propellant in the US was a ternary blend of hydrazine, aniline, and furfuryl alcohol. This blend was used in sounding rockets developed by JPL and Aerojet. The acute and chronic inhalation toxicity of this propellant was tested in animal experiments [2576], and hydrazine was the most toxic constituent of this mixture.

## 10 Environmental Fate and Effects

In view of growing public concern over the environmental effects of hazardous chemicals, and in view of increasing legislative action aimed at the control of chemical hazards, it is important to have a section dedicated to the environmental effects of hydrazine and its derivatives. This information can generally be derived from other paragraphs on toxicity, autoxidation, and so on, but it is worthwhile to consider hydrazine chemistry from the standpoint of an environmental scientist.

Fortunately, and in contradistinction to polychlorinated biphenyl (PCB), dioxin, or dichlorodiphenyltrichloroethane (DDT), little can be said about the environmental persistence of hydrazine and hydrazine derivatives because they degrade so rapidly under the effect of air (oxygen), light, and soil bacteria [2577]. This is one of the most distinct advantages of hydrazine-derived chemicals in numerous agricultural and industrial applications as pesticides, boiler feedwater treatments, or anti-corrosion additives. The biodegradability of hydrazine derivatives is one of the reasons that some hydrazine-based pesticides have been chosen to replace more persistent, chlorinated, or thiophosphate-ester organics that may accumulate in the food chain and/or are suspect endocrine disruptors.

Under the sponsorship of the USAF Civil and Environmental Engineering Development Office (CEEDO, later AFESC-ESL) at Tyndall AFB in Florida, a series of conferences on the environmental chemistry of hydrazine fuels was held in 1977, 1979, and 1987. The proceedings from these three meetings constitute a valuable resource for studying the environmental effects of hydrazine fuels [2578–2580]. During the period in which these conferences were held, the number of industrial and military uses of hydrazines increased substantially [3], and numerous studies on environmental and health effects of hydrazines were in progress [2581]. The concern over hydrazine toxicity eventually led to a lowering of the TLVs for hydrazine exposure at the workplace and to a heightened awareness of the occupational and environmental hazards

of hydrazines. During the period from 1970 through 1985, the USAF Medical Research Laboratory hosted a series of *Annual Conferences on Environmental Toxicology*. Some of these conferences contained several individual papers on hydrazines, although in other years some of these conferences did not deal with hydrazines at all.

The US Environmental Protection Agency (EPA) has issued several *Health and Environmental Effects Profiles* for hydrazines that contain sections on environmental effects in addition to toxicity information [2292]. Howard's *Handbook of Environmental Degradation Rates* gives data for many chemicals, including hydrazine, MMH, UDMH, SDMH, and NDMA [2582].

### 10.1 Potential Environmental Impact of Hydrazine

When hydrazines and hydrazine derivatives were first introduced for a variety of applications, some of which were agricultural applications where it must be expected that crop residues will end up in consumer food, there was little and insufficient understanding of the potential environmental and consumer health implications. This awareness has changed greatly in recent decades. The persistence of hydrazine derivatives in the environment is low compared to other xenobiotic toxicants that have caused similar concern, e.g., DDT or dioxin. Nevertheless, adequate precautions need to be taken to avoid environmental pollution.

Prior to the introduction of the F-16 fighter jet, hydrazine propellants were used only in a small number of rocket launch sites. When the F-16 was introduced, it caused hydrazine (in the form of a 70% aqueous solution) to enter the logistics chain and had to be stored at many airbases, including forward bases during military conflicts. Although thorough planning and preparation of environmental impact statements preceded the introduction of the F-16 [2509], the complexity of the task was underestimated, and the acceptance of the new technology by flight-line maintenance personnel was not unequivocally enthusiastic. Despite the poorly planned fielding of a new hazardous fluid and lack of training in many cases, there were only a few incidents of spillage and accidental vapor exposure. The few incidents that did occur caused the USAF to push for lowered TLVs in the entire industry, although industry knew very well how to safely handle this chemical.

Additional information on the environmental effects of hydrazines is available in [22] including the aquatic toxicity and degradation of hydrazine in water, degradation of hydrazine in surface waters and in sewage treatment plants, adverse effects of hydrazine on plants, hydrazine degradation and environmental fate in soil, and atmospheric decay of hydrazine vapors in air. These sections of the recommended standard reference for information on hydrazine toxicity and environmental effects have not yet been updated.



## 10.2 Environmental Pollution Case Studies

Hydrazines have been used for more than half a century in a wide range of rocket propulsion applications in addition to many commercial applications. It is unfortunate that some locations have experienced pollution incidents in which hydrazines may have entered the environment.

Launch mishaps like the Titan 34D explosions just offshore in California on August 28, 1985, and April 18, 1986, and a later Titan 4A explosion on August 12, 1998, off the coast of Florida resulted in the release of a large cloud of unburnt liquid propellant in the midst of chunks of burning solid propellant. Atmospheric models have been derived to predict the path of the toxic cloud, the chemical reactions in the cloud, and the downwind concentrations where it begins to enter populated areas. The more visible part of these events was the aluminum oxide and hydrogen chloride from the solid propellant boosters and the red cloud from evaporating NTO converting itself to nitrogen dioxide. The Aerozine-50 propellant that may also have been involved in the deflagration was less visible.

A spill of commercial hydrazine hydrate from 16 punctured steel drums in a railroad accident near Sea Cliff, CA, occurred on July 28, 1991. No major environmental damage occurred since the spill site was quickly surrounded by a dam, and leaked hydrazine hydrate was collected in a lined pond and destroyed with hypochlorite solutions.

Several decontamination techniques were used to clean up the stored process waste and tank rinse water from the Rocky Mountain Arsenal Hydrazine Blending and Storage Facility [2023]. Significant NDMA levels persisted in the groundwater below Rocky Mountain Arsenal for many years after the propellant mixing facility was shut down. Air sampling at Rocky Mountain Arsenal Hydrazine Blending Facility continued for several more years while the cleanup was in progress [2064, 2519, 2520]. Intercept wells were sunk to prevent polluted groundwater from diffusing off-site. NDMA-contaminated water collected in these wells could not be cleaned by activated charcoal filters alone.

During the development and production of the TITAN II ICBM, large quantities of Aerozine-50 were consumed at a test site near Denver, CO, which was initially intended for the use of LOX/kerosene only. Many years after the test facilities were decommissioned and contamination from halogenated solvents was found, the USAF started a facility restoration program to make sure that no pollutants would spread from the sites [2583, 2584]. The Agency for Toxic Substances and Disease Registry (ATSDR) evaluated environmental data and exposure information associated with the Air Force Plant PJKS site and determined that the site posed no apparent public health hazard [2585].

### 10.3 Effect of Anhydrous Hydrazine on Bacteria Viability

The concern arose that anhydrous hydrazine in propellant tanks that crash or vent on other planets might harbor terrestrial bacteria that would then propagate on the target planet in their new environment, resulting in false findings of future search for extraterrestrial life. For the purposes of planetary protection, a series of experiments was performed to answer a long-standing question about the potential of bacterial contamination of interplanetary spacecraft from liquid hydrazine residues in propellant tanks vented or crashed on Mars. Spores of *Bacillus atrophaeus* (ATCC No. 9372, also known as *Bacillus subtilis* var. *niger*, and BSN) were exposed to anhydrous hydrazine and survivors were enumerated using the NASA standard planetary protection pour plate assay [2586]. Results indicated that bulk hydrazine rocket propellant may be considered free of living bacterial cells for planetary protection compliance.

Similar results were obtained with bacteria cultures exposed to hydrazine vapor [2587]. The exposure times required to reduce the spore population by a factor of 10, known as the *D*-value, were  $4.70 \pm 0.50$  h at 298 K (25°C) and  $2.85 \pm 0.13$  h at 308 K (35°C). These inactivation rates are short enough to ensure that the bioburden of the surfaces and volumes in a space probe would be negligible after prolonged exposure to hydrazine vapor. Thus, not all of the propellant tubing and internal tank surfaces exposed to hydrazine vapor contribute to the total spore count in hardware sent to other planets.

### 10.4 Atmospheric Dispersion, Decay, and Environmental Fate of Hydrazine

#### 10.4.1 Atmospheric Dispersion of Hydrazine

In the event of a spill and uncontrolled release of hydrazine(s) into the air, the immediate concern is for the safety of the population in the surrounding community. Instructions will need to be given to the hazardous material response team on how wide the evacuation circle should be drawn, depending on the size of the spill, the toxicity of the materials, the meteorological conditions, and the toxicity of the material.

A detailed summary of hazard corridor computer models has already been provided in Section 7.8.3. The models discussed there do not take into consideration that hydrazines react with oxygen in the air and become oxidized and photolyzed while they disperse. Another mode of neutralization is by the reaction of hydrazine with atmospheric carbon dioxide, leading to carbazic acid, a solid of very low volatility that most likely would precipitate as an aerosol, especially on a moist day. Therefore, the predicted hydrazine concentrations at the perimeter of the vapor plume are most likely higher than the actual measurements would show. It has been recommended that future improvements of atmospheric dispersion models include not only dilution, diffusion, and meteorological parameters, but also chemical reactions that could lead to a more rapid decay of hydrazines in the atmosphere [2588, 2589].

In the unusual situation that 1040 kg (2300 lb<sub>m</sub>) of hydrazine flown as part of an auxiliary power generator on board a military aircraft should have to be dumped in case of an emergency, dispersion profiles were calculated for a planned dump (requiring < 5 min) and an emergency dump (lines and pressurization sized for the fastest possible dump within less than 1 min.) [1927].

#### 10.4.2 Hydrazine Dispersion in Atmosphere from Re-entering Spacecraft

A rare case of hydrazine dispersion is the disintegration of satellites or upper stages that still contain varying amounts of residual hydrazine(s), either liquid or even frozen solid. This concern surfaced in 2008 when it became known that a wayward, uncontrollable US military satellite known as US193 that was about to re-enter the atmosphere contained a large tank with 450 kg (1000 lb) anhydrous hydrazine that was most likely frozen because the temperature controls on the satellite were inoperative. It was not possible to predict the time and location of re-entry, but in the worst case it could have re-entered over populated areas. If experts could have assured the authorities that the propellant was not frozen, the liquid propellant would more likely have dispersed in the atmosphere before it hit the ground. Numerous calculations were performed to estimate the chance that the tank and its contents would survive re-entry. One calculation predicted that the titanium shell of the tank would be breached due to re-entry heating and melting, but its frozen contents would not melt fast enough to disperse all the liquid before the tank would hit the ground [2590]. The model would have to be improved by entering the heat capacity of the solid and liquid hydrazine as a function of temperature (instead of a constant number) and by dividing the hydrazine model into several layers instead of one bulk mass. To be on the safe side, the out-of-control US193 satellite was destroyed in orbit by hitting it with an anti-missile missile launched from a ship. The US193 satellite that was destroyed in 2008 by an SM-3 antimissile interceptor at an altitude of 209 km (130 miles) in order to prevent it from re-entering the atmosphere above populated areas, involved most likely frozen hydrazine, and not methylhydrazine [2591].

Any aerodynamic re-entry heating that is enough to heat the second stage structures to beyond the melting point of metals, as evidenced by the meteor-like brightly shining object in the video of a re-entering second stage, is hot enough to destroy any remaining propellant on board. Re-entering first stages remain intact to the point that local residents in the impact area make a business out of salvaging the scrap metal. Looking at the debris collected on the ground from the disintegration of Space Shuttle Columbia during re-entry, spherical tanks are more likely to survive entry intact than other components [2592]. Some of the spherical tanks shown in NASA pictures tied down on a flatbed truck could have been just pressurant gas tanks and not liquid propellant tanks. It is not known whether any of the other tanks were tested for residual propellants that might have survived the re-entry heating. As part of a “design for demise” philosophy, a tankage re-entry survival analysis was performed for the

re-entry of NASA's Global Precipitation Measurement satellite [1690] and other satellites [2593].

A survivability-analysis program has been developed to analyze the ground impact risk of atmospheric re-entry objects, such as satellites or the upper stages of a launch vehicle, which move at or near the orbital velocity [2594]. The aero-thermodynamic load during free fall, the temperature variation due to thermal load, and the phase change after reaching the melting point were integrated into the three-degree-of-freedom trajectory simulation of the re-entry objects to analyze the size and weight of debris surviving re-entry and impacting the ground. The analysis results of the present method for simple-shaped objects were compared with the data predicted by similar codes developed by NASA and ESA and compared to observed actual re-entry orbital objects found on the ground.

The influence of oxidation on the thermal degradation process and material properties under atmospheric entry conditions remains unknown. An experimental investigation examining Ti-6Al-4V oxidation under atmospheric entry conditions was made in a 6-kW solar furnace, as most of the debris found on the ground was made of this material [2595, 2596]. The computer code was applied to the atmospheric re-entry of a generic Ti-6Al-4V tank and would be applicable to all tanks, those containing hydrazine or other propellants.

The controlled release of clouds of rocket propellants in space was planned to be studied during the chemical release experiment flown as payloads in the Space Shuttle payload bay [2597]. The purpose of this experiment was to identify the potential environmental consequences of an inadvertent release of hydrazine rocket propellant in space, during orbital or suborbital operations. The experiment was to be conducted in the thermosphere of outer space, at an altitude of about 300 km. It was planned to eject three Get Away Special satellites (one during the first and two during the second Space Shuttle flight), each containing about 100 lb of the specified hydrazine fuel, plus the required circuitry for tracking and ordinance activation to disperse its contents.

#### 10.4.3 Atmospheric Decay of Hydrazine

The kinetics and reaction products of autoxidation of hydrazine in the vapor phase were already discussed in Section 3.1.1.1. Under laboratory conditions, it is frequently difficult to simulate unconfined free atmosphere conditions and eliminate the wall effects of the reaction vessels used in the apparatus. Available literature attempts to review the significance of laboratory study results for actual unconfined environmental conditions. Ideally, real-life environmental atmospheric decay studies should be conducted in a large outdoor volume, and remote sensing with a LIDAR (Section 3.6.11.2) would greatly facilitate analysis of the environmental pollutant. Fortunately, hydrazines are not very persistent in the atmosphere. At the same time, this makes it difficult to catch and hold them for environmental decay kinetic studies long enough because they may be all gone by natural decay before the experiment is

over. Experimental methods for the study of atmospheric decay of hydrazine vapors in the dark are described in [22].

## 11 Hydrazine Fuel Mixtures

Among the main disadvantages of hydrazine as a fuel are its high freezing point and the difficulty in using it as a regenerative coolant in bipropellant rocket engines. Both of these disadvantages can be overcome by mixing hydrazine with other fuels.

Many studies have been conducted on hydrazine fuel mixture formulation [2598]. Hydrazine fuel mixtures could have been discussed in this book either in the chapter on hydrazine or in the chapter on the fuel that is used as an additive to hydrazine. It was decided to discuss hydrazine fuel mixtures at the end of the chapters on fuels, e.g.,  $\text{NH}_3$ , UDMH, or EDH, that are used as additives, because those are the more volatile or more toxic components ( $\text{NH}_3$ , UDMH) that would determine the handling and safety properties of such mixtures more than hydrazine that accepted these additives.

Hydrazine/ammonia fuel mixtures were already described in the chapter on ammonia. The hydrazine fuel mixtures with UDMH, Aerozine-50 will be discussed in the chapter on dimethylhydrazines, and MHF-3 will be discussed in the chapter on methylhydrazine.

### 11.1 H-70 Hydrazine/Water Fuel Mixture

The physical properties of hydrazine/water mixtures were already described previously in Sections 2.1.2.1 and 2.1.9.4. The most important hydrazine/water mixture is H-70, which is used as a gas generant in gas generators for EPUs in fighter aircraft such as the F-16. This fuel mixture contains 70%  $\text{N}_2\text{H}_4$ , which is just a little more hydrazine than hydrazine hydrate, which contains 64%  $\text{N}_2\text{H}_4$ . Theoretically H-70 could be made from HH100 hydrazine hydrate by adding just a little anhydrous hydrazine to bump the hydrazine content from 64 up to 70%. However, commercial HH100 contains too much carbon dioxide and other contaminants such that the fuel mixture made by this method would not meet criteria of MIL-PRF-87930B. Therefore, H-70 must be made by diluting monopropellant-grade anhydrous hydrazine with carbon-dioxide-free deoxygenated distilled water.

### 11.2 Military Specifications for H-70

The Military Specification for H-70 is essentially a watered-down version of MIL-PRF-26536F with the changed requirements of 69–70%  $\text{N}_2\text{H}_4$  and 30% minimum  $\text{H}_2\text{O}$ . The specification contains several analysis methods for assay and contaminants in H-70.

### 11.3 Other Hydrazine Fuel Mixtures

Numerous other fuels have been tested as additives to hydrazine to improve its freezing point and cooling capability behavior [2598]: Hydrazine and aniline form a eutectic mixture, which freezes at 237 K (−36 °C) and has a composition of 17.3 mass-% hydrazine and 82.7 mass-% aniline. This composition possesses highly improved hypergolic ignition properties with mixed acid and with fuming nitric acid, as compared to aniline alone.

### 11.4 Gelled Hydrazine Fuels

#### 11.4.1 Selection of Gelling Agents

Gelling agents that were proven to work for MMH or UDMH will not necessarily work for hydrazine. The polarity and solvent behavior of hydrazine as a solvent is quite different from that of the alkylhydrazines. One gelling agent evaluated for hydrazine and alkylhydrazines is polyacrylamide [2599].

Gelling agents of polyacrylic acids containing repeating units of



are those sold under the tradenames Carbopol 934, Carbopol 940, and Carbopol 941 with molecular masses of 1–3 million, which are trademarks of the Goodrich Company. Up to 33 mass-% aluminum powder could be suspended in a hydrazine gel with 2% Carbopol 940 [2600].

#### 11.4.2 Gelled Metallized Hydrazine Fuels

An experimental program to prepare thixotropic gels of hydrazine, MMH, and UDMH at ambient temperature included particulate, chemical, and synthetic gellant materials [2601]. Gelation of the liquid fuels was achieved with gellant concentrations as low as 1 mass-% in some cases. Hydrazine hydrate could be gelled by gelling agents like pectin, polyacrylamide (PAA,  $M > 5 \times 10^6$ ), polyvinyl alcohol, carboxymethylcellulose (CMC), hydroxyethyl cellulose (HEC), and ASPAA-II, whereas MMH was successfully gelled by low- and high-substitution methylcellulose, HEC, hydroxypropyl methylcellulose (HPMC), and AS-PAA-II in required concentrations. The gels of UDMH have been prepared using gellants such as Cab-O-Sil, PAA, low- and high-substitution methylcellulose, and HEC. Subsequently, MMH gelled fuel systems with HPMC and ASPAA-II gellants were chosen for metallization due to their low gellant concentration requirement and better gel quality. Metallized heterogeneous gels using up to 40 mass-% of Al or Mg metal powders showed a reduction in required gellant concentration with increasing metallization. The storage studies on gelled systems without metals over a period of 3 months showed good gel stability, but the metallized gels had segregated. A storage life of 3 months is insufficient for most applications. A suggestion

that aged, settled gels could be re-homogenized by stirring is totally unrealistic for most applications.

#### 11.4.2.1 Alumizine

A complete characterization of two specific gel systems, beryllium in anhydrous hydrazine and aluminum in anhydrous hydrazine gelled with Carbopol 940, revealed that the preparation of these gel system is very difficult. The gel characterization included rheology, thermal stability, mechanical stability, storage properties, shock sensitivity, and contamination properties.

There are more detailed studies on metallized MHF-3 fuels because they have a lower freezing point than those with hydrazine (see *Encyclopedia of Liquid Fuels*, chapter “Methylhydrazine”).

#### 11.4.2.2 Gelled Hydrazine/Metal Hydride Fuels

Adding aluminum hydride to hydrazine creates a more energetic fuel, which when burned in a rocket chamber with NTO will allow a specific impulse that is 39% greater than that of a hydrazine fuel in which the aluminum hydride is omitted. Major difficulties have been encountered with hydrazine fuels containing aluminum hydride due to the evolution of gas during storage. The evolution of gas is apparently caused by the catalytic decomposition of hydrazine on the surface of the aluminum hydride. To overcome the gas evolution problem, it has been proposed to coat the aluminum hydride with various polymeric coating materials. The gelation of hydrazine containing aluminum hydride has been accomplished using several different commercially available gelling agents. However, most of these gelling agents are not satisfactory because they are easily shear thinned and have a long recovery time. A poly [(alkyl or aryl)-(alkyl or aryl) semicarbazide] copolymer coating on aluminum hydride eliminated the gas evolution problem and at the same time caused gelling of the hydrazine fuel to eliminate the need for additional gelling agents [2602].

#### 11.4.2.3 Gelled Hydrazinium Nitrate/Hydrazine Solutions

Solutions of HN in hydrazine or hydrazine hydrate can be used as energetic monopropellants or liquid explosives. Many gelling agents that work with plain hydrazine will fail to create a gel in hydrazine or hydrazine hydrate in the presence of hydrazinium ions from hydrazinium salts. A solution (slurry) of 60% HN in 40% hydrazine hydrate was gelled with 0.8% partially hydrolyzed polyacrylamide, 1.2% guar gum, and 1.8% sodium carboxymethyl cellulose [2603].

### 11.5 Hydrazine Fuel Mixtures as Energy Carriers

Hydrazine hydrate and hydrazine mixtures have been tested as fuels in air/hydrazine fuel cells and in internal combustion engines intended for automotive propulsion.

A ternary fuel consisting of 64% hydrazine, 10% ammonia, and 26% water was tested in a stationary internal combustion engine and proposed as an environmentally friendly (no CO<sub>2</sub> emissions) alternative to gasoline [2604].

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# Ionic Liquids

## Ionic Liquids

Ionic liquids have gained importance as potential rocket propellants only during the past twenty years. This is a relatively recent development and ionic liquids are still being actively investigated while this book goes to print.

### 1 Definition of Ionic Liquids

The definition of ionic liquids (ILs) remains somewhat controversial; the scientific community tends to agree that salts that melt below 373 K (100 °C) are considered “ionic liquids.” This is an arbitrary limit and not scientifically founded. A narrower definition is “room-temperature ionic liquids” (RTILs) for those which remain in the liquid state at or below 298 K (25 °C). In order to achieve low melting points, ILs make use of bulky, asymmetric, poorly packing ions to lower their lattice energy. Favorite choices are quaternary ammonium and *N*-heteroaromatic cations. The *N*-heteroaromatic ions have been found to be very energetic when combined with appropriate counter ions. This arises from the numerous energetic N–N and C–N bonds and ring strains which lead to high enthalpies of formation. This property makes them suitable rocket propellants.

A commonly used acronym and abbreviation used for the term **Ionic Liquid** is **IL**. We have opted to use it in this chapter, and **ILs** in the case of the plural, as a means of saving space. Another acronym found in the literature is **RTIL** for **Room Temperature Ionic Liquid**. For use as rocket propellants, we are looking for **Energetic Ionic Liquids**, often abbreviated as **EILs**. In the literature, the term “**IL**” may include inorganic, low-melting salts such as hydroxylammonium nitrate (**HAN**).

One subset of ILs is the family of protic ILs (**pILs**), which are formed via proton transfer from a Brønsted acid to a Brønsted base [1]. As a result, **pILs** possess a proton-donor and a proton-acceptor site, which can build up a hydrogen bond (H-bond) network. However, depending on the compounds present and their **pKs**, the proton transfer may be less than complete, and, as a result, a mixture of two neutral liquids may be encountered. Doubly ionic H-bonds occur when an H-bond forms between a cation and anion, and these are a key feature of ILs [2]. H-bonds depress the melting point and alter the viscosity of imidazolium-based ILs, one of the main groups of ILs.

## 1.1 Introduction

This chapter deals only with organic ILs, and only with their preparation, and physical, thermal-stability, and safety properties. Applications of ILs as monopropellants will be discussed in *Encyclopedia of Monopropellants*. Applications of ILs as fuels in combination with hypergolic oxidizers will be discussed in *Encyclopedia of Hypergolic Bipropellant Combinations*. It is also possible that several ILs that should be listed here have already been described in *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic and Heterocycloaliphatic Amines.” Some of these compounds are referenced repeatedly in this book because they have several applications.

Of all the chapters in this book, this IL chapter was the most difficult one to compile and to bring it up-to-date. This is because the technology is still actively under development and in flux. This chapter is an attempt to collect relevant literature, but it may not be complete. It is hoped that by the time a chapter on ILs as hypergolic fuels is added to a future set *Encyclopedia of Hypergolic Bipropellants* in several years from now, the surge of publications will have settled down and the real potential of these new fuels will become apparent.

The interest in ILs and their applications has led to the development of an extensive and diverse range of organic salts that can support low-melting-point IL phases (with examples ranging from simple mononuclear to complex anions) and the exploration of materials and applications utilizing the novel characteristics of these IL phases, including rocket propellants, explosives, heat-transfer fluids, lubricants, photovoltaics, and battery, capacitor, and fuel-cell electrolytes. In trying to organize the large amount of information that has become available on energetic ILs (EILs) during the past decades, several sorting criteria can be used for the following sections. One way of separating and sorting the information would be according to the intended application: as a rocket propellant, as a fuel for rocket bipropellant combinations, as a monopropellant, or as an explosive. Another way would be according to the number of atoms in the heterocyclic ring that forms the cation of the IL (most have five atoms), and then again by the number of heteroatoms (mostly nitrogen with 1–4 atoms) in the ring. Most of them have three nitrogens in a 5-membered ring placing them in the chapter on imidazole.

ILs consist of cations and anions. Typically, we sort ionic compounds by the cation first and the anion last. The difficulty in writing this chapter of the book is that most publications on ILs deal with more than one compound at the same time, requiring multiple entries in several subsections or they are dealing with the chemical compounds out of sequence from the general sorting scheme. Another way of subdividing the chapters would be to characterize the materials according to their physical, chemical, and safety properties, or by experimental and theoretical methods.

In any case, the literature cited in this book appears in chronological order, with the oldest references first and the most recent ones at the end of each chapter. This section contains mostly general information on ILs that applies to more than

one compound. Publications dealing with synthesis, properties, and applications of a specific IL, most of them heterocyclic compounds, have been moved to the sections in this book where the parent compounds (e.g. imidazole and 5-aminotetrazole) are discussed in systematic order.

In order to develop IL-based energetic materials, one typically looks for nitrogen-rich cations (imidazoles, triazoles, tetrazoles, hydrazine derivatives, and quaternary ammonium salts) in combination with oxygen-rich anions (nitrates, dinitramides, and perchlorates). One also has the option of souping up the performance by changing a traditional IL cation, like an imidazolium anion, into a nitroimidazolium anion by adding nitro groups to the ring structure. Depending on the energy content and the speed of energy release, such materials can behave either as high explosives or as energy-rich fuels. For instance, borohydride anion-based ILs have been proposed as hypergolic fuels for bipropellant combinations. Low vapor pressure and enhanced thermal stability are expected to yield low impact sensitivity of IL-based high-energy materials. Such materials should also retain their performance effectiveness after long-term storage, thus making them suitable for usage with weapons requiring long-term storability.

An advantage of ILs over the propellants they are intended to replace is their low vapor pressure, which makes them safer to handle and has earned them the designation of “green” (i.e. environmentally friendly) propellants. Many ILs solidify (i.e. they transition to a solid-glass state) at temperatures below the freezing point of the hydrazine(s) fuel or hydrazine monopropellant they are intended to replace, reducing the electric power requirements for propellant tanks and line heaters in satellites in cold regions of outer space. A disadvantage of ILs is their higher viscosity than conventional fuels, resulting in poor atomization when sprayed into a combustion chamber or an electrospray colloid thruster, and requiring higher feed pressures to overcome the fluid resistance in the feed system and injectors. The viscosity of a fluid arises from the internal friction of the fluid by mutual attraction of oppositely charged ions, and it manifests itself externally as the resistance of the fluid to flow. IL viscosities at room temperature range from a low of around 10 cPs to values in excess of 500 cPs. IL monopropellants (discussed in more detail in *Encyclopedia of Monopropellants*) have a higher density than hydrazine and a higher volume-specific impulse, which is a desirable property. However, up to now, there are no known catalysts that can spontaneously initiate the decomposition of IL monopropellants at room temperature. The less toxic monopropellants based on ammonium dinitramide (ADN) or HAN, which have now advanced to the status of orbital flight demonstrations, all require external electric power to pre-heat the catalyst and have long pre-heat response times.

Physical properties needed for the evaluation of ILs as rocket propellants are the freezing point (glass-transition point and melting point) and enthalpy of formation. Density is good to have if one wants to compare propellant combinations on the basis of volume-specific impulses. But densities of ILs based on organic heterocyclic amines are all very similar and would be easy to extrapolate. There is a lack of published en-

thalpies of formation for ILs and additional work is required to allow calculation of the specific impulse ( $I_{sp}$ ) for many of the compounds proposed as rocket propellants.

Many ILs are derived from heterocyclic amines, which is one reason why additional information on specific ILs can be found in *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic and Heterocycloaliphatic Amines.” Besides being evaluated as rocket propellants, general interest in ILs as green solvents has increased in recent decades, primarily aiming at replacements for conventional media (solvents and absorbents) in chemical processes. ILs are an exciting class of compounds with unique properties that make them attractive for many other industrial applications, in addition to their proposed use as rocket propellants and explosives. Among their valuable features, an immeasurably low vapor pressure and a liquid state at or near ambient room temperature conditions are of interest to the rocket propellant chemist and safety evaluator. More than half of the literature cited in this chapter does not directly relate to rocket propulsion, but it provides the background information needed to develop more EILs.

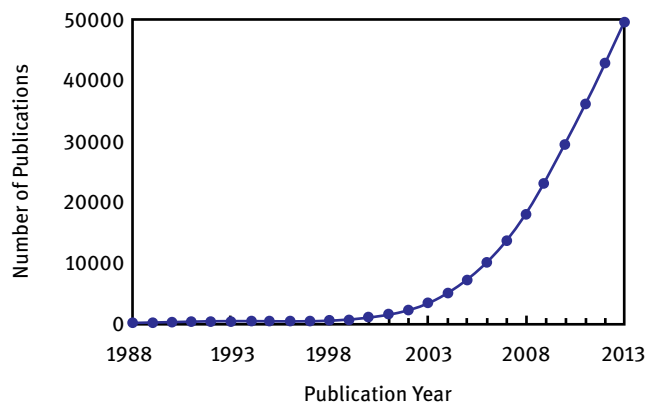
Organic preparative chemists usually put their pride into preparing organic compounds that crystallize nicely and have sharp melting points; the melting point is often used as a criterion for purity. Quite often, the chemist gets frustrated by a compound that does not want to crystallize at room temperature. While this is usually considered a nuisance, now, all of a sudden, the unwillingness of an organic compound to crystallize becomes a desirable virtue if the compound remains a liquid at room temperature and can be used as an IL rocket propellant. Many of the ILs tend to supercool easily, forming glasses at very low temperatures rather than exhibiting sharp crystallization or melting transitions.

Initially, much of the focus in EIL research was on heterocyclic cations, in combination with oxygenated anions like nitrate and perchlorate which frequently have stability and safety problems. Later efforts expanded to other anions that made the liquids suitable as fuels instead of monopropellants or explosives. Other ILs with anions like tetrafluoroborate, hexafluorophosphate, and trifluoromethanesulfonate are of no use as rocket propellants but may serve as intermediates in the synthesis of more EILs.

## 1.2 Summary Information on ILs

For the researcher who intends to examine ILs as a group, the following literature sources may be useful. Some of this literature does not deal specifically with rocket propellants but is more of common interest, including many non-rocket applications of ILs.

The number of publications on ILs has increased exponentially during recent years (Figure 1) [3, 4]. As of August 2013, a search on SciFinder using the key words “ionic liquids” generated a list of 49426 publications. As of February 2021, this number had increased to 118709. Only few of these dealt with rocket propellants or explosives,



**Figure 1:** Total number of publications on ILs. (Reprinted from [3], with permission of ©2014 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

so we selected a few and referenced them here. Most of the literature references on ILs evaluated as rocket propellants in this book are less than ten years old.

In addition to publications in periodicals and presentations at conferences, there are now several books devoted to ILs which are a good starting point for studies on these types of non-volatile rocket propellants. A book that provides many fundamentals about ILs, including history and pioneers was published in 2002 [5]. It lists many applications of ILs, but nothing about their use as rocket propellants. Surprisingly, the entire 3.6-MB book was once available to download for free on the Internet, but this is now a dead link [6].

A chapter in a book on applications of ILs in science and technology [7] gives a very useful overview of ILs for space propulsion applications [8]. It is available for downloading as an open-source document. It contains sections dealing with the use of ILs as monopropellants (HAN- and ADN-based), hypergolic bipropellants, and working fluids in electrospray thrusters.

An excellent summary on ILs for propellant and explosive applications is now available in [9]. This publication with its 158 references is a good starting point for the type of chemistry discussed in this chapter. Chapter 6 “Room temperature ionic liquids” [10] in a book on ILs [11] contains 464 references.

A summary on properties of mixtures of ILs containing information on 39 types of physicochemical properties for 1388 mixtures, including binary, ternary, quaternary, and other mixtures, is based on data gathered from 800 sources [12]. See also [13–17].

The chapter “Design and synthesis of green hypergolic ionic liquid fuels” in the book *High-Energy-Density Fuels for Advanced Propulsion: Design and Synthesis* is a summary of information on ILs and their hypergolic ignition capabilities [18]. In 1998, publication of a new journal, *Green Chemistry*, started which has since published numerous papers on ILs [19].

The National Institute of Science and Technology (NIST), the former National Bureau of Standards, maintains a database, the *NIST Standard Reference Database 147; NIST Ionic Liquids Database – IL Thermo* [20]. IL Thermo is a Web-based ILs database available for free to the public. It aims to provide users worldwide with up-to-date information on publications of experimental investigation on ILs, including numerical values of chemical and physical properties, measurement methods, sample purity, uncertainty of property values as well as many other significant measurement details. The database can be searched by means of the ions constituting the ILs, the ILs themselves, their properties, and references. The inaugural version of the database included data for more than 200 ions and more than 300 ILs as well as their binary and ternary mixtures. It contains well-organized and archived information on current and historical investigations on ILs, detailed descriptions of key elements in the experimental investigations such as sample purification and measurement methods, and up-to-date information on major publications on ILs. As of December 2013, it contained information on 1059 ILs and 796 pure IL compounds. Searching for “dicyanamide” produced 149 results, searching for “imidazolium” produced 2806 results, searching for a specialized item like “1-butyl-3-methylimidazolium dicyanamide” produced 44 results, but searching for “nitrate” failed. The database can be searched according to several criteria:

- Chemical identifier information on ions
- Chemical identifier information on ILs
- Binary mixture systems containing ILs
- Ternary mixture systems containing ILs
- Thermodynamic properties
- Thermochemical properties
- Transport properties

In several instances, it is possible to mix two solid substances and end up with an IL [21].

## 2 ILs Derived from Amines or Amides as Cations

The majority of ILs are derived from amines as cations. In this group, again subdividing according to the source of the cation, the majority of ILs known are derived from cations of heterocyclic amines. The anions with which the cations are paired can be either inorganic or organic. Anions that bring with them available oxygen would be preferred for ILs intended as monopropellants.

## 2.1 ILs Derived from Aliphatic Amines

The first IL considered as a rocket propellant was ethylammonium nitrate (EAN), which has a low melting (glass-transition) point of  $282\text{ K} = 9^\circ\text{C}$ . The properties of EAN were already described in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines.”

Throughout this chapter on ILs, the literature cited refers to either experimental or theoretical computational work on ILs, and sometimes to both modes of investigation. In this chapter, the different modes of investigation have not been separated, but are assembled in random arrangements next to each other in chronological order. Many publications deal with more than one type of IL, so these papers are cited at more than one location.

Classical molecular-dynamics (MD) computational chemistry simulations have been performed on 30 ILs at 298, 333, and 393 K, including ILs containing quaternary tetra-alkylammonium cations and dicyanamide (DCA), tricyanomethanide (TCM), tetracyanoborate, and nitrate anions [22]. The predicted IL density, heat of vaporization, ion self-diffusion coefficient, conductivity, and viscosity were found to be in good agreement with available experimental data.

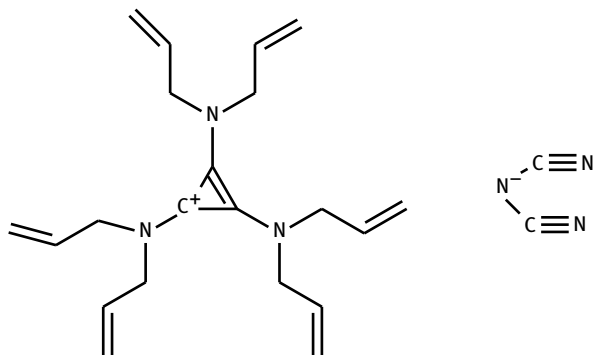
The crystal structure and dimensions of *N,N,N,N*-tetramethylammonium(1+) DCA ionic salt was predicted by MD simulations and was in good agreement with experimental data [23]. Ion-counterion spatial distributions were used to understand the local environment and pairing of both ions in crystalline and liquid phases.

Five pILs with *n*-propylammonium or 3-hydroxypropylammonium as cations, and formate, acetate, or trifluoroacetate as anions, were synthesized and thermophysical properties such as density, viscosity, and velocity of sound were measured at various temperatures ranging from 293 to 343 K at atmospheric pressure [24]. The title of this paper is misleading. It meant to describe hydroxy**alkyl**ammonium ILs and has nothing to do with hydroxylammonium ions. The temperature dependence of experimental density and viscosity were fitted with second-order polynomial and Vogel–Tamman–Fulcher (VFT) equations, respectively. Thermal-decomposition temperature and glass-transition temperature, along with crystallization and melting point, were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The glass-transition temperatures were in the range 249–245 K (–24 to –28 °C).

The IL 2-(dimethylamino)-*N,N,N*-trimethylethanammonium DCA is hypergolic with white-fuming nitric acid (WFNA) and exhibits potential as a green fuel for bipropellants. Four energetic salts (including two ILs) based on 2-(dimethylamino)-*N,N,N*-trimethylethanammonium and *N,N'*-dialkyl-*N,N,N',N'*-tetramethylethane-1,2-diammonium were prepared and characterized by nuclear magnetic resonance ( $^1\text{H}$ - and  $^{13}\text{C}$ -NMR), infrared (IR), and Raman spectroscopy, and elemental analysis [25]. Physicochemical properties such as melting and decomposition temperatures, density, viscosity, enthalpy of formation, detonation performance, and  $I_{\text{sp}}$  were measured or calculated. The salts were stable up to 473 K (200 °C). The resulting ILs had densities from 1.02 to 1.19 g/cm<sup>3</sup> and enthalpies of formation from +85.1 to +154.4 kJ/mol.



Salts of the charge-delocalized cations of the triaminocyclopropenium (tac) family bearing alkyl substituents have been prepared and shown to be air- and water-stable ILs [26]. One example shown in the following structure is tris(dipropenylamino)cyclopropenium dicyanamidate.



The experimental results showed that all of these ILs exhibited the expected hypergolic reactivity with WFNA. Among them, the hypergolic IL based on the cyanoimidazolyl borohydride anion showed excellent properties, including a high onset of decomposition temperature 467 K (194 °C), high density (0.95 g/cm<sup>3</sup>), moderate viscosity (44 MPa · s), a very short ignition delay time (6 ms), and a high  $I_{sp}$  (302 s). This demonstrated its potential use as an environmentally friendly hypergolic fuel.

### 2.1.1 ILs Derived from Methylamine

Methylammonium nitrate melts at 381 K (108 °C) and is widely used as an ingredient in emulsion explosives. Its melting point is just outside the range of what are considered ILs. *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines” contains a complete summary of the properties of methylammonium nitrate.

*Ab initio* molecular-dynamics (AIMD) simulations of the pIL methylammonium nitrate served to explain the effect of hydrogen bonding (H-bonding) on melting points of this relatively simple molecule [27]. It was easier to do these calculations for a simple molecule like methylammonium nitrate than for other ILs. Previous AIMD investigations had focused upon imidazolium-based ILs.

### 2.1.2 ILs Derived from Ethylamine

Ethylammonium nitrate, also known as ethylamine nitrate, EAN, H<sub>3</sub>CCH<sub>2</sub>NH<sub>3</sub>NO<sub>3</sub>, CAS RN [22113-86-6], is the simplest IL and is easy to obtain. The properties of EAN were already described in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines.” Its low melting point has aroused the curiosity of many chemists, but its use as a rocket propellant was not immediately recognized until J. D. Clark in his landmark book, *Ignition!*, commented: “Molten salts are nothing new, but these were the only ones I ever

heard of that were liquid at 25 °C. I've never found a use for the ethylamine compound, but something with such interesting properties ought to be good for something!" [28]. EAN is the first RTIL, with a melting point of 282 K = 9 °C, and it was first reported in 1914 [29].

Surface tensiometry of binary mixtures of EAN, ethanolanmonium nitrate (EtAN), and water revealed a distinctive amphiphilic character for the ethylammonium cation, but not for the ethanolanmonium cation [30]. Results also showed that the surface film incorporates nitrate counter ions, and that electrostatic and H-bonding interactions, rather than alkyl-chain packing, determine the saturated adsorbed film structure and limiting molecule area.

The rheologic properties of five pure pILs, EAN, *n*-propylammonium nitrate (PAN), EtAN, ethylammonium formate (EAF), and dimethylethylammonium formate (DMEAF), were characterized and interpreted by considering the effects of both the H-bond network and the solvo-phobic nanostructure of the liquids [31]. The results demonstrated that these effects are not independent or simply additive. At 293 K (20 °C), EtAN had the highest zero-shear viscosity of 156.1 mPa s, followed by PAN (89.3 mPa s), EAN (35.9 mPa s), EAF (23.1 mPa s), and DMEAF (9.8 mPa s). The primary ammonium ILs behaved as Newtonian fluids at low shear rates, but shear-thinned at high shear rates. The rheology of binary mixtures of these ILs was analyzed and used to demonstrate fundamental differences in the way IL cations and anions interact.

Multiple crystal pathways and crystal polymorphs were observed in pILs, which are liquids at room temperature [32]. The pILs investigated were methylammonium nitrate, dimethylammonium nitrate, EAN, and PAN. Methylammonium nitrate and dimethylammonium nitrate solidified as plastic crystals at room temperature, but EAN and PAN were liquids at room temperature. In spite of its simple molecular structure, complicated phase behaviors such as multiple crystal pathways and crystal polymorphs were observed in liquid EAN at a low temperature. Liquid PAN exhibited low-temperature anomalies similar to those observed with liquid EAN. Rapid proton exchanges, which disturb the crystal nucleation of pILs at room temperature, cause multiple crystal pathways via non-equilibrium states.

Low-melting alkylammonium nitrate ILs are useful as fuels for monopropellants, in combination with ADN or HAN as oxidizers. The melting behavior and thermal-decomposition mechanisms in the condensed phase of ADN/alkylammoniumnitrate mixtures during heating was measured using DSC and TGA-differential thermal analysis (DTA)-mass spectrometry (MS) [33]. Results showed that the melting point of ADN was significantly lowered upon the addition of alkylammonium nitrates with low molecular volumes and low melting points. TGA-DTA-MS results showed that the onset temperature of the thermal decomposition of ADN/alkylammonium nitrate mixtures was similar to that of pure ADN. ADN produced highly acidic products during thermal decomposition in the condensed phase that promoted exothermic reactions, nitration, and nitrosation of amines.

### 2.1.3 ILs Derived from 2-Hydroxyethylamine

One of the first ILs produced was probably 2-hydroxyethylammonium nitrate; also known as aminoethanol nitrate; ethanol, 2-amino-, nitrate (1:1);  $\text{HOCH}_2\text{CH}_2\text{NH}_3\text{NO}_3$ , CAS RN [20748-72-5], melting point (m.p.)  $325\text{--}328\text{ K} = 52\text{--}55\text{ }^\circ\text{C}$ ,  $\rho = 1.390\text{ g/cm}^3$ , in the year 1888 [34]. There are now hundreds of publications on ILs with the 2-hydroxyethylammonium cation, but mostly only with carboxylic acids, with particularly formic acid providing the anion [35, 36]. These ILs may be used as fuels or solvents, but they are not hypergolic. There was only very little work done on 2-hydroxyethylammonium cation paired with oxidizing anions like nitrate, perchlorate, or dinitramide.

The effect of step-by-step replacement of ethyl groups in triethylammonium nitrate by hydroxyethyl groups on properties of the ILs was investigated [37]. There were 32 salts with a melting point below 373 K.

If the remaining two hydrogens on the amino group of 2-hydroxyethylammonium nitrate are also replaced by hydroxyethyl groups, one obtains trihydroxyethylammonium nitrate (TEAN), which has once found extensive use as a fuel in liquid gun propellants (see *Encyclopedia of Monopropellants*).

### 2.1.4 ILs Derived from Other Aliphatic Amines

Three salts based on propan-2-ylidene methanetriamium cations and the DCA anion, *N*-(propan-2-ylidene) methanetriamium DCA, *N,N'*-bi(propan-2-ylidene) methanetriamium DCA, and *N,N',N''*-tri(propan-2-ylidene) methanetriamium DCA, were synthesized and characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, IR, and Raman spectroscopy, elemental analysis, TGA-DTA, and X-ray diffraction (XRD) [38]. Impact sensitivities were  $>40\text{ J}$  by drop hammer tests, which places these salts in the insensitive class. The salts were hypergolic with WFNA.

## 2.2 ILs Derived from O-Alkylhydroxylamines

IL salts derived from *O*-alkylhydroxylamines were already described in *Encyclopedia of Oxidizers*, along with other hydroxylammonium salts. The cations discussed there were derived from *O,O'*-methylenedioxamine,  $\text{H}_2\text{N}-\text{OCH}_2-\text{O}-\text{NH}_2$ , and *O,O'*-ethylenedi(oxamine),  $\text{H}_2\text{N}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{NH}_2$ , organic bases which can form mono- or diprotonated salts. *O,O'*-ethylenedi(oxamine) bis-dinitramide,  $[\text{H}_3\text{NOCH}_2\text{CH}_2\text{ONH}_3][\text{N}(\text{NO}_2)_2]_2$ , melts below 273 K, qualifying it as a RTIL. Its decomposition temperature is  $T_{\text{dec}} = 388\text{--}393\text{ K} = 115\text{--}120\text{ }^\circ\text{C}$ . *N*-Alkylhydroxylamines form IL salts that were already described in *Encyclopedia of Oxidizers*, chapter "Hydroxylammonium Salts."

## 2.3 ILs Derived from Aliphatic Amides

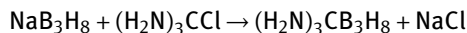
Guanidinium salts like guanidinium nitrate are well crystallized with high melting points. It requires organic substituents on the amido groups and different anions to obtain guanidinium ILs. Functionalized guanidinium ILs containing alkenyl functionalities have been developed as a new class of versatile organic materials, and characterized by measuring melting points, glass-transition temperatures, miscibility, densities, and surface tensions [39]. The physical properties of guanidinium dicyanoamidate ILs are summarized in Table 1

**Table 1:** Physical properties of guanidinium dicyanoamidate compounds.

| Cation              | Melting point |     | Decomposition onset |     | Density           | References |
|---------------------|---------------|-----|---------------------|-----|-------------------|------------|
|                     | K             | °C  | K                   | °C  | g/cm <sup>3</sup> |            |
| Guanidinium         | 330           | 57  | 418                 | 145 | 1.38              | [40]       |
| Aminoguanidinium    | 228           | 55  | 393                 | 120 | 1.41              | [41]       |
| Diaminoguanidinium  | 334           | 61  | 385                 | 112 | 1.36              | [41]       |
| Triaminoguanidinium | 397           | 124 | 423                 | 150 | 1.42              | [42]       |

The triaminoguanidinium dicyanamidate (dicyanamide, DCA) is not an IL but a solid which melts at 397 K (124 °C) and its enthalpy of formation is  $+400 \pm 7$  kJ/mol ( $+95.5 \pm 1.8$  kcal/mol). Since three of the four salts listed in Table 1 had melting points considerably below 373 K (100 °C), hypergolic ignition of the liquids was tested in simple drop tests with WFNA or nitrogen tetroxide (NTO). Details about these tests will be discussed in a future *Encyclopedia of Hypergolic Bipropellant Combinations*. At low temperatures, guanidinium dicyanoamidate exists in two different polymorphic phases with orthorhombic or monoclinic structures. Due to the chemical composition of guanidinium DCA,  $C_3N_6H_6$ , which is formally identical with that of melamine  $C_3N_3(NH_2)_3$ , and its facile conversion into melamine at around 400 K, guanidinium DCA may be suited as a molecular precursor for synthesis of graphitic carbon nitride materials.

Guanidinium octahydrotriborate, containing 13.8 mass-% hydrogen, has been prepared by a simple metathetic reaction



and has been evaluated as a hydrogen storage fluid [43]. Guanidinium octahydrotriborate is an IL with a melting point below 263 K (−10 °C). It decomposes selectively, starting at 343 K (70 °C) and maxing at 383 K (110 °C) to dihydrogen, and would most likely be hypergolic with WFNA or high-test peroxide (HTP).

Four types of guanidinium DCA-based energetic salts were prepared and investigated as energetic additives to the hypergolic IL fuel 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA]) [44]. Their densities, viscosities, heats of formation,  $I_{sp}$ , ignition delay times, melting points, charge distributions, and decomposition temperatures were measured and calculated. The results showed that these salts possessed a high nitrogen content (>66 mass-%N), high density, and high  $I_{sp}$ . Their addition can bring significant improvement to the density and  $I_{sp}$  of [Emim][DCA] and would hardly affect its ignition delay time.

## 2.4 ILs Derived from Heterocyclic Amines

The current section deals only with ILs that have a heterocyclic cation and/or anion. There is some overlap between chapters on ILs, i.e. in *Encyclopedia of Liquid Fuels* in the chapter “Heterocyclic Amines,” here in the chapter “Ionic Liquids,” and in a later set on hypergolic combinations using ILs as fuels. It is common practice to abbreviate the names of heterocyclic ions in ILs by four-letter acronyms. Table 2 is a summary of commonly used acronyms.

**Table 2:** Acronyms used for heterocyclic cations in ILs.

| Acronym         | Complete name                          |
|-----------------|----------------------------------------|
| [Bmim], [C4mim] | 1-butyl-3-methylimidazolium            |
| [Dmim]          | 1- <i>n</i> -decyl-3-methylimidazolium |
| [Emim], [C2mim] | 1-ethyl-3-methylimidazolium            |
| [Hmim]          | 1-methyl-imidazolium nitrate           |
| [Hmim], [C6mim] | 1- <i>n</i> -hexyl-3-methylimidazolium |
| [Mmim]          | 1,3-dimethylimidazolium                |

This first series of sections on ILs deals with preparation and properties of ILs not especially intended as hypergolic fuels or explosives. Later on in this chapter is a series of sections in a very similar sequence, concentrating on ILs intended as hypergolic fuels in bipropellant combinations. There may be some overlap between these two components of this chapter. Separating the ILs intended as hypergolic fuels into a subsection made the large amount of information more manageable.

### 2.4.1 Preparation of ILs Derived from Heterocyclic Amines

The preparation of ILs from the parent heterocyclic amines is usually pretty straightforward: an acid–base reaction of stoichiometric amounts of base and acid, conducted in a solvent as a diluent with adequate cooling to conduct away the heat of neutralization. After removal of the solvent, the salts may or (most often) may not

crystallize. They have a tendency to supercool and may require seed crystals to obtain a solid phase for XRD structure determination at low temperatures. Some do not have a freezing point but only a glass-transition point at low temperatures. In most cases, for rocket applications, the heterocyclic amine forms the cation and it is paired with the anion of a strongly oxidizing inorganic acid, such as nitrate, perchlorate, or dinitramide. Salts that are formed with hexafluorophosphate or tetrafluoroborate anions are of less interest to rocket propulsion. They might be used as intermediates in the synthesis of more energetic compounds or as electrolytes in batteries or capacitors. Other ILs exist where both the cation and the anion are heterocycles.

While first-generation ILs often had at least one inorganic ion, other ILs have now been synthesized that contain azonium cations and azolate anions [45]. Triazole and tetrazole were coupled with 1-ethyl-3-methylimidazolium hydroxide, and the obtained tetrazolium salt was a liquid at room temperature showing a glass-transition temperature at 184 K (−89 °C.)

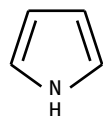
#### 2.4.2 ILs Derived from Azetidine

The parent molecule of azetidinium-derived ILs is azacyclobutane, also known as azetidine, azetane, CAS RN [503-29-7], which was already described in *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic Amines.”

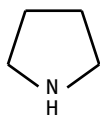
A group of azetidinium-based hypergolic ILs was synthesized and characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and IR spectroscopy, and electrospray ionization mass spectrometry (EIMS) [46]. The ILs were made by quaternizing 1-*n*-butylazetidine with methyl, ethyl, propyl, allyl, propynyl, or butyl iodide or bromide, and replacing the halogenide anion by a reaction with silver DCA. The properties of six synthesized ILs were characterized with respect to liquid range, density, viscosity, enthalpy of formation, and ignition delay time with WFNA. In order to better understand the relation between ring strains and the energy of obtained compounds, the isomers of 1-*n*-butyl-1-propyl-azetidinium dicyanamidate (BPAD) were also synthesized for comparison. It was found that compared with the isomers, BPAD exhibited a much higher enthalpy of formation (difference of +0.78 kJ/g), which indicated that ring strains play an important role in the performance of these energetic compounds. BPAD had the highest enthalpy of formation, +2.17 kJ/g.

#### 2.4.3 ILs Derived from Pyrrolidine

Pyrrolidine is the fully hydrogenated pyrrole.



Pyrrole



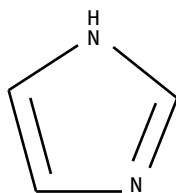
Pyrrolidine

Pyrrolidinium nitrate,  $C_4H_{10}N_2O_3$ , CAS RN [129228-91-7],  $M = 134.13$  is a low-melting IL. Property data for this well-characterized salt have already been summarized in *Encyclopedia of Liquid Fuels*, chapter “Aliphatic Amines.” A batch of pyrrolidinium nitrate exploded while drying it under reduced pressure at 383 K (110 °C), using a rotary evaporator with a silicone oil bath [47]. Therefore, precautions are necessary when working with any amine nitrate or perchlorate.

A family of low-cost and easily prepared azide-functionalized cation-based ILs, including fuel-rich anions, such as nitrate, DCA, and nitrocyanamide anions, were synthesized and characterized [48]. All the DCA- and nitrocyanamide-based ILs exhibited spontaneous combustion upon contact with 100%  $HNO_3$ . The densities of these hypergolic ILs varied within the range 1.11–1.29 g/cm<sup>3</sup>, and the density-specific impulse, predicted based on Gaussian 09 calculations, was between 289.9 and 344.9 s g cm<sup>-3</sup>. The values of these two key physical properties were much higher than those of unsymmetrical dimethylhydrazine (UDMH). 1-(2-Azidoethyl)-1-methylpyrrolidin-1-ium DCA showed excellent properties including the lowest viscosity (30.9 MPa s), a wide liquid operating range (203–478 K = –70 to 205 °C), the shortest ignition delay time (7 ms) with 100%  $HNO_3$ , and a superior density-specific impulse (302.5 s g cm<sup>-3</sup>).

#### 2.4.4 ILs Derived from Imidazole

Imidazole itself is not useful as a rocket propellant. The interest in imidazole(s) as a rocket propellant ingredient stems mostly from the low melting point of the imidazolium salts, which puts them into the category of “ionic liquids.” The most commonly shown structural formula is 1*H*-1,3-imidazole



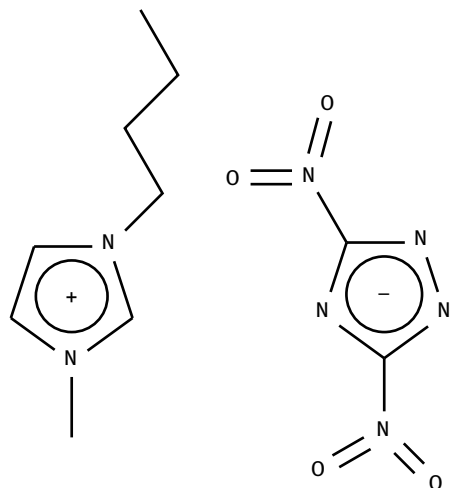
Imidazole

although compounds derived from other imidazoles (2*H*-imidazole and 4*H*-imidazole) are known.

In searching for the ideal IL, the effect of substitution on the heterocyclic ring on physical properties of the resulting salts has been thoroughly investigated. Imidazole-based ILs are of particular interest because they can serve as monopropellants and as working fluids in electrospray colloid thrusters. The IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emim][Im]) has already been used in colloid, or electrospray, thruster applications. Due to their favorable electrochemical properties, several other imidazole-based ILs are under consideration for electrospray propulsion.

#### 2.4.4.1 Preparation of ILs Derived from Imidazole

1-Butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate [Bmim], [C4mim], exhibited an unexpectedly low melting point ( $308\text{ K} = 35^\circ\text{C}$ ) [49, 50]. ILs (defined as having a  $\text{m.p.} < 373\text{ K} = < 100^\circ\text{C}$ ) were obtained with all combinations of the Bmim cation and the heterocyclic azolate anions studied, and with several combinations of tetraethyl or tetrabutylammonium cations and the azolate anions. The  $[\text{C4mim}]^+$  azolates were liquids at room temperature, exhibiting wide liquid ranges and forming glasses upon cooling with glass-transition temperatures in the range of  $220\text{--}191\text{ K}$  ( $-53$  to  $-82^\circ\text{C}$ ).



Analogous tetra-alkylammonium (methyl, ethyl, and *n*-butyl) triazolate salts have also been prepared, but they all melted above  $373\text{ K}$ , and the tetraethylammonium example was characterized by single-crystal XRD.

ILs can be custom-designed to meet certain desired properties by attaching active substituents to an imidazole platform and pairing it with the correct anion [51]. It is not yet possible to accurately predict the thermodynamic properties of ILs just from their chemical structure alone, although attempts in this direction have been made [52].

The molar enthalpy of formation of the IL [Bmim][DCA] was measured by means of combustion calorimetry to be  $+206.2 \pm 2.5\text{ kJ/mol}$  and the molar enthalpy of vaporization was obtained from the temperature dependence of the vapor pressure measured using the transpiration method and found to be  $157.2 \pm 1.1\text{ kJ/mol}$  [53]. The enthalpy of formation of gaseous [Bmim][DCA] is  $+363.4 \pm 2.7\text{ kJ/mol}$ .

Densities and viscosities of 1-butyl-3-methylimidazolium nitrate [Bmim][NO<sub>3</sub>] and its binaries with alcohols (ethanol, 1-propanol, or 1-butanol) were measured at different temperatures [54]. The densities and viscosities of pure ILs were correlated successfully by empirical equations.

Classical MD computational chemistry simulations have been performed on 30 ILs at  $298$ ,  $333$ , and  $393\text{ K}$ , including ILs containing 1-methyl-3-alkylimidazolium,



1-alkyl-2-methyl-3-alkylimidazolium cations with different-length alkyl chains, and DCA, TCM, tetracyanoborate, and nitrate anions [22]. The IL density, heat of vaporization, ion self-diffusion coefficient, conductivity, and viscosity were found to be in good agreement with available experimental data.

Thirty-one salts were synthesized by pairing diverse cations (Bmim, and tetramethyl-, tetraethyl-, and tetrabutylammonium) with azolate anions (5-nitrobenzimidazolate, 5-nitrobenzotriazolate, 3,5-dinitro-1,2,4-triazolate, 2,4-dinitroimidazolate, 4-nitro-1,2,3-triazolate, 4,5-dinitroimidazolate, 4,5-dicyanoimidazolate, 4-nitroimidazolate, and tetrazolate) [55]. These salts were characterized by DSC, TGA, and single-crystal XRD. The azolates in general were surprisingly stable in the systems explored. ILs were obtained with all combinations of the Bmim cation and the heterocyclic azolate anions studied, and with several combinations of tetraethyl- or tetrabutylammonium cations and the azolate anions. Favorable quantitative structure–property relationships (QSPRs) were most often achieved when changing from 4- and 4,5-disubstituted anions to 3,5- and 2,4-disubstituted anions. The most promising anion for use in energetic ILs of those studied here, was 3,5-dinitro-1,2,4-triazolate, based on its contributions to the entire set of desired properties.

1-(2-Hydroxyethyl)-3-methylimidazolium dicyanamidate [C2OHmim][DCA],  $C_8H_{11}ON_5$ , has a density of  $1.12\text{ g/cm}^3$  and a heat capacity of  $1.20\text{ J g}^{-1}\text{ K}^{-1}$ . The standard molar enthalpy of formation of the IL [C2OHmim][DCA] has been determined by means of combustion calorimetry. The heat of combustion of liquid [C2OHmim][DCA] was  $4793.0 \pm 2.1\text{ kJ/mol}$  and the enthalpy of formation was  $+72.9 \pm 2.3\text{ kJ/mol}$  [56]. First-principles calculations of the enthalpy of formation in the gaseous phase have been performed for the ionic species. The combination of combustion calorimetry with the high-level quantum chemical calculations allowed an estimation of the molar enthalpy of vaporization of the IL. The liquid-phase enthalpy of formation of this IL can be estimated by extrapolating from group additivity rules.

Vaporization enthalpies of 1-ethyl-3-methylimidazolium tricyanomethanide [C2mim][C(CN)<sub>3</sub>],  $C_{10}H_{11}N_5$ , CAS RN [666823-18-3], and 1-butyl-3-methylimidazolium tricyanomethanide [C4mim][C(CN)<sub>3</sub>],  $C_{12}H_{15}N_5$ , CAS RN [878027-73-7] were measured in the range 400–453 K by a quartz microbalance method [57]. The enthalpies of formation of the two liquid ILs derived from the heat of combustion in a calorimeter were  $+342.2 \pm 2.5$  and  $+279.2 \pm 2.6\text{ kJ/mol}$ , respectively.

For comparison, the enthalpies of formation of the corresponding DCA salts in the liquid state are [C2mim][N(CN)<sub>2</sub>]  $+235.3 \pm 3.1\text{ kJ/mol}$  and [C4mim][N(CN)<sub>2</sub>]  $+195.0 \pm 2.7\text{ kJ/mol}$  [53, 58]. For comparison, the enthalpies of formation of the corresponding nitrate salts in the liquid state are [C2mim][NO<sub>3</sub>]  $-216.9 \pm 2.0\text{ kJ/mol}$  and [C4mim][NO<sub>3</sub>]  $-261.4 \pm 2.9\text{ kJ/mol}$  [59].

Commercially available 1-butyl-3-methylimidazolium nitrate and 1-ethyl-3-methylimidazolium sulfate were used as fuels for monopropellant blends with HAN as the oxidizer [60–63]. Such mixtures can potentially also be used in electrospay thrusters in dual-mode satellite propulsion systems.

The possibility of forming simple EILs via the straightforward protonation of heterocyclic amines with nitric or picric acid was explored with 1-alkylimidazoles, 1-alkyl-2-methylimidazoles, and nitro-, dinitro-, and dicyano-substituted derivatives of imidazole [64]. The melting points of most of the prepared salts were lower than expected, and of the 30 compounds prepared, more than half were found to melt below 373 K (100 °C). For example, 1-methyl-3*H*-imidazolium nitrate melted at 333 K (60 °C) and its decomposition started at 410 K (137 °C). It was found that energetic electron-withdrawing substituents, such as nitro or cyano, will result in a reduction in nucleophilicity of the heterocycle and an inability to form salts with the acids studied. Unusual thermal behavior was observed with several of the new salts including supercooling and crystallization on heating. Comparison of the singly protonated imidazolium nitrate and picrate salts with their methylated analogs indicated that the protonated ILs did not differ substantially in their melting points from the methylated analogs. However, the thermal stabilities of protonated imidazolium salts were much lower than their alkylated derivatives. Nitrate salts with alkylated cations tended to be more thermally stable than the corresponding picrate salts; however, with protonated cations, the picrate salts tended to be approximately 70–80 °C more stable than the nitrate salts. Accelerating-rate calorimetry (ARC) revealed that alkylated salts decomposed much less exothermically (in some cases endothermically) than the protonated analogs. Among all the analyzed salts, the most energetic materials were 1-methylimidazolium nitrate and 1,2-dimethylimidazolium picrate.

*N,N*-Bis(1*H*-tetrazol-5-yl)amine anions (HBTA<sup>−</sup> and BTA<sup>2−</sup>) were used as nitrogen-rich components for the construction of EILs. Seven ILs, namely, **(1)** 1,3-dimethylimidazolium [C1mim]HBTA, 1-ethyl-3-methylimidazolium **(2)** [C2mim]HBTA, 1-butyl-3-methylimidazolium **(3)** [C4mim]HBTA, 1-hexyl-3-methylimidazolium **(4)** [C6mim]HBTA, 1-methyl-3-octylimidazolium **(5)** [C8mim]HBTA, and 1,2,3-trimethylimidazolium **(6)** [C1Mmim]HBTA cations with the HBTA<sup>−</sup> anion and di-1,2,3-trimethylimidazolium *N,N*-bis(1*H*-tetrazol-5-yl)amine and **(7)** [C1Mmim]<sub>2</sub>BTA were synthesized and characterized by IR and NMR spectroscopy, elemental analysis, and high-resolution MS (HR-MS) [65]. The crystal structures of **(1)** and **(7)** were determined by single-crystal XRD **(1)**: monoclinic, space group *P*2<sub>1</sub>/*n*,  $\rho = 1.511 \text{ g/cm}^3$ ; **(7)** monoclinic, space group *P*2<sub>1</sub>/*c*,  $\rho = 1.221 \text{ g/cm}^3$ . The ILs **1–7** were thermally stable to 493 K (220 °C), and **2–5** were RTILs. The heats of formation of **1–7** obtained by both experimental and theoretical methods were all positive. The ILs **1–7** were insensitive to impact (>40 J) and friction (>360 N). They could be ignited in air. These new EILs contain only C, H, and N, and are of interest as potential propellants with high energy, high thermal stability, low sensitivity to impact and friction, and environmentally friendly decomposition products.

The energy contents of [Emim]<sup>+</sup>-based EILs have been studied via the formation of their ion pair [Emim]<sup>+</sup>[X]<sup>−</sup>, using G3MP2 and density functional theory (DFT) methods [66, 67]. The selected anions included nitrogen-rich derivatives of tetrazolate and triazolate, dinitramidate, and dicyanamidate as well as the conventional anions BF<sub>4</sub><sup>−</sup> and PF<sub>6</sub><sup>−</sup>. The nitrogen enrichment in the system produces EILs which showed compa-

rable and, in some cases, superior thermochemical, fluid, and  $I_{sp}$  properties to conventional ILs. The binding energy values for  $[\text{Emim}]^+[\text{X}]^-$  were in the range of 336–400 kJ/mol at DFT levels, while the atomization procedure used to compute their enthalpy of formation ( $\Delta H_f$ ) at the G3MP2 level produced results in very close agreement with available experimental data (maximum deviation <5%). The  $\Delta H_f$  of conventional ILs is negative whereas that of EILs (167–559 kJ/mol) confirmed their high-energy state. The predicted  $I_{sp}$  of all EILs was slightly lower than hydrazine in monopropellant systems, but a significant increase in  $I_{sp}$  was observed with the addition of HAN. A linear correlation between  $I_{sp}$  and the sum of nitrogen and oxygen mass-% of the EILs was observed. Measured enthalpies of formation for  $[\text{Emim}][\text{DCA}]$  and  $[\text{Bmim}][\text{DCA}]$  are +391.7 and +363.4 kJ/mol, respectively.

The combustion of 1-ethyl-3-methyl imidazolium cyanoborohydride ( $[\text{Emim}][\text{BH}_3\text{CN}]$ ) and 1-allyl-3-ethyl imidazolium cyanoborohydride ( $[\text{AEIM}][\text{BH}_3\text{CN}]$ ), and catalyzed additive mixtures with 95%  $\text{H}_2\text{O}_2$  has been investigated [68]. 1,3-Dimethylimidazolium iodocuprate ( $[\text{dimim}]_n[\text{Cu}_2\text{I}_3]_n$ ) was synthesized and dissolved in ILs. A 2–15 mass-% of  $[\text{dimim}]_n[\text{Cu}_2\text{I}_3]_n$  in  $[\text{Emim}][\text{BH}_3\text{CN}]$  and 15 mass-% of  $[\text{dimim}]_n[\text{Cu}_2\text{I}_3]_n$  exhibited ignition delay time values of 13 and 29 ms under fuel-rich and oxidizer-rich conditions, respectively. These ignition delay time values were 100 times lower than those for the  $[\text{Emim}][\text{BH}_3\text{CN}]$  solvent by itself.  $[\text{dimim}]_n[\text{Cu}_2\text{I}_3]_n$ - $[\text{Emim}][\text{BH}_3\text{CN}]$  solutions have high density ( $>0.98 \text{ g/cm}^3$ ), good thermal stability ( $T_{\text{dec}} > 473 \text{ K} = > 200^\circ\text{C}$ ), and a density-specific impulse 5.6–6.0% higher than that of UDMH.

Two ILs,  $[\text{Emim}][\text{BH}_3\text{CN}]$  and its zwitterion 1-methyl imidazolium borane ( $\text{mimBH}_3$ ), were evaluated as bipropellants with 95%  $\text{H}_2\text{O}_2$  as the oxidizer [69]. A 9 mass-% solution of sodium iodide in  $[\text{Emim}][\text{BH}_3\text{CN}]$  and in a blend of  $[\text{Emim}][\text{BH}_3\text{CN}]$ :furfuryl alcohol (1:1 by mass) had an ignition delay time of ~75 and 56 ms, respectively. These ignition delay times were a hundred times lower than those of the neat fuel  $[\text{Emim}][\text{BH}_3\text{CN}]$ .

It is generally assumed that there is a relationship between the ignition delay time and the viscosity of hypergolic energetic ILs. With this presumption, an investigation was made to obtain the best logical relationships between the ignition delay time, viscosity, and molecular structure of hypergolic imidazolium ILs [70]. The 3D chemical structures of a collected database of 50 imidazolium ILs were encoded into a total number of 3250 diverse types of molecular descriptors, which are representatives of various physicochemical properties of these ILs. A multiple linear regression/artificial neural network (MLR-ANN) statistical approach was applied to obtain the most important molecular descriptors on these relationships. The obtained results for the proposed 3D QSPR models were applied as a criterion for designing new hypergolic imidazolium ILs with the desired short ignition delay time and low viscosity. The predictive ability of the final models derived was evaluated by both internal and external validation methods. This computational method can enable computer-aided molecular design researchers to identify or design new high-energy ILs with optimum physicochemical properties.

#### 2.4.4.2 Thermal Stability of ILs Derived from Imidazole

The thermal stability of ILs is usually determined with the DTA, TGA, DSC, or ARC methods, or by gas evolution volumetric measurements. Because of the unusually high heats of vaporization of RTILs, volatilization of RTILs through thermal decomposition and vaporization of the decomposition products can be significant. Heats of vaporization were determined by a similar method. Upon further heating of cyano-functionalized anionic RTILs in vacuum, their gaseous products were detected experimentally via tunable vacuum ultraviolet (VUV) photonionization (PI) MS [71–73]. Experimental evidence for di- and trialkylimidazolium cations and cyano-functionalized anionic RTILs confirmed that the thermal decomposition occurred primarily via two pathways: deprotonation of the cation by the anion and dealkylation of the imidazolium cation by the anion. Secondary reactions included possible cyclization of the cation and C2 substitution on the imidazolium. Additional evidence supporting these mechanisms was obtained using TGA-MS, gas chromatography MS (GC-MS), and temperature-jump IR spectroscopy. The ability to predict the overall thermal stability in these ILs depends on knowledge of both the basicity of the anions and their nucleophilicity. DFT calculations were conducted to model the decomposition mechanisms, and these could provide a method to predict thermal stabilities for ILs in general.

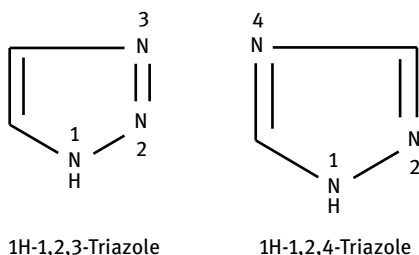
The thermal stability and thermokinetic parameters of 1,3-dimethylimidazolium nitrate, [Mmim]NO<sub>3</sub>, were examined by TGA under non-isothermal conditions in a nitrogen atmosphere [74]. The results showed that [Mmim]NO<sub>3</sub> exhibited three decomposition stages from 366 to 623 K (93.3–350 °C), and the onset temperature of [Mmim]NO<sub>3</sub> was 161–182 °C, depending on the heating rate. The apparent activation energy was 119.0–124.0 kJ/mol and the pre-exponential factor was  $3.6 \times 10^{12} \text{ min}^{-1}$ . Vent-sizing package 2 was employed to acquire the maximum self-heating rate (39828 °C/min) and pressure rise rate (73331 psi/min) for simulating cooling system failure in a closed-vessel practical process. The findings indicated that [Mmim]NO<sub>3</sub> has the possible hazard of a runaway reaction.

In an investigation of the short- and long-term stability of several 1-alkyl-3-methylimidazolium halides, determination of the degradation products, and the elucidation of their decomposition patterns and structure–stability relations, the short-term stability and mechanism of thermal degradation were investigated with a thermal-analysis, single-photon ionization time-of-flight (TOF) MS device [75]. This instrument allowed real-time monitoring of the forming species and allowed tracing of their change during the course of the decomposition. The almost fragment-free soft ionization with VUV photons plays a crucial role. Unfragmented molecules were detected whose formation was only assumed by electron ionization. The main decomposition products of the selected ILs were alkyl imidazoles, alkenes, alkyl halides, and hydrogen halides. Long-term thermal stability was determined based on TGA evaluated with a kinetic model. The time-dependent maximum operation temperatures for these ILs have been calculated.

The thermal stability of [Mmim]NO<sub>3</sub> was investigated by simultaneous TGA and high-pressure DSC [76]. Isothermal experiments indicated that [Mmim]NO<sub>3</sub> might already decompose at a temperature substantially lower than the DSC onset temperature. A pseudo-zero-order-rate expression was applied to characterize the thermal decomposition kinetics of [Mmim]NO<sub>3</sub>. The temperature at which the thermal decomposition of ILs reached 10.0% for a given time of 10 h (T 0.1/10 h) was defined to assess the long-term thermal stability, which should be used as the maximum safe operating temperature of [Mmim]NO<sub>3</sub>.

## 2.5 ILs Derived from Triazole

As already described in detail in *Encyclopedia of Liquid Fuels*, chapter “Heterocyclic Amines,” there are two triazole isomers, 1,2,3-triazole and 1,2,4-triazole.



Both serve as the parent molecule for a multitude of ILs, modified by substituting one, two, or three hydrogens on the ring with melting point-lowering and energy-increasing groups. Most of these are used in the form of triazolium cations.

Drake and co-workers [77, 78] prepared EILs by combining cations containing energetic functionality with relatively small inorganic energetic anions ([NO<sub>3</sub>]<sup>−</sup>, [ClO<sub>4</sub>]<sup>−</sup>, and [N(NO<sub>2</sub>)<sub>2</sub>]<sup>−</sup>). In this work, and related work by Xue, Shreeve, and coworkers [79, 80], energetic low-melting organic salts contained amine-functionalized triazoles and tetrazoles as cations. It was suggested that the ready formation of ILs with these cations appeared to be due to a similarity of topographical shape and charge distribution with conventional IL systems.

### 2.5.1 Triazolium-Based Energetic Ionic Salts

A comparison of the thermal stability of heterocyclic amines has led to the discovery that the incorporation of amino groups into a heterocyclic triazole ring is one of the simplest routes to enhance thermal stability. The *N*-amino group behaves as an electron-withdrawing group in these high-nitrogen heterocycles that, when paired with nitrate, perchlorate, or dinitramide anions, form energetic salts potentially useful as rocket propellants. 4-Amino-1,2,4-triazolium or 1-amino-1,2,4-triazolium

salts are formed by the reaction of 4-amino-1,2,4-triazole or 1-amino-1,2,4-triazole with  $\text{HNO}_3$ ,  $\text{HClO}_4$ , or  $\text{HN}(\text{NO}_2)_2$ , respectively. In addition to the amino substituent on the triazole ring, substitution of additional ring-bound hydrogens with methyl, trifluoromethyl, alkyl, perfluoroalkyl, azido, or azidoethyl groups leads to a wide variety of EILs. Ionic salts containing longer alkyl and polyfluoroalkyl substituents have lower melting points because of less-efficient packing in the solid.

4-Amino-1,2,4-triazole was the readily available starting material for the synthesis of 1-R-4-amino-1,2,4-triazolium bromide salts, which, by subsequent metathesis with the appropriate silver salts, led to several new nitrate, perchlorate, and nitro-cyanamide ILs [81]. Compounds with alkyl side chains including R = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, methylcyclopropyl, 2-propenyl(allyl), and 2-hydroxyethyl were synthesized via this reaction pathway. These ILs were characterized by vibrational spectroscopy, multi-nuclear NMR, elemental analyses, DSC, and impact and friction sensitivity tests. Most of the salts were liquid at ambient temperatures, with melting points well below room temperature. All materials were stable at room temperature and showed no signs of decomposition even after over one year of storage at ambient temperatures.

1,2,4-Triazolium ILs are a practical alternative to imidazolium ILs [82]. Direct quaternization of 1-methyl-1,2,4-triazole with *n*-alkyl methanesulfonates (alkyl = butyl, octyl, and dodecyl) with subsequent metathesis with lithium bis-(trifluoromethanesulfonyl)amide is a convenient, solvent- and halide-free way to obtain 1,2,4-triazolium methanesulfonate ILs in high purity and yield. DSC confirmed that all investigated compounds qualify as ILs. 1-Methyl-4-*n*-dodecyl-1,2,4-triazolium methanesulfonate showed a rather complex thermal behavior involving formation of mesophases. Polarizing optical microscopy showed oily, streaky textures that are characteristic for smectic liquid crystalline phases. Single-crystal XRD structure analysis confirmed formation of a layered structure. All compounds were photoluminescent. All ILs showed an appreciable liquidus range and thermal (up to 260–350 °C) and electrochemical stability.

The  $\Delta H_f$  of some EILs was predicted from the quantum mechanical energies of molecules using an atomization approach [83]. The enthalpies of formation for substituted gas-phase triazolium cations were calculated by G2 and DFT Becke, 3-parameter, Lee–Yang–Parr (B3LYP) methods. The  $\text{N}_3$  and CN substituents at the 1,2,4-triazolium ring's nitrogen atoms led to the highest values of  $\Delta H_f$ .

Hypergolic fuels based on 1-ethyl-4-methyl-1,2,4-triazolium iodide,  $[\text{EMT}]^+[\text{I}]^-$  were synthesized by nucleophilic substitution and characterized by IR and  $^1\text{H}$ -NMR spectroscopy and GC-MS [84]. The hypergolic chemicals  $[\text{EMT}]^+[\text{X}]^-$  ( $\text{X} = \text{CN}^-$ ,  $\text{N}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$ ,  $\text{AlCl}_4^-$ ) were prepared via ion exchange reactions from  $[\text{EMT}]^+[\text{I}]^-$ . The salts were dissolved in 2-hydroxyethylhydrazine (2-HEH), and the decomposition temperature, density, viscosity, and decomposition energy were evaluated to determine their suitability for use as liquid rocket fuels. The ignition delay time of the mixture of hypergolic chemicals with  $[\text{EMT}]^+[\text{N}_3]^-$ ,  $[\text{EMT}]^+[\text{CN}]^-$ ,

$[\text{EMT}]^+[\text{AlCl}_4]^-$ , and  $[\text{EMT}]^+[\text{I}]^-$  using HTP as an oxidizer was 18, 33, 28, and 8 ms, respectively.

*Encyclopedia of Liquid Fuels*, chapter “Heterocyclic Amines” contains a summary of the predicted enthalpies of formation of triazolium salts. Several of these have very low melting points.

## 2.6 ILs Derived from Tetrazole

The high nitrogen content of tetrazole and its derivatives has led to ongoing investigations into their use as potential energetic materials. Some of these derivatives have low melting or glass-transition points and are classified as ILs.

### 2.6.1 ILs Derived from Mono-Substituted Tetrazole

Eight 5-aminotetrazolate (5-AT) salts based on the 1,2,3-trimethylimidazolium (**1**), 1,3-dimethylimidazolium (**2**), 1-ethyl-3-methylimidazolium (**3**), 1-butyl-3-methylimidazolium (**4**), 1-isobutyl-3-methylimidazolium (**5**), 1-(3'-methylbutyl)-3-methylimidazolium (**6**), 1-hexyl-3-methylimidazolium (**7**), and 1-methyl-3-octylimidazolium (**8**) cations have been synthesized and characterized by IR and NMR spectroscopy and elemental analysis [85]. Based on DSC/TGA, these salts decomposed within the temperature range 296–535 K (230–262 °C). Salts **3–8** were very fluent RTILs, whose glass-transition temperatures were quite low. Their viscosities at 303 K (30 °C) were in the range of 92–208 cPs. The standard enthalpy of formation of salts **1–8** was predicted by theoretical methods. Salt (**2**) with the 1,3-dimethylimidazolium cation had the highest positive enthalpy of formation. These 5-AT salts were insensitive to impact (>40 J) and friction (>360 N). Hypergolic reactions of these 5-AT salts with 100%  $\text{HNO}_3$  were also examined but only a few ignited.

### 2.6.2 ILs Derived from Tri-Substituted Tetrazole

1,5-Diamino-4-methyltetrazolium dinitramide melts at <100 °C, which places it in the category of an EIL. One of the first oxygen-balanced ILs in this category was 1-ethyl-4,5-dimethyltetrazolium tetranitratoaluminate [86, 87]. In this IL molecule, the tetranitratoaluminate anion contains 12 oxygen atoms; of these, 10.5 are available to oxidize a fuel cation. The 1-ethyl-4,5-dimethyltetrazolium cation was chosen because of its positive enthalpy of formation and its ability to form an RTIL with the tetranitratoaluminate anion. The resulting energetic salt is a colorless liquid at room temperature. Its spontaneous ignition temperature was 473 K (200 °C). This is the end of the section on ILs based on 5-membered heterocyclic rings. The following sections will describe ILs based on 6-membered heterocyclic rings.

## 2.7 ILs Derived from Pyridines

Pyridinium salts containing cyanoborohydride or DCA anions are hypergolic with the oxidizer red-fuming nitric acid (RFNA). Imidazolium and triazolium compounds are ten times more expensive than pyridinium salts, so there is an economic incentive to thoroughly evaluate pyridinium ILs as hypergolic fuels. Hypergolic ILs containing  $[\text{BH}_3\text{CN}]^-$  have shorter ignition delays (4 ms) and are less expensive than the  $[\text{BH}_2(\text{CN})_2]^-$  anion and less sensitive to water than those with  $\text{BH}_4^-$  and  $[\text{Al}(\text{BH}_4)_4]^-$ . The pyridinium salts of interest are those derived from 4-aminopyridine and quaternized with butyl and allyl chloride [88]. The chloride ion is then replaced by metathetical reactions with silver and sodium salts of the cyan-containing anions. Ignition delays of these fuels with RFNA will be discussed in a future *Encyclopedia of Hypergolic Bipropellant Combinations*.

*N*-Methylpyridinium salts  $[\text{MPy}]^+[\text{X}]^-$  with  $\text{X} = \text{N}_3^-$ ,  $\text{CN}^-$ ,  $\text{ClO}_4^-$ , or  $\text{NO}_3^-$  were prepared via an ion-exchange reaction from  $[\text{MPy}]^+[\text{I}]^-$  and a counter anion [89]. Mixtures of energetic salts were prepared by dissolving the salts in 2-HEH in order to obtain high exclusion properties. The physical and chemical properties of the energetic salt mixtures such as decomposition temperature, density, viscosity, and decomposition energy were evaluated in order to determine their possible usefulness as liquid rocket fuels. The ignition delay times of the energetic salt mixtures with  $\text{H}_2\text{O}_2$  as an oxidizer were 135–167 ms. The properties of the synthesized energetic salts were predicted by Gaussian 09 computational G2 methods.

## 2.8 ILs Derived from Azepanes

The seven-member alicyclic secondary amine, azepane, has been used as starting material for the synthesis of RTILs. Such transformations of this co-product of diamine production processes, generated in large amounts in the polyamide industry, would mitigate its disposal, which usually involves combustion, and convert it to a useful product. Reaction of azepane with 1-bromoalkanes or 1-bromoalkoxyalkanes produced the corresponding tertiary amines with good selectivity; further quaternization reactions with the appropriate methylating agents yielded quaternary azepanium salts:  $[\text{Rmazp}]\text{X}$  ( $\text{R} = \text{alkyl or alkoxyalkyl}$ ;  $\text{X}^- = \text{I}^-$ ),  $[\text{CF}_3\text{COO}]^-$ , or  $[\text{OTf}]^-$  ( $\text{Tf} = \text{trifluoromethylsulfonyl}$ ) [90]. Analogous  $[\text{NTf}_2]^-$  salts have also been produced by metathetic reactions. Liquid temperature ranges were significantly affected by the nature of the anion and the substituents on the azepanium cation core, e.g.  $[\text{CF}_3\text{COO}]^-$  or  $[\text{OTf}]^-$  salts based on cations with alkyl substitution were solids whereas those with alkoxyalkyl substitution were liquid at ambient temperature. The presence of ether linkages in the cationic side chains caused a marked decrease in viscosities and an increase in conductivities.



## 2.9 ILs Derived from Hydrazines

*N,N*-Dimethylhydrazinium DCA and nitrocyanamide ILs were prepared by quaternization of *N,N*-dimethylhydrazine with alkyl halides followed by metathesis reactions with silver DCA or silver nitrocyanamide [91]. Spot plate tests with WFNA as the oxidizer showed that the 14 new *N,N*-dimethylhydrazinium salts were hypergolic with ignition delay times ranging from 22 to 1642 ms.

Enthalpies of formation ( $\Delta H_f$ ) of some EILs were predicted from quantum mechanical energies of molecules using an atomization approach [83]. The enthalpies of formation of *N,N*-dimethylhydrazinium EILs were predicted by a G2 procedure. It was found that the cyanomethyl group on *N,N*-dimethylhydrazinium-based system led to higher enthalpies of formation and increased the efficiency of the propellant.

Hypergolic fuels based on *N,N,N*-trimethylhydrazinium iodide ( $[\text{TMH}]^+[\text{I}]^-$ ) were synthesized by nucleophilic substitution and characterized by IR and  $^1\text{H}$ -NMR spectroscopy and GC-MS [84]. The hypergolic chemicals  $[\text{TMH}]^+[\text{X}]^-$  ( $\text{X} = \text{CN}^-$ ,  $\text{N}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{ClO}_4^-$ , or  $\text{AlCl}_4^-$ ) were prepared via ion exchange reactions from  $[\text{TMH}]^+[\text{I}]^-$  and  $[\text{EMT}]^+[\text{I}]^-$ , respectively. The salts were dissolved in 2-HEH and decomposition temperature, density, viscosity, and decomposition energy were evaluated to determine their suitability for use as liquid rocket fuels. The ignition delay time of the mixture of hypergolic chemicals with  $[\text{TMH}]^+[\text{N}_3]^-$  and  $[\text{TMH}]^+[\text{CN}]^-$  using HTP as an oxidizer was 56 and 97 ms, respectively.

## 3 Anions for ILs

Many ILs described in the literature have inorganic, non-oxidizing anions such as tetrafluoroborate, hexafluorophosphate, trifluoromethylsulfonate ( $[\text{CF}_3\text{SO}_3]^-$ ), or bis-(trifluoromethylsulfonyl)imide. Because these inert ILs are only of academic interest, they are not included in this book. They may be used as intermediates by exchanging the inert anions with oxidizing anions.

### 3.1 ILs with DCA Anions

The chemical literature continues to describe the  $(\text{NC})_2\text{N}^-$  anion as dicyanamide, the same name as the parent acid. This is acceptable, as long as the word “anion” is carried along with it. It seems more reasonable to describe this anion as dicyanamidate, but this nomenclature has not yet taken hold. An alternate name, dicyanoamidate, is rarely found. The common abbreviation for dicyanamidate is dca or DCA.

A convenient source of DCA anions is in the form of calcium or barium dicyanamidate. Hypergolic ILs based on DCA anions are preferred because both the cation and the anion have fuel value.

Dicyanamide anions provide a combustible organic structure, and produce ILs with low viscosities and a wide liquidus range. The book *High-Energy-Density Fuels for Advanced Propulsion* contains a subsection on hypergolic ILs based on DCA anions [18]. All the liquid DCA salts of various imidazolium cations are hypergolic with inhibited red-fuming nitric acid (IRFNA) or WFNA [92]. However, the ignition delays were found to be between 170 and 670 ms, which is far from the required ignition delay time of <5 ms for a safe ignition. For comparison, the ignition delay time of hydrazine with RFNA is 4.8 ms. Importantly, the results showed that the DCA anions may play a key role in the ignition process, whereas the unsaturated substituents have less impact on the ignition delay time. Although the ignition of these DCA-based ILs with WFNA was not rapid, this work, for the first time, reported on the hypergolic properties of DCA salts and provided a new path for IL-based non-toxic hypergolic fuels. Ammonium and hydrazinium salts of DCA are unstable and have a tendency to rearrange to *N*-cyanoguanidine or cyclize to guanazole [93].

### 3.1.1 Reactions of ILs Containing DCA Anions

Understanding the ignition reactions for hypergolic propellants is an important step in developing a complete reaction model that can be used in rocket engine design and optimizing the composition of oxidizer/fuel combinations. An experimental study of the hypergolic reaction of sodium DCA with nitric acid was conducted to investigate reaction mechanisms for hypergolic ignition of this family of ILs [94]. Sodium DCA was used to simplify contributions to products from the cation of the fuel. Gas-phase reaction products were studied using microprobe sampling and MS analysis. In addition, a chemical assay was used to test for the presence of dinitrobiuret, the key intermediate in the proposed mechanism. Most of the results from the study supported a proposed mechanism, but there was no direct evidence for dinitrobiuret.

Four ILs, with a formula of  $[R(H_3C)_2NCH_2CH_2N_3][N(CN)_2]$  ( $R$  = ethyl, *n*-butyl, *n*-hexyl, and *n*-octyl) were synthesized through a metathesis reaction of quaternized *N,N*-dimethyl-2-azidoethylamine (DMAZ) with a different alkyl-chain length from that of silver DCA [95]. The density, dynamic viscosity, and thermal properties of these ILs were measured over a wide temperature range and the effect of the alkyl-chain length was examined. The density decreased, while dynamic viscosity and molar heat capacity increased with the increasing number of carbon atoms in the alkyl chain. The density showed a linear decrease with temperature, and the dynamic viscosity decreased with temperature according to the VFT equation. No melting points were found for these four ILs, except for glass-transition temperatures from 171 to 182 K (−102 to −91 °C). The decomposition temperatures of these four ILs ranged from 514 to 515 K (241–242 °C), independent of the alkyl-chain length.

In order to better understand the reaction dynamics of IL fuels containing DCA anions, MD simulation calculations were performed for two predicted intermediate compounds in nitric acid/DCA-based IL combustion, i.e. protonated DCA (DCAH) and

nitro-dicyanamide-carbonyl (NDC) [96]. Calculations were performed using a ReaxFF reactive force field model. Single-component simulations showed that neat NDC undergoes exothermic decomposition and ignition. Simulations with  $\text{HNO}_3$  were performed at both low and high densities to investigate the reaction in a dense vapor and liquid phase, respectively. Both DCAH and NDC react hypergolically with  $\text{HNO}_3$ , and increased density led to shorter times for the onset of thermal runaway. Contrary to a mechanism proposed by others for DCA combustion, neither DCAH nor NDC was converted to 1,5-dinitrobiuret before thermal runaway. See also [97–106].

Both the DCA anion,  $\text{N}(\text{CN})_2^-$ ,  $\text{DCA}^-$ , and dicyanoborohydride anion,  $\text{BH}_2(\text{CN})_2^-$ ,  $\text{DCBH}^-$ , have the desirable property of imparting hypergolicity to IL fuels. The question remained which of the two was more suited for this task. Direct quantum mechanical dynamics simulations of the reaction of  $\text{HNO}_3$  with  $\text{DCA}^-$  and  $\text{DCBH}^-$  were performed in an attempt to elucidate the primary and secondary reactions in the two reaction systems [107]. Guided by trajectory results, reaction coordinates and potential energy diagrams were mapped out for the oxidation of  $\text{DCA}^-$  and  $\text{DCBH}^-$  by one and two  $\text{HNO}_3$  molecules, respectively, in the gas-phase and condensed-phase ILs. The oxidation of  $\text{DCA}^-$  by  $\text{HNO}_3$  is initiated by proton transfer. The most important pathway leads to the formation of  $\text{O}_2\text{N}-\text{NHC}(\text{O})\text{NCN}^-$ , and the latter reacts with a second  $\text{HNO}_3$  to produce  $\text{O}_2\text{N}-\text{NHC}(\text{O})\text{NC}(\text{O})\text{NH}-\text{NO}_2^-$  ( $\text{DNB}^-$ ). The oxidation of  $\text{DCBH}^-$  by  $\text{HNO}_3$  may follow a similar mechanism to that of  $\text{DCA}^-$ . The theoretical results indicated that the formation of  $\text{DNB}^-$  is exclusively important in the oxidation of  $\text{DCA}^-$ , whereas the same type of reaction is a minor channel in the oxidation of  $\text{DCBH}^-$ . The combination of fast reaction rate constants, large exothermicities of  $\text{H}_2$  elimination, the high heat of combustion of the  $\text{H}_2$  product, and the low viscosity of the  $\text{DCBH}^-$  ILs have resulted in a shortened ignition delay time and enhanced pre-ignition performance of  $\text{DCBH}^-$  over  $\text{DCA}^-$ . Kinetics modeling has simulated the distinctive pre-ignition chemistry of  $\text{DCBH}^-$  and  $\text{DCA}^-$  and explained the different  $\text{HNO}_3$  oxidation kinetics of the two ILs.

A new strategy of cationic functionalization was developed by introducing the energetic nitrate (nitroxyl) group into the cationic units of ILs [108]. Interestingly, the introduction of oxygen-rich nitrate groups into the cationic structure of 12 ILs significantly improved the combustion performance of DCA hypergolic ILs. Ignition delays with WFNA were between 62 and 26 ms. The densities of these ILs were in the range of 1.22–1.39 g/cm<sup>3</sup>, which is much higher than that of UDMH (0.79 g/cm<sup>3</sup>).

### 3.1.2 Thermal Decomposition of ILs with DCA Anions

In an attempt to better understand decomposition mechanisms of  $\text{Emim}^+\text{DCA}^-$  and  $\text{EMmim}^+\text{DCA}^-$ , quasi-classical, direct-dynamics trajectories were calculated by quantum mechanical computational methods [109]. The trajectories showed many dissociation paths for these two ILs. Using trajectory results as a guide, structures of transition states and products that might be important for decomposition of these two

compounds were determined using DFT calculations. On the basis of modeling, initial decomposition paths for energized  $\text{Emim}^+\text{DCA}^-$  correspond to formation of an *N*-heterocyclic carbene and acid pair via transfer of the C2 proton of  $\text{Emim}^+$  to  $\text{DCA}^-$ , and evolution of methylimidazole and ethylimidazole via  $\text{S}_{\text{N}}2$  alkyl abstraction by  $\text{DCA}^-$ . Similar decomposition paths were identified for energized  $\text{EMmim}^+\text{DCA}^-$ , except that the reactivity of C2 of the imidazolium cation was significantly reduced upon substitution of a methyl group for a hydrogen atom at this position.

A droplet of 1-methyl-4-amino-1,2,4-triazolium dicyanamide ( $[\text{MAT}][\text{DCA}]$ ) was acoustically levitated in argon and heated to successively higher temperatures by a carbon dioxide laser [110]. At each temperature, *in situ* Fourier transform infrared (FTIR), Raman, and UV-visible spectra were recorded. The droplet became increasingly yellow before exploding at 400 K to produce a brown foam-like substance and dense smoke. The foam was subsequently studied *ex situ* by X-ray photoelectron and IR diffuse-reflectance spectroscopy, and elemental analysis. The combined spectroscopic analyses suggested that the foam was formed by linking two or more melamine molecules to yield a combination of melem, melon, and possibly graphitic carbon nitride. At least 37% of the  $[\text{MAT}][\text{DCA}]$  liquid was transformed into the stable, solid-state foam, which would be problematic for the use of such an IL-based hypergolic fuel in rocket engines because it might clog the injector orifices.  $[\text{Bmim}][\text{DCA}]$  did not explode and form this type of foam, even at temperatures of up to 430 K.

### 3.2 ILs with Nitrocyanamide Anions

The nitrocyanamide anion ( $[\text{N}(\text{NO}_2)(\text{CN})]^-$ ) is a hybrid between the  $\text{DCA}^-$  anion  $\text{N}(\text{CN})_2^-$  and the dinitramide anion  $\text{N}(\text{NO}_2)_2^-$  [111]. ILs with the nitrocyanamide anion are of interest both as ingredients for monopropellants or explosives and as hypergolic fuels with IRFNA or WFNA. Nitrocyanamide ILs with substituted imidazolium, guanidinium, and tetrazolium cations have been synthesized and characterized [112]. Aminoguanidinium nitrocyanamide crystallized in the triclinic system  $P\bar{1}$ . The results obtained from theoretical calculations based on aminoguanidiniumnitrocyanamide were consistent with single-crystal structure data. These ILs exhibit desirable physicochemical properties, such as low melting points, good thermal stability, and low impact sensitivity. Their energetic performances, including enthalpies of formation, detonation pressures, and detonation velocities, were studied by a combination of theoretical and empirical calculations. The ILs have wide liquid ranges and low viscosities. They were shown to be promising candidates as hypergolic ILs by performing ignition tests with 100%  $\text{HNO}_3$ .

Nine EILs were synthesized by anion exchange reactions between substituted imidazolium, guanidinium, or tetrazolium halides and silver nitrocyanamide ( $\text{Ag}[\text{N}(\text{CN})(\text{NO}_2)]$ ) in methanol. All of the resultant ILs were liquids at room

temperature and had desirable physicochemical properties, such as low melting points ( $m.p. < 183\text{ K} = < -90^\circ\text{C}$ ), good thermal stability ( $T_{\text{dec}} > 523\text{ K} = > 250^\circ\text{C}$ ), low viscosities ( $< 25\text{ mPa s}$ ), and good detonation performance. The ignition delay times of these ILs with WFNA were between 46 and 78 ms, similar to those of [Bmim][N(CN)<sub>2</sub>] (ignition delay = 47 ms). However, guanidinium or tetrazolium nitrocyanoamide ILs were not hypergolic with WFNA.

### 3.3 ILs with Boron-Containing Anions

A wide range of ILs with boron-containing anions have been tested as hypergolic fuels. Many of these compounds have very short ignition delays when they come in contact with WFNA. The boron-containing anions include  $\text{BH}_4^-$ ,  $\text{Al}(\text{BH}_4)_4^-$ ,  $\text{BH}_3\text{CN}^-$ ,  $\text{BH}_2(\text{CN})_2^-$ ,  $\text{BH}_2\text{BH}_3\text{CN}^-$ ,  $\text{BH}_3\text{CNBH}_2\text{CN}^-$ , and  $\text{PH}_2\text{B}_2\text{H}_6^-$ . Additional boron-containing anions are derived from the decaborate anion  $\text{B}_{10}\text{H}_{12}^{2-}$  and its adduct with ammonia,  $\text{B}_{10}\text{H}_{11}\text{NH}_3^-$ .

The presence of B—H bonds in the anion promotes the hypergolicity of ILs, while the introduction of intrinsically electron-rich groups (azide, allyl, propynyl, and B—H bonds) into the heterocyclic ring cation can efficiently shorten the ignition delay time of the ILs.

#### 3.3.1 Tetrahydroborate Anions

Lithium borotetrahydride ( $\text{LiBH}_4$ ) forms adducts with substituted tetrazoles such as 1,5-dimethyltetrazole or 1,5-dimethyltetrazole [113]. Although both complexes are solids at ambient temperature, the goal was to solvate  $\text{LiBH}_4$  at a high mol ratio and the general presence of multiple bonding modes might aid in liquefying these systems.

#### 3.3.2 Dicyanoborohydride Anions

Both the dicyanoamide anion,  $\text{N}(\text{CN})_2^-$ ,  $\text{DCA}^-$ , and the dicyanoborohydride anion,  $\text{BH}_2(\text{CN})_2^-$ ,  $\text{DCBH}^-$ , have the desirable property of imparting hypergolicity to IL fuels. The question remained which of the two was more suited for this task. Direct quantum mechanical dynamics simulations of the reaction of  $\text{HNO}_3$  with  $\text{DCA}^-$  and  $\text{DCBH}^-$  were performed in an attempt to elucidate the primary and secondary reactions in the two reaction systems [107]. Guided by trajectory results, reaction coordinates and potential energy diagrams were mapped out for the oxidation of  $\text{DCBH}^-$  by one and two  $\text{HNO}_3$  molecules, respectively, in the gas-phase and condensed-phase ILs. The oxidation of  $\text{DCBH}^-$  by  $\text{HNO}_3$  may follow a similar mechanism to that of  $\text{DCA}^-$ , producing two analog products:  $\text{O}_2\text{N—NHC}(\text{O})\text{BH}_2\text{CN}^-$  and  $\text{O}_2\text{N—NHC}(\text{O})\text{BH}_2\text{C}(\text{O})\text{NH—NO}_2^-$ . Theoretical calculations supported the enhanced pre-ignition performance of  $\text{DCBH}^-$  over  $\text{DCA}^-$  with WFNA. The combination of fast

reaction rate constants, large exothermicities of  $\text{H}_2$  elimination, the high heat of combustion of the  $\text{H}_2$  product, and the low viscosity of the  $\text{DCBH}^-$  ILs have resulted in a shortened ignition delay time and enhanced pre-ignition performance of  $\text{DCBH}^-$  over  $\text{DCA}^-$ .

The hypergolic ignition process of eight ILs with  $[\text{BH}_3(\text{CN})\text{BH}_2(\text{CN})]^-$  anions with WFNA was experimentally investigated by a droplet test method and safe-distance microscope high-speed photography techniques [114, 115]. Results showed that the hypergolic ignition process of these ILs was of a completely different 3-stage nature. An ultra-fast hypergolic ignition delay ( $<5$  ms) was observed for this family of ILs, based on “Coulomb explosion”-like behavior, in terms of the fast and vigorous ejection of liquid spikes that protruded from the mixing layer. The Coulomb explosion delay time was correlated with the side-alkyl functional group in the cation. In the second stage, liquid spikes that were ejected into the oxidizer pool significantly increased the reactive surface area underneath the liquid surface. As a consequence, local temperature increased and gas-phase intermediate product and oxidizer/fuel vapor accumulated due to the continuous liquid-phase reaction underneath the surface. The ignition delay time decreased with the increase of unsaturation index of the heterocyclic core in the cation. The enthalpies of formation of the ILs for different cation structures were correlated with ignition delay time, which represented both the fuel structure chemistry and the Coulomb explosion-enhanced mixing effect on the overall reactivity of this diffusive system.

Introduction of the cyano group into the anions of borane-based hypergolic fuels can greatly reinforce the hydrolytic stability [116, 117]. A 1-allylimidazole cyano-borane complex had some attractive properties such as water immiscibility and good hydrolytic stability, high density, good thermal stability ( $T_{\text{dec}} = 466 \text{ K} = 193^\circ\text{C}$ , onset), high calculated density impulse, ultra-short ignition delay time (WFNA, 3 ms), and low viscosity (8.4 mPa s).

*In situ* IR spectroscopy techniques and TGA-MS were used to characterize the reactivity of  $\text{Bmim}^+\text{DCBH}^-$ , in comparison to the well-characterized  $\text{Bmim}^+\text{DCA}^-$  IL [118]. TGA measurements determined the enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) to be  $112.7 \pm 12.3 \text{ kJ/mol}$  at 298 K. A rapid-scan FTIR spectrometer was used to track the appearance and disappearance of species in the hypergolic reactions of  $\text{Bmim}^+\text{DCBH}^-$  and  $\text{Bmim}^+\text{DCA}^-$  with WFNA, and in the thermal decomposition of these EILs. Experimental results indicated that the hypergolic reaction of  $\text{Bmim}^+\text{DCBH}^-$  with WFNA generated both common and unique intermediates as compared to previous  $\text{Bmim}^+\text{DCA}^- + \text{WFNA}$  investigations. Nitrous oxide  $\text{N}_2\text{O}$  was generated during both hypergolic reactions indicating that it may play a role in the hypergolic ignition process,  $\text{NO}_2$  was generated in significantly higher concentrations for  $\text{Bmim}^+\text{DCBH}^-$  than for  $\text{Bmim}^+\text{DCA}^-$ ,  $\text{CO}_2$  was only generated for  $\text{Bmim}^+\text{DCA}^-$ , and hydrogen cyanide (HCN) was only generated during thermal decomposition and hypergolic ignition of  $\text{Bmim}^+\text{DCBH}^-$ .

### 3.3.3 Cyclic Boranate Anions

ILs can be formed from heterocyclic amine cations and polyhedral borane anions. The synthesis, structure, and physical properties of nitrogen heterocyclic salts of the polyhedral borane anions (closo-decaborate  $[B_{10}H_{10}]^{2-}$ , closo-dodecaborate  $[B_{12}H_{12}]^{2-}$ , carba-closo-dodecaborate  $[CB_{11}H_{12}]^{-}$ , and their derivatives), and their potential application as ILs and energetic materials, have been reviewed [119].

A series of borohydride cluster-based ILs with excellent hydrolytic and thermal stabilities ( $T_d > 200^\circ\text{C}$ ) and high density ( $1.18\text{ g/cm}^3$ ) were prepared [120]. Upon contact with WFNA or  $N_2O_4$ , these ILs had ultra-short ignition delay times (as short as 1 ms).

### 3.3.4 Substituted Boranate Anions

A series of cyanotetrazolylborohydride (CTB) anion-based ILs was synthesized by a straightforward *N*-hydroboration of tetrazole followed by a salt metathetical reaction [121]. These ILs exhibited remarkably low viscosity ( $<20\text{ mPa}\cdot\text{s}$ ), high density ( $>1.1\text{ g/cm}^3$ ), and ultra-short ignition delay time (as short as 1.4 ms) upon contact with WFNA.

### 3.3.5 Tetrakis(tetrahydroborate)aluminate Anions

ILs with  $Al(BH_4)_4$  anions have high reactivity with oxidizers, but lack other properties to make them practical as liquid propellants. In an attempt to lower the viscosity, neutral  $Al(BH_4)_3$  was mixed with an IL containing the cyanoborohydride anion [113]. ILs with the  $[NCBH_3]^{-}$  anion by itself generally possess very low viscosities ( $\sim 20\text{ cPs}$ ). It was anticipated that the combination of  $[NCBH_3]^{-}$  with  $Al(BH_4)_3$  would produce a new anion of the formula  $[Al(BH_4)_3NCBH_3]^{-}$ . There were indications of a mixed borohydride/cyanoborohydride aluminum compound with a coordination number of seven. Unfortunately, neither the cyanoborohydride approach nor the pure tetrakis/tetrahydroborate aluminate ILs discovered possessed the desirable physical properties for a suitable propellant.

## 3.4 ILs with Anions Derived from Heterocyclic Amines

Surprisingly, while most azotetrazolates exhibit melting points in excess of 423 K ( $160^\circ\text{C}$ ), bis(1-butyl-3-methyl-imidazolium) 5,5'-azotetrazolate is an RTIL with a melting point of 270 K ( $3^\circ\text{C}$ ), [122], similar to its 3,5-dinitrotetrazolate analog which melts at 308 K ( $35^\circ\text{C}$ ), as described in [49].

Twenty-eight energetic salts with tetramethyl-, tetraethyl-, and tetrabutylammonium and 1-butyl-3-methylimidazolium cations paired with 3,5-dinitro-1,2,4-triazolate, 4-nitro-1,2,3-triazolate, 2,4-dinitroimidazolate, 4,5-dinitroimidazolate, 4,5-dicyanoimidazolate, 4-nitroimidazolate, and tetrazolate anions have been pre-

pared and characterized by using DSC, TGA, and single-crystal XRD in order to study the effects of cation and anion type on the physicochemical properties of the resulting crystalline salts or ILs [50]. ILs (defined as having a m.p.  $< 373\text{ K} = < 100^\circ\text{C}$ ) were obtained with all combinations of the 1-butyl-3-methylimidazolium cation ( $\text{C4mim}^+$ ) and the heterocyclic azolate anions studied, and with several combinations of tetraethyl or tetrabutylammonium cations and the azolate anions. The  $\text{C4mim}^+$  azolates were liquids at room temperature exhibiting wide liquid ranges and forming glasses on cooling with glass-transition temperatures in the range of  $220\text{--}191\text{ K}$  ( $-53$  to  $-82^\circ\text{C}$ ), except for the 3,5-dinitro-1,2,4-triazolate salt (m.p.  $306\text{ K} = 33^\circ\text{C}$ ).

The dinitromethanide  $(\text{NO}_2)_2\text{CH}^-$  anion proved to be a useful component of RTILs with substituted imidazolium cations [123]. Delocalization of both the  $(\text{NO}_2)_2\text{CH}^-$  anion and dimethylimidazolium cation was found from single-crystal structure data. Their impact sensitivities were determined and they were found to be insensitive ( $>40\text{ J}$ ).

## 4 Physical Properties of ILs

Physical properties of specific ILs are interspersed as examples in the following sections under their parent amine from which the salts were derived. The most important property of an IL is its melting point (freezing point if it is a liquid at room temperature). Other properties of interest for rocket propellant chemists are the enthalpy of formation and the density. The following sections discuss the physical properties of ILs in general, often with examples for more than one compound. This is why these publications could not be cited at just one location in this chapter.

### 4.1 Melting Points and Phase Changes of ILs

ILs exhibit low-melting-point behavior as a result of disrupting the attractive ion–ion interactions in conventional salts by introducing structural “buffer-zones” of van der Waals-only regions into the ions, principally cations, which suppress crystallization, leading to the formation of either glasses on cooling, or low-lattice energy solids, typical opportunities for both polymorphism and plastic crystal formation. Anions often grouped with these cations are nitrate ( $\text{NO}_3^-$ ), perchlorate ( $\text{ClO}_4^-$ ), and the DCA anion  $\text{N}(\text{CN})_2^-$ .

The liquidus ranges exhibited by ILs can be much greater than those of common molecular solvents. Water, for example, has a liquidus range of  $273\text{--}373\text{ K}$  ( $0\text{--}100^\circ\text{C}$ ). The lower temperature limit of ILs, solidification (either crystallization or glassification), is governed by the structure and interactions between the ions. Phase transitions of ILs are not sharp endotherms on the DSC thermograms, but diffuse, wide peaks extending over a range of 10 degrees. The heat of fusion can also be derived



from the DSC thermograms and is used along with the peak temperature of the phase-change DSC to characterize the compounds. ILs, consisting of totally ionized components and displaying relatively weak ion–ion pairing (in comparison to molten salts), have little or no measurable vapor pressure. In contrast to molecular solvents, the upper liquidus limit for ILs is usually that of thermal decomposition rather than vaporization.

The melting points of organic salts are influenced by the symmetry of the molecule, the flexibility of the alkyl or aryl substituents, and the accessibility of the charges. ILs do not have sharp freezing points, but undergo a gradual transition to a glassy, highly viscous state. The ILs are best characterized by their glass-transition temperature ( $T_g$ ). There are different definitions of the glass-transition temperature. According to one definition,  $T_g$  is the temperature at which the shear viscosity reaches  $10^{12}$  Pa s. Another states that it is the temperature at which the characteristic molecular relaxation time reaches  $\tau_g = 100$  s.

The physical and chemical properties of ILs can be tailored to meet certain application criteria. In most cases, this is achieved by the appropriate selection of the cation and anion pair or by changing the substituents on one or both of the heterocyclic amine rings. A simple chemometric model was used to tune the melting and freezing points of a model IL, [Hmim][NO<sub>3</sub>] [124].

## 4.2 Densities of ILs

Volume parameters for RTILs and salts were developed for 59 of the most common imidazolium-, pyridinium-, pyrrolidinium-, tetra-alkylammonium-, and phosphonium-based RTILs [125]. The mean absolute deviation (MAD) of the densities was  $0.007 \text{ g/cm}^3$ ; for 35 imidazolium-based room-temperature salts, it was  $0.020 \text{ g/cm}^3$ ; and for 150 energetic salts, it was  $0.035 \text{ g/cm}^3$ . The experimental density ( $Y$ ) for an alkylated imidazolium- or pyridinium-based RTIL is approximately proportional to its calculated density ( $X$ ) in the solid state. This method was later extended over a wider range of temperatures and pressures [126].

Although numerous different ILs exist, even basic physical-property data, such as the density and melting point, exist only for relatively few. Derivation of melting-point QSPRs for EILs would therefore greatly aid in the molecular design of new energetic compounds. Samples of ILs based on 1-substituted 4-amino-1,2,4-triazolium bromide and nitrate salts were synthesized and their melting points and densities measured [127]. The molecular geometries of the cations of the ILs were optimized using *ab initio* quantum chemical methods. Melting-point QSPRs were then derived from molecular orbital, thermodynamic, and electrostatic potential (ESP) descriptors, and good correlations with experimental data were achieved. The correlation coefficients for 3-parameter melting-point QSPRs and for 1-parameter density QSPRs exceeded 0.9. Although some of the descriptors that appeared in the QSPRs were designed to describe

chemical reactions, it was inferred that they served in this study only to quantify interactions between the cation and anion.

The liquid density of imidazolium-based ILs was estimated using a combined method that included an artificial neural network and a simple group-contribution method [128]. A total of 1736 data points of density at several temperatures and pressures, corresponding to 131 ILs, was used to train the neural network. The molar mass and the structure of the molecule were given as input variables. New values of density as a function of temperature and pressure for 33 other ILs were predicted, and the results were compared to experimental data from the literature. The results showed that the chosen artificial neural network and the group contribution method represent a viable alternative for the estimation of the liquid density of imidazolium-based ILs, with acceptable accuracy for a wide range of temperatures and pressures (258–393K and 99–206940 kPa, respectively).

A group-contribution model of the  $p$ - $\rho$ - $T$  relation based on a large amount of data by different authors for 1- $C_n$ -3-methylimidazolium-based ILs with  $n = 2, 4$ , and 6, and with the  $N(CN)_2$  anions, describes the dependence of density, isobaric expansivity, and isothermal compressibility on temperature, pressure, the length of the alkyl side chain of the cation, and the anion [129]. This makes it possible to obtain the most reliable values of the density and assess which sets of data can be considered more accurate than others.

### 4.3 Velocity of Sound in ILs

The velocity of sound is an important physical property of any propellant and can be used to derive other properties like adiabatic compressibility or thermal conductivity. A database for the velocity of sound of pure ILs, created by collecting experimental data from literature covering the period 2005–2013, was used to study the effects of temperature and the alkyl-chain length on the velocity of sound and a second-order, corresponding-states, group-contribution computational method was developed to estimate the velocity of sound of new ILs [130]. The velocity of sound can be used to determine the thermal conductivity of ILs based on the Bridgman theory. The calculated values of thermal conductivity showed good agreement with the experimental data.

A review of the literature data on the velocity of sound and ultrasound absorption in pure ILs included an analysis of experimental methods described in the literature to determine the velocity of sound in ILs as a function of temperature and pressure, and the relevance of ultrasound absorption in acoustic investigations [131]. A relation between ion structures and velocities of sound would be useful for predicting the velocity of sound in yet undiscovered ILs.

#### 4.4 Vapor Pressures of ILs

The vapor pressure of ILs is usually below the level at which it can be measured. This is very desirable and is one of the reasons why ILs have received so much attention as potential rocket propellants as they are without respiration toxicity or vapor flammability hazard.

Isolated ion pairs of a reactive hypergolic IL,  $\text{Bmim}^+\text{DCA}^-$ , were generated by vaporizing IL sub-micrometer aerosol particles [132]. The vaporized species were investigated by dissociative ionization with tunable VUV light, exhibiting clear intact cations. Mass spectra of ion-pair vapor from an effusive source of the hypergolic IL showed substantial reactive decomposition due to the internal energy of the molecules emanating from the source. The method of IL sub-micrometer aerosol particle vaporization for reactive ILs such as hypergolic species is a convenient, thermally “cooler” source of isolated intact ion pairs in the gas phase compared to effusive sources.

A neutral, intact ion pair of a vaporized IL,  $\text{Bmim}^+\text{TCM}^-$  was observed in a vacuum chamber using tunable VUV photonionization (PI)-time-of-flight (TOF) mass spectrometry (MS) [71]. The ionization potential (IP) for the ion pair was experimentally determined to be  $6.6 \pm 0.5$  eV. TGA determined the  $\Delta H_{\text{vap}}$  to be  $298 \text{ K} = 143.5 \pm 6.2 \text{ kJ/mol}$ . Vaporization of  $\text{Bmim}^+\text{TCM}^-$  as ion pairs was the dominant mechanism for mass loss under the experimental conditions for VUV PI-TOFMS ( $T = 433 \text{ K}$ ).

Methods for vaporizing ILs with very low vapor pressures were developed using HAN, HEH, ammonium nitrate (AN), and mixtures of these compounds [133]. Models were developed to understand the ionization processes of vaporized ionic mixtures.

#### 4.5 Viscosity of ILs

Ionic liquids are more viscous than most other organic solvents. The higher viscosity is caused by electrostatic attraction between the ions of different charge polarities.

The viscosity of imidazolium-based ILs with four different cations and three different anions was measured at pressures up to 126 MPa and at three temperatures (298, 323, and 343 K) [134]. The high-pressure viscosity of Emim, 1-*n*-hexyl-3-methylimidazolium (Hmim), and 1-*n*-decyl-3-methylimidazolium (Dmim) cations with a common anion, bis(trifluoromethylsulfonyl)imide Tf2N, was measured to determine the alkyl-chain-length effect of the cation. An increase in the alkyl-chain length increased the viscosity at elevated pressures. Dmim exhibited a larger non-linear increase with pressure over the shorter alkyl substituents. Anion effects were investigated with Hmim as a common cation and the anions Tf2N, hexafluorophosphate ( $\text{PF}_6$ ), and tetrafluoroborate ( $\text{BF}_4$ ).  $[\text{Hmim}][\text{PF}_6]$  had the highest viscosity and a very non-linear pressure dependence, even at relatively moderate pressures (of up to 30 MPa), similar to the results for  $[\text{Bmim}][\text{PF}_6]$ .

Melting temperatures, glass-transition temperatures, decomposition temperatures, heat capacities, and viscosities for a large series of pyridinium-based ILs were measured, with data for several imidazolium and quaternary ammonium salts included for comparison [135]. Many of these compounds did not crystallize, but formed glasses at temperatures between 188 and 223 K. Viscosities generally increased with the increasing number and length of alkyl substituents on the cation, with the pyridinium salts typically being slightly more viscous than the equivalent imidazolium compounds.

Density, viscosity, and surface tension data sets of 13 ILs formed by imidazolium, pyridinium, or pyrrolidinium cations paired with dicyanamidate, tetrafluoroborate, thiocyanate, methylsulfate, and trifluoroacetate anions were measured at temperatures between 293 and 363 K [136]. The effect of the IL-forming anion and cation on the physical properties was analyzed systematically. A longer alkyl chain in imidazolium-based ILs was associated with lower density, higher viscosity, and lower surface tension. Density of [C4mim][DCA],  $C_{10}H_{15}N_5$ , at 293.15 K and 100 kPa was  $1.064.4 \pm 0.008 \text{ g/cm}^3$ , and viscosity was  $0.0332 \pm 0.0009 \text{ Pa}\cdot\text{s}$ .

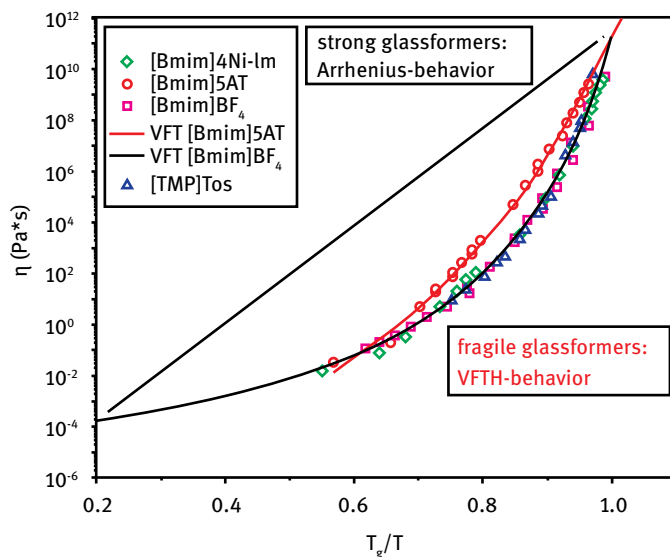
The investigation of the MD of ILs is vital for the fundamental understanding of their physical nature as well as for the successful engineering design in their applications. An in-depth rheological study of two ILs of different nature in a wide frequency and temperature range (up to the glass-transition point and beyond) was performed, utilizing techniques with an oversampling procedure and with adjustment of the instrument compliance [137].

The effect of azolate anion structure on the physical properties of four ILs, specifically on their glassy dynamics and ion interactions, was studied utilizing rheology, X-ray scattering, UV/vis absorption, and *ab initio* calculations [138]. Three of the ILs shared the same Bmim cation. The anions were tetrafluoroborate, 1-butyl-3-methylimidazolium 4-nitroimidazolate, and 1-butyl-3-methylimidazolium 5-aminotetrazolate. The peculiar rheological behavior for these ILs, which deviated from what was expected for molecular glass-formers, included high elasticity in the low-frequency zone and failure of time–temperature superposition. These peculiarities were attributed to specific interactions in the nitrogen-rich planar rings of azolate ILs. X-ray scattering measurements revealed a nanometer-ordered organization in azoliumazolates due to H-bond interactions. This conclusion was also supported by *ab initio* calculations.

In order to compare the viscosities of different ILs, it is possible to plot the logarithm of the viscosity versus the reciprocal absolute temperature normalized by the glass-transition temperature, as shown in Figure 2.

The viscosity of ILs can be lowered by adding graphene as a lubricant, thus improving ignition delays [139]. The viscosity of ILs can be reduced and the ignition delay can be improved by dilution with ethanol [140].

Experimental data for viscosity of 268 typical ILs from 215 literature references were compiled and critically evaluated and the effects of ionic molecular structures on the viscosity of ILs were presented [141]. Water and residual  $Cl^-$  have an effect on the



**Figure 2:** Viscosity versus  $T_g/T$  for the [Bmim]BF<sub>4</sub> (squares), [TMP]Tos (triangles), [Bmim]5AT (circles), and [Bmim]4Ni-lm (diamonds) ILs. (Reprinted from [138], with permission of ©2011 American Chemical Society; permission conveyed through RightsLink). The dashed straight line represents the Arrhenius model, and the solid curved line represents the VFT model.

viscosity of ILs. The parameters of the VFT equation for the temperature dependence of the viscosities of these ILs were reported.

Transport properties include thermal conductivity for heat transfer, viscosity for momentum transfer, and diffusion coefficient for mass transfer. The transport properties are important for all applications of ILs. High viscosity hinders the applications of some of the ILs. A review of the transport properties of pure ILs and mixtures of ILs with other compounds attempted to derive a correlation between the transport properties and the molecular structures [142].

ILs are known to have very high viscosities, which makes it difficult to pump and spray atomize them in a rocket combustion chamber. The rheological behavior of a fluid is an important property that has a distinct impact on its viscosity, mass transfer rates, and fluid dynamics. It is necessary to study the different rheograms and the viscoelastic properties of fluids. A review looked at imidazolium-based combinations of ILs and natural deep eutectic solvents, in terms of different H-bond donors (HBD) and H-bond acceptors (HBA), with different molar ratios of HBA:HBD; the rheological behaviors of these combinations at ambient-temperature conditions and higher temperatures were critically evaluated [143].

## 4.6 Surface Tension of ILs

The pendant drop method has been used for measuring the surface tension of pure ILs in the range of 278–333 K [144]. In addition, densities and thermal-expansion coefficients of these ILs were presented. The values of surface tension were between 25 and 48 mN/m and decreased with temperature. Although this study used ILs that are not useful as rocket propellants, the same method can be used to measure surface tensions of EILs.

Air-liquid interfacial tension data and density data were measured for two ILs with the 1- $C_n$ -3-methylimidazolium cation,  $n=2$  and 4, and the DCA anion at atmospheric pressure in the temperature range 278–356 K [145]. The density was measured using a buoyancy method. An analysis of the experimental density data, using a group-contribution model, performed for eight ILs with the 1- $C_n$ -3-methylimidazolium cation ( $n=2, 4, 6$ ), and the tetrafluoroborate, trifluoromethanesulfonate, and DCA anions, indicated that the uncertainty arising from impurities present in the sample was significant. The model is capable of providing predictions for pure imidazolium-based ILs with the  $\text{BF}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ , and  $\text{N}(\text{CN})_2^-$  anions.

## 4.7 Thermal Conductivities of ILs

Thermal conductivity of ILs is not as important for their use as rocket propellants as it is for their proposed use as thermal storage and heat transfer fluids. The thermal conductivities of ten ILs based on the anions  $\text{C}(\text{CN})_3^-$  (i.e. tricyanomethanide, TCM) and  $\text{B}(\text{CN})_4^-$  (tetracyanoborate), and a homologous series of the [alkyl-mim] $^+$  (1-alkyl-3-methylimidazolium) cations Emim $^+$  (ethyl), Bmim $^+$  (butyl), Hmim $^+$  (hexyl), Omim $^+$  (octyl), and Dmim $^+$  (decyl) were measured by a steady-state guarded parallel-plate instrument in the temperature range 283.15–353.15 K at atmospheric pressure [146]. The measured thermal conductivities of the ILs decreased with increasing temperature and increasing alkyl-chain length of the cation. Regarding the influence of the anion, somewhat smaller values were observed for the  $[\text{B}(\text{CN})_4]^-$ -based ILs than for the  $[\text{C}(\text{CN})_3]^-$ -based ILs carrying the same cation. A simple prediction method for the thermal conductivity of ILs using only information on the molar mass and the density was derived. By the combination of this approach with the temperature dependence of the density, an extended empirical correlation additionally describing the temperature dependence of the thermal conductivity of ILs was selected.

A database for the thermal conductivity of ILs was established by collecting experimental data from the literature covering the period 2007–2013, including 359 data points from 45 ILs, with the objective of studying the relationship between temperature or the alkyl-chain length of the cation and thermal conductivity [147]. A topological index method was proposed to estimate the thermal conductivity of ILs based on the collected data. The total average absolute deviation between the calcu-

lated and literature data was 2.3%. The topological index method guaranteed satisfactory precision with a simple form and can be easily expanded to new types of ILs.

ILs are very viscous and it is difficult to measure their thermal conductivity. In order to fill missing experimental data gaps, an estimation approach has been developed. A structure-interpolating approach was chosen, assigning contributions to thermal conductivity to the individual ions [148]. A total of 375 experimental data points for 39 ILs were used for the development. A detailed error analysis resulted in a combined experimental and predictive uncertainty of 7.96% for unknown ILs. A systematic screening of ILs based on their thermal conductivity is possible.

A simple, general, accurate, and easy-to-use correlation was developed for estimating the thermal conductivities of pure ILs over a wide range of temperatures at atmospheric pressure [149]. The objective was to develop a thermal conductivity correlation which does not require any other physical properties as input parameters, once a single thermal conductivity data point is available. A correlation has been proposed based on 378 thermal-conductivity temperature data points from 44 different IL types. The proposed correlation, in comparison to two well-known and commonly used group-contribution models and one literature correlation, showed much better accuracy with respect to experimental values.

ILs have been considered as replacement materials for halogenated heat transfer fluids. Thermal conductivity and heat capacity must be known for this application and would also be useful for rocket applications. The impact of electronic structure on the heat capacity was confirmed by DFT calculations [150]. The objective of this work was to assess the predictive capabilities of existing models for thermal conductivity and heat capacity, with further improvements based on more accurate investigated structure characterization and reparameterization using group-contribution methodology.

#### 4.8 Electrical Conductivities of ILs

Many ILs have been proposed as electrolytes for batteries and capacitors, and for this application they must have good electrical conductivities and/or dielectric constants. The electrical conductivities of ILs are of primary interest for their use as electrolytes, but are also needed for their use in electrospray colloid thrusters or in the design of electrolytic igniters for monopropellants.

#### 4.9 Thermodynamic Properties of ILs

A few examples of the thermodynamic properties of ILs are listed in this section. More thermophysical property data are listed in the sections for specific ILs. Thermophysical properties of 13 imidazole-derivative ILs were determined by DSC, but only one of those investigated would be of interest as a rocket propellant: [Bmim][DCA], CAS RN

[44824-52-1], is a potential hypergolic fuel for bipropellant engines [151]. It has a glass-transition temperature of 183 K (−90 °C) and a melting point of 267 K (−6 °C). The heat capacity at 298 K is 364.6 J mol<sup>−1</sup> K<sup>−1</sup> and the heat capacity function is

$$C_p = 0.197T + 305.81 \text{ J mol}^{-1} \text{ K}^{-1}.$$

Heat capacities of numerous other ILs were measured, but only few of those are of interest as rocket propellants. Nevertheless, the methods demonstrated for the measurement of heat capacities of these inert ILs can also be applied to EILs.

Heat capacities of five ILs were measured from 283.15 to 358.15 K. The  $C_p$  293.15-K estimated values were about 12% higher than the experimental values. The estimates suggested that heat capacities of ILs do not differ considerably from those typical for molecular liquids. The heats of solution of ILs in water, acetonitrile, and methanol were measured as a function of IL concentration [152].

Heat capacities for nine ILs have been determined with a “three-step” method using two different DSC devices. In addition, the heat capacities of these ILs have been studied by the modulated-temperature DSC method [153]. Heat capacities of nine ILs were measured from 293 to 358 K by using a heat flux DSC device [154].

A computational approach to the prediction of the heats of formation ( $\Delta H_f^\circ$ ) of solid-state energetic salts from electronic structure and volume-based thermodynamics (VBT) calculations used as its starting point reliable  $\Delta H_f^\circ$  data for energetic precursor molecules and ions [155]. An isodesmic crystal is a crystal in which all the bonds have the same electrostatic valency. The  $\Delta H_f^\circ$  of more complex energetic species such as substituted imidazole, 1,2,4-triazole, and tetrazole molecules and ions were calculated in this way and compared to experimental data.

Thermochemical and detonation parameters were calculated for the IL 1-ethyl-3-methyl-*H*-imidazolium perchlorate, [Emim][ClO<sub>4</sub>] and its associated solid [156]. The thermochemical values estimated included: lattice energy,  $U_{\text{POT}}([\text{Emim}][\text{ClO}_4])$  515 ± 67 kJ/mol (123 ± 16 kcal/mol); enthalpy of formation of the gaseous cation,  $\Delta H_f^\circ([\text{Emim}]^+(\text{G})) = +603 \text{ kJ/mol}$  (+144.2 kcal/mol) and anion,  $\Delta H_f^\circ([\text{ClO}_4]^{-}(\text{G})) = -277 \text{ kJ/mol}$  (−66.1 kcal/mol); enthalpy of formation of the solid salt,  $\Delta H_f^\circ([\text{Emim}][\text{ClO}_4](\text{S})) = -230 \pm 67 \text{ kJ/mol}$  (−55 ± 16 kcal/mol) and for the associated IL,  $\Delta H_f^\circ([\text{Emim}][\text{ClO}_4](\text{L})) = -218 \pm 67 \text{ kJ/mol}$  (−52 ± 16 kcal/mol) as well as the corresponding Gibbs energy terms:  $\Delta G_f^\circ([\text{Emim}][\text{ClO}_4](\text{S})) = +121 \pm 67 \text{ kJ/mol}$  (+29 ± 16 kcal/mol) and  $\Delta G^\circ([\text{Emim}][\text{ClO}_4](\text{L})) = +100 \pm 67 \text{ kJ/mol}$  (+24 ± 16 kcal/mol) and the associated standard absolute entropies, of the solid [Emim][ClO<sub>4</sub>],  $S^\circ_{298}([\text{Emim}][\text{ClO}_4](\text{S})) = 347 \pm 17 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  (83 ± 4 cal · K<sup>−1</sup> · mol<sup>−1</sup>). Combustion and detonation parameters were predicted for [Emim][ClO<sub>4</sub>] in its (ionic) liquid form:  $I_{\text{sp}} = 228 \text{ s}$  (monopropellant), detonation velocity ( $V_D$ ) = 5466 m/s, detonation pressure ( $p_{\text{CJ}}$ ) = 99 kbar, and explosion temperature ( $T_{\text{ex}}$ ) = 2842 K.

On the basis of a database of thermodynamic data established for 53 ILs, at least five models that made use of constitutional descriptors gave pretty good predictions for the heats of combustion of ILs [157]. A model for predicting heats of combustion of



ILs has been developed using a multi-linear regression. The model obtained from a set of 40 molecules revealed a good fit with the values in the literature. The heat capacities of pyridinium and imidazolium ILs, including [C4Mim][DCA], can be extrapolated from measured data [158].

The heat of vaporization of *N*-butyl-*N*-methylpyrrolidinium bis(trifluorosulfonyl)imide was found to be  $\Delta H_{\text{vap}}(298.15\text{ K}) = 195 \pm 19\text{ kJ/mol}$ , that of [C4Mim][DCA] was  $\Delta H_{\text{vap}}(298.15\text{ K}) = 174 \pm 12\text{ kJ/mol}$ , and that of *N*-butyl-*N*-methylpyrrolidinium dicyanamide was  $\Delta H_{\text{vap}}(298.15\text{ K}) = 171 \pm 12\text{ kJ/mol}$  [159]. These experimental heats of vaporization, photo ion appearance energies, and *ab initio* calculations corroborate vaporization of these RTILs as intact cation–anion pairs.

A computational method for the prediction of the condensed phase (solid or liquid) heat of formation (HOF) of triazolium-based energetic ionic liquids (EILs) at 298 K was based on the influence of some specific elemental compositions of cations and anions as additive parts [160]. The reported HOF values of 57 different triazolium-based EILs were used to derive a new model. For 34 different triazolium-based EILs, where the outputs of quantum mechanical methods were available, the Root Mean Squared Error (RMSE) of the new model was 156 kJ/mol.

#### 4.10 Computational Modeling Studies of the Molecular Structures of ILs

In addition to experimental investigations for the development of ILs as rocket propellants and for other industrial applications, theoretical studies are aimed at understanding the interaction of ions in the melt that give these liquids their unique physical properties. It is hoped that once the theory of ILs is better understood, that more EILs with physical properties (viscosity) more aligned with conventional rocket propellants can be developed based on predictions from computer calculations (“designer ionic liquids”) and tailored to specific properties needed for a given application.

The thermophysical and transport properties of ILs were theoretically investigated by means of molecular simulation techniques [161–163]. Quantum calculations were used as a support tool to force field development work. The cations studied included imidazolium-, pyridinium-, and triazolium-based structures, with different inorganic anions such as hexafluorophosphate, nitrate, and perchlorate, and one organic anion, bis(trifluoromethanesulfonyl)imide. Force fields for a range of imidazolium-, pyridinium-, and triazolium-based ILs were developed and published. The static properties computed included gravimetric densities, volumetric expansivities, isothermal compressibilities, heat capacities, cohesive energy densities as well as the liquid structure. Analysis of the dynamic properties of IL systems was aimed at information on the rotational dynamics and transport properties such as self-diffusivity. Additional work was done comparing the structures of hydrazinium(1+) nitrate, methylhydrazinium nitrate, and 1,1-dimethylhydrazinium

nitrate, also in comparison to 2-hydroxyethylhydrazinium nitrate (HEHN) which has a very low melting point ( $<248\text{ K}$ ).

The overall objective of the *Design of Energetic Ionic Liquids* challenge project is to characterize, design, and develop ILs as new monopropellants [164]. A fundamental understanding of the (in)stability of ILs, the intrinsic nature of the short- and long-range structure and interactions between the component ions, and identification of the key steps in the initial stages of decomposition and combustion can be achieved by computational chemistry. A hierarchy of computational approaches has been employed to predict the performance of EILs as monopropellants and fuels [164]. This effort included atomistic, high-level quantum chemical methods applied to individual ions and ion clusters, condensed-phase atomistic MD simulations utilizing polarizable force fields, and mesoscale-level simulations of bulk ILs based upon multi-scale coarse-graining techniques.

Electronic structure modeling calculations have been performed on the tetrazolium cation with a variety of substituents [165]. DFT with the B3LYP functional, using the 6-311G(d,p) basis set was used to optimize geometries. Improved treatment of dynamic electron correlation was obtained using second-order perturbation theory based on the Møller-Plesset 2 (MP2) method. Heats of formation of the cation with different substituent groups were calculated using isodesmic reactions and Gaussian-2 calculations on the reactants. In the search of EILs, the cation was paired with oxygen-rich anions, such as  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ , or  $\text{N}(\text{NO}_2)_2^-$ , and these structures were optimized using both DFT and MP2. The reaction pathway may involve a proton transfer from the cation to the anion.

Synthesis and extensive experimental and crystallographic analysis of the properties of protonated ILs, including nitro-substituted 1-alkyl-3-H-imidazolium and 1-alkyl-2-methyl-3-H-imidazolium nitrate and picrate salts, was conducted as part of an investigation of physical and chemical properties directed towards the development of an understanding of the criteria needed to model and predict IL materials incorporating energetic moieties [166].

A computational approach to predict the thermodynamics for forming a variety of imidazolium-based salts and ILs from typical starting materials was based on calculating the gas-phase proton and methyl cation acidities of several protonating and methylating agents, as well as the proton and methyl cation affinities of many important methyl-, nitro- and cyano-substituted imidazoles [167]. These calculated proton and methyl cation affinities of neutrals and anions were used in conjunction with an empirical approach, based on molecular volumes, to estimate the lattice enthalpies and entropies of ILs. A thermodynamic cycle for salt formation can predict the likelihood of success to synthesize a variety of energetic salts including ones with potentially high energy densities. This was then applied to imidazoles (the cation to be formed) with alkyl, nitro, and cyano substituents.

Previous studies of ILs have focused on the decomposition of ion pairs, providing insight into the chemistry of their ignition as high-energy fuels. Beyond this, it has

been attempted to accurately describe larger systems beyond single anion–cation pairs. The fragment molecular orbital (FMO) method, which decomposes a large molecular system (e.g. a cluster, protein, liquid, zeolite, etc.) into small subunits (fragments) that are designed to both retain the high accuracy of the chosen quantum mechanical level of theory while greatly reducing the demands on computational time and resources, was used in studies of ion clusters. Two IL systems, 1,2,4-triazolium dinitramide and 4-amino-1,2,4-triazolium dinitramide, were studied using both *ab initio* MP2 and the MP2 implementation of the FMO method, with each ion chosen as a FMO fragment or monomer [168]. Structures composed of two cations and two anions (tetramers) and larger clusters of three cations and three anions (hexamers) were optimized. Single-point energy calculations were then performed for comparison with the fully *ab initio* results. Comparing the energies from FMO2 and FMO3, it could be seen immediately that the FMO method captures the total energy very well, within 2 kcal/mol in the worst case. For the tetramers, both FMO2 and FMO3 were in good agreement; the FMO2 errors were less than 1 kcal/mol relative to the fully *ab initio* results.

The molecular structure of cations and anions of EILs can be optimized by molecular design [169]. Energetic salts satisfy requirements, such as high power, high density, insensitivity, thermal stability, and environmental friendliness.

MD simulation calculations of ILs containing the Bmim cation and nitrate, azide, or DCA anions were conducted. A comparison of thermodynamic properties, such as densities, enthalpies of vaporization, and ion-binding energies as well as structural correlations obtained from simulations at atmospheric pressure and over the temperature range 298–393 K, demonstrated that ILs with the  $\text{N}(\text{CN})_2$  anion had significantly different characteristics from those of ILs with the  $\text{N}_3$  and  $\text{NO}_3$  anions [170]. This trend was further manifested in dynamical properties characterized by self-diffusion coefficients and molecular rotational relaxation times. For [Bmim][ $\text{NO}_3$ ], the simulations gave a value for  $\Delta H_{\text{vap}}$  of +145.8 kJ/mol, which was in good agreement with the experimental value (+162.4 kJ/mol). The experimental value of  $\Delta H_{\text{vap}}$  for [Bmim][ $\text{N}_3$ ] was very similar to the value of +152.5 kJ/mol predicted from simulations at 298 K. The predicted  $\Delta H_{\text{vap}}$  for [Bmim][ $\text{N}(\text{CN})_2$ ] was +195.3 kJ/mol.

## 5 Chemical Properties of ILs

Some of the very first ILs used heterocyclic cations, and tetrachloroaluminate, hexafluorophosphate, or bis(trifluoromethyl)sulfonylamidate,  $[(\text{F}_3\text{CSO}_2)_2\text{N}]^-$ , as the anions. This was useful for battery electrolytes, but not suitable for rocket propellants. Only after these salts were formulated with oxidizing anions (with some unfortunate accidents occurring in the lab), did the rocket propulsion community become aware of their potential as rocket propellants. As an example, the Emim cation was paired with many different anions and the melting points were compared to understand the effect of molecular structure on melting point [171].

## 5.1 Thermal Stability of ILs

The thermal stability of ILs is remarkable. The nature of the ILs, containing organic cations, restricts upper stability temperature limits. Pyrolysis generally occurs at 623–723 K (350–450 °C) if no other lower temperature decomposition pathways are accessible. Oxidizing anions will lower the thermal stability. In most cases, decomposition occurs with complete thermolysis and volatilization of the component fragments.

Arrhenius-type reaction rate parameters for the initiation reactions governing the thermal decomposition of several EILs, 4-amino-1,2,4-triazolium nitrate (4ATN) and HEHN, were determined by experimental and numerical techniques [172]. The supplementary, less energetic compounds studied for comparison were 4-amino-1,2,4-triazolium chloride (4ATCl) and AN. The reaction rate parameters were obtained by an algorithm that compared the difference between the experimental and simulated species evolution profiles from the decomposition process. The rates of decomposition were measured by confined rapid thermolysis (CRT). The decomposition process was then simulated by applying conservation and equilibrium equations to the condensed and gas phases individually. The processes governing the decomposition of these energetic compounds were found to be autocatalytic in nature, and the autocatalytic agents were the strong acids generated by the initial decomposition step. The activation energy ( $E_{\text{act}}$ ) and pre-exponential factor  $A$  for the unimolecular decomposition step for 4ATN, HEHN, and 4ATCl were 167–188 kJ/mol and  $1016 \text{ s}^{-1}$ , respectively, similar to previously determined values for AN.

The thermal stability data of ILs were collected in a summary publication with attention to the experimental set-up [173]. Both ramped temperature and isothermal TGA methods, along with state-of-the-art methods such as TGA-MS and pyrolysis-GC, were used to characterize the thermal stability of ILs. The strengths and weaknesses of the different methodologies known to date demonstrated that analysis methods should be in line with the application. The combination of data from advanced analysis methods would allow us to obtain in-depth information on the degradation processes. In conjunction with computational methods, the kinetics and thermodynamics of thermal degradation can be revealed step by step. The better understanding of the behavior of ILs at high temperatures allows for selective and application-driven tailored design of ILs as well as mathematical prediction of their properties.

It was attempted to predict decomposition temperatures of imidazolium-based EILs. The first simple model was based only on the number of some of atoms in cationic and anionic structures [174]. Later, a suitable correction term was added in the second correlation to adjust the predicted results for the presence of some specific cation/anion moieties. The measured data of 164 different types of imidazolium-based EILs were used to derive the new correlations. The predicted results have confirmed that insertion of a correcting function in the second correlation can provide better accuracy of the estimations. These models were also tested and compared with one of the best available group-contribution methods (where this method can be applied), for 17 additional imidazolium-based EILs containing complex molecular structures.

Rapid-scan FTIR spectroscopy and TOFMS were used to study the thermal decomposition of three imidazolium-based ILs, with Emim as the cation and  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$  as the anions, at heating rates of 2000 K/s and temperatures up to 708 K (435 °C) in an ambient inert gas at 1 atm [175]. The evolution of gas-phase species indicated that the most probable sites for proton transfer and subsequent secondary reactions were primarily the methyl group, and secondarily the ethyl group. The ring appeared to remain intact, as there was no evidence of the formation of HCN, imines, or related products. The nitrate group in [Emim] $\text{NO}_3$  served as a strong oxidizer and reacted strongly with the methyl/ethyl groups at the elevated temperatures to produce combustion products.

Although the following paper deals only with ILs with non-energetic anions, the insight gained about the thermal stability of the cations is also useful for developing other (energetic) ILs. Thermal decomposition of a series of imidazolium-type IL samples was studied by pyrolysis-GC at 823 K (550 °C) [176]. As for the imidazolium halides, haloalkanes and 1-alkylimidazoles corresponding to the alkyl substituents were mainly formed through the nucleophilic attacks of halide ions to the alkyl groups followed by C–N bond cleavage, along with a small number of alkenes. Meanwhile, in the case of the ILs with  $\text{BF}_4$ ,  $\text{PF}_6$ , and  $\text{CF}_3\text{SO}_3$  anions, corresponding alkenes were predominantly produced along with 1-alkylimidazoles rather than haloalkanes. As for the samples with a longer alkyl group, the pyrolyzates reflecting the C–C bond scissions in the alkyl groups were also formed to some extent. Imidazole rings did not split under the experimental conditions at around 823 K (550 °C).

Thermal stability and thermal decomposition kinetics of  $[\text{Bmim}^+][\text{N}(\text{CN})_2^-]$  were investigated using both isothermal and non-isothermal TGA under high pure nitrogen as the carrier gas [177]. The long-term TGA studies revealed that the highest storage temperature should be 383 K = 110 °C, at which  $[\text{Bmim}^+][\text{N}(\text{CN})_2^-]$  lost less than 10% by mass in 10 h. The non-isothermal activation energy was  $147 \pm 2$  kJ/mol.

The maximum operation temperatures (MOT) of the cyano-based ILs, [Emim][DCA], [Bmim][DCA], 1-ethyl-3-methylimidazolium thiocyanate ([Emim][SCN]), [Bmim][SCN], and [Emim][TCM] have been determined using dynamic and isothermal TGA and specific heats from 296.2 to 372.2 K have been measured using DSC [178]. The MOT for [Emim][TCM] was found to be the highest, the MOT for [Emim][DCA], [Bmim][DCA], and [Bmim][SCN] was a little lower, and the [Emim][SCN] MOT was the lowest.

ILs have low vapor pressure and high heats of vaporization, so volatilization of RTILs in a flame front occurs only through thermal decomposition and vaporization of the decomposition products. A useful approach to predict decomposition mechanisms of IL systems is via quasi-classical, direct-dynamics trajectory simulations, where the motion of the molecule is followed, allowing the molecule to show the observer what the preferred reaction pathways are [72]. The direct-dynamics method dispenses with the potential energy surface. Instead, it calculates the energies, force constants, and Hessian equations on the fly using quantum chemistry methods. This method becomes computationally attractive when the dimensionality of the system increases,

particularly for RTILs, which typically contain 10 or more heavy atoms. Dynamics simulations allows the partitioning of the energy generated by exothermic reactions into vibrational, rotational, and translational degrees of freedom, thereby increasing the chance of locating new reaction pathways in the system. Several likely reaction mechanisms in the thermal decomposition of RTILs were identified by this method.

The decomposition pathways and the associated chemical kinetic parameters of energetic ionic salts based on nitrogen-rich heterocycles were studied to simulate their combustion characteristics [179]. The reaction mechanisms of four major families of energetic ionic salts, explored by various experimental and numerical techniques, were reported in detail. Droplets of [MAT][DCA] were acoustically levitated in argon and heated to successively higher temperatures by a carbon dioxide laser [110].

## 5.2 Computational Chemistry of Reactions with ILs

Whenever it becomes too difficult to examine decomposition and combustion reactions in the laboratory, computational chemistry is stepping in and trying to fill this gap of information.

MD simulations based on both electronically non-polarizable and polarizable models have been carried out to investigate the IL 1-hydroxyethyl-4-amino-1,2,4-triazolium nitrate [180]. The intent in this work was to not only provide simulation data but also to provide insight into the relationship between molecular structure, dynamics, and other useful physical properties for this class of ILs. Replacing the ethyl group in 1-ethyl-4-methyl-1,4-imidazolium nitrate by a 2-hydroxyethyl group created an IL with an interwoven network of H-bonds, which was simulated by MD calculations and the predicted glass-transition temperature closely matched that one measured by experiments.

Most borohydride-rich hypergolic ILs were very sensitive to water, but a few special examples displayed good hydrophobicity and remained very stable in air even after a month or more. The reasons behind their hydrolytic stability are unclear. Several calculation methods including ESPs, molecular orbital energy gaps, and interaction energy were used in an attempt to explain the water stability of eight typical borohydride-rich hypergolic ILs [181]. The results demonstrated that negatively charged anions with a high absolute ESP (not extrasensory perception!) values usually reacted more easily with positively charged water. The large molecular orbital energy gap with the BPB<sup>−</sup>, BCNBCN<sup>−</sup>, CTB<sup>−</sup>, and BTB<sup>−</sup> anions was related to the high degree of difficulty of interactions between anions and water, leading to a better hydrolytic stability of borohydride-rich anions. On the other hand, the relatively water-sensitive borohydride-rich anions, BH<sub>4</sub><sup>−</sup> and BH<sub>3</sub>CN<sup>−</sup>, generally had lower interaction energy with water than stable anions such as BPB<sup>−</sup> and BCNBCN<sup>−</sup>. Studies on their stepwise hydrolysis mechanism demonstrated that, in the case of all the reactions, the first step is the rate-determining step and high energy barrier values of anions correspond to good hydrophobicity.

Protonation of the anion in an IL plays a key role in the hypergolic reaction between ILs and oxidizers such as WFNA. The de-protonation energy of a set of cations has been calculated by an *ab initio* computational method to investigate the influence of the cation on the protonation reaction [182]. Specifically, guanidinium, dimethyltriazanium, triethylamine, N-ethyl-N-methyl-pyrrolidinium, N-ethyl-pyridinium, 1,4-dimethyl-1,2,4-triazolium, 1-ethyl-4-methyl-1,2,4-triazolium, and 1-butyl-4-methyl-1,2,4-triazolium were studied. The net proton transfer energy from the cations to a set of previously studied anions was calculated, demonstrating an inverse correlation between the net proton transfer energy and the likelihood that the cation/anion combination will react hypergolically with WFNA.

## 6 Combustion of ILs

### 6.1 Autoignition Temperatures of ILs

On the one hand, we want the autoignition temperature of ILs in air to be very high, in order to improve their safety and handling properties. On the other hand, these liquids may be difficult to ignite in a rocket engine when they are supposed to burn. In order to identify the initiation and secondary reactions in the condensed phase that lead to the ignition and combustion of ILs, and better understand the effects of the structure of the cation on these reactions and the amount of energy needed for ignition, two primary experimental approaches were applied: (1) laser heating coupled with tandem MS and (2) CRT coupled with FTIR and TOF MS [183]. The compounds studied using this method included: 1-ethyl-3-methyl-imidazolium nitrate, 4-amino-1,2,4-triazolium nitrate, 1-methyl, 4-amino-1,2,4-triazolium nitrate, 2-amino-4,5-dimethyl tetrazolium nitrate and 1-amino-4,5-dimethyl tetrazolium nitrate.

ILs have long been labeled and described as “not flammable” due to their low vapor pressures and measured flash points. Although so far (2013) no industrial accident involving an IL has been listed, two recently informally reported laboratory incidents during and just after synthesis of ILs containing a nitrate anion (e.g. EAN) have occurred in the EU. Both these incidents resulted in explosion events, confirming that the explosion hazard of ILs must not be neglected. More frequently, self-sustained or piloted combustion of some ILs has been shown as a potential incident scenario in some experiments. In most cases, rapid exothermic decomposition occurs when ILs with a high nitrogen content are taken to high temperatures and the subsequent decomposition products are sensitive to ignition and combustion. The ignition and combustion of non-propellant, commercially available ILs was tested by means of a fire propagation apparatus [184]. The flammability behavior of ILs is more like that of a polymer than that of a flammable liquid. The main hazard is the toxic fumes that develop during smoldering, oxygen-starved combustion.

The combustion of energetic imidazolium- or hydrazinium-based ILs may tend to be explosive even in a vacuum [185]. Burning tests performed on 4-amino-1-methyl-

1,2,4-triazolium nitrate led to a flame temperature of 2200 K [186, 187]. EILs based on 4-amino-1,2,4-triazole, with 12 different combinations of substituents (alkyl, hydroxyalkyl, methoxyalkyl, allyl, and cyanoalkyl) as cations and nitrate, dinitramide, or perchlorate as anions, were synthesized and their decomposition and combustion reactions were investigated [188].

In some cases, ILs are even combustible by design when they are intended for use as monopropellants as alternatives to hydrazine. Ultimately, once the various molecular bonds reach their thermal decomposition temperature in these carbon-based ILs, smaller and more flammable molecules could be released that lead to combustion similar to polymer combustion. These examples show that traditional flashpoint-type tests are not adequate in most cases to properly characterize the fire hazard. The flashpoint of ILs in relation to their decomposition was investigated by the estimation of vapor pressure and by the use of TGA, DSC, FTIR, and flash point analyzer apparatus [189].

This is related to a finding that ILs do not behave as traditional flammable liquids where the fire results from the combustion of the vapor phase of the concerned chemical. The flammability hazard of ILs must be revisited because they show a burning behavior more closely comparable to that of polymers rather than that of flammable solvents.

The safety of ILs relating to physicochemical hazards is very rarely investigated as it is usually perceived as a non-issue due to the lack of traditional flash points for these liquids. However, it is justified to take a detailed look at the physicochemical properties of ILs in the context of separation and purification technologies, sort out misleading from true general statements regarding their actual safety, discuss physicochemical hazard rating systems and their limitation in the context of overall risk evaluation, in addition to reporting on the early findings of a joint initiative regarding the development of predictive tools for heats of combustion of ILs and the experimental results obtained by pyrolysis combustion flow calorimetry on the effective rate of heat release from ILs in fire conditions [190].

The fundamental flammability properties of IL chemicals were determined through the use of a pyrolysis combustion flow calorimeter and a fire propagation apparatus [191]. Results so far confirmed that the combustibility potential as well as the fire behavior must be assessed on a case-by-case approach, and this is often dictated by the chemical structure of the IL. The study also illustrated how the data obtained characterize the comprehensive physicochemical hazard profiles of ILs.

## 6.2 Suspensions of Fuel Particles in ILs

4-Amino-1-methyl-1,2,4-triazolium dicyanamidate was used as an IL to suspend ball-milled nanoboron particles, creating a fuel with a very high heat of combustion suitable for air-breathing engines [192]. The IL not only suspends the particles during ball-milling, but also protects the freshly formed surface from oxidation which would



otherwise detract from the heat of combustion of the slurry [193]. A typical slurry would contain 10 mass-% boron. It can also be used as a bipropellant fuel with NTO or RFNA as the oxidizer.

The structure of two different EILs and the nature of their binding to elemental boron surfaces were investigated by a combination of X-ray photoelectron and IR spectroscopy, zeta potential measurements, TGA, and calculations based on first-principles theory [194]. It was found that both [MAT][DCA] and [Bmim][DCA] ILs bind to boron well enough to resist removal by ultrasonic washing and protect the boron surface from oxidation during exposure of the washed powder to the air. The data suggested that both the cation and the anion of the ILs interact with the boron surface.

## 7 Safety Properties of ILs

ILs have been advertised as the ultimate safe rocket propellants and battery electrolytes, due to their low or non-existent vapor pressure and flammability. However, some investigators have overlooked the fact that many ILs (including those that are commercially available) are potentially explosive due to the presence of oxidizing ions and the positive enthalpy of formation of the heterocyclic ring compounds [47, 185].

### 7.1 Flammability of ILs

RTILs have been identified as non-volatile, non-flammable compounds with a wide range of applications. However, numerous thermal studies have identified volatile decomposition products and a source for fuel, raising questions regarding the fire hazard of ILs. The flammability properties of imidazolium-based ILs have been measured using cone calorimetry and microscale combustion calorimetry [195]. The combustion data were compared to flashpoints estimated from the TGA data. The resulting flammability properties of ILs were comparable to aliphatic hydrocarbon plastics (polyethylene and polyamide) and were lower than those of high-boiling organic solvents.

### 7.2 Explosive Properties of ILs

Besides the ILs that are being developed as replacements for 1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) and are intended as explosives, some EILs may constitute an unexpected explosive hazard in the laboratory. A batch of the pIL pyrrolidinium nitrate exploded while drying it under reduced pressure at 383 K (110 °C) using a rotary evaporator with an oil bath [47].

## 8 Toxicity of ILs

Many ILs are intended to replace more toxic propellants. They have been described as “green” (i.e. environmentally friendly) propellants. Before ILs are allowed to be widely used with relaxed safety precautions regarding personnel-protective equipment, it would be wise to make sure that there are no hidden, yet unrecognized and unanticipated risks in producing, handling, and disposing of these compounds. Appendix F of a report on environmentally sustainable liquid gas generator formulations [196] contains a summary of the toxicity of candidate propellant ingredients, also published as a separate report [197].

## 9 Environmental Impact of ILs

Byproducts of the synthesis of ILs need to be disposed of in a safe manner, and this may complicate the overall equation of environmental benefits of switching to ILs. For comparison, the only byproduct in the synthesis of hydrazine hydrate by the Raschig method is sodium chloride brine which is easy to dispose of. The synthesis of heterocyclic amines produces a wide array of byproducts which must be disposed of as hazardous materials.

A systematic investigation of the biodegradability of pyrrolidinium-, morpholinium-, piperidinium-, imidazolium-, and pyridinium-based IL cations substituted with different alkyl or functionalized side chains was performed by specific analysis and/or their ultimate biodegradability using biochemical oxygen-demand tests according to the Organisation for Economic Co-operation and Development (OECD) guideline 301F [198]. Biological transformation products were investigated using MS. A comparison of the biodegradation potential of these ILs showed that, for all five compound groups, representatives can be found that are readily or inherently biodegradable, thus permitting the structural design of ILs with a reduced environmental hazard. If spilled in surface waters, most heterocyclic ILs are actually more persistent than hydrazine because they autoxidize more slowly.

The life-cycle environmental impacts of ionic salts and liquids like high-energy materials, propellants, and explosives have not been sufficiently studied. Environmental impacts arise both from the release of these energetic materials themselves as well as from the byproducts of their synthesis. ILs require multi-step synthesis operations and none of the steps operates at 100% yield, leaving byproducts and contaminants along the way which need to be disposed of. A cradle-to-grave life-cycle environmental impact study looked at the production of the energetic ionic salt 1,2,3-triazolium nitrate and compared it to a traditional energetic material, TNT [199]. The results indicated that the production processes of ionic salts may have a significantly higher environmental footprint than conventional energetic materials. The conclusion was the same across all nine impact categories analyzed and can be directly attributed to

the energy-intensive steps needed to prepare ionic salts (liquids) and their precursors. The findings suggested that ionic energetic materials may have a higher environmental impact than TNT from a complete life-cycle perspective.

Motivated by the prevailing need for a sustainable development and taking the principles of *Green Chemistry* as a starting point, conditions regarding a sustainable product design for ILs were reviewed with a focus on environmental risk [200]. Cytotoxicity testing and first indicative results from a genotoxicity study extend the present knowledge, also with regard to the possible effects on humans. The structural variability of commercially available ILs leads to consequences for an integrated risk assessment accompanying the development process of ILs. The side-chain effect on toxicity for imidazolium-type ILs required more complex biological testing. Also, the influence of anions on cytotoxicity was examined for the first time. Testing of presumed metabolites of the imidazolium-type cations showed a significantly lower biological activity in cytotoxicity studies than their parent compounds. In addition to the risk analysis, a life-cycle analysis for the multi-objective problem of designing ILs was described and an eco-friendly design scheme for ILs was proposed.

ILs were initially proposed as replacements for conventional organic solvents. However, their chemistry and range of applications has expanded remarkably and offers unexpected opportunities in numerous fields, ranging from electrochemistry to biology and rocket propulsion. As a consequence of ILs advancing towards potential and actual applications, a comprehensive determination of their environmental, health, and safety impacts is now required. A critical review aimed to present an overview of the current understanding of the toxicity and environmental impact of the principal IL groups, and it highlighted some emerging concerns [201]. Each cation type was considered separately, examining the significance of the biological data, and identifying the most critical questions, some yet unresolved. The need for more studies, and greater detail, was emphasized.

## 10 ILs as Rocket Propellants

ILs are an exciting class of compounds with unique properties that make them attractive for many industrial applications. Among their valuable features, an immeasurably low vapor pressure and a liquid state at or near-ambient room temperature conditions are of interest to the rocket propellant chemist. For a rocket propellant chemist, EILs can be divided into two categories: potential bipropellant fuels (hypergolic systems) and monopropellants (self-oxidizing systems). The first category encompasses a wide range of cations, from N-rich ammonium and hydrazinium, to tetrazolium and other cationic *N*-heteroaromatic rings as well as various anions, such as nitro- and cyano-containing or borohydride-based anions. The energetic behavior of such bipropellant fuels requires a reaction with a liquid oxidizer. The second category consists of an ionic pair made up of a combustible N-rich cation with an oxidizing acid anion, which

make these EILs stoichiometrically oxygen-balanced (or nearly oxygen-balanced) and prone to self-oxidation.

The research on EILs typically involves aliphatic or heterocyclic amines as the cation. For aliphatic amines, the cation may be formed from 1,2-bis(oxyamine)-ethane, 1,2-bis(oxyamine)propane, or dimethyl(azidoethyl)amine. For heterocyclic amines, imidazolium, triazolium, or tetrazolium cations are combined with DCA, tetrazolate, or other anions to make fuels and oxidizing acids (nitrate, perchlorate, trinitromethide, and dinitramide) for monopropellants and explosives [202]. Many are salts which are liquids at room temperature and are being evaluated as monopropellants by themselves (if they have nitrate or perchlorate ions), as fuels for HAN- or hydroxylammonium perchlorate (HAP)-based monopropellants, as replacements for monomethylhydrazine (MMH) as a hypergolic fuel in bipropellant combinations, and as working fluids for colloid thrusters [81, 171, 203–206]. EILs with a high nitrogen content offer several potential advantages over traditional monopropellants such as hydrazine and storable fuels such as methylhydrazine. These are the types of ILs and propellants discussed here. A logical approach to achieve targeted combinations of physical and chemical properties by tuning the selection of the cation and anion independently is described in [207]. This publication, with 80 references, contains sections on triazolium-based ionic salts, tetrazole-based, urotropinium-based, tetrazine-based, azetidinium-based, picrate-based, and imidazolium-based salts as well as polynitrogen compound-containing salts. However, most of these have melting points above 373 K (100 °C) and are not in the category of ILs. Another good survey paper is [208]. Both publications offer very good summaries of energetic ionic solids and liquids including work done through 2006.

Other publications, mostly collections of presentation charts, are useful introductions to the study of ILs as rocket propellants, describing early advances of this technology, providing updates on the current status of the research, and outlining targets for future exploration [209–212]. A summary review with 26 references of IL rocket propellant work done by the Shreeve group in Idaho and others was published in 2013 and is a good survey and status report as of that year [213].

An excellent summary in the field of EILs with 98 references was published in 2014 [3]. This is a good introduction and explains that the intrinsic properties of ILs, e.g. low vapor pressures, high thermal stabilities, and low melting points, make them ideal candidates for minimizing or even eliminating the hazardous conditions associated with handling, processing, and transporting conventional storable rocket propellants. In order to achieve low melting points, ILs make use of bulky, asymmetric, poorly packing ions to lower their lattice energy. Favorite choices are quaternary ammonium and *N*-heteroaromatic cations. The *N*-heteroaromatic ions have been found to be energetic when combined with appropriate counter-ions. This arises from the numerous energetic N–N and C–N bonds which lead to high heats of formation.

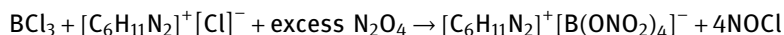
IL rocket propellant development projects are in progress in many countries in the world, including Germany, France [214], Russia, Japan, and China [215].

## 11 ILs as Monopropellants

Historically, most anions paired with IL cations were either non-oxidizing ( $\text{BF}_4^-$  and  $\text{PF}_6^-$ ) or moderately oxidizing ( $\text{NO}_3^-$  and  $\text{ClO}_4^-$ ) anions carrying insufficient oxygen to achieve complete combustion of the organic skeleton and appending alkyl groups. Searching for anions that carry sufficient oxygen to achieve complete combustion to carbon monoxide, carbon dioxide, nitrogen, and water has led to the identifications of polynitrato or polyperchlorato complex anions with very high oxygen contents.

While most ILs are underoxidized with a negative oxygen balance, making them more useful as fuels in bipropellants than as monopropellants in their own right, combining a heterocyclic cation with an oxygen-rich anion like tetranitratoaluminate can create oxygen-balanced ILs and potential IL monopropellants where one does not have to mix water-soluble oxidizers and fuels. One of the first oxygen-balanced ILs in this category was 1-ethyl-4,5-dimethyltetrazolium tetranitratoaluminate [86, 87]. In this IL molecule, the tetranitratoaluminate anion contains 12 oxygen atoms; of these, 10.5 are available to oxidize a fuel cation. A 1-ethyl-4,5-dimethyltetrazolium cation was chosen because of its positive enthalpy of formation and ability to form an RTIL with the tetranitratoaluminate anion. The resulting energetic salt is a colorless liquid at room temperature. Its spontaneous ignition temperature is 473 K (200 °C).

One of the EILs is described in a patent [216]. One of the examples listed in this patent is Emim tetranitratoborate,  $[\text{C}_6\text{H}_{11}\text{N}_2][\text{B}(\text{ONO}_2)_4]$ , which can be prepared in a one-step process through the reaction of Emim chloride, boron trichloride, and excess dinitrogen tetroxide.



The products of the reaction are easily separated, because nitrosyl chloride is highly volatile and easily removed from the desired reaction product, which, as an IL, has essentially no vapor pressure. Other oxygen-rich anions proposed for such propellants are  $\text{P}(\text{ONO}_2)_6^-$ ,  $\text{B}(\text{OCIO}_3)_4^-$ ,  $\text{Al}(\text{OCIO}_3)_4^-$ , and  $\text{Ti}(\text{ONO}_2)_5^-$ .

HEHN is an IL that does not readily crystallize at room temperature. Solutions of HEHN can be decomposed on Shell 405 catalysts [217, 218]. The 2-HEH dinitrate reacts with Shell 405 catalysts in a similar fashion. HEHN has also been considered and tested as a bipropellant fuel in combination with RFNA, NTO, or 98% HTP [219].

It is difficult to see anything novel in a 2014 patent claiming an EIL catalytic decomposition gas generator using stoichiometric and non-stoichiometric mixtures of EILs and iridium catalysts [220]. One of the monopropellants claimed is a mixture of 2-HEHN and 2-HEH dinitrate. Virtually all aspects of this patent have been described in the open literature, in particular 2-HEHN has been patented as a fuel in monopropellants with iridium catalysts and is described in previous articles [221].

A dual-mode spacecraft might use monopropellants for high-thrust maneuvers and electrical propulsion for low-thrust, long burn-time maneuvers. Imidazole-based

ILs were investigated in terms of dual-mode chemical monopropellant and electro-spray rocket propulsion capabilities [222]. The ILs [C4mim][DCA], C4mim nitrate, and Emim ethylsulfate meet or exceed the storability properties of hydrazine, and their electrochemical properties indicate that they may be capable of electro-spray emission in the purely ionic regime. These liquids were projected to have a 13–23% reduced monopropellant propulsion performance in comparison to hydrazine due to the prediction of solid carbon formation in the exhaust. The use of these ILs as a fuel component in a binary monopropellant mixture with HAN would deliver a 1–4% improved  $I_{sp}$  over some other “green” monopropellants. Also, this avoids volatility issues and reduces the number of electro-spray emitters by 18–27% and the power required by 9–16%, with oxidizing IL fuels providing the greatest savings. A fully oxygen-balanced IL will exceed the state-of-the-art performance in both modes but will require advances in hardware technology in both modes to achieve minimum functionality and meet mission-life requirements.

The high combustion temperature of IL monopropellants make the use of typical ignition catalyst beds prohibitive, since conventional catalysts cannot withstand the elevated temperatures. Laboratory studies were conducted using alternative ignition techniques such as laser-induced-spark ignition and hot-wire ignition [223]. Ignition delay, defined as the time between the introduction of the ignition source and the first sign of light emission from a developing flame kernel, can be measured using Schlieren visualization. An optically accessible, liquid monopropellant burner was planned to be used to determine propellant burn rates as a function of pressure and initial propellant temperature via high-speed imaging through the chamber’s windows.

In an effort to find less-toxic monopropellants as replacements for hydrazine and less sensitive and with lower combustion chamber temperatures than AF-M315E, material candidates based on ILs were evaluated as possible hydrazine replacements [196]. The target combustion chamber temperature was <1450 K. The target viscosity was <1000 cPs. The program evaluated cations from the triazole, tetrazole, pyrimidinium, hydrazide, and imidazole family, and the perchlorate, dinitramide, and nitrate anions. Initial evaluations examined the performance, sensitivity, catalytic response, thermal stability, and toxicity of each candidate. Overall, the triazoles and hydrazides exhibited acceptable properties. Both candidate families exhibited good ignition, enthalpy of formation, and reactivity. The imidazoles were the first to be eliminated from further evaluations due to poor performance. The tetrazoles were eliminated due to insufficient thermal stability and the pyrimidium salts due to poor catalytic ignition. Nitrates were determined as the only acceptable cation. Perchlorates were eliminated due to environmental concerns (HCl in the exhaust) while dinitramides exhibited an unacceptably low onset of exotherm temperatures. The 1-methyl-4-amino-1,2,4-triazolium nitrate candidate was selected because of its good performance. A carbohydrazinium nitrate formulation was selected because of

its high performance and the commercial availability and low cost of carbohydrazide. A diluted AF-M315 formulation was included due to its high maturity level and ability to meet the targeted flame temperature requirement. Candidate fuel ingredients were selected from a list of 51 chemicals, many of these being ILs. Theoretical rocket performance and combustion chamber temperatures were calculated for HAN/H<sub>2</sub>O in combination with 36 of these fuels. HEHN was included as a baseline. A new propellant formulation contained HAN and 1-(2-hydroxyethyl)-4-amino-1,2,4-triazolium nitrate. Rocket engine test results with four of these new monopropellants will be discussed in *Encyclopedia of Monopropellants*.

Multi-mode space propulsion systems are being proposed that combine high- $I_{sp}$  electric propulsion and high-thrust chemical propulsion. The most important attribute of this concept is a shared propellant feed system capable of both modes of propulsion, which adds to mission flexibility. One promising approach is a catalytic monopropellant thruster paired with an electrospray electric thruster. Previous research has identified an IL consisting of 41 mass-% Emim ethyl sulfate and 59% HAN as a promising propellant candidate. The burn rate of this monopropellant was measured through pressure-based and high-speed imaging methods in a fixed-volume chamber at pressures from 0.5 to 10 MPa [224, 225]. The burn rate of the multi-mode monopropellant was found to follow an exponential law given by

$$r_b = 5.35P^{1.11}$$

between 0.5 and 3 MPa, and it was approximately constant at  $142 \pm 29$  mm/s between 3 and 10 MPa.

During the discussion of HAN-based monopropellants with ionized fuels (fuel salts), we already pointed out that these solutions have unique properties which place them in the category of ILs, in particular if they are formulated without any water. HAN and many nitrate salts form low-melting eutectics which can be described as ILs.

Otherwise, the research on EILs typically involves triazolium or imidazolium salts which are liquids at room temperature and are being evaluated as monopropellants by themselves (if they have nitrate, dinitramide, or perchlorate ions), as fuels for HAN- or HAP-based monopropellants, and as working fluids for colloid thrusters. EILs with a high nitrogen content offer several potential advantages over traditional monopropellants like hydrazine. These are the types of propellants (all those not using HAN) discussed here. ILs as monopropellants can be decomposed on platinum group-supported catalysts similar to those used for hydrazine or ADN- or HAN-based monopropellants [226].

## 12 ILs as Hypergolic Fuels

Initially, much of the work on EILs was on heterocyclic cations in combination with oxygenated anions such as nitrate or perchlorate, which frequently had stability and safety problems. ILs can also be used as low-volatility, low-toxicity fuels in hypergolic or non-hypergolic bipropellant combinations.

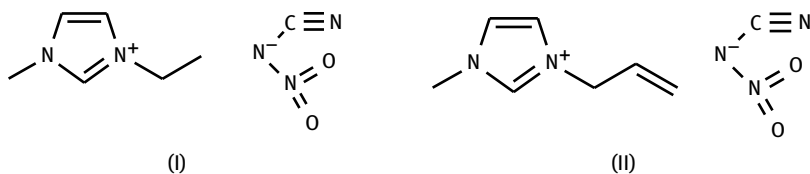
In a bipropellant system with ILs used as fuels, it is not necessary to use an oxygen-balanced IL. One can avoid oxygen-carrying anions completely, which, other things being equal, should make handling much safer because the fuel and the oxidizer are chemically and physically separated. In an ionic salt system, the positive charge of the cation makes it more resistant toward oxidation. Consequently, electron- and fuel-rich anions are much easier to oxidize and thus would seem to hold the potential to promote hypergolic ignition.

Because the ILs are very viscous, it is difficult to achieve complete mixing of IL hypergolic fuels with the oxidizers, for instance WFNA, NTO, or HTP. Even more difficult would be to achieve mixing between an IL fuel and an IL oxidizer and get them to ignite hypergolically without a significant ignition delay and ignition pressure spike. The first attempts to achieve hypergolic ignition with WFNA or RFNA and ILs were not very encouraging, but led the way to substantial improvements in shortening the ignition delay [227].

The basic molecule design strategy to make hypergolic ILs is to incorporate reactivity in the cation and/or anion through the incorporation of chemical bonds known to induce a hypergolic reaction with common oxidizers, such as the  $\text{N}-\text{C}\equiv\text{N}$  bond, e.g. in  $[\text{DCA}]^-$ , or  $\text{B}-\text{H}$  bonds, e.g. the  $[\text{B}(\text{CN})_2\text{H}_2]^-$  anion or the boronium cation [228]. Even with this designed reactivity, many other physical and chemical properties, such as viscosity or density, play a large role in the mixing, ignition, and combustion processes that occur upon contact. It is hard to predict which cations should be paired with already-known hypergolic anions and whether the modified physical properties or the introduced functional groups can take the credit for any enhanced reactivity.

One of the few hypergolic ILs derived from an aliphatic amine instead of a heterocyclic amine is 2-azidoethyltrimethylammonium nitrocyanamidate [229]. Its ignition delay with WFNA was of the order of 8 ms, equal to that of MMH. Another IL, bis(2-azidoethyl)dimethylammonium DCA, also gave a useful IL hypergolic fuel with an ignition delay of 20 ms. One azido group can add approximately 280 kJ/mol to the heat of formation of a molecule. In contrast, in the absence of azide functional groups, some imidazolium ILs, based on the nitrocyanamidate anion only, displayed relatively longer ignition delay times (e.g. 78 ms for 1-methyl-3-ethylimidazolium nitrocyanamidate **(I)** and 46 ms for 1-methyl-3-acrylimidazolium nitrocyanamidate **(II)**) [112].





Although both hypergolic ILs (**I** and **II**) are liquids at room temperature and also exhibited relatively low viscosities (23 and 44 cPs at 298 K = 25 °C, respectively), their long ignition delay time (>45 ms) significantly decreased their practical application potentials as hypergolic fuels.

ILs previously proposed as hypergolic fuels for the replacement of hydrazine, MMH, or UDMH must have low volatility and favorable fluid transport properties. While many IL-forming anions {e.g., azide  $[\text{N}_3]^-$ , dicyanamidate  $[\text{N}(\text{CN})_2]^-$ , nitrocyanamidate  $[\text{N}(\text{CN})(\text{NO}_2)]^-$ , and dicyanoborohydride  $[\text{B}(\text{CN})_2\text{H}_2]^-$ } have been shown to be hypergolic with nitric acid or hydrogen peroxide, many other practical properties must also be considered in the design of hydrazine replacements.

*N,N*-Dimethylhydrazinium DCA and nitrocyanamide ILs were prepared by quaternization of UDMH with alkyl halides, followed by metathesis reactions with silver DCA or silver nitrocyanamide, and then evaluated as hypergolic fuels [230]. The key physicochemical properties, such as melting point and decomposition temperatures, density, viscosity, heat of formation, detonation pressure and velocity, and  $I_{\text{sp}}$  were measured or calculated. Spot plate droplet tests with WFNA as an oxidizer showed that the 14 new *N,N*-dimethylhydrazinium salts are hypergolic, with ignition delay times ranging from 22 to 1642 ms, suggesting that some may have potential as non-volatile bipropellant fuels.

Fourteen different ionic salts were prepared with tetramethylguanidinium, alkyl- and amino-1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and alkyl-1,5-diazabicyclo[4.3.0]non-5-ene (DBN) as the cations, and DCA and cyanoborate as anions, characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and IR spectroscopy, and HR-MS, and evaluated as hypergolic fuels [231]. Their physicochemical properties such as thermal properties, density, viscosity, heats of formation,  $I_{\text{sp}}$ , and ignition delay time were characterized or calculated. Among the 14 new organic ionic materials, 11 salts were liquids at room temperature, and all exhibited good thermal stability. The densities of these ionic compounds ranged from 1.00 to 1.22 g/cm<sup>3</sup>, and their enthalpies of formation varied between -38.0 and +478.6 kJ/mol. Surprisingly, most of these new ILs exhibited an unexpected high thermal stability of >280 °C. These novel IL materials had extremely low vapor pressures, short ignition delay times upon contact with WFNA, and high thermal stability. See also [232–235].

Chemists worldwide have been motivated to develop alternative, environmentally friendly hypergolic IL propellants as fuels. Anions of these salts, which include DCA, dicyanoborate, cyanoborate, azide, nitrate, aluminum borohydride, nitrocyanamide, etc., appear to play the major role in determining hypergolic ignition properties. Although cations play a lesser role, they are most frequently nitrogen-containing

alkyl and heterocyclic species, e.g. substituted alkyl ammonium, imidazolium, imidazolium-substituted compounds with alkyl, vinyl, or propargyl groups [236].

A report on methods for predicting hypergolic-mixture flammability limits contains a good historical summary of ILs as hypergolic fuels their thermodynamic properties and flammabilities, and predicted flame temperatures when in contact with various oxidizers [237].

The previous section discussed ILs as hypergolic fuels for bipropellant combinations without narrowing the discussion down to a specific group of cations or anions. The following sections deal with ILs as hypergolic fuels where the cation and/or the anion are identified. The ultimate goal would be to not only replace toxic fuels with less toxic IL hypergolic fuels, but to replace both conventional hypergolic fuels and oxidizers with ILs that have very low vapor pressures [238].

## 12.1 ILs as Hypergolic Fuels, Sorted by Cations

The structures of heterocyclic ring amines with various substituents attached to the ring determine the ignition delays of various ionic liquids with oxidizers like WFNA, RFNA, or HTP. Substituents with unsaturated alkyl groups attached to a ring structure like imidazole make good hypergolic fuels [228, 239].

### 12.1.1 IL Hypergolic Fuels Derived from Ethylenediamine

Four energetic salts (including two ILs), based on 2-(dimethylamino)-*N,N,N*-trimethylethanaminium and *N,N'*-dialkyl-*N,N,N',N'*-tetramethylethane-1,2-diaminium, were prepared and characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, IR, and Raman spectroscopy, and elemental analysis, melting and decomposition temperatures, density, viscosity, enthalpy of formation, detonation performance, and  $I_{\text{sp}}$  [25]. With thermal stability up to 473 K (200 °C), the resulting ILs showed densities from 1.02 to 1.19 g/cm<sup>3</sup> and heats of formation from +85.1 to +154.4 kJ/mol. The IL-2-(dimethylamino)-*N,N,N*-trimethylethanaminium DCA is hypergolic with WFNA and exhibited good potential as a green fuel for bipropellant combinations.

### 12.1.2 IL Hypergolic Fuels Derived from Imidazole

Alkylimidazolium bromides are useful precursors for the synthesis of EILs by metathetical reactions with silver nitrate, DCA, nitrocyanamide, or perchlorate [240].

The hypergolic reactions of 1[Amim][DCA], [Emim][DCA], and [Bmim][DCA] with nitric acid were investigated [241]. [Amim][DCA] was characterized by DSC, TGA, and density. Rheological measurements were performed on pure and gelled [Amim][DCA] with silicon dioxide nanoparticles. The enthalpy of formation was calculated from the heat of combustion and the performance with nitric acid was calculated. The calculated results for ILs were compared to MMH and UDMH, which they are intended to replace. The mass-specific impulse of [Amim][DCA] is lower than that of MMH and

UDMH. However, the volume-specific impulse of [Amim][DCA] is higher than that of the traditional hypergolic fuels.

DCA-based ILs containing mono- and dicationic counterparts were synthesized and characterized [242]. The physical properties of these salts, including thermal stability, melting point, density, and viscosity, are highly dependent on the structure of the cation and the type of anion. Spot plate droplet tests were used to investigate the hypergolic properties of these ILs. All of the synthesized compounds showed hypergolic activity upon contact with WFNA.

A QSPR modeling method was developed for predicting the ignition delay time of 31 hypergolic imidazolium IL derivatives with WFNA as the oxidizer [243]. Chemical structures of these ILs were encoded into several sets of molecular descriptors, representing various physical and chemical properties of these molecules. A total of 1447 molecular descriptors with different types (e.g. constitutional, functional group counts, and geometrical descriptors) were selected and calculated. A combination of stepwise and best-subset regression approaches was used to determine the molecular descriptors which have the strongest influences on the ignition delay time of hypergolic imidazolium IL derivatives. The derived model displayed a good predictive ability, arising from the determination coefficient corresponding to the leave-one-out cross-validation technique. The predictive power of the proposed method was evaluated using several different techniques and this method can be used as a reliable tool for designing improved hypergolic ILs.

A new set of synthesized ILs combined the advantages of conventional rocket propellants with the energy characteristics of acetylene derivatives [244]. N-alkylated imidazoles (alkyl = ethyl, butyl) have been synthesized and alkylated with propargyl bromide followed by metathesis using silver DCA. Modified hypergolic drop tests of N-ethyl (IL-1) and N-butyl propargylimidazolium (IL-2) ILs with WFNA were performed using high-speed shadowgraph imaging to visualize the ignition process. The temperature rise due to ignition was monitored with a 2-color photodetector. It was shown that the ignition delay was shorter for IL-1 than for IL-2. The ignition of IL-1 occurred in two stages, whereas the combustion of IL-2 proceeded smoothly without secondary flashes.

The anions  $\text{DCA}^-$ ,  $\text{CBH}^-$  and cations  $\text{Emim}^+$  and  $\text{Amim}^+$  were mixed in different ratios to form hypergolic ionic mixtures and their viscosity, density, decomposition temperature, and  $I_{\text{sp}}$  were determined and calculated [245]. Ignition delay times were measured by a spot plate drop test recorded by a high-speed camera. The results indicated that ionic nature and ionic ratio were two decisive factors for the properties of ionic mixtures. Specifically, mixture [Emim][CBH]0.7[DCA]0.3 possessed the shortest ignition delay time of 3 ms with WFNA as the oxidizer, which was shorter than that of pure IL [Emim][DCA] (32 ms) or [Emim][CBH] (8 ms) alone. However, with a reverse ratio of anions, the mixture [Emim][CBH]0.3[DCA]0.7 possessed a very long ignition delay time of 373 ms and showed a different phenomenon in the ignition process. TGA indicated that mixture [Emim][CBH]0.7[DCA]0.3 decomposed faster than mixture [Emim][CBH]0.3[DCA]0.7. As a new design strategy, hypergolic IL mixtures

can not only combine properties of different ions, but can also show a more favorable performance in a specific ionic ratio than each parent IL by itself.

Three hypergolic ILs, from the cation Amim combined with the DCA, CBH, or SCN anions, were prepared and evaluated as hypergolic fuels [228]. Their viscosity, density, melting point, energy properties, and  $I_{sp}$  were measured and calculated. A hypergolicity evaluation scheme was established to predict the hypergolicity and guide the design of new hypergolic ILs. See also [246].

### 12.1.3 IL Hypergolic Fuels Derived from Triazole

Bipropellant ILs that react hypergolically with WFNA were tested to gain a fundamental understanding of the ignition of EILs with WFNA [247]. The effects of cation and anion structure on initiation reactions, and the subsequent reactions leading to ignition for representative compounds in three classes of compounds (amino-1,2,4 triazoles, amino-1,2,3-triazoles, and amino-tetrazoles) were investigated. Thermal decomposition of the EILs, 1-methyl-4-amino-1,2,4-triazolium nitrate and 1-amino-3-methyl-1,2,3-triazolium nitrate, was studied by CRT. In the FTIR spectrum of species from CRT of 1-methyl-4-amino-1,2,4-triazolium nitrate at 593 K (320 °C) and 1 atm, nitric acid with several rovibrational bands from 1700 to 800  $\text{cm}^{-1}$  and an overtone above 3500  $\text{cm}^{-1}$ , was immediately discernable as a major species. The other major species detected were  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and  $\text{CO}_2$ . Also identified were small quantities of isocyanic acid (HNCO) and HCN. In order to explain the effects of substituents, the decomposition products and their temporal evolution over a range of temperatures were analyzed.

### 12.1.4 IL Hypergolic Fuels Derived from Tetrazole

A series of hypergolic (2-methyltetrazol-5-yl)diazotates have been synthesized by treatment of ammonia, hydrazine, guanidine, aminoguanidine, diaminoguanidine, and triaminoguanidine with (2-methyltetrazol-5-yl)diazotatic acid [248]. The melting points of these salts were between 98 and 194 °C, so they are not ILs. These energetic salts showed remarkably short ignition delay times by droplet test with WFNA. All compounds were fully characterized using IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy, DSC and, in the case of aminoguanidinium (2-methyltetrazol-5-yl)diazotate and diaminoguanidinium (2-methyltetrazol-5-yl)diazotate, single-crystal XRD.

### 12.1.5 IL Hypergolic Fuels with Boron-Containing Cations

Two series of boronium-cation-based ILs were prepared and characterized by  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{11}\text{B}$ -NMR and IR spectroscopy, DSC, and elemental analysis [249]. The structure of bis(1-methyl-1*H*-imidazole-3-yl)dihydroboroniumdicyanoborohydride (5a) was determined by single-crystal XRD. The densities of these ILs ranged from 1.05 to 1.28  $\text{g}/\text{cm}^3$ , and the enthalpies of formation, predicted on the basis of Gaussian 03 calculations, were between -164.6 and +430.5 kJ/mol. Bis(1-allyl-1*H*-imidazole-3-

yl)dihydroboroniumdicyanoborohydride exhibited the lowest viscosity (35 mPa s) and shortest ignition delay time (14 ms) when in combination with WFNA.

Hypergolic ILs based on the [imidazolyl–amine–BH<sub>2</sub>]<sup>+</sup> cation combined with fuel-rich anions, such as the N(CN)<sub>2</sub><sup>−</sup> and BH<sub>3</sub>CN<sup>−</sup> anions, were synthesized and characterized. As expected, all of the ILs exhibited spontaneous combustion upon contact with WFNA. The densities of these ILs varied from 0.99 to 1.12 g/cm<sup>3</sup>, and the enthalpies of formation, predicted based on Gaussian 09 calculations, were between −707.7 and +241.8 kJ/mol. 1-Allyl-1*H*-imidazole-3-yl-(trimethylamine)-dihydroboronium DCA exhibited the lowest viscosity (168 MPa s), good thermal properties ( $T_g < 203\text{ K} = < -70\text{ }^\circ\text{C}$ ,  $T_{dec} > 403\text{ K} = > 130\text{ }^\circ\text{C}$ ), and the shortest ignition delay time (18 ms) with WFNA [250–252].

Boronium cation-based ILs exhibited relatively low viscosities and short ignition delay times in combination with WFNA [249]. Two series of boronium cation-based ILs were prepared and fully characterized by <sup>1</sup>H-, <sup>13</sup>C- and <sup>11</sup>B-NMR and IR spectroscopy, DSC, and elemental analysis. The structure of bis(1-methyl-1*H*-imidazole-3-yl)dihydroboronium dicyanoborohydride was determined by single-crystal XRD. The densities of these ILs ranged from 1.05 to 1.28 g/cm<sup>3</sup>, and the heats of formation, predicted on the basis of Gaussian 03 calculations, were predicted to be between −164.6 and +430.5 kJ/mol. Bis(1-allyl-1*H*-imidazole-3-yl)dihydroboronium dicyanoborohydride exhibited the lowest viscosity (35 mPa s) and shortest ignition delay time (14 ms) in combination with 100% HNO<sub>3</sub>. It had a melting point of less than 193 K (−80 °C), a low viscosity of 35 MPa s at 298 K (25 °C), and its ignition delay time was 14 ms when WFNA was used as the oxidizer. In this hypergolic salt, both the boronium cation and the dicyanoborate anion contain two B–H bonds, which is probably an important contributor to the hypergolicity of this IL. See also [253].

Phosphorus is common in pyrotechnic igniters, but is not a preferred element to have in rocket propellants. ILs with bis(borano)hypophosphite anions [254] or boranophosphate ions [255] are hypergolic with WFNA or HTP.

## 12.2 ILs as Hypergolic Fuels, Sorted by Anions

The hypergolic activity of ILs with NTO, RFNA, or WFNA, or even HTP is usually determined by the type of the more mobile anion than by the asymmetric cation. The following section provides a listing of candidate hypergolic fuels arranged by the common anion.

### 12.2.1 ILs with DCA Anions as Hypergolic Fuels

[Bmim][DCA], CAS RN [44824-52-1], is a potential hypergolic fuel for bipropellant engines [99, 151]. Its density at 297 K (24 °C) is 1.0580 g/cm<sup>3</sup> and at 355.8 K (82.7 °C) it is 1.0258 g/cm<sup>3</sup>. It has a glass-transition temperature of 183 K (−90 °C) and a melting point of 267 K (−6 °C).

The patent literature describes numerous hypergolic bipropellants formed by combining an IL fuel having a DCA anion and a nitrogen-containing heterocyclic cation, with a liquid oxidizer, more specifically, an IL fuel that contains at least one DCA anion and a nitrogen-containing heterocyclic-based cation selected from the group comprising imidazolium, triazolium, pyrrolidinium, pyridinium, and tetrazolium [256].

The Air Force Research Laboratory (AFRL) conducted a program to develop the capacity to experimentally determine and theoretically validate hypergolic ignition mechanisms in ILs, to provide a roster of hypergolicity of hydrazine, MMH, and triazolium IL–oxidizer pairs, to provide ignition mechanisms for a reference set of IL–oxidizer reactions with time-resolved spectroscopic techniques, theoretically validate predictions for experimental results, and develop a predictive model to suggest targets for future development and screening for IL synthesis candidates [209, 257].

In order to more accurately measure ignition delays with IL fuels in comparison to other hypergolic fuels, the AFRL developed an ignition delay tester using a line-of-sight electro-optical circuitry with a direct digital readout and an additional oscilloscope recording that can be used to measure total ignition and chemical delay times for screening candidate fuels [258]. A falling drop interrupts a light beam and starts a counter. A photodiode detects the first flash of light and stops the counter. The use of a 1-MHz time base gives the chemical delay directly in microseconds upon subtraction of counter 1 from counter 2. The ignition delay of WFNA/MMH measured for comparison was 14.7 ms, but ignition delays of WFNA with IL fuels were substantially longer. The properties of six imidazolium DCA salts with different alkyl group substituents are summarized in Table 3.

**Table 3:** Properties of 3-methylimidazolium DCA salts with different alkyl group substituents

| 1-R-3-methylimidazolium           | Glass temperature |     | Melting point |     | Decomposition onset |      | Viscosity at 298 K (25 °C) | Ignition delay, ms |      |
|-----------------------------------|-------------------|-----|---------------|-----|---------------------|------|----------------------------|--------------------|------|
|                                   | K                 | °C  | K             | °C  | K                   | °C   |                            | IRFNA              | WFNA |
| 1-allyl-                          | 188               | –85 | —             | —   | 480                 | +207 | 42                         | 625                | 43   |
| 1-(3-butenyl)-                    | 183               | –90 | —             | —   | 483                 | +210 | 27                         | 670                | —    |
| 1-propargyl-                      | 212               | –61 | 290           | +17 | 417                 | +144 | 110                        | 170                | 15   |
| 1-(2-butenyl)-                    | —                 | —   | 322           | +49 | 452                 | +179 | —                          | —                  | —    |
| 1-(2-pentenyl)-                   | —                 | —   | 332           | +59 | 457                 | +184 | —                          | —                  | —    |
| 1-methyl-4-amino-1,2,4-triazolium | 207               | –66 | —             | —   | 416                 | +143 | 92                         | —                  | —    |

Data sources: [92, 259, 260]

An investigation was conducted to study the hypergolicity of selected DCAs, e.g. commercially available [Bmim][DCA], and the AFRL developed AF-IL-617, with common oxidizers [261]. Diluents, particularly water and methanol, were introduced into the

fuel in an effort to understand the effect of dilution on the ignition delay. The water dilution limit at which ignition would still occur was obtained for the two DCA-based fuels with WFNA. Controlled droplet experiments were conducted with high-speed photography at 1040 frames/s to establish the ignition delays. A single run consisted of dispensing a small droplet of fuel into a cuvette with typically 250 or 500  $\mu\text{L}$  of oxidizer. The bulk of the testing focused upon two work-horse DCA-based fuels: [Bmim][DCA] (BMIMDCA) and AF-IL-617. BMIMDCA is commercially available, and AF-IL-617 was developed in-house at the AFRL. The oxidizers of interest were WFNA, HAN, S-HAN-5, dinitrogen tetroxide, and 93% hydrogen peroxide. The experiment utilized a syringe pump with a 10- $\mu\text{L}$ , glass hypodermic syringe to dispense the fuel droplet into the pool of oxidizer in a cuvette 4.6 cm below. The drop test was recorded at 1040 frames/s with a monochrome high-speed digital camera.

A new class of RTILs that can ignite hypergolically with WFNA was tested [97, 98]. Fast ignition of DCA ILs when mixed with nitric acid was different from the reactivity of the IL azides, which showed high reactivity with nitric acid, but did not ignite. Rapid-scan FTIR spectroscopy of the pre-ignition phase indicated the evolution of  $\text{N}_2\text{O}$  from both the DCA and azide RTILs. There was evidence for the evolution of  $\text{CO}_2$  and  $\text{HNCO}$  with similar temporal behavior to  $\text{N}_2\text{O}$  from reaction of the DCA ILs with nitric acid. Evolution of  $\text{HN}_3$  was detected from the azides. No evolution of  $\text{HCN}$  from the DCA reactions was detected. From the FTIR observations, biuret reaction tests, and *ab initio* calculations, a mechanism was proposed for the formation of  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{HNCO}$  from the DCA reactions during pre-ignition. For the DCA-based ILs, the anion is responsible for inducing the ignition, while the cation may play only a secondary role in influencing the ignition delay time.

IL hypergolic fuels are already safer than many of the hypergolic fuels they are intended to replace, but they are still liquids that can leak. To make the fuels even safer and leak-proof, they can be gelled. Unfortunately, the increased viscosity causes longer ignition delays. The spray formation, atomization, mixing, and hypergolic ignition of gelled IL and the ignition of liquid and gelled methylethyl imidazolium DCA with nitric acid were tested [262, 263]. Sprays of propellant ignited in an ambient-pressure, optically accessible chamber, and high-speed video and optical sensors provided data on the speed of ignition events.

ILs derived from combinations of alkylammonium, hydrazinium, guanidinium, and hydrazidinium cations with DCA anions were tested for their reactivity toward hypergolic oxidizers [41]. This particular publication is a very thorough description of synthesis efforts to develop IL hypergolic fuels, with 47 literature references. For synthesizing a combustible IL with fuel qualities, the frequently used anions, nitrate, perchlorate, or dinitramide, had to be replaced with a combustible anion like DCA ( $\text{N}\equiv\text{C}$ ) $_2\text{N}^-$ . In looking for alkyl groups in alkylamines that are likely to react hypergolically with WFNA, a variety of primary, secondary and tertiary amines with alkenyl (vinyl or acryl) or alkynyl (propargyl) groups were prepared and their DCA salts prepared and tested. It was known that  $\text{C}=\text{C}$  bonds, such as those in

furfuryl alcohol or vinylisobutyl ether, promote hypergolic ignition. About half of the materials were RTILs with melting points ranging between 269 and 301 K (−4 and 28 °C). Most of the liquids had acceptably low viscosities between 26 and 120 cPs. Table 4 gives a summary of some of the salts investigated. Unfortunately, several of the unsaturated compounds had a tendency undergo cyclization reactions and formed heterocyclic-ring compounds with less desirable properties.

**Table 4:** ILs evaluated as hypergolic fuels.

|                                                           | Melting point |     | Onset of decomp. |     | Viscosity at 298 K |
|-----------------------------------------------------------|---------------|-----|------------------|-----|--------------------|
|                                                           | K             | °C  | K                | °C  | cPs                |
| <b>Primary amines</b>                                     |               |     |                  |     |                    |
| 1 Ethylammonium dicyanamidate                             | 319           | 46  | 359              | 86  | a                  |
| 2 Acrylammonium dicyanamidate                             | 284           | 11  | 351              | 78  | 95                 |
| 3 3,4-butenyl dicyanamidate                               | b             | b   | 348              | 75  | 120                |
| 4 2-hydroxyethylammonium dicyanamidate                    | 287           | 14  | c                | c   | 106                |
| <b>Secondary amines</b>                                   |               |     |                  |     |                    |
| 5 Diacrylammonium dicyanamidate                           | 310           | 37  | 344              | 71  | 37 <sup>b</sup>    |
| <b>Tertiary amines</b>                                    |               |     |                  |     |                    |
| 6 Dimethylacrylammonium dicyanamidate                     | b             | b   | 381              | 108 | c                  |
| 7 Dimethyl-2-azidoethylammonium dicyanamidate             | 289           | 16  | 368              | 95  | 74                 |
| <b>Quaternary alkylammonium salts</b>                     |               |     |                  |     |                    |
| 8 Trimethylacrylammonium dicyanamidate                    | 301           | 28  | 502              | 229 | 26 <sup>b</sup>    |
| 9 Trimethyl-2-azidoethylammonium dicyanamidate            | 289           | 16  | 460              | 187 | 81                 |
| 10 Trimethyl cyanomethylammonium dicyanamidate            | 395           | 122 | 449              | 176 | a                  |
| 11 Trimethyl-2-cyanoethylammonium dicyanamidate           | 352           | 79  | 386              | 113 | a                  |
| 12 Dimethyldiacrylammonium dicyanamidate                  | b             | b   | 473              | 200 | 37                 |
| 13 Dimethyldipelarginylammonium dicyanamidate             | 347           | 74  | 428              | 155 | a                  |
| 14 Dimethylacrylpelarginylammonium dicyanamidate          | 296           | 23  | 445              | 172 | 111                |
| 15 Dimethylacryl-2-hydroxyethylammonium dicyanamidate     | 269           | −4  | 466              | 193 | 87                 |
| 16 Dimethylcyanomethyl-2-azidoethylammonium dicyanamidate | d             | d   | 373              | 100 | a                  |
| 17 Dimethylacrylcyanomethylammonium dicyanamidate         | 308           | 35  | 417              | 144 | a                  |
| 18 Tetrapelarginylammonium dicyanamidate                  | 386           | 113 | 420              | 147 | a                  |

<sup>a</sup> solid; <sup>b</sup> supercooled liquid; <sup>c</sup> not determined; <sup>d</sup> not observed

Data source: [41]



Guanidinium and mono-, di-, or triaminoguanidinium dicyanoamides had melting points above room temperature, but three of the four salts had melting points below 373 K (100 °C) (Table 5). The DCA anion was chosen not only because it is a fuel-rich anion but also because IL dicyanoamides have some of the lowest viscosities among known ILs. Only a few of the DCA ILs ignited hypergolically with WFNA. It was proposed that the tests be repeated with IRFNA instead of WFNA and to also test with HTP. It was not possible to identify the “magic trigger group” that causes all IL fuels to become hypergolic fuels. See also [264].

**Table 5:** Properties of guanidinium dicyanoamides.

| Compound                         | Melting point |     | Decomp. onset |     | Density<br>g/cm <sup>3</sup> |
|----------------------------------|---------------|-----|---------------|-----|------------------------------|
|                                  | K             | °C  | K             | °C  |                              |
| Guanidinium dicyanoamide         | 330           | 57  | 418           | 145 | 1.38                         |
| Aminoguanidinium dicyanoamide    | 328           | 55  | 393           | 120 | 1.41                         |
| Diaminoguanidinium dicyanoamide  | 334           | 61  | 385           | 112 | 1.36                         |
| Triaminoguanidinium dicyanoamide | 397           | 124 | 423           | 150 | 1.42                         |

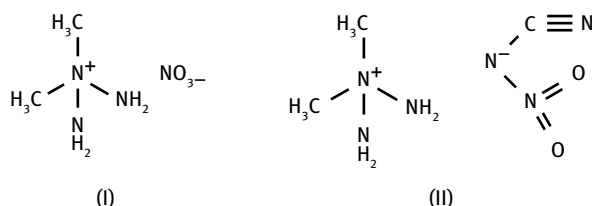
Data source: [265]

Imidazolium-based ILs were first considered because they generally possess greater stability than their triazolium or tetrazolium analogs. Unsaturated side chains, such as allyl, propargyl, and 2-butenyl, were selected because it was hoped that they would initiate or promote hypergolic ignition [92, 266]. It has been demonstrated in the past that unsaturated, especially acetylenic, compounds show a tendency to hypergolicity and can even be used as fuel additives to promote hypergolic ignition. Examples are furfuryl alcohol and Visol-1 (isobutylvinylether). 1-R-3-methylimidazolium DCAs with unsaturated R side chains were prepared and tested for hypergolic ignition with WFNA and RFNA. The physical properties and ignition delays are summarized in Table 3. Most substituted imidazolium DCAs are true room-temperature liquids.

Bipropellant ILs that react hypergolically with WFNA were tested to gain a fundamental understanding of the ignition of EILs with WFNA [247]. The effects of cation and anion structure on initiation reactions, and subsequent reactions leading to ignition for representative compounds in three classes of compounds (amino-1,2,4 triazoles, amino-1,2,3-triazoles and amino-tetrazoles) were investigated. In order to explain the effects of substituents, the decomposition products and their temporal evolution over a range of temperatures were analyzed. To gain further insight into the mechanism of decomposition, simplified kinetic models were developed and overall kinetic parameters were derived. The second major research objective was to study the hypergolic reaction mechanism for DCA-based ILs by analyzing the species produced during hypergolic ignition. A postulated key intermediate was dinitrobiuret. Another intermediate is HNCO.

ILs with the DCA anion have been shown to exhibit hypergolic properties and instantaneous ignition when in contact with WFNA. Such liquids tend to have low volatilities, and high thermal and chemical stabilities, and often exhibit wide liquid ranges; this could allow utilization of these substances as bipropellant fuels in a variety of environmental conditions [267, 268]. Dicyanoborates with substituted *N*-acyclic, *N*-cyclic, and azolium cations can be synthesized in water.

A new class of hypergolic ionic salts with the 2,2-dialkyltriazanium cation was reported to be capable of igniting rapidly with WFNA [269, 270]. 2,2-Dimethyltriazanium nitrate (**I**) displayed the shortest ignition delay time of 4 ms but, unfortunately, it is a solid at room temperature and it does not melt until it is heated to 372 K (99 °C).



When the 2,2-dialkyltriazanium cation was used in combination with the nitrocyanamidate (**II**) instead of the nitrate anion, the resulting IL turned out to be a true liquid at room temperature (m.p. = 273 K = -0.2 °C) and also exhibited excellent hypergolic properties. For example, when WFNA or N<sub>2</sub>O<sub>4</sub> was used as the oxidizer, the ignition delay time of this IL was 16 and 8 ms, respectively.

Fourteen *N,N*-dimethylhydrazinium DCA and nitrocyanamidate ILs were prepared by quaternization of *N,N*-dimethylhydrazine (UDMH) with alkyl halides, followed by metathetical reactions with silver DCA or silver nitrocyanamidate [91]. The key physicochemical properties, such as melting point and decomposition temperatures, density, viscosity, heat of formation, detonation pressure and velocity, and *I*<sub>sp</sub>, were measured and/or calculated to study the impact of anions and alkyl-substituted hydrazinium cations on these properties. Droplet ignition delay tests with WFNA as the oxidizer showed that these new *N,N*-dimethylhydrazinium salts were hypergolic, with ignition delay times ranging from 22 to 1642 ms. Of these, *N,N,N*-trimethylhydrazinium DCA and *N,N,N*-trimethylhydrazinium nitrocyanamidate gave ignition delays of 58 and 126 ms, respectively. The replacement of -NH<sub>2</sub> with a methyl group in the cation resulted in the significant increase in the ignition delay time, i.e. 16 versus 126 ms, indicating that the structure of two or three adjacent nitrogen atoms in the cation is favorable for the shorter ignition delay time of hypergolic ILs.

It was attempted to use DFT tight-binding MD (DFTB-MD) simulations to study the initial stages of hypergolic reactions between an EIL and nitric acid [271, 272]. Calculations were performed at various temperatures, and various reaction mechanisms were identified. The reaction products, such as H<sub>2</sub>O, HNCO, and CO<sub>2</sub>, predicted by DFTB-MD simulations were in agreement with the experiments reported by the AFRL.

The reaction mechanism is very complex and it changes with temperature. The energy gap between the highest occupied molecular orbitals (HOMO) of anions and the lowest occupied molecular orbitals (LUMO) of  $\text{HNO}_3$  was used as a parameter for interaction between a base and an acid. Based on molecular orbital calculations, a design guideline for hypergolic ILs was developed [273].

The QSPR represents a simplified design approach for quantitatively predicting the ignition delay times based on linear correlations using a set of descriptors, which define electrostatics, H-bonding, and other structural features of the ILs [274]. Experimental ignition delay times for a set of 41 ILs were collected for QSPR development. Experimental measurements of the ignition delay times were then correlated to theoretical descriptors determined from quantum mechanical calculations. A number of multi-descriptor linear equations were analyzed by regression of the ignition delay data, showing reasonable agreement. The ignition delay values were observed to spread over a wide range, in large part due to the presence of oxygen in the fuel molecule. A brief overview of ILs as hypergolic fuels is provided in a series of lecture slides from an Advanced Energetic Materials Synthesis Workshop held in 2011 [275].

It was found that reactions between DCA-based ILs, e.g. [Emim][DCA] or [Bmim][DCA] and WFNA, always yielded a precipitate that was composed of cyclic triazines including melamine and its polymers [99, 276]. Indication was that about 25% of the IL was converted into the precipitate during the ignition. Evidence showed that polymerization occurred even at lower concentration of reagents (e.g. the reaction of DCA with aqueous  $\text{HNO}_3$  solution), when neither hypergolic ignition nor notable heating of the reaction mixture took place. Electrospray ionization MS showed that, during the hypergolic reaction, the  $\text{HNO}_3$  and IL cation (e.g.  $\text{Emim}^+$ ) first undergo an ion exchange, i.e.  $\text{Emim}^+$  pairs with  $\text{NO}_3^-$  to form water-soluble [Emim][ $\text{NO}_3$ ] and  $\text{HN}(\text{CN})_2$ , followed by the rapid self-polymerization of  $\text{HN}(\text{CN})_2$  to yield a precipitate (melamine and its oligomers) under conditions of instant high temperature and strong acidic environment.

Hypergolic ignition of two hypergolic ILs [Emim][DCA] and [Bmim][DCA] was tested with three oxidizers (WFNA, RFNA, and NTO) [277]. A drop test system was designed to control the collision event of a single droplet of fuel with an oxidizer pool in a reproducible way. The results showed that the hypergolic ignition process of [Emim][DCA] with WFNA is quite similar to that of MMH–WFNA. Combined with thermophysical properties of hypergolic ILs, a mechanism for the hypergolic ignition process of [Emim][DCA] – WFNA was proposed. Hypergolicity of different propellant combinations was tested to investigate the influence of the oxidative capacity of oxidizers and the cation structure of ILs.

The low vapor toxicity of ILs make them attractive replacements for hydrazine in rocket applications. However, ILs will fail to fulfill their promise unless toxic hypergolic oxidizers like  $\text{HNO}_3$  or  $\text{N}_2\text{O}_4$  can be replaced with safer alternatives. By their very nature, all rocket oxidizers are hazardous and so, reducing the hazards, even though the resulting materials might not be completely harmless, is at the heart of green initia-

tives in propulsion. A significant step to a lower toxicity bipropellant system would be the demonstration of hypergolicity (spontaneous ignition) between an IL and a safer oxidizer like hydrogen peroxide. Outside of cryogenics, hydrogen peroxide seems to be promising, with its less toxic vapor and corrosivity and its environmentally benign decomposition products. Up until 2011, no IL had been reported to be reliably hypergolic with  $\text{H}_2\text{O}_2$ , but additional work is in progress [278, 279]. A number of imidazolium ILs with azide, cyanamdate, nitrocyanamdate, and boranate anions and adducts with aluminum boranate were tested with 90 and 98%  $\text{H}_2\text{O}_2$ , but ignition was very slow, of the order of several seconds, if it ignited at all.

A selection of substituted imidazolium cations was prepared and paired with known hypergolic anions (DCA) and more recently employed anions (vinylgous DCA and  $N,N'$ -dicyanoformamidinate) in the synthesis of ILs that might be useful as hypergolic fuels [280].

1-Butyl-3-methylimidazolium tetrafluoroborate, which is not hypergolic with WFNA by itself, could be hypergolized by dissolving nitrogen–boron compounds in the IL [281]. The solids ammonia borane (a), hydrazine borane (b), and hydrazine bis(borane) (c) were all found to exhibit hypergolic behavior with WFNA with ignition delays of 80, 4, and 12 ms, respectively. They are soluble in 1-butyl-3-methylimidazolium tetrafluoroborate. Dissolving ammonia borane or hydrazine borane in the non-hypergolic IL resulted in hypergolic solutions (ignition delays of 88 and 390 ms with WFNA, respectively). ILs containing the DCA anion instead of the tetrafluoroborate anion were also good solvents for the three B–N compounds and reacted hypergolically with WFNA. Dissolving boranes in the DCA liquids reduced the ignition delays of the ILs significantly, with values ranging from 3 to 34 ms.

A detailed chemical kinetics model has been built to examine the gas-phase chemistry between  $\text{HNCO}$ , WFNA,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , and water at low-to-medium temperatures (ambient to 423 K) [282, 283]. This kinetics model was supposed to explain the gas-phase ignition observed during hypergolic ignition of the IL  $[\text{Bmim}][\text{DCA}]$  with WFNA. Ignition is predicted to occur via an exothermic reaction between  $\text{HNCO}$  and nitric acid ( $\text{HONO}_2$ ), and subsequent  $\text{HONO}_2$  thermal decomposition that has  $\text{NO}_2$  and  $\text{OH}$  radicals as the primary chain carriers. A detailed understanding of the initiation processes in the liquid phase is needed, as the  $[\text{Bmim}][\text{DCA}]$  and WFNA begin to react to produce the above pre-ignition species for the proposed chemical kinetics model to describe the ignition behavior of the system.

Hypergolic bipropellant fuels that are self-igniting with  $\text{N}_2\text{O}_4$  as the oxidizer can be made from protonated alkylhydrazides, carbohydrazide, or di- and triaminoguanidinium as the cation, and DCA or TCM as the anion [264]. Details about these ILs are summarized in *Encyclopedia of Liquid Fuels*, chapter “Amides and Imides.”

MD simulations of mixtures of the RTILs  $[\text{Bmim}][\text{DCA}]$  and  $[\text{Bmim}][\text{NO}_3]^-$  with WFNA have been performed utilizing quantum chemistry computations [284]. Experimentally, it has been observed that  $[\text{Bmim}][\text{DCA}]$  exhibits hypergolic behavior when mixed with  $\text{HNO}_3$  while  $[\text{Bmim}][\text{NO}_3]^-$  does not. The structural, thermodynamic, and

transport properties of the IL/ $\text{HNO}_3$  mixtures have been determined from equilibrium MD simulations over the entire composition range (pure IL to pure  $\text{HNO}_3$ ) based on bulk simulations. Additional (non-equilibrium) simulations of the composition profile for IL/ $\text{HNO}_3$  interfaces as a function of time have been utilized to estimate the composition-dependent, mutual-diffusion coefficients for the mixtures. The latter have been employed in continuum-level simulations to examine the nature (composition and width) of the IL/ $\text{HNO}_3$  interfaces on the millisecond time scale.

Similar quantum chemistry-based force field calculations have been performed for the hydrazinium, methylhydrazinium, and dimethylhydrazinium cations in combination with the nitrate, azide, DCA, or 5-azidotetrazolate anions [285]. Calculations were performed on the neutral precursors, ions, and cation–anion complexes. Seven different ionic systems have been investigated:  $\text{N}_2\text{H}_5\text{NO}_3$ ,  $(\text{CH}_3)_2\text{N}_2\text{H}_4\text{NO}_3$ ,  $(\text{CH}_3)_2\text{N}_2\text{H}_3\text{NO}_3$ ,  $\text{N}_2\text{H}_5\text{CN}_7$ ,  $(\text{CH}_3)_2\text{N}_2\text{H}_4\text{N}_3$ ,  $(\text{CH}_3)_2\text{N}_2\text{H}_3\text{N}_3$ , and  $\text{N}_2\text{H}_5\text{N}(\text{CN})_2$ . For all of these, except  $(\text{CH}_3)_2\text{N}_2\text{H}_3\text{NO}_3$  and  $\text{N}_2\text{H}_5\text{N}(\text{CN})_2$ , calculations of a single, gas-phase ion pair predicted spontaneous deprotonation of the cation. Crystal-lattice parameters obtained from MD simulations were compared with experiments for ionic crystals of these seven systems, with the experimentally determined crystal structure of  $\text{N}_2\text{H}_5\text{N}(\text{CN})_2$  as an example, which enabled comparison of the simulation and experiment for this compound.

In a very thorough re-evaluation of a wide range of heterocyclic amine cations and various anions previously shown to impart hypergolicity to ILs, a total of 13 halide salt precursors were synthesized through typical quaternization reactions between the neutral heterocycles and respective alkylating agents such as iodomethane, chloroethane, 1-chlorobutane, 1-bromobutane, 1-chloro-2-methoxyethane, allyl chloride, or propargyl bromide [286, 287]. Typical quaternization reactions were conducted by first dropwise adding 1.1 mol excess of the alkylating agent under a constant stream of argon to a round-bottom flask containing the pure heterocycle while stirring at 273 K (0 °C). The reaction mixture was then slowly heated to a gentle reflux for between 24 and 96 h and monitored by  $^1\text{H}$ -NMR until no unreacted heterocycles could be detected. Saturated solutions of the halide precursors in methanol were added to the suspensions of a 1.1 mol excess of the corresponding silver salt delivering the anion. The mixtures were then allowed to stir at 298 K (25 °C) for at least 3 days. The metathesis reactions were monitored via  $^1\text{H}$ -NMR by observing the upfield shift of the azolium peaks until only a single set of cation peaks was present. A total of 38 salts (32 liquids and 6 solids) were isolated from 13 cations and 3 anions and characterized by IR and NMR. Upon the removal of excess silver salts, each isolated IL was extensively dried under high vacuum ( $\sim 1 \times 10^{-4}$  mm Hg) while being stirred and heated at 323–343 K (50–70 °C) for between 7 and 10 days. Additionally, each salt was freeze-thawed 3 times to remove any entrapped gases and trace amounts of volatiles. Melting points or glass-transition temperatures for the combinations of 13 amines (11 five-membered and 2 six-membered heterocyclic amines) and three anions were tabulated. Each salt was characterized by DSC and TGA to determine melting temperature ( $T_m$ ), glass-tran-

sition temperature ( $T_g$ ), and onset of thermal decomposition, which were assembled in a table. The highest melting points were observed for salts of the same cation with azide anions. The lowest-melting IL ( $T_m = -55^\circ\text{C}$ ) was *N*-butyl-*N*-methyl-pyrrolidinium DCA. Many of the salts were hygroscopic and it was difficult to remove the last traces of water. Although 32 liquids were obtained, 14 of these exhibited no observable melting or glass transitions, which might be a result of the hygroscopic nature of these compounds. Even trace amounts of water could interfere with a glass or melting transition. Viscosity, density, and ignition delay with WFNA of 12 ILs were measured and tabulated. Ignition delays ranged from 19 to 151 ms. Surprisingly, the IL that had the lowest ignition delay was 1-propargyl-3-methyl-imidazoliumDCA, with a value of only 19 ms, although it had the second-highest reported melting point of any of the DCA-based ILs ( $290\text{ K} = 17^\circ\text{C}$ ) and a moderately high viscosity (31.7 cPs). The same functional group that promoted faster ignition (19 ms) also contributed to a higher viscosity (31.5 cPs), higher melting point ( $290\text{ K} = 17^\circ\text{C}$ ), and lower thermal stability ( $470\text{ K} = 197^\circ\text{C}$ ). All allyl-substituted cations had ignition delays of 31 ms or less.

Many ILs containing the DCA anion exhibit hypergolic ignition when exposed to WFNA. However, the ignition delay is often about 10 times longer than the desired 5 ms for rocket applications, so that improvements are needed. Experiments have suggested both a mechanism for the early reaction steps and also that additives such as decaborane can reduce the ignition delay. The mechanisms for reactions of nitric acid with both  $\text{DCA}^-$  and protonated DCAH were examined using accurate wavefunction quantum chemical computational methods [101]. Complexation of  $\text{DCA}^-$  or DCAH with borane clusters  $\text{B}_{10}\text{H}_{14}$  or  $\text{B}_9\text{H}_{14}^-$  was found to modify these mechanisms slightly by changing the nature of some of the intermediate saddle points and by small reductions in the reaction barriers.

The transport properties of DCA ILs are significant for their applications as solvents, electrolytes, and hypergolic fuels in bipropellants. Several transport properties of four DCA ILs ( $[\text{C4mim}][\text{N}(\text{CN})_2]$ ,  $[\text{C4m2im}][\text{N}(\text{CN})_2]$ ,  $\text{N4442}[\text{N}(\text{CN})_2]$ , and  $\text{N8444}[\text{N}(\text{CN})_2]$ ) including viscosity, conductivity, and electrochemical property at different temperatures were examined and related to the chemical structure of the ionic salts [288]. The melting points, temperature-dependent viscosities, and conductivities revealed the structure–activity relationship of four DCA ILs. From the Walden plots, the imidazolium cations exhibit stronger cation–anion attraction than the ammonium cations. DCA ILs have relatively high values of electrochemical windows, which makes them potential candidates for electrolytes in electrochemical applications. The electrochemical properties of the DCA ILs are dominated by the cationic structures. A correlation of the cationic structure–transport property relationships of DCA ILs was developed, which will be useful for designing new functionalized ILs to fulfill specific requirements. See also [236, 289].

Ignition delays of three DCA-based ionic liquids with different cations, 1-allyl-3-methyl imidazolium ([Amim]), 1-ethyl-3-methylimidazolium ([Emim]) and 1-butyl-3-methyl-imidazolium ([Bmim]) with WFNA were measured in a single droplet test

apparatus [290]. The experimental results indicated that short-chain alkyl and unsaturated alkyl substituents in cations are favored for short hypergolic ignition delays.

The ignition delays of two EILs (1-butyl-1-methylimidazolium dicyanamide,  $\text{Bmim}^+\text{DCA}^-$ ) and 1-butyl-1-methylpyrrolidinium dicyanamide ( $\text{Bmpy}^+\text{DCA}^-$ ) with WFNA were measured in a 100%  $\text{N}_2$  atmosphere and then again in a 25%  $\text{N}_2\text{O}$  and 75%  $\text{N}_2$  atmosphere [291]. The addition of  $\text{N}_2\text{O}$  was found to decrease the average ignition delays for both EILs.

### 12.2.2 ILs with Nitrodicyanomethanide Anions as Hypergolic Fuels

Twelve IL salts with nitrodicyanomethanide and dinitrocyanomethanide anions paired with 1,5-diamino-4-methyltetrazolium, 1,4-dimethyl-5-aminotetrazolium, 1,4,5-trimethyltetrazolium, 1-methyl-4-amino-1,2,4-triazolium, 1,4-dimethyltriazolium and 1,3-dimethylimidazolium cations have been prepared through metathesis reactions of equivalent silver(I) salts with corresponding iodide salts in acetonitrile [292]. The relationships between key physical properties, such as melting point, thermal stability, and density and their structures were examined. The structures of 1,5-diamino-4-methyltetrazolium-based salts were further confirmed by single-crystal XRD. The densities and standard enthalpies of formation were calculated. All of the salts had higher enthalpies of formation than the nitrate analogs.

### 12.2.3 ILs with Boron-Containing Anions as Hypergolic Fuels

Tri(hexyl)-tetradecyl-phosphonium tetraboranoaluminate  $(\text{C}_6\text{H}_{13})_3(\text{C}_{14}\text{H}_{29})\text{P}^+\text{Al}(\text{BH}_4)_4^-$  or oxygen-balanced 1-ethyl-4,5-dimethyltetrazolium tetranitratoaluminate  $\text{Al}(\text{NO}_3)_4$  will react hypergolically with 98%  $\text{H}_2\text{O}_2$  [293].

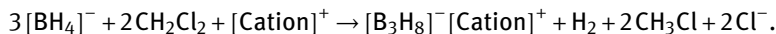
A series of hypergolic CTB anion-based ILs was synthesized by a straightforward N-hydroboration of tetrazole followed by a salt metathesis reaction [121]. The salts exhibited remarkably low viscosity ( $<20\text{ mPa}\cdot\text{s}$ ), high density (often  $>1.1\text{ g/cm}^3$ ), and ultra-short ignition delay time (as short as 1.4 ms) upon contact with WFNA.

A series of hypergolic ILs based on the cyano(1*H*-1,2,3-triazole-1-yl) dihydroborate anion were synthesized by introducing the  $[\text{BH}_2\text{CN}]$  moiety into the 1,2,3-triazole anion [294]. This introduction improved the hypergolic ignition property and decreased the viscosity of IL fuels. The synthesized series of hypergolic ILs exhibited wide liquid operating ranges ( $>220^\circ\text{C}$ ), high densities ( $>1\text{ g/cm}^3$ ), low viscosities (as low as 23 cPs), and ignition delay times as short as 5 ms by WFNA as the oxidizer. These ILs can also be ignited upon contact with a 90 mass-%  $\text{H}_2\text{O}_2$  oxidizer in the presence of a trace of iodine. See also [253, 295].

### 12.2.4 ILs with Tetrahydroborate Anions as Hypergolic Fuels

A series of pure  $\text{BH}_4^-$  ILs with 1-butyl-2,3-dimethylimidazolium (Bmmim), 1-ethyl-3-methylimidazolium (Emmim), 1-propyl-1-methylpiperidinium (PropMPip), and 1-butyl-1-methylpyrrolidinium (BMP) cations were prepared [265]. All synthesized ILs

were well soluble in  $\text{CH}_2\text{Cl}_2$ . A facile route to  $[\text{B}_3\text{H}_8]^-$  ILs with  $\text{Bmmim}^+$ ,  $\text{Emmim}^+$ ,  $\text{PropMPip}^+$ , and  $\text{NBu}_4^+$  was developed, in which  $\text{Na}[\text{BH}_4]$  reacts *in situ* (enhanced by ultrasound) with the solvent  $\text{CH}_2\text{Cl}_2$  as the oxidizing agent to give the triborate IL in high yield and purity according to the equation:



This reaction path was further investigated by additional NMR spectroscopic experiments, powder-XRD analysis, and quantum chemical DFT calculations.

Borohydride ILs and borane–IL solutions meet nearly all of the desired important criteria for well-performing hypergolic non-toxic fuels [296]. Ignition delay times are superior to those of any known hypergolic IL and may thus be possible replacements for hydrazine, MMH, or UDMH as bipropellant fuels.

Borohydride-containing ILs have been synthesized using a more efficient synthetic pathway that does not require liquid ammonia and halide precursors [297]. Among the eight new compounds, 1-allyl-3-*n*-butyl-imidazolium borohydride and 1,3-diallylimidazolium borohydride exhibited very short ignition delay times of 8 and 3 ms, respectively. The borohydride ILs are viscous compounds. 1,3-Diallylimidazolium tetrahydroborate had the lowest viscosity at 175 mPa s and the shortest ignition delay of 3 ms. The hydrolytic stability of borohydride compounds has been greatly improved by attaching long-chain alkyl substituents to the imidazole ring. 1,3-Di-(*n*-octyl)-imidazolium tetrahydroborate is a water-stable borohydride-containing IL. 1,3-Di-(*n*-butyl)-imidazolium tetrahydroborate is a unique example of a borohydride liquid crystal. These ILs have some unusual advantages, including negligible vapor pressures, good ignition delay times, and reduced synthetic and storage costs, thereby showing good application potential as environmentally friendly fuels in bipropellant formulations. See also [298].

A series of *N*-alkylimidazole borane compounds with zwitterionic structure has been synthesized and characterized [251, 252]. The borohydride  $-\text{BH}_3^-$  group is attached to the carbon in the 2-position between the two nitrogen atoms in the imidazole ring. The positive charge oscillates in the ring between the nitrogen atoms. These compounds are potential hypergolic fuels owing to their excellent physicochemical properties including low melting points, high thermal stability, low viscosities, and unique hypergolic reactivity.

A family of hydrophobic borohydride-rich ILs was developed, one of which, *N*-allylpyridinium, exhibited the shortest ignition delay times of 1.7 ms and the lowest viscosity (10 mPa s) of hypergolic ILs, demonstrating their great potential as faster-igniting rocket fuels to replace toxic hydrazine derivatives in liquid bipropellant formulations [299]. Comparing the stabilities of previously reported ILs with hydrogen-rich anions, i.e. typical  $\text{BH}_4^-$  and  $\text{BH}_2(\text{CN})_2^-$ , partial replacement of negatively charged hydrogen atoms on the boron atom with electron-withdrawing cyano groups can significantly improve the water stability of the resulting hypergolic ILs. In the design strategy of borohydride-rich anions, creating a cyano-bridged



dicyanodiboranate anion  $[\text{BH}_3(\text{CN})\text{BH}_2(\text{CN})]^-$ , one cyano group can serve as a stabilizing ligand to bridge two hydrogen-rich  $\text{BH}_3$  and  $\text{BH}_2\text{CN}$  moieties, while both cyano groups as electron-withdrawing groups play a role in improving the chemical stability of negatively charged hydrogen atoms. Quaternized alkylimidazolium, pyridinium, and pyrrolidinium salts with the  $[\text{BH}_3(\text{CN})\text{BH}_2(\text{CN})]^-$  anion all had melting and glass-transition points between 251 and 236 K (–22 and –37 °C) and good thermal stability.

#### 12.2.5 ILs with Borane Cluster Anions as Hypergolic Fuels

Nonaborane and decaborane cluster anions  $[\text{B}_9\text{H}_{14}]^-$  and  $[\text{B}_{10}\text{H}_{13}]^-$  can form stable solutions in ILs or certain molecular solvents, leading to enhanced ignition in known hypergols (fuels that spontaneously ignite upon contact with an oxidizer), or induced hypergolicity in certain non-hypergolic solvents [300, 301]. It was attempted to achieve hypergolic ignition between 1-methyl-3-sulfoimidazolium nitrate as the oxidizer and [3-butyl-1-methylimidazolium] $[\text{B}_6\text{H}_7]$  as the fuel, and indeed they ignited [238].

The compounds described in the following sections are solids and do not belong in this section on ILs. They are just mentioned here because the mechanisms leading to hypergolic ignition are similar to those observed with ILs. Imidazole-substituted decaborane, 6-exo,9-exo-bis(imidazole) decaborane, was used as a hypergolic “trigger” component in combination with energy-rich but non-hypergolic nitrobenzene or pyrazine to create hypergolic co-crystals [302]. Other hypergolic solids were made from metal–organic frameworks [303].

Closo-dodecahydroborate salts with guanidinium-and aminotetrazolium-based cations were synthesized, crystallized, and characterized, but they have high melting points, all above 497 K (224 °C) [304]. The salts were readily produced in good yields by metathesis (ion exchange) reactions, depending on the water solubility of the dodecahydroborate salts. Water-insoluble salts were synthesized from the potassium or sodium salts by a simple metathesis reaction with the corresponding halide of the desired organic cation. Water-soluble salts were prepared via two consecutive metathesis reactions: the halide was first converted to the corresponding sulfate, which, in turn, was reacted with barium dodecahydroborate, yielding the water soluble organic closo( $\text{B}_{12}\text{H}_{12}$ ) $_2^-$  salt and the insoluble  $\text{BaSO}_4$ . The thermal stabilities of these compounds were established by TGA. The enthalpies of combustion of representative salts were determined using constant-volume bomb calorimetry. The data showed that these salts possess relatively high heats of combustion ( $\Delta U_c$ , ca. 35 kJ/g), and have the potential to serve as green high-energy materials.

#### 12.2.6 ILs with Other Boron-Containing Anions as Hypergolic Fuels

Tetrahydroborate anions can be combined with other anions in an effort to lower the freezing point and viscosity of ILs. Phosphorus is not a preferred element to have in rocket fuels, but boranophosphate ILs have been evaluated as hypergolic rocket fuels [255].

From a rocket performance standpoint, it is not a good idea to replace hydrogen in boranate anions with iodine but, apparently, this substitution which results in ILs of organic amines with periodoborane anions ( $[\text{B}_{12}\text{I}_{12}]^{2-}$ ) enables hypergolic reactions with hydrogen peroxide [305, 306].

### 12.2.7 ILs with Cyanoborate Anions as Hypergolic Fuels

To achieve very short ignition delay times, *N,N*-dimethyl-*N*-butylhydrazinium dicyanoboranate,  $[(\text{C}_4\text{H}_9)(\text{CH}_3)_2\text{NNH}_2]^+[\text{BH}_2(\text{CN})_2]^-$  and *N,N*-dimethyl-*N*-acrylhydrazinium dicyanoboranate  $[(\text{C}_4\text{H}_9)(\text{CH}_3)_2\text{NNH}_2]^+[\text{BH}_2(\text{CN})_2]^-$  ILs, all of which had low melting points of  $<353\text{ K}$  ( $<80^\circ\text{C}$ ), were designed and synthesized [307]. All these ILs were air- and water-stable and exhibited good thermal stability, and their onset of decomposition temperature was higher than  $473\text{ K}$  ( $200^\circ\text{C}$ ). More importantly, they exhibited relatively low viscosities of  $<40\text{ MPa}\cdot\text{s}$  and can also ignite rapidly with WFNA in 5 ms. In comparison with other hypergolic ILs, which contain the more common anions, e.g. DCA or nitrocyanamidate anions, these dicyanoborate-based ILs had lower or similar melting points, higher thermal stability, lower viscosities and, most importantly, much shorter ignition delay times.

Cyanoborohydride-(cyanoboranate)-based ILs have hypergolic ignition properties and performances comparable to hydrazine derivatives [308]. They have negligible vapor pressure, short ignition delay times, and tolerable synthesis and storage costs, thereby showing good application potential as environmentally friendly fuels in bipropellant rockets.

The oxidation of levitated 1-butyl-3-methylimidazolium dicyanoborate ( $[\text{Bmim}][\text{DCBH}]$ ) or 1-allyl-3-methylimidazolium dicyanamide ( $[\text{Amim}][\text{DCA}]$ ) droplets by  $\text{NO}_2$  vapor was monitored using FTIR, Raman, and UV-visible spectroscopic methods [102, 309, 310].

Furfuryl alcohol has been used as a solvent for an IL,  $[\text{Emim}][\text{BH}_3\text{CN}]$ , together in different volume proportions (80:20, 70:30, 60:40, 50:50, and 40:60), forming a hypergolic fuel [311]. The blends exhibited good stability (chemical and thermal), low viscosity ( $\eta < 15\text{ mPa}\cdot\text{s}$ ), high density ( $\rho > 1\text{ g/cm}^3$ ), short ignition delay, and high performance in comparison to UDMH.

Two hydrophobic imidazolylidene-cyanoborane complexes were prepared by reaction of imidazolium iodide with  $\text{NaBH}_3\text{CN}$  [116]. These two compounds were characterized using IR and  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy, HR-MS, and XRD. The compound was hypergolic with WFNA and was immiscible with water, had a wide liquid range ( $T_g = 251\text{ K} = -22^\circ\text{C}$ ), short ignition delay time (13 ms), high density ( $0.98\text{ g/cm}^3$ ), and good density impulse ( $\rho I_{sp} = 347\text{ s g cm}^{-3}$ ).

### 12.2.8 ILs with Azide Anions as Hypergolic Fuels

Several imidazolium-based IL azides with saturated and unsaturated side chains were prepared and their physical and structural properties were investigated [312, 313]. The hypergolic ignition reactivity of these new as well as some previously

reported IL azides with  $\text{N}_2\text{O}_4$  and IRFNA was studied. With IRFNA and  $\text{N}_2\text{O}_4$ , all compounds reacted vigorously, with copious production of red fumes but without ignition. The initial heat release during these reactions did not result in hypergolic ignition of the material under the tested conditions.

Atomistic MD simulations were performed on the ILs [Bmim][ $\text{N}_3$ ], 1-butyl-2,3-dimethylimidazoliumazide [BMmim][ $\text{N}_3$ ], and 1-butynyl-3-methyl-imidazoliumazide [Bumim][ $\text{N}_3$ ] [314]. Good agreement between the experimentally determined and simulated crystal structure of [Bumim][ $\text{N}_3$ ] as well as the liquid-state density and ionic conductivity of [BMmim][ $\text{N}_3$ ] was achieved. Methylation of Bmim (yielding BMmim) resulted in dramatic changes in ion-structuring in the liquid and slowing of ion motion. Conversely, replacing the butyl group of Bmim with the smaller 2-butynyl group resulted in an increase of ion dynamics.

### 12.3 Other ILs as Hypergolic Fuels

ILs can contain dissolved metal salts, which catalyze decomposition of hydrogen peroxide and makes the fuel hypergolic with hydrogen peroxide [315]. Dissolving iodocuprate salts in [Emim] $^+$ [ $\text{H}_3\text{BCN}$ ] $^-$  and [mim][ $\text{BH}_3$ ] ILs produces fuels which are hypergolic with highly concentrated 95%  $\text{H}_2\text{O}_2$  oxidizer, with the ignition delay times down to 14 ms [316]. See also [231, 263, 274, 279, 317].

### 12.4 Amine Boranes as Hypergolic Fuels

Amine boranes may not qualify as ILs, but they are closely related to ILs with boron and nitrogen in their molecular structure [318]. A series of asymmetric monoimidazolium dihydroboronium-based ILs were synthesized from amine–boranes and characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and IR spectroscopy, elemental analysis, or HR-MS [319]. Compared with the symmetric bis(imidazolium)dihydroboronium-based ILs, these new ILs exhibited improved properties, with shorter ignition delay times, higher densities, and lower phase-transition temperatures.

A series of new amine borane/cyanoborane zwitterionic compounds was developed as hypergolic ILs [320]. The UDMH-based zwitterions, UDMH-borane and UDMH-bis(borane), displayed a strikingly lower ignition delay time of 2.2 and 2 ms, respectively, and a high  $I_{\text{sp}}$  of 241 and 245 s, respectively. The pyridinium–cyanoborohydride had a higher enthalpy of formation (146 kJ/mol) than UDMH. All the developed compounds had a higher density than UDMH. The chemical stability of UDMH-borane was investigated at different environmental conditions. It was found to be stable for longer duration. Short ignition delay, good thermal and chemical stability, positive heat of formation, high  $I_{\text{sp}}$ , ease of synthesis, and commercially available starting materials are some of the promising features of these compounds.

### 13 ILs as Working Fluids for Electric Propulsion

Colloidal thrusters are electrostatic accelerators of charged liquid droplets. One advantage of colloid engines for very small thrust levels is the fact that no gas-phase ionization is involved. Electrospray atomization delivers the small particle size required for efficient operation.

The negligible vapor pressure, substantial electrical conductivity, and thermal stability of ILs make them ideal candidates for electrospray space propulsion applications. An overview was provided covering current requirements in space propulsion, and it summarized the virtues of IL-propelled electrospray thrusters [321]. The physics associated with single cone-jet electrosprays was reviewed and recent developments with respect to IL ion sources were reported. Specific examples of MS measurements of charged particle emission from IL cone-jets included positive and negative ion emissions from [Emim][BF<sub>4</sub>], [Emim][Im], and [Emim][NO<sub>3</sub>].

ILs are suitable for electric space propulsion applications due to their high conductivity and negligible vapor pressure. The HAN-based AF-M315E is a promising monopropellant that has been successfully demonstrated for high-thrust chemical thruster operation. Dual-mode propulsion concepts in which AF-M315E would also be used for a high- $I_{sp}$  electrospray thruster operation are under evaluation. Quantum mechanical and classical MD calculations are being undertaken for likely ionic products of the AF-M315E propellant electrosprayed from an externally wetted tungsten emitter [322]. Quantum mechanical calculations determined that all assigned ion clusters observed experimentally are thermally stable at the operating temperature of 313 K. Proton transfer reactions occurring in the liquid phase of AF-M315E were found to play an important role in the observed ion distributions. Ionic clusters did not contain water or hydroxylammonium.

Chemical monopropellant and electrospray thrusters can both use ILs as propellants, lending themselves to the development of a dual-mode system. Several propellant candidates for a dual-mode electrospray-monopropellant micropropulsion system have been identified [323]. Reducing the number and size of hydrocarbon groups and increasing the highly electronegative species, such as oxygen and nitrogen, reduces the propensity of formation of solid carbon in the monopropellant exhaust. This also increases the surface tension and specific conductivity of the propellant, improving the thrust level for a given applied voltage in the electrospray mode.

### 14 Other Applications of ILs

There are many proposed new non-rocket applications for ILs, foremost being the battery electrolyte applications from which much of the research into ILs originated. Some of the knowledge gained about other applications of ILs may benefit their development as rocket propellants and vice versa [16]. The use of ILs as catalysts and/or solvents in synthesis reactions yielding high added-value products has also been pro-

posed. ILs can be coated in a thin layer on high-surface-area catalyst supports and serve as the medium in which reactions take place at an accelerated rate. These are called supported ILs [324]. ILs can also be used as working fluids for colloid thrusters. If we used them as conventional rocket fuels, they would be gone in a flash, in particular if they are a mix of a combustible fuel cation and an oxidizing anion. Most ILs are derived from the salts of heterocyclic amines.

### 14.1 EILs as Explosives

As is often the case, the propellant chemist trying to develop a more energetic rocket propellant is treading a thin line, easily overstepped, and can end up developing a liquid explosive instead. The story of ILs is no exception.

The US military is searching for replacements for TNT for use in melt-castable explosives. The AFRL has investigated the feasibility of replacing TNT with an IL (m.p.  $< 373\text{ K} = < 100\text{ }^{\circ}\text{C}$ ) [325]. The approach focused on synthesizing triazolium-based salts that have the appropriate physical and safety properties, thermal stability, and theoretical performance to potentially replace TNT. Individual salts selected from several families of energetic triazolium salts synthesized at the AFRL were shown to have high densities and relatively high heats of formation, and passed acceptance criteria of thermal stability tests.

The patent literature describes IL explosives consisting of eutectic mixtures of triazolium salts, such as 4-amino-1,2,4-triazolium perchlorate (4-ATP), 4-amino-1,2,4-triazolium nitrate (4-ATN), 1-H-1,2,4-triazolium perchlorate (TP), 1-amino-3-methyl-1,2,3-triazolium nitrate (1-AMTN) and 1-methyl-4-amino-1,2,4-triazolium perchlorate (MATP) [326]. Typical examples are eutectic mixtures of 4-ATP/4-ATN (70/30), 4-ATP/4-ATN (30/70) and 4-ATP/TP (30/70).

### 14.2 EILs as Gas Generants

Under a US Army STTR contract, C3 Propulsion, in cooperation with the Center for Green Manufacturing of the University of Alabama, proposed designing, developing, and demonstrating the feasibility of an on-demand gas generator, based on an IL monopropellant, that would supply pressures up to 24.1 MPa (3500 psi) and be suitable for pressurizing liquid and gelled fuel and oxidizer tanks in pressure-fed liquid-propellant missiles [327].

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# Jet Fuels

## Introduction

The *Encyclopedia of Liquid Fuels* contains eight chapters dealing with hydrocarbon fuels. The topic of hydrocarbon fuels had to be subdivided into several smaller chapters that were easier to arrange in alphabetical order in five subvolumes of equal size. The titles of the eight hydrocarbon chapters are: “Alkanes,” “Alkenes and Alkynes,” “Aromatic Hydrocarbons,” “Cycloaliphatic Hydrocarbons,” “Hydrocarbons,” “Jet Fuels,” “Kerosenes,” and “Ramjet Fuels.”

## 1 Jet Fuels

This chapter on jet fuels, obviously fuels for air-breathing jet engines and not for rocket engines, may seem out-of-place in the *Encyclopedia of Rocket Propellants*, but there are so many similarities between jet fuel kerosenes and rocket engine fuel kerosenes that it is justifiable to include jet fuels here. The hydrocarbons are in many cases the same; it is just the composition of the mixtures that is different. Furthermore, analytical methods used for either type of fuel are the same. The same comments apply to ramjet fuels, which are described in a chapter of their own. Otherwise ramjet fuels would have been included here under “Jet Fuels.” Quite often jet fuels have been used as rocket fuels because they were readily available.

New types of jet propulsion, such as in rotating detonation engines and pulsejet engines, require unique hydrocarbon fuels, and the designers of those engines need a good source of physical properties of fuels to choose from.

The most frequently referenced set of specifications for hydrocarbon fuels is the one created by US military agencies for jet fuels described by the letters JP followed by a number designation (JP = jet propellant). JP-1 was the first kerosene propellant to be described by a specification. Neither JP-1 nor JP-2 found widespread application and the two specifications are now only of historical interest. JP-3 is a kerosene with a very wide boiling range. Because of its higher vapor pressure, its composition changes significantly if allowed to spend time in unpressurized fuel tanks in airplanes flying at high altitude; thus, it was only allowed to be used in airplanes that did not cruise at very high altitudes. The JP-3 specification was later replaced by JP-4 which has a lower vapor pressure and can be flown at higher altitudes. For many decades JP-4 was the most frequently used jet fuel in military aircraft.

Air/kerosene fuel mixtures are flammable and explosive. In spite of padding the tanks with “vitiated air” to lower the oxygen concentration, there have been 17 fuel tank ignition events on commercial airplanes since 1959 that have resulted in 542 fatalities and 11 airplane losses. On the military side, there have been 12 airplane losses

on the military version of the B-707 and the B-52. Both JP-4 and Jet A were gradually being replaced in the wake of an accident in a Boeing 747-131 commercial passenger plane on TWA flight 800 in 1996, where an unknown source of ignition caused one of the fuel tanks to explode in flight with a loss of life of all passengers and crew on board. Another loss of a B-52 bomber was caused by a lightning strike igniting fuel vapors in the tanks. Subsequently, fuels have been reformulated and efforts have been made to inert the vapor space above the fuel in the fuel tanks with nitrogen or vitiated air. Because JP-4 was widely available, many rocket engine tests have been conducted with JP-4 although it was not really intended as a rocket fuel, but only as a fuel for air-breathing jet engines.

JP-5 has a higher freezing point than JP-4 and a narrower boiling range, from 473 to 563 K (200 to 290 °C), compared to JP-4 (413 to 553 K = 140 to 280 °C). A similarly narrow boiling range is reported for RP-1 which is the main hydrocarbon fuel used in many US launch vehicles. For quick calculations, RP-1 can be assumed to have the gross formula  $C_{11.74}H_{21.83}$  and a mean molecular mass of 163 g/mol.

## 2 Jet Fuel Kerosene JP-4

The first turbojets flying after WW II used MIL-F-5616 (JP-1) fuel. However, it was quickly recognized that large fleets of jet aircraft operating under all-out emergency conditions would consume considerably more JP-1 fuel than would be available from crude petroleum with existing refinery equipment at that time. As a result, during the next several years, an intense effort was devoted to the development of a turbojet fuel specification that satisfied both performance as well as availability considerations. An original proposal for JP-3 fuel was made in January 1947. A second revision of the JP-3 specification was made in March 1949. The JP-3 specification remained unaltered until May 1951, at which time the mercaptan sulfur content was limited to a maximum of 0.005 mass-%. This revision was due to corrosion problems, possible rubber swell problems, and objectionable odors that were being encountered during engine tests. Considerable opposition to the high volatility of the fuel arose because of the excessive entrainment losses that occurred during rapid climb with vented tanks. A less volatile fuel obtained the designation JP-4. The change in Reid vapor pressure was accompanied by the elimination of the 90% distillation requirement and the addition of a maximum limit of 250 °F on the 10% distillation point. The limitation of the 10% point, in effect, placed a more precise restriction on the minimum volatility of the fuel, since the accuracy of the Reid vapor pressure determination is questionable at pressures as low as 13.8 kPa (2 psia). The change in volatility also required new specific gravity limits. In December 1953, the JP-4 specification was altered to eliminate the 10% and end-point requirements and to add limiting values on the 20, 50, and 90% points on the distillation curve [1].

JP-4, also known under the designation NATO F40, has been the most widely used fuel for air-breathing turbine jet engines for several decades, but between 1980 and 1991 it was gradually replaced by JP-8 which is a more narrow cut of kerosene distillates. The Military Specification described JP-4 as a “wide cut, gasoline type” fuel and marked it as “inactive for new design.” JP-4 is rarely used any more, although it is possibly still used in developing countries with less stringent requirements for quality of jet fuel.

There exists a large database on properties of JP-4, and although JP-4 is no longer in use, the literature on JP-4 is compiled here because a comparison of JP-4 with other grades of kerosenes is very educational. Thus, this section is mostly of historical interest. JP-4 is not going to be used any more as a rocket propellant in the U.S., but in the early years, in particular before the arrival of RP-1, numerous rocket engine tests were run with JP-4 as the kerosene fuel that was most readily available. A complete set of physical properties of JP-4 is useful. In some cases where more recent data are not available, one can extrapolate to properties of other kerosenes.

## 2.1 Production of JP-4

JP-4 and other kerosenes used as jet or rocket fuels are (were) processed from crude oil petroleum by distillation, desulfurization, and hydrogenation. Some JP-4 fuel blending stocks were hydrogen-treated to prevent the formation of gums and peroxides after manufacture.

## 2.2 Physical Properties of JP-4

There is a vast amount of data on physical properties of JP-4, but because the MIL-DTL-5642W (former MIL-F-5624C) tolerances for composition and other properties of JP-4 are fairly wide, the physical properties of a specific sample can vary widely as well. In some cases, properties of JP-4 derived from coal instead of petroleum were compared to those of traditional grades of JP-4. Physical properties of JP-4 are summarized in Table 1 and reference [2].

Although all fuel samples may have been within the fairly wide specification limits for JP-4, the properties of JP-4 supplied by refineries may have changed over the course of several years, depending on the source of petroleum and the methods of processing in the refineries. For several decades, the USAF Defense Fuel Supply Center (DFSC) collected and analyzed historical JP-4 samples from the field using 17 specification tests in order to identify trends in the composition and physical properties of this fuel, for instance [7].

Samples of JP-4, JP-5, and JP-8 were analyzed and new analytical methods were developed in support of programs for studying fuel combustion behavior, turbine en-



**Table 1:** Physical properties of JP-4.

| Property                                         | SI units                                        | Other units                                                          | References |
|--------------------------------------------------|-------------------------------------------------|----------------------------------------------------------------------|------------|
| Freezing point                                   | <223 K                                          | <-50 °C = <-58 °F                                                    | [3]        |
| Boiling range                                    | 333–518 K                                       | 60 to 245 °C = 140 to 473 °F                                         |            |
| Density                                          | 0.751 to 0.802 g/cm <sup>3</sup>                | 46.88 to 50.07 lb <sub>m</sub> /ft <sup>3</sup>                      |            |
| Vapor pressure at 37.8 °C                        | 14 to 21 kPa                                    | 105 to 157 mm Hg                                                     |            |
| Vapor pressure at 300 K                          | 12.04 kPa                                       | 90 mm Hg                                                             | [4]        |
| Density at 300 K                                 | 0.7527 g/cm <sup>3</sup>                        | 46.99 lb <sub>m</sub> /ft <sup>3</sup>                               | [4]        |
| Kinematic viscosity at 300 K                     | 0.924 mm <sup>2</sup> /s                        | 0.924 cSt                                                            | [4]        |
| Dynamic viscosity at 298 K                       | 870 μPa s                                       | 0.879 cPs                                                            |            |
| Surface tension at 300 K                         | 23.27 mN/m                                      | 23.27 dyn/cm                                                         | [4]        |
| Thermal conductivity                             | 0.14 W m <sup>-1</sup> K <sup>-1</sup> at 298 K | 0.079 BTU h <sup>-1</sup> ft <sup>-1</sup> °F <sup>-1</sup> at 77 °F | —          |
| Heat capacity $c_p$                              | 2.1 J g <sup>-1</sup> K <sup>-1</sup> at 298 K  | 0.50 BTU lb <sup>-1</sup> °F <sup>-1</sup> at 77 °F                  | —          |
| Enthalpy of formation $\Delta H_f^{298}$         | -22723 J/mol                                    | -388.8 cal/g                                                         | [5]        |
| Lower (net) heat of combustion $\Delta H_{comb}$ | >42.8 MJ/kg                                     | >18413 BTU/lb                                                        | [3]        |
|                                                  | 43.603 MJ/kg                                    | 18758 BTU/lb                                                         | [4]        |
| Autoignition temperature                         | 503 K                                           | 229 °C = 445 °F                                                      | [6]        |
| Flash point                                      | 244 K                                           | -29 °C = -20 °F                                                      | [6]        |

gine design, and other fuel-related technologies [8]. Data obtained on most samples included hydrocarbon-type analysis (Modified ASTM D 2789 and Monsanto Method 21-PQ-38-63), simulated distillation (ASTM D 2887-73), heat of combustion (ASTM D 240-76), true vapor pressure, kinematic viscosity (ASTM D 445-79), surface tension (capillary rise method), and density. See also [9].

### 2.2.1 Density of JP-4

The range of density variations among several samples of JP-4 and their dependence on temperature is illustrated in Figure 1.

### 2.2.2 Vapor Pressure of JP-4

The vapor pressure of two different density (41 and 51 API) JP-4 samples was measured over the range from 311 to 644 K (100 to 700 °F) and the curve for the less volatile 41 API fuel is shown in Figure 2, with the Reid vapor pressure (RVP) as auxiliary variable [10]. The volume average boiling point for the API 41 fuel was 475 K (395 °F), and for the API 51 fuel it was 431 K (316 °F).

### 2.2.3 Viscosity of JP-4

The viscosity of JP-4 is illustrated in Figure 3 in comparison to that of JP-3 and JP-5. This is an average of many samples and one must expect significant variations from sample to sample.

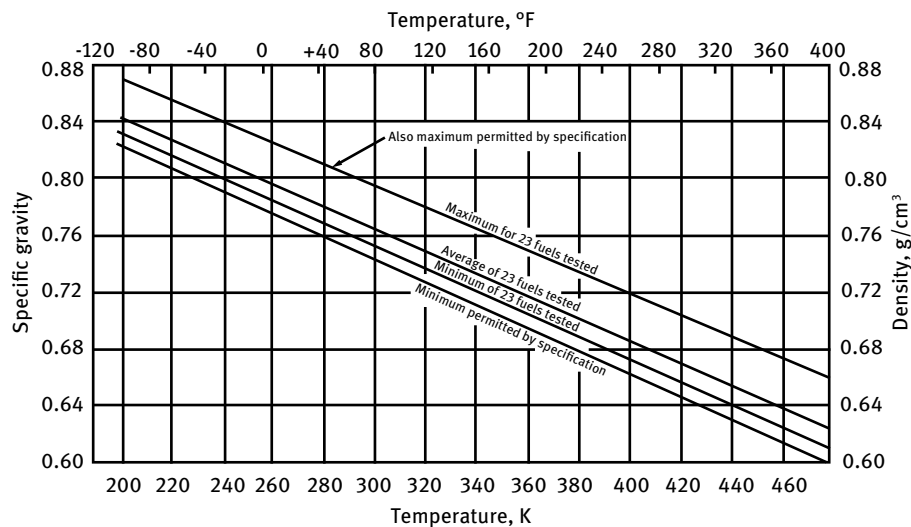


Figure 1: Density of MIL-F-5624C (JP-4) fuel. (Reproduced and modified from [1].)

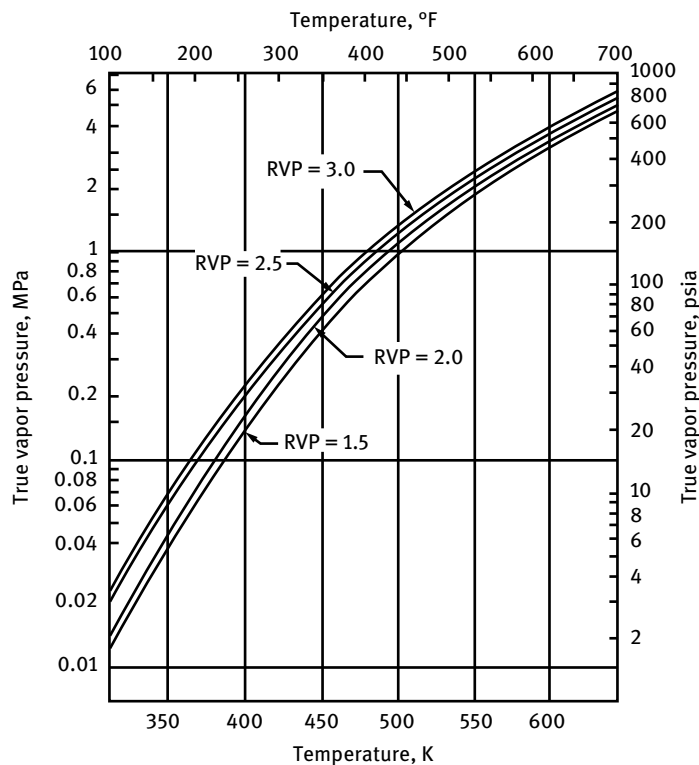
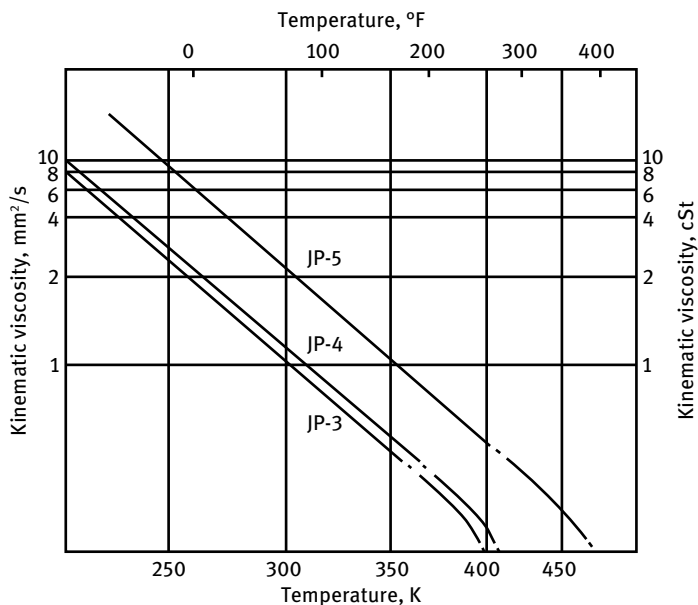


Figure 2: Vapor pressure of JP-4. (Republished and modified from [10], with permission of ©1954 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)



**Figure 3:** Kinematic viscosity of JP-4, JP-3, and JP-5. (Reproduced and modified from [1].)

Furthermore, the flow properties of JP-4 with entrained gas bubbles is different from those of a bubble-free liquid [11]. The dynamic viscosity of JP-4 at 298 K is 0.879 cPs.

#### 2.2.4 Surface Tension of JP-4

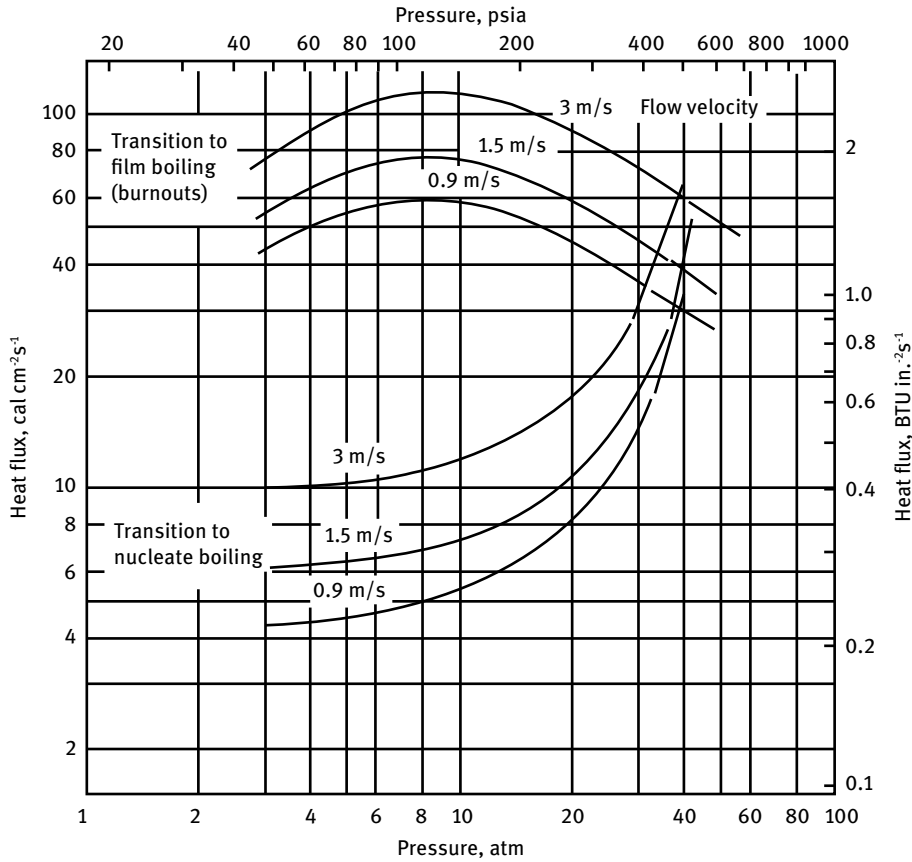
The surface tension of JP-4 at 300 K was reported as 23.27 mN/m = 23.27 dyn/cm [4].

#### 2.2.5 Thermal Conductivity of JP-4

The thermal conductivity of JP-4 at 300 K was reported as 0.14 W m<sup>-1</sup> K<sup>-1</sup> at 298 K = 0.079 BTU h<sup>-1</sup> ft<sup>-1</sup> °F<sup>-1</sup> at 77 °F [12].

#### 2.2.6 Heat Transfer Coefficient of JP-4

Heat transfer to subcritical JP-4 was studied using a transparent annular test section with an electrically heated, stainless steel tube [10]. Heat transfer data were obtained in the non-boiling, nucleate boiling, and film boiling regions for velocities from 0.9 to 12 m/s (3 to 40 ft/s) and pressures from 207 to 3447 kPa (30 to 500 psia). Burnout data were obtained over the same range of variables. The heat flux values were increased until either the tube failed or the limit of power generation was reached, which was approximately 1634 W/cm<sup>2</sup> (10 BTU in.<sup>-2</sup> s<sup>-1</sup>). The troublesome phenomenon of coking was studied visually and by the use of colored films. The dependence of the heat trans-



**Figure 4:** Effect of pressure and flow velocity on heat transfer to JP-4. (Republished and modified from [10], with permission of ©1954 American Institute of Aeronautics & Astronautics; permission conveyed through Copyright Clearance Center Inc.)

fer to JP-4 on pressure and flow velocity in a cooling channel in a rocket engine and the variation of nucleate boiling range with pressure is illustrated in Figure 4.

In the non-boiling regime of forced convection, the heat transfer to JP-4 can be represented by a Sieder–Tate equation with an accuracy of  $\pm 11\%$

$$Nu = 0.0213 Re^{0.8} Pr^{0.33} \left( \frac{\eta_m}{\eta_{wall}} \right)^{0.14}$$

where  $Nu$  is the Nusselt number,  $Re$  is the Reynolds number,  $Pr$  is the Prandtl number,  $\eta_m$  is the viscosity of the medium at the center of the flow and  $\eta_{wall}$  is the viscosity of the fluid near the wall. The transition from non-boiling heat transfer to nucleate boiling occurs at higher and higher pressures the lower the flow velocity is and vice versa.

In the regime of nucleate boiling, the influence of flow velocity is not as pronounced as the influence of pressure (see Figure 4, lower group of curves). The transition to film boiling, which is accompanied by a drop in heat transfer and can lead to burnout of the wall in critical locations at the upper limit of nucleate boiling, is not as strongly dependent on the local pressure.

## 2.2.7 Thermodynamic Properties of JP-4

### 2.2.7.1 Heat of Combustion of JP-4

There exists a wide variety of heat of combustion data for JP-4, depending on the source of the samples analyzed. The MIL SPEC requirement for the heat of combustion of JP-4 per MIL-DTL-5624W is a minimum of 42.8 MJ/kg (18413 BTU/lb). The NASA CEA input calculation for the enthalpy of formation of JP-4 (and RP-1) was based on a heat of combustion of 18640 BTU/lb [5]. One of the summary publications for kerosene properties [13] gives a heat of combustion of 18701.30 BTU/lb, which is the value accepted in reference [2].

The heating value of JP-4 and similar kerosenes is mostly a function of the hydrogen content of the fuel. The heating value can be estimated from an empirical equation

$$Q_{\text{net}} = 35.08 + 0.5849H$$

where  $Q_{\text{net}}$  is the heating value in MJ/kg and  $H$  is the hydrogen content in mass-%.

### 2.2.7.2 Enthalpy of Formation of JP-4

It is difficult to calculate the enthalpy of formation of a mixture of hydrocarbons that varies over such a wide range as JP-4 does. The enthalpy of formation is derived from the heat of combustion which varies just as much.

The standard enthalpy of formation of JP-4 was reported as  $-6124.80 \text{ cal/mol}$  for a molecular mass of  $14.027 \text{ g/mol}$ , which translates to a enthalpy of formation of  $-437 \text{ cal/g} = -1828 \text{ J/g}$  [13]. It is not meaningful to give enthalpy of formation of a mixture in terms of energy per mol because the molecular mass and empirical formula used by different investigators varies from case to case. Another source gave the enthalpy of formation of JP-4 as  $-1903 \text{ J/g} = -818 \text{ BTU/lb}$  [6]. However, the PEPCODED.DAT list gives an enthalpy of formation of  $-281 \text{ cal/g} = -1176 \text{ J/g}$  for a JP-4 fuel with a density of  $0.0254 \text{ lb/in.}^3 = 0.7031 \text{ g/cm}^3$ , which is quite different [14].

The NASA CEA input list [5] assumes a JP-4 enthalpy of formation of  $-22723 \text{ kJ/mol} = -1626.7 \text{ J/g} = -388.8 \text{ cal/g}$ , which is based on a heat of combustion of 18640 BTU/lb, assuming an empirical formula of  $\text{C}_{11}\text{H}_{1.9423}$  and a molecular mass of  $13.9688 \text{ g/mol}$  for a fuel with a density of  $0.773 \text{ g/cm}^3$ . This number is between that of [13] and [14]. They assume that the same data are valid for RP-1.

2.2.7.3 Enthalpy of Evaporation of JP-4

The latent enthalpy of evaporation of JP-4 and JP-5 as a function of temperature is illustrated in Figure 5.

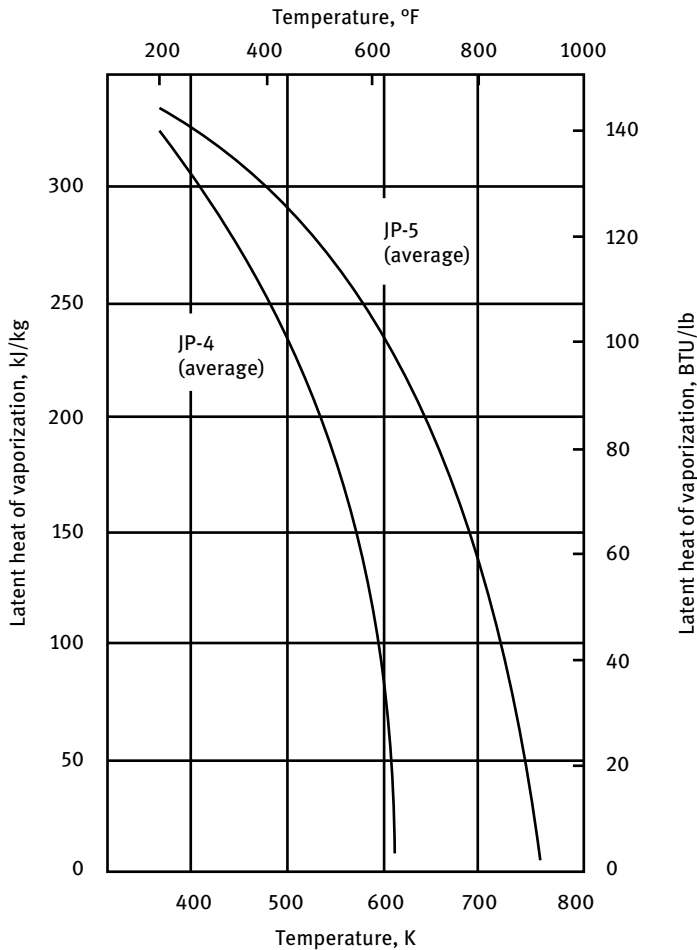
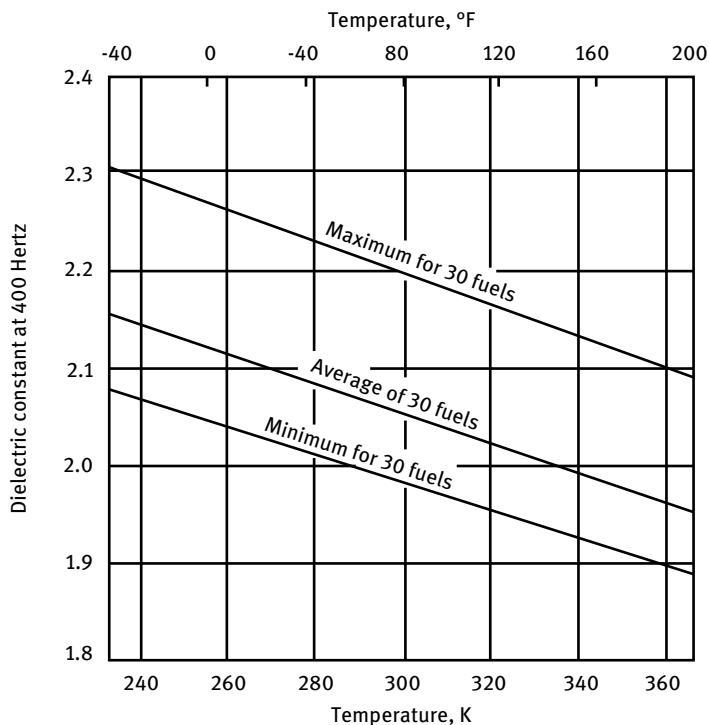


Figure 5: Latent enthalpy of evaporation of JP-4 and JP-5. (Reproduced and modified from [1].)

2.2.8 Dielectric Constant of JP-4

The dielectric constant of JP-4 as a function of temperature is illustrated in Figure 6, based on the analysis of 30 samples, all within the specification limits of MIL-F-5624C. Measuring the dielectric constant of fuels is a tool for purity control and an indication



**Figure 6:** Dielectric constant of JP-4 as a function of temperature. (Reproduced and modified from [1].)

of the likelihood of building up dangerous electrostatic charges which may lead to accidental ignition in air.

## 2.3 Chemical Properties of JP-4

The empirical formula for JP-4 can be described as  $C_{9.5}H_{18.9}$  corresponding to a molecular mass of 133.1 g/mol. JP-4 was described as a high volatility, low freezing point fuel composed of approximately 65% gasoline and 35% kerosene.

### 2.3.1 Specifications for JP-4 and JP-5

The Military Specification for JP-4 is combined with that for JP-5. The most recent revision was MIL-DTL-5624W in 2016 [3]. As the last letter of the specification number indicates, this specification has gone through many revisions. The specification requirements for JP-4 are listed in Table 2.

**Table 2:** Specification requirements for JP-4 and JP-5.

| Property                                                                     | GRADE JP-4            | GRADE JP-5      | ASTM or IP test method                                                 |
|------------------------------------------------------------------------------|-----------------------|-----------------|------------------------------------------------------------------------|
| Total acid number, mg KOH/g, max.                                            | —                     | 0.015           | D3242                                                                  |
| Aromatics, vol.-%, max.                                                      | 25.0                  | 25.0            | D13191                                                                 |
| Aromatics, vol.-%, max.                                                      | 26.52                 | 26.52           | D6379 <sup>a</sup>                                                     |
| Sulfur, mercaptan, mass-%, max.                                              | 0.003                 | 0.002           | D32271                                                                 |
| Doctor test                                                                  | Negative              | Negative        | D4952                                                                  |
| Sulfur, total, mass-%, max.                                                  | 0.30                  | 0.20            | D129, D1266, D2622,<br>D3120, D42941 or D5453<br>D861, D7345 or D28875 |
| Distillation temperature, °C                                                 |                       |                 |                                                                        |
| Initial boiling point                                                        | Report                | Report          |                                                                        |
| 10% recovered, temp.                                                         | Report                | 205 max.        |                                                                        |
| 20% recovered, temp.                                                         | 90 min.,<br>145 max.  | Report          |                                                                        |
| 50% recovered, temp.                                                         | 110 min.,<br>190 max. | Report          |                                                                        |
| 90% recovered, temp.                                                         | 245 max.              | Report          |                                                                        |
| End point, max. temp.                                                        | Report                | 300 max.        |                                                                        |
| Residue, vol.-%, max. (for D86)                                              | 1.5                   | 1.5             |                                                                        |
| Loss, vol.-%, max. (for D86)                                                 | 1.5                   | 1.5             |                                                                        |
| Flash point, °C, min.                                                        | —                     | 60.0            | D56, D931 or D3828                                                     |
| Density, at 15 °C, kg/L, min. (API max.)                                     | 0.751<br>(57.0)       | 0.788<br>(48.0) | D1298, D40521 or D7777                                                 |
| kg/L, max. (API min.)                                                        | 0.802<br>(45.0)       | 0.845<br>(36.0) |                                                                        |
| Vapor pressure, at 37.8 °C, kPa, min.<br>max.                                | 14<br>21              | —<br>—          | D323 or D51911                                                         |
| Freezing point, °C, max.                                                     | −50                   | −46             | D23861, D59728, D7153<br>or D7154                                      |
| Viscosity, at −20 °C, max., mm <sup>2</sup> /s                               | —                     | 7.0             | D445                                                                   |
| Net heat of combustion, MJ/kg, min.                                          | 42.8                  | 42.6            | D3338/D3338M, D4529<br>or D4809                                        |
| Hydrogen content, mass-%, min.                                               | —                     | 13.4            | D3701, D5291 or D71711                                                 |
| Smoke point, mm, min. or                                                     | 25.0                  | 25.0            | D1322                                                                  |
| Smoke point, mm, min.                                                        | 18.0                  | 18.0            | D1322                                                                  |
| Naphthalene, vol.-%, max.                                                    | 3.0                   | 3.0             | D1840                                                                  |
| Copper strip corrosion, 2 h at 100 °C, max.                                  | No. 1                 | No. 1           | D130                                                                   |
| Thermal stability <sup>c</sup> : change in pressure<br>drop, mm Hg, max. and | 25                    | 25              | D3241                                                                  |
| Tube deposit code, less than, or                                             | 3 <sup>b</sup>        | 3 <sup>b</sup>  | D3241 Annex A1                                                         |
| Average deposit thickness, nm, over area<br>of 2.5 mm <sup>2</sup> , max.    | —                     | 85              | D3241 Annex A2                                                         |
| Existent gum, mg/100 mL, max.                                                | 7                     | 7               | D381 or IP 540                                                         |



Table 2: (continued)

| Property                                            | GRADE JP-4 | GRADE JP-5 | ASTM or IP test method   |
|-----------------------------------------------------|------------|------------|--------------------------|
| Fuel system icing inhibitor: vol.-% min.            | 0.10       | 0.08       | D5006                    |
| Fuel system icing inhibitor: vol.-% max.            | 0.15       | 0.11       |                          |
| Fuel electrical conductivity: allowable range, pS/m | 150 to 600 | —          | D2624                    |
| Particulate matter (gravimetric), mg/L, max.        | 1          | 1          | ASTM D2276 or ASTM D5452 |

<sup>a</sup> When using D6379 results, the higher maximum total aromatics limit shall apply

<sup>b</sup> If the visual rating of the heater tube shows peacock (P) or abnormal (A) type deposits, the fuel sample is not acceptable

<sup>c</sup> The thermal stability test shall be conducted using ASTM D3241 at a test temperature of 260°C.

The aromatic content of JP-4 has been historically quite low, around 11 vol.-%. Conversion from high volatility JP-4 to lower volatility JP-8, which is similar to commercial Jet A-1, as the primary USAF aircraft turbine fuel had been under consideration since 1978. The strong motives for the change were NATO standardization and reduced combat vulnerability. In addition, the crude oil strategic supply situation had led to considerations to determine the extent to which USAF fuel specifications can be broadened to increase the yield from available petroleum crudes and, ultimately, to permit production from other sources such as coal, oil shale, and tar sands or alcohol from fermentation.

Distillate hydrocarbon fuels are being considered for many hypersonic vehicle and space planes. Characterization of the composition of fuels is complicated by the relatively loose specifications and the variations encountered in the fuels from day-to-day and refinery-to-refinery. A version of ASTM D2425 was used to characterize a number of jet fuels from a recent world fuel survey, as well as a number of specialty kerosene fuels, such as RP-1 and JP-7 [15]. These data were useful for combustion physical property modeling, as well as developing “surrogates” for testing of kerosene fuels.

Additives found in JP-4 include MIL-PRF-25017 Inhibitor, Corrosion/Lubricity Improver, Fuel Soluble (NATO S-1747) and MIL-DTL-85470 Inhibitor, Icing, Fuel System, High Flash, (NATO S-1745).

Antioxidants are added to freshly processed JP-4 before the fuel is exposed to air during storage and transfer. Antioxidants are methyl-*tert*-butylphenols. The antioxidant concentration is limited to not less than 17.2mg nor more than 24.0mg of active ingredient per liter of fuel.

### 2.3.2 Surrogate Fuel Mixtures for JP-4

Because of the complexities involved in measuring and modeling the performance and properties of finished fuels, the fuel science community must often use surrogate mixtures as substitutes, especially in the absence of consensus standard mixtures. While surrogate mixtures are often formulated on the basis of the ability of a particular mixture to reproduce a particular property, there is usually a desire to employ surrogate mixtures that are physicochemically authentic. This means that, provided that the primary purpose is satisfied, researchers are inclined to choose mixtures that have physical and chemical properties appropriate to the finished fuel.

A mixture of 14 different, pure hydrocarbons was developed based on the distillation curve and compound class composition as a laboratory-reproducible surrogate fuel with properties very similar to those of JP-4 [16].

Two surrogate fuel mixtures were developed using a model-based optimizer to emulate the fuel properties affecting the spray development and gas phase ignition of a conventional jet fuel [17]. The first surrogate, UM1, was a mixture of *n*-dodecane/iso-cetane/methylcyclohexane/toluene (0.3844/0.1484/0.2336/0.2336 mol fraction), while the second, UM2, was a mixture of *n*-dodecane/iso-cetane/decalin/toluene (0.2897/0.1424/0.3188/0.2491 mol fraction). The surrogates contained hydrocarbon species that are available in existing chemical mechanisms, and emulate both the physical and chemical properties of a representative real jet fuel, Jet A POSF-4658. POSF-4658 is suitable as a surrogate target fuel since the properties of POSF-4658 are representative of a nominal Jet A, and a wide range of experimental POSF-4658 data is readily available, including multiple ignition delay measurements. While the UM1 surrogate gave a much tighter match for temperature-independent properties, UM2 was shown to better emulate liquid density and volatility, properties which are known to be important for spray predictions under engine conditions. Ignition delay times predicted with a detailed chemical mechanism under diesel conditions showed reasonable agreement with shock tube and rapid compression machine experiments.

### 2.3.3 Analysis of JP-4

The list of test methods for qualification of JP-4 (or JP-5) in MIL-DTL-5624W extends over 3½ pages [3]. Most of those test methods are documented ASTM test methods.

### 2.3.4 Thermal Stability of JP-4

During heat transfer measurements in the laboratory as well as in real airborne life application, carbon deposits as a result of incipient hydrocarbon decomposition will interfere with the heat transfer or clog passaged and increase pressure drops. Carbon deposits are good insulators and will reduce the amount of heat flowing through the wall. Pyrolysis of JP-4 and carbon deposition can start at wall temperatures of 753 to 923 K (480 to 650 °C), depending on the quality of the propellant [18].

Similar measurements and observations were made for JP-3 [19–22]. Carbon deposition can occur above 673 K (400 °C) and can become a real problem. Using the heat transfer data thus obtained in the laboratory, one can design and size a cooling system for LOX/JP-3 or N<sub>2</sub>O<sub>4</sub>/JP-3 rocket engines that are regeneratively cooled with JP-3 [23].

## 2.4 Toxicity of JP-4

Because the composition of JP-4 with and without additives may vary widely, depending on where the samples are taken, it is difficult to establish a safe limit for inhalation of JP-4 vapors at the place of employment [24]. The same concern applies to other kerosenes that are now replacing JP-4 in the inventory of military supplies. The recommended threshold limit value (TLV) for JP-4 is 2.5 mg/L.

Male and female Fischer-344 rats, female C57BL/6 mice, and male and female beagle dogs were divided into three treatment groups and exposed nearly continuously (23 h/day, 7 days/week) to JP-4 jet fuel vapor at concentrations of 0, 500, and 1000 mg/m<sup>3</sup> for 90 days [25]. At exposure termination, all dogs and 1/3 of the rodents were euthanatized and the remaining animals were held for either a 19- or 21-month post-exposure tumorigenesis observation period. Pathologic findings in male rats revealed treatment-related renal toxicity consistent with male rat oc2M-globulin nephropathy. No treatment-related respiratory toxicity was noted in any species. This study did not demonstrate target-organ toxicity or carcinogenesis which could be extrapolated to other species. A very detailed toxicological profile of JP-4 was published which also included toxicity data for JP-7 [26].

The relative potency of three jet fuels (JP-4, JP-8, and JP-8+100) to cause respiratory tract sensory irritation was studied by administering vapor only or vapor/aerosol mixtures for 30 min periods by means of a head-only exposure system to groups of four mice [27].

## 2.5 Environmental Impact of JP-4 Spills

Although JP-4 is no longer used, information on environmental impact of JP-4 spills is summarized here because similar consequences may be observed in the event of spills of other kerosenes, including RP-2. JP-4 and several other kerosenes were examined to measure the effects of potential environmental contamination resulting from these fuels on fresh water fish and aufwuchs [28]. Besides JP-4, the materials evaluated included RJ-4, RJ-5, methylcyclohexane, and JP-9. The toxicity of JP-4 would differ from that of other kerosenes if the additives turn out to be more toxic than the hydrocarbon base by itself. The water extract of the water-soluble fraction of JP-4 was still toxic to small fish [29, 30].

## 2.6 Safety Properties of JP-4

### 2.6.1 Flash Point of JP-4

The flash point of JP-4 can vary widely, depending on the exact composition of the fuel. It depends on the most volatile component of the hydrocarbon mixture that makes up JP-4 and similar jet fuels. The published flash point value for JP-4 is 244 K ( $-29^{\circ}\text{C} = -20^{\circ}\text{F}$ ) [6].

### 2.6.2 Flammable Range of JP-4 Vapors

The flammability limits of JP-4 and JP-5 are listed in Table 3.

**Table 3:** Flammability limits of JP-4 and JP-5.

| Fuel               | Flammability limits |      |                |      |
|--------------------|---------------------|------|----------------|------|
|                    | Volume percent      |      | Fuel:air ratio |      |
|                    | Lean                | Rich | Lean           | Rich |
| JP-4               |                     |      |                |      |
| Minimum volatility | 0.74                | 5.34 | 0.035          | 0.26 |
| Maximum volatility | 0.90                | 6.15 | 0.035          | 0.25 |
| Average volatility | 0.80                | 5.63 | 0.035          | 0.26 |
| JP-5               |                     |      |                |      |
| Minimum volatility | 0.57                | 4.38 | 0.035          | 0.28 |
| Maximum volatility | 0.62                | 4.68 | 0.035          | 0.28 |
| Average volatility | 0.60                | 4.53 | 0.035          | 0.28 |

Data source: [1]

### 2.6.3 Autoignition Temperature of JP-4

The autoignition temperature of flammable liquids is determined in accordance with ASTM Method E659-78 (1994) [31]. Literature data for autoignition temperature of JP-4 are summarized in Table 4.

**Table 4:** Autoignition temperature of JP-4 and JP-5.

| Fuel     | Autoignition temperature |                    |                    | References |
|----------|--------------------------|--------------------|--------------------|------------|
|          | K                        | $^{\circ}\text{C}$ | $^{\circ}\text{F}$ |            |
| JP-4     | 524                      | 251                | 484                | [1]        |
| Kerosene | 522                      | 249                | 480                | [32]       |
| JP-5     | 518–520                  | 245–247            | 473–477            | [1]        |

### 3 Jet Fuel Kerosene JP-5

JP-5 fuel, used from 1952 to the present by the US Navy, has a 333 K (140 °F) (minimum) flash point temperature. This kerosene fuel is currently the US Navy's primary fuel and was developed mainly due to fire safety concerns aboard ships. This fuel has a freezing point temperature of 227 K (−51 °F). JP-5 does not have the anti-static additive as JP-4 and JP-8 have.

The physical properties of JP-5 and other kerosene fuels can vary considerably yet still lie within the military specification (MIL-DTL-5624W; March 2016) [1, 33]. JP-5, also known under the designation NATO F44, has been described in the Military Specification as “high flash point, kerosene type.”

#### 3.1 Physical Properties of JP-5

Physical properties of JP-5 are listed in Table 5 and reference [34].

##### 3.1.1 Density of JP-5

The military specification MIL-DTL-5624W requires that the density of JP-5 at 288 K must be in the range from 788 to 845 kg/m<sup>3</sup> = 0.788 to 0.845 g/cm<sup>3</sup> [3]. The variation of the density of numerous samples of JP-5, all within the MILSPEC limits, and their dependence on temperature, is illustrated in Figure 7. A typical sample of JP-5 had a density of 0.82 g/cm<sup>3</sup>, which is close to the average for 62 samples analyzed.

##### 3.1.2 Vapor Pressure of JP-5

The vapor pressure of JP-5 as a function of temperature is illustrated in Figure 8. The vapor pressure of a typical sample of JP-5 at 332 K was reported as 0.69 kPa (5.2 mm Hg) [3].

##### 3.1.3 Viscosity of JP-5

The kinematic viscosity of JP-5 as a function of temperature is shown in Figure 9. The military specification MIL-DTL-5624W requires that the kinematic viscosity of JP-5 at 253 K must not be higher than 7.0 mm<sup>2</sup>/s (7 cSt at −20 °C) [3].

##### 3.1.4 Surface Tension of JP-5

The surface tension of a typical sample of JP-5 at 298 K was reported to be 23.6 mN/m (23.6 dyn/cm at 25 °C) [1].

**Table 5:** Physical properties of JP-5.

| Property                                                | SI units                                                                         | Other units                                                                                 | References |
|---------------------------------------------------------|----------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|------------|
| Molecular mass for $C_{12}H_{24}$                       | 168.32 g/mol                                                                     | 5.9411 mol/kg                                                                               |            |
| Molecular mass for $C_{11}H_{1.9185}$                   | 13.9448 g/mol                                                                    | 71.71 mol/kg                                                                                | [5]        |
| Freezing point                                          | 227 K                                                                            | $<-46^{\circ}\text{C} = <-50.8^{\circ}\text{F}$                                             | [3]        |
| Boiling range                                           | 478–573 K                                                                        | 205–300 $^{\circ}\text{C}$                                                                  |            |
| Density at 288 K                                        | 788–845 kg/m <sup>3</sup>                                                        | 0.788–0.845 g/cm <sup>3</sup>                                                               |            |
| Boiling range                                           | 455–530 K                                                                        | 360–495 $^{\circ}\text{F}$                                                                  | [6]        |
| Vapor pressure at 332 K                                 | 0.69 kPa                                                                         | 0.10 psia at 138 $^{\circ}\text{F}$                                                         | [1]        |
| Density at 298 K                                        | 0.820 g/cm <sup>3</sup>                                                          | 51.2 lb <sub>m</sub> /ft <sup>3</sup> , 6.84 lb <sub>m</sub> /gal at 77 $^{\circ}\text{F}$  | [34]       |
| Kinematic viscosity at 298 K                            | 2.6 mm <sup>2</sup> /s                                                           | 2.6 cSt at 77 $^{\circ}\text{F}$                                                            | [34]       |
| Kinematic viscosity at 253 K                            | 7.0 mm <sup>2</sup> /s max.                                                      | $<7$ cSt at $-20^{\circ}\text{C}$                                                           | [3]        |
| Surface tension at 298 K                                | 23.6 mN/m                                                                        | 23.6 dyn/cm at 25 $^{\circ}\text{C}$                                                        | [1]        |
| Thermal conductivity                                    | 0.14 W m <sup>-1</sup> K <sup>-1</sup>                                           | 0.079 BTU h <sup>-1</sup> ft <sup>-1</sup> $^{\circ}\text{F}^{-1}$ at 77 $^{\circ}\text{F}$ |            |
| Dielectric constant                                     | 2.15 at 400 Hz                                                                   | —                                                                                           |            |
| Heat capacity $c_p$ at 298 K                            | 1.9 J g <sup>-1</sup> K <sup>-1</sup>                                            | 0.46 BTU lb <sub>m</sub> <sup>-1</sup> $^{\circ}\text{F}^{-1}$                              | [34]       |
| Enthalpy of formation $\Delta H_f^{298}$                | -22183 J/mol for a molecular mass of 13.9448 corresponding to $C_{11}H_{1.9185}$ | -1591 J/g = -380 cal/g                                                                      | [5]        |
|                                                         | -1719 kJ/kg                                                                      | -739 BTU/lb                                                                                 | [6]        |
|                                                         | -1720 J/g                                                                        | -411 cal/g for a fuel with a density of 0.0296 lb <sub>m</sub> /in. <sup>3</sup>            | [14]       |
| Lower (net) heat of combustion $\Delta H_{\text{comb}}$ | $>42.6$ MJ/kg                                                                    | $>18327$ BTU/lb                                                                             | [3]        |
|                                                         | 42.4 MJ/kg                                                                       | 18241 BTU/lb                                                                                | [6]        |
|                                                         | 43.170 MJ/kg                                                                     | 18560 BTU/lb <sub>m</sub>                                                                   | [1]        |
| Volumetric heat of combustion                           | 34800 MJ/m <sup>3</sup>                                                          | 125000 BTU/gal.                                                                             | [6]        |
| Autoignition temperature                                | 497 K                                                                            | 435 $^{\circ}\text{F}$                                                                      | [6]        |
| Flash point                                             | 334 K                                                                            | 142 $^{\circ}\text{F}$                                                                      | [6]        |
| Flash point                                             | $>333$ K                                                                         | $>60^{\circ}\text{C}$                                                                       | [3]        |

### 3.1.5 Thermal Conductivity of JP-5

The thermal conductivity of a typical sample of JP-5 at 298 K was reported as 0.14 W m<sup>-1</sup> K<sup>-1</sup> (0.079 BTU h<sup>-1</sup> ft<sup>-1</sup>  $^{\circ}\text{F}^{-1}$  at 77  $^{\circ}\text{F}$ ) [1].

### 3.1.6 Thermodynamic Properties of JP-5

#### 3.1.6.1 Heat Capacity of JP-5

The isobaric heat capacity  $c_p$  of JP-5 at 298 K is 1.9 J g<sup>-1</sup> K<sup>-1</sup> (0.46 BTU lb<sub>m</sub><sup>-1</sup>  $^{\circ}\text{F}^{-1}$ ).

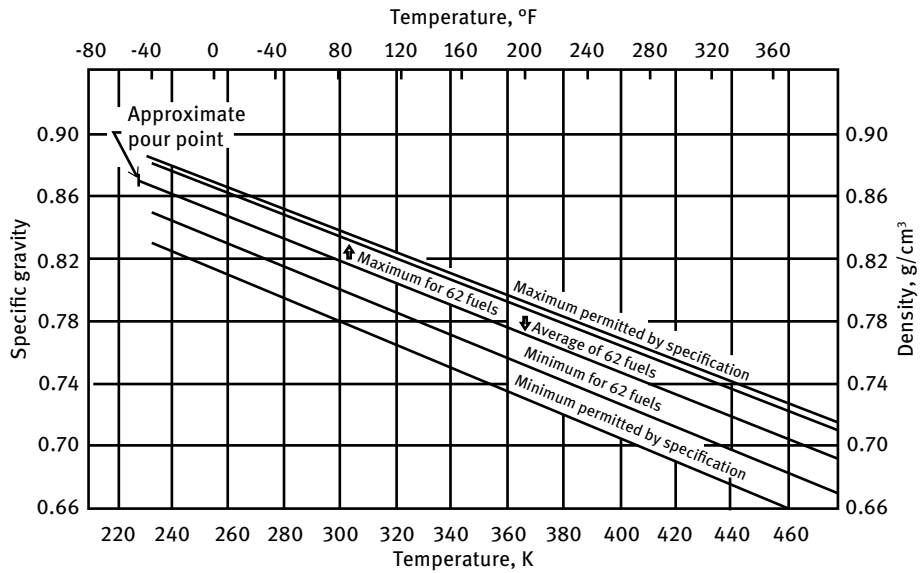


Figure 7: Density of MIL-F-5624C (JP-5) fuel. (Reproduced and modified from [1].)

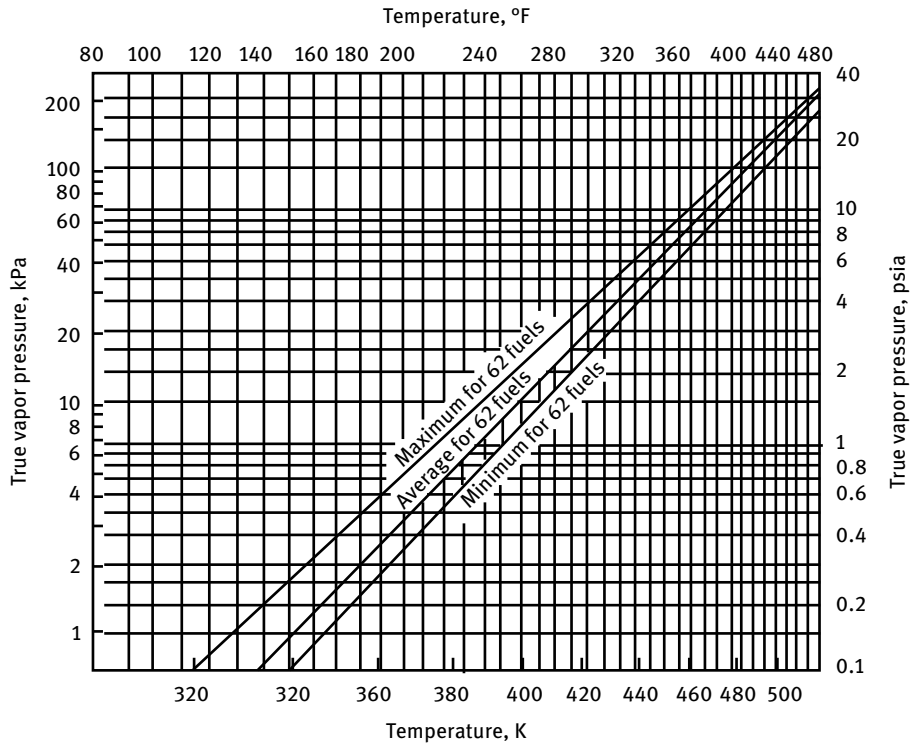
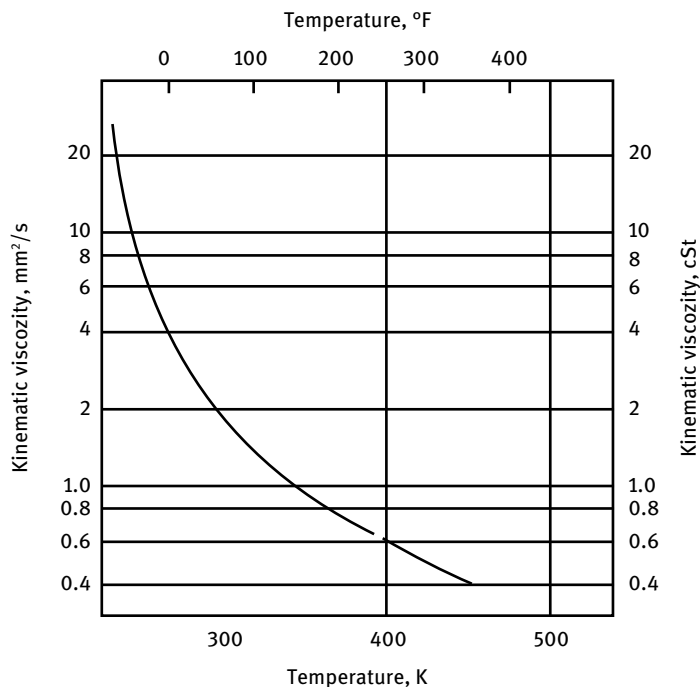


Figure 8: Vapor pressure of MIL-F-5624C (JP-5) fuel. (Reproduced and modified from [1].)



**Figure 9:** Kinematic viscosity of JP-5 as a function of temperature. (Reproduced and modified from [33].)

### 3.1.6.2 Heat of Combustion of JP-5

The heat of combustion of JP-5 varies with the source of the material. The military specification MIL-DTL-5624W requires that the net heat of combustion of JP-5 must be at least 42.6 MJ/kg (18327 BTU/lb) [3].

### 3.1.6.3 Enthalpy of Formation of JP-5

The enthalpy of formation of JP-5 varies with the source of the material and is calculated from the heat of combustion. The NASA CEA program uses an enthalpy of formation of  $-22183 \text{ J/mol}$  for a molecular mass of  $13.9448 \text{ g/mol}$  corresponding to an empirical formula of  $\text{C}_{11}\text{H}_{1.9185}$  which translates into  $\Delta H_f^{298} = -1591 \text{ J/g} = -380 \text{ cal/g}$  [5]. This number was derived from a heat of combustion of  $18600 \text{ BTU/lb}_m$ .

### 3.1.6.4 Enthalpy of Evaporation of JP-5

A graph showing the latent enthalpy of evaporation of JP-5 in comparison to that of JP-4 was already shown in Section 2.2.7.3. A similar graph has already been published (Figure 3 on page 12 of [33]).



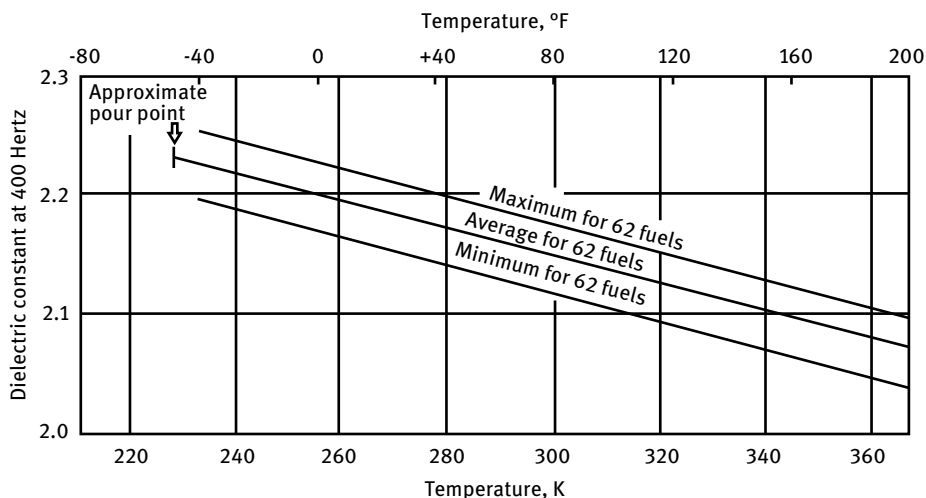
### 3.1.7 Electrical Properties of JP-5

#### 3.1.7.1 Electric Conductivity of JP-5

The electrostatic charge buildup hazard properties of JP-5 fuel derived from alternate (non-petroleum) sources were determined [35]. Two properties, electrical conductivity and electrostatic charging tendency, were measured on seven samples. Five coal-derived fuels and one sample derived from tar sands exhibited properties similar to jet fuels derived from petroleum and hence should not develop unusual ignition hazards in field handling. A JP-5 produced from shale had higher values of conductivity and charging tendency than petroleum-derived fuels, but the combination of the two properties indicated that no abnormal electrostatic hazards should be encountered.

#### 3.1.7.2 Dielectric Constant of JP-5

The dielectric constant of JP-5 as a function of temperature is illustrated in Figure 10, based on the analysis of 62 samples, which were all within the specification limits of MIL-F-5624C [3].



**Figure 10:** Dielectric constant of JP-5 as a function of temperature. (Reproduced and modified from [1].)

### 3.1.8 Critical Point Properties of JP-5

The following critical point properties were obtained for JP-5 [36]:

$$t_{\text{crit.}} = 675 \text{ K} = 402^\circ\text{C}$$

$$P_{\text{crit.}} = 2.27 \text{ MPa} = 22.4 \text{ atm}$$

## 3.2 Chemical Properties of JP-5

### 3.2.1 Specifications for JP-5

The Military Specification for JP-5 is combined with that for JP-4. The most recent revision was MIL-DTL-5624W (March 2016) [3]. As the last letter of the specification number indicates, this specification has gone through many revisions. The specification requirements for JP-5 were already listed in Table 2 along with those of JP-4.

A maximum of 50 vol.-% of the finished fuel may consist of synthesized paraffinic kerosene (SPK) blend components derived from Fischer–Tropsch (FT)-produced SPK or hydroprocessed esters and fatty acids (HEFA). FT-SPK blend components shall conform to the requirements in ASTM D7566 Annex A1. SPK blend components derived from HEFA shall conform to requirements in ASTM D7566 Annex A2. A maximum of 10 vol.-% of the finished fuel may consist of synthesized iso-paraffins blend components derived from hydroprocessed fermented sugars.

Antioxidants are usually added to freshly processed JP-5 before the fuel is exposed to air during storage and transfer. Antioxidants are methyl-*tert*-butylphenols. The antioxidant concentration is limited to not less than 17.2mg nor more than 24.0mg of active ingredient per liter of fuel.

### 3.2.2 Thermal Decomposition of JP-5

A test program was conducted to determine the thermal stability and heat transfer characteristics of JP-5 and several other kerosene-type fuels which vary in composition and tendency to form deposits [37]. Tests were conducted over the temperature range 425 to 870 K for durations up to 32h in small-diameter, resistively heated tubes at typical aircraft engine operating conditions. A detailed mapping of the thermal decomposition characteristics of JP-5 was performed to evaluate the importance of key operating conditions such as temperature, pressure, flowrate, and test duration, and to establish a database for estimating the relative performance of new fuels in comparison to JP-5. Fuel decomposition rates varied among fuels, and the relationship between the “breakpoint temperature” (determined according to ASTM D3241) and the rate of coke deposition was investigated.

A model was developed for predicting the thermal decomposition rates of aviation fuels like JP-5 [38]. The thermal deposition model was incorporated into an existing computational fluid dynamics (CFD) code that could solve the Reynolds-averaged conservation equations of mass, momentum, and energy. The decomposition chemistry was modeled by three global Arrhenius expressions in which the fuel decomposition was assumed to be due to an autoxidation reaction with dissolved oxygen. The deposition process was modeled by assuming that all deposit-forming species transported to the wall adhered and formed a deposit. Verification of the model required the determination of the following parameters for a given fuel, in this case JP-5: (1)

the pre-exponential constant and activation energy for the wall reaction, (2) the pre-exponential constant and activation energy for the bulk autoxidation reaction, and (3) the pre-exponential constant and activation energy for the precursor decomposition reaction.

### 3.2.3 Analysis of JP-5

The list of test methods for qualification of JP-5 (or JP-4) in MIL-DTL-5624W extends over several pages. Most of those test methods are documented ASTM test methods. The list of analytical methods used for the characterization of JP-5 to verify compliance with MIL-DTL-5624W is 2½ pages long [3]. The most fundamental method used for characterization of hydrocarbon fuel blends is the distillation fraction curve, measuring the amount of distillate that has collected while the temperature in the vapor phase is rising, and also measuring the amount of less volatile residue left behind at the upper end of the distillation range.

### 3.3 Materials Compatibility with JP-5

The compatibilities of several dozen lubricants and elastomers with JP-5 were evaluated in immersion tests. Parker Fuelube, Carbowax 1500, and MIL-L-6032 lubricants are compatible with JP-5 fuel. No corrosion was promoted by contact of JP-5 fuel with metallic compounds. Teflon, fluorosilicone rubber, polyethylene, Buna N, and Kel-F elastomers are compatible with JP-5 fuel [33].

### 3.4 Toxicity of JP-5

A very detailed summary of toxicity hazards of JP-5 (as well as JP-8 and Jet A) is available from NIOSH Agency for Toxic Substances and Disease Registry, Division of Toxicology and Human Health Sciences [39]. Although JP-5 and Jet A fuels have been used for over 60 years and JP-8 was identified by the Department of Defense as its single military fuel over 30 years ago, as of 2017 there were only very little specific data on the toxicity of kerosene-based jet fuels in humans. Limited information is available on the carcinogenic potential of jet fuels in humans. Studies in laboratory animals have examined the toxicity of JP-5, JP-8, and Jet A fuels following inhalation, oral, or dermal exposure and have reported a number of targets of toxicity, including the lungs, liver, skin, immunological system, nervous system, and developing organism. Although renal effects have also been observed in male rats exposed to JP-5 or JP-8, the lesions are considered to be characteristic of  $\alpha_2\mu$ -globulin nephropathy, which is only observed in male rats and is not considered to be toxicologically relevant to hu-

mans. JP-5 was not carcinogenic in mice in a 2-year dermal bioassay. Increases in skin tumors were observed in mice dermally exposed to Jet A for 52–62 weeks; however, tumors were only observed at concentrations resulting in significant skin damage (inflammation and necrosis). Similarly, increased numbers of skin tumors were observed in mice that received applications of undiluted kerosene on the skin for 2 years, but this occurred only in the presence of moderate-to-marked skin damage. No inhalation or oral studies evaluated the carcinogenicity of JP-5, JP-8, or Jet A in laboratory animals; no increases in tumor incidences were observed in rats administered kerosene by gavage for 2 years. No human studies have examined the potential of JP-5, JP-8, or Jet A to induce respiratory effects. Studies in rats, mice, rabbits, and pigs demonstrated the dermal toxicity of topically applied JP-5, JP-8, and Jet A. Similar effects have been observed for all three fuel types.

### 3.5 Safety Properties of JP-5

#### 3.5.1 Flammability Limits of JP-5

The flammability limits of JP-5 were already listed in Table 3 along with those of JP-4. A typical JP-5 fuel has a vapor pressure of about 69 Pa (0.01 psia) at 289 K (60 °F), equivalent to a fuel : air ratio of about 0.003. This is well below the lean limit, and the tank's free space will be non-flammable provided that liquid fuel is not dispersed as a mist in this space. As is known, fuel mists in air are nearly as flammable as fuel vapors in air, and a fuel tank containing JP-5 fuel at 289 K (60 °F) can be flammable if shaken sufficiently to disperse liquid fuel droplets through the tank's free space. The temperature of JP-5 fuel must be raised to about 330 K (135 °F) before the vapor pressure becomes sufficient to exceed the lean-limit concentration.

#### 3.5.2 Flash Point of JP-5

The flash point of JP-5 determined in accordance with ASTM D56, D931, or D3828 must be above 333 K (60 °C) to meet requirements of MIL-DTL-5624W. Other sources gave a flash point of 334 K (61 °C) [6].

#### 3.5.3 Autoignition Temperature of JP-5

Data for the autoignition temperature of JP-5 were already shown in Table 4 together with the data for JP-4. The autoignition temperature of JP-5 is 497 K (435 °F) [6].

## 4 Jet Fuel Kerosene JP-7

JP-7 is a kerosene fuel with properties quite similar to those of RP-1. Its specification [40] was created to provide a fuel with high thermal stability for use in the supersonic SR-71 Blackbird. It is interesting to compare the various requirements that led to the development of various operational jet fuels, that is, comparing JP-7 to (US) Jet A (European Jet A-1), Jet Propellant JP-4 (European F-40), JP-5 (European F-44), JP-8 (F-34), JP-TS (US only), and JP-8+100 (US only) [41]. The composition of aviation fuels has generally been determined by specifications that are primarily based upon operational requirements. These include heat content, fluidity, corrosion protection, and stability. Successful demonstration of hydrocarbon-fueled hypersonic technology was achieved with a flight test of an X-51A Waverider vehicle burning JP-7, but JP-7 is no longer in production [42].

Although JP-7 also meets the operational demands for hypersonic aircraft (Mach 5+), this fluid is no longer produced. There was a proposal in the hypersonic vehicle community to replace JP-7 with the rocket propellant RP-2; however, research and testing was necessary to determine whether this substitution would be possible [43]. The advanced distillation curve method was applied to a representative sample of the hypersonic vehicle fuel JP-7 in comparison to RP-2.

### 4.1 Physical Properties of JP-7

Properties of JP-7 are summarized in reference [44].

#### 4.1.1 Freezing (Melting) Point of JP-7

The maximum allowed freezing (melting) point of JP-7 specified per MIL-DTL-38219D is 229.8 K ( $-43.3^{\circ}\text{C}$ ) [40]. A typical freezing point of JP-7 is 229 K ( $-44^{\circ}\text{C} = -47.5^{\circ}\text{F}$ ).

#### 4.1.2 Boiling Range of JP-7

The boiling range of JP-7 per MIL-DTL-38219D is 455–561 K ( $182\text{--}288^{\circ}\text{C} = 360\text{--}550^{\circ}\text{F}$ ) [40].

#### 4.1.3 Density of JP-7

The density of JP-7 at 288 K ( $15^{\circ}\text{C}$ ) specified per MIL-DTL-38219D is  $0.779\text{--}0.806\text{ g/cm}^3$  [40].

#### 4.1.4 Vapor Pressure of JP-7

The minimum required vapor pressure of JP-7 per MIL-DTL-38219D is 20.7 kPa at 422 K (149 °C) and 331 kPa at 533 K (260 °C) [40]. A typical measured vapor pressure of JP-7 was 0.048 kPa at 298 K (0.36 mm Hg at 25 °C).

#### 4.1.5 Viscosity of JP-7

The maximum allowed kinematic viscosity of JP-7 at 253 K (−20 °C) per MIL-DTL-38219D is 8.0 mm<sup>2</sup>/s (8 cSt). Typical kinematic viscosity of JP-7 is about 1.775 mm<sup>2</sup>/s at 298 K (1.775 cSt at 25 °C).

#### 4.1.6 Surface Tension of JP-7

The surface tension of a sample of JP-7 was measured as 0.002255 mN/m at 298 K (0.002255 dyn/cm at 25 °C) [44].

#### 4.1.7 Heat Transfer Coefficient of JP-7

Heat transfer and flow instabilities in supercritical fuels in vertical tubes with upward flow were studied with JP-7 or methylcyclohexane as the test fluids with heat fluxes of 250 kW/m<sup>2</sup> and nominally turbulent ( $N_{Re} \sim 30000$ ) conditions [45]. At times, complete flow reversals with pressure amplitudes of 540 kPa (80 psid) and fluid exit temperature fluctuations of 100 °C were observed.

A series of electrically heated tube experiments was conducted to investigate the potential of JP-7 as a coolant under aerodynamic heating conditions of a Mach 8 scramjet propulsion system [46, 47]. The heat transfer capabilities, carbon deposition, and material compatibility of JP-7 at surface temperatures up to 1200 K (927 °C) were tested in 3.17-mm (0.125-in.) diameter tubes of 304 SS, Inconel 617, Haynes 188, Haynes 230, and 50150 moly-rhenium. The heat transfer to the coolant was modeled well by a Dittus-Boelter correlation at lower heat fluxes. At higher heat fluxes, audible instabilities were observed and corresponded to a significant enhancement in the coolant heat transfer rates. The carbon deposition rates in these tests were comparable to those in previous experiments at lower heat fluxes and much longer residence times. This result suggested that alternative paths of the deposition mechanism may be enhanced under high heat flux test conditions. Microscopic investigation of the test tubes after the experiments indicated that there was a significant layer of ordered carbon deposits that had not been seen in the tests at lower heat flux.

#### 4.1.8 Thermodynamic Properties of JP-7

##### 4.1.8.1 Heat Capacity of JP-7

The heat capacity of JP-7 is  $c_p = 2.025 \text{ J g}^{-1} \text{ K}^{-1}$  at 298 K ( $0.484 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$  at  $25^\circ\text{C}$ ) [44].

##### 4.1.8.2 Enthalpy of Formation of JP-7

The enthalpy of formation of liquid JP-7 is  $\Delta H_f^{298} = -1799 \text{ J/g} = -430 \text{ cal/g}$  calculated from the heat of combustion [48].

##### 4.1.8.3 Heat of Combustion of JP-7

The minimum net heat of combustion of JP-7 per MIL-DTL-38219D is  $43.5 \text{ MJ/kg} = 18700 \text{ BTU/lb}$  [40]. The volumetric net heat of combustion of JP-7 is  $34000 \text{ MJ/m}^3 = 124600 \text{ BTU/gal}$ .

##### 4.1.8.4 Enthalpy of Evaporation of JP-7

Assuming that the gross formula of JP-7 is  $\text{C}_{12}\text{H}_{25}$  and using correlation gas chromatography (GC) and nuclear magnetic resonance (NMR) spectrometry, the vaporization enthalpy of JP-7 was predicted to be  $341 \text{ kJ/kg}$  [49].

#### 4.1.9 Critical Point Properties of JP-7

The critical point properties of JP-7 were measured and calculated. A critical temperature of  $678 \text{ K}$  ( $761^\circ\text{F}$ ) was measured and a critical temperature of  $673 \text{ K}$  ( $751^\circ\text{F}$ ) and critical pressure of  $2.10 \text{ MPa}$  ( $305 \text{ psia}$ ) was calculated from boiling range data and density. The critical density is  $0.792 \text{ g/cm}^3$  at  $298 \text{ K}$  ( $49.5 \text{ lb}_\text{m}/\text{ft}^3 = 6.62 \text{ lb}_\text{m}/\text{gal}$  at  $77^\circ\text{F}$ ).

#### 4.2 Chemical Properties of JP-7

The empirical gross formulas for JP-7 cover a wide range of compositions. The proposed formulas are  $\text{C}_{12.5}\text{H}_{26}$ ,  $\text{C}_{12.1}\text{H}_{24.4}$ ,  $\text{C}_{12.3}\text{H}_{25.5}$ , and  $\text{C}_{15.1}\text{H}_{32.7}$ . The molecular mass is different for each of these formulas. One must not report thermophysical properties in terms of property per mol without specifying the average molecular mass this property was calculated for. JP-7 is a hydrocarbon-based kerosene fraction with a low volatility and high thermal stability. JP-7 was developed in the 1950s to meet the more stringent requirements necessary for the development of high-altitude reconnaissance aircraft that fly at speeds exceeding Mach 3. The extreme temperatures encountered due to the heat transmitted from compressed air on the aircraft, and air resistance, required the development of fuels with improved thermal stability and higher flash points. Although JP-7 also meets the operational demands for hypersonic aircraft (Mach 5+), this fluid is no longer produced. There may still be a desire in the hypersonic vehicle community to replace JP-7 with the rocket propellant RP-2. However, research and testing

would be necessary to determine whether this substitution will be possible. The advanced distillation curve method was used to characterize a representative sample of the hypersonic vehicle fuel JP-7 [43]. Specifically, the thermodynamically consistent distillation curve and the composition channel were used to characterize the curve in terms of composition and available energy content. The results were compared with previous measurements performed on the rocket propellants RP-1 and RP-2 to provide a basis of comparison among these fuels in terms of the fundamental thermophysical properties.

#### 4.2.1 Specifications for JP-7

JP-7 was a fuel created from special blending stocks to create a fuel with low vapor pressure, high thermal oxidation stability, and low volatility. It was developed for the SR-71 Blackbird in the 1960s but is no longer used. The specification requirements (chemical composition, physical properties, test methods) for JP-7 per MIL-DTL-38219D [40] are listed in Table 6.

JP-6 per MIL-J-2565 was a kerosene-based fuel developed in 1956 for the XB-70 Valkyrie aircraft. JP-6 was intended for the high altitude bomber, being similar to JP-5 but with a lower freezing point and improved thermal oxidative stability. When the XB-70 program was cancelled, the JP-6 specification, MIL-J-25656, was also cancelled.

#### 4.2.2 Composition of JP-7

To prevent the formation of gums and peroxides, one of the following antioxidants shall be blended into the fuel immediately after it is processed and before it is exposed to air. The antioxidant shall be added to the fuel at a concentration of 24 mg of inhibitor (not including weight of the solvent) per liter of fuel:

- a. 2,6-di-*tert*-butyl-4-methylphenol
- b. 2,4dimethyl-6-*tert*-butylphenol
- c. 2,6-di-*tert*-butylphenol
- d. Mixed *tert*-butylphenol composition:
  - 75% 2,6-di-*tert*-butylphenol
  - 10–15% 2,4,6-tri-*tert*-butylphenol
  - 10–15% *ortho-tert*-butylphenol

#### 4.2.3 Analysis of JP-7

Analysis methods for JP-7 are described in the MIL SPEC MIL-DTL-38219D [40].



**Table 6:** JP-7 chemical and physical requirements and test methods per MIL-DTL-38219D.

| Requirements                                                    | Minimum           | Maximum               | ASTM Standards test methods  |
|-----------------------------------------------------------------|-------------------|-----------------------|------------------------------|
| Aromatics, vol.-%                                               |                   | 5                     | D1319                        |
| Mercaptan sulfur, mass-% <sup>a</sup>                           |                   | 0.001                 | D3227                        |
| Sulfur, total, mass-%                                           |                   | 0.1                   | D1266, D2622, D3120 or D4294 |
| Distillation temperature, °C <sup>b</sup>                       |                   |                       | D86                          |
| Initial boiling point                                           | 182               |                       |                              |
| 10% recovered                                                   | 196               |                       |                              |
| 20% recovered <sup>c</sup>                                      | 206               |                       |                              |
| 50% recovered                                                   | Report            |                       |                              |
| 90% recovered                                                   | 260               |                       |                              |
| End point                                                       | 288               |                       |                              |
| Residue, vol.-%                                                 |                   | 1.5                   |                              |
| Distillation loss, vol.-%                                       |                   | 1.5                   |                              |
| Flash point, K (°C)                                             | 333 (60)          |                       | D93                          |
| Density, at 288 K (15 °C), kg/L                                 | 0.779             | 0.806                 | D1298 or D4052               |
| Vapor pressure, kPa at 422 K (149 °C)                           | 20.7 <sup>d</sup> |                       |                              |
| Vapor pressure, kPa at 533 K (260 °C)                           | 331 <sup>d</sup>  |                       |                              |
| Freezing point, K (°C)                                          |                   | 229.8 K<br>(−43.3 °C) | D2386                        |
| Viscosity, mm <sup>2</sup> /s, at 253 K (−20 °C)                |                   | 8.0 <sup>e</sup>      | D445                         |
| Net heat of combustion, MJ/kg (BTU/lb)                          | 43.5<br>(18700)   |                       | D2382 or D3338               |
| Hydrogen content, mass-%                                        | 14.40             |                       | D3343 or D3701               |
| Copper strip corrosion, at 100 °C (212 °F)                      | 1 <sup>b</sup>    |                       | D130                         |
| Thermal stability, JFTOT, change in pressure drop in 5 h, mm Hg |                   | 25.0                  | D3241                        |
| JFTOT, delta TDR Spun                                           |                   | 12                    | D3241                        |
| Existent gum, mg/100 mL                                         |                   | 5.0                   | D381                         |
| Particulate matter, mg/L, origin                                |                   | 0.3                   | D2276 or D5452               |
| Particulate matter, mg/L, destination                           |                   | 0.5                   | D2276 or D5452               |
| Water reaction, interface rating                                |                   | 1 <sup>b</sup>        | D1094                        |
| Separation rating                                               |                   | (2)                   |                              |
| Water separator index                                           | 85                |                       | D3948                        |
| Fuel system icing inhibitor, vol.-%                             | 0.10              | 0.15                  | D5006                        |

<sup>a</sup> The mercaptan determination may be waived at the option of the inspector if fuel is “Doctor Sweet” when tested in accordance with ASTM D4952.

<sup>b</sup> A condenser temperature of 0 to 4.4 °C (32 to 40 °F) shall be used. To insure accurate IBP data, the operator must cut back on the heating rate when the vapor/condensate ring rises to within about 25 mm (1 in.) of the vapor tube. The reduced heating rate allows the thermometer to more accurately reflect the true vapor temperature when the first condensate is collected.

<sup>c</sup> The temperature reading at the 20 percent recovered point shall be corrected for the emergent stem in accordance with ASTM E77, paragraph 7, Treatment of Data.

<sup>d</sup> Test shall be performed in accordance with the vapor pressure test in Appendix A or Appendix C of this specification.

<sup>e</sup> Until an ASTM thermometer calibrated for the −20 °C condition becomes available, this test may be conducted at −34.5 °C (−30 °F) with a maximum allowable viscosity of 15.0 centistokes

#### 4.2.4 Thermal Stability of JP-7

Experimental studies have shown that trace amounts of fuel-soluble metal compounds can be very detrimental to the thermal stability of JP-7. Adverse effects on fuel thermal stability have been demonstrated by gas-driven fuel coker tests on JP-7 fuels containing as little as 15 to 25 parts per billion of added iron or copper, or 100 to 250 parts per billion of added zinc or lead [50]. The true threshold concentrations were generally lower, since the added metal tended to disappear from fuel samples during storage and handling. The ambiguities in metal content hinder any clear correlation and make it impractical to recommend metal-content limits for fuel quality control.

Thermal cracking of JP-7 flowing through a heated tube was investigated as a possible high temperature heat sink for supersonic aircraft [51]. It was found that the endothermicity of the reactions was on the order of 697 kJ/kg (300 BTU/lb), much less than the theoretical maximum of 3487 kJ/kg (1500 BTU/lb). The decrease from the theoretical value was due to significant formation of saturated species and aromatics. The endothermic heat of reaction peaks at 40–60% conversion for both pure hydrocarbons and hydrocarbon fuel mixtures. The heat of reaction ranges from 323–930 kJ/kg (100–400 BTU/lb) of fuel converted. This heat of reaction is much smaller than the maximum calculated by assuming 100% ethylene formation 3487 kJ/kg (1500 BTU/lb). Increasing conversion above 60% leads to decreased reaction endothermicity due to increased formation of saturated products. Pressure had little effect between 1.38 and 6.89 MPa (200 and 1000 psig).

#### 4.3 Toxicity of JP-7

A very detailed toxicological profile of JP-7 was published which also included toxicity data for JP-4 [26].

#### 4.4 Safety Properties of JP-7

##### 4.4.1 Flash Point of JP-7

The flash point of JP-7 is 333 K (60 °C = 140 °F).

##### 4.4.2 Autoignition Temperature of JP-7

The autoignition temperature of JP-7 in air is 514 K (241 °C = 465 °F). Electrostatic discharges with a spark energy of 0.2 mJ are sufficient to ignite JP-7 vapors in air.

##### 4.4.3 Flammable Range of JP-7 Vapors

The flammable range of JP-7 vapors in air is from 0.6 to 4.6 vol.-%.

## 5 Jet Fuel Kerosene JP-8

JP-8 was first introduced at NATO bases in 1978 and is currently the US Air Force's primary fuel. JP-8 is very similar to Jet A-1. JP-8, however, contains an icing inhibitor, corrosion/lubricity enhancer, and anti-static additive. Conversion to JP-8 was virtually complete in 1995 and was accomplished for fire safety and combat survivability reasons.

JP-8 (MIL-DTL-83133E, NATO code F-34) is the current US Air Force fuel for essentially all aircraft and ground vehicles [52]. As the "single fuel for the battlefield," the US Army plans to transition to a single fuel, JP-8, for all ground vehicles and aircraft. US Navy aircraft typically fly on JP-8 from land bases, but use a higher flash point fuel (JP-5) when based on carriers.

JP-8 is essentially commercial kerosene Jet A/Jet A-1 fuel with three military-specified additives: a corrosion inhibitor/lubricity improver, an anti-static additive, and a fuel system icing inhibitor. JP-8 replaced JP-4 in general Air Force use in the 1980s, primarily to reduce the risk of fire encountered with the low-flash-point JP-4. JP-TS and JP-7 are specialty fuels used for the U-2 and SR-71, respectively.

In 1979, USAF operations within the United Kingdom were converted from JP-4 (NATO designation F-40) to JP-8 (NATO F-34). NATO and USAF operations in Europe converted to JP-8 by the end of 1988. Gradually all USAF operations in the Pacific (Japan, Korea, and Okinawa) converted to JP-8 by 1991. Eventually USAF also converted continental US (CONUS) operations to JP-8. Although not widely used within the CONUS, Jet A-1 is the primary commercial jet fuel for the rest of the free world. In NATO, much of the JP-8 will be procured and shipped as Jet A-1, with the special additives, required to convert the Jet A-1 into JP-8, injected into the fuel prior to its delivery to air bases [53]. A synthetic fuel with JP-8 properties was made by the Fischer-Tropsch process and was compared to JP-8 made from petroleum [54].

### 5.1 Physical Properties of JP-8

The physical properties of JP-8 are listed in Table 7. Models were developed to represent the thermophysical properties of aviation kerosenes described under the umbrella names of Jet A and JP-8 [54, 55]. Measurements included the chemical analysis of finished fuels, studies of the thermal decomposition of fuels and components, measurement of the volatility, density, velocity of sound, viscosity, and thermal conductivity of finished fuels and their selected components. The modeling efforts included the development of equations of state for a suite of potential surrogate components, and the development of models based on the Helmholtz free energy equation of state. A GC-MS analysis of a typical sample of JP-8 showed about 50 peaks in the fractogram, most of which could be identified by MS. Properties of pure methylcyclohexane and

**Table 7:** Physical properties of JP-8.

| Property                                         | SI units                                 | Other units                                                           | References     |
|--------------------------------------------------|------------------------------------------|-----------------------------------------------------------------------|----------------|
| Molecular mass                                   | 151.7 g/mol                              | 6.5919 mol/kg                                                         |                |
| Freezing point                                   | <226 K                                   | <-47 °C                                                               | MIL-DTL-83133J |
| Boiling range                                    | 473–573 K                                | 200–300 °C                                                            |                |
| Density at 288 K                                 | 0.775–0.840 g/cm <sup>3</sup>            | —                                                                     |                |
| Vapor pressure at 300 K                          | 2.13 kPa                                 | 16 mm Hg                                                              | [4]            |
| Density at 300 K                                 | 0.7295 g/cm <sup>3</sup>                 | 45.54 lb <sub>m</sub> /ft <sup>3</sup>                                | [4]            |
| Kinematic viscosity at 300 K                     | 1.849 mm <sup>2</sup> /s                 | 1.849 cSt                                                             | [4]            |
| Kinematic viscosity                              | <8.0 mm <sup>2</sup> /s at 253 K         | <8 cSt at -20 °C                                                      | MIL-DTL-83133J |
| Surface tension at 300 K                         | 25.85 mN/m                               | 25.85 dyn/cm                                                          | [4]            |
| Thermal conductivity at 300.7 K and 0.781 MPa    | 0.1157 W m <sup>-1</sup> K <sup>-1</sup> | 0.0668949612 BTU ft h <sup>-1</sup> ft <sup>-2</sup> °F <sup>-1</sup> | [54]           |
| Thermal conductivity at 298 K                    | 0.1145 W m <sup>-1</sup> K <sup>-1</sup> | 0.0662 BTU h <sup>-1</sup> ft <sup>-1</sup> °F <sup>-1</sup>          | [44]           |
| Heat capacity $c_p$ at 298 K                     | 1.980 J g <sup>-1</sup> K <sup>-1</sup>  | 0.473 cal g <sup>-1</sup> °C <sup>-1</sup> at 25 °C                   | [44]           |
| Enthalpy of formation $\Delta H_f^{298}$         | -1634 J/g                                | -390 cal/g                                                            | [48]           |
| Lower (net) heat of combustion $\Delta H_{comb}$ | 43.21 MJ/kg                              | 18589 BTU/lb                                                          | [4]            |
| Autoignition temperature                         | 497–511 K                                | 435–460 °F                                                            | [44]           |
| Flash point                                      | 311 K                                    | 100 °F                                                                |                |

propylcyclohexane were measured so they could be used as constituents of surrogate fuel mixtures.

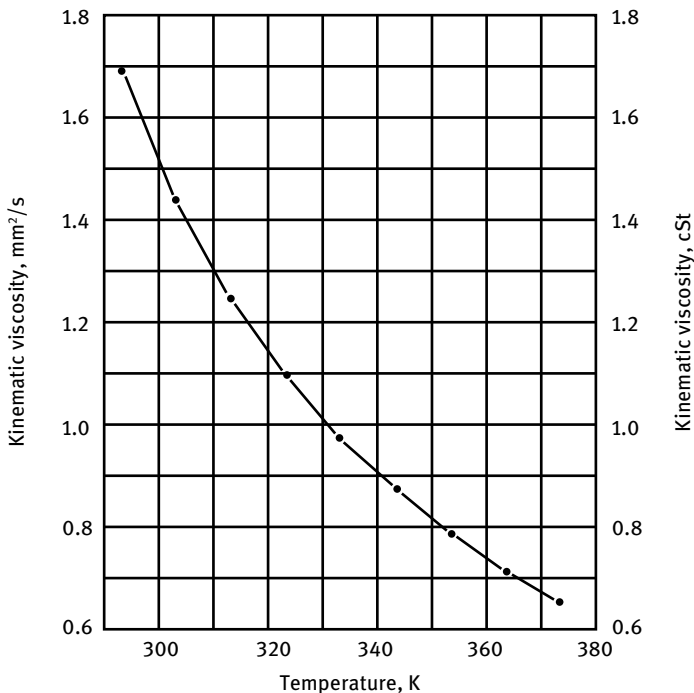
Additive packages are used with aviation kerosenes to achieve performance enhancements, such as higher or lower operating temperatures or increased lubricity. An additive that is used to increase operating temperatures for heat sink applications is the +100 additive that is added to JP-8. As part of an effort to characterize JP-8, the effect of the +100 additive on the volatility of JP-8 was measured by using the composition-explicit or advanced distillation curve approach [56]. It was found that the vaporization temperatures increased modestly in the early stages of the distillation but the difference disappeared after the 70% distillate fraction. Selected components of the additive were tracked through the distillation curve and related the concentration to the temperature data grid. This allowed the determination of the heaviest components of the additive which were concentrated late in the distillation curve and a significant quantity in the recovered residue.

### 5.1.1 Density of JP-8

The density range of JP-8 specified by MIL-DTL-83133J is 0.775–0.840 g/cm<sup>3</sup> at 288 K (15 °C).

### 5.1.2 Viscosity of JP-8

Per MIL-DTL-83133J, the maximum allowed kinematic viscosity of JP-8 at 253 K ( $-20^{\circ}\text{C}$ ) is  $8.0\text{ mm}^2/\text{s}$  (8 cSt). The kinematic viscosity of JP-8 was measured in the range 300–547 K and at pressures up to 50 MPa [54]. The kinematic viscosity of JP-8 as a function of temperature is shown in Figure 11. Similar data are available for a synthetic JP-8 type fuel with a designation of S-8 made by the Fischer–Tropsch process.



**Figure 11:** Kinematic viscosity of JP-8 as a function of temperature. (Reproduced and modified from [54].)

### 5.1.3 Surface Tension of JP-8

The surface tension of JP-8 at 300 K was reported as  $25.85\text{ mN/m} = 25.85\text{ dyn/cm}$  [4].

### 5.1.4 Thermal Conductivity of JP-8

The thermal conductivity of JP-8 was measured over a range from 300 to 547 K at pressures up to 50 MPa [54]. The thermal conductivity of JP-8 at 300.7 K and a pressure of 0.781 MPa was  $0.1157\text{ W m}^{-1}\text{ K}^{-1}$ . The thermal diffusivity of JP-8 at 298 K is  $8.7 \times 10^{-8}\text{ m}^2/\text{s}$ .

### 5.1.5 Thermodynamic Properties of JP-8

#### 5.1.5.1 Heat Capacity of JP-8

The heat capacity of JP-8 can be calculated from the least-squares generated equation for the heat capacity at ambient pressure [54]:

$$C_p/C_p^0 = (2.193 \pm 0.0055) + (3.996 \pm 0.0011) \times 10^{-3} (T/T_0 - 1)$$

where  $C_p/C_p^0$  is the ratio of heat capacities at temperature  $T$  in relation to the heat capacity at a reference temperature  $T_0$  (in kelvin).

#### 5.1.5.2 Heat of Combustion of JP-8

The minimum lower (net) heat of combustion of JP-8 as specified by MIL-DTL-83133J is 42.8 MJ/kg (18413 BTU/lb).

#### 5.1.5.3 Enthalpy of Evaporation of JP-8

Assuming that the gross chemical formula of JP-8 is  $C_{11}H_{21}$ , and using correlation GC and NMR, the evaporation enthalpy of JP-8 was predicted to be 441 kJ/kg [49].

### 5.1.6 Critical Point Properties of JP-8

The critical temperatures of some petroleum- and coal-derived jet fuels were measured using a rapid heating sealed tube method [57]. A critical property estimation method was used to calculate the critical temperatures and pressures of the jet fuel samples. Five other methods were also used to estimate the critical temperatures of these fuels. While most of the estimation methods gave satisfactory predictions of the critical temperatures of the petroleum-derived jet fuels, they were not able to predict the results for the coal-derived jet fuels. The larger differences between the measured and estimated critical temperatures for the coal-derived fuels were attributed to the different composition of these fuels, dominated by cycloalkanes. On the basis of properties of the compounds found in the coal-derived jet fuels, a new correlation was proposed to calculate the critical temperatures of the coal-derived jet fuels. Six petroleum-derived jet fuels (designated as JP-8P, JP-8P2, Jet A, Jet A-1, JP-7, and JPTS) and three coal-derived jet fuels (JP-8C, JP-8CA, and JP-8CB) were used. The petroleum-derived jet fuels were composed mainly of long-chain paraffins, while JP-8C consisted mainly of monocyclic and bicyclic alkanes and some two-ring hydroaromatic compounds. The compositions of JP-8CA and JP-8CB were similar to that of JP-8C, although JP-8CA contained higher concentrations of low-boiling-point compounds, while JP-8CB was richer in high-boiling-point compounds. A sealed tube method was used to measure the critical temperatures of the jet fuels. This method consisted of sealing a certain amount of sample in a glass tube with a volume which was approximately equal to the critical volume of the sample at the critical temperature and then heating it rapidly in a furnace until the critical point was reached. The critical temperature of JP-8 is 666–684 K (740–772 °F) and the critical pressure is 2.344 MPa (340 psia).

## 5.2 Chemical Properties of JP-8

### 5.2.1 Specifications for JP-8

The properties of JP-8 are specified in MIL-DTL-83133J, Detail Specification: Turbine Fuel, Aviation, Kerosene Type, JP-8 (NATO F-34), NATO F-35, and JP-8+100 (NATO F-37) (16 December 2015) (Table 8). This specification covers three grades of kerosene type aviation turbine fuel: JP-8 (NATO F-34), NATO F-35, and JP-8+100 (NATO F-37).

**Table 8:** JP-8 Chemical and physical requirements and test methods per MIL-DTL-83133J.

| Property                                                           | Min.  | Max.              | ASTM or IP test method                                                  |
|--------------------------------------------------------------------|-------|-------------------|-------------------------------------------------------------------------|
| Color, Saybolt <sup>a</sup>                                        |       |                   | D156 <sup>b</sup> or D6045                                              |
| Total acid number, mg KOH/g                                        | 0.015 |                   | D3242                                                                   |
| Aromatics, vol.-%                                                  | 25.0  |                   | D1319                                                                   |
| Sulfur, total, mass-%                                              | 0.30  |                   | D129, D1266, D2622, D3120 <sup>c</sup> ,<br>D4294 <sup>b</sup> or D5453 |
| Sulfur, mercaptan, mass-%<br>or Doctor test <sup>d</sup>           |       | 0.002<br>negative | D3227 <sup>b</sup><br>D4952                                             |
| Distillation temperature, °C                                       |       |                   | D86 <sup>b</sup> , D2887, or D7345                                      |
| Initial boiling point <sup>a</sup>                                 |       |                   |                                                                         |
| 10% recovered                                                      |       | 205               |                                                                         |
| 20% recovered <sup>a</sup>                                         |       |                   |                                                                         |
| 50% recovered <sup>a</sup>                                         |       |                   |                                                                         |
| 90% recovered <sup>a</sup>                                         |       |                   |                                                                         |
| Final boiling point                                                |       | 300               |                                                                         |
| Residue, vol.-%                                                    |       | 1.5               |                                                                         |
| Loss, vol.-%                                                       |       | 1.5               |                                                                         |
| Flash point, °C                                                    | 38    |                   | D56, D93 <sup>b</sup> , D3828 or IP 170                                 |
| Density                                                            |       |                   |                                                                         |
| Density, kg/L at 15 °C or                                          | 0.775 | 0.840             | D1298, D4052 <sup>b</sup> or D7777                                      |
| Gravity, API at 60 °F                                              | 37.0  | 51.0              |                                                                         |
| Freezing point, °C                                                 |       | −47               | D2386 <sup>b</sup> , D5972, D7153 or D7154                              |
| Viscosity, at −20 °C, mm <sup>2</sup> /s                           |       | 8.0               | D445 <sup>b</sup> or D7042                                              |
| Net heat of combustion, MJ/kg                                      | 42.8  |                   | D3338, D4529 or D4809 <sup>b</sup>                                      |
| Hydrogen content, mass-%                                           | 13.4  |                   | D3343, D3701, D5291 or D7171 <sup>b</sup>                               |
| Smoke point, mm, or                                                | 25.0  |                   |                                                                         |
| Smoke point, mm, and                                               | 19.0  |                   | D1322                                                                   |
| Naphthalenes, vol.-%                                               | 3.0   |                   | D1322 or D1840                                                          |
| Calculated cetane index <sup>a</sup>                               |       |                   | D976 or D4737                                                           |
| Copper strip corrosion, 2 h at 100 °C                              |       | No. 1             | D130                                                                    |
| Thermal stability (2.5 h at 260 °C)                                |       |                   | D3241                                                                   |
| Change in pressure drop, mm Hg                                     |       | 25                |                                                                         |
| Tube rating: One of the following requirements shall be met:       |       |                   |                                                                         |
| (1) Annex A1 VTR or                                                | <3    |                   |                                                                         |
| (2) Annex A3 ETR or Annex A2 ITR                                   |       |                   |                                                                         |
| average deposit thickness, nm, over<br>area of 2.5 mm <sup>2</sup> | 85    |                   |                                                                         |

**Table 8:** (continued)

| Property                                        | Min. | Max. | ASTM or IP test method      |
|-------------------------------------------------|------|------|-----------------------------|
| Fuel system icing inhibitor, vol.-%             | 0.07 | 0.10 | D5006                       |
| Fuel electrical conductivity, pS/m <sup>e</sup> |      |      | D2624                       |
| Existent gum, mg/100 mL                         |      | 7    | D381 <sup>b</sup> or IP 540 |
| Water reaction interface rating                 |      | 1b   | D1094                       |
| Microseparometer rating                         |      |      | D3948 or D7224 <sup>b</sup> |

<sup>a</sup> To be reported – not limited.

<sup>b</sup> Referee Test Method.

<sup>c</sup> The sulfur content detection range for ASTM D3120 is 3.0 to 1000 mg/kg.

<sup>d</sup> If the Doctor Test results in a failure ('positive' result), then mercaptan sulfur content shall be determined by the referee test method ASTM D3227.

<sup>e</sup> The conductivity must be between 150 and 600 pS/m for JP-8 (NATO F-34) and between 50 and 600 pS/m for NATO F-35, at ambient temperature or 29.4 °C (85 °F), whichever is lower, unless otherwise directed by the procuring activity. In the case of JP-8+100 (NATO F-37), JP-8 with the thermal stability improver additive (see Section 3.3.6 of MIL-DTL-83133), the conductivity limit must be between 150 and 700 pS/m at ambient temperature or 29.4 °C (85 °F), whichever is lower, unless otherwise directed by the procuring activity.

Conventional petroleum-derived jet fuel is the most broadly specified fuel. The density range for JP-8 (and Jet A as specified in ASTM D165515) is greater than that of RP-1 by a factor of four. JP-8 specification properties are measured for each batch procured by the Defense Energy Support Center (DESC) and published annually in the Petroleum Quality Information System (PQIS). The report summarizes procurement quantities and specification properties for several product grades and includes statistics (historical trends, geographical region, number of analyses, minimum, maximum, mean, and weighted mean values) useful for assessing fuel variability. The only hydrocarbon composition quantity measured is total aromatic compounds, which for JP-8 was at a weighted mean of 17.92 vol.-% in 2008 [58]. Describing fuel composition by hydrocarbon type distribution is a practical approach for comparing complex kerosenes, particularly since performance is often related to compound classes rather than particular species. The introduction of hydrocarbon class requirements in fuel specifications (cycloparaffin content is limited to 15% by volume for Fischer–Tropsch synthetic paraffinic kerosene blend stocks in jet fuel) leads to increased relevance of compositional descriptions via compound type. The 2006 World Fuel Sampling Program collected 54 fuel samples (JP-8, Jet A, Jet A-1) worldwide, compiling numerous property and performance data which included fuel compositional analysis by hydrocarbon class according to ASTM D2425.



### 5.2.2 Composition of JP-8

The average composition and minimum and maximum property numbers observed in delivered JP-8 and Jet A accumulated during a decade of observation were compared to the specification limits for JP-8 [53]. For comparison, the study also included the average properties of Jet A fuels prior to the addition of the additives.

#### 5.2.2.1 Antioxidants

Immediately after processing and before the fuel is exposed to the atmosphere (such as during rundown into feed/batch tankage), an approved antioxidant formulation or combination of approved antioxidant formulations are added in order to prevent the formation of gums and peroxides after manufacture. The concentration of antioxidant to be added shall be:

- a. Not less than 17.2 milligrams (mg) nor more than 24.0 mg of active ingredient per liter (L) of fuel to all JP-8 fuel that contains blending stocks that have been hydrogen treated or SPK derived from hydrotreated, hydrocracked, or hydroisomerized products of a Fischer–Tropsch or HEFA process.
- b. At the option of the supplier, not more than 24.0 mg of active ingredient per liter of fuel may be added to JP-8 fuels that do not contain hydrogen-treated blending stocks or SPK-derived from hydrotreated, hydrocracked, or hydroisomerized products of a Fischer–Tropsch or HEFA process.

#### 5.2.2.2 Antioxidant Formulations

The following antioxidant formulations are approved:

- 2,6-di-*tert*-butyl-4-methylphenol
- 6-*tert*-butyl-2,4-dimethylphenol
- 2,6-di-*tert*-butylphenol
- 75% min. 2,6-di-*tert*-butylphenol, 25% max. *tert*-butylphenols and tri-*tert*-butylphenols
- 72% min. 6-*tert*-butyl-2,4-dimethylphenol, 28% max. *tert*-butyl-methylphenols and *tert*-butyl-dimethylphenols
- 55% min. 2,4dimethyl-6-*tert*-butylphenol and 15% min. 2,6-di-*tert*-butyl-4-methylphenol and 30% max. mixed methyl and dimethyl *tert*-butylphenols

JP8+100 contains dispersants (surface active agents with fuel soluble tail), antioxidants (2,6-di-*tert*-4-methylphenol), and metal deactivators which function by forming a chelate with the metal.

### 5.2.3 Surrogate Fuel Mixtures for JP-8

Because of the complexities involved in measuring and modeling the performance and properties of finished fuels, the fuel science community must often use surrogate mixtures as substitutes, especially in the absence of consensus standard mixtures. While surrogate mixtures are often formulated on the basis of the ability of a particular mixture to reproduce a particular property, there is usually a desire to employ surrogate mixtures that are physicochemically authentic. This means that, provided that the primary purpose is satisfied, researchers are inclined to choose mixtures that have physical and chemical properties appropriate to the finished fuel.

Jet A and JP-8 consist of complex mixtures of higher order hydrocarbons, including alkanes, cycloalkanes, and aromatic molecules. Surrogate mixtures were needed to represent JP-8 fuels and to discuss a general detailed chemical kinetic model for jet fuels. A surrogate blend of six pure hydrocarbons was found to adequately simulate the distillation and compositional characteristics of a practical JP-8 [59]. A hierarchically constructed kinetic model already available for the oxidation of alkanes and simple aromatic molecules (benzene, toluene, ethylbenzene, xylene, etc.) was extended to include methylcyclohexane and tetralin as new reference fuel components. The kinetic model was validated through comparisons with experimental data for the pure components and it was also used to verify and predict the structures of laminar premixed flames of different pure components as well as conventional kerosene fuels.

Surrogate fuel mixtures were developed for a synthetic fuel meeting JP-8 criteria made from coal by the Fischer–Tropsch process [60]. The properties of the surrogate model were then compared with experimental density, sound speed, viscosity, thermal conductivity, and distillation curve data for the real fuel.

Experimental and numerical studies were carried out to develop a surrogate that can reproduce selected aspects of combustion of kerosene jet fuels, in particular Jet A1, Jet A, and JP-8 [61]. Surrogate fuels are defined as mixtures of few hydrocarbon compounds with combustion characteristics similar to those of commercial fuels. A mixture of 80 mass-% *n*-decane and 20 mass-% 1,2,4-trimethylbenzene, called the Aachen surrogate, was selected for consideration as a possible surrogate of kerosene. Combustion experiments were carried out employing a counterflow configuration. The fuels tested were real kerosene and the Aachen surrogate. Critical conditions of extinction, autoignition, and volume fraction of soot measured in laminar non-premixed flows burning the Aachen surrogate were found to be similar to those in flames burning kerosene. A chemical kinetic mechanism was developed to describe the combustion of the Aachen surrogate. This mechanism was assembled using previously developed chemical kinetic mechanisms for the components: *n*-decane and 1,2,4-trimethylbenzene. The combined mechanisms were validated using experimental data obtained from shock tubes, rapid compression machines, jet stirred reactor, burner-stabilized premixed flames, and a freely propagating premixed flame. Numerical calculations were performed using the chemical kinetic

mechanism for the Aachen surrogate. The calculated values of the critical conditions of autoignition and soot volume fraction agreed well with experimental data.

#### 5.2.4 Analysis of JP-8

The analytical methods used to verify compliance of JP-8 with the requirements of MIL-DTL-83133J are spelled out in MIL-DTL-83133J.

- a. Acid Number. The acid number controls the amount of acidic components in the fuel, carried over from the crude oil, formed or added in refinery processes, or added after processing. The specification level is 0.015 mg KOH/g fuel.
- b. Aromatics Content. Aromatics are unsaturated, cyclic hydrocarbons that are excellent solvents, have a strong odor (hence the name aromatics), and have poor combustion performance. As the solvency of aromatics causes some elastomers to swell excessively, specifications typically limit aromatics content to 20 to 25 vol.-%. The poor combustion performance of aromatics is another reason for limiting aromatics content of jet fuels. None of the JP-8 fuels tested during a field survey exceeded or even closely approached the specification limit of 25% aromatics [53]. The average aromatics content of JP-8 was slightly less than that for Jet A (16.4 vs. 17.8 vol.-%.)
- c. Olefins Content. Olefins are chain and branched chain paraffins that have double carbon bonds. As the double carbon bonds cause olefins to be less stable, olefins are limited to 5 vol.-%. Average olefins content of JP-8 and Jet A during a field study was 1.0 and 1.2 vol.-%, respectively. However, the accuracy of the test method used to measure olefins content is poor, so the differences in the average values is meaningless. As the most likely source of olefins is cracked petroleum stocks, the specification limit on olefins effectively limits the use of thermally and catalytically cracked stocks.
- d. Sulfur Content. Sulfur is limited in jet fuels because of its corrosivity and the noxious nature of its combustion products. The specification limit for JP-8 and Jet A is 0.3 mass-%. During a field study, both JP-8 and Jet A had average sulfur contents well below specification limits, but JP-8 averaged 0.08 vs. 0.05 mass-% for Jet A.
- e. Mercaptan Sulfur Content. Mercaptan sulfur is one of the most noxious forms of sulfur, both in odor and in corrosiveness. During a field survey, none of the JP-8 fuels exceeded the specification limit of 0.002 mass-%, and the average mercaptan sulfur content of JP-8 was only slightly less than that for Jet A, which has a specification limit of 0.003 mass-%.
- f. Distillation Range. The distillation ranges for JP-8 and Jet A are identical. None of the JP-8 fuels tested approached either the maximum allowable 10% recovered temperature or the end point temperature.
- g. Flash Point. The average flash point for Jet A was significantly higher than for JP-8. This correlated with the higher average distillation temperatures of Jet A.

- h. Gravity. All JP-8 fuels met the gravity limits. As API gravity is inversely related to specific gravity, the higher average API gravity for JP-8, as compared to Jet A, meant that JP-8 was less dense than Jet A. The higher density of Jet A correlated with the higher distillation range and aromatics content of Jet A.
- i. Freezing Point. Aside from additives, the major difference between JP-8/Jet A-1 and Jet A is the freezing point requirement. All JP-8 fuels tested had freezing points of 226 K ( $-47^{\circ}\text{C}$ ) or below. With a maximum allowable freezing point of 233 K ( $-40^{\circ}\text{C}$ ), the average Jet A freezing point was 228 K ( $-45^{\circ}\text{C}$ ).
- j. Viscosity. Engine starting and altitude relight performance requires excellent fuel atomization, and atomization is a function of viscosity. Although the viscosity limit for JP-8, Jet A-1, and Jet A is the same, viscosity tends to correlate with freezing point, density, and distillation range. The average viscosity of numerous samples of JP-8 collected in a field survey was less than for Jet A [53].
- k. Smoke Point. The smoke point is the maximum flame height (in millimeters) that can be obtained without smoking, using a standard wick lamp. Smoke point correlates with fuel combustion performance in gas turbine engines. A high smoke point insures that the fuel will burn with a minimum of exhaust smoke and minimum heat transferred to the combustor liner via radiation.
- l. Hydrogen Content. The hydrogen content of jet fuels correlates with fuel combustion performance. For the JP-8 fuels the mass percent hydrogen is calculated using ASTM D 3343. During a 1988 field survey, all JP-8 fuels met or exceeded the minimum allowable hydrogen content of 13.4 % required by specification MIL-T-83133B.
- m. Heat of Combustion. The calorific value of a fuel can be measured directly in a calorimeter or estimated using correlations based on other fuel measurements. During a 1988 field survey, all but one JP-8 met or exceeded the minimum specification limit of 42798 kJ/kg (18400 BTU/lb). The JP-8 fuels had a slightly higher heat of combustion than Jet A fuels.
- n. Thermal Oxidative Stability. Jet fuel is the primary coolant for airframe, engine components, and engine lubricant. As aircraft become more complex and engine fuel flow rates decrease with increasing engine efficiencies, fuel temperatures increase. Fuel must withstand these higher temperatures without forming deposits within the fuel system. A jet fuel thermal oxidative tester (JFTOT) test apparatus is used to insure that each batch of fuel has acceptable stability. The JFTOT monitors the formation of deposits on a heated, polished aluminum tube and plugging of a filter downstream of the heated tube. The tube deposit must be less than code 3 (a dark tan) and the pressure drop across the filter must not exceed 25 mm of mercury.
- o. Existent Gum. Jet fuels are good solvents and may contain quantities of dissolved polymeric gums and resins, which can form deposits within the fuel system and combustor. To analyze for existent gum, a sample of the fuel is evaporated and the remaining residue is weighed.

- p. **Particulate Matter.** This test measures the quantity of solid particulates by filtering 3.78 L (1 gallon) of fuel through a 0.8-micron pore size filter membrane, which is weighed before and after the filtration.
- q. **Filtration Time.** Department of Defense (DoD) jet fuel specifications limit the time required to filter 3.78 L (1 gallon) of jet fuel through a 0.8-micron filter. This test is run in conjunction with the particulate matter test. The purpose of this test is to insure that the fuel does not contain contaminants that will rapidly plug the filters and filter-water separators in the bulk fuel storage and servicing systems at Air Force bases. The contaminants that can plug filters include solid particulates (sand, rust, fibers, etc.), precipitates from refinery treating solutions left in fuels, and reaction products of fuel corrosion inhibitors (fatty acids that have reacted with water and metals to form gelatinous soap-like materials).
- r. **Water Separation Index.** The most common and potentially serious contaminant in jet fuel is water. Filter-water coalescer/separator devices are used in the base fuel servicing systems to remove particulates and undissolved water. The water is removed by coalescence, i.e., small water droplets coalesce to form large droplets that are then separated by gravity and hydrophobic filter media. However, coalescence of water can be degraded or prevented by trace quantities of surface active (surfactants, emulsifiers) materials in the fuel. The water separation index (modified) apparatus consists of a miniature coalescer device through which a sample of the fuel, emulsified with water, is passed. The ability of the coalescer to remove the water is then determined. A water separation index modified (WSIM) rating of 100 is excellent; a rating of less than 70 is cause for concern. As fuel additives affect the WSIM, different limits are placed on the fuel, depending on which additives are present. With corrosion inhibitor (CI) but not the static dissipator additive present, a minimum WSIM of 70 is allowed. The presence of the corrosion inhibitor does significantly lower the WSIM. The average WSIM value of 95 for the Jet A fuels (which normally do not contain corrosion inhibitor additives) is essentially the same as for the JP-8 fuels that do not contain a corrosion inhibitor additive.
- s. **Fuel Additives.** JP-8 requires, as mandatory additives, fuel system icing inhibitor, corrosion inhibitor/lubricity improver, and static dissipator additives, and their concentrations need to be monitored. Antioxidants are optional unless the fuel has been hydrogen treated, in which case the antioxidant is also mandatory. The metal deactivator additive is optional.

Several improvements in the measurement of distillation curves for complex fluids were introduced [62]. The modifications to the classical measurement provided for (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis); (2) temperature measurements that are true thermodynamic state points; (3) temperature, volume, and pressure measurements of low uncertainty suitable for an equation of state development; (4) consistency with a century of historical data; (5) an assessment of the energy content of each distillate fraction; (6)

a trace chemical analysis of each distillate fraction; and (7) a corrosivity assessment of each distillate fraction. The most significant modification was achieved with a new sampling approach that allowed precise qualitative as well as quantitative analyses of each fraction, on the fly. The new method was applied to the measurement of rocket propellant, military aviation fuel JP-8, and also to a coal-derived fuel developed as a potential substitute. Each fraction of the distillation was chemically characterized.

### 5.2.5 Thermal Stability of JP-8

The object of a research program was to determine which components of an oxidized fuel are most responsible for deposits on hot engine parts [63]. A 5° boiling range cut of a JP-8 fuel was oxidized with air at 373 K (100 °C) and then fractionally distilled (separated) at 25 and 5 mm Hg pressure into (essentially) recovered fuel, a high-boiling fraction (containing monomeric oxidation products), and a residue (containing bi-functional and polymeric materials). Restoration of polymeric oxidation products to the original or recovered fuels greatly increased deposit formation in the jet fuel thermal oxidation tester (JFTOT) per ASTM D 3241, but restoration of monomeric oxidation products had little effect.

JP-8 was not initially formulated to serve as an endothermic fuel. A program to develop and demonstrate the endothermic potential of JP-8 for hypersonic scramjet cooling used a high-pressure bench-scale reactor to determine the overall heat sinks (including magnitude of endotherms), endothermic reforming products, and coking rates for this fuel. Endothermic reforming of hydrocarbon fuels is an enabling technology for high-speed flight. The successful implementation of this technology is predicated on the exploitation of existing multi-component fuels and their decomposition with inexpensive, readily available catalysts.

An additive package was developed for JP-8 which offers a  $55\text{ K} = 55\text{ °C}$  ( $100\text{ °F}$ ) increase in the bulk maximum temperature from 436 to 491 K (= from 163 to 218 °C = from 325 to 425 °F) and improves the heat sink capability by 50% [64, 65]. Major advances made during the development of JP-8+100 fuel included the development of several new quantitative fuel analysis tests, a free radical theory of autooxidation, adaptation of new chemistry models to computational fluid dynamics programs, and a non-parametric statistical analysis to evaluate thermal stability. Hundreds of additives were tested for effectiveness, and a package of additives was then formulated for JP-8 fuel. This package has been tested for fuel system materials compatibility and general fuel applicability. The flight testing has shown an improvement in thermal stability of JP-8 fuel. This improvement has resulted in a significant reduction in fuel-related maintenance costs and a threefold increase in mean time between fuel-related failures.

Hydrogen donor compounds and compounds with similar chemical characteristics (decahydroquinoline and cyclodecane) have been used as thermal stabilizers in JP-8+100 fuel. Decalin (a mixture of *cis*- and *trans*-stereoisomers of bicyclo[4.4.0]-

decane) and tetrahydroquinoline (THQ) were evaluated at various concentrations in JP-8+100 fuel and stressed to temperatures up to 873 K (600°C) for 6 h in a flowing reactor system in order to measure thermal oxidative and pyrolytic deposition for all fuel/additives mixtures, the conversion percentages, and composition of the stressed fuel's gaseous and liquid products [66]. *cis*-Decalin and *trans*-decalin were assessed individually to determine whether their thermal stability activities in a static reactor are correlatable to a flowing system and to compare with the performance of the decalin mixture.

The effects of fuel composition changes on jet fuel thermal stability were experimentally investigated [67]. A High Reynolds Number Thermal Stability test device was used to evaluate thermal stability of JP-8 fuels. The experiment consisted of an electrically heated, stainless steel capillary tube with a controlled fuel outlet temperature. An optical pyrometer monitored the increasing external temperature profiles of the capillary tube as deposits build inside during each test. Multiple runs of each fuel composition provided results on measurement repeatability. Testing at two different facilities provided data on measurement reproducibility. The technique was able to distinguish between thermally stable and unstable compositions of JP-8 and intermediate blends made by combining each composition.

### 5.2.6 Oxidation of JP-8

The preignition oxidation reactivity behaviors of five JP-8 samples, three Jet A samples, one JP-7 sample, and four JP-8 surrogate mixtures were studied in a pressurized flow reactor in the low- and intermediate-temperature regime (600–800 K) [68]. No significant differences in the low-temperature oxidation behavior were observed between Jet A and JP-8, suggesting that the two fuels can be used interchangeably for surrogate development.

## 5.3 Toxicity of JP-8

To reduce fuel fouling in US Navy and Air Force aircraft systems and to provide additional heat sink and thermal stability for future systems, the Air Force was developing an improved JP-8 jet fuel called JP-8+100. Two companies developed additive packages that were tested in aircraft systems. To determine whether the additive packages will produce adverse health effects for flightline personnel, acute toxicity testing was performed on JP-8 and two JP-8+100 jet fuels from different suppliers [69]. A single oral dose of 5 mg jet fuel/kg body weight to five male and five female Fischer-344 rats, and a single dermal application of 2 g jet fuel/kg body weight applied to five male and five female New Zealand White rabbits resulted in no deaths. No signs of toxic stress were observed, and all animals gained weight over the 14-day observation periods. Single treatment of 0.5 mL neat jet fuel to rabbit skin produced negative results for skin ir-

ritation. Guinea pigs failed to elicit a sensitization response following repeated skin applications of the jet fuels. Inhalation vapor exposure to JP-8 or JP-8+100 (samples from two different suppliers) resulted in LC50 values of >3.43, >3.52, and >3.57 mg/L, respectively. LC50 values for aerosol exposure to JP-8 and JP-8+100 (samples from two different suppliers) were >4.44, >4.39, and >4.54 mg/L, respectively. Under the conditions of these tests, the additive packages did not potentiate the acute effects normally associated with JP-8 jet fuel exposure.

The relative potency of three jet fuels (JP-4, JP-8, and JP-8+100) to cause respiratory tract sensory irritation was studied by administering vapor only or vapor/aerosol mixtures for 30 min periods by means of a head-only exposure system to groups of four mice [27].

A very detailed summary of toxicity hazards of JP-8 (as well as JP-5 and Jet A) is available from NIOSH Agency for Toxic Substances and Disease Registry, Division of Toxicology and Human Health Sciences [39]. Although JP-8 was identified by the Department of Defense as its single military fuel over 30 years ago, as of 2017 only very little specific data on the toxicity of kerosene-based jet fuels in humans were available. Most of the studies focused on the potential neurotoxicity of JP-8 fuel. Single studies in humans exposed to JP-8 fuel reported increases in white blood cell neutrophil and monocyte levels with no change in lymphocyte subpopulations and an inverse association between aliphatic hydrocarbons in exhaled breath and serum levels of luteinizing hormone. However, exposure to JP-8 was not associated with higher odds of menstrual disorders. Limited information is available on the carcinogenic potential of jet fuels in humans. Studies in laboratory animals have examined the toxicity of JP-8, JP-5, and Jet A fuels following inhalation, oral, or dermal exposure and have reported a number of targets of toxicity, including the lungs, liver, skin, immunological system, nervous system, and developing organism. Although renal effects have also been observed in male rats exposed to JP-8 or JP-5, the lesions are considered to be characteristic of  $\alpha_2\mu$ -globulin nephropathy, which is only observed in male rats and is not considered to be toxicologically relevant to humans. Increases in skin tumors were observed in mice dermally exposed to Jet A for 52–62 weeks; however, tumors were only observed at concentrations resulting in significant skin damage (inflammation and necrosis). Similarly, increased numbers of skin tumors were observed in mice that received applications of undiluted kerosene on the skin for 2 years, but this occurred only in the presence of moderate-to-marked skin damage. No inhalation or oral studies evaluated the carcinogenicity of JP-8, JP-5, or Jet A in laboratory animals; no increases in tumor incidences were observed in rats administered kerosene by gavage for 2 years. No human studies have examined the potential of JP-5, JP-8, or Jet A to induce respiratory effects. Studies in rats, mice, rabbits, and pigs demonstrated the dermal toxicity of topically applied JP-8, JP-5, and Jet A. Similar effects have been observed for all three fuel types.



## 5.4 Safety Properties of JP-8

The US Air Force change from JP-4 to JP-8 was a positive step for aircraft safety but not to the point that fuel fire/explosion safety features such as anti-static additives, fuel tank inerting, explosion suppressant foam, bonding and grounding, and the complete elimination of ignition sources in and around fuel systems can be abandoned.

### 5.4.1 Flash Point of JP-8

An American Society of Testing and Materials (ASTM) test method is used to determine the flash point temperature: The test fuel is placed in a container and slowly and uniformly heated with its temperature monitored. Periodically as the temperature is increased, an ignition source is inserted into the container and this is repeated until the lowest temperature where a flash (light) occurs is identified. This temperature is defined as the flash point temperature. Since this ASTM test is conducted at ambient conditions, the amount of oxygen present is fixed and the ignition source is specified. As the pressure in the fuel tank of aircraft is reduced during aircraft ascent, the effective flash point temperature is lowered. In the case of TWA-800 at 13800 ft, the effective flash point of the fuel was lowered by about 8.3 °C (15 °F). At sea level some fuels may even be non-flammable, but may become flammable at higher altitude.

JP-8 at a specific temperature above its flash point temperature is just as flammable as JP-4 at the same delta temperature above its flash point. The safety advantage of JP-8 over JP-4 is that the ambient temperature and fuel operational temperatures are generally below the flash point of JP-8. The specification MIL-DTL-83133J prescribes a flash point for JP-8 of at least 311 K (38 °C). In the presence of buildup of electrostatic charges, a spark with only 0.20 mJ is sufficient to ignite JP-8 vapors in air.

### 5.4.2 Flammable Range of JP-8 Vapors

The flammable range of JP-8 vapors in air is 0.6–4.7 vol.-%. While it is true that the vapor pressure of JP-8 is less than that of JP-4, it is still possible, given the right conditions, that there are enough explosive vapors in a nearly empty fuel tank with JP-8 fuel to permit ignition that leads to a catastrophic explosion [70, 71].

By the mid 1990s most Air Force bases changed to JP-8, which resulted in a reduction of aircraft mishaps and damage caused by fuel combustion as the initial cause or as a secondary effect. Obviously under the right circumstances all fuels burn. A perfect example is the TWA-800 accident (17 July 1996) in which 230 people perished as a result of an in-flight explosion of the aircraft's center wing tank. While the tank contained only unusable fuel, it was in fact the vapors from Jet A (a fuel which exhibits very similar physical properties and combustion characteristics as JP-8) which exploded in the empty portion of the tank known as the "ullage."

Whatever ignited the fuel vapor/air mixture may never be determined; however, the fact that a catastrophic explosion occurred with Jet A fuel is significant in that a similar set of circumstances can potentially also occur with JP-8 and cause the same tragic results. The safety advantage of JP-8 over JP-4 is that the ambient temperature and fuel operational temperatures are generally below the flash point of JP-8.

Both the Air Force and commercial aircraft operators would prefer a fuel like JP-5 with a flash point above 333 K (140 °F), but JP-5 fuel availability is scarce and cost is prohibitive. Although Navy aircraft currently operate on JP-5 fuel, the Navy still expends significant effort addressing aircraft fire issues.

## 5.5 Fuel Mixtures with JP-8

Fuel mixtures with JP-8 were often evaluated as a means of increasing the heat of combustion of JP-8 or lowering the freezing points of other fuels. Fuel mixtures of JP-8 with other fuels include those with high-density terpene dimer fuels [72].

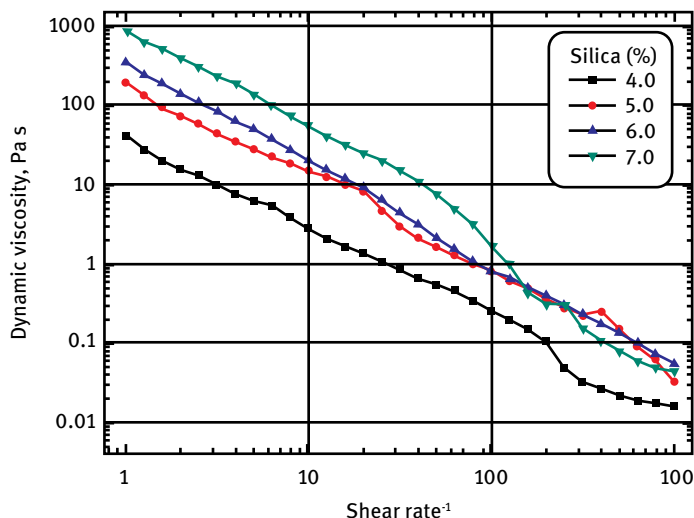
### 5.5.1 Gelled Kerosene JP-8

Fumed silica, also known under the trade name Cab-O-Sil<sup>®</sup>, is a useful gelling agent for fuels as well as oxidizers. The rheological behavior of gelled JP-8 turbine fuel with fumed silica as a gelling agent was measured and the optimal gel mixing process, gel stability, and rheological parameters showed a significant influence of the added silica amount [73, 74].

The rheological behavior of gelled rocket propellant RP-1 and JP-8 with fumed silica as a gelling agent has been measured and an optimal mixing process has been selected. The rheological parameters of the gelled kerosene showed a significant influence of the added amount of silica in comparison to the ungelled pure liquids [75] (Figure 12).

The rheology and droplet burning behaviors of JP-8 gelled with fumed silica were compared to those of methylhydrazine (MMH) gelled with hydroxypropyl cellulose [76]. Droplets of gelled MMH burning in air swelled and had a flexible droplet surface, whereas burning kerosene droplets gelled with fumed silica had a rigid silica structure which remained unburned.

The droplet burning of gelled JP-8 in air was studied at ambient pressure [77]. Based on a rheological characterization of gelled JP-8 turbine fuel using fumed silica as a gelling agent, single droplet combustion experiments have been conducted. Combustion experiments have shown a typical  $d^2$ -law behavior with considerable influence of the gelling agent. A higher amount of gellant agent resulted in a reduced burning rate. Droplet size as well as droplet temperature during combustion depended strongly on the consistency of the gel.



**Figure 12:** Viscosity of gelled JP-8 as a function of shear rate and silica amount. (Reproduced and modified from [75] with permission from W. E. Anderson.)

Gelled JP-8 has been used to study the rheological behavior of gelled hydrocarbons using 4 to 7 mass-% of fumed silica as the gelling agent [78]. Viscosity, stability, thixotropic behavior, and the viscoelastic properties of the gel through their storage and loss moduli were measured as a function of the amount of gelling agent added. Differential scanning calorimetry measurements showed only a slight influence of the amount of gelling agent on the enthalpy of vaporization of the gels. The ungelled hydrocarbons had a higher enthalpy of vaporization than the gels.

### 5.5.2 Injectors for Gelled Kerosene JP-8

Gelled fuels may be safer to handle, but they are more difficult to burn and to atomize into small droplets. One type of injector that has been tested for gelled propellants is the like-on-like impinging jet injector [79]. Disintegration of individual water jets and liquid sheets formed by jet-on-jet impingement was studied with jet velocities in the range of 0.9–37 m/s (3–122 feet/s) and compared to known water correlations for selected velocities. The laminar sheet shape is predicted and compared to high speed images of the experimental sheet to help ensure proper alignment and operation of the impinging jet system. A JP-8 and 5% fumed silica gelled mixture impingement study was conducted as a first step toward producing and injecting gelled hypergolic bipropellant reactants through this injector. The gelled-impingement sheet disintegration was observed and compared to water data collected in the same apparatus.

## 6 Jet Fuel JP-9

JP-9 is a blend of the three components and was developed to meet the requirements for an air-launched cruise missile. JP-9, a three-component blend consisting of 65–70% JP-10, 10–12% methylcyclohexane to increase volatility, and 20–25% RJ-5 (to be described in *Encyclopedia of Liquid Fuels*, chapter “Ramjet Fuels”) to boost energy content, was developed to meet the fuel specifications; its properties are described in Table 9. This fuel is not practical because of the high cost and abandonment of RJ-5 supply route.

**Table 9:** Physical properties of JP-9.

| Property                                 | SI units                                          | Other units                                                 | References |
|------------------------------------------|---------------------------------------------------|-------------------------------------------------------------|------------|
| Molecular mass for $C_{10.2}H_{16}$      | 138.64 g/mol                                      | 7.2129 mol/kg                                               | [6]        |
| Density                                  | 0.938 kg/L at 298 K                               | 0.938 g/cm <sup>3</sup> at 298 K                            | [80]       |
| Melting point                            | <219 K                                            | <−65 °F                                                     | [6]        |
| Boiling range                            | 372 to 558 K                                      | 210 to 545 °F                                               |            |
| Vapor pressure                           | 1.7 kPa at 298 K                                  | 0.24 psia at 77 °F                                          | [80]       |
| Kinematic viscosity                      | 3.18 mm <sup>2</sup> /s at 298 K                  | 3.18 cSt at 77 °F                                           | [82]       |
|                                          | <50 mm <sup>2</sup> /s at 219 K                   | <50 cSt at −54 °C                                           |            |
|                                          | <12 mm <sup>2</sup> /s at 255 K                   | <12 cSt at −18 °C                                           |            |
| Surface tension                          | 31.7 mN/m at 298 K                                | 31.7 dyn/cm at 25 °C                                        | [80]       |
| Thermal conductivity                     | 0.11 W m <sup>−1</sup> K <sup>−1</sup> at 298 K   | 0.065 BTU h <sup>−1</sup> ft <sup>−1</sup> °F <sup>−1</sup> |            |
|                                          |                                                   | at 77 °F                                                    |            |
| Dielectric constant                      | 2.33 at 298 K (25 °C)                             | —                                                           |            |
| Heat capacity $c_p$                      | 1.55 kJ kg <sup>−1</sup> K <sup>−1</sup> at 298 K | 0.371 BTU lb <sub>m</sub> <sup>−1</sup> °F <sup>−1</sup>    | [80, 83]   |
|                                          |                                                   | at 77 °F                                                    |            |
| Enthalpy of formation $\Delta H_f^{298}$ | −757.0 kJ/kg                                      | −18.09 kcal/100 g                                           | [83]       |
|                                          | −772 kJ/kg                                        | —                                                           | [6]        |
| Upper heat of combustion                 | 44710 kJ/kg                                       | 1068.6 kcal/100 g                                           | [83]       |
| Lower (net) heat of combustion           | 42215 kJ/kg                                       | 1008.9 kcal/100 g                                           |            |
| Autoignition temperature                 | 523 K                                             | 482 °F                                                      | [6]        |
| Flash point                              | 294 K                                             | 70 °F                                                       |            |

### 6.1 Preparation of JP-9

JP-9 can be prepared by mixing 65–70 mass-% JP-10, 20–25 mass-% RJ-5, and 10–12 mass-% methylcyclohexane. In an effort to measure physical properties of JP-9 within the range of MIL-SPEC tolerances as a function of composition, 12 JP-9 mixtures were made starting with four different batches of RJ-5 [80]. Blends of the

fuel components were prepared which covered but did not exceed the specified composition range for JP-9 fuel.

## 6.2 Physical Properties of JP-9

Physical properties of JP-9 are summarized in Table 9 and reference [81].

### 6.2.1 Thermodynamic Properties of JP-9

#### 6.2.1.1 Heat Capacity of JP-9

The heat capacity of JP-9 as a function of temperature between 260 and 360 K can be calculated from the following equation [83]:

$$c_p = 0.09299 + 0.001006 T$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin.

#### 6.2.1.2 Heat of Combustion of JP-9

The gross heat of combustion of JP-9 is  $44.711 \pm 0.003 \text{ kJ/kg}$  ( $10686.16 \pm 0.78 \text{ cal/g}$ ), and the net heat of combustion of JP-9 is  $42.21 \pm 0.01 \text{ kJ/kg}$  ( $10089.5 \pm 2.4 \text{ cal/g}$ ) [83]. An earlier report from the same source gave the heat of combustion of JP-9 as  $10089.3 \pm 2.4 \text{ cal/g}$  [84].

## 6.3 Chemical Properties of JP-9

The empirical formula of JP-9 is  $\text{C}_{10.2}\text{H}_{16}$ . The chemical composition of JP-9 is 65–70 mass-% JP-10, 20–25 mass-% RJ-5, and 10–12 mass-% methylcyclohexane. An out-of-date specification MIL-P-87107B (USAF) (March 1979) once covered both JP-9 and JP-10 but it has been superseded by MIL-DTL-87107E [82] which covers JP-10 only.

## 6.4 Safety Properties of JP-9

### 6.4.1 Fire Hazard Properties of JP-9

The flash point of JP-9 per MIL-P-87107B was supposed to be between 16 and 27°C (60 and 80 °F).

### 6.4.2 Environmental Impact of JP-9 Spills

JP-9 and several other kerosenes were examined to measure the effects of potential environmental contamination resulting from these fuels on fresh water fish and aufwuchs [28]. Besides JP-4, the materials evaluated included RJ-4, RJ-5, methylcyclohexane, and JP-4.

## 7 Jet Fuel JP-10

JP-10 is a military missile fuel, used in many cruise missiles (e.g., Tomahawk, ALCM, ACM). JP-10 is a single component fuel, *exo*-tetrahydro-di(cyclopentadiene), *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane, in contrast to the other, JP-type jet fuels (e.g., JP-8 or JP-7) which are multi-component petroleum distillates. JP-10 is a single component (*exo*-)isomer. The *endo*-isomer is a solid at room temperature and is not used for JP-10. JP-10 has a very low freezing point (194 K = -79 °C) and a density almost 20% higher than JP-8. The main ingredient of JP-10 consists mostly of *exo*-tetrahydro-dicyclopentadiene, C<sub>10</sub>H<sub>16</sub>, CAS RN [2825-82-3], which is a synthetic isocyclic (alicyclic) hydrocarbon (see chapter “Cycloaliphatic Hydrocarbons”). JP-10 per MIL-DTL-87107E may contain antioxidant and fuel system icing inhibitors, which may slightly change its physical and chemical properties.

### 7.1 Production of JP-10

JP-10 is made by adding 90–110 ppm (by mass) antioxidant and 0.10–0.15 vol.-% fuel system icing inhibitors to *exo*-tetrahydrodicyclopentadiene.

### 7.2 Physical Properties of JP-10

Physical properties of JP-10 are summarized in Table 10 and would be mostly identical with the properties of *exo*-tetrahydrodicyclopentadiene (chapter “Cycloaliphatic Hydrocarbons”). Based on their titles, many publications describe the chemical studied as JP-10, but it is doubtful that they actually had military grade JP-10 with antioxidant and icing inhibitor in their laboratory. Most of those experiments were probably made with more or less pure *exo*-tetrahydrodicyclopentadiene without any additives. Not knowing the actual composition of the samples tested (additives or no additives), we have entered references to the publications into those sections where the title of the publication directed us to. This may result in publications with properties of otherwise identical chemicals to be found in different sections of this book. Thus, one will want

**Table 10:** Physical properties of JP-10.

| Property                          | SI units                                            | Other units                                                                                           | References  |
|-----------------------------------|-----------------------------------------------------|-------------------------------------------------------------------------------------------------------|-------------|
| Molecular mass for $C_{10}H_{16}$ | 136.2340 g/mol                                      | 7.3403 mol/kg                                                                                         |             |
| Freezing point                    |                                                     | $<-79^{\circ}\text{C} = <-110^{\circ}\text{F}$                                                        | [82]        |
| Freezing point                    | 183.2 K                                             | $-89.95^{\circ}\text{C}$                                                                              | [86]        |
| Boiling point                     | 455 K                                               | $182^{\circ}\text{C} = 359^{\circ}\text{F}$                                                           | [6]         |
| Density at 288 K                  | 0.934–0.943 g/cm <sup>3</sup>                       | —                                                                                                     | [82]        |
| Density at 298 K                  | 0.9314 g/cm <sup>3</sup>                            | —                                                                                                     | [87]        |
| Kinematic viscosity at 233 K      | 19 mm <sup>2</sup> /s                               | 19 cSt                                                                                                | [6]         |
| Kinematic viscosity at 219 K      | <40 mm <sup>2</sup> /s                              | <40 cSt                                                                                               | [82]        |
| Kinematic viscosity at 255 K      | <10 mm <sup>2</sup> /s                              | <10 cSt                                                                                               |             |
| Surface tension at 298 K          | 30.4 mN/m                                           | 30.4 dyn/cm at $25^{\circ}\text{C}$                                                                   | [80]        |
| Thermal conductivity              | 0.115 W m <sup>-1</sup> K <sup>-1</sup>             | 0.0664 BTU h <sup>-1</sup> ft <sup>-1</sup> °F <sup>-1</sup>                                          | [85]        |
| Dielectric constant               | 2.46 at 298 K                                       | —                                                                                                     | [80]        |
| Index of refraction               | $n_D^{20} = 1.4872$                                 | —                                                                                                     | [84]        |
| Heat capacity $c_p$ at 298 K      | 1.569 J g <sup>-1</sup> K <sup>-1</sup>             | 0.375 cal g <sup>-1</sup> °C <sup>-1</sup>                                                            | [88]        |
| Enthalpy of formation             | -902 kJ/kg<br>-774 J/g                              | -388 BTU/lb<br>-185 cal/g for a fuel<br>with a density of<br>0.0336 lb <sub>m</sub> /in. <sup>3</sup> | [6]<br>[14] |
| Lower (net) heat of<br>combustion | >42.1 MJ/kg<br>42.4 MJ/kg                           | >18100 BTU/lb<br>18241 BTU/lb                                                                         | [82]<br>[6] |
| Volumetric heat of<br>combustion  | 39600 MJ/m <sup>3</sup><br>>39400 MJ/m <sup>3</sup> | 142000 BTU/gal<br>>141500 BTU/gal                                                                     | [6]<br>[82] |
| Autoignition temperature          | 518 K                                               | 474 °F                                                                                                | [6]         |
| Flash point                       | 326 K                                               | 128 °F                                                                                                | [6]         |
| Flash point                       | >327.5 K                                            | >54.4 °C = 130 °F                                                                                     | [82]        |

to examine both sections, this one under JP-10 here and the other in the section on *exo*-tetrahydrodicyclopentadiene. The two sections will complement each other and there may be some duplication of information.

The physical properties of *exo*-tetrahydrodicyclopentadiene (THDCPD) as a pure compound (without any additives) are described in chapter “Cycloaliphatic Hydrocarbons.” A very detailed characterization of thermochemical and thermophysical properties of JP-10 performed in 2006 was done on JP-10 samples taken from the flight line, but it was not known whether this particular sample contained any additives or not [85]. Most likely they did contain additives and the investigator should have identified them.

### 7.2.1 Freezing Point of JP-10

The freezing point of JP-10 is not specified by MIL-DTL-87107E but must not be higher than 183.2 K ( $-89.9^{\circ}\text{C}$ ). However, one source [89] gave the freezing point of JP-10 as

194 K (−79 °C), which is higher than the temperature found in other sources. One source measured the freezing point of JP-10 at 200 K (−73 °C). JP-10 was added to RJ-5 in an effort to lower the freezing point of RJ-5. The freezing points of XTHDCPD/PHDNBD (JP-10/RJ-5) mixtures were measured over a wide range of compositions [90]. There was very little difference among the viscosity-composition isotherms for the three PHDNBD isomers.

### 7.2.2 Density of JP-10

The density of JP-10 specified per MIL-DTL-87107E is 0.934–0.943 g/cm<sup>3</sup> at 288 K (15 °C). Dicyclopentadiene and dimethylcyclopentadiene, for example, have comparable high densities of 0.974 and 0.940 g/cm<sup>3</sup>, respectively, at 293 K (20 °C), while the densities of gasoline and aviation fuel kerosene are substantially lower. The density of JP-10 as a function of temperature is listed in Table 11.

**Table 11:** Density of JP-10 as a function of temperature.

| Temperature |    | Density           |
|-------------|----|-------------------|
| K           | °C | g/cm <sup>3</sup> |
| 278         | 5  | 0.9462            |
| 288         | 15 | 0.9377            |
| 298         | 25 | 0.9314            |
| 318         | 45 | 0.9166            |
| 338         | 65 | 0.9017            |

Data source: [87]

The density and the absolute and kinematic viscosity of JP-10 in the temperature range from 233–373 K (−40 to +100 °C) at atmospheric pressure was measured in a Stabinger viscodensimeter (Anton Paar SVM 3000) as well as a Sound Speed Analyzer DSA 5000 [85]. The density decreased almost linearly with temperature, as shown in Figure 13.

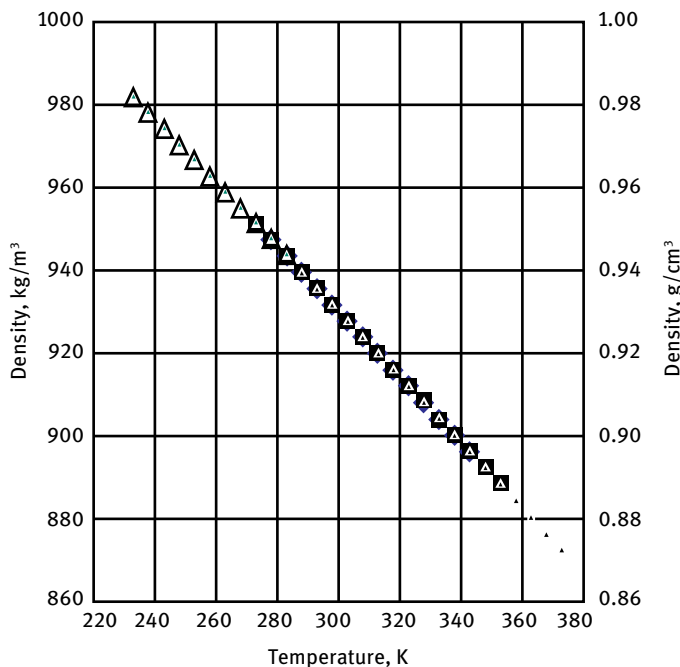
The density of JP-10 was expressed by the polynomial equation

$$\rho = a_0 + a_1\tau + a_2\tau^2$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $\tau = T/T_c$  is the reduced temperature (temperature divided by the critical temperature) and  $a_0$ ,  $a_1$ , and  $a_2$  are constants:  $a_0 = 1153.0412$ ;  $a_1 = -192.47447$ ;  $a_2 = -9.3825928$ .

Densities of JP-10 at temperatures from 270 to 470 K and at pressures up to 30 MPa were measured with two vibrating-tube densimeters [89]. Correlations were reported that represented the temperature and pressure dependence of the experimental density data within their estimated uncertainty. The properties of JP-10 were compared to





**Figure 13:** Density of JP-10 as a function of temperature. (Reproduced and modified from [85].)

those of other previously measured jet and rocket fuels, such as RP-1 and Jet A. The density of JP-10 is much higher than the density of RP-1 (Figure 14).

Density data for compressed JP-10 were correlated with a Tait equation

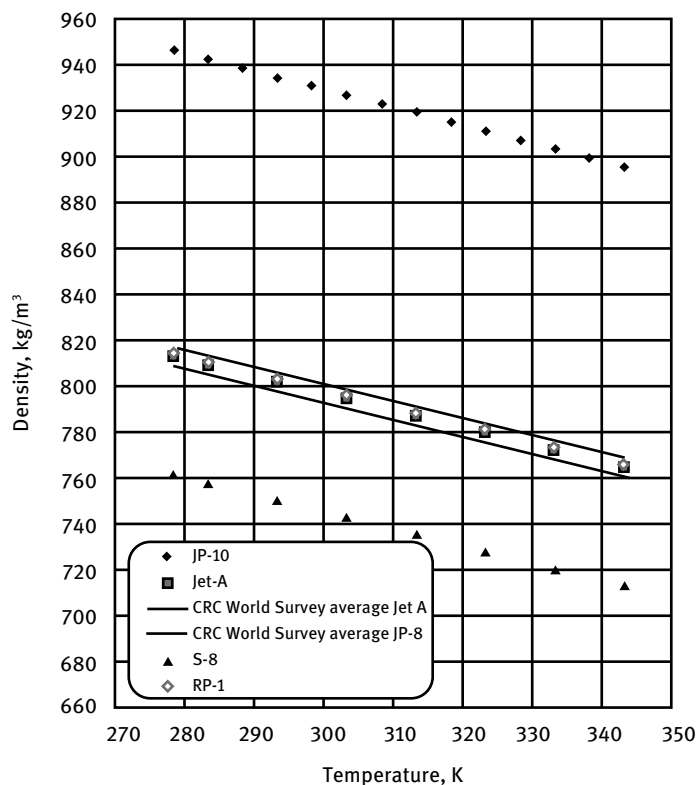
$$\rho = \frac{\rho_{\text{ref}}}{1 - C \ln\left(\frac{P + D}{P_{\text{ref}} + D}\right)}$$

where  $\rho$  is the density in  $\text{g/cm}^3$ ,  $\rho_{\text{ref}}$  is the density at the reference state,  $P$  is the pressure in MPa,  $P_{\text{ref}}$  is the reference pressure = 0.083 MPa, and  $C$  is a constant  $C = 79.18232 \times 10^{-3}$ .  $D$  is the Tait parameter to be calculated from a quadratic polynomial

$$D = 417.1 - 370.4 \times T_r + 86.24 \times T_r^2$$

where  $T_r$  is the reduced absolute temperature  $T$  divided by 273.15 K.

The density of JP-10 at 267 to 873 K under pressures of 0.70 to 6.00 MPa was measured using a gamma-ray radial method calibrated with water, cyclohexane, and a mixture of *n*-heptane and *n*-octane [91]. This method was based on the attenuation theory of gamma rays. Two empirical correlations were used to fit the liquid and gas density data separately. The isobaric thermal expansion of the liquid was calculated. The densities of liquid JP-10, ranging from 267.9 to 562.1 K under 0.70 MPa, 267.3 to



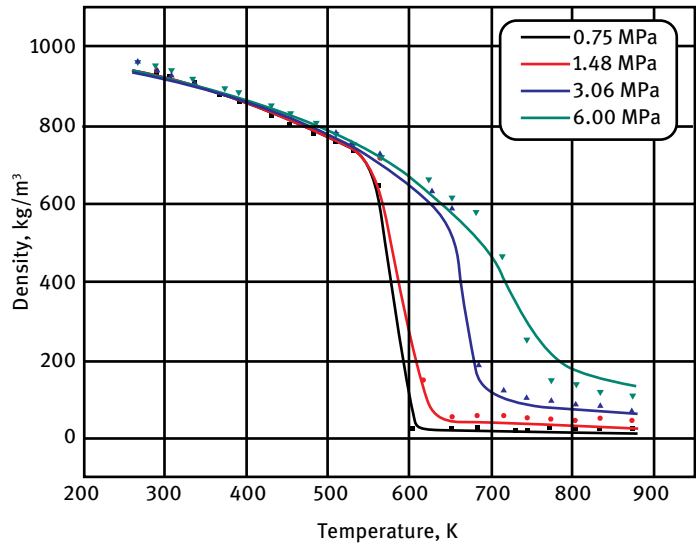
**Figure 14:** Measured and extrapolated density data of JP-10 compared to those of other fuels as a function of temperature at ambient pressure. (Reprinted and adapted from [89], with permission from ©2011 American Chemical Society; permission conveyed through RightsLink.)

563.8 K under 1.48 MPa, 267.9 to 651.9 K under 3.06 MPa, and 267.3 to 681.8 K under 6.00 MPa, were fitted by third-order polynomials as

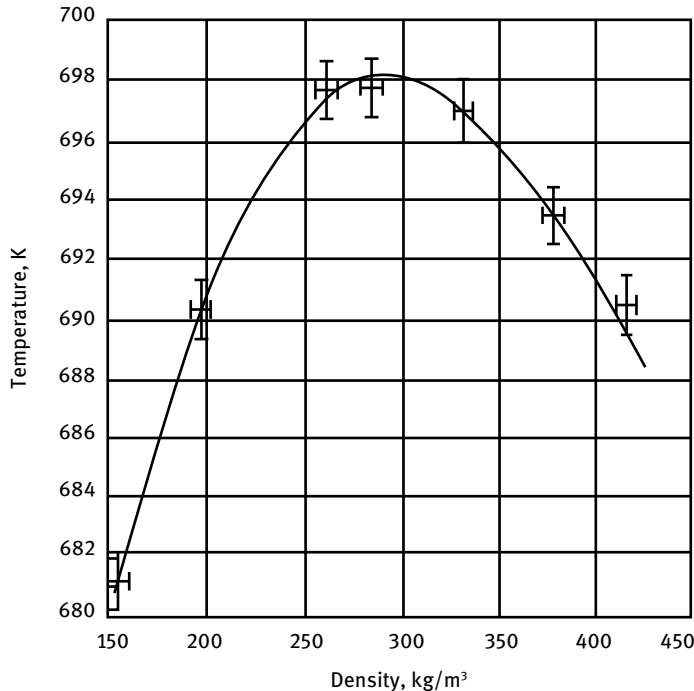
$$\rho = 1853.6 - 6.4515T + 0.0153T^2 - 1.3517 \times 10^{-5}T^3$$

where  $\rho$  represents density of liquid JP-10 in  $\text{kg/m}^3$ , and  $T$  represents temperature in kelvin. The predicted density curves in different colors versus temperature under different pressures and measured density points under experimental pressures are shown in Figure 15.

The density of subcritical JP-10 under saturated vapor pressure conditions was calculated and is illustrated in Figure 16. For comparison, the vapor–liquid coexistence plot given in Figure 16 shows a critical temperature,  $T_c = 698 \text{ K}$ , with a corresponding critical density  $\rho_c = 285 \text{ kg/m}^3$ . Similar charts are available for tetralin and toluene.



**Figure 15:** Predicted density curves of JP-10 versus temperature under different pressures and measured density points under experimental pressures. (Reprinted and adapted from [91] with permission from ©2019 American Chemical Society; permission conveyed through RightsLink.)



**Figure 16:** Vapor–liquid coexistence region of JP-10. (Reproduced and modified from [92].)

### 7.2.3 Vapor Pressure of JP-10

The vapor pressure of JP-10 is governed by its main ingredient, *exo*-tetrahydrodicyclopentadiene (see chapter “Cycloaliphatic Hydrocarbons”). The vapor pressure of JP-10 determined in an apparatus with a vapor : liquid volume ratio of 0.28 is listed in Table 12.

**Table 12:** Vapor pressure of JP-10 as a function of temperature.

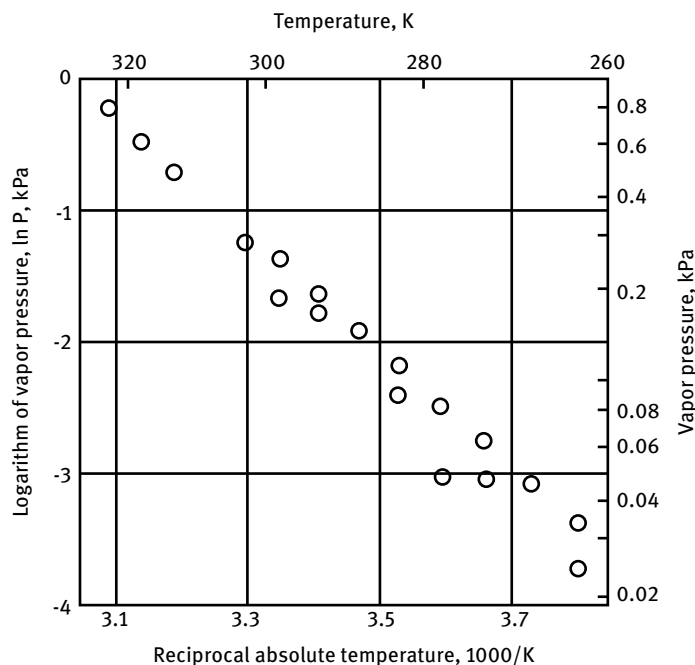
| Temperature |    | Vapor pressure |       |
|-------------|----|----------------|-------|
| K           | °C | kPa            | mm Hg |
| 273         | 0  | 4.26           | 32    |
| 298         | 25 | 5.73           | 43    |
| 323         | 50 | 8.26           | 62    |
| 348         | 75 | 13.3           | 100   |

Data source: [87]

The dependence of the vapor pressure of JP-10 on temperature can be expressed by a Cox equation

$$\ln(P/P_c) = (1 - 1/T_r) \exp(2.39742 - 1.28961T_r + 0.90779T_r^2)$$

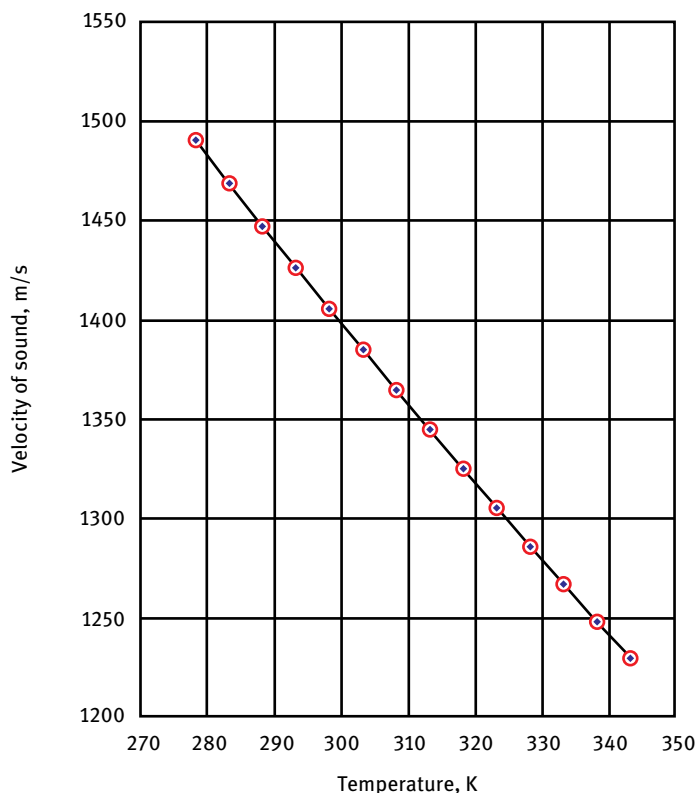
where the reduced temperature is  $T_r = T/T_c$ ,  $T$  is the temperature in kelvin,  $T_c$  is the critical temperature = 698 K and  $P_c$  is the critical pressure = 3733 kPa [92]. Figure 17 shows experimental data for measured vapor pressure of JP-10.



**Figure 17:** Vapor pressure of JP-10 as a function of temperature. (Reproduced and modified from [93].)

#### 7.2.4 Velocity of Sound and Compressibility of JP-10

A sound speed analyzer (Anton Paar DSA 5000) was used to measure the velocity of sound and the density of several JP-10 samples at atmospheric pressure in the temperature range 278–343 K (5–70 °C) [85]. The velocity of sound decreased almost linearly with temperature (Figure 18).

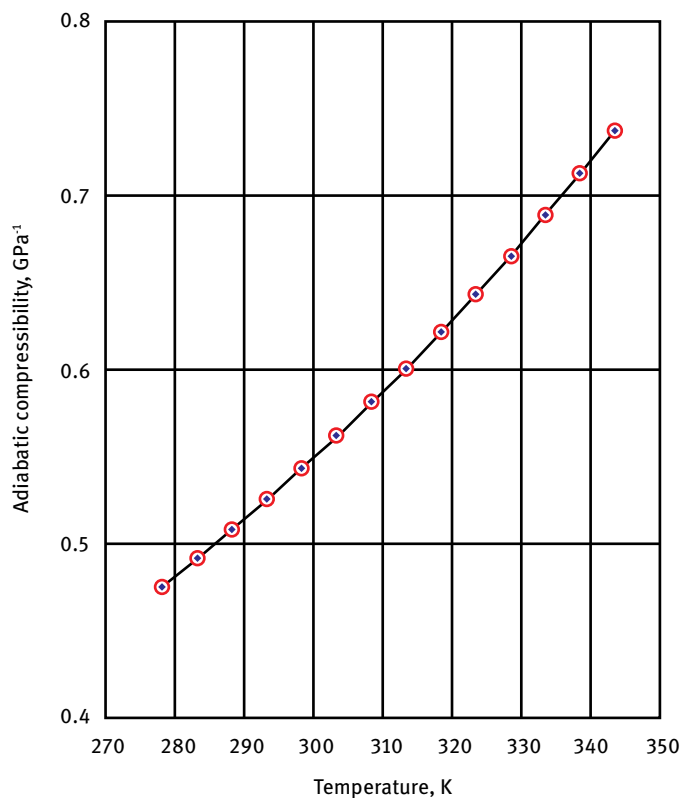


**Figure 18:** Velocity of sound in JP-10 as a function of temperature. (Reproduced and modified from [85].)

The adiabatic compressibility of JP-10 was derived from velocity of sound data using the known correlation between the two properties (Figure 19). Adiabatic compressibilities were calculated from the measured densities and velocity of sound according to the thermodynamic relation

$$k_s = -\frac{\left(\frac{\partial V}{\partial P}\right)_s}{V} = \frac{1}{\rho w^2}$$

where  $V$  denotes volume,  $P$  is the pressure,  $\rho$  is the density, and  $w$  is the velocity of sound. The subscript  $s$  indicates “at constant entropy.”

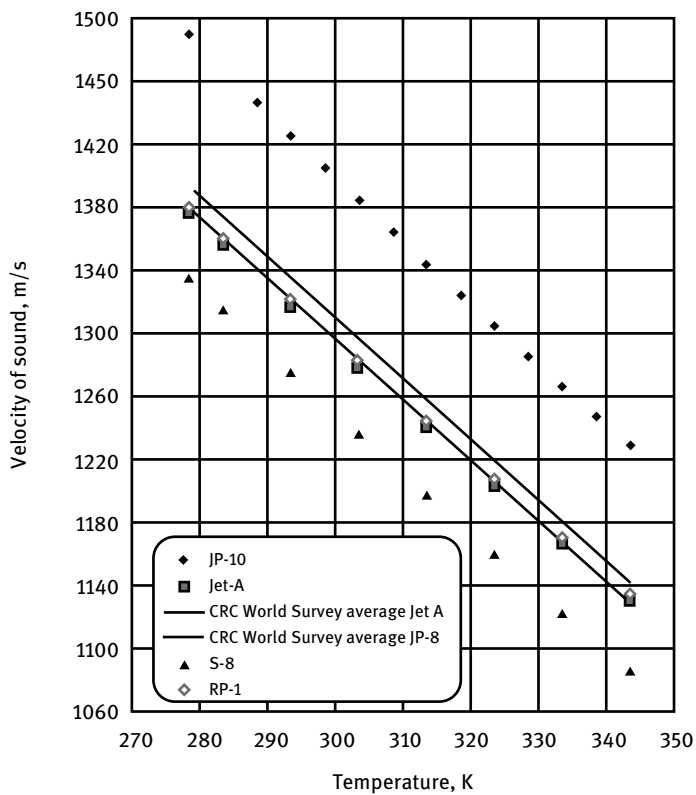


**Figure 19:** Adiabatic compressibility of JP-10 as a function of temperature. (Reproduced and modified from [85].)

The velocity of sound in JP-10 was measured with a propagation time method at ambient pressure from 278 to 343 K [89]. The results for density and velocity of sound at ambient pressure were combined to obtain the adiabatic compressibility. The velocity of sound properties of JP-10 were compared to those of other previously measured jet and rocket fuels such as RP-1 and Jet A (Figure 20). The velocity of sound in JP-10 is higher than the velocity of sound in other fuels.

### 7.2.5 Viscosity of JP-10

The viscosity of *exo*-THDCPD and its mixtures with PHDNBD was measured over a wide range of temperatures. The kinematic viscosity of JP-10 as a function of temperature is listed in Table 13.



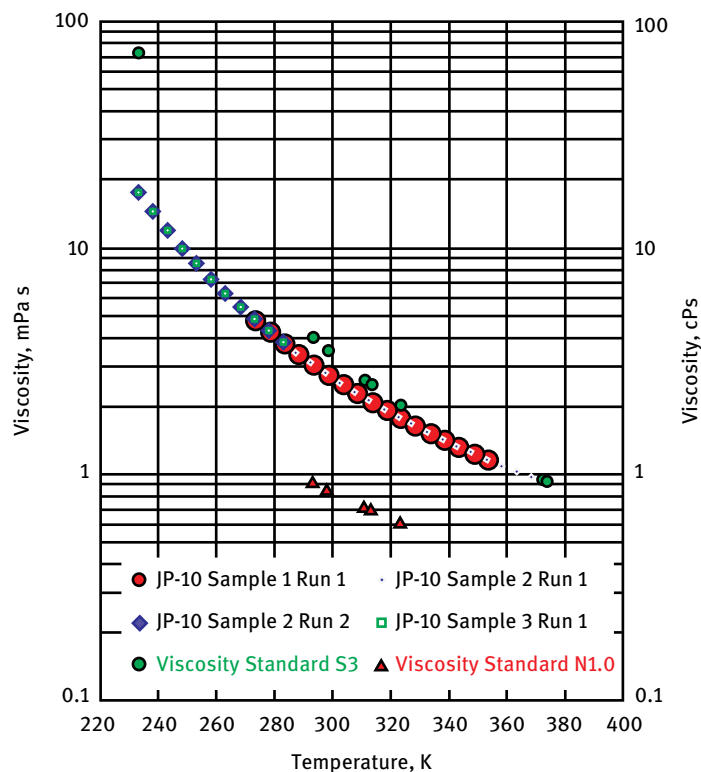
**Figure 20:** Measured velocity of sound data of JP-10 as a function of temperature at ambient pressure compared to those of other jet fuels. (Reprinted and adapted from [89], with permission from ©2011 American Chemical Society; permission conveyed through RightsLink.)

**Table 13:** Viscosity of JP-10 as a function of temperature.

| Temperature |      | Kinematic viscosity |      |
|-------------|------|---------------------|------|
| K           | °C   | mm <sup>2</sup> /s  | cSt  |
| 253         | −20  | 8.84                | 8.84 |
| 273         | 0    | 5.08                | 5.08 |
| 294.2       | 21.1 | 3.26                | 3.26 |
| 310.9       | 37.8 | 2.37                | 2.37 |

Data source: [87]

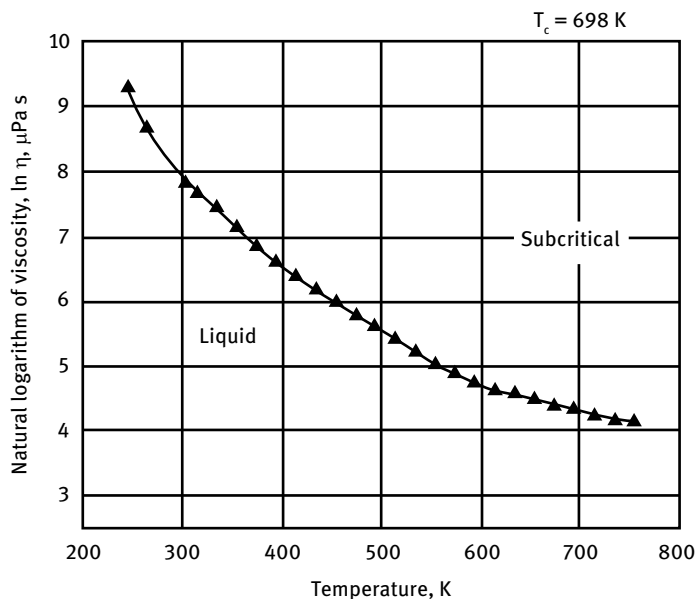
The viscosity of JP-10 was measured with a Stabinger viscodensimeter SVM 3000 on three samples from the same stock to assess the repeatability of the instrument [85]. Four runs were carried out in the combined temperature range from 233 to 373 K. The dynamic viscosity curve as a function of temperature measured in the Stabinger viscodensimeter SVM 3000 is shown in Figure 21. The measurement data points fall on top of each other, showing good reproducibility. Two standard fluids, one more viscous and one less viscous, were tested to calibrate and verify proper operation of the instrument.



**Figure 21:** Dynamic viscosity of JP-10 as a function of temperature. (Reproduced and modified from [85].)

The viscosities of JP-10 were measured using a two-capillary method at 242.7–753.3 K under pressures of 0.69–6 MPa [94]. After the viscosity of pure *n*-octane was measured and compared with literature data, the measurement system was calibrated, and the average absolute deviation and the maximum absolute deviation were found to be 0.71 and 1.35%, respectively. Yaws' equation and Bruno's equation were used to cor-





**Figure 22:** Viscosity of JP-10 at 3 MPa as a function of temperature. (Reprinted and adapted from [94], with permission from ©2017 American Chemical Society; permission conveyed through RightsLink.)

relate the experimental data. The data measured at a pressure of 3 MPa are shown in Figure 22. The data extend into the critical region.

### 7.2.6 Surface Tension of JP-10

The surface tension of JP-10 is listed in Table 14.

**Table 14:** Surface tension of JP-10 as a function of temperature.

| Temperature |    | Surface tension |        |
|-------------|----|-----------------|--------|
| K           | °C | N/m             | dyn/cm |
| 298         | 25 | 0.0321          | 32.1   |
| 323         | 50 | 0.0298          | 29.8   |
| 348         | 75 | 0.0274          | 27.4   |

Data source: [87]

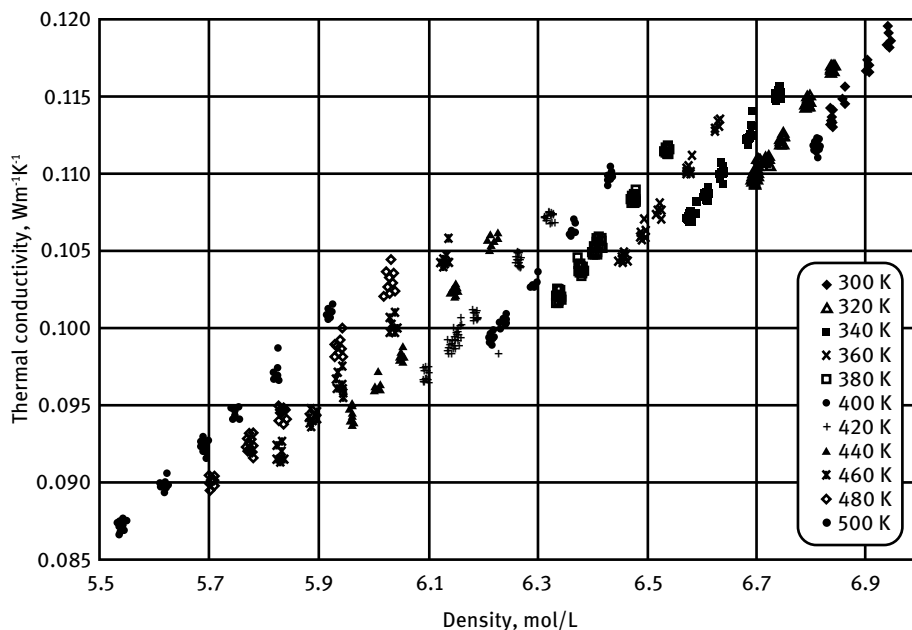
### 7.2.7 Pressurant Gas Solubility in JP-10

The solubility of nitrogen, oxygen, and carbon dioxide in JP-10 (*exo*-tetrahydrodicyclopentadiene) in the temperature range from 293 to 343 K was measured in intervals of

10 K and in the pressure range from 0.5 to 7.5 MPa [95]. The solubility of the three gases in JP-10 in the studied temperature and pressure range decreased in the order carbon dioxide > oxygen > nitrogen. Henry's constants and the thermodynamic properties of solvation were calculated from the solubility data.

### 7.2.8 Thermal Conductivity of JP-10

Transient hot-wire measurements of the thermal conductivity of the JP-10 liquid sample were made along 11 isotherms at temperatures from 300 to 500 K with pressures up to 30 MPa [85]. The thermal conductivity was illustrated in Figure 23 as a function of density, not temperature. This is not a very convenient format if the user needs thermal conductivity as a function of temperature at constant pressure (sea level atmospheric pressure).



**Figure 23:** Thermal conductivity of JP-10 as a function of density. (Reproduced and modified from [85].)

### 7.2.9 Thermodynamic Properties of JP-10

Thermodynamic properties of pure *exo*-tetrahydrodicyclopentadiene, the main constituent of JP-10, are discussed in chapter “Cycloaliphatic Hydrocarbons.” Since JP-10 is 99+% *exo*-tetrahydrodicyclopentadiene, its thermodynamic properties will be the same as those of *exo*-tetrahydrodicyclopentadiene. A very detailed characterization

of thermodynamic properties of JP-10 was done on a sample of JP-10 taken from the flight line, but it was not known whether this particular sample contained any additives or not [85].

### 7.2.9.1 Heat Capacity of JP-10

A high-temperature/high-pressure sample cell developed for use with a DSC has been used to determine the liquid-phase heat capacities and critical properties for toluene, tetralin, and JP-10 [92]. The results for toluene and tetralin compared very favorably with available literature values, while no reliable literature data for JP-10 to compare to were available.

The results of heat capacity measurements of subcritical JP-10 at saturation pressure between 300 and 690 K were only given in table format (Table 15) [92]. It would have been more practical to give the parameters for a curve-fitted polynomial equation.

The heat capacity of JP-10 as a function of temperature in the range 260–465 K can be expressed by the following equation [88]:

$$c_p = 0.10423 + 0.76872 \times 10^{-3}T + 0.46992 \times 10^{-6}T^2$$

**Table 15:** Heat capacity of JP-10 at constant volume and under saturation pressure conditions.

| Temp., K | $C_V/R$ | $C_\sigma/R$ | Temp., K | $C_V/R$ | $C_\sigma/R$ |
|----------|---------|--------------|----------|---------|--------------|
| 300      | 27.37   | 27.37        | 500      | 40.60   | 40.67        |
| 310      | 28.11   | 28.11        | 510      | 41.21   | 41.30        |
| 320      | 28.83   | 28.83        | 520      | 41.82   | 41.93        |
| 330      | 29.55   | 29.55        | 530      | 42.43   | 42.56        |
| 340      | 30.25   | 30.25        | 540      | 43.04   | 43.20        |
| 350      | 30.95   | 30.95        | 550      | 43.66   | 43.85        |
| 360      | 31.64   | 31.64        | 560      | 44.28   | 44.52        |
| 370      | 32.32   | 32.32        | 570      | 44.91   | 45.20        |
| 380      | 32.99   | 32.99        | 580      | 45.55   | 45.91        |
| 390      | 33.65   | 33.66        | 590      | 46.22   | 46.66        |
| 400      | 34.31   | 34.32        | 600      | 46.90   | 47.45        |
| 410      | 34.96   | 34.97        | 610      | 47.61   | 48.30        |
| 420      | 35.61   | 35.62        | 620      | 48.37   | 49.22        |
| 430      | 36.25   | 36.26        | 630      | 49.17   | 50.25        |
| 440      | 36.88   | 36.90        | 640      | 50.03   | 51.44        |
| 450      | 37.51   | 37.53        | 650      | 50.99   | 52.85        |
| 460      | 38.14   | 38.17        | 660      | 52.06   | 54.62        |
| 470      | 38.76   | 38.79        | 670      | 53.29   | 57.05        |
| 480      | 39.38   | 39.42        | 680      | 54.80   | 60.96        |
| 490      | 39.99   | 40.05        | 690      | 56.86   | 70.62        |

$R = 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$ ; Subscript  $\sigma$  = saturation pressure conditions

Data source: [92]

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin. For a temperature of 298 K, this equation gives a heat capacity of  $1.569 \text{ J g}^{-1} \text{ K}^{-1} = 0.375 \text{ cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$

#### 7.2.9.2 Enthalpy of Formation of JP-10

Literature data for the enthalpy of formation of JP-10 differ substantially:  $-902 \text{ J/g} = -388 \text{ BTU/lb}$  [6] and  $-774 \text{ J/g} = -185 \text{ cal/g}$  for a fuel with a density of  $0.0336 \text{ lb}_m/\text{in.}^3$  given in [14]. The enthalpy of formation of JP-10 would essentially be identical with that of *exo*-tetrahydrodicyclopentadiene for which a heat of combustion of  $10682.01 \pm 0.90 \text{ cal/g} = 1457.68 \pm 0.33 \text{ kcal/mol}$  was reported which leads to an enthalpy of formation of  $-122.8 \pm 1.5 \text{ kJ/mol} = -29.35 \pm 0.35 \text{ kcal/mol} = -901 \text{ J/g} = -215 \text{ cal/g}$  [84].

#### 7.2.9.3 Enthalpy of Fusion of JP-10

The heat of fusion of JP-10 would essentially be the same as that of *exo*-tetrahydrodicyclopentadiene which is  $1.2 \text{ kJ/mol}$  at  $183.2 \text{ K}$ .

#### 7.2.9.4 Enthalpy of Evaporation of JP-10

The enthalpy of evaporation of JP-10 would essentially be the same as that of *exo*-tetrahydrodicyclopentadiene which is  $53.4 \pm 0.8 \text{ kJ/mol}$  ( $10.40 \pm 0.2 \text{ kcal/mol}$ ) at  $443 \text{ K}$  [96].

#### 7.2.9.5 Heat of Combustion of JP-10

The upper heat of combustion of JP-10 was measured at  $42.81 \text{ MJ/kg}$  [87].

#### 7.2.10 Index of Refraction of JP-10

The index of refraction of JP-10 was reported as  $n_D^{20} = 1.4872$  [97].

#### 7.2.11 Critical Point Properties of JP-10

The following values of the critical parameters should be used for all property calculations from the equation of state:

- $T_c = 698 \text{ K}$
- $P_c = 3.733 \text{ MPa}$
- $\rho_c = 2.16 \text{ mol/dm}^3$

while other sources [92] gave the critical point properties of JP-10 as

- $T_c = 698 \text{ K}$
- $P_c = 3.733 \text{ MPa}$
- $\rho_c = 285 \text{ kg/m}^3$

### 7.2.12 Molecular Structure of JP-10

Some publications deal with the molecular structure of what the authors called “JP-10.” There is no molecular structure of JP-10 because in the exact sense of the definition JP-10 is a mixture and not a pure compound. The molecular structure of *exo*-tetrahydrodicyclopentadiene (tricyclo[5.2.2.1.0<sup>2,6</sup>]decane) is discussed in chapter “Cycloaliphatic Hydrocarbons.”

## 7.3 Physical Properties of JP-10 Mixtures

Numerous mixtures of JP-10 with other hydrocarbons have been characterized in an effort to develop improved or more economical fuels for cruise missiles and other air-breathing propulsion applications. The densities and viscosities of the binary mixtures of JP-10 with *n*-octane and JP-10 with *n*-decane were determined from 293.15 to 313.15 K at atmospheric pressure, over the entire composition range [98]. Excess volumes  $V_m^E$  of the binary mixtures were calculated. The experimental data indicated that the addition of *n*-alkanes has a distinct effect on the density and viscosity of JP-10, and  $V_m^E$  values of the binary systems were negative. Experimental data were fitted to the Redlich–Kister equation, and the adjustable parameters and the standard deviations between experimental and calculated values were estimated. Viscosity data have been correlated with several semi-empirical equations, and the Grunberg–Nissan equation gave satisfactory results.

Densities and viscosities of *exo*-tetrahydrodicyclopentadiene plus *n*-undecane and *exo*-tetrahydrodicyclopentadiene plus *n*-tetradecane mixtures were measured at different temperatures (293, 298, 303, and 313 K) and atmospheric pressure over the entire composition range [99]. The excess molar volumes ( $V_m^E$ ) and deviations in viscosity  $\delta\eta$  for the mixtures were calculated from the experimental data and fitted to the Redlich–Kister equation, and the regression coefficients and the standard deviations of the fits were given. The viscosity data were correlated with several semi-empirical equations, and the double-parameter McAllister equation gave satisfactory results. Similar experiments were conducted with mixtures of *exo*-tetrahydrodicyclopentadiene with *n*-butanol and *exo*-tetrahydrodicyclopentadiene with *n*-pentanol [100]. Similar experiments were conducted with mixtures of *exo*-tetrahydrodicyclopentadiene with methyl *tert*-butyl ether or ethyl *tert*-butyl ether [101]. The excess molar volumes were negative over the entire range of composition.

Bubble-point vapor pressures and densities for the binary mixtures of propylene glycol monomethyl ether (PGME) and *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane (JP-10) were measured over the whole composition range [102]. The Antoine equation was fitted to the experimental vapor pressure data and the parameters were calculated. The excess molar volumes for the mixtures were calculated from the density data and were negative. The flash points of the binary mixtures of PGME and JP-10 were measured by a closed-

cup flash point analyzer and predicted from vapor pressures using Wilson and the regular solution models. It was found that PGME can effectively adjust the volatility and flash point of hydrocarbon fuels.

The thermal decomposition of JP-10, *iso*-octane and their mixtures was examined in a stainless steel tubular reactor at temperatures from 883 to 963 K [103]. The conversions of components, and the yields of gas and liquid products for each sample were determined in detail. The addition of *iso*-octane can promote the decomposition of JP-10. One possible mechanism has been proposed to demonstrate the initiation effect of *iso*-octane on the decomposition of JP-10. For the possible pathways, the rate constants of the H-abstraction reactions between the alkyl radicals obtained from C—C bond fission of *iso*-octane and the H atoms of JP-10 were calculated using density functional theory (DFT). Combining the quantum calculations and experimental observations, the formation of some decomposition products in the JP-10/*iso*-octane mixtures can be predicted.

## 7.4 Chemical Properties of JP-10

The chemical gross formula for THDCPD, the main ingredient of JP-10, is  $C_{10}H_{16}$  with 11.84 mass-% hydrogen and a molecular mass of 136.24 g/mol. THDCPD is an isomer of adamantane, limonene, pinene, and camphene.

### 7.4.1 Composition of JP-10

The main ingredient of JP-10 is *exo*-tetrahydrodicyclopentadiene (*exo*-THDCPD), also described as tricyclo[5.2.1.0<sup>2,6</sup>]decane. The properties of THDCPD as a pure compounds are described in chapter “Cycloaliphatic Hydrocarbons.” JP-10 may contain 90–110 ppm (by mass) of an antioxidant. JP-10 may contain a 0.10–0.15 vol.-% of a fuel system icing inhibitor (FSII). JP-10 is not a complex mixture but rather a simple fluid where the major “impurity” is typically the *endo* isomer.

A sample of JP-10 analyzed at NIST by GC-MS contained 1% adamantane and 2.5% of the *endo* isomer of tetrahydrodicyclopentadiene which eluted after the main peak of *exo*-tetrahydrodicyclopentadiene [85]. In addition, there were several peaks of trace contaminants eluting ahead of *exo*-tetrahydrodicyclopentadiene, the main peak in this category was decahydronaphthalene (decalin). Other trace contaminants included 2-methyl-bicyclo[3.2.1]octane, 2-ethyl-bicyclo[2.2.1]heptane, *endo*-2,2,3-trimethyl-bicyclo[2.2.1]heptane, *cis*-1methyl-4-(1-methylethenyl)cyclohexane and 2,6-dimethyl-bicyclo[3.2.1]octane.

### 7.4.2 Specification Requirements for JP-10

Specification requirements for JP-10 are listed in MIL-DTL-87107E [82].

#### 7.4.2.1 Antioxidants

The following active inhibitors shall be blended separately or in combination into the fuel in total concentration of 90 parts per million (minimum) to 110 parts per million (maximum), by weight, not including weight of solvent, in order to prevent the formation of polymeric oxidation products:

- a. 2,6-*tert*-butyl-4-methylphenol
- b. 6-*tert*-butyl-2,4-dimethylphenol
- c. 2,6-di-*tert*-butylphenol

#### 7.4.2.2 Fuel System Icing Inhibitor

Fuel system icing inhibitor (FSII) shall only be used at the request of the user. When requested by the user, the FSII shall conform to MIL-DTL-85470. The requirement for adding fuel system icing inhibitor to JP-10 was eliminated during revision D of MIL-DTL-87107D.

#### 7.4.3 Thermal Decomposition of JP-10

This section overlaps significantly with chapter “Cycloaliphatic Hydrocarbons” about the thermal decomposition of *exo*-tetrahydrodicyclopentadiene (THDCPD). Most investigators made no distinction between JP-10 and pure THDCPD when actually JP-10 may contain additives that influence its thermal decomposition and autoxidation behavior.

The thermal decomposition of JP-10 has been thoroughly investigated. The literature references to numerous publications on experimental studies of JP-10 decomposition are discussed here in chronological order. There is also a section on theoretical studies on JP-10 decomposition (Section 7.4.3.3).

Establishment of an accurate kinetic mechanism for JP-10 pyrolysis and oxidation would require identification of the initial products of JP-10 thermal decomposition. A high-speed UV absorption kinetic spectrograph can be used with a tube to rapidly acquire spectra to measure and identify these initial products at combustion temperatures [104]. Using this kinetic spectrograph, the high-temperature UV absorption spectra for a variety of hydrocarbon species related to the decomposition of JP-10 have been measured. These species included benzene, cyclopentene, propene, ethylene, 1,3-butadiene, cyclopentadiene, and undecomposed JP-10. Few of these spectra had been previously measured at high temperature. By comparison of these spectra to the absorption spectrum of JP-10 decomposition products, evidence of cyclopentene as an initial decomposition product with near unity yield was found.

The thermal decomposition of JP-10 at 623–698 K (350–425 °C) was studied by enclosing samples in CRES-316L stainless steel bomblets (“cells”) consisting of 6.4 cm lengths of high pressure tubing (0.64 cm external diameter, 0.18 cm internal

diameter) that were sealed on one end with a stainless steel plug welded by a clean tungsten-inert-gas (TIG) process [85]. Each cell was connected to a high-pressure valve at the other end. Each cell and valve was capable of withstanding a pressure in excess of 105 MPa at the desired temperature. The cells were maintained at the reaction temperature for a specified period of time ranging from 4 min to 20 h. After the desired time period, the cells were removed from the thermal block and quenched in water at room temperature. The thermally stressed JP-10 was then recovered from the cells and analyzed by GC-MS. The early eluting pyrolysis products were *n*-propane, *n*-butane, cyclopentane, methyl cyclopentane, 1-methyl cyclopentene, benzene, ethyl cyclopentane, ethylidene cyclopentane, toluene, *n*-propyl cyclopentane, *cis*-bicyclo[3.3.0]oct-2-ene, ethyl benzene, *o*-xylene, octahydropentylene, and 3-methyl cyclooctane. The thermal decomposition reaction rate constants were 648 K (375 °C)  $0.00111 \text{ min}^{-1}$ , 673 K (400 °C)  $0.00437 \text{ min}^{-1}$ , 698 K (425 °C)  $0.01518 \text{ min}^{-1}$ .

The product distribution and kinetics of thermal cracking of JP-10 were investigated in an annular tubular reactor at atmospheric pressure in the temperature range of 903–968 K [105]. No inerts were added as diluents to the feed stream entering the reactor. The major decomposition products were methane, ethylene, propylene, cyclopentene, cyclopentadiene, benzene, and toluene. The pre-exponential factor, activation energy, and overall reaction order for thermal cracking of JP-10 were determined by non-linear regression analysis to be  $2.4 \times 10^{13} (\text{m}^3/\text{mol})^{0.1} \text{ s}^{-1}$ , 256.2 kJ/mol, and 1.1, respectively.

The decomposition of JP-10 was studied in a small flow tube pyrolysis reactor over the temperature range up to 1700 K with reactor dwell times on the millisecond time scale [106]. For comparison, the decomposition behavior of cyclopentadiene, dicyclopentadiene, and benzene was studied under identical conditions. Products of pyrolysis were identified by chemical ionization and electron impact ionization mass spectrometry. On the experimental time scale, JP-10 began to decompose above 900 K and was completely decomposed by the time 1300 K was reached. In the initial decomposition, the principal products were cyclopentadiene, benzene, propyne, and  $\text{C}_4\text{H}_x$ . At high temperatures, the cyclopentadiene decomposed as well, and the principal species observed were benzene, acetylene, and ethylene. From the combination of electron impact (EI) and chemical ionization (CI) mass spectra, it was confirmed that the  $\text{C}_6$  product observed was benzene, with few if any other  $\text{C}_6\text{H}_x$  products. Similarly, the  $\text{C}_5$  product was cyclopentadiene, with no cyclopentene or other  $\text{C}_5\text{H}_x$  products. The observed product distribution was inconsistent with both equilibrium speciation and predictions of existing JP-10 decomposition kinetic models.

Thermal cracking of JP-10 was studied in a batch reactor at different pressures [107]. The reactor effluent was quenched and collected at room temperature and atmospheric pressure. The gaseous and liquid components were quantitatively determined by GC and GC/MS. The conversion of JP-10 proceeded relatively slow at atmospheric pressure but increased under pressure. With an increase of the pressure,



the relative content of ethene or propene decreased and that of methane, ethane, or propane increased simultaneously. In the liquid products, cyclopentane, cyclopentene, 1,3-cyclopentadiene, and *cis*-bicyclo[3.3.0]oct-2-ene were found to be the major components. Substituted cyclopentene, benzene, toluene, and naphthalene were also observed at high pressures and temperatures. A probable mechanism for the thermal cracking of JP-10 was proposed to explain the product distribution. The process of isomerization might be dominating for liquid product formation during the thermal cracking under elevated pressures.

Molecular dynamics (MD) simulations using the ReaxFF reactive force field method were carried out to investigate the initiation mechanisms and kinetics associated with the pyrolysis of JP-10 (*exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane) [108]. It was found that the primary decomposition reactions involve either (1) dissociation of ethylene from JP-10, resulting in the formation of a C<sub>8</sub> hydrocarbon intermediate, or (2) the production of two C<sub>5</sub> hydrocarbons. ReaxFF MD calculations gave good agreement with experiments for the product distribution as a function of temperature. On the basis of the rate of consumption of JP-10, an activation energy of 244 kJ/mol (58.4 kcal/mol) for the thermal decomposition of this material was calculated, which was consistent with a strain-facilitated C—C bond cleavage mechanism in JP-10. This compared well with the experimental value of 261 kJ/mol (62.4 kcal/mol).

JP-10 pyrolysis was performed in a continuous flow tubular reactor near atmospheric pressure in the temperature range of 930–1080 K, a conversion range of 4–94%, and two dilution levels of 7 and 10 mol-% JP-10 in nitrogen [109]. Identification and quantification of the pyrolysis products of JP-10 were done by online two-dimensional GC with a time-of-flight MS and a flame ionization detector. JP-10 started to react at 930 K and was fully converted by the time it reached 1080 K. Among the more than 70 species up to C<sub>14</sub>H<sub>10</sub> that were identified and quantified, tricyclo[5.2.1.0<sup>2,6</sup>]dec-4-ene was identified for the first time, indicating the importance of bimolecular H-abstraction reactions in the consumption of JP-10. Critical assessment of the experimental data with the JP-10 combustion model developed by Magoon et al. in 2012 [110] showed that the model predictions of JP-10 agreed reasonably well. The new and highly detailed experimental data helped in understanding the thermal decomposition chemistry of JP-10 and can be used to validate future kinetic models of JP-10 pyrolysis.

Shock tube experiments and kinetic modeling efforts on the pyrolysis and combustion of JP-10 were performed at 6–8 atm using 2000 ppm of JP-10 in air over a temperature range of 1000–1600 K for pyrolysis and oxidation equivalence ratios from 0.14 to 1.0 [111]. GC/MS was used to identify and quantify the products within the shocked samples, enabling the tracking of product yield dependence on equivalence ratio as well as identifying several new intermediates that form during JP-10s decomposition. A detailed, comprehensive model of JP-10 combustion and pyrolysis kinetics was constructed with the help of RMG, an open-source Reaction

Mechanism Generation software package. The resulting model, which included 691 species reacting in 15518 reactions, was extensively validated against the shock tube experimental dataset as well as newly published flow tube pyrolysis data from [109, 112]. .. Most of the important rate coefficients were computed using quantum chemistry. The model succeeded in identifying all major pyrolysis and combustion products and captured key trends in the product distribution. Simulated ignition delays agreed within a factor of 4 with most experimental ignition delay data gathered from literature. The presented experimental work and modeling efforts yielded new insights on JP-10s complex decomposition and oxidation chemistry, and identified key pathways towards aromatics formation.

Two sets of experiments were performed to examine the high-temperature pyrolysis of tricyclo[5.2.1.0<sup>2,6</sup>]decane (JP-10) in high-temperature reactors over a temperature range of 1100–1600 K in the Advanced Light Source (ALS), and a temperature range of 927 to 1083 K in the National Synchrotron Radiation Laboratory (NSRL), with residence times of a few tens of microseconds (ALS) to typically 144 ms (NSRL) [113]. The products were identified *in situ* in supersonic molecular beams via single photon vacuum ultraviolet photoionization coupled with mass spectroscopic detection in a reflectron time-of-flight mass spectrometer. These studies were designed to probe the initial (ALS) and also higher order reaction products (NSRL) formed in the decomposition of JP-10, including free radicals and thermally labile closed-shell species. Altogether 43 reaction products were detected and quantified including C<sub>1</sub>–C<sub>4</sub> alkenes, dienes, C<sub>3</sub>–C<sub>4</sub> cumulenes, alkynes, enynes, diynes, cycloalkenes, cyclodienes, aromatic molecules, and most importantly, free radicals such as ethyl, allyl, and methyl produced at shorter residence times. At longer residence times, the predominant fragments were molecular hydrogen, ethylene, propene, cyclopentadiene, cyclopentene, fulvene, and benzene. Accompanied by electronic structure calculations, the initial JP-10 decomposition via C–H bond cleavages resulting in the formation of the initial six C<sub>10</sub>H<sub>15</sub> radicals was found to explain the formation of all products detected in both sets of experiments. These radicals were not stable under the experimental conditions and further decomposed via C–C bond  $\beta$ -scission processes. These pathways resulted in ring opening in the initial tricyclic carbon skeletons of JP-10. Intermediates accessed after the first  $\beta$ -scission can further isomerize or dissociate. Complex PAH products in the NURLS experiment (naphthalene, acenaphthylene, biphenyl) are likely formed via molecular growth reactions at longer residence times.

A multi-wavelength, multi-species laser was used to study the pyrolysis of JP-10 fuel [114]. Increasingly sophisticated multi-wavelength approaches were used to measure the species resulting from JP-10 pyrolysis in a shock tube at 2.7 atm near 1330 K. Laser absorption measurements in the far-IR region produced species time histories for ethylene and cyclopentadiene. Measurements of methane time histories were made in the mid-IR region.

Cetyl-hyperbranched polyethyleneimine (CHPEI) synthesized from the modification of hyperbranched polyethyleneimine (HPEI) with a lipophilic alkyl chain was used as a novel macroinitiator to accelerate the thermal cracking of hydrocarbon fuels and improve the cooling capacity for aircraft heat exchangers [115]. The pyrolysis performances under supercritical conditions (4.0 MPa and 873–973 K = 600–700 °C) of JP-10 with CHPEI and the monomer triethylamine were compared in an electrically heated alloy tube. Both types of initiators with C–N bonds can promote the thermal cracking of JP-10, while CHPEI with a large molecular weight showed a crack-promoting effect similar to that of triethylamine with adding only one-tenth of the amount of the latter. As a typical example, the addition of 0.20 mass-% CHPEI increased the conversion rate of JP-10 from 16.4 to 33.9%, and the corresponding heat sink was improved from 1.96 to 2.18 MJ/kg at 948 K (675 °C). On the basis of investigations on the intermediate species from different decomposition pathways of JP-10, it was shown that CHPEI accelerates the thermal cracking of JP-10 by generating free radicals to participate in the H-abstraction reaction of JP-10.

#### 7.4.3.1 Catalyzed Decomposition of JP-10

Catalytic cracking of JP-10 and other hydrocarbons can lower the operating temperature of endothermic cooling jackets on hypersonic missiles and create more readily combustible fuel mixtures. Catalytic cracking of JP-10 is an important technology to improve its cooling or heat sink capacity. The following references to catalytic cracking of JP-10 are arranged in chronological order.

The decomposition of JP-10 through thermal and catalytic cracking at elevated temperatures using a bench-top reactor system with industrial zeolite catalysts was studied in a system that had the capability to vaporize liquid fuel at precise flowrates while maintaining the flow path at elevated temperatures and pressures for extended periods of time [116, 117]. A gas chromatograph with a capillary column and flame ionization detector, connected to the reactor output, was used to analyze the reaction products. The conversion rate and product compositions were determined as functions of the fuel metering rate, reactor temperature, system backpressure, and zeolite type. An additional study was carried out to evaluate the feasibility of using pre-mixed rich combustion to partially oxidize JP-10. A mixture of partially oxidized products was initially obtained by rich combustion in air/JP-10 mixtures for equivalence ratios between 1 and 5. Following the first burn, air was added to the products, creating an equivalent stoichiometric mixture. A second burn was then carried out. Pressure histories and schlieren video images were recorded for both burns. The results were analyzed by comparing the peak and final pressures to computed thermodynamic predictions.

Catalytic pre-cracking of JP-10 could provide a more easily detonated mixture of light olefin products for pulse detonation engines. A mixture of mostly light hydrocarbons has the added benefit of being less prone to coking than a product mixture

heavy in aromatics. Several heterogeneous catalytic cracking tests of JP-10 have been done using a benchtop tubular reactor and the products were analyzed with GC/MS and GC [118]. Two forms of nanocrystalline zeolites and three forms of silico-alumino-phosphates successfully catalyzed the thermal cracking of JP-10. Both zeolite catalysts converted over 90% of JP-10 within a ~3-s residence time into a mixture of hydrocarbon products consisting mainly of  $C_4$  and lower chain hydrocarbons ( $C_3$  to  $C_1$ ).

Thermal breakdown and oxidation of JP-10 in the presence of nanoparticulate  $CeO_2$  and  $Fe_2O_3$  was studied in a small alumina flow-tube reactor with dwell time durations around 1 ms [119]. Decomposition products were analyzed by an *in situ* mass spectrometer. In the absence of any oxidizer, JP-10 pyrolyzed at temperatures above ~900 K to a variety of hydrocarbon fragments. In the absence of  $O_2$ , both  $CeO_2$  and  $Fe_2O_3$  oxidized JP-10 efficiently, with decomposition onset temperatures up to 300 K lower than in a clean alumina flow tube under identical flow conditions and substantial conversion to products such as water,  $CO_2$ , CO, and formaldehyde. Under such non-catalytic conditions, the  $CeO_2$  or  $Fe_2O_3$  was reduced and deactivated by the reaction with JP-10. Decomposition of JP-10 in the presence of stoichiometric amounts of  $O_2$  was also studied, with and without  $CeO_2$  present. In absence of  $CeO_2$ , some oxidation products were observed; however, the rate-limiting step appeared to be pyrolysis of JP-10, and pyrolysis products dominated for temperatures up to 1200 K. When both  $O_2$  and  $CeO_2$  were present, oxidation was clearly catalytic, i.e., oxidation was initiated by the reaction of JP-10 with  $CeO_2$ , which is then reoxidized by  $O_2$ .

JP-10 has significant sensible heat sink capacities and may undergo endothermic chemical cracking for hypersonic aircraft applications without the problems associated with other endothermic fuels. Chemical initiators may accelerate the rate of cracking reactions and reduce the required temperatures in a hypersonic aircraft heat exchanger/reactor. On the other hand, with the addition of an initiator some other basic properties of JP-10 may change, such as volatility, which is directly related with ignition performance and combustion problems. Tributylamine (TBA) can be used as an effective initiator. TBA and JP-10 blended fuel were evaluated as a potential fuel for hypersonic aircraft [120]. The bubble-point vapor pressures and equilibrium temperatures for mixtures of JP-10 and TBA with different mass fractions were measured by comparative ebulliometry with inclined ebulliometers. Vapor pressures and equilibrium temperatures were correlated by Antoine's equation with satisfactory precision. Bubble-point lines of pressure versus composition at different temperatures and temperature versus composition at different pressures were obtained. The mixtures exhibited positive deviations from Raoult's law. It was shown that the addition of TBA does not have a distinct effect on the vapor pressure and the phase equilibrium behavior of JP-10.

Compared to thermal cracking of JP-10, the conversion ratio of catalytic cracking JP-10 over ZSM-5 molecular sieves in the temperature range from 773 to 923 K (500 to 650°C) is substantially enhanced [121]. The predominant products of the catalytic

cracking were methane, ethane, ethylene, propane, propylene, benzene, and benzenoid hydrocarbons. It was found that indene and naphthalene, which have negative effects on the combustion quality, were produced because of a hydrogen transfer reaction at high temperatures. High conversion ratio and low content of aromatics could not be obtained at the same time. A reaction mechanism of the catalytic cracking of JP-10 was proposed based on both the measured product composition and quantum mechanical calculation.

A pseudohomogeneous method of catalytic decomposition of JP-10 was developed using well-dispersed nickel nanoparticles [122]. Compared with thermal decomposition, catalytic reaction of JP-10 on nickel nanoparticles exhibited remarkably enhanced rates of conversion. The content of hydrogen and alkene of catalytic reaction products was higher than that of thermal decomposition at temperatures from 813 to 873 K (540 to 600 °C).

Quasi-homogeneous catalytic cracking of hydrocarbon fuels using dispersible zeolite is an effective way to improve their cooling capacity for future hypersonic aircraft. Hydrocarbon dispersible beta nanozeolites were hydrothermally synthesized [123]. IR and TGA analyses indicated that these zeolites have more organic groups anchored on their surface than other zeolites, leading to a higher external surface area and better dispersibility in JP-10. Experiments with the quasi-homogeneous catalytic cracking of JP-10 were conducted in an electrically heated tube in the laboratory under a pressure of 4 MPa. The heat sink capacity of JP-10 reached 2800 kJ/g at 973 K (700 °C) using 100 ppm zeolite as a quasi-homogeneous additive, achieving high catalytic cracking conversion of 63% and high alkenes selectivity (57% in the gaseous products), compared with both thermal cracking or catalytic cracking of JP-10 with other zeolites. The good catalytic performance may be attributed to the high external surface area and good dispersibility in JP-10.

The catalytic cracking of JP-10 at 773 K (500 °C) with a mass hourly space velocity of  $22.56 \text{ h}^{-1}$  over nanosheets gave a conversion of 45%, which was 77% higher than that obtained over a conventional zeolite catalyst (CZ-25, 25%), and the deactivation rate was relatively low (only two-thirds that of CZ-25) [124]. Characterization of the catalysts using ammonia temperature-programmed desorption measurements and FTIR spectroscopy indicated that the better catalytic performance may be attributed to more Brønsted acid sites on the external surface, which is favorable for the larger molecules (like JP-10), and higher accessibility of acid sites in the micropores of nanosheets due to the shorter diffusion path (less than 2.0 nm). The enhanced diffusion of JP-10 over nanosheets also leads to high olefin yields, and better coking tolerance through prevention of secondary reactions.

The cracking of JP-10 with and without the hydrogen form of Y-type zeolite (H-Y zeolite) as catalysts was determined over a wide range of operating conditions relevant to endothermic fuels using both a fixed bed reactor and a microflow tube reactor [125]. The predominant reaction during supercritical pyrolytic cracking was carbon-carbon

bond cleavage to form the primary products of cyclopentadiene and cyclopentene. In contrast, the predominant reaction during supercritical catalytic cracking was the formation of secondary products such as naphthalene and substituted indenenes from primary products via molecular growth reactions. Turnover frequencies for the cracking of JP-10 over H-Y zeolite under supercritical conditions were obtained and used to determine the apparent activation energy of JP-10 cracking over H-Y ( $186 \pm 9$  kJ/mol). Atmospheric microflow tube reactor results were obtained to better understand the flow residence time and transport effects, and they showed that catalytic cracking slightly decreased the endothermic cooling capacity as compared to pyrolytic cracking at similar levels of conversion. However, at similar levels of conversion, the addition of a catalyst reduced cracking temperatures by 210 K.

Cetyl-hyperbranched polyethyleneimine (CHPEI) synthesized from the modification of hyperbranched polyethyleneimine with a lipophilic alkyl chain was used as a macroinitiator to accelerate the thermal cracking of hydrocarbon fuels and improve the cooling capacity for aircraft heat exchangers [115]. The rate of pyrolysis under supercritical conditions (4.0 MPa, and 873–973 K = 600–700 °C) of JP-10 (*exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane) with CHPEI and the monomer triethylamine were compared in an electrically heated alloy tube. Both types of initiators with C–N bonds can promote the thermal cracking of JP-10, while CHPEI with a large molecular weight showed a similar crack-promoting effect to that of triethylamine with adding only one-tenth of the amount of the latter. As a typical example, the addition of 0.20 mass-% CHPEI increased the conversion rate of JP-10 from 16.4 to 33.9%, and the corresponding heat sink was improved from 1.96 to 2.18 MJ/kg at 948 K (675 °C). CHPEI accelerated the thermal cracking of JP-10 by generating free radicals to participate in the H-abstraction reaction of JP-10.

#### 7.4.3.2 Coke Deposition During JP-10 Decomposition

The fouling of JP-10 on the inner surface of CRES-316L tubes was investigated at wall temperatures from 533 to 623 K (260 to 350 °C) and at 3.84 MPa with a flow rate of 0.5 mL/min for 24 h [126]. The fouling of JP-10 was influenced by wall temperature, fuel temperature, and the type of metal surface. The average values of coke deposits were measured to be between 7.52 and 10.67  $\mu\text{g}/\text{cm}^2$  by a carbon burn-off method, and the maximum values of local coke deposits and average values of coke deposits increased with the wall temperature. At 573–623 K (300–350 °C) the locations of peak deposition shifted upstream as the wall temperature increased. The nature and morphology of deposits were characterized by field emission scanning electron microscopy and temperature programmed oxidation profiles, and the deposits of JP-10 were mainly in the form of amorphous carbon. Structurally more ordered deposits were also found, and it could be caused by the catalysis of iron and nickel in metal surfaces.

Coking of three model compounds for hydrocarbon fuels: *n*-heptane, cyclohexane, and tricyclo[5.2.1.0<sup>2,6</sup>]decane (JP-10), during their thermal cracking processes un-

der supercritical conditions (873 K, 4.1 MPa) was investigated and the compositions of the thermal cracking products were analyzed by GC-MS [127]. The morphology and microstructures of the cokes were characterized by SEM, TEM, DSC, and XRD. The results showed that chemical structures play important roles in the thermal stability and coking property of the fuels. The thermal cracking conversion of *n*-heptane was the highest, and the coke yield of JP-10 was highest under the same conditions. It was observed that the morphologies of the cokes produced from the thermal cracking of three fuels were quite different. Cokes from *n*-heptane, cyclohexane, and JP-10 were in the forms of carbon nanofilaments, carbon nanotubes, and irregular carbon particles, respectively.

#### 7.4.3.3 Computational Chemistry Studies of JP-10 Decomposition

Computational chemistry with quantum chemical calculations was used to identify the weakest chemical bonds in the *exo*-tetrahydrodicyclopentadiene (JP-10) molecule where bond breakage was most likely to occur first on heating. Density functional theory (DFT) calculations have been carried out to investigate the thermal cracking pathways of JP-10 [128]. Several thermal cracking mechanisms were proposed, as reported previously [107]. Using DFT calculations, the potential energy profiles of the possible thermal cracking pathways for all of the diradicals obtained from homolytic C—C bond cleavage of JP-10 were derived. The predicted products of the different thermal cracking pathways were in good agreement with previous experimental observations.

A detailed kinetic model for the thermal decomposition of JP-10 was constructed using a combination of automated mechanism generation techniques and *ab initio* calculations [112]. Rate coefficients for important unimolecular initiation routes of *exo*-THDCPD were calculated using the multi-reference method CAS-PT2, while rate coefficients for the various primary decompositions of the *exo*-THDCPD-derived monoradicals were obtained using CBS-QB3. Rate-of-production analysis showed the importance of four dominating JP-10 decomposition channels. The model predictions agreed well with five independent experimental data sets for JP-10 pyrolysis that covered a wide range of operating conditions ( $T = 300 - 1500$  K,  $P = 300$  Pa to  $1.7 \times 10^5$  Pa, dilution = 0.7–100 mol-% JP-10, conversion = 0–100%) without any adjustment of the model parameters. A significant part of the model comprised secondary conversion routes to aromatic and polyaromatic hydrocarbons and could, thus, be used to assess the tendency for deposit formation in fuel-rich zones of endothermic fuel applications.

The hybrid chemistry (HyChem) approach has been proposed previously for combustion chemistry modeling of real, liquid fuels of a distillate origin. The applicability of the HyChem approach was tested for single-component fuels using JP10 as the model fuel [129]. The method remained the same: an experimentally constrained, lumped single-fuel model describing the kinetics of fuel pyrolysis was combined with a detailed foundational fuel chemistry model. Due to the multi-ring molecular structure of JP10, the pyrolysis products were found to be somewhat different from those

of conventional jet fuels. The lumped reactions were therefore modified to accommodate the fuel-specific pyrolysis products. The resulting model showed generally good agreement with experimental data, which suggested that the HyChem approach is also applicable for developing combustion reaction kinetic models for single-component fuels.

Theoretical calculations of the rate constants and product branching ratios in the pyrolysis of *exo*-tetrahydrodicyclopentadiene (JP-10) and its initial decomposition products at combustion-relevant pressures and temperatures were performed and compared to the experimental results from the reported molecular beam photoionization mass spectrometry study of the pyrolysis of JP-10 [113, 130]. The results allowed a quantitative assessment of the decomposition mechanisms of JP-10 by a direct comparison with the nascent product distribution, including radicals and thermally labile closed-shell species, detected in the short-residence-time molecular beam photoionization mass spectrometry experiment. In accord with the experimental data, the major products predicted by the theoretical modeling included methyl radical ( $\bullet\text{CH}_3$ ), acetylene ( $\text{C}_2\text{H}_2$ ), vinyl radical ( $\bullet\text{C}_2\text{H}_3$ ), ethyl radical ( $\bullet\text{C}_2\text{H}_5$ ), ethylene ( $\text{C}_2\text{H}_4$ ), allyl radical ( $\bullet\text{C}_3\text{H}_5$ ), 1,3-butadiene ( $\text{C}_4\text{H}_6$ ), cyclopentadienyl radical ( $\bullet\text{C}_5\text{H}_5$ ), cyclopentadiene ( $\text{C}_5\text{H}_6$ ), cyclopentenyl radical ( $\bullet\text{C}_5\text{H}_7$ ), cyclopentene ( $\text{C}_5\text{H}_8$ ), fulvene ( $\text{C}_6\text{H}_6$ ), benzene ( $\text{C}_6\text{H}_6$ ), toluene ( $\text{C}_7\text{H}_8$ ), and 5-methylene-1,3-cyclohexadiene ( $\text{C}_7\text{H}_8$ ). Ethylene, allyl radical, cyclopentadiene, and cyclopentenyl radical were significant products at all combustion-relevant conditions, whereas the relative yields of the other products depended on temperature. The most significant temperature trends predicted were increasing yields of the  $\text{C}_2$  and  $\text{C}_4$  species and decreasing yields of the  $\text{C}_1$ ,  $\text{C}_6$ , and  $\text{C}_7$  groups with increasing temperature. The calculated pressure effect on the rate constant for the decomposition of JP-10 via initial C—H bond cleavages became significant at temperatures above 1500 K. The initially produced radicals will react away to form closed-shell molecules, such as ethylene, propene, cyclopentadiene, cyclopentene, fulvene, and benzene, which were observed as the predominant fragments in the long-residence-time experiment. The calculated rate constants and product branching ratios should prove useful to improve the existing kinetic models for the JP-10 pyrolysis.

Functionalized graphene sheets (FGS) have proven to be an effective nanoparticle additive to enhance decomposition of jet fuels. The reactive force field (ReaxFF) molecular dynamics (MD) simulation was used to investigate the initiation mechanisms of JP-10 pyrolysis and oxidation with FGS in comparison with normal JP-10 reactions [131]. ReaxFF calculations were performed to study the transition state and energy barrier for key initiation reactions in order to reveal the catalytic effect of FGS on JP-10 pyrolysis and oxidation. The results showed that both pyrolysis and oxidation of JP-10 can be advanced and enhanced in the presence of FGS, leading to earlier decomposition of JP-10 at a lower temperature and a faster reaction rate. It was found that the OH functional group on the FGS not only advanced the initiation of JP-10 but also



participated in various intermediate reactions to further enhance the pyrolysis and oxidation of JP-10. The dehydrogenation of JP-10 without FGS was only observed at very high temperatures. Deeper insight into the enhancement resulting from the FGS was provided through the analysis of the results of transition state and energy barrier for key initiation reactions. It was found that JP-10 decomposition initiated by OH or H on the FGS occurred at a lower energy barrier than unimolecular decomposition or through reaction with O<sub>2</sub>, thereby changing and enhancing the JP-10 initiation.

#### 7.4.4 Ignition of JP-10 in Air

Although the combustion of JP-10 in air is planned to be discussed in a future set of the *Encyclopedia of Rocket Propellants*, some chemical reactions that may lead to ignition of JP-10 vapors in air, an important step in the use of JP-10 in propulsion systems, are already discussed here. Ignition delay times and OH concentration time histories for JP-10/O<sub>2</sub>/Ar mixtures have been measured behind reflected shock waves over the temperature range of 1200–1700 K, pressure range of 1–9 atm, fuel concentrations of 0.2 and 0.4%, and stoichiometric ratios of  $\Phi = 0.5, 1.0$  and 2.0 [132]. Fuel concentrations were measured in the shock tube using laser absorption at 3.39  $\mu\text{m}$ , ignition times were determined using CH emission, and OH concentration histories were inferred from narrow-linewidth continuous wave (CW) laser absorption measurements near 306 nm. The laser measurements also revealed evidence for a long-lived JP-10 decomposition product with strong absorption near 306 nm. A kinetic model for JP-10 oxidation was developed using global decomposition reactions proposed by others. This modeling gave good agreement with the ignition times at higher pressures, and sensitivity studies using this model indicated the possible important role of C<sub>2</sub> chemistry in JP-10 decomposition.

A pressure-dependent, detailed chemical kinetic mechanism that describes the combustion of JP-10 was developed through the use of dynamic trajectory analysis to identify potential reaction pathways, *ab initio* chemistry calculations to determine thermochemical properties and kinetic rates, and *ab initio* chemistry and group additivity theory to calculate transport properties [133]. A comparison of predicted and measured values for ignition delay and species profiles from the literature showed good agreement. In addition, new data for species profiles were developed.

#### 7.4.5 Electron Impact Ionization of JP-10

The ionization of JP-10 (C<sub>10</sub>H<sub>16</sub>, *exo*-tricyclo[5.2.1.0<sup>2,6</sup>]decane) by electron impact has been studied using Fourier transform mass spectrometry [134]. This is similar to what happens to JP-10 vapors in the inlet section of a mass spectrometer. Absolute total and partial ionization cross-sections have been measured as functions of the electron energy in the range of 10–200 eV. The major channel of parent ion fragmentation at low energies (<27 eV) produced C<sub>9</sub>H<sub>13</sub><sup>+</sup>, and at higher energies, C<sub>5</sub>H<sub>7</sub><sup>+</sup>. Several possible fragmentation mechanisms were proposed.

The plasma cracking of *exo*-tetrahydrodicyclopentadiene (JP-10) ( $C_{10}H_{16}$ ) was investigated using a quadrupole mass spectrometer [135, 136]. The relative densities of the JP-10 molecule and its principal decomposition products, including  $H_2$ , were determined for varying radiofrequency (rf) powers in the range of 3–30 W, using the measured ion intensities combined with ionization cross section data from the literature. The extent of the cracking of JP-10 and the formation of  $H_2$  as functions of the intensity of the applied rf power were discussed.

#### 7.4.6 Analysis of JP-10

The components of four samples of JP-10 were analyzed by GC/MS [137]. The purity of JP-10 fuels was measured with an external standard method. Results showed that JP-10 contains not only the main component *exo*-tetrahydrodicyclopentadiene, but also decahydronaphthalene, *endo*-tetrahydrodicyclopentadiene, adamantane, and their methylated homologues. The suitable concentration range for the external standard method to measure the purity of JP-10 is 0.5–20 mg/mL. This method is supposed to be reliable, accurate, and can be used for determining the purity of JP-10.

### 7.5 Materials Compatibility of JP-10

The fuel system icing inhibitor (FSII) in JP-10 fuel was found to corrode aluminum components in missile fuel systems during long-term storage under an anhydrous nitrogen atmosphere [138–140]. Previous investigations into fuel-system corrosion had used extreme conditions such as high FSII concentration or temperature to accelerate corrosion. Electrochemical impedance spectroscopy (EIS) was used to determine the corrosion rate on Al 2024, Al 6061, Al A357, and Al 7075 as a function of additive type and concentration under conditions similar to those found in actual use.

To explore the possibility of using advanced surface engineering techniques (ASETs) to solve the friction and wear problems caused by the poor lubricity of pure, low-viscosity aviation fuel JP-10, polished M50 bearing steel sample surfaces were treated with nitrogen ion implantation, TiAlN coating deposition, and Ta coating deposition followed by high current pulsed electron beam (HCPEB) irradiation, respectively [141]. Boundary tribological behaviors of these ASET-treated and untreated steel samples sliding in pure JP-10 against a  $Si_3N_4$  ball (ball-on-disc model) were investigated under 2.0 GPa in the atmosphere and the friction tests indicated that significant reductions, although to different extents, in friction and wear were achieved by these modified surfaces. Simultaneously considering the tribological performance and potential pollution caused by wear debris to JP-10, HCPEB-treated Ta coating with a lowest average friction coefficient of 0.11 and a specific wear rate of around zero was the best to offset the inadequate lubricity of JP-10 by itself under laboratory conditions.

## 7.6 Toxicity of JP-10

Pregnant ICR mice were given oral doses of 0.2, 0.4, 0.6, and 0.8 mL/kg of JP-10 on days 6 through 9 of gestation [142]. No significant differences were found between controls and experimental groups in mean implants/female, mean viable fetuses/litter, mean resorptions/litter, frequency of resorptions, frequency of soft tissue anomalies, and frequency of skeletal anomalies. Mean fetal weight was significantly heavier in the 0.2 and 0.4 mL/kg groups. This effect is difficult to explain when the 0.6 and 0.8 mL/kg groups showed no increase in fetal weight.

The effect of JP-10, the major component of cruise missile fuel, on the development of embryonic rats was evaluated. Pregnant females were exposed via inhalation to 600 ppm or orally dosed with 250, 500, or 1000 mg JP-10/kg on gestation days 6–15 [143, 144]. In a separate experiment, both fetal and maternal blood levels of JP-10 were monitored during an inhalation exposure. Moderate signs of toxicity including tremors and convulsions were observed in the pregnant females receiving the higher doses. JP-10 was not selectively embryotoxic in the rat when administered by gavage or inhalation. Blood levels of JP-10 in the fetuses was about one half the maternal blood levels at steady state.

## 7.7 Fire Hazard Properties of JP-10

### 7.7.1 Limits of Flammability of JP-10

The flammability limits of air/JP-10 vapor mixtures were near those of gaseous air/*n*-decane mixtures. However, the maximum explosion pressure and the maximum rate of pressure rise of air/JP-10 vapor mixtures were much higher than those of gaseous air/*n*-decane mixtures.

### 7.7.2 Autoignition Temperature of JP-10 in Air

The autoignition temperature of JP-10 in air is 518 K = 474 °F [6].

### 7.7.3 Flash Point of JP-10

The TAG flash point of JP-10 is 323.6 K (50.5 °C). The Military Specification MIL-DTL-87107E requires that the flash point of JP-10 must be above 327.5 K = 54.4 °C = 130 °F.

### 7.7.4 Explosion of Air/JP-10 Vapor Mixtures

Additional discussion of explosions of air/JP-10 vapor mixtures will be provided in a future set of *Encyclopedia of Rocket Propellants*. An examination of the flammability of JP-10 included maximum explosion pressure, maximum rate of pressure rise,

and limiting flammability concentrations [145]. Through a series of experiments, the influences of the concentration of gaseous JP-10 in air on the explosion pressure and on the rate of explosion pressure rise have been analyzed. The explosion pressure of gaseous air/JP-10 mixtures reached their highest values at a concentration of 1.88%. The variation trends in the explosion pressure and the rate of pressure rise of gaseous air/JP-10 mixtures with vol.-% appeared similar. When the vol.-% of gaseous JP-10 was in the range 0.5–1.8%, the explosion pressure and the rate of pressure rise for gaseous air/JP-10 mixtures increased with the vol.-%, while in the range 1.8–5% these parameters decreased with the vol.-%. The flammability limits of air/JP-10 vapor mixtures were near those of gaseous air/*n*-decane mixtures. However, the maximum explosion pressure and the maximum rate of pressure rise of air/JP-10 vapor mixtures were much higher than those of gaseous air/*n*-decane mixtures.

### 7.7.5 Explosion of Air/JP-10 Aerosol Mixtures

The flammable range for JP-10 vapor in air is 0.7–5.3 vol.-% at standard temperature and pressure (STP), but the flammable range of JP-10 aerosol sprays in air is much wider. The explosion parameters of vapor/liquid two-phase JP-10/air mixtures were determined in a 20-L cylindrical vessel for two sets of JP-10/air mixtures at different fuel concentrations, with mean aerosol droplet diameters of 20 and 35  $\mu\text{m}$  [146]. The explosion temperature, pressure and lower flammability limits were measured and analyzed. The peak overpressures,  $\sim 0.85$  MPa, for 20 or 35  $\mu\text{m}$  diameter droplets were very similar and occurred at a vapor equivalent of 1.6 vol.-% ( $600 \text{ g/m}^3$ ) JP-10, just a little on the fuel-rich side of the stoichiometric composition (1.48 vol.-%), within 100 ms from ignition. The pressure rise rate for 35- $\mu\text{m}$  droplets maxed at 90 MPa/s. This information is of interest for the design of air/JP-10 pulse detonation engines.

## 7.8 Fuel Mixtures with JP-10

Additions of cycloalkanes enhance the endothermic fuel capabilities of JP-10 [147]. The bubble-point vapor pressure, density, and viscosity for binary mixtures of tricyclo[5.2.1.0<sup>2,6</sup>]decane (JP-10) with methylcyclohexane (MCH) were measured at several temperatures [148]. The correlation between vapor pressures and equilibrium temperatures of each mixture was performed and the Antoine equation parameters were given correspondingly. The experimental vapor liquid equilibrium data were correlated with the Wilson model. From the density and viscosity data, excess volume and viscosity deviation,  $\Delta\eta$ , for the binary mixtures were calculated and fitted with the Redlich–Kister equation. The viscosities were correlated with several semi-empirical equations. The excess molar volumes and the viscosity deviations were negative over the entire composition range.

Densities, viscosities, and refractive indices were measured for the binary system of tricyclo[5.2.1.0<sup>2,6</sup>]decane with cyclohexane, methylcyclohexane, ethylcyclohexane, butylcyclohexane, or 1,2,4-trimethylcyclohexane at temperatures from 293 to 318 K and at atmospheric pressure with  $p = 0.1$  MPa [149]. The excess molar volumes ( $V_mE$ ), the viscosity deviations ( $\Delta\eta$ ), and the refractive index deviations ( $\Delta nD$ ) were then calculated. The changes of  $V_mE$  and  $\Delta\eta$  with the composition were fitted to the Redlich–Kister equation. The values of density, viscosity, and refractive index increase continuously with the increase of mol fraction of tricyclo[5.2.1.0<sup>2,6</sup>]decane and decrease with the rise of temperature. The  $V_mE$  and  $\Delta\eta$  are all negative over the whole composition range for these five binary systems which is typical for molecular interactions in binary systems.

The fundamental physical properties including density, viscosity, refractive index, and relative permittivity have been measured for binary mixtures of *exo*-tetrahydrodicyclopentadiene (JP-10) with four octane isomers (*n*-octane, 3-methylheptane, 2,4-dimethylhexane and 2,2,4-trimethylpentane) over the whole composition range 293–313 K and at atmospheric pressure  $p = 0.1$  MPa [150]. The values of excess molar volume, viscosity deviation ( $\Delta\eta$ ), refractive index deviation ( $\Delta nD$ ), and relative permittivity deviation ( $\Delta\epsilon_r$ ) were then calculated. All of the values of  $V_mE$  and  $\Delta\eta$  were observed to be negative, while those of  $\Delta nD$  and  $\Delta\epsilon_r$  were close to zero. The negative values of  $V_mE$  and  $\Delta\eta$  are conducive to high-density and low flow-resistance of fuels, which is favorable for advanced hydrocarbon fuels.

Density, viscosity, and vapor pressure of binary mixtures of *exo*-tetrahydrodicyclopentadiene (JP-10) with isopropyl ether were measured between 293 and 313 K over the entire composition range [151]. Densities and viscosities of a 50/50 by volume mixture of JP-10 and a turpentine dimer fuel have been measured in the compressed-liquid state from 270 to 470 K, 0.5 to 45 MPa, and at ambient pressure from 263.15 to 373.15 K [152]. Ambient pressure dynamic viscosity was measured over the same temperature range. Results of the mixture measurements were compared with previously measured densities of the individual components, turpentine dimer fuel and JP-10.

The heat of combustion of JP-10 or quadricyclane can be increased by dissolving acetylene in the fuel. The solubility of acetylene in JP-10 or quadricyclane can be enhanced by adding triethylamine [153]. The solubility of acetylene in JP-10 at 298 K and pressures up to 200 kPa was studied. The molar concentration of acetylene in JP-10 at a pressure of 100 kPa reached 0.60 mol-% prior to addition of the amine. The solubility of acetylene in the presence of triethylamine showed that such additives could increase significantly the solubility of acetylene in the fuel.

## 7.9 Applications of JP-10

### 7.9.1 Gelled JP-10

Like all kerosenes, JP-10 can be gelled and its heat of combustion can be increased by suspending metal powders in the gel. The high viscosity of the gel will prevent the heavier metal particles from settling during storage or high-g acceleration.

Surface-modified boron nanoparticles (NPs) were added to jet fuel JP-10 with tri-octylphosphine oxide as the stabilizer which inhibited particle contact and agglomeration [154]. After 6 weeks, a suspension with 12.7 mass-% boron nanoparticles was still completely dispersed in the fuel. Addition of 12.7 mass-% boron increased the density and volumetric energy from 0.93 g/mL and 39.4 MJ/L to 0.98 g/mL and 43.4 MJ/L, respectively. The suspension flowed freely like liquid fuel and had relatively low viscosity at low temperature.

JP-10 supramolecular gel propellants were prepared by dissolving the low-molecular mass gelator 1,1',1''-[(2,4,6-trioxo-1,3,5-triazinane-1,3,5-triyl)tris-(hexane-6,1-diyl)]tris(3-octadecyl-urea) (HDIT-18) in JP-10 [155]. The critical gelator concentration for JP-10 was as low as 0.0638 mass-%. The JP-10 supramolecular gel propellants exhibited high thermal stability. Scanning electron microscopy (SEM) studies revealed that the gelator molecules self-assembled into 1–3  $\mu\text{m}$  fibers in JP-10. Rheological studies showed that the JP-10 supramolecular gels were thixotropic and shear-thinning (for a shear rate range from 0.3 to 30  $\text{s}^{-1}$ ). The dynamic strain sweep test showed that the critical strain percentage of the gel materials was 1%.

### 7.9.2 Metallized JP-10

Nanofluid fuels were examined through theoretical and experimental methods. Theoretical calculations showed that aluminum is very effective in improving the volumetric specific impulse and density of JP-10 [156]. A surface-modification method was developed to stabilize Al nanoparticles in fuel, and oleic acid was the most effective coating agent. The surface modification inhibited the contact and agglomeration of nanoparticles and maintained them stably dispersed in fuel. With the addition of 30% Al, the density and volumetric energy of JP-10 was increased by 20 and 10%, respectively, and the fuel can flow freely. Combustion tests showed that the combustion efficiency of Al nanoparticles was higher than 95%, with density specific impulse of JP-10 being increased by 15% through the addition of 16% Al nanoparticles.

Nanosize aluminum (16 mass-%) was suspended in JP-10 and 2 mass-% of a surfactant was used to reduce the agglomeration of nanoparticles. Combustion of metalized fuel, as well as pure JP-10, was carried out in a small-scale combustor [157]. The oxygen-to-fuel ratios were set at 1.7, 1.8, and 1.9. The effect of water injection during combustion was also tested. The pressures at the combustion chamber and nozzle exit, along with the thrust, were measured during the combustion and intervals of true values of the specific impulse were presented. The results

showed that a 3 to 9% improvement in combustion efficiency was achieved with the JP-10-based slurry when compared to pure JP-10. However, the specific impulse could be increased only when the combustion-induced heat release was improved enough to overcome the two-phase loss. Depositions at different positions were collected after combustion for deep analysis by XRD, TGA, SEM, and laser light scattering. A relatively high oxidation rate of the aluminum was obtained in tests without water injection, and the solid particles were mainly spherical and 100–300 nm in size. In the tests with water injection, stable combustion and increased thrust were achieved, whereas the combustion efficiency and specific impulse were decreased and the size of the particles was increased due to the addition of water.

D-gluconic acetal supramolecular organic gelators can form gels with JP-10 [158]. Rheological measurements showed that G8 gel exhibited good mechanical strength at a concentration of 2 mass-%, while G18 gel had a remarkable yield stress. JP-10 gels showed thixotropy with high viscosity, especially for the G8-based gel, which had an instantaneous recovery ratio. The CGC (critical gelator concentration) of G8 was less than 0.1 mass-%. G18 can gel JP-10 at room temperature, which was the first example of room temperature gel propellant formed by a supramolecular gelator. Nano accelerants (Al, B) can be dispersed into the gel propellant system, which can be stable for months. The presence of 50 nm Al powder in G8-based gels can significantly increase its mechanical strength, yield stress, and viscosity, as well as thixotropy. Addition of nano-aluminum to JP-10 increased the heat of combustion and enhanced the combustion behavior in air [159].

## 8 Commercial Fuel Jet A

Commercial fuel Jet A is rarely used as a rocket propellant. Some of its properties are listed here only for comparison to some of the other kerosene fuels. Jet A specification fuel has been used in the United States since the 1950s, whereas Jet A-1 is the standard specification fuel used in the rest of the world other than the former Soviet Union states where TS-1 is the most common standard. Both Jet A and Jet A-1 have a flash point higher than 311 K (38 °C = 100 °F), with an autoignition temperature of 383 K (210 °C = 410 °F). Jet A is used as the fuel in the South Korean KSLV-II launch vehicle with LOX as the oxidizer.

### 8.1 Physical Properties of Jet A

Although this is primarily a book on rocket propellants, we include jet engine fuels here because in the early years, any kerosene—including blends similar to what is now designated Jet A—was used for rocket engine tests, mostly because it was readily available. There are numerous publications dealing with the properties of kerosene

Jet A fuel. The primary difference between Jet A and Jet A-1 is the lower freezing point of Jet A-1. Jet A freezes at 233 K ( $-40^{\circ}\text{C} = -40^{\circ}\text{F}$ ), whereas Jet A-1 freezes at 226 K ( $-47^{\circ}\text{C} = -53^{\circ}\text{F}$ ). Without going into details, we list a few references here which will be useful to our readers for future study [160]. A synthetic fuel, S-8, similar to JP-8, was derived from the Fischer–Tropsch process. Clearly, rocket propellants are not used as fuels for air-breathing commercial transport planes; however, as there is some overlap in the methods for evaluation of the thermal stability of these fuels that can be applied to both rocket fuels and jet engine fuels, they are included here.

## 8.2 Chemical Properties of Jet A

### 8.2.1 Composition of Jet A

The chemical composition of Jet A is essentially identical with that of JP-8, except that Jet A does not contain any of antioxidant and anticorrosive additives. The primary difference in chemical composition between Jet A and Jet A-1 is the mandatory addition of an anti-static additive to Jet A-1.

### 8.2.2 Surrogate Fuel Mixtures for Jet A

Because of the complexities involved in measuring and modeling the performance and properties of finished fuels, the fuel science community must often use surrogate mixtures as substitutes, especially in the absence of consensus standard mixtures. While surrogate mixtures are often formulated on the basis of the ability of a particular mixture to reproduce a particular property, there is usually a desire to employ surrogate mixtures that are physicochemically authentic. This means that, provided that the primary purpose is satisfied, researchers are inclined to choose mixtures that have physical and chemical properties appropriate to the finished fuel.

Surrogate mixture models were developed to represent the thermophysical properties of two samples of aviation turbine fuel Jet A [161]. One sample was a composite of numerous batches from multiple manufacturers and was considered to be a representative fuel. A second sample, while still meeting the fuel specifications, contained a lower than normal aromatic content and was selected to demonstrate some of the compositional variability seen among different batches of Jet A fuel. A surrogate for each fuel was developed with a procedure that incorporated experimental data for the density, sound speed, viscosity, thermal conductivity, cetane number, and the volatility (as indicated by advanced distillation curves) for samples of the two fuels. The surrogates were simple mixtures containing eight or fewer components, yet they can represent the thermophysical properties of actual real fluids that are very complex mixtures of hundreds of components.

The advanced distillation curve method was used as a means to evaluate the physicochemical authenticity of surrogate mixtures. While the strategy outlined here



can be used for any family of surrogates, it was applied to surrogate mixtures for Jet A/JP-8. Mixtures were divided into two groups: (1) simple surrogate mixtures with up to three components, and (2) complex surrogate mixtures with more than three components [162].

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# Kerosenes

## Introduction

The *Encyclopedia of Liquid Fuels* contains eight chapters dealing with hydrocarbon fuels. The topic of hydrocarbon fuels had to be subdivided into several smaller chapters that were easier to arrange in alphabetical order in five subvolumes of equal size. The titles of the eight hydrocarbon chapters are: “Alkanes,” “Alkenes and Alkynes,” “Aromatic Hydrocarbons,” “Cycloaliphatic Hydrocarbons,” “Hydrocarbons,” “Jet Fuels,” “Kerosenes,” and “Ramjet Fuels.” The current chapter, “Kerosenes,” is an introduction to the chemistry and applications of hydrocarbons with high boiling points.

## 1 Kerosenes

This chapter on kerosenes is closely related to other chapters in the *Encyclopedia of Liquid Fuels*, such as the chapters on hydrocarbons, alkanes, cycloaliphatic hydrocarbons, aromatic hydrocarbons, jet fuels, and ramjet fuels. Various grades of kerosenes have been used for propulsion since petroleum fuels were first discovered. Most of the kerosenes in the early days were of the diesel fuel grade. Eventually, different grades of kerosene for jet fuel became available and many of those were used as rocket propellant fuels as well because they were readily available [1–4]. Efforts are continuing to improve the performance of kerosene fuels [5]. See also Sargent [6] and McCoy [7]. It is sometimes useful to look back at the history of kerosenes as military jet fuels to better understand their limitations and to appreciate the work that has been done to improve them [8, 9]. To some extent the improved kerosenes for rocket engines have benefited from this development, which was predominantly aimed at improving fuels for airbreathing jet engines.

There are many more publications on the properties of kerosenes as aircraft fuels than there are publications on kerosenes as rocket fuels. Literature summaries of the physical properties of kerosenes, regardless of what stimulated their creation in the first place, are useful for both applications and a short list of these publications (some now only of historical value) is offered here [10–15].

Some of these hydrocarbon fuels were also evaluated as fuels for pulse detonation engines or rotating detonation engines, which will be described in future volumes of the *Encyclopedia of Rocket Propellants*, such as *Encyclopedia of Non-Hypergolic Bipropellant Combinations*.

Until the 2010s, it was common practice to design booster stage rocket engines so that they would be used only once and then discarded. One of the limiting issues that prevented the reusability of those liquid oxygen (LOX)/kerosene engines was coke

deposition in the cooling channels of regeneratively cooled engines. Both design changes and strict use of thermally more stable kerosenes have enabled reusable launch vehicles. The three special grades of RP-1 listed in Table 1 were evaluated for use in reusable engines.

**Table 1:** Sulfur content of RP-1 grades

| Total Sulfur (TS) content, ppm | RP-1 Grade     |
|--------------------------------|----------------|
| < 500                          | Standard       |
| < 30                           | TS-30          |
| < 5                            | TS-5           |
| < 0.1                          | UL (Ultra-Low) |

The selection criteria for kerosenes as rocket fuels evolved gradually while a better understanding of the effects of molecular composition on the quality of heat transfer in regeneratively cooled engines developed and methods for the avoidance of coke deposition were found.

In the early days of rocketry, for logistic and economic reasons, it appeared desirable to design large rocket engines to operate on cheap, readily available hydrocarbon fuels without considerations of their source and reproducibility. When this shift in fuel was attempted, serious difficulties were encountered. This led to a considerable effort to improve the propellant performance by various means, including additives to the fuel. The shift to hydrocarbon fuels was accomplished with relatively little difficulty in engines employing liquid oxygen as the oxidizer. The absence of major difficulties at this stage probably inspired a false feeling of confidence that large rocket engines could satisfactorily employ any current specification air-breathing jet engine fuel. Until then, no specification existed for a hydrocarbon fuel specifically for rocket engines. Specification MIL-F-25576A for RP-1 fuel, originally issued 8 May 1956, represented the first concrete result of a joint effort by the Air Research and Development Command and Rocketdyne to arrive at a hydrocarbon fuel composition that would best suit the needs of large rocket engines as opposed to airbreathing jet engines.

The significance of composition and physical properties of blended hydrocarbon fuels on the performance of large rocket engines was investigated early on [16]. Results of a research program conducted at Rocketdyne to study the effects of the systematic variation of the fuel molecular type and molecular weight in bipropellant turbine gas generators and model rocket thrust chambers showed that a high aromatic content is deleterious to the performance of these combustion devices. Bipropellant turbine gas generators operate under very fuel-rich conditions to limit the exhaust gas temperature to the range that the pump turbine blades can tolerate. Soot formation is inevitable under these fuel-rich conditions. A highly naphthenic fuel within

the kerosene boiling range represents the best compromise among satisfactory thrust chamber and gas generator performance and good physical properties. Application of these criteria led to the development of RP-1 rocket fuel and Specification MIL-F-25576A, which was still new in the mid-1950s. In addition to kerosene fuel blends, pure heptane, *iso*-octane, *iso*-pentane, toluene, and methylcyclohexane were tested as model fuel compounds.

From a historical viewpoint it is interesting to learn that the word “kerosene” was once a trademark, registered as a <sup>TM</sup> trademark in 1854, and for several years, only the North American Gas Light Company and the Downer Company were allowed to call their lamp oil “Kerosene<sup>TM</sup>” in the United States [17].

## 2 Physical Properties of Kerosenes

Because the chemical composition of petroleum fractions differs substantially depending on the source of the crude oil, the chemical composition of hydrocarbon fuels is not used as a quality criterion. For each intended application a different set of physical and chemical property specifications has been created that serves for the procurement and the quality control of stored and transported fuels. A summary of physical properties of kerosenes used for air-breathing engines is given in Table 2. Some of these are the numbers contained in fuel specifications and may not necessarily represent average measured properties of currently used fuel blends. Other numbers are the results of field surveys, with numerous samples taken from the flight line.

### 2.1 Density and Coefficient of Thermal Expansion of Kerosenes

Because the chemical composition of kerosenes differs from sample to sample, it is difficult to assemble a list of physical properties for engineering calculations. It has been attempted to establish a correlation of physical properties (examples are coefficient of thermal expansion, thermal conductivity and heat capacity shown below) by normalizing them in relation to the density of the sample, which is easy to determine. As an example of a physical property correlated to the density, Table 3 gives the coefficient of thermal expansion  $\beta = 1/V \, dV/dt$  for four kerosenes of different densities.



Table 2: Summary of physical properties of kerosenes.

| Property                                             | JP-4                               | JP-5                            | JP-7                              | JP-9                              | JP-10                           | RJ-4                            | RJ-5                            | RJ-6                            |
|------------------------------------------------------|------------------------------------|---------------------------------|-----------------------------------|-----------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Specification                                        | MIL-DTL-5624W                      | MIL-DTL-5624W                   | MIL-DTL-38219D                    | P-87107B                          | P-87107B                        | F-82522A                        | Draft                           | Draft                           |
| Molecular formula                                    | C <sub>9.5</sub> H <sub>18.9</sub> | C <sub>12</sub> H <sub>24</sub> | C <sub>12.5</sub> H <sub>26</sub> | C <sub>10.2</sub> H <sub>16</sub> | C <sub>10</sub> H <sub>16</sub> | C <sub>12</sub> H <sub>20</sub> | C <sub>14</sub> H <sub>18</sub> | C <sub>12</sub> H <sub>17</sub> |
| Molecular mass                                       | 133                                | 168                             | 176                               | 138.4                             | 136                             | 164                             | 186                             | 161                             |
| Freezing point, K                                    | <244                               | 224                             | 227                               | <219                              | 183                             | 227                             | 244                             | 219                             |
| Freezing point, °F                                   | <-72                               | -55                             | -50                               | <-65                              | -130                            | -50                             | -20                             | -65                             |
| Boiling range, K                                     | 333–512                            | 455–530                         | 462–524                           | 372–558                           | 455                             | 480–494                         | 533–558                         | 455–558                         |
| Boiling range, °F                                    | 141–463                            | 360–495                         | 373–484                           | 210–545                           | 360                             | 405–430                         | 500–545                         | 360–545                         |
| Viscosity, cSt at 233 K                              | 4.5                                | 17                              | 17                                | 24                                | 19                              | 60                              | 2000                            | 140                             |
| = -40 °F                                             |                                    |                                 |                                   |                                   |                                 |                                 |                                 |                                 |
| Volumetric net heat of combustion, MJ/m <sup>3</sup> | 32900                              | 34800                           | 34700                             | 39700                             | 39600                           | 39600                           | 44900                           | 42400                           |
| Volumetric net heat of combustion, BTU/gallon        | 118000                             | 125000                          | 124600                            | 142500                            | 14200                           | 142000                          | 161900                          | 152000                          |
| Enthalpy of formation, kJ/kg                         | -1903                              | -1719                           | -2079                             | -772                              | -902                            | -982                            | +86                             | -309                            |
| Enthalpy of formation, BTU/lb                        | -818                               | -739                            | -894                              | -332                              | -388                            | -422                            | +37                             | -133                            |
| Auto-ignition temperature, K                         | 502                                | 497                             | 497                               | 523                               | 518                             | 602                             | 507                             | 505                             |
| Auto-ignition temperature, °F                        | 445                                | 435                             | 435                               | 482                               | 474                             | 625                             | 453                             | 450                             |
| Flash point, K                                       | 244                                | 334                             | 338                               | 294                               | 326                             | 344                             | 377                             | 334                             |
| Flash point, °F                                      | -20                                | 142                             | 150                               | 70                                | 128                             | 160                             | 220                             | 142                             |

BTU = British thermal unit  
Data source: [7]

**Table 3:** Coefficient of thermal expansion for four kerosenes of different densities.

| Temperature |       | Density               |                       |                       |                       |
|-------------|-------|-----------------------|-----------------------|-----------------------|-----------------------|
| K           | °C    | g/cm <sup>3</sup>     |                       |                       |                       |
|             |       | 0.78                  | 0.80                  | 0.82                  | 0.84                  |
| 255.3       | -17.8 | $9.05 \times 10^{-4}$ | $8.65 \times 10^{-4}$ | $8.80 \times 10^{-4}$ | $7.96 \times 10^{-4}$ |
| 310.9       | +37.8 | $1.02 \times 10^{-3}$ | $9.60 \times 10^{-4}$ | $9.10 \times 10^{-4}$ | $8.68 \times 10^{-4}$ |
| 366.1       | 93.0  | $1.13 \times 10^{-3}$ | $1.06 \times 10^{-3}$ | $9.94 \times 10^{-4}$ | $9.40 \times 10^{-4}$ |

Data source: [18]

The North American petroleum industry often uses the American Petroleum Institute (API) scale to describe the density of petroleum distillates. The physical density can be converted to degree API by using the following formula:

$$^{\circ}\text{API} = (141.5/\rho \text{ at } 15.6^{\circ}\text{C}) - 131.5$$

where  $^{\circ}\text{API}$  is the degrees on the API scale and  $\rho$  is the density at  $288.7\text{ K} = 15.6^{\circ}\text{C}$  in  $\text{g/cm}^3$ .

## 2.2 Equation of State of Kerosenes

It is difficult to obtain accurate equations of state for kerosenes such as RP-1 or JP-8 because the composition of the samples may vary from case to case. The equations of state of surrogate fuel mixtures with known compositions can be predicted from empirical data bases and theoretical correlations [19]. The NIST ThermoData Engine is a large electronic database containing experimental data with detailed descriptions of relevant metadata that incorporates expert-system software to automatically generate dynamically on-demand equations of state [20]. The resulting equation of state (EOS) formulations for pure chemical compounds are used to develop a surrogate mixture model to represent the volatility behavior, as expressed by the distillation curve, of paraffinic fuels.

## 2.3 Compressibility of Kerosenes

The velocity of sound and the adiabatic compressibility for JP-3 and JP-4 are summarized in Table 4.

**Table 4:** Velocity of sound and adiabatic compressibility of JP-3 and JP-4.

|               | Density at 25 °C,<br>g/cm <sup>3</sup> | Velocity of sound at 25 °C,<br>m/s | Adiabatic compressibility,<br>m <sup>2</sup> /kg |
|---------------|----------------------------------------|------------------------------------|--------------------------------------------------|
| JP-3 Sample a | 0.7590                                 | 1196.5 ± 1                         | 8.41 × 10 <sup>-9</sup>                          |
| JP-3 Sample b | 0.7682                                 | 1233.8 ± 2                         | —                                                |
| JP-4 Sample a | 0.7757                                 | 1242.2 ± 1                         | 8.40 × 10 <sup>-9</sup>                          |
| JP-4 Sample b | 0.7762                                 | 1242.3 ± 1                         | —                                                |

Data sources: [21–23]

The isothermal compressibility coefficient of RP-1 is  $4 \times 10^{-6} \text{ psi}^{-1}$ . The temperature change of RP-1, entering the system at 288 K, as the result of adiabatic compression while passing through a pump were calculated to be 0.3 °C for every 0.68 MPa = 6.8 atm = 100 psia pressure increase [24]. This is only a very small change, but nevertheless it can have an effect on some of the temperature-dependent phenomena in a liquid propellant feed system (oscillations, cavitation).

When measuring the compressibility of RP-1, it was difficult to account for the chemical composition, which varied from sample to sample. A better correlation was possible by introducing a new temperature-dependent auxiliary parameter  $J$ , which is the volume modulus [25]:

$$J = \frac{1}{\rho \sqrt{\log 1000v}}$$

where  $\rho$  is the density in g/cm<sup>3</sup> at 288.7 K = 15.6 °C = 60 °F and  $v$  is the kinematic viscosity in cSt at 310.9 K = 37.8 °C = 100 °F. For the density range allowed for RP-1, the kinematic viscosity at 310.9 K = 37.8 °C = 100 °F is between 3.185 and 1.25 cSt. See Table 5.

**Table 5:** Isothermal compressibility of RP-1.

| Temperature, °C | 0                                                       | 30    | 75    | 150  | 225  | 300  |
|-----------------|---------------------------------------------------------|-------|-------|------|------|------|
| $J^a$           | Isothermal compressibility in $1/\text{at} \times 10^4$ |       |       |      |      |      |
| 0.64            | 0.556                                                   | 0.631 | 0.774 | 1.15 | 1.73 | 2.74 |
| 0.66            | 0.562                                                   | 0.638 | 0.792 | 1.18 | 1.79 | 2.86 |
| 0.68            | 0.567                                                   | 0.648 | 0.806 | 1.21 | 1.85 | 2.97 |
| 0.70            | 0.571                                                   | 0.655 | 0.824 | 1.24 | 1.90 | 3.09 |
| 0.72            | 0.576                                                   | 0.667 | 0.840 | 1.28 | 1.96 | 3.20 |

<sup>a</sup>  $J$  is a temperature-dependent volume modulus auxiliary parameter defined above.

Data Source: [25]

## 2.4 Thermal Conductivity of Liquid Kerosenes

The thermal conductivity of liquid kerosene can be calculated from the following empirical formula:

$$\lambda = \frac{0.278226 \times 10^{-3}}{\rho} (1 - 5.4 \times 10^{-4} t)$$

where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$ ,  $\rho$  is the density in  $\text{g/cm}^3$ , and  $t$  is the temperature in  $\text{°C}$ . The thermal conductivity of four kerosenes with different densities is listed in Table 6.

**Table 6:** Thermal conductivity of four kerosenes with different densities.

| Temperature |     | Thermal conductivity, $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$ <sup>a</sup> |                         |                         |                         |
|-------------|-----|--------------------------------------------------------------------------------------|-------------------------|-------------------------|-------------------------|
| K           | °C  | Density, $\text{g/cm}^3$                                                             |                         |                         |                         |
|             |     | 0.78                                                                                 | 0.80                    | 0.82                    | 0.84                    |
| 273         | 0   | $0.3567 \times 10^{-3}$                                                              | $0.3476 \times 10^{-3}$ | $0.3394 \times 10^{-3}$ | $0.3311 \times 10^{-3}$ |
| 366         | 93  | $0.3388 \times 10^{-3}$                                                              | $0.3303 \times 10^{-3}$ | $0.3223 \times 10^{-3}$ | $0.3146 \times 10^{-3}$ |
| 477         | 204 | $0.3174 \times 10^{-3}$                                                              | $0.3094 \times 10^{-3}$ | $0.3019 \times 10^{-3}$ | $0.2947 \times 10^{-3}$ |

<sup>a</sup> calculated from the equation above.

Data source: [18]

The thermal conductivity of D. Eng. R. D. 2495, a kerosene with a boiling range of 443 to 523 K (170 to 250  $\text{°C}$ ) once used in the UK, was measured between 288 and 598 K (15 and 325  $\text{°C}$ ) and 0.1–20.3 MPa (1–200 atm) [26].

## 2.5 Heat Transfer Properties of Kerosenes

Kerosenes are often used as a regenerative coolant in very large rocket engines, such as the F-1 used in the SATURN-V Apollo-era launcher and the Russian RD-180 used in ATLAS-V EELV. The heat transfer properties of kerosenes need to be known in order to accurately size the cooling channels and select the operating conditions in a regeneratively cooled rocket engine. The operating conditions must be selected such as to avoid the formation of coke in the cooling channels. Heat transfer to kerosenes becomes unpredictable in supercritical regimes [27].

The convective heat transfer and pressure drop characteristics of a kerosene hydrocarbon fuel were investigated in an electrically heated minichannel with an inside diameter of 2.0 mm, within the range of fuel temperature 298–873 K (25–600  $\text{°C}$ ) at near-critical pressures [28]. In the single-phase liquid flow, considerable free convec-

tion in laminar flow stabilizes the flow at Reynolds numbers up to 3600, the heat transfer coefficients can be predicted by Gnielinski correlation with deviations no more than 20%, but at  $Re > 4000$  heat transfer enters a different regime. The adiabatic friction factor agreed with the Moody diagram and Blasius correlation at laminar and turbulent flow. As fuel temperature approached the pseudo-critical point, a peak and trough in heat transfer coefficients were recorded. First, heat transfer was enhanced by boiling or pseudo-boiling at the relevant pressures. As fuel temperature increased, heat transfer deteriorated, accompanied by acoustic flow instability and a peculiarly diabatic pressure drop deduction due to the steep thermodynamic properties. The heat transfer and flow stability were regained as the bulk fuel temperature increased to above the pseudo-critical points. Upon increasing the pressure, the singularities of heat transfer and fluid flow gradually disappeared.

The heat transfer characteristics of hydrocarbon fuels were investigated in short horizontal tubes with an inside diameter of 1.0 mm [29]. The experiments were conducted in test tubes that were 46 and 116 mm in length at a supercritical pressure of 3.0 MPa. The experimental parameters included a liquid velocity of 0.21–1.20 m/s, an inlet fluid temperature of 298–673 K, and various heat fluxes. Different heat transfer regions were designated based on the heat transfer behavior. Heat transfer was improved by thermophysical property variation, thermoacoustic oscillation, and endothermic reactions of the hydrocarbons. Heat transfer deterioration was characterized by gas resistance and coke deposition in the boundary fluid layer. The maximum safe ratios between heat flux and mass flow rate at various velocities and inlet fluid temperatures were determined and could be used as design criteria.

The design of cooling channels in regenerative cooling systems for scramjets or rockets requires knowledge of heat transfer properties of kerosenes. Correlations for heat transfer in kerosene flowing upward and downward in vertical tubes were developed and four existing correlations were assessed against available experimental data [30]. To further improve the prediction accuracy of the heat transfer of supercritical kerosene, a new dimensionless parameter ( $Q_i$ ) relevant to the heat flux was proposed and introduced into the development of a new correlation. Verification showed that the new correlation is more accurate than existing correlations.

An experimental investigation was performed on the convection heat transfer of a supercritical hydrocarbon fuel in a long capillary tube [31]. The horizontal test tube had an inner diameter of 1 mm and a length-to-diameter ratio of 980, dimensions that are close to those of practical interest heat-transfer channels in the thermal management system for hypersonic vehicles. The heat-transfer regions of hydrocarbon fuel were classified into initial heat transfer, normal heat transfer, enhanced heat transfer, and deteriorated heat transfer. The heat transfer coefficients of hydrocarbon fuels are affected by large variations in thermo-physical properties and buoyancy effects.

Under certain conditions of initial fluid temperature, the difference between wall temperature and fluid temperature, and above certain temperatures near the criti-

cal temperature, destructive pressure oscillations may occur in most fluids, including kerosenes. Pressure oscillations increase the rate of heat transfer. There are additional publications studying this phenomenon in specific kerosenes, such as RP-1 or RP-3.

Pressure oscillations in supercritical Jet-A fuel flowing through four parallel, heated tubes connected to common manifolds have been observed [32]. Tests were performed with fuel inlet temperatures ranging from 366 to 589 K (200 to 600 °F). Each tube received 2.26 kg/h of fuel. Tubes were heated by blowing 728–739 K (850–870 °F) hot nitrogen over them. Oscillations occurred when fuel inlet temperature was at least 422 K (300 °F). Amplitudes increased as fuel inlet temperature was increased. Maximum amplitudes encountered had frequency content ranging from 0.5 to 3 Hz for all oscillating cases.

Nucleate boiling heat transfer may induce oscillations under near-boiling conditions in any fluid, including kerosenes. The thermo-acoustic instability and heat transfer coefficients of an endothermic hydrocarbon fuel were investigated in a horizontal mini tube at supercritical pressures [33].

Experiments examining thermo-acoustic instability of hydrocarbon fuel flowing in horizontal circular tubes under various conditions indicated that there is a transition from stability to thermo-acoustic instability [34]. Results obtained with the method of Multi-Scale Shannon Wavelet Entropy based on Wavelet Transform Correlation Filter and Multi-Scale Shannon Entropy demonstrated that the induction of thermo-acoustic instability from noise and weak signals can be detected and the differences among stable operation, the transition phase, and the fully developed instability can be identified. The method can alert designers that thermo-acoustic instability of hydrocarbon fuel flowing in scramjet cooling channels may occur. The mass flow rate and the inlet pressure determine the point of transition to thermo-acoustic instability. This investigation of thermo-acoustic instability dynamic characteristics at supercritical pressures based on the wavelet entropy method defined the safe scramjet fuel flow rate, which can ensure stable fuel flow in regenerative cooling channels.

## 2.6 Thermodynamic Properties of Liquid Kerosenes

### 2.6.1 Heat Capacity of Liquid Kerosenes

The specific heat of liquid kerosene within the range 273 to 700 K can be calculated from the following formula (accurate to  $\pm 2\%$ ) [18]:

$$c_p = \frac{1}{\sqrt{\rho_{15.6}}} \left[ 0.388 + 4.5 \times 10^{-4} \times (1.8t + 32) \right]$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$ ,  $t$  is the temperature in  $^\circ\text{C}$ , and  $\rho$  is the density in  $\text{g/cm}^3$ . This equation gives the values summarized in Table 7. The specific heat

**Table 7:** Heat capacity of four liquid kerosenes with different densities.

| Density<br>g/cm <sup>3</sup> | Temperature |      | Liquid heat capacity                 |                                   |
|------------------------------|-------------|------|--------------------------------------|-----------------------------------|
|                              | K           | °C   | cal g <sup>-1</sup> °C <sup>-1</sup> | J g <sup>-1</sup> K <sup>-1</sup> |
| 0.78                         | 288.7       | 15.6 | 0.470                                | 1.97                              |
| 0.78                         | 298.1       | 25   | 0.479                                | 2.00                              |
| 0.78                         | 373.1       | 100  | 0.547                                | 2.29                              |
| 0.80                         | 288.7       | 15.6 | 0.464                                | 1.94                              |
| 0.80                         | 298.1       | 25   | 0.473                                | 1.98                              |
| 0.80                         | 373.1       | 100  | 0.540                                | 2.26                              |
| 0.82                         | 288.7       | 15.6 | 0.458                                | 1.92                              |
| 0.82                         | 298.1       | 25   | 0.467                                | 1.95                              |
| 0.82                         | 373.1       | 100  | 0.534                                | 2.23                              |
| 0.84                         | 288.7       | 15.6 | 0.453                                | 1.89                              |
| 0.84                         | 298.1       | 25   | 0.461                                | 1.93                              |
| 0.84                         | 373.1       | 100  | 0.527                                | 2.21                              |

Data source: [18]

of kerosene vapor can be extrapolated from the following equation (not very accurate, only good for first-order estimates):

$$c_p(\text{vapor}) = c_p(\text{liquid}) - 0.09/\rho.$$

The isobaric specific heat capacity of a kerosene-type hydrocarbon fuel at temperatures from 330 to 900 K and operating pressures from 1.96 to 4.93 MPa was measured using a flow calorimeter, which was based on the energy conservation theory [35]. The isobaric specific heat capacity data had an expanded relative uncertainty of 2.54%. The reliability and accuracy of the flow calorimeter measurement was verified using water, *n*-hexane, and binary mixtures of *n*-heptane + *n*-octane, and methanol + acetone respectively. In addition to kerosene, the isobaric specific heat capacities of a type of endothermic hydrocarbon fuel were measured and  $C_p$ - $T$  diagrams were plotted at sub- and supercritical pressures.

### 2.6.2 Enthalpy of Formation of Liquid Kerosenes

Because kerosenes are mixtures of hydrocarbons, thermodynamic properties that are usually reported on a per mole basis are difficult to compare. It would be more meaningful to list the enthalpy of formation on a mass basis (typically per 100 g). Different investigators have used different gross formulas and different formula weights (masses) for kerosenes. For instance, JP-4 has been described as CH<sub>2</sub>, C<sub>9</sub>H<sub>17</sub>, or C<sub>9.5</sub>H<sub>18.9</sub> and for each of these gross formulas the enthalpy of formation would be different if it was reported in the kJ/mol format. Enthalpy of formation data for kerosenes are compared in Tables 8 and 9.

**Table 8:** Air-breathing fuel properties.

| Fuel | Molecu-<br>lar mass | Empirical chemical<br>formula       | Enthalpy of forma-<br>tion $\Delta H_f$ |          | Net heat of<br>combustion |                     | Stoichiometric<br>fuel: air mass ratio |
|------|---------------------|-------------------------------------|-----------------------------------------|----------|---------------------------|---------------------|----------------------------------------|
|      | g/mol               |                                     | kJ/mol                                  | cal/mol  | kJ/kg                     | BTU/lb <sub>m</sub> |                                        |
| JP-4 | 14.027              | CH <sub>2</sub>                     | -25.63                                  | -6124.8  | 43499                     | 18701               | 0.067558                               |
| JP-5 | 13.926              | CH <sub>1.9</sub>                   | -22.55                                  | -5390.3  | 43164                     | 18557               | 0.068290                               |
| JP-7 | 173.439             | C <sub>12.3</sub> H <sub>25.5</sub> | -316.08                                 | -75544.7 | 43894                     | 18871               | 0.067194                               |
| RJ-5 | 186.676             | C <sub>14</sub> H <sub>18.375</sub> | +30.37                                  | +7259.1  | 41607                     | 17888               | 0.072638                               |

BTU = British thermal unit

Data source: [36]

**Table 9:** Enthalpy of formation data for kerosenes.

| Compound                                         | Formula                           | Enthalpy of formation |           | Density           |                                  |
|--------------------------------------------------|-----------------------------------|-----------------------|-----------|-------------------|----------------------------------|
|                                                  |                                   | kJ/kg                 | cal/100 g | g/cm <sup>3</sup> | lb <sub>m</sub> /in <sup>3</sup> |
| JP4 (Liquid turbojet fuel)                       | C <sub>9</sub> H <sub>17</sub>    | -11.76                | -281      | 0.7031            | 0.0254                           |
| JP5 (Bert Stull)                                 | C <sub>10</sub> H <sub>19</sub>   | -17.20                | -411      | 0.8193            | 0.0296                           |
| JP5 (Mont Stevens Standard)                      | C <sub>10</sub> H <sub>19</sub>   | -16.19                | -387      | 0.8193            | 0.0296                           |
| JP-10 ( <i>Exo</i> -Tetrahydrodicyclopentadiene) | C <sub>10</sub> H <sub>16</sub>   | -7.74                 | -185      | 0.9300            | 0.0336                           |
| RJ4(MIL-F-82522A.TH-Dimer)                       | C <sub>12</sub> H <sub>20</sub>   | -8.28                 | -198      | 0.9245            | 0.0334                           |
| RJ4(MIL-F-82522A.TH-Dimer)                       | C <sub>12</sub> H <sub>20</sub>   | -11.42                | -273      | 0.9245            | 0.0334                           |
| RJ5 (Shelldyne-H)                                | C <sub>140</sub> H <sub>184</sub> | +4.48                 | +107      | 1.0795            | 0.039                            |
| RP-1                                             | C <sub>1</sub> H <sub>2</sub>     | -56.07                | -1340     | 0.7999            | 0.0289                           |
| RP-1 (RPL)                                       | C <sub>100</sub> H <sub>195</sub> | -15.10                | -361      | 0.7999            | 0.0289                           |

Data source: [37]

### 2.6.3 Enthalpy of Evaporation of Liquid Kerosenes

For a crude approximation, the enthalpy of evaporation of kerosene at sea-level pressure can be expressed as a function of the liquid density and the temperature [18]:

$$\Delta H_{\text{evap.}} = \frac{0.5556}{\rho} [110.9 - 0.09(1.8t + 32)]$$

where  $\Delta H_{\text{evap}}$  is the enthalpy of evaporation in cal/g,  $t$  is the temperature in °C, and  $\rho$  is the density in g/cm<sup>3</sup>.

Correlation-gas chromatography was used to predict the evaporation enthalpy of complex fuels such as RP-1, JP-7, and JP-8 [38]. Evaporation enthalpies of 308, 341, and 441 kJ/kg were predicted assuming average compositions of C<sub>12</sub>H<sub>23.4</sub>, C<sub>12</sub>H<sub>25</sub>, and C<sub>11</sub>H<sub>21</sub> respectively. The hydrogen-to-carbon (H/C) ratio in these fuels has been measured by <sup>1</sup>H nuclear magnetic resonance (NMR), and an average molecular weight has been determined using gas chromatography (GC). Some variance in composition with the literature values has been observed. The predicted vaporization enthalpies were



compared with those in the literature. The effect of GC detector bias in evaluating the molar fraction of each hydrocarbon present, as a function of size, was tested and determined to have a relatively small effect on the vaporization enthalpy. Additional heat of sublimation data of hydrocarbons are available at Chickos and Acree [39].

## 2.7 Critical Point Properties of Kerosenes

The critical point properties of kerosenes are listed in Table 10.

**Table 10:** Critical point properties of kerosenes.

| Compound | $T_{\text{crit}}$<br>K | $p_{\text{crit}}$<br>MPa | References |
|----------|------------------------|--------------------------|------------|
| RP-1     | 676–689                | 2.140–2.170              | —          |
| JP-4     | Variable               | Variable                 | —          |
| JP-5     | 675                    | 2.27                     | [40]       |
| JP-8     | 666–684                | 2.344                    | [41]       |

## 2.8 Chemical Properties of Kerosenes

Hydrocarbons can be gases, liquids, or solids. At room temperature, alkanes with 5–16 carbon atoms in linear chains are liquids. The general gross formula for alkanes is  $C_nH_{2n+2}$ , the general gross formula for alkenes is  $C_nH_{2n}$ , and the general gross formula for alkynes is  $C_nH_{2n-2}$ .

The constituents of kerosene fuels can be generally classified in the following categories:

1. Hydrocarbon (HC) types
  - a. Paraffins ( $C_nH_{n+2}$ ) are mostly desirable as the main constituents of kerosenes such as JP-4 or RP-1. Paraffin alkanes are the natural constituent of many crude oils (aka “feedstocks”). Alkanes have the highest H/C ratio, which is a measure of the energy content of the fuel and is also regarded as a good indicator of stability. The paraffin fraction in crude oil can be increased by hydrotreating, thereby saturating the aromatic and olefin types. Depending on pressure and flow rate, paraffins are resistant to cracking at temperatures  $< 811$  K. The biggest problem with normal paraffins is their relatively high freezing point. This potential problem is eliminated by mixing normal paraffins with branched paraffins, which maintain the desired properties of the paraffin, but with better low temperature properties.
  - b. Naphthenes or cycloparaffins ( $C_nH_{2n}$ ) are desirable constituents for rocket propellant fuels. Naphthenes are natural constituents of some crude oils. The

naphthenes fraction depends on the origin of the feedstock. Naphthenes are more thermally stable than paraffins and may passivate reactive hydrocarbon constituents formed in heated fuel. Highly branched cycloparaffins have extremely low freezing points due to the asymmetry of the molecule. The ideal kerosene fuel would be a mixture of the branched and cyclic paraffins. Increasing the naphthenic content improves the thermal stability of the fuel. This can be accomplished by either using naphthenic crude oil feedstocks available on the West Coast, or by catalyzed isomerization during the refinement process (which might elevate fuel cost).

- c. Aromatics are undesirable for rocket propellant fuels. Aromatics are natural constituents of many crude oils. A low H-number or H/C ratio is a characteristic of a high fraction of aromatics in the fuel. Aromatics have poor ignition and combustion properties, increase flame radiation (which can produce plume heating issues in the rocket exhaust) and can cause deposition of coke at temperatures greater than  $\sim 533\text{K}$ . Aromatics are not desirable components for any fuel used in gas turbines or rocket engines. Aromatics content can be minimized by hydrotreating to form the corresponding naphthenes.
  - d. Olefins are highly undesirable in any fuel mixture, jet engine fuel, or rocket fuel. Olefins are highly unstable and are not a large natural constituent of crude oil. The olefin fraction in crude oil can be minimized/eliminated by hydrotreating. Olefins will degrade in ambient temperature storage to produce insoluble gums in fuels.
2. Non-hydrocarbon (HC) types
- a. Sulfur is a highly undesirable constituent of hydrocarbon fuels. Sulfur is a natural constituent of most (“sour”) crude oils in the form of thiols/mercaptans, sulfides, and thiophenes. Thiols and sulfides are primary initiators in the degradation process by producing reactive hydrocarbon constituents. This is specifically prevalent when exposed to copper-based alloys (i.e., coolant liners), where the sulfur reacts to form  $\text{Cu}_2\text{S}$  deposits and corrosion on the metal. The sulfur content becomes more troublesome at fuel temperatures  $> 644\text{K}$ . Sulfur-containing components can be minimized by hydrotreating to remove thiols and sulfides.
  - b. Dissolved oxygen in kerosene is undesirable but is usually introduced into kerosene by exposure to ambient air. Oxygen plays a role in the thermal stability of the fuel, but is a transient phenomenon that is a function of the storage history of the fuel. Oxygen reacts with unstable constituents and contributes to decomposition by producing reactive contaminants during storage. Sparging with nitrogen gas can remove dissolved oxygen from the fuel. Sparging is a physical process that involves bubbling nitrogen through the fuel for a period of time. The nitrogen gas will replace the dissolved oxygen in the fuel.

- c. Gums in kerosene are highly undesirable. Gums are higher molecular weight residues formed during the refining process or introduced into fuel from contaminated storage tanks and transfer lines. Originally, gums were thought to be mainly formed from olefin polymerization. Gums can contribute to the formation of deposits on metal surfaces and fouling. Gums are susceptible to thermal decomposition.

### 2.8.1 Thermal Decomposition of Kerosenes

The thermal decomposition of kerosenes is a standard process in petroleum refining in order to obtain lower boiling fuels. The product distribution and the kinetics of cracking of kerosene were investigated in a pilot plant under varying conditions of residence time, temperature, total pressure, and dilution close to those used in industrial operations [42]. The influences of feed composition, total pressure, and inlet partial pressure on the product distribution were determined. Kinetics of the cracking of individual components in the kerosene mixture were also calculated.

New challenges to increase aircraft speeds and engine efficiencies are increasing vehicle aerodynamic friction heat loads. Exotic alloys have been used for the shell of supersonic airplanes such as the X-15 and the SR-71/YF-12 (Black Bird). The leading edges may have to be cooled to prevent them from losing structural integrity and melting. Especially at higher Mach numbers, fuel is an attractive heat sink. For many vehicle applications, utilization of this heat sink would increase fuel temperatures beyond the limits of thermal stability, typically 643–673 K (370–400 °C). As temperatures increase beyond about 753 K (480 °C), this heat addition can lead to thermal/catalytic cracking of the fuel, leading to an “endothermic” fuel. The principal barrier to the use of high-temperature fuels is the deposition of carbonaceous material on heat exchanger passages, filters, fuel injectors, and other fuel system components [43].

There is concern that rocket engine regenerative cooling system performance and reliability may be negatively impacted by compositional variation even for kerosene fuels meeting existing specification limits. One must identify all potential compositional variations and quantify their influence on cooling characteristics. Rocket-grade kerosene is not typically quality tested for thermal stability or material compatibility prior to delivery and use in current launch vehicles. Specifically, RP-1 is not tested and RP-2 is tested only using American Society for Testing and Materials (ASTM) D3241 (Standard Test Method for Thermal Oxidation Stability of Aviation Turbine Fuels [Jet Fuel Thermal Oxidation Tester, JFTOT, Procedure]), but results are only reported, not constrained by specification limits. The JFTOT procedure, as specified in MIL DTL-25576E, is unable to adequately discriminate between thermally stable rocket fuels that have been shown in higher fidelity testing to perform differently or even fail.

The pyrolysis of a jet fuel consisting mostly of *n*-alkanes was experimentally and numerically studied in a tube reactor heated by fluidized sand under supercritical conditions [44]. The pyrolysis of aviation kerosene at different temperatures (798–873 K =

525–600 °C in 25° increments) and flow rates (1–6 mL/min) were experimentally studied under supercritical pressures (3.5 MPa) and the conversion rates and product distributions under different conditions were measured. The equivalent residence time was calculated by computational fluid dynamics (CFD) simulations with the concept of equivalent volume. On this basis, a molecular kinetic reaction model including 16 substances and 11 reactions was developed. The experimental and predicted results using the developed kinetics model agreed well, with deviations of less than 10% at conversions of up to 70%. The pyrolysis model was also used in modeling fuel flowing and pyrolysis in an electrically heated tube showing conversion prediction errors of less than 15% and fuel and wall temperature prediction deviations less than 20 K, which was a significant improvement over a previous model.

### 2.8.2 Coke Deposition of Hydrocarbon Fuels

Coking, with regard to hydrocarbon fuels, has been defined as the deposit formation of mostly solid-state carbon in the cooling channels of a hydrocarbon fuel-cooled combustion chamber. Coke formation appears to be influenced by the following parameters:

- a. Hydrocarbon fuel composition. For example, because of its inherent stability, the composition of methane is less prone to coking than higher-molecular-weight hydrocarbons. Liquid fuel high-temperature stability can be predicted from an *a priori* knowledge of the primary hydrocarbon types present in the fuel.
- b. Operating fuel pressure
- c. Hot wall temperature
- d. Catalytic activity of fuel-wetted surface material (i.e., copper alloy coolant liners promote faster deposit formation than stainless steel)
- e. Fuel flow velocity (i.e., fast-flowing fuel reduces the residence time for which the fuel is exposed to the hot wall)

Coking is undesirable for several reasons. Even present as a thin surface coating, it can restrict the flow of heat to the bulk coolant, thus causing coolant channel temperature increases, which ultimately cause failure and burnout. In larger quantities, coke deposition could progressively restrict the flow of fuel through the coolant passages and increase the pressure drop.

#### 2.8.2.1 Methods for Determination of Coke Deposition

Thermal stability of kerosenes is critical to prevent coke deposition in the channels of a regenerative cooling system. This property is very difficult to determine and it is difficult to obtain reproducible results. Methods for the quantitative determination of a tendency of a hydrocarbon fuel blend toward coke deposition have evolved during the past six decades. Some of these older methods are now only of historical interest.

Comparisons were made between the visual results obtained with a coker and the results obtained with a small, highly-instrumented Minex heat exchanger [45]. The comparisons showed that a reasonable correlation between the results obtained with the heat exchanger and with the coker may be achieved if three or more coker tests are analyzed on the basis of tube wall temperature versus deposit rating. By measuring the thickness of the film deposited and by knowing the effect of this thickness on heat transfer, a thermal conductivity can be calculated.

Six different jet fuels were tested for their resistance to thermal coke deposition by two versions of the CRC modified coker and the Minex heat exchanger [46]. The test results were compared by plotting the coker deposit code rating versus coker–preheater-tube wall temperature. The temperature of the tube wall, where large quantities of deposits form, was compared with the temperature of the Minex fuel outflow, where tube fouling due to deposits occurs. Fouling was indicated by a change in the measured heat transfer coefficient. The relative ranking of the six fuels was the same on the Minex as on the helium-driven modified coker. The pump-driven modified coker, however, gave a relative ranking that correlated with neither the Minex nor the gas-driven coker. It was concluded that the pump-driven modified coker was not a satisfactory test tool for fuels with a resistance to thermal degradation above 533 K (500 °F). It was apparent that the pump on the coker was affecting the test results when fuels of high thermal stability were tested. The most obvious reason for this effect was that the fuels with thermal stability above 533 K (500 °F) were treated to remove trace materials, and that these trace materials provide a degree of boundary lubrication in the pump. Without this degree of boundary lubrication, the coker pump may wear and release wear products (metal particles) that affect the test results.

The test recommended to measure the thermal stability of kerosenes is the JFTOT. Although the majority of the test methods described here were developed for jet engine fuels, they can be equally well used for evaluating the thermal stability of kerosenes for rocket engines.

The thermal stability test is conducted in accordance with a modified version of (IAW) ASTM D 3241 (JFTOT). The JFTOT test conditions are:

- a. Heater tube temperature at maximum point:  $628\text{ K} = 355^\circ\text{C} = 671^\circ\text{F}$
- b. Fuel system pressure:  $3.45\text{ MPa} = 34\text{ atm} = 500\text{ psi}$
- c. Fuel flow rate:  $3.0\text{ mL/min}$
- d. Test duration: 300 min
- e. Quantity of test fuel: 1 L

The heater tube is inspected after the test and the amount of coke formed is rated visually on a scale. The post-test heater tube is rated for deposits using the Alcor Mark 8A Tube Deposit Rater (TDR). The Alcor Mark 8A TDR is described in ASTM D 3241.

Comparisons were made between the JFTOT and the ASTM-CRC Coker Test (D 1660), which could be replaced with a new laboratory test device [47]. The JFTOT represents another method for rating the deposit-forming tendencies of

hydrocarbon fuels. It utilizes the same principle as the ASTM CRC Coker with certain improvements and was expected to be comparable with the Coker in ranking fuels. The JFTOT has the following operating advantages over the Coker: smaller sample size, shorter test time, easier operation, better tube temperature control, higher temperature capability, and higher fuel system pressure to minimize two-phase flow. The precision of determining maximum deposits is about the same with both tests. Precision of measuring test filter pressure drop in the JFTOT is significantly better than the Coker. The precision of measuring “breakpoint” temperature in the JFTOT is significantly better than the Coker. The JFTOT operated at a heater tube control temperature of 516 K (243 °C) should provide the same pass–fail criteria as the Coker operated at a fuel outflow control temperature of 422 K (149 °C). A light-reflectance method for rating tube deposits was found to be more precise than the visual method used with the Coker. Although there is a general relationship between the two rating methods, they are not exactly interchangeable.

The Visual Rating method and the ALCOR Mark 8A Tube Deposit Rater, used to rate deposits that form on the JFTOT heater tubes, were compared with each other and with measurements of the deposit thickness [48]. An Auger Electron Spectrometer, used in conjunction with an ion gun (AES/Ion Gun), was used to measure the deposit thickness and composition. Both the Visual Rating method and the Mark 8A Tube Deposit Rater were found to correlate with deposit thickness measurements to a limited degree. The AES/Ion Gun method proved to be a useful laboratory tool for measuring the thickness of coke deposits and the elemental composition of deposits (except for hydrogen and helium). Deposits that have a spectrum of colors (i.e., peacock or rainbow-type colors) were found to be considerably thicker than Code 3 deposits. Thin-film light interference (similar to colors of oil sheen on water) was found to be the cause of the peacock colors associated with these deposits.

Earlier research performed by Shell Research sought to compare the performance of fuels in the JFTOT with that in a simulated engine oil cooler. However, the agreement between the rigs was poor and initial attempts to improve the correlation by modifying various JFTOT operating parameters were ineffective. Later, those same operating parameters were readdressed in more detail, in order to determine the physical and chemical factors that control fuel response in the JFTOT [49]. Flowrate experiments and activation energy measurements indicated not only that the JFTOT’s response to a fuel depends on the relative roles of chemical reaction and physical transport, but more significantly, the contribution of the two effects is fuel dependent. Studies of test section metallurgy revealed that although differences between aluminum and stainless steel were clearly discernible under certain conditions, such differences became irrelevant as fuel degradation proceeds and the metal surface becomes lacquered. The findings provided an explanation as to why no improvement could be made in the correlations exhibited by earlier experiments. Development of a different small-scale thermal stability test was suggested.

One measure of the thermal stability of aviation fuels is the quantity of deposits formed on heated metal surfaces. In accelerated stability tests conducted in accordance with the JFTOT procedure (ASTM D3241), the rating methods involve either visual comparisons or measurement of reflected light by the TDR, both of which are sensitive to deposit color and surface texture. Deposits formed on stainless-steel JFTOT heater tubes have been examined by the TDR, a gravimetric carbon combustion method, and two new non-destructive techniques for determining deposit volumes based on measurements of dielectric strength and optical interference [50]. Measurements of total carbon content by combustion were used as a reference. It was found that the dielectric and interference methods correlated well with the combustion analyses and each other, whereas the total TDR often yielded misleading results.

It was demonstrated that a Fourier transform-infrared (FT-IR) fiber optic probe and a quartz crystal microbalance (QCM) probe could be used to measure deposit formation from thermal stressing of jet fuels in a high-temperature, high-pressure flow system [51]. These probes were designed, constructed, and tested in an existing Fuel Stability Test System that had an FT-IR Attenuated Total Reflectance (ATR) circle cell monitoring the stressed fuel after cooling to ambient temperature. It was demonstrated that both the FT-IR fiber optic probe and the QCM probe could successfully differentiate between a 'stable' and an 'unstable' fuel. The results from the QCM probe tests indicated that the drop in frequency for this particular probe resulted from viscosity dampening and not the mass of the film. The changes in the bulk fuel composition from thermal stressing were measured with the ATR circle cell, and were found to be significantly different from the changes in the deposit layer composition measured by the fiber-optic probe.

A series of heat transfer tests with methane, propane, No. 21 high-density kerosene, aerokerosene, and rocket kerosene was conducted at pressures of 0.5–30 MPa, flow velocities of 2–106 m/s, and heat fluxes up to 66 MW/m<sup>2</sup> in stainless-steel and copper tubes, and the deposit formation rates for kerosene in tubes were measured [52]. Forced convective heat-transfer correlations were obtained for liquid methane, propane, and kerosene, up to extreme heat fluxes at which test tubes burnt out. The test results indicated that heat-transfer coefficients of methane and propane decreased at high wall temperatures, and that the coefficients of kerosene increased under similar conditions because of boiling. No coking was detected in methane tests. Coking temperature and coking rates were determined for kerosene in stainless-steel tubes.

A series of heat-transfer tests was conducted with JP-7, JP-8, JP-8+100, JP-10, and RP-1 in resistively heated tube sections to simulate conditions encountered in regeneratively cooled rocket engines [53]. Six tests were conducted for each fuel using a half-factorial test matrix with fuel average velocities set at 7.6 and 22.8 m/s (25 and 75 ft/s), wall temperatures of 672 and 811 K (750 and 1000 °F), and OFE 101 copper and stainless steel 304 as tube materials. Test section average pressure and fuel bulk outlet tempera-

ture were held constant at 6.8 MPa (1000 psi) and 533 K (500 °F), respectively whereas target run times for all tests were 20 min. Carbon deposition rates for all tests were comparable ( $\sim 100 \mu\text{g cm}^{-2} \text{h}^{-1}$ ) with the exception of the JP-8/JP-8+100 copper tests, which yielded deposition rates an order of magnitude greater ( $\sim 1000 \mu\text{g cm}^{-2} \text{h}^{-1}$ ). The heat-transfer data collected from all tests could be well correlated by a standard pipe flow equation, which yielded an  $R^2$  value of 0.96.

A laboratory-scale flow reactor was used to subject small amounts (approximately 1 ml) of deoxygenated hydrocarbon fuels to controlled conditions of temperature and residence-time-at-temperature at constant pressure (3.44 MPa = 34 atm) in the liquid or supercritical phase [54]. The reactor was made of CRES-316 HPLC tubing. The thermal stability of the fuels, as well as the thermal fragmentation products of each fuel was measured using an in-line analytical system, as well as off-line GC analysis of products. Some of the candidate materials tested (quadricyclane and bicyclopropylidene) showed only marginal thermal stability with major decomposition occurring below 673 K (400 °C) with only  $\sim 3$ -s residence time. Other candidate materials (JP-10, RP-1, RG-1, RJ-6, and RJ-7) showed excellent thermal stability and little decomposition even at 873 K (600 °C). Results showed the pyrolytic stability of candidate materials relative to each other, and provided insights into the mechanisms of thermal decomposition for specific fuel candidates.

An experimental research program to investigate the thermal performance of several candidate hydrocarbon rocket fuels used a series of test rigs of increasing complexity and fidelity to one after another screen identified fuels without the cost and complexity of a full engine system level test [55, 56]. Results of small-scale thermal decomposition experiments utilizing a System for Thermal Decomposition Studies test rig provided an initial evaluation of the thermal stability performance of fuels from very small fuel samples. Measurements of heat transfer coefficient and the effect of wall temperature, flow velocity, and wetted material on deposit formation in heated test channels were obtained from larger rigs, such as the NASA/GRC Heated Tube Facility and the Air Force Rocket Propulsion Laboratory (AFRPL)/PRS High Heat Flux Facility. Two major types of devices were used to obtain high-heat-flux-relevant conditions: electrically heated tubes and heated copper blocks. Electrically heated tubes generate heat by passing electrical current through a metal tube instead of wrapping it with a heater coil and are predominantly used to obtain high-heat-flux heat-transfer data [57].

Conduction heated rigs, such as Aerojet's Carbothermal test rig, developed under the Hydrocarbon-Materials Fuel/Chamber-Liner Compatibility Program in the late 1980s (NAS3-25070), offer the advantage of significantly lower electrical power requirements to generate simulation of high-heat-flux test conditions in cooling channels. AFRPL/PRS has undertaken design and construction of a conduction heated, High Heat Flux Facility, based on the Carbothermal test rig and incorporating extension of maximum-heat-flux test capability to  $16342 \text{ W/cm}^2$  (100 British thermal units [BTU] in  $^{-2} \text{ s}^{-1}$ ).



Until 2004, none of the existing thermal stability test rigs had the ability to accurately simulate the high heat flux conditions that will exist in the cooling channels of new high-pressure hydrocarbon engines. The Air Force Research Laboratory (AFRL) at Edwards AFB designed a High Heat Flux Facility (HHFF) using experience gained from past thermal stability test rig experiments [58]. In order to design a facility capable of simulating the higher heat fluxes expected in the channels, CFD++, a Metacomp Technologies Inc. computational fluid dynamics software suite, was employed to optimize the design prior to manufacture. Conjugate heat-transfer calculations were performed in a single computational domain containing the copper heater block and the fluid channel of the new test rig design. The parameters of interest during each experiment were the heat-transfer coefficient, the degree of coking and corrosion in the channel, and the pressure drop as a function of heat flux, wall temperature, Reynolds number, channel material, fuel composition, and pressure.

The JFTOT is a thermal stability test that measures the tendency for fuel to form deposits and delivers a pass/fail grade for each fuel tested. However, the extent of oxidation and the corresponding deposition occurring in the JFTOT is not fully understood. A JFTOT Model Mark II was modified to include a bulk outlet temperature measurement and a downstream oxygen sensor to measure bulk oxygen consumption [59]. Results showed a direct relationship between the bulk outlet temperature and JFTOT setpoint temperature with the bulk outlet less than the setpoint temperature. Several fuels were tested at varying setpoint temperatures with complete oxygen consumption by 593 K (320 °C) and a wide range of oxygen consumption from 10–85% at 533 K (260 °C). Simulations of coke deposition were of the right order of magnitude and matched the deposit profile of comparable experimental ellipsometry data.

### 2.8.2.2 Kinetics of Thermal Decomposition of Kerosenes

Fuel concentration time-histories and overall rates of gas-phase RP-1, RP-2, JP-7, *n*-dodecane, and 1,2,3,4-tetrahydroquinoline decomposition reactions were measured using laser absorption in an aerosol shock tube and a heated high-pressure shock tube [60–63]. Experiments were performed with 0.1 to 0.6% fuel/argon mixtures for temperatures between 1000 and 1400 K and pressures from 0.3 to 5.1 MPa (3 to 51 atm). Fuel concentration was measured by infrared laser absorption at 3.39  $\mu\text{m}$ . Fuel-removal data for *n*-dodecane were used to determine the unimolecular decomposition rate constant for the reaction *n*-dodecane  $\rightarrow$  products.

The thermal decomposition kinetics of JP-7, JP-TS, and JP-900 were studied at 648, 673, 698, and 723 K (375, 400, 425, and 450 °C) in stainless-steel bomblet reactors [64]. In all cases, the pressure before decomposition was adjusted to 34.5 MPa (5000 psi). Decomposition as a function of time at each temperature was quantified by analyzing the thermally stressed liquid phase using GC. These results were used to determine global first-order rate constants that approximate the overall decomposition rate of each fuel. For JP-7, these first-order rate constants ranged from  $1.79 \times 10^{-5} \text{ s}^{-1}$  at 648 K (375 °C) to  $3.02 \times 10^{-4} \text{ s}^{-1}$  at 723 K (450 °C). For JP-TS, the rate constants were between

$1.74 \times 10^{-5} \text{ s}^{-1}$  at 658 K (375 °C) to  $2.70 \times 10^{-4} \text{ s}^{-1}$  at 723 K (450 °C). For JP-900, the rate constants ranged from  $1.03 \times 10^{-5} \text{ s}^{-1}$  at 648 K (375 °C) to  $3.60 \times 10^{-4} \text{ s}^{-1}$  at 723 K (450 °C). At all temperatures studied, these three fuels have similar rate constants for thermal decomposition; with only one exception, the values of  $k'$  were identical within the combined uncertainty. The rate constants for the decomposition of RP-2, a fuel being considered as a replacement fuel for hypersonic vehicles, were similar within the temperature range studied. Considering the time needed for 1% of the sample to decompose ( $t_{0.01}$ ), we find that required instrument residence times range from 16 min at 648 K (375 °C) to 30 s at 723 K (450 °C). The rate constants as well as the Arrhenius parameters can be used to design and plan physical property measurements at additional temperatures.

### 2.8.2.3 Experimental Study of Coke Deposition in Regeneratively Cooled Rocket Engines

There are numerous test methods for the measurement of the coking (“fouling”) tendency of hydrocarbon fuels subjected to high temperatures in contact with metal surfaces. Some tests measuring the rates of coke deposition were combined with an evaluation of the compatibility with and potentially catalytic activity of the metals from which cooling channels in rockets are built. The test methods were already described in Section 2.8.2.1 above. The following is a summary of results obtained by various investigators with several fuels using different experimental methods. Sections on thermal stability and coke deposition of specific hydrocarbon fuels will follow under the headings of individual hydrocarbon fuels.

Oxidation and condensation products of a standard jet fuel at 463–473 K (190–200 °C) have been concentrated and fractionated to give materials of average molecular weight of  $>300$  by (1) precipitation from pentane and (2) gel permeation chromatography [65]. Heating fuel with stainless steel wool and oxygen at 473 K (200 °C) formed insoluble deposits that could be removed only by heating in air. A deposit from a simulated fuel manifold has been analyzed.

A high-pressure fuel coking test apparatus was used to evaluate thermal decomposition (coking) limits and carbon deposition rates in heated copper tubes for two hydrocarbon fuels, RP-1 and commercial-grade propane [66, 67]. Tests were conducted using JP-7 and chemically pure propane as being representative of more refined cuts of the baseline fuels. A parametric evaluation of fuel thermal stability was performed at pressures of 136 to 340 atm, bulk fuel velocities in the range 6–30 m/s, and tube wall temperatures within the range 422–811 K. The effect of the inside wall material on deposit formation was evaluated in selected tests using nickel-plated tubes. The results of the tests indicated that substantial deposit formation occurred with RP-1 fuel at wall temperatures between 600 and 800 K, with peak deposit formation occurring near 700 K. No improvements were obtained when deoxygenated JP-7 fuel was substituted for RP-1. The carbon deposition rates for the propane fuels were generally higher than those obtained for either of the kerosene fuels at any given wall tempera-

ture. Plating the inside wall of the tubes with nickel was found to significantly reduce carbon deposition rates for RP-1 fuel.

An experimental research program was undertaken to investigate the thermal stability and heat-transfer characteristics of several hydrocarbon fuels under conditions that simulate high-pressure, rocket engine cooling systems [68–70]. The rates of carbon deposition in heated copper and nickel-plated copper tubes were determined for RP-1, propane, and natural gas using a continuous flow test apparatus that permitted independent variation and evaluation of the effect on deposit formation of wall temperature, fuel pressure, and fuel velocity. The effects of fuel additives and contaminants, cryogenic fuel temperatures, and extended duration testing with intermittent operation were examined. Parametric tests to map the thermal stability characteristics of RP-1, commercial-grade propane, and natural gas were conducted at pressures of 6.9 to 13.8 MPa, bulk fuel velocities of 30 to 90 m/s, and tube wall temperatures within the range 230 to 810 K. Tests were run in which propane and natural gas fuels were chilled to 230 and 160 K respectively. Corrosion of the copper tube surface was detected for all fuels tested. Plating the inside of the copper tubes with nickel reduced deposit formation and eliminated tube corrosion in most cases. The lowest rates of carbon deposition were obtained for natural gas, and the highest rates were obtained for propane. For all fuels tested, the forced-convection heat-transfer film coefficients were satisfactorily correlated using a Nusselt–Reynolds–Prandtl number equation.

Coking and heat transfer characteristics of three hydrocarbon fuels in heated tubes were compared. RP-1, RP-1/DAH, and JP-7 hydrocarbon fuels were tested in electrically heated tubes to determine and compare their heat-transfer characteristics and thermal stability [71]. Tube materials of Ni 200 and SS 347 were used, and coolant-side wall temperatures of 644, 755, and 866 K (371, 482, and 593°C) were tested. Fuel flow conditions were set to match the conditions in the regenerative coolant channels of typical LOX/hydrocarbon expendable rocket engine systems. Results showed that JP-7 has a 4.5% higher specific heat capacity than RP-1 and very little coke deposition on the tube walls. The specific heat of the RP-1/DAH fuel was similar to that of the RP-1 fuel. The coke deposition of the RP-1/DAH fuel, however, was much heavier than that of the baseline RP-1 fuel. It was evident throughout the Ni 200 tubes in nodules that grew as high as 0.041 mm above the surface.

A materials compatibility and thermal stability investigation was conducted under environmental conditions similar to those encountered in regeneratively cooled rocket engines using five common liquid hydrocarbon fuels and two structural materials [72]. Scanning-electron microscopic analysis in conjunction with energy dispersive spectroscopy (EDS) was used to characterize the condition of the tube inner wall surface and any carbon deposition or corrosion that was formed during selected runs. Results showed that the carbon deposition process in stainless-steel tubes was relatively insensitive to fuel type or test condition. The deposition rates were comparable for all fuels and none of the stainless steel test pieces showed any signs of corrosion. For tests conducted with copper tubing, the sulfur content of the fuel had a significant impact

on both the condition of the tube wall and carbon deposition rates. Carbon deposition rates for the lowest sulfur fuels (2 ppm) were slightly higher than those recorded in the stainless-steel tubes with no corrosion observed on the inner wall surface. For fuels with slightly higher sulfur content (25 ppm), nodules that intruded into the flow area were observed to form on the inner wall surface. These nodules induced moderate increases in tube pressure reduction. The highest sulfur content fuels (400 ppm) produced extensive wall pitting and dendritic copper sulfide growth that was continuous along the entire tube wall surface, resulting in an inability to maintain flow rate owing to rapidly increasing test section pressure drops. Accompanying this corrosion were carbon deposition rates an order of magnitude greater than those observed in comparable stainless-steel tests. The results of this investigation showed that trace impurities in fuels (i.e., sulfur) can significantly impact the carbon deposition process and produce unacceptable corrosion levels in copper-based structural materials.

In the regeneratively cooled combustion chambers of liquid rocket engines using hydrocarbon fuels, coking occurs as the wall temperature increases, which results in coke deposition on the wall of cooling channels. This phenomenon reduces the cooling capability of the coolant, which finally causes damage to the combustor by overheating of the chamber wall. An electrically heated tube was used to simulate a regeneratively cooled channel and investigate the compatibility of copper alloys with hydrocarbon fuel Jet A-1 [73].

Parameters identified or suggested to influence fuel thermal stability and deposit formation include overall fuel chemical composition, specific fuel constituents such as additives (beneficial) and contaminants (detrimental), the effect of compositional variability on system-level cooling performance, primary fluid, and thermal conditions e.g., pressure, surface temperature, etc., and surface material composition and treatment. The need for an experimental approach capable of rapid, multi-parametric investigations of these and other factors influencing fuel thermal performance and cooling capability was addressed. Standard test methods existing a decade ago were incapable of achieving the very hot operating environments of cooling systems for advanced engines, and operational thermal stability tests are often accompanied by high associated costs and relatively long turnaround times. Under a collaborative research and development effort conducted by the AFRL and Johns Hopkins University/Chemical Propulsion Information Analysis Center, a rocket fuel thermal stability experiment has been designed and constructed in order to allow rapid assessment of fuel thermal integrity. It was hoped that this test will eventually qualify as an apparatus around which a standard method for thermal stability can be developed. The CRAFTI (Compact Rapid Assessment of Fuel Thermal Integrity)-based apparatus may be included in future fuel specifications as a thermal performance requirement.

The US Air Force (USAF) started an Aerospace Fuels Quality Test and Model Development program to identify conditions in kerosene fuels that may negatively impact or even jeopardize cooling system performance and reliability owing to compositional variations of fuels meeting existing specification limits and to mature and refine fuel

quality assurance practices for rocket-grade kerosene [74, 75]. Another objective was to develop predictive models correlating fuel composition with observed behavior in a cooling channel. An experimental apparatus was designed and constructed for the purpose of evaluating the effects of fuel purification technologies on thermal stability and material compatibility. This CRAFTI method was modified and extensively characterized under the AF project. In this versatile convective heat transfer experiment, fuel is pressurized by a positive displacement dual-syringe pump and flows through an ohmically heated test article, a tube. Electrical current is maintained via control of the dual power supplies, resulting in constant power during the test. Backpressure is held constant by an electropneumatically controlled dome loaded backpressure regulator. Downstream heat exchangers in series cool the effluent fuel to safe levels prior to sampling. The experiment is conducted in vacuum to reduce heat loss to surroundings, minimize oxidation of test article surfaces, and isolate the operator from potential hazards. Combined control of fuel flowrate, test article geometry, and supply power defines surface temperature profile, which in turn determines fuel exit bulk temperature. Recorded data include flow rate, power supply current and voltage, fuel inlet and exit bulk temperature, fuel pressure, and test article outer surface temperature, measured at 1.3-cm (0.5-in.) increments. To demonstrate overall CRAFTI repeatability, a series of ten runs was conducted using a specific RP-2 fuel under standard test conditions over a period of approximately 1 year. These runs were interspersed among nearly 50 others, many of which employed relatively high sulfur and aromatic content fuels. The ability of CRAFTI to reproduce carbon deposit behavior after a full year of testing with a variety of special blends, treated fuels, and worst case formulations, without full disassembly or extensive cleaning, indicated its excellent potential as a standard test method. Additional hydrocarbon fuel characterization was done using GC  $\times$  GC-TOFMS (time-of-flight mass spectrometry) with a reverse column configuration to enhance separation and optimize selectivity for the 19 fuel samples evaluated. In this configuration, the first dimension column had a polar stationary phase and the second dimension column had a non-polar stationary phase.

Based on results obtained with the CRAFTI apparatus, a Thermal Integrity Index was proposed as the quantifiable measure of fuel thermal stability for a future specification test. Additional discussion of results obtained with this apparatus is presented in subsequent sections on specific kerosene fuels.

### 2.8.3 Radiolysis of Kerosenes

One-hundred-milliliter samples of RP-1 generate 50.3 mL of radiolytic off-gas (measured at 298 K and 101 kPa (25°C and 1 atm)) when irradiated to  $8.5 \times 10^6$  rads with gamma rays [76]. When approximately 5 mass-% of an efficient, olefinic, free-radical scavenger was added to the samples, the off-gas volume produced by RP-1 fuel was reduced by 18.7% whereas those of hydrazine and Hydyne fuels were not reduced. These scavenging effects show that RP-1 fuel decomposes radiolytically by both free-radical

(18.7%) and molecular mechanisms, and that hydrazine and Hydryne fuels decompose entirely by a molecular or ionic mechanism. See also [77].

#### 2.8.4 Specifications for Kerosenes

Because commercially used liquid hydrocarbons are very rarely pure chemical compounds but are usually very complex mixtures of up to several hundred organic compounds, it is important to manufacture and procure fuels with reproducible properties. Military specifications specify the most important properties of the fuel mixtures, but still leave a wide range of variability from one producer to another. In 1944, the US first published specification AN-F-32 for JP-1, a kerosene jet fuel. This specification was changed to MIL-F-5616 in 1950. Many more specifications have been issued and updated in the interim.

Table 11 is an alphabetical summary with a brief description of the various kerosene fuels in the JP and RP series with number designations, some of which have been discontinued and are now only of historical interest. Although most of them are distillate ranges of naturally occurring petroleum, several are synthetic hydrocarbons with well-defined chemical structures, and although most of them were formulated to meet requirements of air-breathing jet engines, many have been used as rocket fuels because of their ready availability. However, one must remember that performance evaluation criteria for fuels for air-breathing jet engines and oxidizer-carrying rocket engines are quite different, the former going mostly by heat of combustion and density, whereas the latter need hydrogen-rich fuels to lower the mean molecular mass of the combustion products. The physical and chemical property requirements for hydrocarbons as rocket propellants and jet engine fuels are described in the Military Specifications:

Because kerosenes are mixtures and not a pure compound, their physical and chemical properties vary widely and are specified in industrial and military specifications, depending on the intended application. The most common fuel for jet engines is (was) JP-4. The most common fuel for rocket engines is (was) RP-1. Another summary table gives a partial list of kerosene specifications as they were in use in the 1960s. Table 12 gives the specification properties of some of the most commonly used kerosenes at that time. This table is now only of historical interest because many specifications have changed or have been canceled in the meantime. Specification limits for aerospace fuels are listed in Table 13. One of the older sources of information on foreign specifications for jet propellants is the book by Ragozin [78]. The foreign specifications for jet engine fuels have undergone many changes during the past century, just as the US specifications have evolved over time [79].

**Table 11:** Listing of kerosene designations.

| Designation      | Composition description                                                                                       | Specification <sup>a</sup> | Intended use                          |
|------------------|---------------------------------------------------------------------------------------------------------------|----------------------------|---------------------------------------|
| JP-1             | Narrow cut, low freezing point and high flash point                                                           | MIL-F-5616C (1944)         | Air-breathing jet engines             |
| JP-2             | Wider cut, unsuitable viscosity and flammability                                                              | MIL-F-5624C (1945)         |                                       |
| JP-3             | Wide-cut distillate fuel with a vapor pressure comparable with that of aviation gasoline                      | AN-F-58 (1947)             |                                       |
| JP-4             | MIL-F-5624A specification revision allowed the use of “cracked” materials in the formulation of JP-3 and JP-4 | MIL-F-5624C                | XB-70 bomber                          |
| JP-5             | High flash point kerosene. US Navy ship-board use                                                             | MIL-F-7914 (1952)          |                                       |
| JP-6             | Special fuel                                                                                                  | MIL-J-25656 (1956)         |                                       |
| JP-7             | Low vapor pressure and improved thermal oxidative stability. Low aromatics                                    | MIL-T-38219 (1970)         | SR-71 Hypersonic vehicle              |
| JP-8             | Lower vapor pressure than JP-4. Similar to commercial Jet A-1. It replaced JP-4 except in arctic regions      | MIL-DTL-83133A (1979)      | All land-based jet engines            |
| JP-9             | Ternary blend of Shelldyne-H, methylcyclohexane, and TH-MCPD                                                  | MIL-P-87107B (1979)        | ALCM                                  |
| JP-10            | exo-Tetrahydrodi(cyclopentadiene)                                                                             | MIL-P-87107B (1979)        | Cruise missiles, Tomahawk             |
| Jet-A and Jet-A1 | Commercial jet fuel                                                                                           | ASTM-D-1655                | Air-breathing jet engines             |
| RJ-1             | High-boiling-range kerosene                                                                                   | MIL-F-25558 (1956)         | Ramjet engines, Navaho cruise missile |
| RJ-4             | Tetrahydromethylcyclopentadiene dimer                                                                         | MIL-F-82522A (1971)        | Air-breathing ramjet engines          |
| RJ-5             | Hydrogenated dimers of norbornadiene, Shelldyne-H                                                             | Development                | Air-breathing ramjet engines          |
| RJ-6             | Mixture of RJ-5 and JP-10                                                                                     | Development                | Air-breathing ramjet engines. ASALM   |
| RP-1             | High-boiling-range kerosene                                                                                   | MIL-DTL-25576C (1967)      | Regeneratively cooled rocket engines  |
| RP-2             | High-boiling-range kerosene, low sulfur                                                                       |                            |                                       |
| RP-3             | High-boiling-range kerosene                                                                                   |                            |                                       |

<sup>a</sup> Historical, not the most recent

**Table 12:** Specifications for kerosene fuels (historical listing).

| Country                                             | USA            | USA            | USA            | USA            | USA                           | USA            | UK       | France         | France |
|-----------------------------------------------------|----------------|----------------|----------------|----------------|-------------------------------|----------------|----------|----------------|--------|
| Common designation                                  | JP-1           | JP-3           | JP-4           | JP-5           | RP-1                          | JP-4B          | Air-3405 | Air-3407       |        |
| MIL specification                                   | MIL-F-5616C    | MIL-F-5624C    | MIL-F-5624C    | MIL-F-7914     | MIL-R-25576B,<br>MIL-F-25576A | DERD-2486      |          |                |        |
| Corresponding NATO specification                    | F-33           |                | F-40           | F-42           |                               |                |          |                |        |
| Boiling range, °C                                   | —              | —              | 104 to 280     | 200 to 290     | 177 to 275                    | —              | —        | —              | —      |
| % Distillate gone over up to this boiling point, °C |                |                |                |                |                               |                |          |                |        |
| 10%                                                 | <210           | —              | <121           | <210           | —                             | <121           | —        | <120           |        |
| 20%                                                 | —              | <116           | <144           | —              | —                             | <144           | <200     | —              |        |
| 50%                                                 | —              | <177           | <188           | —              | —                             | <188           | —        | —              |        |
| 90%                                                 | <255           | <243           | <243           | —              | —                             | <248           | —        | <275           |        |
| Final boiling temperature                           | <300           | <315           | <288           | 288            | —                             | <288           | <300     | <290           |        |
| Distillation residues, mass-%                       | <3             | <3             | <3             | <3             | —                             | <3             | <3.5     | —              |        |
| Vapor pressure at 311 K = 38°C, mm Hg               | —              | 260 to 380     | 100 to 150     | 15 to 20       | —                             | 100 to 150     | —        | 107 to 160     |        |
| Density at 288.6 K = 15.5°C, g/cm <sup>3</sup>      | 0.780 to 0.850 | 0.740 to 0.780 | 0.750 to 0.802 | 0.780 to 0.845 | 0.803 to 0.815                | 0.750 to 0.802 | —        | 0.740 to 0.825 |        |
| Flash point, °C                                     | >46            | —              | —              | >60            | >43                           | —              | >40      | —              |        |
| Aromatics, vol.-%                                   | <20            | <25            | <25            | <25            | —                             | <25            | <20      | <25            |        |



Table 12: (continued)

| Country                                        | USA              | USA    | USA                  | USA              | USA   | UK     | France           | France |
|------------------------------------------------|------------------|--------|----------------------|------------------|-------|--------|------------------|--------|
| Lower heat of combustion, kcal/kg <sup>a</sup> | >10170           | >10270 | >10220               | >10170           | —     | >10220 | >10150           | >10200 |
| Beginning crystallization, °C                  | < -60            | < -60  | < -60                | < -40            | < -40 | < -60  | < -40            | < -60  |
| Sulfur content, mass-%                         | <0.20            | <0.40  | <0.40                | <0.40            | <0.40 | <0.40  | <0.20            | <0.4   |
| Mercaptan sulfur, mass-%                       | <0.005           | <0.005 | <0.005               | <0.005           | —     | <0.005 | <0.005           | <0.005 |
| Kinematic viscosity, at ___ °C, cSt            | <10<br>(at -40°) | —      | <0.9 cPs<br>(at 20°) | <16<br>(at -34°) | —     | —      | <6<br>(at -18°C) | —      |
| Resinous residue, mg/100 ml propellant         | <5               | <7     | <7                   | <7               | —     | <7     | <6               | <10    |
| Acidity, mg KOH/g propellant                   | <0.1             | <0.1   | <0.1                 | <0.1             | —     | <0.1   | <0.1             | —      |
| Bromine number                                 | <5               | <5     | <5                   | <5               | —     | <5     | —                | <3     |
| Unsaturated hydrocarbons, mass-%               | <5               | <5     | <5                   | <5               | —     | <5     | —                | —      |

MIL = military, KOH = potassium hydroxide

<sup>a</sup> Must always specify if this is upper or lower heat of combustion!

Data source: [78]

**Table 13:** Specification limits for aerospace fuels.

|                                         | ASTM                | JP-5          | Jet A              | JP-7        | JP-8        | RP-1                   | RP-2               |
|-----------------------------------------|---------------------|---------------|--------------------|-------------|-------------|------------------------|--------------------|
| Specification                           | Method              | MIL-DTL-5624U | ASTMD1655-15       |             |             | [80]                   | [80]               |
| Requirement, units                      | Distillation, °C    |               |                    |             |             |                        |                    |
| IBP                                     | D86                 | report        | —                  | >182        | report      | report                 | report             |
| 10% recovered                           | D86                 | <205          | <205               | >196        | <205        | (185–210) <sup>a</sup> | (185–210)          |
| 20% recovered                           | D86                 | report        | —                  | >206        | report      | —                      | —                  |
| 50% recovered                           | D86                 | report        | report             | report      | report      | report                 | report             |
| 90% recovered                           | D86                 | report        | report             | <260        | report      | report                 | report             |
| End point                               | D86                 | <300          | <300               | <288        | <300        | <274                   | <274               |
| Density at 15 °C, kg/L                  | D1298               | 0.788–0.845   | 0.775–0.840        | 0.779–0.806 | 0.775–0.840 | 0.799–0.815            | 0.799–0.815        |
| Viscosity at –20 °C, mm <sup>2</sup> /s | D445                | <8.5          | <8.0               | <8.0        | <8.0        | <16.5 <sup>b</sup>     | <16.5 <sup>b</sup> |
| Flash point, °C                         | D93 <sup>c</sup>    | >60           | >38                | >60         | >38         | >60                    | >60                |
| Freezing point, °C                      | D2386 <sup>d</sup>  | <–46          | <–40 <sup>e</sup>  | <–43.3      | <–47        | <–51                   | <–51               |
| Lower (“net”) heat of combustion, MJ/kg | varies <sup>f</sup> | >42.6         | >42.8              | >43.5       | >42.8       | >43.0                  | >43.0              |
| Hydrogen, mass-%                        | varies <sup>g</sup> | >13.4         | >13.4 <sup>h</sup> | >14.4       | >13.4       | >13.8                  | >13.8              |
| Aromatics, vol.-%                       | D1319               | <25.0         | <25.0              | <5          | <25         | <5                     | <5                 |
| Olefins, vol.-%                         | D1319               | —             | —                  | —           | —           | <2.0                   | <1.0               |

Table 13: (continued)

|                          | ASTM                | JP-5                | Jet A               | JP-7                  | JP-8                  | RP-1    | RP-2     |
|--------------------------|---------------------|---------------------|---------------------|-----------------------|-----------------------|---------|----------|
| Total sulfur, mass-%     | varies <sup>l</sup> | <0.3                | <0.3                | <0.1                  | <0.3                  | <0.003  | <0.00001 |
| Mercaptan sulfur, mass-% | D3227               | <0.002 <sup>j</sup> | <0.003 <sup>j</sup> | <0.001 <sup>j</sup>   | <0.002 <sup>j</sup>   | <0.0003 |          |
| JFTOT ΔP change, mm Hg   | D3241 <sup>k</sup>  | <25                 | <25                 | <25 (355 °C, 300 min) | <25 (260 °C, 150 min) | —       | report   |

IBP = initial boiling point, JFTOT = Jet Fuel Thermal Oxidation Tester

Notes:

<sup>a</sup> Parentheses denote unit conversion from detail specification.

<sup>b</sup> Maximum value at –30 °F (–34 °C) is given.

<sup>c</sup> D56 is preferred method for Jet A.

<sup>d</sup> JP-5 also allows D5972; Jet A also allows D5972, D7153, and D7154.

<sup>e</sup> Jet A-1 value: –47 °C

<sup>f</sup> JP-5, Jet A: D4809, D3338, or D4529; RP-1/RP-2: D240

<sup>g</sup> JP-5: D3701; JP-8: D3701, D3343, or D7171; RP-1/RP-2: D3343

<sup>h</sup> Value provided is for JP-8 (MIL-DTL-831 33H).

<sup>i</sup> JP-5: D1266, D2622, D3120, D4294, or D5453; Jet A: D1266, D2622, D4294, or D5453; RP-1: D5453 or D5623; RP-2: D4045 or D5623

<sup>j</sup> Alternatively, D4952 can be used with sweet/negative result.

<sup>k</sup> JP-5, Jet A: 260 °C for 150 min; RP-2: 355 °C for 300 min.

### 2.8.5 Analysis of Kerosenes

A group-type analysis of hydrocarbons in a complex jet fuel may be more useful than attempting to analyze every component because such an attempt inevitably leaves a large portion of the fuel unidentified. Although it may be difficult to accurately determine the identity of a particular compound, that compound can often be classified as belonging to a group or compound class because of its chromatographic retention and mass spectral properties. Compound class quantitation is often capable of relating compositional information to fuel properties.

In rocket kerosenes, 150 to 200 components are usually detected. If one is lucky, 80% of these components can be identified by GC-MS, for instance, in the Russian Naftil fuel [81]. To construct correlations with the results of traditional methods of analysis, the identified compounds are usually split into groups according to chemical structure. Most often, three to eight groups are used.

Two-dimensional gas chromatography (GC  $\times$  GC) is a technique capable of providing this group-type separation and quantitation in jet fuels. This technique was used to examine a large set of fuels (Jet A, Jet A-1, JP-5, and JP-8, primarily) from petroleum sources and non-petroleum alternative sources, such as synthetic paraffinic kerosene [82]. By comparing results from GC  $\times$  GC analysis with those of established techniques and model compound studies, it was found that the accuracy of GC  $\times$  GC for this sort of group-type analysis is excellent.

#### 2.8.5.1 Assay Analysis of Kerosenes

Because liquid hydrocarbons very rarely are pure chemical compounds, but usually are very complex mixtures of up to several dozens of organic compounds, it is important to have uniform and accurate analytical methods to analyze fuels and obtain the same results, regardless of whether the analysis is done at the manufacturer, the intermediate dealer, or the end user. The task of the analytical methods is to verify the quality of the fuel with reproducible properties from batch to batch or from one supplier to another. Military specifications specify the most important properties of the fuel mixtures, but still leave a wide range of variability from one producer to another. Accurate and precise analytical methods help to narrow this range of variability. Many analytical methods for hydrocarbons as rocket propellants are described in the Military Specifications, for instance:

- Propellant, Kerosene, Grade RP-1, Spec MIL-P-25576
- Propellant, Jet Fuel, Grade RJ-1, Spec MIL-F-25558

In addition to verifying the assay and nominal properties, analytical methods also need to determine the amount of additives and possible undesirable contaminants.

#### 2.8.5.2 Distillation Curves for Analysis of Kerosene Mixtures

The boiling range of kerosene mixtures is quantified by fractionated distillation and MIL specifications specify the temperature ranges within which certain fractions of

distillate have to go over. These analysis methods are described in ASTM and API procedures, such as ASTM D86, ASTM D7345, or ASTM D2887.

Methods are sought that can provide a link between chemical composition and physical property information and provide the ability to calculate thermodynamic and transport properties for complex heterogeneous streams. One such technique was based on the advanced distillation curve (ADC) method, which separates complex fluids by distillation into fractions that are sampled, and for which thermodynamically consistent temperatures are measured at atmospheric pressure [83, 84].

### **2.8.5.3 Comparison of Different Grades of Kerosene**

A comparative evaluation of Russian kerosene and US RP-1 to support integration of Russian propulsion elements into the US space program followed a two-prong approach to provide better understanding of the differences. First, laboratory analysis provided insight into chemical and physical properties, and the theoretical rocket performance difference between the two fuels [85]. Second, hot fire testing provided performance and engine operational data with the two fuels. Analysis of the data showed three major differences: Russian kerosene is 3% more dense than RP-1, it has 21% less sulfur content, and the temperature rise with Russian kerosene through the cooling jacket is lower. No significant difference in the characteristic exhaust velocity,  $c^*$ , was found. The advantages and disadvantages of eventually using Russian kerosene in US vehicles and the impacts of using RP-1 with Russian engines can thus be evaluated.

### **2.8.5.4 Detection of Kerosene Vapors**

Because kerosenes have a low toxicity and relatively low volatility (compared with gasoline), there may be a relatively lax attitude toward monitoring the kerosene concentrations in the air of work areas. Only a few instruments for continuous monitoring of kerosene concentrations are in use.

A rocket kerosene vapor detector consisting of a light source, gas absorption cell, IR sensor, electric circuitry, and data collecting and processing system was designed based on non-dispersive infrared using an electrically modulated IR source and an IR filter [86]. The instrument had the advantages of great sensitivity, long life span, and rapid response. Kerosene vapors in contaminated soil and in the air above contaminated soil can be detected with a quartz crystal resonator on a piezo sensor [87].

### **2.8.6 Additives to Kerosenes**

Commercial hydrocarbon fuels may contain a wide range of different additives that are supposed to improve their performance for an intended application under given circumstances, but may interfere with their application as rocket propellants.

### 2.8.6.1 Anti-Icing Water Precipitation Additives

Alkanes are immiscible with water, but they possess a very small and often troublesome solubility for water. Hydrocarbons that have absorbed water from the air or have been exposed to water by accident may be saturated with water at room temperature. As soon as the temperature drops, water will come out of the solution and either form a puddle of water at the bottom of the tank or, worse yet, form ice crystals suspended in the fluid. Ice crystals in jet engine fuel or rocket fuel may clog filters and orifices. Often alcohols are added to hydrocarbon fuels to prevent water and ice precipitation. The water content must be analyzed and kept below a certain limit [88].

### 2.8.6.2 Antioxidants

Alkanes that are free from unsaturated compounds are stable in air. However, most commercially used hydrocarbon fuels contain varying percentages of unsaturated compounds that may autoxidize and polymerize, forming less soluble resins. Commercial grades of kerosene often contain anti-oxidants that are supposed to prevent resin formation.

Anti-oxidants may be added separately or in combination to the propellant in total concentrations not in excess of 8.4 lb of inhibitor (not including the weight of the solvent) per 1000 barrels of propellant (9.1g/100 US gal) in order to prevent the formation of gum:

- a. 2,6-di-*tert*-butyl-4-methyl phenol
- b. *N,N'*-di-*sec*-butyl-paraphenylenediamine
- c. 2,4-dimethyl-6-*tert*-butyl phenol
- d. 2,6-di-*tert*-butyl phenol

A metal deactivator, *N,N'*-disalicylidene-1,2-propanediamine, may be added in an amount not to exceed 2 pounds of active ingredient per 1000 barrels of propellant (2.2g/100 US gal).

A dye, methyl derivative of azobenzene-4-azo-2-naphthol, shall be added in an amount not to exceed ½ ounce (wt) per 1000 US gallons of RP-1 propellant. Dye shall not be added to RP-2 propellant.

Oxidation and polymerization inhibitors are hydroquinone or *tert*-butylcatechol. 4-*tert*-Butylcatechol is added as a stabilizer and an inhibitor of polymerization to butadiene, styrene, vinyl acetate, and other reactive hydrocarbons. It is 25 times more effective than hydroquinone for a polymerization inhibitory effect.

### 2.8.6.3 Corrosion Inhibitors

Santolene C, which was a phosphorus-containing dimer of linoleic acid, has been renamed/replaced by HITEC E515 (formerly Santolene C). HITEC E515 is a corrosion/wear inhibitor comprising dilinoleic acid and diamyl phenol acid phosphate in a kerosene-based hydrocarbon solvent. In December 2007, HITEC E515 corrosion inhibitor was replaced by HITEC E580, as HITEC E515 is no longer available.

#### 2.8.6.4 Static Dissipator Additives

Hydrocarbons are normally non-conductive to electricity. Flowing hydrocarbons in poorly grounded equipment may build up electrostatic charges and sparks from discharges may cause ignition in the presence of hydrocarbon vapors and air. Commercial grades of hydrocarbons may contain additives to provide marginal electrical conductivity to the liquid, just enough to prevent the build-up of electrostatic charges.

#### 2.8.6.5 Cetane Number Improvers

Kerosene that is intended to be used as diesel fuel may contain cetane number improvers, in particular in Arctic regions.

#### 2.8.6.6 Droplet Dispersion by Micro-Explosion Additives

Various types of kerosene-soluble organic azides and diazides, both aliphatic and aromatic azides, have been tested as additives to fuels (diesel engine fuels, jet engine fuels and rocket engine fuels) to enhance droplet break-up and dispersion in a flame zone. The types of azides used for this type of application have already been described in chapter “Azides and Azido Compounds.”

The combustion of such fuels with additives and the effect on droplet dispersion will be described in a future set of the *Encyclopedia of Rocket Propellants*, namely in *Encyclopedia of Non-Hypergolic Bipropellant Combinations*. The rates of fuel droplet evaporation can be improved by up to two orders of magnitude by the addition of organic azides. Diazidoalkane fuel additives were investigated as a method of improving the performance of LOX/RP-1 booster engines by causing microexplosions of evaporating fuel droplets. Compared with neat RP-1, the azide additives have greater fuel density and allow an increase in theoretical specific impulse for mixture ratios below 2.6. 1,10-Diazidodecane was used for the initial evaluation in four hot fire tests using subscale combustor hardware to determine the effect of diazidodecane on combustion performance. The density of diazidodecane is 20% higher than that of neat RP-1. 1,10-Diazidodecane is a clear liquid and is completely miscible with RP-1. See also [89, 90].

### 2.9 Handling of Kerosenes

#### 2.9.1 Facilities for Kerosene Storage and Transfer

The number one requirement for design of hydrocarbon storage and transfer facilities is the leak-proof design and the prevention of the escape of hydrocarbon vapors into the environment. In due consideration of the fire and explosion hazards in connection with hydrocarbons, all facilities should be properly grounded to prevent build-up of electrostatic charges and protected against lightning strike. Electrical equipment in the vicinity of hydrocarbon storage and transfer facilities must be spark-proof.

### 2.9.2 Fire Fighting of Kerosene Fires

Because hydrocarbons are not miscible with water and float on top of water while continuing to burn, water is not a very effective fire-fighting agent against hydrocarbon fires. Foam, carbon dioxide, and bicarbonate dust dry chemical fire extinguishers are more effective than water against hydrocarbon fires.

The most difficult fires to fight are those in launch vehicles that also contain an oxidizer. Launch mishaps are dramatic and there is very little one can do other than allowing the fuel to burn out and possibly cool surrounding structures with a water curtain. The water can have only a cooling action and will not extinguish the flames as long as there is oxidizer available.

## 2.10 Safety Properties of Kerosenes

The safety properties of jet fuels for the AF were reviewed with primary emphasis on JP-5 and JP-4 fuels. JP-5, a jet fuel that has a lower volatility than JP-4, was compared with JP-4 for AF jet aircraft operations. In the assessment of the data on the two fuels, special effort was made to determine whether there are 'fire-safety' advantages to be gained by the AF from the use of JP-5 instead of JP-4. From the study of pertinent technical information available and actual operational experience of the AF, it was suggested that use of a lower-volatility fuel such as JP-5 would have contributed little, if any, improvement in the AF flight safety record as of the mid-1960s. There was concern that the use of a fuel with lower volatility might reduce the military flight performance capability of certain types of AF aircraft. In spite of this critical assessment, the USAF switched from JP-4 to JP-8 or JP-8+100 during the following decades.

### 2.10.1 Flammability Limits of Kerosenes

Vapors of hydrocarbons mixed with air are flammable and potentially explosive. The exact flammable limits depend on the composition, and in particular on the boiling range of the kerosene blend.

### 2.10.2 Flash Points of Kerosenes

Flash point temperature is the lowest temperature where a fuel will give off sufficient vapors for ignition under ambient conditions. It is related to the lower flammability limit of fuels in air. There are two types of flash point measurement apparatus: open cup and closed cup. Flash point temperature is used by the National Fire Protection Association, and in the Hazardous Substance Classification Act to differentiate the relative fire hazards of fluids. The higher the flash point temperature, the less hazardous the fluid [91].



### 2.10.3 Pool Burning of Kerosene Spills in Air

It has been attempted to reduce the fire hazard of spilled kerosene by gelling it. Gelling would reduce the rate at which spilled hydrazine spreads over a large area and would reduce the rate of evaporation of spilled fuel. The speed of flame spreading over a gelled JP-4 oil-in-water emulsion held in a pool was observed by movie film recording [92]. The temperatures on and above the surface of the gel from the time when the flame front arrived to the time when it faded was measured with an array of thermocouples fixed in place. The flame-spreading velocity of JP-4 can be reduced by gelling down from one-tenth to one-twentieth of that of the original ungelled JP-4.

Flash points of oil-in-water gelled fuels with single and multiple components, and of commercial fuels were measured by the Tag Closed-Cup method and compared with those of neat, ungelled hydrocarbon fuels [93]. A dispersive-type infrared gas analyzer was used to measure the temperature dependence of the equilibrium vapor concentration of the emulsified fuel. Ignition aspects of an emulsified fuel pool surface were compared with those for neat liquid fuel. The effect of emulsification on the elevation of flash point was analyzed in terms of the reduction of fuel vapor pressure owing to solubilization in emulsion. Another finding was that by heating the surface locally, the emulsified fuel pool could be easily ignited, probably because of the considerable reduction of heat loss from the hot region as there existed no internal convection flow, even when the initial temperature of the emulsion was quite low and the flash point of neat hydrocarbon fuel was higher than the ambient temperature.

The influences of the initial temperature and the oil content of oil/water emulsions on flame-spreading velocity were investigated [94]. Characteristics of flame spreading upward and downward along an inclined pool were examined by altering the inclination angle and comparing results with those of a horizontal pool.

## 2.11 Toxicity of Kerosenes

### 2.11.1 Inhalation Toxicity of Kerosenes

Alkanes are not very toxic. Inhalation of air containing more than 1000 ppm alkane vapors can cause euphoric states of poisoning and at even higher concentrations the vapors will be narcotic.

Such high concentrations are not likely to be achieved with kerosenes used as rocket propellants because the vapor pressure is pretty low. Therefore, inhalation protection is usually not required when handling kerosenes at the tank farm or the rocket test site.

However, aromatic hydrocarbons, most of all benzene itself, are toxic. Inhalation or skin resorption of benzene can cause blood disorders and damage the bone tissues where the red blood cells are formed. Benzene is now categorized as a known human carcinogen. Acute and chronic inhalation toxicity, oncogenic exposures, and muta-

genic screening animal exposure tests were described and emergency exposure limits were established for JP-9, RJ-5, methylcyclohexane, and JP-10 [95].

### 2.11.2 Cutaneous Toxicity of Kerosenes

Careless spills of hydrocarbons on the skin may extract the skin grease and the skin will become brittle and cracked. In extreme cases vesicles may develop in the exposed skin. Liquid JP-4 spilled into the eyes causes instant irritation and lacrimation, most likely because of some of the additives in the commercially formulated jet fuel. Incidents of JP-4 spilled in the eye have not left any permanent damage. Nevertheless, wearing safety glasses where JP-4 is transferred under pressure is recommended.

### 2.11.3 Environmental Impact of Kerosene Spills

Kerosene spills on the ground cause ground water pollution and may kill some soil bacteria. Other bacteria can be enticed to digest hydrocarbons and used for bioremediation of kerosene spills.

Nutrients such as nitrogen and phosphorus are necessary for effective biodegradation of spilled hydrocarbons in the soil. These nutrient compounds are frequently injected into the contaminated subsurface to enhance *in situ* biodegradation. The effect of residual sub-surface hydrocarbon (kerosene) contamination on the transport of an electron acceptor ( $\text{NO}_3^-$ ) and a nutrient ( $\text{NH}_4^+$ ) was investigated [96]. Soil column experiments were conducted using uncontaminated and contaminated soil, and a one-dimensional solute transport model with multi-process non-equilibrium sorption was used to predict the breakthrough curves. The presence of kerosene contamination was found to cause an earlier breakthrough time for  $\text{NO}_3^-$  relative to the uncontaminated soil, which was predicted by the transport model. The exchange isotherm involving  $\text{NH}_4^+$  was not affected by the presence of kerosene.

## 2.12 Fuel Mixtures with Kerosenes

The kerosenes JP-4, RP-1 and others are good rocket propellants because they are readily available. The storability and ease of handling make them very attractive. The main disadvantage of kerosenes is that they are not hypergolic with most of the common oxidizers. The only oxidizers that are hypergolic with kerosenes are fluorine and some of the fluorine oxidizers such as chlorine trifluoride or chlorine pentafluoride. There have been numerous attempts to hypergolize kerosenes by adding hypergolizing additives to either the fuel or the oxidizer. Other additives to kerosenes were made with the intent to increase their heat of combustion (see Section 2.12.3) or improve their ignition properties (e.g., amine nitrates) [97].

### 2.12.1 Hypergolization of Kerosenes

There have been numerous attempts to hypergolize kerosenes by adding hypergolizing additives to either the fuel or the oxidizer or both. One hypergolizing additive to the fuel, unsymmetrical dimethylhydrazine (UDMH), has actually seen flight application.

#### 2.12.1.1 Hypergolization of Kerosene by the Addition of UDMH

Kerosene has been hypergolized by the addition of unsymmetrical dimethylhydrazine to render it hypergolic with red fuming nitric acid (RFNA) or white fuming nitric acid (WFNA). There were two types of UDMH/JP-4 blends, one with 17% UDMH and one with 40% UDMH, as specified by Specification MIL-P-26694B. JP-X Type I is a mixture of 60% JP-4 and 40% UDMH and was used in the BOMARC booster [98, 99]. The NIKE-AJAX missile fuel was JP-X Type II with 17% UDMH in JP-4 [4].

#### Physical Properties of Kerosene/UDMH Mixtures

The physical properties of JP-4/UDMH mixtures with 17 to 40% UDMH are summarized in chapter “Dimethylhydrazines.” Unsymmetrical dimethylhydrazine is only marginally miscible with JP-4. It is important that the fuel and the additive remain completely mixed over the entire range of service temperatures. The problem is that small quantities of water addition cause the binary solution to break into two phases, which is not acceptable and would prevent the missile from igniting when commanded to launch (similar phase separation problems are encountered with Gasohol in automobiles). For a mixture containing 17% UDMH in JP-4, only 0.2% water causes phase separation at 233 K (−40 °C). When the mixture contains 40% UDMH, it tolerates 1% water at 233 K. Mixtures containing 40 mass-% UDMH in JP-4 are more moisture tolerant, and will tolerate up to 5 mass-% water without phase separation at 233 K (−40 °C).

#### Chemical Properties of Kerosene/UDMH Mixtures

The compositions of JP-X mixtures were specified by Military Specification MIL-P-26694B – Propellant, JP-X (JP-4 + UDMH) [100]. These specifications covered three types of JP-X. The nominal composition limits and purity requirements of these three types of JP-X are listed in Table 14.

The ignition properties of this fuel with hypergolic oxidizers will be described in the forthcoming *Encyclopedia of Hypergolic Bipropellant Combinations*. Even smaller additions of UDMH to kerosenes (insufficient to achieve hypergolic ignition) improve the stability of combustion of kerosenes with WFNA or RFNA [101]. A fuel mixture containing 17 mass-% UDMH in JP-4 with the designation M-3 was used in the NIKE-AJAX Surface-to-Air-Missile [102, 103]. The mixture, containing 40 mass-% UDMH and 60 mass-% JP-4, had the designation JP-X.

**Table 14:** Composition limits and purity requirements of hypergolized kerosene per MIL-P-26694B.

| Constituent            | Distillation limit | Unit              | Type I      | Type II     | Type III      | Analytical method          |
|------------------------|--------------------|-------------------|-------------|-------------|---------------|----------------------------|
|                        |                    |                   |             |             |               |                            |
| JP-4 per MIL-T-5624    |                    | Mass-%            | 40 ± 1      | 17.0 ± 0.3  | 50.0 ± 2.0    | —                          |
| UDMH per MIL-P-25604   |                    | Mass-%            | 59 min      | 83.0 ± 0.3  | 48 min        | Potassium iodate titration |
| Distillation           | 10% point          | °F                | 155 maximum | 245 maximum | not specified | —                          |
|                        | 35% point          | °F                | 170 max.    | —           | —             | —                          |
|                        | 50% point          | °F                | 300 maximum | 340 maximum | —             | —                          |
|                        | 70% point          | °F                | 370 maximum | —           | —             | —                          |
|                        | 90% point          | °F                | 470 maximum | 466 maximum | —             | —                          |
| Density at 298 K       |                    | g/cm <sup>3</sup> | 0.746–0.788 | 0.749–0.792 | 0.746–0.786   | ASTM D941-55               |
| No phase separation at |                    | °F                | –65 maximum | —           | –65 maximum   | —                          |
| Particulate            |                    | mg/L              | 10 maximum  | 10 maximum  | 10 maximum    | ASTM D-2276-65T            |

### Analysis Methods for Kerosene/UDMH Mixtures

Because the water content of these mixtures had to be measured frequently to make sure the fuel would not segregate at low temperatures, a field method for the determination of water in M-3 and JP-X was developed. It was a gasometric method, based on the reaction of a fuel sample with an excess of calcium hydride. Calcium hydride would react with water and develop hydrogen gas, which was captured in a gas burette [104].

#### 2.12.1.2 Hypergolization of Kerosene by Suspension of Metal Hydrides

A very unusual method for hypergolizing kerosenes is the suspension of finely divided alkali metal hydrides. Alkali metal colloidal suspensions or alkaline earth metal hydrides do not dissolve in kerosene, but they are inert to dry hydrocarbons and can be stored under dry hydrocarbon oil indefinitely. Suspensions of alkali metal hydrides in kerosene are hypergolic with WFNA and have very short ignition delays. These suspensions are easy to prepare, and only a small percentage of hydride additives is needed [105]. It is a disadvantage that the hydrides settle within less than an hour if the kerosene is not gelled. It is not practical to continuously stir the fuel just prior to launch to keep the particles in suspension. If the kerosene/hydride suspension is not gelled or agitated, the powder would settle at the bottom of the tank. The first slug of fuel drained from the tank would consume all the hydride. It would achieve the first ig-

nitition, but the engine may not be restartable or the remainder of the fuel may develop combustion instabilities. In addition, the hydride sludge may clog pumps or orifices.

A student group at the University of Stuttgart, Germany, tested small rocket engines with WFNA and sodium hydride suspensions in kerosene, achieving hypergolic ignition. Commercial kerosene usually contains some moisture, which would deactivate the sodium hydride. Pre-drying the kerosene with calcium hydride, decanting it, and then adding the sodium hydride slurry were recommended. An attempt was also made to slow down the settling of the sodium hydride suspension by increasing the density of the fuel.

### 2.12.2 Gelled Kerosene (Without Suspended Solids)

Most of the work on gelled kerosene has been done to suspend metal or metal hydride powder to improve the fuel properties of kerosene by making them hypergolic with nitric acid or to increase the specific impulse. Some work has been done on gelling kerosene as a means of reducing leakage in case an aircraft tank gets punctured by shrapnel while in battle. Much of this work is related to the work on gelled jet fuels to reduce the fire hazard in case of airplane crashes on the ground. As opposed to a Newtonian fluid, for a non-Newtonian liquid the viscosity  $\eta$  is dependent on the applied shear rate  $\dot{\gamma}$ . For the characterization of Newtonian and non-Newtonian fluids without a yield point, the power-law model (Ostwald–de Waele model) is the most common correlation:

$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

where  $K$  is the consistency index and  $n$  is the power law index of the fluid. For  $n = 1$  Eq. (1) describes a Newtonian fluid. However, shear thinning (thixotropic) behavior is given for a power-law index  $0 < n < 1$ , and shear thickening (dilatant behavior) for  $n > 1$ .

There are numerous publications on the rheology of gelled liquids, in particular those exhibiting thixotropic behavior (“non-Newtonian fluids”), which relate to all gelled propellants, but very often include work on gelled kerosenes or gelled ethanol [106–110].

The viscosity of thixotropic fuels is dependent on the shear rate. Pumping gelled propellants requires higher feed pressures than pumping ungelled propellants. Injection of gelled propellants into combustion chambers results in different modes of droplet break-up.

Description of properties of gelled kerosene and metallized gelled kerosene in this chapter of the book would normally be restricted to selection of gelling agents, preparation of gels, viscosity and rheology of gels, droplet evaporation, segregation under high acceleration, and storage life (limited by “syneresis”) of gels. In several instances these publications deal not only with the aforementioned topics but also proceed to burning the gelled kerosene either in a laboratory apparatus or in a jet or rocket engine. Several publications in this dual-topic category are therefore discussed both here

and will eventually reappear in *Encyclopedia of Non-Hypergolic Bipropellant Combinations*, for the combustion of gelled propellants.

A numerical algorithm was developed for the steady, incompressible, isothermal, laminar flow of a power-law, shear-thinning gel propellant in a converging injector [111]. Such equations would apply to all gelled propellants, but would most likely be used for gelled kerosenes first. The effect of the injector geometry and the flow rate on the velocity and viscosity fields was evaluated for different gelled propellants. In comparison with a straight-passage injector, a convergent one can produce an additional decrease in the mean apparent viscosity of the fluid. The mean apparent viscosity decreased significantly by increasing the convergence angle of the injector. In general, increasing the gel flow rate resulted in a decrease in the mean apparent viscosity of the fluid. Increasing the gellant content of gel propellants resulted in an increase in the fluid viscosity, which decreased when the gel flowed through the injector. Gels of different gellant content that flow through the same geometry injector exhibited similar relative reduction in viscosity.

In bipropellant systems, in particular those with pressure-fed propellants, it is desirable that both oxidizer and fuel should have similar rheological properties, although an exact match is not required [112]. Gelled JP-8 and RP-1 fuels have been used to study the rheological behavior of gelled hydrocarbons using 4–7 mass-% of fumed silica as the gelling agent [113]. Viscosity, stability, thixotropic behavior, and the viscoelastic properties of the gel through their storage and loss moduli were measured as a function of the amount of gelling agent added. Differential scanning calorimetry measurements showed only a slight influence of the amount of gelling agent on the enthalpy of vaporization of the gels. The ungelled hydrocarbons had a higher enthalpy of vaporization than the gels.

Isolated fuel droplets were held in place to investigate experimentally the combustion process of gelled propellants under normal gravity conditions in air [114]. Phase separation of the gel propellant components leading to bubble nucleation, vapor jetting, and microexplosions were found to be the main phenomena involved during the combustion period. The effect of gellant concentration on the burning rate constant as well as flame structure was examined. The burning rate constant decreased with an increase in the gellant concentration. The decrease in the calorific value of the increasing gellant concentrations was most likely one of the reasons for this variation. The flame exhibited a triple flame structure for all the cases for both zones with free radicals as well as visible luminous flames.

Collision of two droplets is a fundamental form of droplet interaction in the spraying droplet flow field in the injector of rocket engines. An axi-symmetric form of the Navier–Stokes equations based on the *volume of fluid* method was used to study the central collision mechanism of two gel droplets with equal diameters and to track the evolution of the gas–liquid free interface [115]. The model was validated by experimental results on Newtonian liquids. Phenomena of rebound, coalescence, and reflexive separation of droplets after collision were investigated, and structures of the compli-

cated flow fields during the collision process were analyzed. Results showed that the maximum shear rate appears at the point where the flow is redirected and accelerated. Rebound of droplets is determined by the Weber number and viscosity of the fluid. It was concluded that the gel droplets are easier to rebound than the base fluid droplets. The results showed that the alternating appearance along with the deformation of droplets in the radial and axial direction is the main characteristic of the droplet coalescence process. The reflexive separation process of droplets can be divided into three distinctive stages including the radial expansion, the recovery of the spherical shape, and the axial extension and reflexive separation. The maximum deformation of droplets appeared in the radial expansion stage.

In order to investigate the evaporation characteristics of a single kerosene gel droplet, an isolated kerosene gel droplet with an initial diameter of ~2mm was suspended at the welding point of a thermocouple wire, and was suddenly exposed to an elevated temperature (within the range 373–773 K = 100–500 °C) at atmospheric pressure (0.1MPa) under normal gravity [116]. The droplet-changing process was recorded by a high-speed imaging system. The results indicated that the evaporation process of a single gel droplet can be divided into three stages: **(1)** the stage of the evaporation of kerosene; **(2)** the stage of the gellant layer formation; **(3)** the stage of the swelling of the gellant layer and microexplosions taking place. Several unique phenomena, such as bubble nucleation, gellant layer formation, disruption of gellant layer, and slight explosion of the initial droplet, were observed. The initial evaporation rate of kerosene gel resembled the evaporation rate of a pure kerosene droplet at a relatively low temperature. However, micro-explosions would occur once the environmental temperature exceeded the boiling point of kerosene.

### 2.12.3 Metal Suspensions in Kerosenes

Ever since the first tests with liquid rocket engines, there have been numerous attempts to improve the performance of LOX/kerosene by the addition of metal powders that have a high heat of combustion. Some of the first tests of this kind actually firing a LOX/kerosene/Al rocket engine were conducted by the famous rocket pioneer Eugen Sänger in Austria in the 1930s [117, 118]. A term coined for these suspensions (English synonym: slurries) in German was “Kerosol” which may be somewhat misleading because nothing was dissolved.

The performance of kerosene as a fuel for bipropellant combination can be enhanced by suspending finely distributed metal powders, preferably aluminum or beryllium. In order to prevent the metal powder from settling during storage, the mixture has to be gelled. The amount of metal that can be added is limited by the increasing viscosity of these blends, making them hard to pump and inject into a combustion chamber [119, 120].

In addition to using metallized kerosene slurries in rocket engines, these fuel mixtures were also evaluated in air-breathing ramjets or in afterburners. It would be diffi-

cult to use them in turbocompressor jet engines because the condensed exhaust products (mostly aluminum oxide) would sandblast the turbine blades and would deposit in undesirable locations. Metallized kerosene slurries for ramjets (no moving parts) and rocket engines were developed at NASA in the US and at LRBA in Vernon (France). It is difficult to achieve complete combustion of metal particles within the short dwell time in the combustion zone. While burning, many metal particles become coated with a layer of high-melting oxides that impede further combustion. The combustion of metal slurries in hydrocarbons will be discussed in more detail in *Encyclopedia of Non-Hypergolic Bipropellant Combinations*.

A compilation of physical and performance data for both neat and heterogeneous propellants in bipropellant rocket and air-augmented rocket applications with emphasis on the air-augmented cases contained physical and thermochemical properties for the neat liquid fuels and oxidizers, including boiling point, freezing point, density, enthalpy of formation, vapor pressure, critical properties, enthalpy of vaporization, viscosity, and specific heat [121]. Physical properties for the heterogeneous fuels included composition, density, graphs of shear stress versus shear rate and temperature, mechanical and thermal stability, specific heat, thermal conductivity, and enthalpy of formation. The performance applications featured bipropellant operation, augmented boost, an air-augmented cruise case in a ducted rocket configuration, and the ramjet mode of operation. The results of the theoretical calculations on performance included maximum density, specific impulse, bulk density, mixture ratio, air ratio, and burnout velocity.

Stable suspensions of aluminum and boron carbide in various hydrocarbons have been prepared for use as ramjet fuels and fundamental chemical and physical properties of these suspensions related to Navy storable propellant criteria were measured [122]. Total burning times of concentrated dust particle flames of carbon, boron, boron carbide, and aluminum at atmospheric pressure in air were examined and compared, and the implications of these dry burning rates with respect to the combustion efficiencies of metal particles in gelled fuels in ramjet missiles were discussed.

In spite of ongoing efforts to develop metallized kerosene slurries, the efforts that have been going on for more than half a century have not produced any flight application or fielding of metallized kerosene rocket or air-breathing propulsion systems and it is doubtful they ever will. Being fully aware of these many futile attempts to get metallized hydrocarbon gels to fly, an attempt has been made here to gather information from the literature and assemble it in a useful format just to prevent the mistakes of the past from being repeated by future generations of propellant chemists. Our collection is incomplete. There are so many references on metallized hydrocarbon and hydrazine, methylhydrazine (MMH), or UDMH gels that they would fill a book by themselves.

There is another chapter on the combustion of metallized kerosene slurries in the forthcoming *Encyclopedia of Non-Hypergolic Bipropellant Combinations*. Owing to the



higher viscosity and two-phase nature of these gels, injection and atomization of fuel sprays in a combustion chamber are difficult tasks.

### 2.12.3.1 Metal Selection for Kerosene Slurries

The additives with high heats of combustion are boron, aluminum, and possibly magnesium. Beryllium would be a good additive if it were not for the toxicity. The solids loading of the metallized gels cannot exceed 60% because such gels could no longer be pumped because of their high viscosity. Usually, smaller metal loadings, within the range 10–20%, are sufficient to achieve a significant improvement of performance.

Suspending metals in kerosene not only makes them more energetic, it can also make them hypergolic with nitric acid as the oxidizer. Finely suspended lithium metal makes kerosene hypergolic with WFNA or RFNA [123].

### 2.12.3.2 Nano-Metals Suspended in Kerosene

In the most recent decade, nano-metals have received a substantial amount of interest for various propulsion applications in gelled and solid propellants. The advantages of aluminum as a nano-metal (“Alex<sup>®</sup>”) over regular vacuum-dispersed aluminum are more complete combustion and higher burning rates.

The heat of combustion of every ingredient by itself and a mixed nano-aluminum/kerosene gel system was measured [124]. It is surprising that the mass-specific heat of combustion of the nano-aluminum/kerosene gel system decreased with an increase in nano-aluminum powder content in the gel system. The reason is that the heat of combustion of nano-aluminum powder is lower than that of kerosene. But the density and volume-specific heat of combustion of the systems increase with an increase in nano-aluminum powder content.

Nano-aluminum suspensions in kerosene with a gelling agent were prepared by means of electromagnetic stirring and ultrasonic agitation [125]. With increasing nano-aluminum powder content, the required amount of gellant to form a stable nano-aluminum/kerosene gel system decreased. When the content of nano-aluminum powder was >6%, no further gellant was needed, which indicated that nano-aluminum powder itself acted as a gellant. However, the normal micron-sized aluminum powder cannot act as a gellant. The ultrasonic agitation of nano-aluminum in kerosene achieved a better suspension than electromagnetic stirring. The optimal dispersion time needed to form a nano-aluminum-kerosene gel was 8–10 min by means of ultrasonic agitation.

### 2.12.3.3 Gelling Agents for Kerosene Slurries

A wide range of gelling agents has been evaluated as a means of suspending metal powders in kerosenes and other liquid fuels.

In the early years of rocket propulsion in the 1930s, Sanger tested metal salts of fatty acids (“metal soaps”), latex rubber, Oppanol<sup>®</sup> and other polymers in order to slow down the sedimentation of metal particles. Oppanol<sup>®</sup> B (Producer: BASF)

is a series of medium- and high-molecular-weight polyisobutenes, with an average molecular weight between 40000 and 4000000.

THIXCIN R (Producer: Elementis in the UK) is a non-hygroscopic organic derivative of hydrogenated castor oil that imparts a high degree of thixotropic thickening in mineral and silicone oils, as well as low-polarity aliphatic solvents. Thixatrol ST is an amide of ricinolic acid. These gelling agents need extra time for swelling, deagglomeration, and activation before a stable gel is formed. Other gelling agents are metal soaps, salts of long-chain carbonic (“fatty”) acids such as aluminum octanoate. Even without the addition of suspended metal particles, there may be some incentive to use gelled hydrocarbons, mostly to reduce spillage in the case of a leak and to reduce slosh in the case of launch phase instabilities.

A study of the physical properties of slurries of commercial magnesium, aluminum, and boron powders (particle size 10–66  $\mu\text{m}$ ) suspended in MIL-F-5624-grade JP-3 fuel used metal soaps (magnesium stearate or aluminum octoate) to stabilize the slurries [126]. Physical properties measured included density, apparent viscosity, apparent surface tension, storability, and fuel-flow characteristics. Several of the prepared slurries had physical properties acceptable for combustion research and limited flight use.

Fumed silica, also known under the trade name Cab-O-Sil<sup>®</sup>, is a useful gelling agent for fuels as well as oxidizers. The rheological behavior of gelled JP-8 turbine fuel and gelled rocket propellant RP-1 with fumed silica as a gelling agent was measured and the optimal gel mixing process, gel stability, and rheological parameters showed a significant influence of the added silica amount [127, 128].

The rheology and droplet-burning behaviors of JP-8 and RP-1 gelled with fumed silica were compared with those of MMH gelled with hydroxypropyl cellulose [129]. Droplets of gelled MMH burning in air swelled and had a flexible droplet surface, whereas burning kerosene droplets gelled with fumed silica had a rigid silica structure that remained unburned.

#### 2.12.3.4 Gelled Metallized Kerosene Slurries

There are countless patents on metallized gelled fuels, describing various gelling agents and stabilizing additives. Many of those patents are purely speculative and repetitive, and probably very few were ever put into practice (Table 15). It is obvious that the patent examiners were not trained propellant chemists and that they should have rejected many of these vague patents.

**Table 15:** Summary of patents on metallized kerosene slurries.

| Author                 | Year | Metal(s)  | Gelling agents           | References |
|------------------------|------|-----------|--------------------------|------------|
| Martin                 | 1961 | Mg, Al    | Polyethylene             | [130]      |
| Whaley                 | 1961 | B, Al, Mg | Polyethylene, oleic acid | [131]      |
| White, Chin, and Jones | 1966 | Al, Mg    | Bentone 34               | [132]      |

The higher the density of the hydrocarbon in which the metal particles are suspended, the less likely the metal particles are to settle out of suspension in a gravity field, and the less gelling agent would be needed. In addition to conventional kerosenes such as JP-4 or RP-1, high-energy, high-density hydrocarbon fuels have also been evaluated for gelled metallized fuel formulations and the energy density of those fuels can be increased further by suspending metals or boron in these fuels. Gelled high-density fuels with high volumetric heating values are of interest for extending the range of air-breathing tactical ramjets. High-density liquid hydrocarbons containing suspended metal powders are of interest for applications in air-launched, volume-limited missiles. These fuels must exhibit suitable physical properties over a wide temperature range, long-term storage stability, low toxicity, a very low degree of manufacturing and handling hazard, and very high volumetric heats of combustion.

#### 2.12.3.5 Gelled Boron Kerosene Slurries

Boron-hydrocarbon slurry fuels were prepared, containing 50–60 mass-% of boron powder of 1- $\mu\text{m}$  average particle size in JP-4 and JP-5 fuels [133]. The boron-hydrocarbon mixtures were fluidized by glycerol sorbitan laurate, a surface-active agent, and stabilized by aluminum octoate, a gelling agent. The useful life of a slurry was approximated by the age at which the settled portion of the slurry could no longer be readily redispersed. Satisfactory stability for up to 6 months was observed for several slurries, but some of these slurries were still in a satisfactory physical state after 6 months. The viscosity at low rates of shear varied with the age of the slurry, but did not follow the same pattern for all slurries. The apparent viscosity of the slurry at a low rate of shear increased with increasing boron and aluminum octoate concentrations, but decreased with increasing concentration of glycerol sorbitan laurate. The JP-5 slurries seemed to exhibit a slightly higher viscosity than the corresponding JP-4 slurries, probably because of the higher density of the JP-5.

Surface-modified boron nano-particles were added to jet fuel JP-10 with trioctylphosphine oxide as the stabilizer, which inhibited particle contact and agglomeration [134]. After 6 weeks, a suspension with 12.7 mass-% boron nano-particles was still completely dispersed in the fuel. The addition of 12.7 mass-% boron increased the density and volumetric energy from 0.93 g/ml and 39.4 MJ/l to 0.98 g/ml and 43.4 MJ/l respectively. The suspension flowed freely like liquid fuel and had relatively low viscosity at low temperatures. Boron-kerosene slurries have been tested in ramjet combustors (This may be included in a future *Encyclopedia of Non-Hypergolic Bipropellant Combinations*).

#### 2.12.3.6 Gelled Magnesium Kerosene Slurries

As magnesium is a relatively inexpensive material and in air-breathing engines it has a greater heat of combustion per pound of air than aluminum, the experimental investigation of magnesium slurries has progressed farther than those of either aluminum

or boron. NACA conducted numerous experiments with magnesium slurries, describing the preparation and stabilization of the gels, combustion experiments, and showing examples of pumps, valves, and combustion chambers for metallized kerosenes [135].

A study of the effect of magnesium particles of various equivalent diameters on the apparent viscosity, sedimentation rate, and redispersibility of petrolatum-stabilized magnesium-JP-4 slurries used powders with equivalent diameters of 2.8, 3.7, 7.2, 9.3, 12, and 14.8  $\mu\text{m}$  [136]. As the average particle size of metal was increased from 2.8 to 14.8  $\mu\text{m}$  in slurries containing the same concentration of magnesium, minimums were observed in the apparent viscosity–magnesium concentration curves. Data were also presented showing the effect of various magnesium concentrations with constant particle diameters on these physical properties.

Kerosene JP-4/Mg slurries have been prepared and tested in rocket engines. Ball-milling 200-mesh magnesium powder in JP-4 containing a wetting agent resulted in a useful metallized slurry [137]. Flight testing of magnesium slurries was done in ram-jets [138].

Attempts have been made to reduce the viscosity and improve the pumpability of gels by adding surfactants [139]. For example, the apparent viscosity of a slurry consisting of 49% Mg in JP-1 could be reduced by using 3–5% of a surfactant additive.

In a study of the use of surface-active additives to reduce the viscosity of thick slurries consisting of 50% by weight of 1.5- $\mu\text{m}$  magnesium powder in *n*-decane, it was found that as the slurry became increasingly fluid the magnesium tended to settle more quickly [140]. The viscosity of the slurry was dependent on the concentration and composition of the additive. Removal of part of the moisture (or perhaps other adsorbed components of the air) from the magnesium powder prior to the addition of the *n*-decane resulted in a product with lower viscosity. A complete summary of effects of metal loading, particle size, and additives on viscosity and settling rates of magnesium–kerosene slurries, illustrated with several graphs, was provided in Barnett et al. [141].

Slurry fuels containing extremely small particles of magnesium were prepared by concentrating the dilute slurry product resulting from the shock-cooling of magnesium metal vapors with a liquid hydrocarbon spray [142]. Ninety-five percent by weight of the solid particles formed by this process passed through a 100-mesh screen. The screened product was concentrated by means of a bowl-type centrifuge from 0.5 to more than 50% by weight of solid content to form an extremely viscous, clay-like mass. By the addition of a surface-active agent, this viscous material could be converted into a pumpable slurry fuel. The high viscosity and the two-phase composition of magnesium slurries make it difficult to achieve good atomization and small droplet spray patterns when injected into a combustion chamber [143]. The dielectric constant of metal slurries can be measured as a method for measuring the metal loading and the settling rate of metal slurries in kerosene [144].

### 2.12.3.7 Gelled Aluminum Kerosene Slurries

#### Micron-sized Aluminum–Kerosene Slurries

Butyl-decyl-thiomethylphosphonate was used as a gelling agent for dispersing aluminum in a thixotropic fuel [145]. In an effort to formulate and characterize the properties of Al/RP-1 and non-metallized RP-1 gelled propellants for rocket propulsion systems, 24 different compositions of gelled fuels have been formulated with 5 and 16  $\mu\text{m}$  atomized aluminum powder in RP-1 [146]. The total solids loading in the propellants varied from 5 to 60 mass-%. Storage tests evaluating the stability and rheological characteristics of the fuels showed that the physical separation of the solids occurred in fuels with less than 50 mass-% solid concentration.

The performance of kerosene as a fuel for bipropellant combination can be enhanced by suspending finely distributed metal powders, preferably aluminum or beryllium. In order to prevent the metal powder from settling during storage, the mixture has to be gelled. The amount of metal that can be added is limited by the increasing viscosity of these blends, making them hard to pump and inject into a combustion chamber [119, 120]. Fumed silica Cab-O-sil, ethylcellulose, methylcellulose, agar agar, polypropylene glycol, hydroxymethyl cellulose, carboxymethyl cellulose, and clay were tested as gelling agents for kerosene and UDMH. Agar agar or methylcellulose gave no gelation at 7.5% in kerosene. Cab-O-sil and polypropylene glycol at 7% gave only partial gelation. An organophilic clay complex with polypropylene glycol gave a gel that could be loaded with 30 or 40% 15- $\mu\text{m}$  size aluminum powder. The viscosity values deduced from a Brookfield viscometer and from a rheogram against shear rate or rotations per minute showed that metallized kerosene gels containing 30 and 40% aluminum showed a drastic decrease in viscosity with an increase in shear rate or rotations per minute. Viscosity values had a decreasing trend with increase in temperature, though not very marked.

Aluminum powder made by explosively vaporizing electrically heated aluminum wire (Alex) can be gelled in kerosene using fumed silica as the gelling agent [147]. The metal loading and the higher viscosity make it difficult to achieve small droplet size when injecting metallized gelled kerosenes into a rocket combustion chamber. The spray characteristics of an aluminized gel were tested with an impinging jet like-on-like injector [148, 149].

JET A-1 (JP-8) gels were prepared using inorganic (fumed silica) and organic (Castor oil derivatives and aluminum octanoate) gelling agents [150, 151]. The main parameters varied were dissolver disk rotational speed, dissolver diameter, gellant particle size, gellant content, and temperature history of gelation. Gel stability was investigated in conventional and optical centrifuge tests with rotor speeds up to 3000 rpm at accelerations up to 2500 g, and it was shown that all the aluminum/kerosene gels were stable below 100 g. Viscosity measurements were performed using rotational cone and plate viscosimeters. All gels showed strong shear-thinning behavior. The results could be fitted to existing viscosity laws and were used to compute the predicted pressure drop in gelled propellant rocket injectors and propellant feed lines.

The spray patterns of aluminized gelled Jet A-1 kerosene were examined as a function of shear rates and metal content [152]. Decreasing dynamic shear viscosity values were found with increasing shear rates and increasing viscosity values with increasing Al content. A high-speed camera study of the atomization behavior of the gels with a doublet like-on-like impinging jet injector under ambient conditions with varying pressure and temperature showed different break-up modes of the jets. Low-density decane-based slurries were prepared with powders of mechanically alloyed Al/Li, nano-composite 2B+Ti, and pure aluminum [153].

The combustion of metallized hydrocarbon slurries will be discussed in more detail in a future volume of the *Encyclopedia of Rocket Propellants*, namely in *Encyclopedia of Non-Hypergolic Bipropellant Combinations*.

### Nano-Sized Aluminum-Kerosene Slurries

Nano-aluminum has been extensively studied as an additive to solid propellants, and can also be used as an additive to kerosene. This is probably mostly done for the use of metallized kerosenes in ramjets, but will also be useful for metallized kerosenes in rocket engines. Addition of nano-aluminum to kerosene would not only increase its volume-specific heat of combustion but also shorten the ignition delays in burners. In a ramjet, poor mixing of fuels and air and insufficient flame holding can cause loss of stability and flameout.

The evaporation characteristics of kerosene droplets containing dilute concentrations (0.1, 0.5, and 1.0 mass-%) of ligand-protected aluminum nanoparticles (n-Al) suspended on a silicon carbide fiber were studied at different ambient temperatures (673–1073 K = 400–800 °C) [154]. The evaporation behavior of pure and stabilized kerosene droplets was also examined for comparison. The results showed that at relatively low temperatures (673–873 K = 400–600 °C), the evaporation behavior of suspended kerosene droplets containing dilute concentrations of nano-Al was similar to that of pure kerosene droplets and exhibited two-stage evaporation following the classical  $d^2$ -law. However, at relatively high temperatures (973–1073 K = 700–800 °C), bubble formation and micro-explosions were observed, which were not detected in pure or stabilized kerosene droplets. For all nano-Al suspensions, regardless of the concentration, the evaporation rate remained higher than that of pure and stabilized kerosene droplets within the range 673–1073 K = 400–800 °C. At relatively low temperatures, the evaporation rate increased slightly. At very high temperatures (700–800 °C), the melting of nano-Al particles led to substantial enhancement of evaporation. The maximum increase in the evaporation rate (57%) was observed for the 0.5% nano-Al suspension at 1073 K (800 °C).

The effects of high ambient temperatures and various concentrations of nanoparticles on the auto-ignition and combustion characteristics of heptane-based nano-fluid droplets were examined using single, heptane ( $n\text{-C}_7\text{H}_{16}$ ) droplets containing 0.5, 2.5, or 5.0 mass-% of nano-Al mounted on a silicon carbide fiber that was exposed to a rapid increase in temperature, (from room temperature to temperatures within

the range 873–1123 K = 600–850 °C) at atmospheric pressure, and the auto-ignition and combustion characteristics were observed [155]. The ignition delay, burn rate, and combustion characteristics of pure and stabilized heptane droplets were also examined for comparison.

Nano-powder materials and dispersants were evaluated for enhanced kerosene fuels with higher particle loading fractions [156]. All commercially available nano-sized aluminum particles examined were found to be unsuitable in the as-delivered state for making metallized gelled kerosene. A high fraction of the particles were in the form of undispersable permanent agglomerates made up of many primary particles, represented as an Average Agglomeration Number significantly greater than 10. After removal of the oversized agglomerates through settling and filtration, only an unacceptably small percentage of material remained in the dispersed state (often with a 90% loss).

### 3 Rocket-Grade Kerosene RP-1

It was always assumed that the abbreviation RP stands for **R**ocket **P**ropellant, but other interpretations are **R**efined **P**etroleum-1 (RP-1).

#### 3.1 Production of RP-1

RP-1 is produced by refining crude petroleum feed stocks, in particular hydrotreating by reduction with hydrogen over catalysts. That treatment reduces the sulfur and aromatics content and totally eliminates any olefin content.

As of 2004, there was one vendor for RP-1 in the US, Haltermann Products of Channelview, TX (near Houston, now a division of Monument Chemicals, Inc.), which has been the sole vendor of RP-1 for at least 16 years. Production has been around 300000 gallons/year. It appears that even if the requirements for RP-1 should increase by a factor of 100, sufficient capability for producing this fuel is available in the USA.

In the years leading up to the selection of RP-2, three different grades of RP-1 were specified with an eye toward decreasing the sulfur concentration specification limits: TS-30 (**T**otal **S**ulfur less than 30 ppm, mass/mass, which was similar to typical as-delivered RP-1), TS-5 (**T**otal **S**ulfur less than 5 ppm, mass/mass), and UL RP-1 (**U**ltra**L**ow sulfur, less than 100 ppb, mass/mass). Experience showed that ultralow sulfur RP-1 showed significant performance benefits over TS-5 with only marginally greater costs; thus, this fluid (ultralow) was eventually selected to become “RP-2” (and the RP-1 sulfur limit was lowered from 500 to 30 ppm, mass/mass). Thus, RP-1 and RP-2 have emerged as the primary kerosene rocket propellants for use in US rocket motors. It is noted that the specification for RP-1 and RP-2 allowable aromatic content are the same; however, a lower aromatic content is commonly found in RP-2. Other specifi-

cation limits, including those related to the distillation behavior, viscosity, density, freezing point, and net heat of combustion, are identical for RP-1 and RP-2.

### 3.2 Physical Properties of RP-1

Physical properties of RP-1 and RP-2 were measured and are now available on-line in the NIST Reference Fluid Thermodynamic and Transport Properties (RefProp) computer program [157, 158]. The free NIST mini-REFPROP, which can be downloaded from the web [159], does not contain RP-1 or RP-2 but contains *n*-dodecane as an example. The properties of *n*-dodecane are very similar to those of RP-1 and RP-2 and *n*-dodecane is a constituent of both RP-1 and RP-2.

Because the physical properties of RP-1 and RP-2 can vary over a wide range (within the range specified by MIL-SPEC), surrogate mixtures prepared from known amounts of pure hydrocarbons are sometimes used to calibrate instruments or to standardize analytical methods (see Section 3.3.3).

The density and viscosity, the thermal conductivity of liquid and solid RP-1, the linear coefficient of thermal expansion, the specific heat, and cubical coefficient of thermal expansion of liquid and solid RP-1 were determined [160]. These data are included in Table 16.

The density, velocity of sound, and viscosity of two RP-1 and RP-2 samples were measured with three different instruments [163, 164]. Data at ambient atmospheric pressure were obtained with a rapid characterization instrument from 278 to 343 K that measured both the velocity of sound and density of the liquids. In parallel, adiabatic compressibilities were derived from that data. Densities of the compressed liquids were measured in an automated apparatus from 270 to 470 K and at pressures up to 40 MPa. Viscosities of the two liquids were measured in an open gravitational capillary viscometer at ambient atmospheric pressure from 293 to 373 K. Correlations have been developed to express the measured properties within the estimated uncertainties of the experimental data and to allow extrapolations beyond the range of the measurements. The designation RP-1 has been around for a very long time, but the property requirements of the fuel it describes have changed over time [165]. A melting (freezing) point of a sample of RP-1 was reported to be 224 K (−56 °F), but the MIL SPEC required freezing temperature is 222 K maximum (−60 °F maximum) [85].

#### 3.2.1 Density of RP-1

One of the oldest density determinations of RP-1 found a density of  $0.7987 \pm 0.0005 \text{ g/cm}^3$  at 298 K (25 °C) [160]. The density as a function of temperature within the range 228 to 298 K (−45 to +25 °C) can be calculated from the equation:

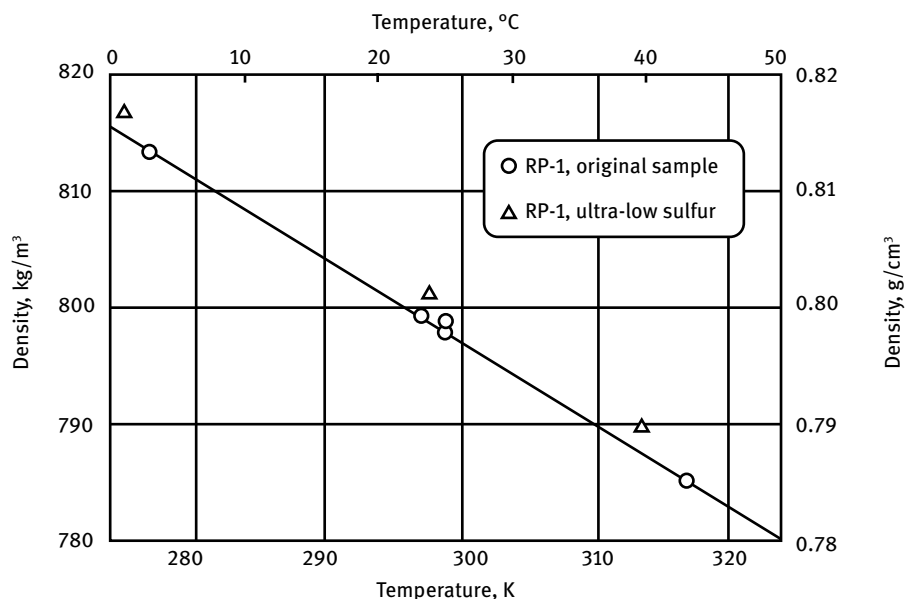
$$\rho = 0.7987 - 0.0036(t - 25.0)$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $t$  is the temperature in °C.



**Table 16:** Physical properties of RP-1.

| Property                                                              | SI units                                        | Other units                                                                                               | References |
|-----------------------------------------------------------------------|-------------------------------------------------|-----------------------------------------------------------------------------------------------------------|------------|
| Freezing point                                                        | 224 K                                           | −56 °F                                                                                                    | [85]       |
|                                                                       | < 222 K                                         | < −60 °F                                                                                                  | [80]       |
| Boiling range                                                         | 455–547 K                                       | 360–525 °F                                                                                                | [80]       |
| Density at 298 K                                                      | 0.7987                                          | —                                                                                                         | [160]      |
|                                                                       | ± 0.0005 g/cm <sup>3</sup>                      |                                                                                                           |            |
| Cubical coefficient of thermal expansion of liquid from −40 to +25 °C | —                                               | $(8.7 \pm 0.1) \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$                                              | [160]      |
| Linear coefficient of thermal expansion of solid from −190 to −50 °C  | —                                               | $(61 \pm 4) \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$                                                 | [160]      |
| Adiabatic compressibility                                             | $6.41 \times 10^{-7} \text{ kPa}^{-1}$ at 294 K | —                                                                                                         | [161]      |
| Isothermal compressibility                                            | $5.8 \times 10^{-7} \text{ kPa}^{-1}$ at 283 K  | —                                                                                                         |            |
| Velocity of sound, liquid, at 298 K                                   | 1300 m/s                                        | —                                                                                                         | [161]      |
| Vapor pressure                                                        | 2.1–5.5 kPa at 293 K                            | 0.3–0.8 psia at 68 °F                                                                                     | [160]      |
| Kinematic viscosity                                                   | 2.45 mm <sup>2</sup> /s at 293 K                | 2.45 cSt at 68 °F                                                                                         | [160]      |
| Kinematic viscosity                                                   | < 16.5 mm <sup>2</sup> /s at 239 K              | < 16.5 cSt at −30 °F                                                                                      | [80]       |
| Dynamic viscosity at 293 K                                            | —                                               | 1.96 cPs                                                                                                  | [160]      |
| Thermal conductivity, liquid                                          | —                                               | $(332 \pm 5) \times 10^{-6} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^{\circ}\text{C}^{-1}$ at 28 °C    | [160]      |
| Thermal conductivity, solid                                           | —                                               | $(6.4 \pm 1.0) \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ }^{\circ}\text{C}^{-1}$ at −78 °C | [160]      |
| Heat capacity $c_p$ , at 301 K                                        | —                                               | $0.53 \text{ cal g}^{-1} \text{ }^{\circ}\text{C}^{-1}$                                                   | [160]      |
| Enthalpy of formation $\Delta H_f^{298}$                              | −5606 J/g                                       | −1340 cal/g                                                                                               | [37]       |
|                                                                       | −24717.7 J/mol                                  | −5.908 kcal/mol                                                                                           | [162]      |
| Lower (net) heat of combustion $\Delta H_{\text{comb}}$               | 43328 kJ/kg                                     | 18640 BTU/lb                                                                                              | [85]       |
| Flash point                                                           | > 333 K                                         | > 140 °F                                                                                                  | [80]       |



**Figure 1:** Density of RP-1. (Reproduced and modified from [166].)

The density of RP-1 was determined by the Archimedes method with an aluminum sinker between 274 and 316 K [166] (Figure 1). The density can be calculated from the equation:

$$\rho = 815.2 - 0.6778t - 5.316 \times 10^{-4}t^2$$

where  $\rho$  is the density in kg/m<sup>3</sup> and  $t$  is the temperature in °C.

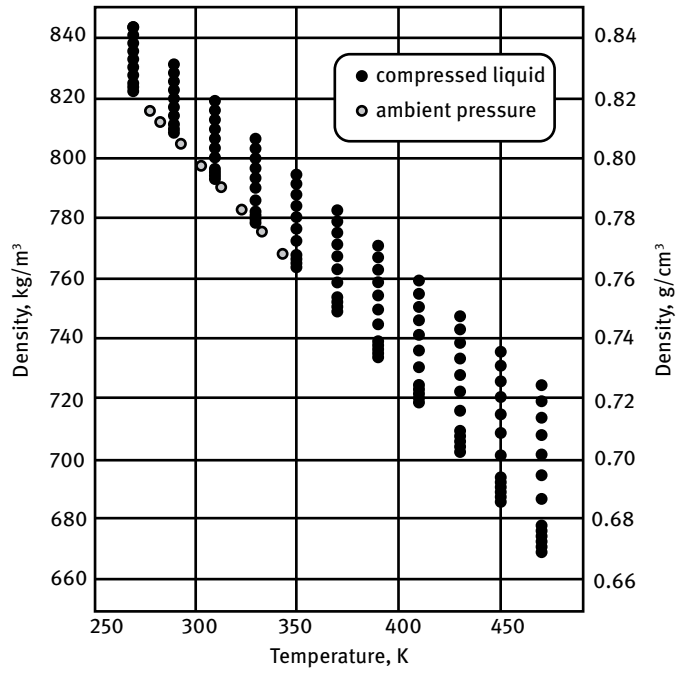
The density of RP-1 has been measured with a density and sound speed analyzer DSA 5000, Anton-Paar Corporation from 278 to 343 K at ambient (0.083 MPa) pressure and compressed liquid density measurements were made with a fully automated densimeter for elevated pressures between 0.083 and 40 MPa [163, 164]. The density of RP-1 as a function of temperature and pressure is illustrated in Figure 2. In Figure 2, the highest pressurized data point was taken at 40 MPa and the lowest data point was taken at 0.5 MPa.

The density of RP-1 at atmospheric pressure can be calculated from the equation:

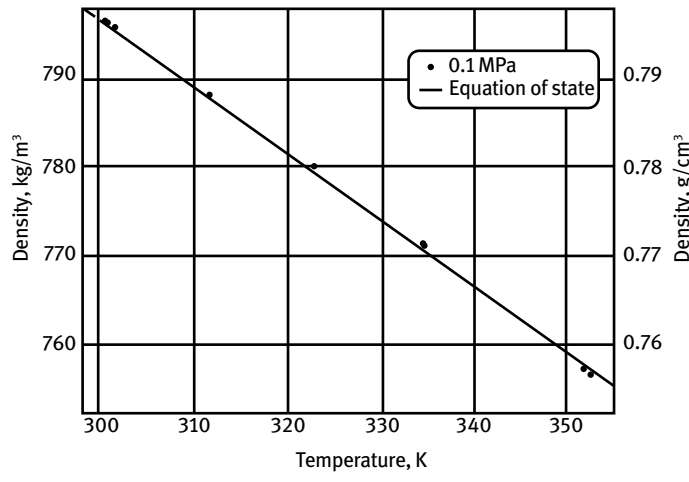
$$\rho = 287.67129 \times 0.53365016^{-\left[1 + \left(\frac{1-T}{574.26284}\right)^{0.6288664}\right]}$$

where  $\rho$  is the density in kg/m<sup>3</sup> and  $T$  is the temperature in kelvin.

The density of RP-1 has been measured with a constant-volume piezometer immersed in a precision liquid thermostat within the temperature range 301 to 745 K and at pressures up to 60 MPa [167]. The uncertainty of density, pressure, and tempera-



**Figure 2:** Density of RP-1 as a function of temperature and pressure. (Republished and modified from [163].)

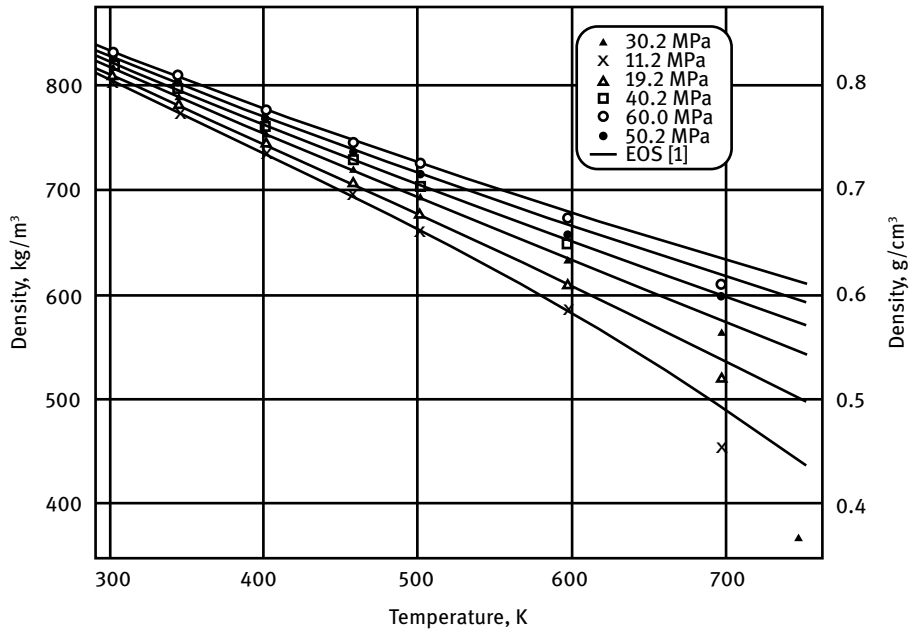


**Figure 3:** Measured and calculated density of RP-1 as a function of temperature at ambient atmospheric pressure. (Reprinted and modified from [167], with permission from ©2010 Elsevier; permission conveyed through RightsLink.)

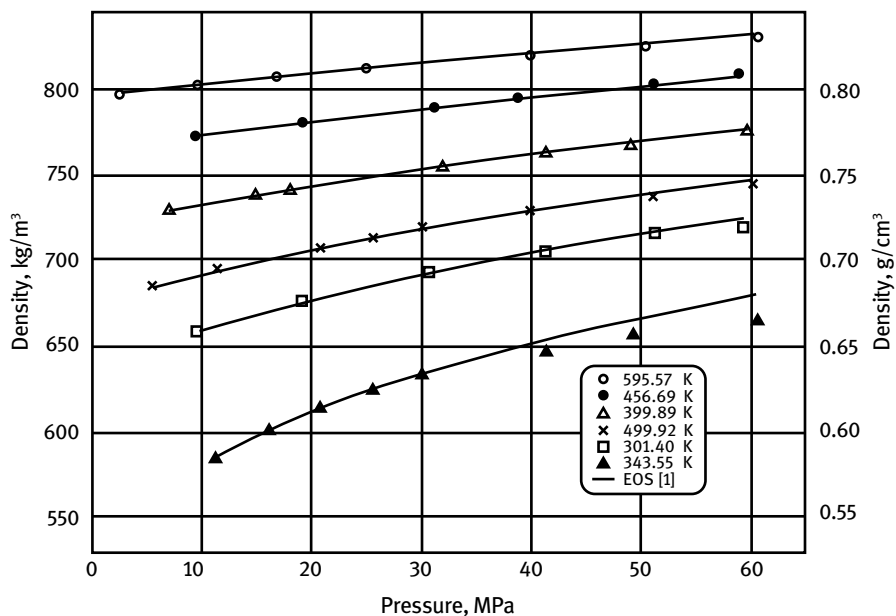
**Table 17:** Densities of RP-1 as a function of temperature at atmospheric pressure.

| Temperature<br>K | Density<br>g/cm <sup>3</sup> |
|------------------|------------------------------|
| 300.55           | 0.7966                       |
| 300.75           | 0.7965                       |
| 301.40           | 0.7959                       |
| 311.55           | 0.7881                       |
| 322.85           | 0.7800                       |
| 334.50           | 0.7712                       |
| 334.55           | 0.7710                       |
| 351.80           | 0.7568                       |
| 352.55           | 0.7562                       |

Data source: [167]

**Figure 4:** Measured and calculated values of density of RP-1 as a function of temperature at various selected isobars (interpolated data). (Reprinted and modified from [167], with permission from ©2010 Elsevier; permission conveyed through RightsLink.)

ture measurements were estimated to be 0.1%, 0.05%, and 15 mK respectively. The measured values of density were compared with data reported in the literature and with values calculated from a surrogate mixture model (via the equation of state). The average absolute deviation (AAD) between the presented data and the values reported in the literature was only 0.13% (Figure 3; Table 17). In addition to density as a function



**Figure 5:** Measured and calculated values of density of RP-1 as a function of pressure at various isotherms. (Reprinted and modified from [167], with permission from ©2010 Elsevier; permission conveyed through RightsLink.)

of temperature at ambient atmospheric pressure, densities were measured at elevated temperatures and elevated pressures under conditions similar to those encountered in the cooling channels of bipropellant rocket engines (Figures 4 and 5; Table 18).

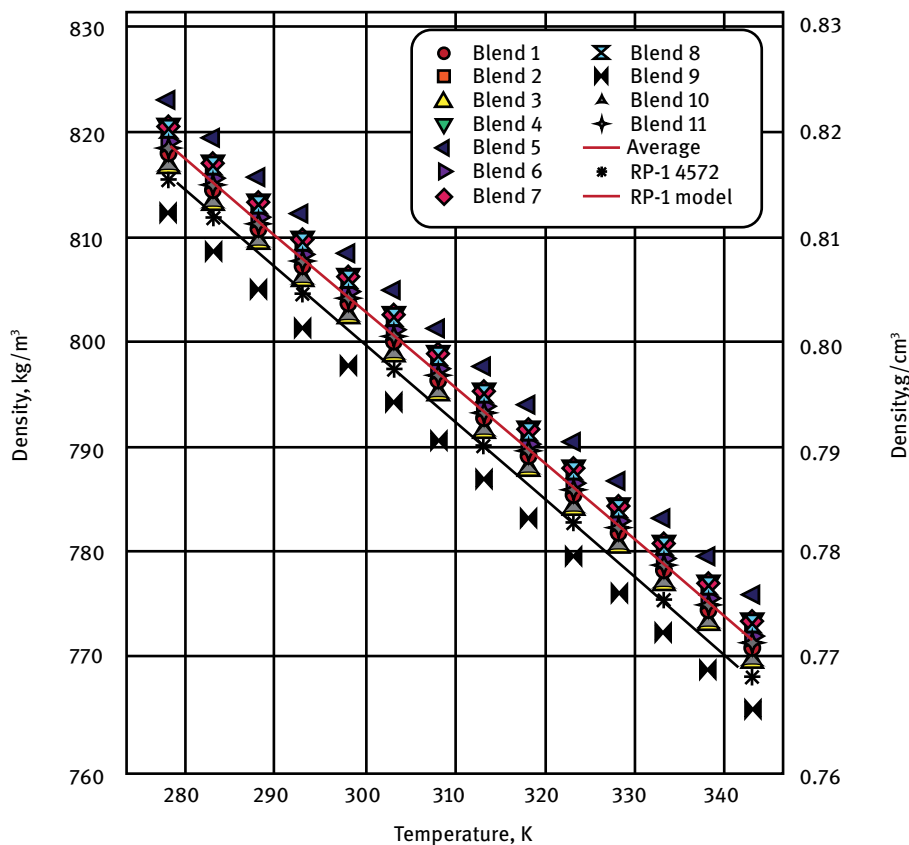
The density of eleven synthetic samples of RP-1 was measured using a commercial density and sound speed analyzer, the DSA 5000 from Anton Paar, which could simultaneously measure these two properties over the temperature range 278 to 343 K [161] (Figure 6). The variability observed in density over the 11 RP-1 samples was relatively constant as a function of temperature, ranging from 1.3% at 278 K to 1.4% at 343 K. The average density is shown as a red solid line.

**Table 18:** Densities of RP-1 at elevated temperatures and pressures.

| Temperature, K      | Pressure, MPa | Density, g/cm <sup>3</sup> |
|---------------------|---------------|----------------------------|
| 301.4               | 2.53          | 0.7976                     |
|                     | 9.63          | 0.8024                     |
|                     | 16.83         | 0.8069                     |
|                     | 25.01         | 0.8120                     |
|                     | 40.02         | 0.8196                     |
|                     | 50.42         | 0.8251                     |
|                     | 60.72         | 0.8303                     |
| 399.89              | 7.003         | 0.7293                     |
|                     | 14.94         | 0.7395                     |
|                     | 18.04         | 0.7425                     |
|                     | 32.03         | 0.7552                     |
|                     | 41.39         | 0.7616                     |
|                     | 49.10         | 0.7672                     |
|                     | 59.80         | 0.7751                     |
| 499.92              | 9.603         | 0.6590                     |
|                     | 19.08         | 0.6765                     |
|                     | 30.71         | 0.6935                     |
|                     | 41.40         | 0.7050                     |
|                     | 51.33         | 0.7161                     |
|                     | 59.39         | 0.7195                     |
| 695.10 <sup>a</sup> | 11.22         | 0.4536                     |
|                     | 16.26         | 0.5012                     |
|                     | 21.32         | 0.5322                     |
|                     | 24.83         | 0.5472                     |
|                     | 30.84         | 0.5636                     |
|                     | 41.08         | 0.5843                     |
|                     | 50.18         | 0.5976                     |
| 745 <sup>a</sup>    | 59.79         | 0.6074                     |
|                     | 11.28         | 0.2673                     |
|                     | 15.59         | 0.2958                     |
|                     | 23.54         | 0.3394                     |
|                     | 30.05         | 0.3677                     |
|                     | 40.84         | 0.4006                     |

<sup>a</sup> Incipient decomposition of RP-2

Data source: [167]



**Figure 6:** Density of RP-1 as a function of temperature. (Reproduced and modified from [161].)

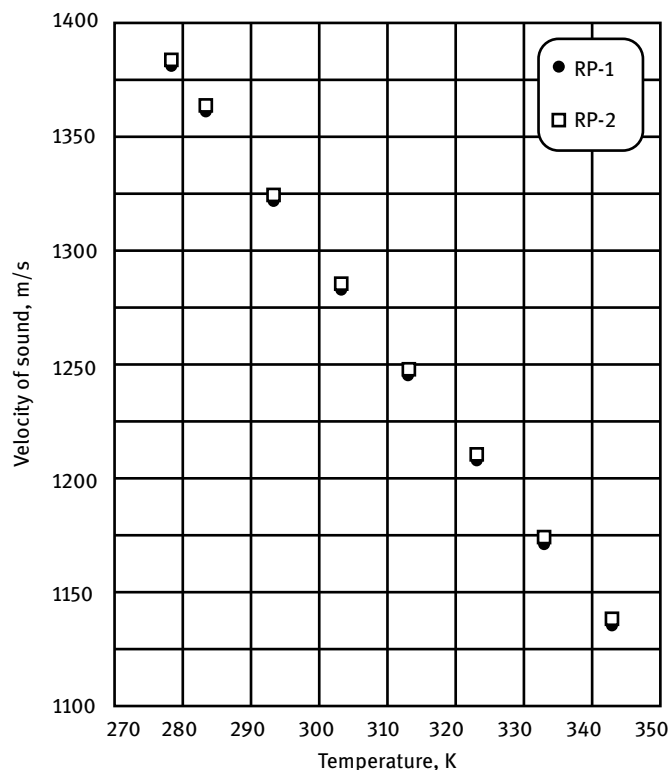
### 3.2.2 Velocity of Sound and Compressibility of RP-1

The velocity of sound in RP-1 and RP-2 was measured with a density and sound speed analyzer DSA 5000, Anton-Paar Corporation, at ambient (0.083 MPa) pressure [163]. The velocity of sound of RP-1 and RP-2 as a function of temperature is illustrated in Figure 7.

Adiabatic compressibilities in liquids can be calculated from sonic velocity data with the aid of the following equation:

$$\beta_a = \frac{1}{\rho c^2}$$

where  $\beta_a$  is the adiabatic compressibility in  $\text{m}^2/\text{N}$ ,  $\rho$  is the density in  $\text{g}/\text{m}^3$ , and  $c$  is the velocity of sound in  $\text{m}/\text{s}$ . The adiabatic compressibility of RP-1 and RP-2 is illustrated in Figure 8.



**Figure 7:** Velocity of sound of RP-1 and RP-2 as a function of temperature. (Reproduced and modified from [163].)

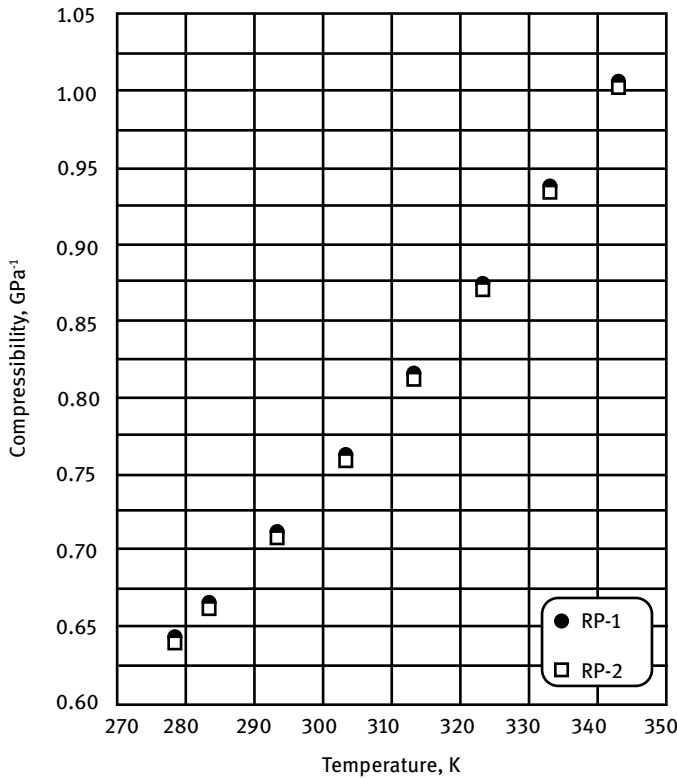
The temperature dependence of the velocity of sound of RP-1 can be expressed by the polynomial equation:

$$v = 2797.7044 - 6.1546685 T + 3.8195817 \times 10^{-3} T^2$$

where  $v$  is the velocity of sound in m/s and  $T$  is the temperature in kelvin.

In a similar series of tests, the velocity of sound of 11 synthetic samples of RP-1 was again measured using a commercial density and sound speed analyzer, the DSA 5000 from Anton Paar, which could simultaneously measure these two properties over the temperature range from 278 to 343 K [161] (Figure 9). The variability observed in sound speed over the 11 RP-1 samples was relatively constant as a function of temperature, ranging from 0.6% at 278 K to 0.8% at 343 K. The average velocity of sound is shown as a red solid line.

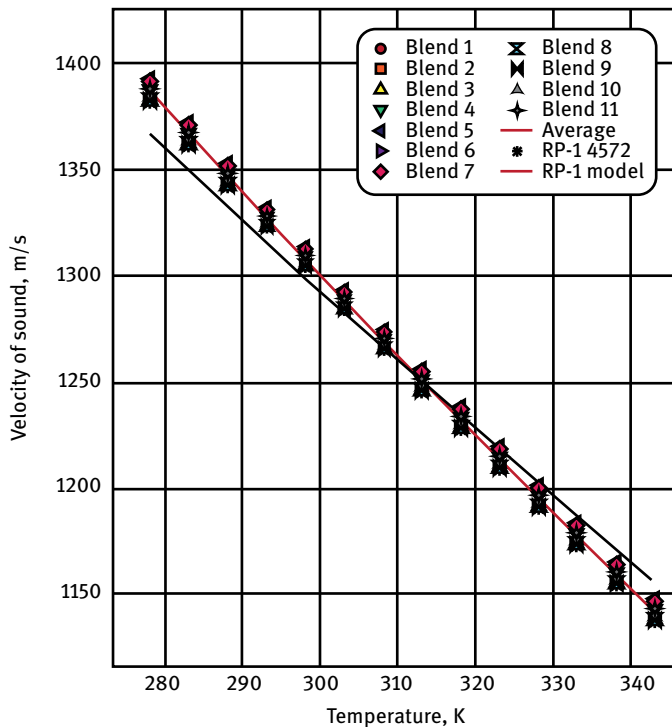




**Figure 8:** Adiabatic compressibility of RP-1 and RP-2. (Reproduced and modified from [163].)

Based on the velocity of sound data shown in Figure 9, the adiabatic compressibility of RP-1 was calculated using known equations. The adiabatic compressibility of RP-1 as a function of temperature is shown in Figure 10. The average compressibility is shown as a red solid line. Single-point adiabatic compressibility of RP-1 was listed as  $6.41 \times 10^{-7} \text{ kPa}^{-1}$  at 294 K and single-point isothermal compressibility of RP-1 was listed as  $5.8 \times 10^{-7} \text{ kPa}^{-1}$  at 283 K.

Generally, as a first approximation, it has been assumed that kerosenes with the same density and viscosity all have the same compressibility and coefficients of thermal expansion. This assumption has been applied to RP-1 [25]. Figure 11 shows the isothermal compressibility of RP-1 as a function of temperature. The auxiliary variable is Jessup's volume modulus. Numerical data for isothermal compressibility of RP-1 are listed in Table 19. These are the same numbers that Figure 11 is based on. The numbers



**Figure 9:** Velocity of sound in RP-1 as a function of temperature. (Reproduced and modified from [161].)

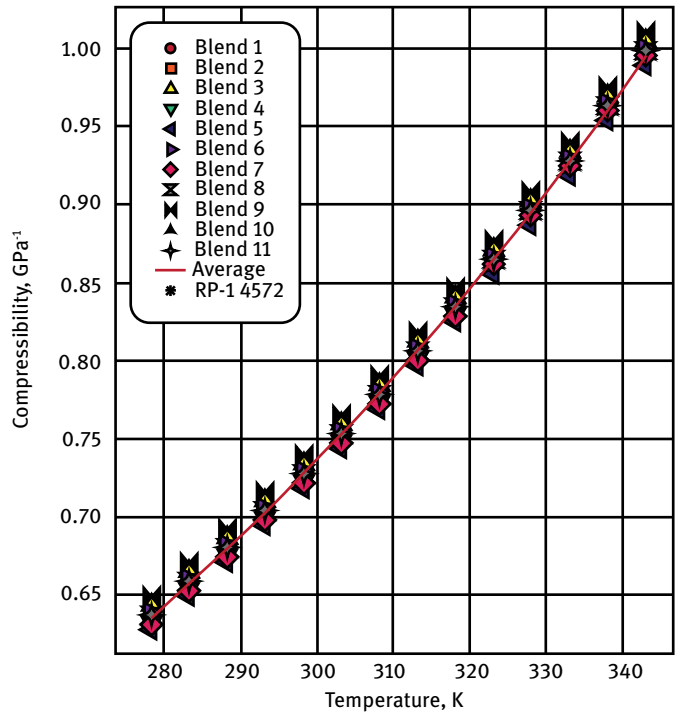
next to the curves in Figure 11 are the numbers in the first column of Table 19. Jessup's volume modulus is defined as:

$$J = \frac{1}{d \sqrt{\log(1000 \times S)}}$$

where  $d$  is the density at 289 K (60 °F) and  $S$  is the kinematic viscosity at 311 K (100 °F).

### 3.2.3 Vapor Pressure of RP-1

The vapor pressure of RP-1 varies widely, depending on the source of the propellant. Even samples that meet the fractionated distillation curve requirements of the MIL-SPEC may differ from one sample to another when measuring the vapor pressure as a function of temperature. When developing surrogate fuels, the formulators have tried to match the vapor pressure curves of RP-1 and the surrogate, but that is not always a close match. There are surprisingly few data on vapor pressure of RP-1 (or

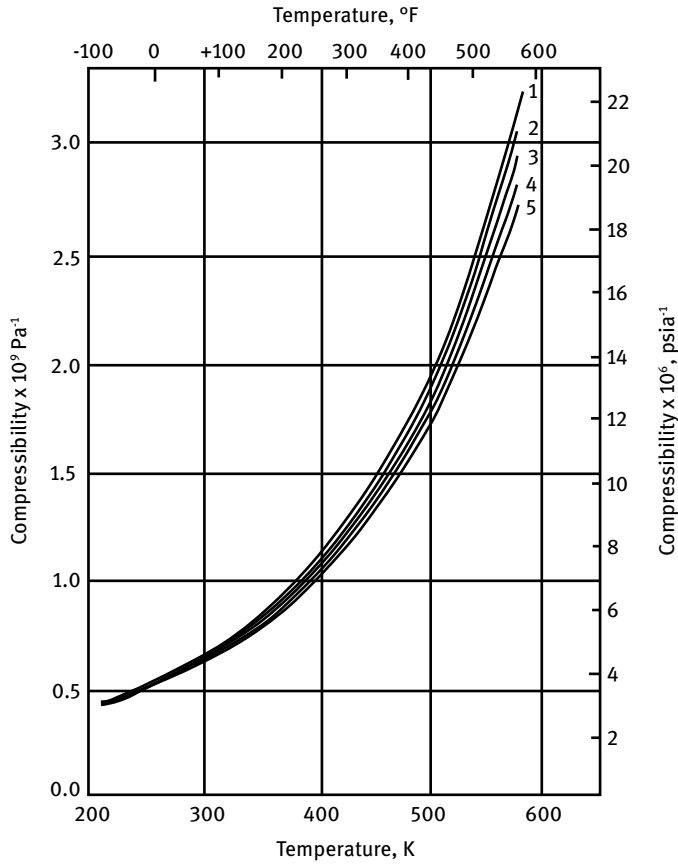


**Figure 10:** Adiabatic compressibility of RP-1 as a function of temperature. (Reproduced and modified from [161].)

**Table 19:** Isothermal compressibility of RP-1.

| No. | Jessup's<br>volume<br>modulus | Compressibility unit: 10 <sup>-7</sup> kPa <sup>-1</sup> |       |       |       |       |       |
|-----|-------------------------------|----------------------------------------------------------|-------|-------|-------|-------|-------|
|     |                               | Temperature                                              |       |       |       |       |       |
|     |                               | 32                                                       | 86    | 167   | 302   | 437   | °F    |
|     |                               | 0                                                        | 30    | 75    | 150   | 225   | °C    |
|     |                               | 273.1                                                    | 303.1 | 348.1 | 423.1 | 498.1 | K     |
| 1   | 0.64                          | 5.48                                                     | 6.22  | 7.64  | 11.31 | 17.11 | 26.97 |
| 2   | 0.66                          | 5.54                                                     | 6.29  | 7.80  | 11.63 | 17.62 | 28.20 |
| 3   | 0.68                          | 5.60                                                     | 6.39  | 7.95  | 11.96 | 18.20 | 29.30 |
| 4   | 0.70                          | 5.64                                                     | 6.47  | 8.12  | 12.27 | 18.78 | 30.45 |
| 5   | 0.72                          | 5.68                                                     | 6.58  | 8.28  | 12.60 | 19.36 | 31.61 |

Data source: [25]



**Figure 11:** Isothermal compressibility of RP-1 as a function of temperature. (Republished and modified from [25], with permission of ©1959 American Institute of Aeronautics & Astronautics; permission conveyed through Copyright Clearance Center Inc.)

RP-2) in the literature. If no other data are available, the vapor pressure of *n*-dodecane can be used as a surrogate fluid. The vapor pressure of RP-1 as a function of temperature has been measured before and after trace volatiles were removed (Figure 12). The center curve showing the average vapor pressure after trace volatiles are removed is generally used for calculations.

### 3.2.4 Viscosity of RP-1

The viscosity of RP-1 was measured by an open gravitational capillary Ubbelohde viscometer by a method described in ASTM method D 445-03 [166]. The kinematic viscosity of RP-1 as a function of temperature is shown in Figure 13.

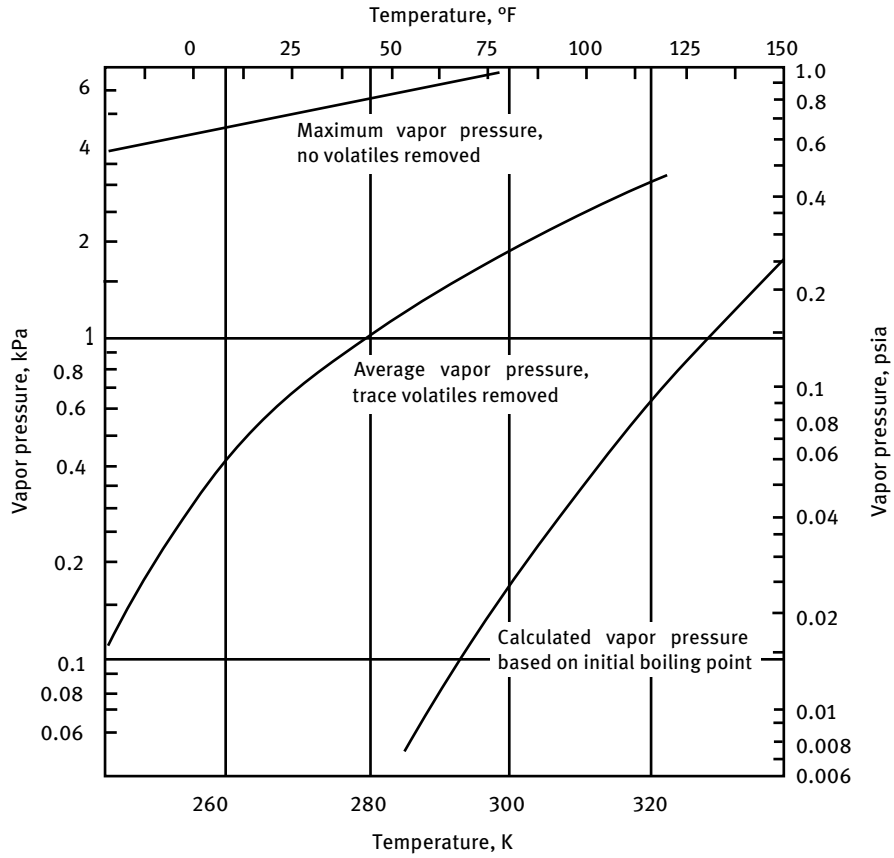


Figure 12: Vapor pressure of RP-1 before and after removing trace volatiles.

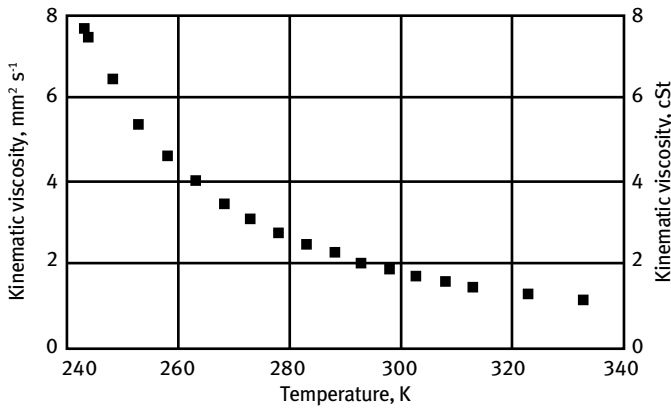


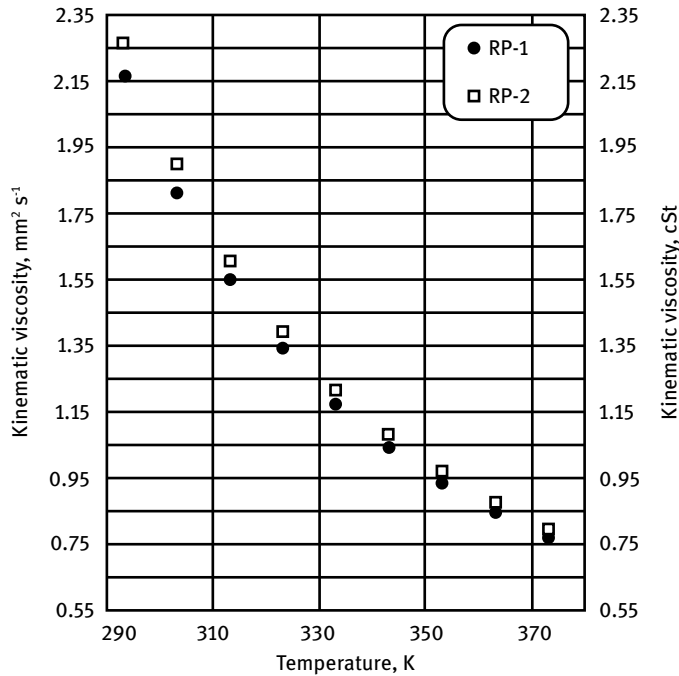
Figure 13: Kinematic viscosity of RP-1 as a function of temperature. (Reproduced and modified from [166].)

The viscosity of two RP-1 and RP-2 samples have been measured in an open gravitational capillary viscometer at ambient atmospheric pressure from 293 to 373 K [163, 164] (Table 20 and Figure 14). Correlations have been developed to express the measured properties within the estimated uncertainties of the experimental data and to allow extrapolations beyond the range of the measurements.

**Table 20:** Viscosity of RP-1

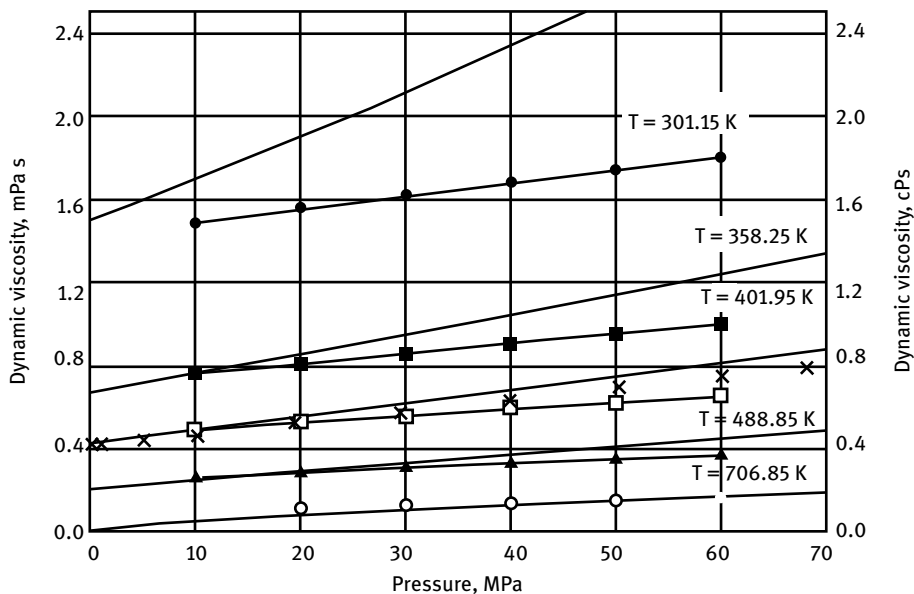
| Temperature $T$ | Kinematic viscosity $\nu$<br>$\text{mm}^2 \text{s}^{-1}$ | Dynamic viscosity $\eta$<br>$\text{mPa s}$ |
|-----------------|----------------------------------------------------------|--------------------------------------------|
| 373.15          | 0.7678                                                   | 0.5727                                     |
| 363.15          | 0.8445                                                   | 0.6362                                     |
| 353.15          | 0.9335                                                   | 0.7103                                     |
| 343.15          | 1.042                                                    | 0.8007                                     |
| 333.15          | 1.173                                                    | 0.9100                                     |
| 323.18          | 1.341                                                    | 1.050                                      |
| 313.12          | 1.549                                                    | 1.225                                      |
| 303.18          | 1.814                                                    | 1.447                                      |
| 293.38          | 2.166                                                    | 1.743                                      |

Data source: [163,164]



**Figure 14:** Kinematic viscosity of RP-1 and RP-2 as a function of temperature. (Modified from [163, 164].)

The viscosity of RP-1 has been measured with a capillary flow technique at high temperatures and high pressures [168]. Measurements were made at seven isobars (0.101, 10, 20, 30, 40, 50, and 60 MPa) over the temperature range 301 to 744 K, up to thermal decomposition temperature. The combined expanded uncertainty of the viscosity, pressure, and temperature measurements at 0.95 confidence level with a coverage factor of  $k=2$  was estimated to be 2%, 0.05%, and 0.02 K respectively. The reliability and accuracy of the experimental method and correct operation of the experimental apparatus were confirmed with comparison measurements on pure toluene for two selected isotherms of 583.15 and 603.15 K at pressures between 10 and 40 MPa. The experimental and calculated values for the viscosity of pure toluene from NIST/REFPROP showed excellent agreement within their experimental uncertainty. The measured values of viscosity for RP-1 were compared with the values predicted from a surrogate mixture model (NIST/REFPROP). The significant effect of thermal decomposition (thermal stress) on the measured values of viscosity of RP-1 at high temperatures (above 650 K) limited the upper temperature up to which measurements could be extended. As Figure 15 shows, at constant temperatures the viscosity of RP-1 increases almost linearly with increasing pressure. Also, Figure 15 demonstrates that the experimental rate of pressure changes  $(\partial\eta/\partial P)_T$  along the various isotherms (dotted lines) is considerably different from the predictive behavior of  $\eta$ - $P$  isotherms (solid lines), especially at low temperatures. The measured values of the viscosity of

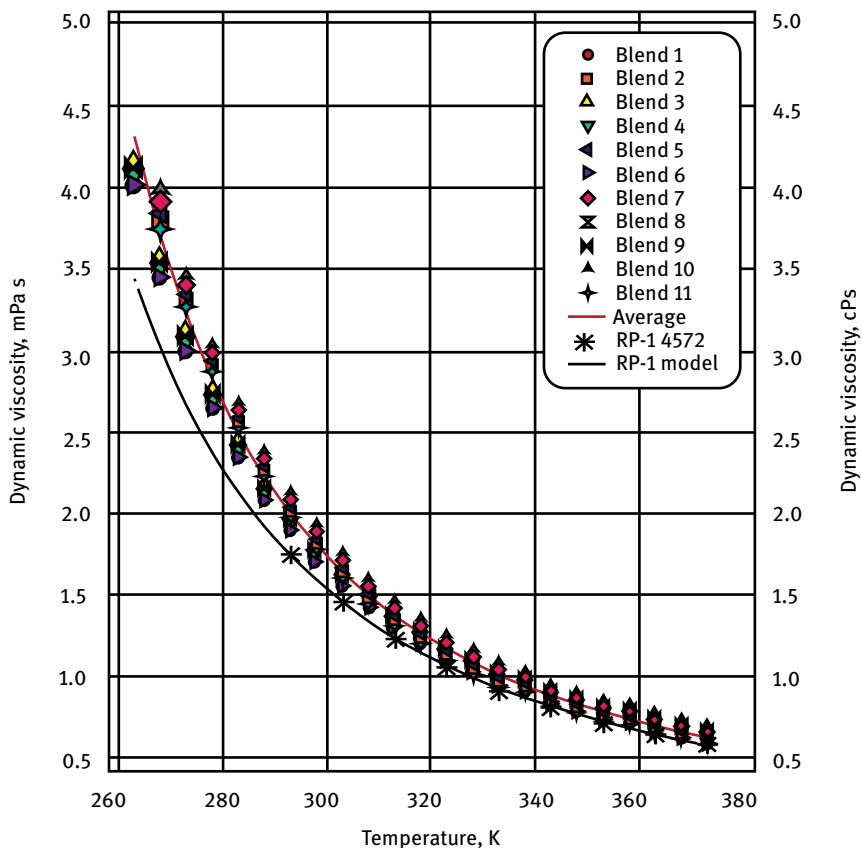


**Figure 15:** Isotherms of dynamic viscosity of RP-1 as a function of pressure. (Reprinted and modified from [168], with permission from ©2019 Elsevier; permission conveyed through RightsLink.)

RP-1 can be best represented by fitting  $\ln \eta$  to a linear Arrhenius correlation model, which is consistent with the theory of rate processes.

Comparing viscosity of RP-1 according to Abdulagatov and Akhmedova-Azizova [168] with viscosity data for RP-2 reported by Laesecke and Cousins [169], it appears that at all pressures RP-2 has a higher viscosity than RP-1.

The viscosity and density of 11 synthetic samples of RP-1 were measured using a commercial viscodensimeter, the SVM 3000 from Anton Paar, which can simultaneously measure viscosity and density over the temperature range 263 to 373 K and at ambient pressure. Density was measured with a vibrating-tube densimeter made of borosilicate glass. Viscosity was measured with a Stabinger rotating concentric cylinder viscometer [161] (Figure 16). The variability observed in dynamic viscosity over the 11 RP-1 samples was significantly larger than that observed for either density or velocity of sound and, unlike the previous properties, it changed considerably with temperature. The overall variability for the 11 samples ranged from 14.1% at 263 K to



**Figure 16:** Dynamic viscosity of RP-1 as a function of temperature. (Reproduced and modified from [161].)



6.2% at 373 K. The mean dynamic viscosity is shown as a solid red line. A similar graph is available for kinematic viscosity on the same samples.

Single-point kinematic viscosity data for RP-1 were reported as  $3.02 \times 10^{-6} \text{ m}^2/\text{s}$  ( $3.02 \text{ cSt}$ ) at 274 K and  $2.17 \times 10^{-6} \text{ m}^2/\text{s}$  ( $2.17 \text{ cSt}$ ) at 323 K [85]. Historical data for absolute viscosity of RP-1 are displayed in Figure 17.

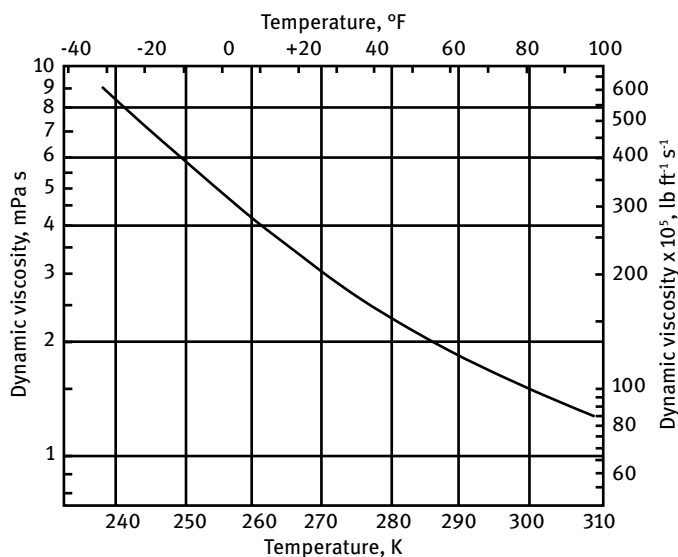
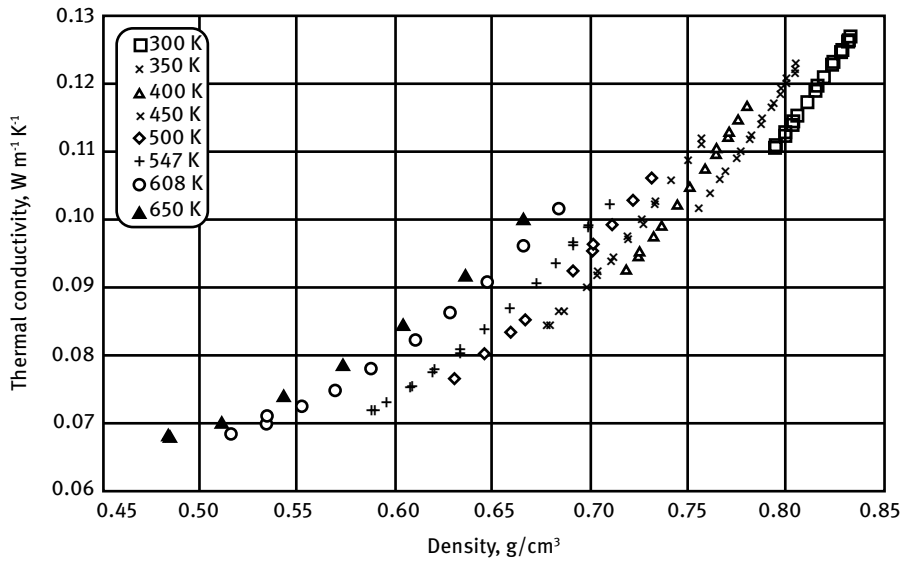


Figure 17: Historical data for absolute viscosity of RP-1.

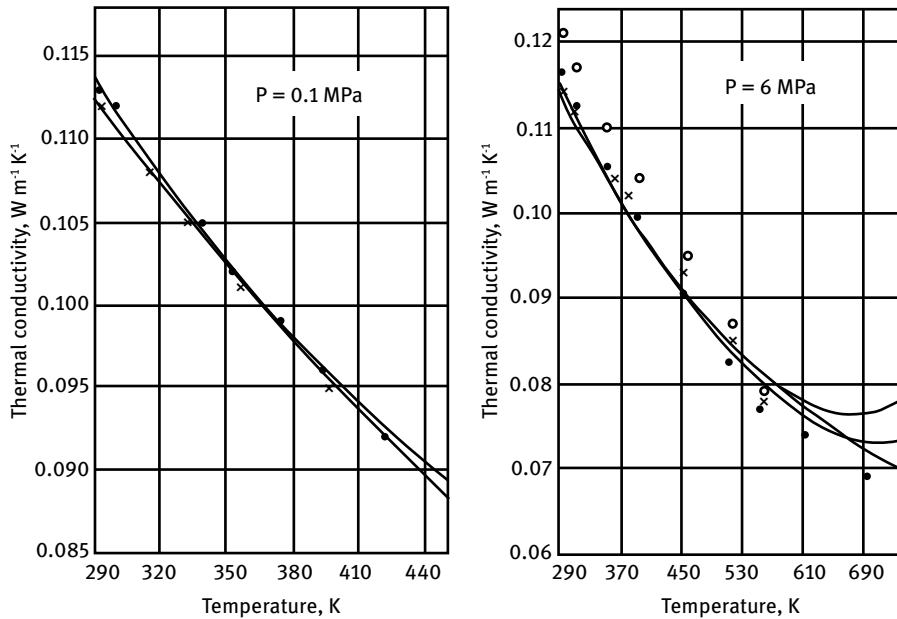
### 3.2.5 Thermal Conductivity of RP-1

The thermal conductivity of RP-1 was measured with a hot wire method at pressures up to 70 MPa [85]. Measurements were made at increasing temperatures on the original sample from 300 to 600 K. At the end of the experiments, in particular those at higher temperatures, the hot wires were encrusted with coke deposits, which hindered further measurements. The thermal conductivity of RP-1 at very high pressures is illustrated in Figure 18, which shows the sample density instead of pressure on the abscissa axis of the graph. Thermal conductivity increased with increasing pressure and with temperature. Density decreased with increasing temperature.

The thermal conductivity of liquid RP-1 was measured by a coaxial-cylinder (steady-state) technique. With this method, the heat generated in an inner emitting cylinder is conducted radially outward through the narrow, fluid-filled annulus to a coaxial receiving cylinder [170]. The gap between cylinders (thickness of the liquid annulus) was  $d = 0.97 \times 10^{-3} \text{ m}$ . The measured values of thermal conductivity of RP-1 agreed well (within 1.0%) with the reported literature data and the values calculated with a reference correlation equation for a surrogate hydrocarbon mixture. The RP-1

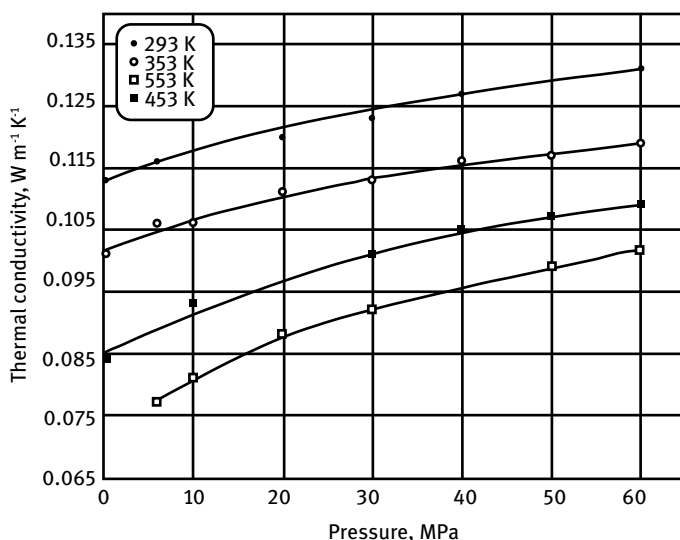


**Figure 18:** Thermal conductivity of RP-1 at very high temperatures and pressures. (Reproduced and modified from [166].)



**Figure 19:** Thermal conductivity of RP-1 as a function of temperature for two different pressures, 0.1 and 6 MPa. (Reprinted and adapted from [170], with permission from ©2009 American Chemical Society; permission conveyed through RightsLink.)

sample measured in this work came from the same batch as that used by Magee et al. [166]. The thermal conductivity of RP-1 as a function of temperature is shown in Figure 19 for two different pressures, 0.1 and 6 MPa. The data points marked with three different symbols are from three consecutive runs with fresh samples. The solid line is what is expected for a surrogate model from Magee et al. [166] and the dashed lines are what is expected for a surrogate model from Huber et al. [19]. The two curves are very similar, except that one is for sea-level atmospheric pressure and the other is for high pressure (6 MPa). Figure 20 shows the thermal conductivity of RP-1 as a function of pressure for four isotherms.



**Figure 20:** Thermal conductivity of RP-1 as a function of pressure for four isotherms. (Reprinted and adapted from [170], with permission from ©2009 American Chemical Society; permission conveyed through RightsLink.)

### 3.2.6 Heat Transfer Coefficient of RP-1

A series of tests to measure the heat transfer in RP-1 and to examine coking problems were performed in a NASA Heated Tube Test Facility [171]. The facility simulates regenerative cooling by flowing room-temperature RP-1 through resistively heated copper tubing. A regression analysis was performed on the data to determine the heat transfer correlation for the Nusselt number as a function of Reynolds and Prandtl numbers. Each measurement and calculation was analyzed to identify sources of uncertainty, including RP-1 property variations. Density, enthalpy, thermal conductivity, and viscosity data for RP-1 fuel were used to calculate several parameters, including the Re and Pr numbers used in the heat transfer correlation. Although RP-1 has been used extensively in the rocket industry, these properties have not been closely studied at tem-

peratures and pressures above standard conditions. Data from a prediction model, which relates properties to a known reduced state based on the principal of corresponding states, was used to determine fluid properties in the data reduction. Similar models and limited data are available for comparison, but the data are quite different from each other. The temperature at the inner wall of the tube was calculated by modeling the resistivity of the tube, the energy input, and the outer wall temperature. The difference between the inner and outer wall temperatures is about 5.5 K (10 °F). The uncertainty in the inner wall temperature from modeling assumptions in this calculation was estimated as  $\pm 1.1$  K ( $\pm 2$  °F). The enthalpy at the inlet of the tube was determined from the fluid temperature and the property data. Downstream from this point, the enthalpy was calculated at the location of each thermocouple by modeling the energy input over each section of the tube. The mean fluid temperature at each location was then determined from the enthalpy using the property data. Assuming a reasonably good model, the uncertainty of this calculation was estimated to be about 3%. It was shown that the overall systematic uncertainty in a predicted Nu number can be as high as 35%. The random uncertainty in the heat transfer correlation is significant and can be as high as 12%. The overall uncertainty in Nu number is the RSS of the random and systematic components and could be as high as 36%. This has a significant impact on engine design parameters. Additional (somewhat outdated) information on heat transfer to RP-1 is published in Greenfield [172], Hines [173], and Seader and Wagner [174].

While studying the heat transfer to RP-1 or diethylcyclohexane under supercritical conditions and with very high wall temperatures, the investigators noticed audible pressure oscillations within the frequency range from 1 to 10 kHz, which led to improved heat transfer, but also caused severe cavitation erosion damage of the surface of the metal tubes [175]. The amplitude of the oscillations was  $\pm 1.4$  MPa ( $\pm 14$  atm). It is suspected that such oscillations in the cooling jackets can couple with combustion oscillations in the combustion chamber and lead to undesirable or even dangerous overall combustion instabilities. The heat-transfer oscillations started only after the heat transfer exceeded a certain reproducible threshold. If the inlet temperature of RP-1 is 339 K (66 °C), the pressure is 4.83 MPa (47.7 atm), the flow velocity 11.9 m/s, and the temperature difference  $T_{\text{wall}} - T_{\text{fluid}} = 278$  K (278 °C); the nominal heat transfer is  $326 \text{ W cm}^{-2}$  ( $= 78 \text{ cal cm}^{-2} \text{ s}^{-1}$ ). Once the temperature difference  $T_{\text{wall}} - T_{\text{fluid}}$  exceeds 340 K (340 °C), heat transfer increases steeply and oscillations can occur. The vibration produced audible noise, increased heat transfer, and resulted in tube splits and pinhole leaks. Similar observations were made with other hydrocarbons [33] and liquid hydrogen.

### 3.2.7 Thermodynamic Properties of RP-1

#### 3.2.7.1 Heat Capacity of RP-1

Heat capacities at constant pressure were measured with a flow calorimeter that operates at conditions up to 671 K and 60 MPa. The isobaric heat capacity of RP-1 has been measured with a vacuum adiabatic calorimeter immersed in a precision liquid thermostat within the temperature range 293 to 671 K and at pressures up to 60 MPa [176]. The uncertainty of heat capacity, pressure, and temperature measurements were estimated to be 2–2.5%, 0.05%, and 15 mK respectively. The measured values of heat capacity were compared with the values calculated from a surrogate mixture model (EOS). The AAD between these data and the values calculated with an EOS was 0.81%. Table 21 gives the measured heat capacity for a wide range of temperatures and pressures. The heat capacity as a function of temperature is an almost linear function, with deviations at the upper end of the temperature range, as illustrated in Figure 21 for two different pressures, 20 and 40 MPa.

**Table 21:** Experimental isobaric heat capacities of RP-1.

| <i>T</i> , K | Isobaric heat capacity, <i>c<sub>p</sub></i> , kJ kg <sup>−1</sup> K <sup>−1</sup> |                    |        |        |        |        |        |
|--------------|------------------------------------------------------------------------------------|--------------------|--------|--------|--------|--------|--------|
|              | 0.1 MPa                                                                            | 10 MPa             | 20 MPa | 30 MPa | 40 MPa | 50 MPa | 60 MPa |
| 293.76       | 2.016                                                                              | 2.015              | 2.010  | 2.007  | 2.004  | 2.002  | 2.000  |
| 334.15       | 2.151                                                                              | 2.153              | 2.143  | 2.140  | 2.135  | 2.130  | 2.127  |
| 373.42       | 2.298                                                                              | 2.305              | 2.296  | 2.285  | 2.280  | 2.275  | 2.270  |
| 434.65       | —                                                                                  | 2.531              | 2.498  | 2.488  | 2.477  | 2.473  | 2.467  |
| 475.45       | —                                                                                  | 2.699              | 2.655  | 2.641  | 2.631  | 2.622  | 2.613  |
| 535.32       | —                                                                                  | 2.965              | 2.884  | 2.864  | 2.850  | 2.840  | 2.831  |
| 576.63       | —                                                                                  | 3.229              | 3.081  | 3.029  | 2.979  | 2.968  | 2.940  |
| 633.84       | —                                                                                  | 3.565              | 3.290  | 3.162  | 3.120  | 3.110  | 3.080  |
| 671.42       | —                                                                                  | 3.810 <sup>a</sup> | 3.310  | 3.190  | 3.145  | 3.122  | 3.100  |

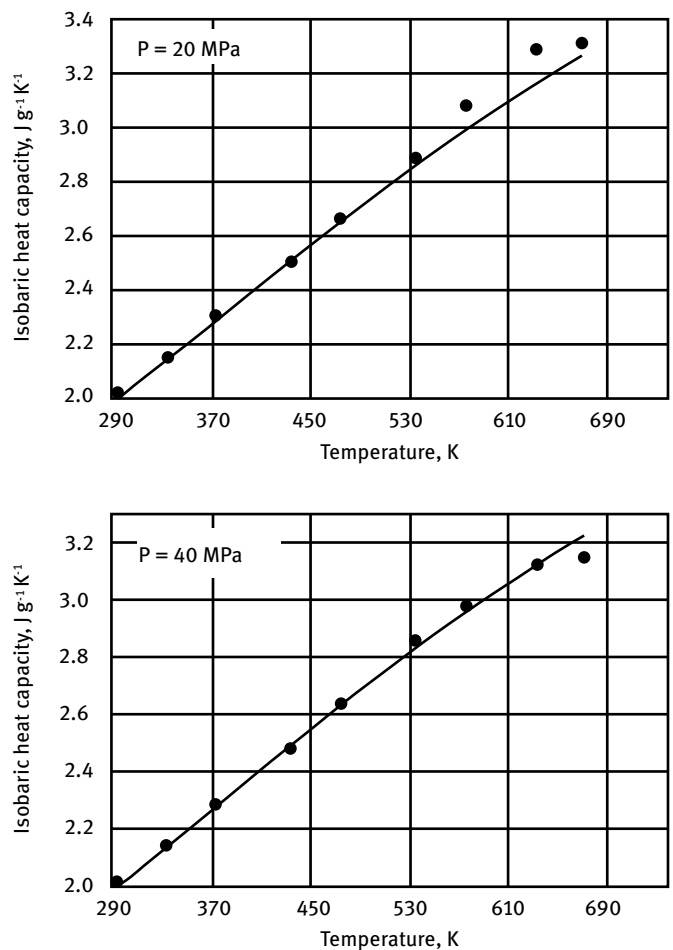
<sup>a</sup> Incipient decomposition of RP-1 (uncertainty is 5–15% and more)

Data source: [176]

#### 3.2.7.2 Enthalpy of Formation of RP-1

The NASA CEC program assumes a formula of C<sub>1</sub>H<sub>1.95</sub> and an enthalpy of formation of −24717.7 kJ/kg mol for RP-1 [162]. The US Navy PEP Program offered two very different sets of data for RP-1 [37] (Table 22).

The different heats of formation when reported in units of kJ/mol are often based on different assumptions for the average molecular mass of RP-1. One avoids this variability by working only with the mass-specific enthalpy of formation, which still varies between −2540 kJ/kg (−60.6 kcal/100 g), assuming C<sub>7.060190</sub>H<sub>14.97479</sub>, and −1760 kJ/kg (−42.0 kcal/100 g) assuming CH<sub>1.9063</sub>, depending on which source one can trust.



**Figure 21:** Measured and calculated values of the isobaric heat capacity of RP-1 as a function of temperature at two selected isobars. (Reprinted and modified from [176], with permission from ©2011 Elsevier; permission conveyed through RightsLink.)

**Table 22:** Enthalpy of formation of RP-1.

| Compound   | Formula                           | Enthalpy of formation |       |
|------------|-----------------------------------|-----------------------|-------|
|            |                                   | kJ/kg                 | cal/g |
| RP-1       | C <sub>1</sub> H <sub>2</sub>     | −5607                 | −1340 |
| RP-1 (RPL) | C <sub>100</sub> H <sub>195</sub> | −1510                 | −361  |

### 3.2.7.3 Enthalpy of Evaporation of RP-1

Assuming that the gross formula of RP-1 is  $C_{12}H_{23.4}$ , the enthalpy of evaporation of RP-1 was predicted to be 308 kJ/kg based on NMR and GC measurements [38]. Other sources reported heats of vaporization between 246 and 291 kJ/kg.

### 3.2.7.4 Heat of Combustion of RP-1

The upper heat of combustion of RP-1 (gross) is 46309 kJ/kg at 298 K (19923 BTU/lb). The lower heat of combustion of RP-1 is (net) 43328 kJ/kg (18640 BTU/lb) [85]. A chemical GC-MS analysis of a specific sample of RP-1 was followed by determination of the heat of combustion in a calorimeter [166].

### 3.2.8 Optical Properties of RP-1

Knowledge of the refractive indices of rocket propellants is of great importance in many engineering and scientific applications. For example, optical constants are needed to calculate the focusing of a laser beam used to ignite rocket fuels inside an engine. These optical parameters are not directly measurable, but can be derived from measured quantities such as the transmission and reflection coefficients.

Complex index-of-refraction values of RP-1 were measured at several different laser wavelengths of 0.193  $\mu\text{m}$  (ArF excimer), 0.4765  $\mu\text{m}$  (argon ion), 0.488  $\mu\text{m}$  (argon ion), 0.5145  $\mu\text{m}$  (argon ion), 0.532  $\mu\text{m}$  (Nd-YAG, frequency doubled), 0.6328  $\mu\text{m}$  (He-Ne), 1.064  $\mu\text{m}$  (Nd-YAG), and 10.5915  $\mu\text{m}$  ( $\text{CO}_2$ ), and the imaginary part of the index of refraction ( $k$ ) was determined by traditional transmission methods [177]. The refractive index of RP-1 varied between 1.44 and 1.50 within the wavelength range 0.1–10  $\mu\text{m}$ .

### 3.2.9 Critical Point Properties of RP-1

The critical temperature of RP-1 was listed as 676 to 689 K, with a critical pressure of 2140 to 2170 kPa.

## 3.3 Chemical Properties of RP-1

### 3.3.1 Contaminant Levels in RP-1

Over the course of several decades, the tolerable sulfur concentration in kerosene for rocket engine use has been lowered from 500 to 30 ppm to 1 ppm and may eventually end up within the ppb range.

### 3.3.2 Chemical Composition of RP-1

A GC-MS analysis of RP-1 revealed at least 24 major constituents (peak area counts in excess of 1%) ranging from  $C_{11}$  fluids such as 2,6-dimethylnonane to  $C_{14}$  fluids such as

2-methyltridecane that represented about 40% of the total area counts [178, 179]. Overall, the sample showed approximately 350 peaks that could be easily distinguished from noise level and perhaps twice that number that were slightly above noise level. The predominant species were linear and branched paraffins, and one- and two-ring cyclic paraffins of 11–14 carbon atoms. Aromatics and olefins were not found in this sample, but aromatics and olefins were reported by other investigators.

A long-established hydrocarbon fuel, RP-1 continues to be widely used as the kerosene component in some rocket propulsion systems. The desire in recent years to re-use rocket engines many times, rather than a single time, has led to reformulations of RP-1 and to the formulation of RP-2. In terms of processing, increased hydro-treating of the component feedstock fluids used in the manufacture of RP-1 can lower the sulfur, olefin, and aromatic content significantly. The resulting fuels have demonstrably lower metal corrosion effects and are thus more amenable to multiple use rocket engines. The reformulated RP-1 mixtures have been extensively studied in terms of thermophysical properties, combustion processes, and kinetics and performance. Still unknown is how compositional variability resulting from the various blending strategies affects both the properties and the ability to correctly predict the fluid behavior with mathematical models. In trying to develop a predictive procedure, 11 batches of RP-1 were prepared to represent the range of formulation recipes [180–182]. The density, velocity of sound, and viscosity of these same 11 samples were later measured and reported [161]. These results were already shown here in individual property sections for RP-1 (see Section 3.2). For each of these representative formulations, the compositional variability was tested with the ADC method. This method is an improvement of classical distillation curve techniques. It features: **(1)** a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis); **(2)** temperature measurements that are true thermodynamic state points that can be modeled with an EOS; **(3)** temperature, volume, and pressure measurements of low uncertainty suitable for EOS development; **(4)** consistency with a century of historical data; **(5)** an assessment of the energy content of each distillate fraction; **(6)** trace chemical analysis of each distillate fraction; and **(7)** corrosivity assessment of each distillate fraction. All applicable data channels of the ADC method were used to show the compositional variability of RP-1 and to show how the variability impacts predictive modeling. It was concluded that the variabilities of RP-1 and RP-2 were significant and perhaps higher than expected.

During the past decade several important improvements were introduced into the measurement of distillation curves for complex fluids. One method was a significant improvement over previous approaches, featuring a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis) and an assessment of the energy content of each distillate fraction, among other features [183]. One modification was achieved with a new sampling approach that allowed precise qualitative as well as quantitative analyses of each fraction, on the fly. This method was applied to the measurement of a wide variety of fluids, including hydro-



carbons, gasoline, jet fuel, diesel fuels (both petroleum-derived and biodiesel), crude oils, RP-1, RP-2, and TS-5. Not only the distillation curves but also the composition-explicit information was used to characterize distillate cuts in terms of composition and available energy content. The measure used for the fluid energy content was the composite enthalpy of combustion for each component selected for identification in each distillate fraction. Overall, the distillation curves and enthalpy data for RP-1, RP-2, and TS-5 were remarkably similar.

Although the range of compositional variability observed for JP-8 is not expected for RP-1, manufacturing process changes and fluctuating feedstock availability can cause subtle compositional variation, which may cause concern for some applications. Whether or not these changes are consequential from an engine or vehicle standpoint depends on the system. Maintaining fuel integrity is universally important for launch applications as vehicle and payload development time and cost are invaluable, especially for manned missions. For the development of new engines, re-examination of the variability in fuel composition, and especially its impact on properties and performance, must be done periodically and repeatedly. Table 23 summarizes literature references for RP-1 hydrocarbon class composition [184].

**Table 23:** Reported RP-1 hydrocarbon class composition.

| Hydrocarbon type<br>Composition    | References     |        |                  |        |                  |
|------------------------------------|----------------|--------|------------------|--------|------------------|
|                                    | [85]           | [185]  | [3]              | D2425  |                  |
|                                    | Vol.-%         | Vol.-% | Mass-%           | Vol.-% | Vol.-%           |
| <i>n</i> -Paraffins                | —              | —      | 2.1              | —      | 7                |
| <i>iso</i> -Paraffins              | —              | —      | 27.1             | —      | 42               |
| Total paraffins                    | 39             | 42     | 29.2             | 39     | 49               |
| <b>Cyclics</b>                     |                |        |                  |        |                  |
| Cycloparaffins (nc) <sup>a</sup>   | 41             | 25     | 36.3             | —      | 36               |
| Dicycloparaffins (c) <sup>a</sup>  | 14             | 20     | 22.3             | —      | 11               |
| Tricycloparaffins (c) <sup>a</sup> | 3              | 4      | 3.8              | —      | 2                |
| Total cyclics                      | 58             | 49     | 62.4             | 58     | 49               |
| <b>Aromatics</b>                   |                |        |                  |        |                  |
| Alkylbenzenes                      | —              | 3.1    | —                | —      | 2.4              |
| Indans + tetralins                 | —              | 1.7    | —                | —      | <0.5             |
| Naphthalene                        | —              | 0      | —                | —      | <0.5             |
| Naphthalenes                       | —              | 4.2    | —                | —      | <0.5             |
| Total aromatics                    | 3 <sup>b</sup> | 9      | 8.4 <sup>c</sup> | 3      | 3.5 <sup>d</sup> |

<sup>a</sup> nc denotes non-condensed; c denotes condensed

<sup>b</sup> Reported as: Total Aromatics/Detectable Naphthalene (2.00/1.50)

<sup>c</sup> ASTM D1319 analysis gives 2.3 vol.-% total aromatics

<sup>d</sup> Obtained with ASTM D6379

Data source: [184]

The composition of seven synthetic fuel mixtures representing a wide range of RP-1 properties was compared with the results of GC-MS-IR analysis of real samples of RP-1 [161].

### 3.3.3 Surrogate Mixtures Representing RP-1

Because the composition of commercial samples of RP-1 may vary widely depending on source and processing techniques, surrogate mixture recipes (“models”) have been developed that can be used to reproducibly reconstitute a mixture of hydrocarbons in the laboratory, starting with known amounts of pure hydrocarbons as ingredients. Whereas real-world RP-1 may contain up to several hundred constituents, surrogate mixtures would normally contain no more than 20 ingredients. Such surrogate mixtures can then be used to calibrate instruments, and to compare analytical methods, for instance, in a nation-wide round-robin analysis effort. Although surrogate mixtures are often formulated on the basis of the ability of a particular mixture to reproduce a particular property, there is usually a desire to employ surrogate mixtures that are physico-chemically authentic. This means that, provided that the primary purpose is satisfied, researchers are inclined to choose mixtures that have physical and chemical properties appropriate to the finished fuel. Such mixtures have been synthesized for RP-1 and several other kerosene types [186].

Other proposed recipes for surrogate mixtures for RP-1 were published [185]. The first step in developing surrogate fluid mixture for RP-1 was a thorough chemical analysis by GC-MS of a specific RP-1 fuel sample provided by the Fuels Branch of the Air Force Research Lab, Wright-Patterson AFB, OH, which gave 37 constituent fluids [166]. A detailed analysis shortened this list to 20 potential constituent fluids for a surrogate mixture. The lightest component identified was neohexane, and the heaviest was hexadecane. The list included linear and branched alkanes, mono and bicyclic paraffins, aromatics, and linear and branched olefins. The final mixture contained 14 constituent fluids, and represented the density to within 0.3%, the heat capacity to within 7%, the thermal conductivity to within 3%, the viscosity to within 3% at atmospheric pressures, and 10% at 60 MPa, and the boiling point at local atmospheric pressure to 0.5%. It had an overall molar mass of 164.6, a H/C ratio of 1.95, and an approximate chemical formula of  $C_{11.8}H_{23.0}$ . The overall composition was (by mol-%) 27.4% alkanes, 26.6% alkenes, 18.5% monocyclic paraffins, 22.4% bicyclic paraffins, and 5.1% aromatics. This mixture was intended as a surrogate; it did not have the actual mixture composition, but rather a mixture that approximated the behavior of a particular RP-1 sample that was investigated.

Surrogate hydrocarbon fuel mixture models were developed to represent the thermophysical properties of two kerosene rocket propellants, RP-1 and RP-2 [19]. The surrogates were developed with a procedure that incorporated experimental data for the density, sound speed, viscosity, thermal conductivity, and the ADCs for samples of the two fuels. The surrogate for RP-1 contained four components (numbers in mo-

lar fractions) 0.354  $\alpha$ -methyldecalin, 0.150 5-methylnonane, 0.183 *n*-dodecane, and 0.313 heptylcyclohexane. Comparisons with experimental data demonstrated that the models were able to represent the density, sound speed, viscosity, and thermal conductivity of both fuels to within (at a 95% confidence level) 0.4, 2, 2, and 4% respectively. The volatility behavior, as measured by the ADCs, is reproduced to within 0.5%.

In continuation of this work, two different surrogate mixtures for RP-1 were formulated, one containing olefins and aromatics, the other not containing any of these [187]. Experimental and calculated thermophysical properties of two samples of RP-1 obtained from different batches of RP-1 that exhibit compositional variations were compared. One sample was atypical, owing to a high olefin content. The greatest effects of this significant compositional variability were seen in the viscosity and the distillation curve. The effects of compositional variations were shown for several thermophysical properties including density, sound speed, viscosity, thermal conductivity, and volatility (as expressed by the distillation curve).

Compositional variability of aerospace kerosene formulations influence performance or the design of practical combustion devices, particularly as relatively extreme operating conditions can result in increased sensitivity to small variations in composition-related physical properties. Twelve laboratory-scale RP-1 fossil-fuel-derived surrogate formulations were prepared that met specification requirements but were blended from nine chemically unique feedstocks, thereby representing the expected compositional variation for currently produced fuel [184]. Chemical composition was characterized in terms of hydrocarbon types and was compared between the various formulations. Composition explicit distillation curve, density, viscosity, heat of combustion, and hydrogen content were determined for each of the 12 blends and several other RP-1 samples carried along for comparison.

#### 3.3.4 Specifications for RP-1

Military specifications for RP-1 have undergone many changes during the past decades. The first release of the RP-1 specification (MIL-F-25576A) was issued on 3 January 1957. The specification restricted levels of olefins (<1.0% by weight), aromatics (<5.0 by weight), and dissolved sulfur (<0.05% by weight), and alleviated most of the performance degradation problem due to soot, coking, and gum deposits. Combined with other specifications regarding hydrocarbon constituents, density range, and heat of combustion, it also ensured repeatable propulsion performance within acceptable limits. In Table 24, an attempt is made to give a chronological list of MIL SPECS for RP-1 that may have been in effect at one time or another.

**Table 24:** Military specifications for rocket-grade kerosene RP-1 and RP-2.

| Designation               | Pages | Date issued   | Changes made                     |
|---------------------------|-------|---------------|----------------------------------|
| MIL-P-25576               | —     | —             | —                                |
| MIL-P-25576A              | —     | —             | —                                |
| MIL-P-25576B              | —     | January 1959  | —                                |
| MIL-P-25576C              | 8     | February 1967 | —                                |
| MIL-P-25576C Amendment 1  | 1     | November 1967 | —                                |
| MIL-P-25576C Amendment 2  | 1     | June 1982     | Olefins limit raised to 2 vol.-% |
| MIL-DTL-25576D            | 12    | May 2005      | Addition of RP-2 as a new grade  |
| MIL-DTL-25576E            | 11    | April 2006    | Dye addition mandatory for RP-1  |
| MIL-DTL-25576E (Notice 1) | 1     | January 2011  | —                                |

Starting with MIL-DTL-25576D, this specification now covers two grades of rocket propellant kerosene for use in rocket engines:

RP-1 Normal production, total sulfur content of 30 mg/kg (maximum), suitable for most uses;

RP-2 Processed RP-1, total sulfur content of 100 µg/kg (maximum).

The specification requirements of RP-1 and RP-2 are listed in Table 25 [80].

In looking at the requirements for RP-1 and RP-2, the sulfur content has been limited because sulfur corrodes copper-containing engine components and may affect the thermal stability of kerosenes [188]. In particular, the main difference between RP-1 and RP-2 is the lower sulfur content in RP-2 that has been reduced by hydrogenation treatment. The desulfurization treatment is also called “sweetening,” which is a process to remove the sour (acidic, sulfur-bearing) contaminants in petroleum products. Sulfur that is contained in mercaptans and thiophenes is more difficult to remove.

The aromatics content has been limited because aromatics (xylene, tetralin) and olefins contain less hydrogen and result in higher average molecular mass of the exhaust products in a rocket engine. For the same reason, the hydrogen content has been specified to be a minimum of 13.8 mass-%. For comparison, a hydrocarbon with the gross formula  $\text{CH}_2$ , the simplified gross formula for hydrocarbons, contains 14.37 mass-% hydrogen. Olefins have been limited because they may autoxidize during storage and form resins that may clog filter screens and injector orifices.

The flash point for both grades of RP has been limited to above 333 K (140 °F) because a higher content of combustible volatiles with lower flash points would change the stoichiometry (shift it to fuel-rich) in the vapor phase at ignition when kerosene is first injected into a rocket engine, and because a fuel-rich mixture is more difficult to ignite.

**Table 25:** Specification requirements of RP-1 and RP-2 per MIL-DTL-25576E.

| Property                                                    | Limits            |               | ASTM Test method    |
|-------------------------------------------------------------|-------------------|---------------|---------------------|
|                                                             | RP-1              | RP-2          | D 86                |
| <b>Distillation</b>                                         |                   |               |                     |
| Initial boiling point, °F                                   | Note <sup>a</sup> | a             |                     |
| Fuel evaporated, 10%, °F                                    | 365–410           | 365–410       |                     |
| Fuel evaporated, 50%, °F                                    | a                 | a             |                     |
| Fuel evaporated, 90%, °F                                    | a                 | a             |                     |
| End point, °F                                               | 525 maximum       | 525 maximum   |                     |
| Residue, vol.-%                                             | 1.5 maximum       | 1.5 maximum   |                     |
| Distillation loss vol.-%                                    | 1.5 maximum       | 1.5 maximum   |                     |
| Specific gravity, 60/60 °F                                  | 0.799–0.815       | 0.799–0.815   | D 1298 <sup>b</sup> |
| Existent gum, mg/100 mL                                     | 1 maximum         | 1 maximum     | D 381               |
| Sulfur, total, mg/kg                                        | 30 maximum        | 0.1 maximum   | D 5623 <sup>c</sup> |
| Mercaptan-sulfur, mg/kg                                     | 3 maximum         | <sup>d</sup>  | D 3227              |
| Freezing point, °F                                          | –60 maximum       | –60 maximum   | D 2386              |
| Thermal value: Net heat of combustion, BTU/lb               | 18500 minimum     | 18500 minimum | D 240               |
| Viscosity at –30 °F, cSt                                    | 16.5 maximum      | 16.5 maximum  | D 445               |
| Aromatics, vol.-%                                           | 5.0 maximum       | 5.0 maximum   | D 1319              |
| Olefins, vol.-%                                             | 2.0 maximum       | 1.0 maximum   | D 1319              |
| Hydrogen content, mass-%                                    | 13.8 minimum      | 13.8 minimum  | D 3343              |
| Copper strip corrosion                                      | 1 maximum         | 1 maximum     | D 130 <sup>e</sup>  |
| Water reaction interface                                    | <sup>f</sup>      | <sup>f</sup>  | D 1094              |
| Flash point, °F                                             | 140 minimum       | 140 minimum   | D 93                |
| Particulate, mg/L                                           | 1.0 maximum       | 1.0 maximum   | D 5452              |
| <b>Thermal Stability tested by JFTOT</b>                    |                   |               |                     |
| JFTOT, change in pressure drop ( $\Delta P$ ) in 5 h, mm Hg | <sup>d</sup>      | a             | D 3241 <sup>g</sup> |
| JFTOT, delta TDR spun                                       | d                 | a             |                     |

JFTOT = Jet Fuel Thermal Oxidation Tester, ASTM = American Society for Testing and Materials

<sup>a</sup> Report only<sup>b</sup> ASTM D 4052 may be used. In case of a dispute, ASTM D 1298 shall be the referee<sup>c</sup> ASTM D 4045 may be used for RP-2 grade. ASTM D 5453 may be used for RP-1 grade. In case of a dispute, ASTM D 5623 shall be the referee<sup>d</sup> Not required<sup>e</sup> Follow the procedures specific to kerosene<sup>f</sup> See MIL-DTL-25576E section 3.2.1 for requirements and section 4.3.2.1 for exceptions to ASTM D 1094<sup>g</sup> For specific test conditions see MIL-DTL-25576E section 4.3.2.2.

### 3.4 Analysis of RP-1

Eighty-seven [189] different hydrocarbons have been identified in RP-1, the fractions of which could change from one batch to another.

### 3.4.1 Copper Strip Corrosion

Copper strip corrosion is a semi-technical subjective test that appears to have little relevance in an advanced fuel specification. It was developed in the 1940s to ensure that the fuels are not too acidic. The test involves soaking a polished copper coupon in the test fuel for 2 h at 212°F, after which the specimen is evaluated against a standard. It is not sure whether any fuel sample has ever failed this test, even fuels with over 500 ppm sulfur.

### 3.4.2 Gas Chromatography

Ongoing efforts in predicting fuel chemical and physical behavior through modeling put greater emphasis on attaining detailed and accurate actual fuel properties and fuel composition information. Traditionally, one-dimensional GC combined with MS has been employed to provide chemical composition information. Building on approaches that make use of GC-MS, comprehensive two-dimensional (2D) gas chromatography combined with time-of-flight mass spectrometry (GC  $\times$  GC-TOFMS) using a reversed column format RTX-wax column for the first dimension, and an RTX-1 column for the second dimension provides substantially more chemical composition information about these complex fuels [190]. By applying chemometric data analysis, specifically partial least-squares (PLS) regression analysis, it was possible to readily model (and correlate) the chemical compositional information provided by the use of GC  $\times$  GC-TOFMS to RP-1 fuel property information such as density, kinematic viscosity, net heat of combustion, hydrogen content, etc. This method readily identified compounds that contribute significantly to measured differences in fuel properties based on results from the PLS models.

The GC  $\times$  GC-TOFMS data were analyzed using PLS regression chemometric analysis to model and predict ADC data for ten RP-1 fuels that were previously analyzed using the ADC method [191]. The PLS modeling provided insight into the chemical species that impact the ADC data. The PLS modeling correlated compositional information found in the GC  $\times$  GC-TOFMS chromatograms of each RP-1 fuel, and their respective ADC, and allowed prediction of the ADC for each RP-1 fuel with good precision and accuracy. The root-mean-square error of calibration ranged from 0.1 to 0.5°C, and was typically below ~0.2°C, for the PLS calibration of the ADC modeling with GC  $\times$  GC-TOFMS data, indicating a good fit of the model to the calibration data.

Partial least squares analysis of rocket propulsion fuel data using diaphragm valve-based comprehensive two-dimensional GC coupled with flame ionization detection introduced a new method for comprehensive GC  $\times$  GC separations with application of high-temperature diaphragm valves for in-oven modulation for GC  $\times$  GC, providing an alternative to other GC  $\times$  GC methods that used cryogenic fluids and MS [192]. For comparison, using PLS analysis, the GC  $\times$  GC-FID (flame-ionization detector) signal of the entire 2D separations was regressed against the same ASTM values, yielding a linear trend for the three compound classes (alkanes, cycloalkanes,

and aromatics). A more detailed PLS analysis was undertaken of the compounds classes (*n*-alkanes, *iso*-alkanes, mono-, di-, and tri-cycloalkanes, and aromatics), and of physical properties previously determined by ASTM methods (such as net heat of combustion, hydrogen content, density, kinematic viscosity, sustained boiling temperature and vapor rise temperature). Results from these PLS studies using the relatively simple and inexpensive GC  $\times$  GC-FID instrumental platform were compared with previously reported results using the GC  $\times$  GC-TOFMS instrumental platform.

Improvements in the method and apparatus used for the measurement of distillation curves for complex hydrocarbon fluid mixtures included the addition of a composition-explicit channel of data, improved temperature control and measurement, and improved and less uncertain volume measurement [179]. The improved approach was applied to two complex hydrocarbon fluids, RP-1 and a synthetic JP-8 that was designated as S-8. Modern versions of RP-1 are produced from a narrow-range kerosene fraction that is processed to reduce unsaturated compounds and also sulfur-containing hydrocarbons. S-8 is a synthetic substitute for fluids such as JP-8 and Jet-A. It is produced with the Fischer-Tropsch process from natural gas. As these new and reformulated fluids gain increasing application, especially in aviation/aerospace, it will be increasingly important to have material characterization test procedures that are reproducible and that have a sound and fundamental basis. This will allow modeling of the properties and guide further refinement of these fuels. GC-MS-IR analysis of RP-1, RP-2, and TS5 and showed 20–30 major peaks that were all identified and listed in a table with their retention times and CAS RN numbers for further identification [183].

### 3.4.3 Distillation Curves

It is common practice to characterize the boiling temperature range of hydrocarbon mixtures by distillation curves, measuring the fraction of a sample that has distilled over in specific temperature ranges. These methods are specified in ASTM D86.

The compositional variability of 11 orthogonal batches of RP-1 that were prepared to represent the range of formulation recipes was assessed with ADC metrology [181, 182]. This method is an improvement of classical boiling curve techniques. The temperature grid of the ADC was used to conclude that the variabilities of RP-1 and RP-2 are significant, and perhaps higher than expected.

## 3.5 Thermal Stability of RP-1

Carbon deposition in cooling channels of LOX/RP-1 engines has been a problem for a long time, but because these engines in expendable launch vehicles were used only once, little effort was made to correct this situation [193]. It was only when launch vehicles became reusable that the coke deposition problem got serious attention.

A laboratory-scale flow reactor was developed to subject small amounts (approximately 1 mL) of deoxygenated fuels to controlled conditions of temperature and residence-time-at-temperature at constant pressure (34 atm) in the liquid or supercritical phase [54]. The reactor was made from 316 stainless steel HPLC tubing. Using an in-line analytical system and off-line chromatographic analysis of products, the thermal stability of the parent material, as well as the thermal fragmentation products of each fuel, was measured. Some of the candidate materials tested showed only marginal thermal stability with major decomposition occurring before 673 K (400 °C; ~3 s residence time). Other fuels (JP-10, RP-1, RG-1, RJ-6, and RJ-7) showed excellent thermal stability with little decomposition even at 873 K (600 °C). Results showed the pyrolytic stability of candidate materials relative to each other, and provided insights into the mechanisms of thermal decomposition for specific fuel candidates.

A series of electrically heated tube tests was performed at the NASA Glenn Research Center's Heated Tube Facility to investigate the effects that sulfur content, test duration, and tube material may have on the overall thermal stability and materials compatibility characteristics of RP-1 [194]. Scanning-electron microscopic (SEM) analysis, in conjunction with EDS, was used to characterize the condition of the tube inner wall surface and any carbon deposition or corrosion formed during these runs. Results of the parametric study indicated that tests with standard RP-1 (total sulfur ~23 ppm) and pure copper tubing were characterized by a deposition/deposit shedding process, producing local wall temperature swings as high as 278 K (500 °F). The effect of this shedding was to keep total carbon deposition levels relatively constant for run times from 20 min up to 5 h, though increasing tube pressure drops were observed in all runs. Reduction in the total sulfur content of the fuel from 23 ppm to <0.1 ppm resulted in the elimination of deposit shedding, local wall temperature variation, and the tube pressure drop increases that were observed in standard sulfur level RP-1 tests. Results of the study were consistent with previously published heated tube data that indicated that small changes in fuel total sulfur content can lead to significant differences in the thermal stability of kerosene type fuels and their compatibility with copper-based materials. In conjunction with the existing thermal stability database, these findings provided insight into the feasibility of cooling a long-life, high-performance, high-pressure liquid rocket combustion chamber and nozzle with RP-1 or RP-2.

The global decomposition kinetics of RP-1 were investigated by measuring the decomposition of RP-1 at elevated temperatures (that is, under thermal stress) as a function of time and then deriving a global pseudo-first-order rate constant that described the overall mixture decomposition [195]. Although not as rigorous as a component-by-component kinetics analysis, this approach was nevertheless considered instructive and can be used to guide the aforementioned property measurements. Decomposition measurements were made at 648, 673, 698, and 773 K (375, 400, 425, and 500 °C) for two separate samples of RP-1. One sample was a typical batch, showing the expected fractions of paraffins, cycloparaffins, olefins, and



aromatics. The other was an off-specification batch that had unusually high olefin and aromatic contents. Decomposition rate constants ranged from  $6.92 \times 10^{-5} \text{ s}^{-1}$  at 648 K (375 °C) to  $1.07 \times 10^{-3} \text{ s}^{-1}$  at 773 K (500 °C). Although the primary purpose of this work was to establish operating ranges for the property measurements, the results clearly have implications in other facets of RP-1 applications. These applications include establishing operating ranges for supercritical fluid heat sink regimes, setting residence times in cooling channels of engines, and similar applications. In addition to the study of decomposition kinetics, a chemical analysis was done of the vapor phase that was produced upon thermal stress.

The effects of fuel composition changes on rocket fuel thermal stability were experimentally investigated [196]. A High Reynolds Number Thermal Stability test device was used to evaluate thermal stability of JP-8 and RP-1 fuels. The experiment consisted of an electrically heated, stainless steel capillary tube with a controlled fuel outlet temperature. An optical pyrometer monitored the increasing external temperature profiles of the capillary tube as deposits build inside during each test. Multiple runs of each fuel composition provided results on measurement repeatability. Testing at two different facilities provided data on measurement reproducibility. The technique was able to distinguish among standard RP-1 rocket fuels and those having reduced sulfur levels. Carbon burn-off analysis of residue in the capillary tubes on the RP-1 fuels correlated well with the external temperature results.

The thermal decomposition of RP-1, RP-2, and mixtures of RP-2 with three different additives has been investigated [197]. The mixtures with RP-2 contained 5% 1,2,3,4-tetrahydronaphthalene (tetralin), 5% 1,2,3,4-tetrahydroquinoline (THQ), or 256 mg/l of the additive used to make JP-8+100. Decomposition reactions were performed in stainless steel ampoule reactors at temperatures from 648 to 723 K (375 to 450 °C). All of the reactions were run with an approximate initial pressure of 34.5 MPa (5000 psi). After each reaction the thermally stressed liquid phase was analyzed by GC. For RP-1 and RP-2, the increase in a suite of light decomposition products was used to derive global, pseudo-first-order rate constants that approximated the overall rate of decomposition. For RP-2, decomposition rate constants ranged from  $1.33 \times 10^{-5} \text{ s}^{-1}$  at 648 K (375 °C) to  $5.47 \times 10^{-4} \text{ s}^{-1}$  at 723 K (450 °C). The rate constants for RP-1 decomposition were not significantly different [198]. The addition of THQ and tetralin had a significant effect on the decomposition of RP-2. Compared with neat RP-2, the addition of 5% THQ slowed the decomposition by an order of magnitude, whereas the addition of 5% tetralin slowed the decomposition by approximately 50%.

An apparatus was designed that would subject flowing hydrocarbons to thermal stresses similar to those experienced in regenerative cooling channels of rocket engines [199]. The volatility of thermally stressed samples of RP-1 and RP-2 rocket propellant kerosenes was measured by use of an ADC method [200]. Measuring the properties of thermally stressed kerosene was motivated by the use of kerosenes as a coolants prior to combustion in the engines. Samples of RP-1 and RP-2 were stressed at 748 and 783 K (475 and 510 °C), at a pressure of 17 MPa (2500 psi), for residence times of 0.5 min.

Volatility measurements revealed significant changes early in the distillation curves, becoming very pronounced at the higher temperature. The volatility measurements were supplemented with chemical analyses and a calculation of the enthalpy of combustion as a function of the distillate volume fraction. It was noted that the increase in volatility can be explained by the significant increase of very light (lower molecular mass) components produced during the thermal stress. It was noted that the enthalpy of combustion followed the same pattern as the volatility, the same as what was reported in previous studies.

Measurements of fuel decomposition and ethylene evolution time histories during decomposition of RP-fuel vapors and their possible surrogate components were carried out between 1000 and 1500 K in two shock tubes, the Aerosol Shock Tube, for experiments between 4 and 8 atm, and the High Pressure Shock Tube, for experiments between 18 and 51 atm [201–203]. From these measurements, overall fuel decomposition rates for six fuels (RP-1, RP-2, JP-7, *n*-dodecane, methylcyclohexane, and *iso*-cetane) were determined and ethylene yields for four of these fuels (RP-1, *n*-dodecane, methylcyclohexane, and *iso*-cetane) were determined. An RP-1 decomposition surrogate was formulated based on three targets: compound class, overall fuel decomposition rate, and ethylene yield. This resulted in a surrogate containing 32% *n*-dodecane, 59% methylcyclohexane, and 9% *iso*-cetane, which would closely resemble RP-1. The activation energies of kerosene decomposition are summarized in Table 26.

**Table 26:** Activation energies of kerosene decomposition.

| Fuel               | $E_a$<br>kJ/mol | Temperature range<br>K | Pressure range<br>atm |
|--------------------|-----------------|------------------------|-----------------------|
| <i>n</i> -Dodecane | $213 \pm 15$    | 1110–1500              | 4–46                  |
| RP-1               | $263 \pm 7$     | 1000–1370              | 4–51                  |
| RP-2               | $250 \pm 23$    | 1050–1370              | 6.4–7.6               |
| JP-7               | $287 \pm 19$    | 1080–1180              | 4.5–5.2               |
| MCH                | 207             | 1250–1520              | 18.7–12.3             |
| <i>iso</i> -Cetane | 244             | 990–1240               | 20.3–22.5             |

Data source: [201,202]

Measurements were made at ambient pressure of the thermophysical properties density, velocity of sound, and viscosity, and the derived property adiabatic compressibility, for the same thermally unstressed and stressed RP-1 and RP-2 fuel samples [204]. The reactor that was built to thermally stress the fuels had been described in detail elsewhere [199]. The fuel was pressurized by use of a high-pressure syringe pump and then delivered to a high-temperature reactor capable of generating controlled temperatures up to 873 K (600 °C). Downstream of the reactor, the fluid was delivered to a chilled water bath heat exchanger to cool the fluid and quench any further decompo-

sition reactions. The cooled fluid was then directed through a back-pressure regulator and into a collection vessel. The combination of the syringe pump and back-pressure regulator allowed the operator to control the residence time of the fluid in the reactor by providing controlled, constant flow rates at a wide range of nominal pressures. For this work, the RP-1 and RP-2 samples were both thermally stressed for 0.5 ( $\pm 0.05$ ) min at a constant pressure of 17 ( $\pm 0.1$ ) MPa and at two temperatures, 748 and 783 K (475 and 510 °C). Density, velocity of sound, and viscosity were measured for samples of RP-1 and RP-2 that had been stressed for 0.5 min. at 748 and 783 K (475 and 510 °C) at a pressure of 17 MPa. Density and velocity of sound were measured from 278 to 323 K (5 to 50 °C) for samples stressed at 748 K (475 °C) and from 278 to 308 K (5 to 35 °C) for samples stressed at 783 K (510 °C). Viscosity was measured from 263 to 323 K (−10 to +50 °C) and 263 to 308 K (−10 to +35 °C) for the samples stressed at 748 and 783 K (475 and 510 °C) respectively. All measurements were made at ambient atmospheric pressure ( $\sim 83$  kPa). The densities of stressed samples were lower than those of the unstressed samples. For both RP-1 and RP-2, the densities of the thermally stressed samples were lower relative to their respective unstressed samples, but the magnitudes of those decreases in density were different for the two fuels. For RP-1, the two thermally stressed samples had similar densities. In contrast to RP-1, the thermally stressed RP-2 samples had densities that were more significantly different from one another, varying by 0.4% at 278 K (5 °C) and 0.6% at 308 K (35 °C). Consequently, relative to unstressed RP-2, RP-2-TS-475 had densities that were 0.8–0.9% lower and RP-2-TS-510 had densities that were 1.2–1.4% lower. As RP-1 and RP-2 decompose, the concentrations of smaller, more volatile molecules increase. The sound speeds of the thermally stressed samples were lower relative to their respective unstressed samples for both RP-1 and RP-2. Relative to unstressed RP-2, RP-2-TS-475 had sound speeds that were 1.2–1.6% lower and RP-2-TS-510 had sound speeds that were 3.2–3.7% lower. For both RP-1 and RP-2, the dynamic viscosities of the thermally stressed samples were considerably lower relative to their respective unstressed samples, with the TS-510 samples showing the most significant deviations. RP-1-TS-475 values were 12–14% lower than unstressed RP-1, and RP-1-TS-510 values were 38–39% lower. Relative to unstressed RP-2, RP-2-TS-475 had dynamic viscosities that were 15–17% lower and RP-2-TS-510 had values that were 40–41% lower.

During regenerative cooling in rocket engines, the extreme temperatures can have significant effects on the fuel composition. Extreme temperatures can result in coking and the fouling of cooling channels. In addition, the decomposition of the fuel can lead to changes in the fuel properties that can affect the fuel performance. Thermally stressed RP-1 and RP-2 were generated at two temperatures, 748 and 783 K (475 and 510 °C) and thermophysical property measurements were performed to characterize the resulting fluids [205]. The measurements included chemical composition, thermal decomposition reaction rate constants, volatility, density, velocity of sound, adiabatic compressibility, dynamic viscosity, and kinematic viscosity. There was a significant increase in volatility with thermal stress, the effect at 783 K (510 °C) being more strik-

ing, with the production of a significant dissolved gaseous fraction. For the other properties (except for adiabatic compressibility) there was a decrease in the respective properties with thermal stress.

The change in fuel composition and molecular structure after passing through the regenerative cooling channels of a rocket engine may have a significant impact on heat release, flame propagation, and mass burning rates in these highly turbulent combustion systems stemming from modifications to fuel chemistry and molecular/thermal diffusivity. Therefore, the effect of endothermic reactions on the subsequent combustion behavior of the reacted (thermally stressed) fuel mixture was experimentally examined [206]. The objective of the study was to investigate: **(1)** the degree of thermal decomposition that a fuel can experience when used in a typical regenerative cooling system at high pressure and temperature; and **(2)** the impact that this thermal decomposition has on fundamental combustion properties for three hydrocarbon model fuels selected as surrogates for RP-1: *n*-heptane, *n*-dodecane, and Jet A. A counterflow flame burner was used to investigate the extinction strain rates of neat *n*-heptane, *n*-dodecane, and Jet A.

The pyrolysis of RP-1 was investigated by reactive molecular dynamics simulations with ReaxFF force field [207]. The initial reactivity differences between a three-component surrogate model and a more complex 24-component model were observed in a series of heat-up and isothermal pyrolysis simulations performed using the GPU-enabled computer code GMD-Reax. The RP-1 conversion in the three-component surrogate was slower than that of the 24-component model. The maximal weight fraction difference for RP-1 consumption can be up to 21.2% in heat-up simulations and 22.3% in isothermal simulations. The reaction analysis facilitated by the code VARxMD further revealed the differences in pyrolysis intermediates, products, and reaction pathways between the two RP-1 models. Normal paraffin reactions of the two RP-1 models were similar owing to the similar fuel structures of normal alkanes. For branched paraffin reactions, the pyrolysis of the multi-branched fuel component of *iso*-cetane in the three-component surrogate produces 2-methylpropene, which is not a major pyrolysis product in the 24-component model, mainly owing to a lack of quaternary carbon with methyl side chains in the branched paraffin components. Compared with the reactions of methylcyclohexane, the only cycloparaffin in the three-component surrogate, more versatile ring opening reactions of cycloparaffins can occur in the 24-component model that will generate more dienes and cyclohexene from the double-ring fuel structures. The results suggested that the reactive molecular dynamics simulations of multi-component model with rich chemical structures closer to real fuel components have the potential as an alternative approach for evaluating reactivity in fuel pyrolysis.

### 3.6 Materials Compatibility with RP-1

Materials compatibility of hydrocarbon fuels (Mil-Spec RP-1, *n*-dodecane, propane, and methane) in contact with copper-based combustion chamber liner materials (OFHC, NASA-Z, and ZrCu coppers) was tested using two different methods [208]. Static tests, in which copper coupons were exposed to fuel for long durations at constant temperature and pressure, provided compatibility data in a precisely controlled environment. Dynamic tests, using the Aerojet Carbothermal Test Facility, provided fuel and copper compatibility data under realistic booster engine service conditions. Tests were conducted using very pure grades of each fuel and fuels to which a contaminant, e.g., ethylene or methyl mercaptan, was added to define the role played by fuel impurities. It was found that each of the copper materials exhibited similar compatibility behavior. However, there were significant differences among the various hydrocarbon fuels tested. In RP-1, carbon deposits were formed above  $T_{\text{wall}} = 578 \text{ K}$  (580 °F) and copper corrosion was observed with sulfur contents above 50 ppm. The result of this deposition process was the formation of a chemically complex, thin, but very tenacious, tar on all exposed copper surfaces. This tar inhibited heat transfer, but had little effect on the flowrate or pressure drop through the channel during the dynamic tests. Copper(I) sulfide is the corrosion product. This corrosive process roughened the copper surfaces, and substantially increased the pressure drop through the cooling channel. It did not have a major impact on the heat-transfer characteristics of the channel. Protective gold or platinum coatings were evaluated to prevent both carbon deposits and copper corrosion. RP-1 was much more stable in Hastelloy-X than in NASA-Z alloy. Additional work was performed under an extension of this contract [209, 210].

### 3.7 Safety Properties of RP-1

#### 3.7.1 Flammability of RP-1 Vapors in Air

Because the content of light boiling hydrocarbons in RP-1 may vary, it is difficult to exactly determine generally valid numbers for flash point and limits of flammability in air. It varies widely from sample to sample.

#### 3.7.2 Suppression of Flammability of RP-1

Experimental studies were carried out to determine the quantities of helium, nitrogen, carbon dioxide, and/or trifluorobromomethane needed for suppressing ignition of mixtures of oxygen with RP-1 under conditions of turbulent flow in a tube measuring 15 cm (6 in) in diameter [211]. The results indicated that on a weight basis the order of effectiveness of the various agents was  $\text{He} \gg \text{N}_2 > \text{CF}_3\text{Br} > \text{CO}_2$  for RP-1. The quantities of agents required were large enough to preclude widespread in-flight applications to

inert leakage once it is detected. The principal utility of inerting processes is probably only in connection with fire prevention during static firing and prelaunch operations on the ground.

### 3.8 Gelled Kerosene RP-1

#### 3.8.1 Metallized Gelled RP-1

##### 3.8.1.1 Aluminized Gelled RP-1

Aluminum slurries in kerosenes have been tested as rocket propellants since the early 1930s (see Section 2.12.3). The types of kerosenes were not very well characterized in those early years. Probably, more testing has been done with aluminized undefined kerosenes and JP-4 than with RP-1. The work described in the following references was done specifically with gelled RP-1. There have not been any flight applications of metallized RP-1.

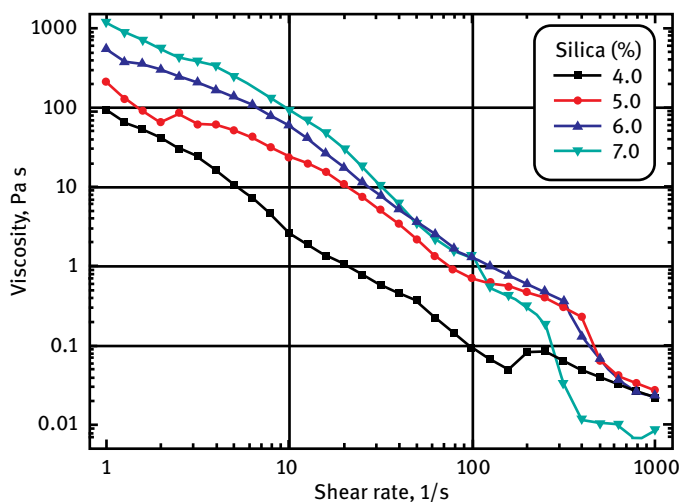
Fumed silica as a gelling agent is not readily wetted by kerosene and conventional kitchen-type rotary mixers do not give uniform gels. Improved dispersion of gellant and added metal powder were achieved with resonant acoustic mixing [212]. The rheology and high-g centrifuge stability of kerosene gelled with EH-5 fumed silica and metallized with nano-aluminum L-Alex<sup>®</sup> powder were measured with different gelling agent loadings, but mostly the same metal loading of ~30%. A surfactant was used to help wet the nanoparticles to aid in the uniform dispersion in the gelled propellant.

The rheological behavior of gelled RP-1 and JP-8 with fumed silica as a gelling agent has been measured and an optimal mixing process has been selected [213]. The rheological parameters of the gelled kerosene showed a significant influence of the added amount of silica in comparison with the ungelled pure liquids (Figure 22). Similar measurements were made with JP-8 instead of RP-1.

The rheology and droplet burning behaviors of RP-1 gelled with fumed silica were compared with those of MMH gelled with hydroxypropyl cellulose [129]. Droplets of gelled MMH burning in air swelled and had a flexible droplet surface, whereas burning kerosene droplets gelled with fumed silica had a rigid silica structure that remained unburned.

Gelled RP-1 has been used to study the rheological behavior of gelled hydrocarbons using 4–7 mass-% of fumed silica as the gelling agent [113]. Viscosity, stability, thixotropic behavior, and the viscoelastic properties of the gel through their storage and loss moduli were measured as a function of the amount of gelling agent added. Differential scanning calorimetry measurements showed only a slight influence of the gelling-agent amount on the enthalpy of vaporization of the gels. The ungelled hydrocarbons had a higher enthalpy of vaporization than the gels.

Fumed silica, also known under the trade name Cab-O-Sil<sup>®</sup>, is a useful gelling agent for fuels as well as oxidizers. The rheological behavior of gelled JP-8 turbine fuel



**Figure 22:** Viscosity of gelled RP-1 as a function of shear rate and silica amount. (Reproduced and modified from [213] with permission dated 11-Feb-2021.)

and gelled rocket propellant RP-1 with fumed silica as a gelling agent was measured and the optimal gel mixing process, gel stability, and rheological parameters showed a significant influence of the added silica amount [127, 128].

### 3.8.1.2 Nano-Aluminum in Metallized RP-1 Gels

A constant volume bomb was used to measure the ignition delay of nano-aluminum metallized RP-1 injected into the air-filled bomb containing air at controlled temperature and pressure [214]. Time was measured from the first movement of the piston injecting the fluid into the chamber to the first noticeable pressure rise. The ignition delay times were measured for RP-1 with and without various amounts of added aluminum and at different temperatures, pressures, and gas compositions in the bomb.

Aluminum as an additive to fuels is a highly energetic metal that can react with a wide variety of oxidizers to produce propellants with a high specific impulse. When added to kerosene rocket fuel, aluminum substantially increases theoretical volumetric density  $I_{sp}$ , potentially reducing the size of tankage and overall system weight. However, depending on the particle size, aluminum tends to agglomerate in burning liquid hydrocarbon droplets, delaying combustion within the engine, reducing the delivered performance. Gels were formulated of 0, 25, 30, and 55 mass-% Alex<sup>®</sup> nano-aluminum powder suspended in RP-1 using a combination of wetting and gelling agents [215, 216]. The viscosities of such gels was measured as a function of aluminum content, temperature, and shear rate and were found to be non-Newtonian, so-called yield-pseudoplastic. At loadings greater than 30 mass-% Alex<sup>®</sup> no additional gellant was necessary to achieve dynamic stability as measured

by centrifuging the gels at 1300 rpm for 1 h. In contrast, micron size aluminum gels required 5% fumed silica as a gellant to achieve dynamic stability, as did the gels containing only 5% Alex<sup>®</sup>. Ignition delay of Alex<sup>®</sup>/RP-1 gels were determined in a laboratory bomb over the temperature range 673–873 K (400–600 °C) and compared with RP-1 gels without any aluminum and with neat RP-1. The data showed that nano-aluminum could be completely consumed during the interval of spraying in a short laboratory bomb. Moreover, the combustion of Alex<sup>®</sup> accelerated the ignition of the RP-1.

### 3.9 Applications of RP-1

There are dozens of launch vehicles that have used or are currently using RP-1 or its low-sulfur derivative RP-2 as the standard storable hydrocarbon fuel. On more than one occasion there were attempts to formulate hydrocarbon fuels that might have advantages over either RP-1 or RP-2, and lead to a gradual replacement of these fuels.

## 4 Rocket-Grade Kerosene RP-2

### 4.1 Physical Properties of RP-2

Physical properties of RP-1 and RP-2 were measured and are now available on-line in the NIST Reference Fluid Thermodynamic and Transport Properties (REFPROP) computer program [158].

#### 4.1.1 Density of RP-2

The density of RP-2 has been measured with a density and sound speed analyzer DSA 5000, Anton-Paar Corporation, at ambient (0.083 MPa) pressure and compressed liquid density measurements were made with a fully automated densimeter at elevated pressures between 0.083 and 40 MPa [163, 164]. The density of RP-2 as a function of temperature and pressure is illustrated in Figure 23. The solid circle high-pressure data points are for pressures between 0.5 and 40 MPa.

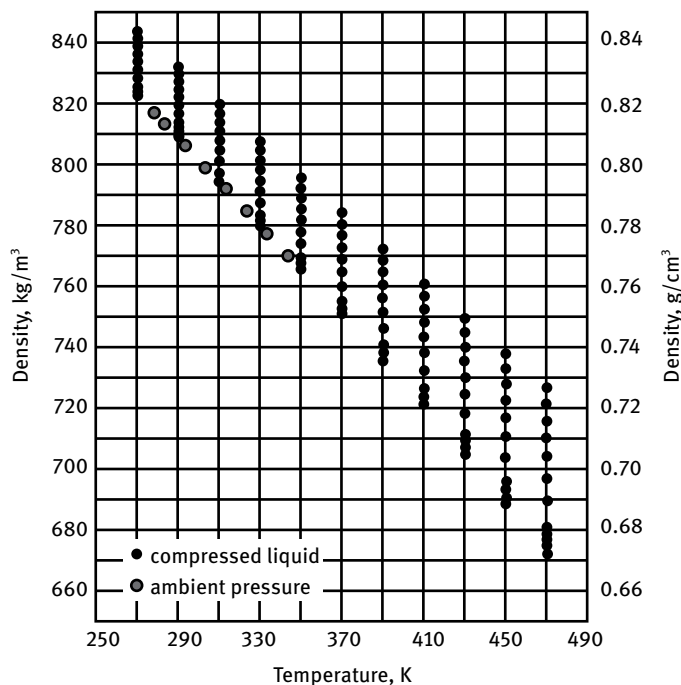
The density of RP-2 at atmospheric pressure can be calculated from the equation:

$$\rho = 288.12529 \times 0.53412256^{-\left[1 + \left(\frac{1-T}{575.46086}\right)^{0.62514441}\right]}$$

where  $\rho$  is the density in kg/m<sup>3</sup> and  $T$  is the temperature in kelvin.

The density of two RP-2 samples was measured at temperatures up to 573 K and pressures up to 100 MPa [217]. A high-temperature, high-pressure (HTHP) variable volume, windowed densimeter was used to determine the density. The experimental den-





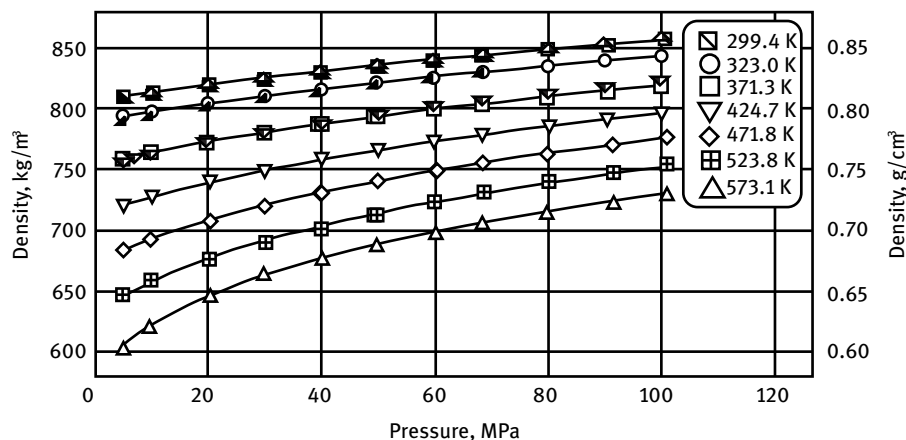
**Figure 23:** Density of RP-2 as a function of temperature and pressure. (Modified from [163].)

sity data were satisfactorily correlated by the modified Tait equation that provided a means for interpolating the density within the experimental conditions investigated in this study. The lines in Figure 24 show the fit of the Tait correlation to the experimental data. The HTHP perturbed-chain statistical associating fluid theory, Peng–Robinson (PR), and HTHP volume-translated PR equations of state were used to model RP-2 density over the entire temperature and pressure ranges. The densities of the two RP-2 samples were compared and contrasted with those reported by Outcalt et al. (2009) to highlight the impact of compositional differences on the observed RP-2 densities.

#### 4.1.2 Velocity of Sound and Compressibility of RP-2

The velocity of sound of RP-2 was measured with a density and sound speed analyzer DSA 5000, Anton-Paar Corporation, at ambient (0.083 MPa) pressure [163, 164]. The velocity of sound of RP-1 and RP-2 as a function of temperature is illustrated in Figure 7 (in the section on RP-1). The temperature dependence of the velocity of sound of RP-2 can be expressed by the polynomial equation:

$$v = 2809.8695 - 6.2215696 T + 3.9342693 \times 10^{-3} T^2$$



**Figure 24:** Density of RP-2A as a function of temperature and pressure. (Reprinted and modified from [217], with permission from ©2019 Elsevier; permission conveyed through RightsLink.)

where  $v$  is the velocity of sound in m/s and  $T$  is the temperature in kelvin. Adiabatic compressibilities in liquids can be calculated from sonic velocity data with the aid of the following equation:

$$\beta_a = \frac{1}{\rho c^2}$$

where  $\beta_a$  is the adiabatic compressibility in  $\text{m}^2/\text{N}$ ,  $\rho$  is the density in  $\text{g}/\text{m}^3$ , and  $c$  is the velocity of sound in m/s. The adiabatic compressibility of RP-1 and RP-2 was already illustrated in Figure 8 (above).

#### 4.1.3 Vapor Pressure of RP-2

There is a lack of vapor pressure data on RP-1 and RP-2. Vapor pressure of these kerosenes varies widely depending on composition of the mixture of up to 100 different hydrocarbons.

#### 4.1.4 Viscosity of RP-2

The viscosity of an RP-2 sample has been measured in an open gravitational capillary viscometer at ambient atmospheric pressure from 293 to 373 K [163, 164] (Table 27 and Figure 14).

Expanding on earlier viscosity measurements of rocket propellants from 293 to 373 K at atmospheric pressure, the viscosity of RP-2 was measured at temperatures from 270 to 425 K and at pressures up to 137 MPa using an oscillating-piston viscometer [169] (Figure 25). The pressure was changed in increments of 10 MPa between 10 and 130 MPa. The instrument was modified and recalibrated at the National Institute of

Table 27: Viscosity of RP-2.

| Temperature<br>$T$ | Kinematic viscosity $\nu$<br>$\text{mm}^2 \text{s}^{-1}$ | Dynamic viscosity $\eta$<br>$\text{mPa s}$ |
|--------------------|----------------------------------------------------------|--------------------------------------------|
| 373.16             | 0.7916                                                   | 0.5918                                     |
| 363.15             | 0.8735                                                   | 0.6595                                     |
| 353.15             | 0.9683                                                   | 0.7383                                     |
| 343.15             | 1.078                                                    | 0.8298                                     |
| 333.15             | 1.215                                                    | 0.9446                                     |
| 323.15             | 1.390                                                    | 1.091                                      |
| 313.15             | 1.607                                                    | 1.272                                      |
| 303.15             | 1.897                                                    | 1.516                                      |
| 293.15             | 2.267                                                    | 1.828                                      |

Data source: [163,164]

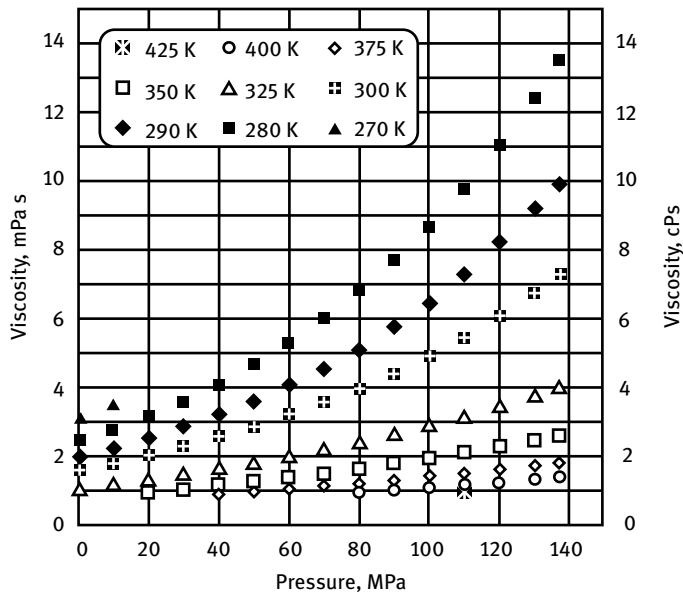


Figure 25: Viscosities of RP-2 as a function of temperature and pressure. (Reproduced and modified from [169].)

Standards and Technology with *n*-dodecane as a known reference fluid over the full temperature and pressure range. Based on the recalibrations, the repeatability of the measurements was found to be approximately 3%, whereas the uncertainty of the instrument was estimated at 5%. The measured viscosities of RP-2 were compared with values calculated with a five-component surrogate mixture model developed

at the National Institute of Standards and Technology. The experimental data have a stronger pressure dependence than the mixture model and are up to 29% higher at high compressions.

#### 4.1.5 Heat-Transfer Coefficient of RP-2

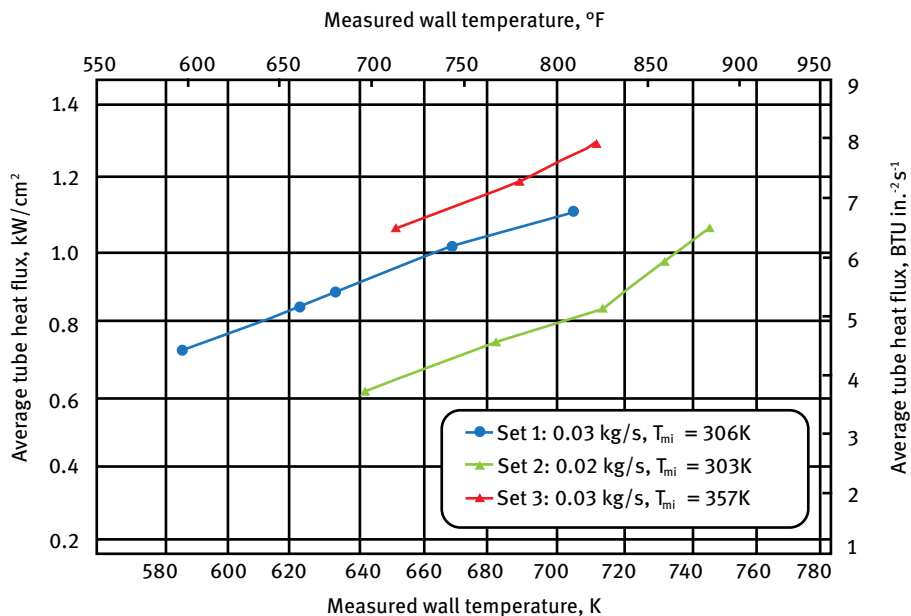
Heat-transfer characteristics of RP-2 experiments were conducted at the Air Force Research Laboratory's HHFF, located at Edwards AFB, CA [218]. The HHFF was designed to explore many fuel-related rocket engine design considerations (e.g., high aspect ratio cooling channels, various fuel thermal stability issues, material compatibility, heat-transfer capability, effects related to dissolved oxygen or specific sulfur species contained within the fuel, etc.). The Air Force has been studying RP-2 (ultra-low sulfur RP-1) to establish an accurate baseline for future experiments in the HHFF. These initial experiments were conducted using low overall heat fluxes and wall temperatures. Results from these experiments demonstrated the facility's ability to produce repeatable data sets, as well as to maintain a constant heat source temperature throughout the test.

The heat-transfer characteristics of RP-2 were examined in the AFRPL HHFF under conditions simulating those encountered in the cooling channels of a real rocket engine [219]. Short-duration thermal stressing tests provided heat-transfer information that closely followed existing empirical correlations for RP-1. Effects of wall temperature, bulk temperature, and flow rate on heat transfer were observed and were consistent with expected behavior. The heat flux increased with increasing wall temperatures (Figure 26).

Average convective heat-transfer coefficient was measured for several short-duration tests, and non-dimensionalized heat transfer (Nusselt number) was compared with an existing empirical correlation for RP-1. Good agreement with the correlation was seen when the experimental data were corrected for inner (wetted) wall temperature, which was shown to vary substantially around the circumference of the tube wall. Longer-duration tests at elevated wall temperatures provided the first steps in identifying the conditions under which solid carbon deposits may form.

The AFRL HHFF simulates cooling channel conditions in a subscale environment [220]. It operates at up to 31 MPa (4500 psi) channel pressure, 480 K (400 °F) bulk fluid temperature,  $>0.075$  kg/s ( $>10$  lb<sub>m</sub>/min.) flow rate, 870 K (1100 °F) wall temperature with 25 PID-controlled heaters that maintain the block temperature. It also has O<sub>2</sub> sparging capability, vacuum environment simulation, and can operate for long test durations at high heat fluxes. Following each test the test section is segmented into 2.5-cm (1-in.) segments that are individually examined under the microscope and analyzed for coke deposition.

A series of electrically heated tube tests were performed at NASA GRC's Heated Tube Facility to investigate the thermal stability and heat transfer of RP-2 as a fuel for



**Figure 26:** Average tube heat flux as a function of wall temperature for short duration tests in copper tube at varying flow conditions. (Reproduced and modified from [219].)

next-generation regeneratively cooled, reusable hydrocarbon boost engines [221]. The effects of duration, operating condition and test piece material on the overall thermal stability and materials compatibility characteristics of RP-2 were evaluated using copper and 304 stainless steel test sections. The copper tests were run at a pressure of 6.8 MPa (1000 psia), heat flux up to 9.8 MW/m<sup>2</sup> (6.0 BTU in.<sup>-2</sup> s<sup>-1</sup>), and wall temperatures up to 911 K (1180 °F). Preliminary results, using measured wall temperature as an indirect indicator of the carbon deposition process, showed that in copper test pieces above approximately 728 K (850 °F), RP-2 begins to undergo thermal decomposition resulting in local carbon deposits. Wall temperature traces showed significant local temperature increases followed by near instantaneous drops, which were attributed to the carbon deposition/shedding process in previous investigations. These findings gave an insight into the feasibility of cooling a long-life, high-performance, high-pressure liquid rocket combustor and nozzle with RP-2.

A model was developed of the steady three-dimensional combined flow of fluid, heat, and electricity in an experimental apparatus designed to test the fuel thermal stability of RP-2 [222]. A numerical simulation was performed for the purposes of model validation and assessment of the detailed thermal characteristics of the apparatus. Conjugate heat transfer and electric current flow of rocket-grade kerosene (RP-2) flowing in an electrically heated tube was simulated. The model and

boundary conditions were selected so as to simulate an experimental case reported in the fuel thermal stability literature. The model included steady, incompressible, variable-density turbulent flow inside the tube, thermally coupled with steady heat conduction, and electric current flow in the solid copper apparatus. Temperature dependences of fluid and solid thermodynamic and transport properties were included in the model. The tube inner wall surface roughness was adjusted in order to match the cooling efficacy of the fuel in the simulation with that observed in the experiment. The simulation predicted an RP-2 temperature rise in agreement with the experiment, and a tube wall thermal state largely in agreement with the experiment. The simulation results were used to identify critical regions of excessive temperature, current flux density, and Joule heating concentration in the experimental apparatus. The predicted tube wall temperatures at each end of the heated portion of the tube were significantly less than the experimentally observed values. The predicted temperatures of the thermal chokes contacting the tube were considerably lower than the experimentally observed values. It was suggested that an unmodeled, unrecognized thermal resistance or resistive heating source may have been present in the experiment.

#### **4.1.6 Thermodynamic Properties of RP-2**

Thermodynamic properties of RP-2 are essentially identical to those of RP-1.

### **4.2 Chemical Properties of RP-2**

#### **4.2.1 Chemical Composition of RP-2**

The GC analytical results for RP-2 were similar to those for RP-1. There were 28 major constituents (peak area counts in excess of 1%) ranging from 2,6-dimethylnonane to *n*-hexadecane. The major constituents comprised linear and branched paraffins, and one- and two-ring cyclic paraffins containing 11-16 carbon atoms with no significant aromatic or olefin content [183]. Changes in the measurement of distillation curves for complex fluids were a significant improvement over previous approaches, featuring a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis) and an assessment of the energy content of each distillate fraction, among other features. The most significant modification was achieved with a different sampling approach that allowed precise qualitative as well as quantitative analyses of each fraction, on the fly. This method was applied to the measurement of a wide variety of fluids, including hydrocarbons, gasoline, jet fuel, diesel fuels (both petroleum-derived and biodiesel), and crude oils, and in particular to representative batches of RP-1, RP-2, and TS-5. Not only the distillation curves but also the composition-explicit information was used to characterize distillate cuts in terms of composition and available energy content by adding up the composite enthalpy of combustion

for each component selected for identification in each distillate fraction. The distillation curves and enthalpy data for all three fluids were very similar. Table 28 shows a comparison of composition of RP-2 and RP-1.

**Table 28:** RP-1/RP-2 comparison (ASTM D2425).

| Summarized D2425 (vol.-%) | RP-1/5235 | RP-2/5433 |
|---------------------------|-----------|-----------|
| Paraffins                 | 44        | 63        |
| Cycloparaffins            | 33        | 18        |
| Dicycloparaffins          | 16        | 14        |
| Tricycloparaffins         | 2.8       | 4.7       |
| Alkylbenzenes             | <0.5      | <0.5      |
| Indans and tetralins      | <0.5      | <0.5      |
| Indenes $C_nH_{2n-10}$    | <0.5      | <0.5      |
| Naphthalene               | <0.5      | <0.5      |
| Acenaphthenes             | <0.5      | <0.5      |
| Acenaphthylenes           | <0.5      | <0.5      |
| Tricyclic aromatics       | <0.5      | <0.5      |
| Monoaromatics (vol.-%)    | <0.2      | 0.2       |
| Diaromatics (vol.-%)      | <0.2      | <0.2      |
| Total aromatics (vol.-%)  | <0.2      | 0.2       |
| Total saturates (vol.-%)  | >99.8     | 99.8      |

Data Source: [219,220]

#### 4.2.2 Surrogate Mixtures Representing RP-2

Because of the complexities involved in measuring and modeling the performance and properties of finished fuels, the fuel science community must often use surrogate mixtures as substitutes, especially in the absence of consensus standard mixtures. Although surrogate mixtures are often formulated on the basis of the ability of a particular mixture to reproduce a particular property, there is usually a desire to employ surrogate mixtures that are physico-chemically authentic. This means that, provided that the primary purpose is satisfied, researchers are inclined to choose mixtures that have physical and chemical properties appropriate to the finished fuel.

Surrogate hydrocarbon fuel mixture models were developed to represent the thermophysical properties of two kerosene rocket propellants, RP-2 and RP-1 [19]. The surrogates were developed with a procedure that incorporated experimental data for the density, sound speed, viscosity, thermal conductivity, and the ADCs for samples of the two fuels. The surrogate for RP-2 contained five components (numbers are molar fractions):  $\alpha$ -methyldecalin (0.354), *n*-dodecane (0.158), 5-methylnonane (0.084), 2,4-dimethylnonane (0.071), and heptylcyclohexane (0.333). Comparisons with experimental data demonstrated that the models were able to represent the density, velocity of sound, viscosity, and thermal conductivity of both fuels to within (at a 95% confi-

dence level) 0.4, 2, 2, and 4% respectively. The volatility behavior, as measured by the ADCs, was reproduced to within 0.5%.

#### 4.2.3 Specifications for RP-2

The composition of RP-2 is a sub-set of the specification for RP-1, as described in MIL-DTL-25576E [80].

#### 4.2.4 Analysis of RP-2

The list of analytical methods used for the characterization of RP-2 to verify compliance with MIL-DTL-25576E is one page long [80]. The most fundamental method used for characterization of hydrocarbon fuel blends is the distillation fraction curve, measuring the amount of distillate that has collected while the temperature in the vapor phase has been rising, and also measuring the amount of less volatile residue left behind at the upper end of the distillation range. Most of those test methods are documented ASTM test methods.

#### 4.2.5 Thermal Stability of RP-2

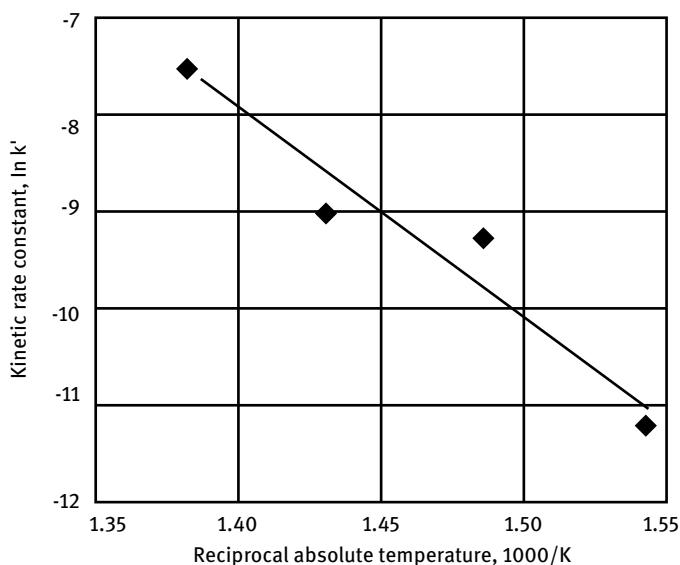
Thermal stability and heat transfer characteristics of RP-2 were examined in the AFRPL HHFF under conditions simulating those encountered in the cooling channels of a real rocket engine [219]. RP-2 was thermally stressed while flowing through circular copper tube test sections. Short-duration thermal stressing tests provided heat-transfer information that closely followed existing empirical correlations for RP-1. Effects of wall temperature, bulk temperature, and flow rate on heat transfer were observed and were consistent with expected behavior. Longer-duration tests at elevated wall temperatures provided the first steps in elucidating the conditions under which solid carbon deposits form. The test sections were analyzed post-test with optical and scanning electron microscopy and carbon deposition burn-off for signs of coke formation. The results from these analyses indicate the presence of solid carbon deposition for high-wall temperature tests exceeding 30 min in duration, although further testing is required to make more conclusive comparisons.

The thermal decomposition of RP-2, and mixtures of RP-2 with three different additives has been investigated [197, 223]. The mixtures with RP-2 contained 5% 1,2,3,4-tetrahydronaphthalene (tetralin), 5% THQ, or 256 mg/L of the additive used to make JP-8+100. Decomposition reactions were performed in stainless steel ampoule reactors at temperatures from 648 to 723 K (375 to 450 °C). All of the reactions were run with an approximate initial pressure of 34.5 MPa (5000 psi). After each reaction the thermally stressed liquid phase was analyzed by GC. For RP-2, the increase in a suite of light decomposition products was used to derive global, pseudo-first-order rate constants that approximated the overall rate of decomposition. The addition of THQ and tetralin had a significant effect on the decomposition of RP-2. Compared with neat



RP-2, the addition of 5% THQ slowed the decomposition by one order of magnitude, whereas the addition of 5% tetralin slowed the decomposition by approximately 50%.

The decomposition kinetics of RP-2 was studied at 648, 673, 698, and 723 K (375, 400, 425, and 450 °C) in comparison with RP-1 [198]. All of the decomposition reactions were performed in stainless-steel ampule reactors. At each temperature, the extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase by GC. These data were used to derive global pseudo-first-order rate constants that approximate the overall rate of decomposition for the fuel. For RP-2, decomposition rate constants ranged from  $1.33 \times 10^{-5} \text{ s}^{-1}$  at 648 K (375 °C) to  $5.47 \times 10^{-4} \text{ s}^{-1}$  at 723 K (450 °C) (Figure 27). There was no significant difference between RP-1 and RP-2 in this test.



**Figure 27:** Rate constants of RP-2 thermal decomposition. (Reproduced and modified from [158].)

The activation energy derived from the slope of the Arrhenius graph shown above was  $180 \pm 30 \text{ kJ/mol}$ . One use of these rate constants is for the design and planning of physical property measurements at high temperatures. On the basis of the amount of time required for 1% of the sample to decompose ( $t_{0.01}$ ), allowable instrument residence times ranged from 15 min. at 648 K (375 °C) to 0.3 min. at 723 K (450 °C).

Hydrogen donors increase thermal stability by interrupting radical decomposition pathways. The effect of three potential stabilizing additives on the thermal decomposition of RP-2 was investigated in stainless steel reactors [224]. The additives were THQ, 1,2,3,4-tetrahydronaphthalene (tetralin), and the additive package that is used to make JP-8+100 (herein referred to as the “+100 additive”). For mixtures of RP-2

with THQ and tetralin, the concentration of additive was 5% by mass. The mixture of RP-2 with the +100 additive contained only 256 mg/L of the additive (the same concentration used to make JP-8+100). Decomposition reactions were performed at 648, 673, 698, and 723 K (375, 400, 425, and 450 °C) in stainless steel reactors. At each temperature, the extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase using GC. The results with each additive were compared with the decomposition of neat RP-2 under the same conditions. The addition of 5% THQ slowed the rate of decomposition by approximately one order of magnitude. The addition of 5% tetralin slowed the rate of decomposition by approximately 50%. At the low concentration tested, the +100 additive did not significantly change the thermal stability of the RP-2.

The stabilizing additive THQ was identified as a potential stabilizer for RP-2, but previous tests were done at only one concentration of this additive. In order to determine the minimum effective additive level, the thermal stability of RP-2 with varying concentrations of THQ was investigated [225]. The mixtures (% by mass) were RP-2 + 0.1% THQ, RP-2 + 0.5% THQ, RP-2 + 1% THQ, and RP-2 + 5% THQ. These were thermally stressed in sealed stainless-steel reactors at 673 K (400 °C) for 1–4 h. The approximate initial pressure at the reaction temperature was 34.5 MPa (5000 psi). The extent of decomposition as a function of time was determined by analyzing the thermally stressed liquid phase using GC. The results with each THQ mixture were compared with the thermal stability of neat RP-2 under the same conditions. The thermal stability of the mixtures showed a clear dependence upon the concentration of THQ. For example, the addition of 5% THQ slowed the rate of decomposition by approximately one order of magnitude, and the addition of 0.5% THQ slowed the rate of decomposition by approximately 50%. Another potential stabilizing additive evaluated was *trans*-decahydronaphthalene (decalin). Unlike THQ, the addition of 5% decalin to RP-2 had no significant effect on the thermal stability of RP-2.

A series of tests were performed in NASA GRC's Heated Tube Facility to study the heat-transfer and thermal-stability behavior of RP-2 under conditions similar to those found in rocket engine cooling channels [226]. Using resistively heated copper tubes in a vacuum chamber, flowing RP-2 was heated to explore thermal effects under a wide range of test conditions. Wall temperature (728–839 K = 850–1050 °F) and bulk fluid temperature (422–533 K = 300–500 °F) were varied to define thermal decomposition and stability at each condition. Flow velocity and pressure were fixed at 22.8 m/s (75 ft/s) and 6.8 MPa (1000 psia) respectively. Five different batches of RP-2 were tested under identical conditions to examine any thermal-stability differences resulting from batch-to-batch compositional variation. Among these tests was one with the potential coke reducing additive THQ. Although pure copper tubes were used for the majority of tests, two exploratory tests were performed with a copper alloy known as GRCo-42. Each tube was instrumented with 15 thermocouples to examine the temperature profile, and carbon deposition at each thermocouple location was determined post-test in an oxidation furnace. In many tests, intermittent local temperature increases were

observed visually and in the thermocouple data. These hot spots did not appear to correspond to a higher carbon deposition.

Measurements were made at ambient pressure of the thermophysical properties density, velocity of sound, and viscosity, and the derived property adiabatic compressibility, for the same thermally unstressed and stressed RP-2 fuel samples [204]. The fuel was pressurized by use of a high-pressure syringe pump and then delivered to a high-temperature reactor capable of generating controlled temperatures up to 873 K (600 °C). Downstream of the reactor, the fluid was delivered to a chilled water bath heat exchanger to cool the fluid and quench any further decomposition reactions. The cooled fluid was then directed through a back-pressure regulator and into a collection vessel. The combination of the syringe pump and back-pressure regulator allowed the operator to control the residence time of the fluid in the reactor by providing controlled, constant flow rates at a wide range of nominal pressures. For this work, the RP-2 samples were thermally stressed for 0.5 ( $\pm 0.05$ ) min at a constant pressure of 17 ( $\pm 0.1$ ) MPa and at two temperatures, 748 and 783 K (475 and 510 °C). Density, velocity of sound, and viscosity were measured for samples of RP-2 that had been stressed for 0.5 min at 748 and 783 K (475 and 510 °C) at a pressure of 17 MPa. Density and velocity of sound were measured from 278 to 323 K (5 to 50 °C) for samples stressed at 748 K (475 °C) and from 278 to 308 K (5 to 35 °C) for samples stressed at 783 K (510 °C). Viscosity was measured from 263 to 323 K (−10 to +50 °C) and 263 to 308 K (−10 to +35 °C) for the samples stressed at 748 and 783 K (475 and 510 °C) respectively. All measurements were made at ambient atmospheric pressure ( $\sim 83$  kPa). The densities of stressed samples were lower than those of the unstressed samples. For both RP-1 and RP-2, the densities of the thermally stressed samples were lower relative to their respective unstressed samples, but the magnitudes of those decreases in density were different for the two fuels. For RP-1, the two thermally stressed samples had similar densities. In contrast to RP-1, the thermally stressed RP-2 samples had densities that were more significantly different from one another, varying by 0.4% at 278 K (5 °C) and 0.6% at 308 K (35 °C). Consequently, relative to unstressed RP-2, RP-2-TS-475 had densities that were 0.8–0.9% lower and RP-2-TS-510 had densities that were 1.2–1.4% lower. As RP-2 decomposed, the concentrations of smaller, more volatile molecules increased. The sound speeds of the thermally stressed samples were lower relative to their respective unstressed samples for both RP-1 and RP-2. Relative to unstressed RP-2, RP-2-TS-475 had sound speeds that were 1.2–1.6% lower and RP-2-TS-510 had sound speeds that were 3.2–3.7% lower. For both RP-1 and RP-2, the dynamic viscosities of the thermally stressed samples were considerably lower relative to their respective unstressed samples, with the TS-510 samples showing the most significant deviations. Relative to unstressed RP-2, RP-2-TS-475 had dynamic viscosities that were 15–17% lower and RP-2-TS-510 had values that were 40–41% lower.

In order to identify compositional changes that could improve the thermal stability of RP-2, the effect of different types of alkanes on the thermal stability of RP-2 was investigated [227]. The proportion of linear, branched, or cyclic alkanes was in-

creased by mixing RP-2 with one of the following alkanes (25% by mass): *n*-dodecane, *n*-tetradecane, 4-methyldodecane, 2,6,10-trimethyldodecane, or 1,3,5-triisopropylcyclohexane. These mixtures were thermally stressed in stainless steel ampule reactors at 673 K (400 °C, 752 °F) for up to 4 h. After each reaction, the stressed fuel was analyzed by GC with flame ionization detection. The decomposition kinetics of each added alkane was determined from the decrease in its chromatographic peak. The overall decomposition kinetics of each fuel mixture was determined from the increase in a suite of chromatographic peaks that correspond to light, liquid phase decomposition products. These data are compared with similar data for neat RP-2.

As of 2014, there existed no standardized test methods to quantify the thermal stability of a kerosene fuel. Advancements in fuel processing, analysis, and thermal performance testing have provided insight into the conditions, influences, and pathways of troublesome fuel thermal decomposition in liquid rocket engine cooling systems. Multiple parameters have been identified or suggested/suspected to influence fuel thermal stability. These include overall fuel chemical composition in terms of hydrocarbon classes, the role of specific fuel constituents such as additives (beneficial) and contaminants (detrimental) on deposit formation, the effect of compositional variability on system-level cooling performance, primary fluid and thermal effects (e.g., pressure, surface temperature, etc.) determining the limitations of fuel use for a given application or environment, and coolant channel surface material composition, roughness, and treatment. Existing standard test methods are incapable of replicating the operating environments of cooling systems for advanced engines, and operational thermal stability tests are often accompanied by high associated costs and relatively long turnaround times. The proposed Compact Rapid Assessment of Fuel Thermal Integrity (CRAFTI) test methods are envisioned to be included in future fuel detail specifications for thermal performance requirements.

## 5 Chinese Aviation-Grade Kerosene RP-3

Kerosene RP-3 is used mainly in China for air-breathing turbine jet and ramjet engine propulsion. It is not known as a rocket propellant. This type of kerosene was repeatedly referred to as an “endothermic fuel.” It is assumed that it undergoes endothermic chemical changes (cracking) if used as a coolant at high temperatures.

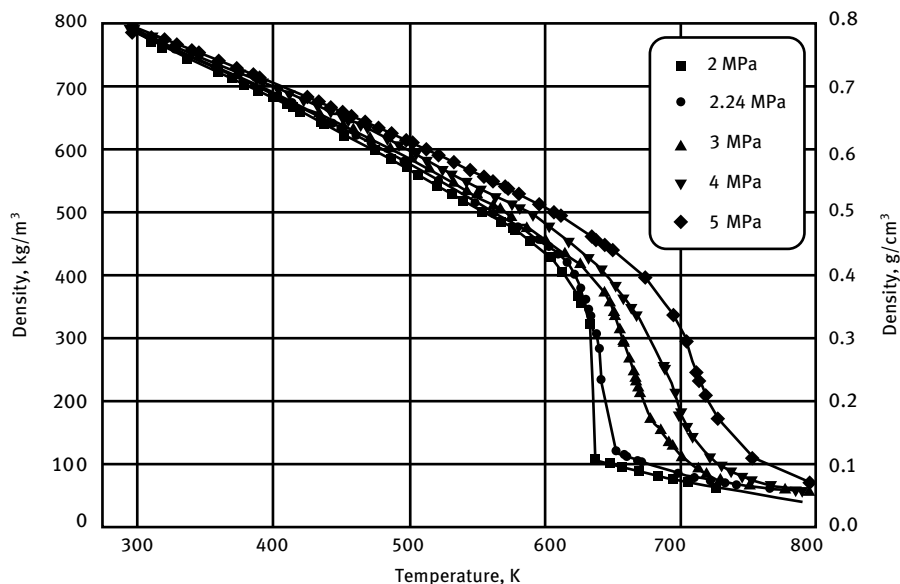
Nobody is planning to use RP-3 in the US, so why would we go to the trouble of listing it here? There are hundreds of publications investigating RP-3, but only a few of those are listed here. This is done for a reason similar to the argument why we included Russian kerosenes in our review. Although we may never see any RP-3 in our laboratory, the techniques used in other countries to characterize and improve hydrocarbon fuels may also be applicable to our grades of RP and JP. It would be interesting to compare the properties of RP-3 with US kerosenes such as JP-4, JP-5, and JP-8 in side-by-side tests. There may be some commonalities.

## 5.1 Physical Properties of RP-3

It appears that most of the recently published reports on the physical properties of RP-3 deal only with the fuel in the near-critical or super-critical state and accurate properties at room temperature and over the entire normal liquid range are difficult to find.

### 5.1.1 Density of RP-3

The density of RP-3 at sub- and super-critical conditions at 295 to 796 K under pressures from 0.1 to 5 MPa was measured using a dynamic density measurement method that was based on mass conservation equation and that can be applied to the density measurement of single-phase flow including supercritical fluids [228]. As shown in Figure 28, the density drops abruptly as the temperature approaches the critical temperature. The uncertainty of the measurement was within  $\pm 0.635\%$  according to error analysis. The results were fitted as polynomials to analyze deviations. For the 265 experimental data points, the AAD and the maximum absolute deviation (MAD) were 0.539 and 3.29% respectively. In addition, the isobaric thermal expansion coefficient  $\alpha_P$  was derived from the fitted values of the density.



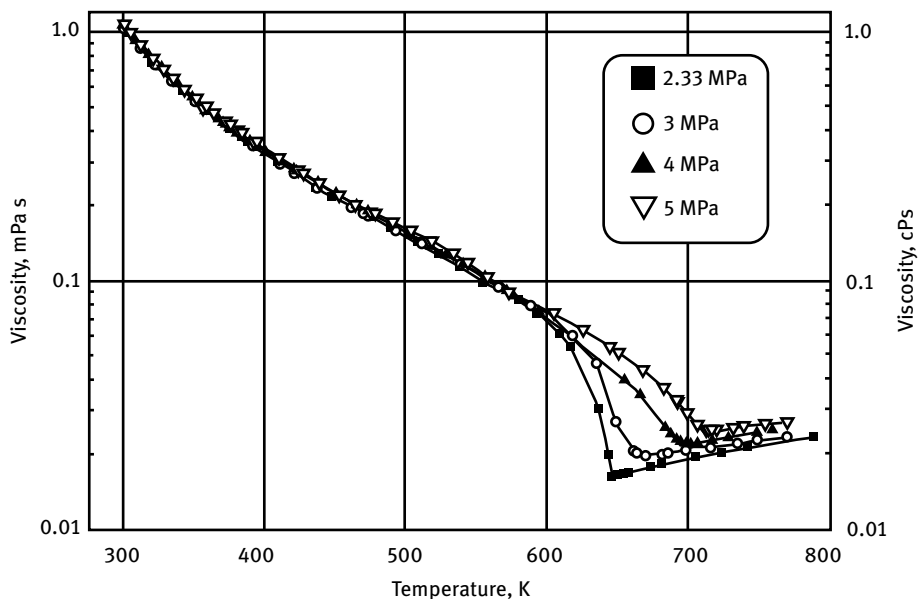
**Figure 28:** Density variations of RP-3 versus temperature under different pressures. (Reprinted and adapted from [228], with permission of ©2011 American Chemical Society; permission conveyed through RightsLink.)

It appears that a developmental fuel called Endothermic Hydrocarbon Fuel-Tianjin University (EHF-TU) is a narrow cut of distillates taken from RP-3, consisting mainly of naphthenic hydrocarbons (51.3%), alkanes (48.2%), and aromatic hydrocarbons (0.5%) with a boiling range of 455–528 K. A list of constituents showed 21 hydrocarbons (0.3 to 22 mass-%). The main constituent was *n*-dodecane. The density of EHF-TU has been measured at temperatures of 303 to 765 K and pressures of 3 to 7 MPa [229], varied from 759 to 134 kg/m<sup>3</sup>, and is similar to that of RP-3. The critical pressure of EHF-TU is about 1.913 MPa, which is below that of RP-3.

### 5.1.2 Viscosity of RP-3

The viscosity of RP-3 under critical and supercritical conditions over a temperature range of 298 to 788 K under pressures from 2.33 to 5 MPa was measured by expanding the classical capillary viscosity measurement method, and it can be applied to the viscosity measurement of single-phase flow, including supercritical fluids [230]. In these experiments, the total pressure drops of long and short measurement tubes were measured simultaneously. The uncertainty of the measurement was within  $\pm (2.1 \text{ to } 6.4)\%$  ( $k = 2$ ) according to error analysis. The results were fitted as polynomials to analyze deviations. Out of 219 points, 205 points were within the  $\pm 5\%$  error band, which is 93%. Figure 29 shows the dynamic viscosity variations of RP-3 versus temperature under different pressure conditions. Like other pure fluids, the dynamic viscosity of RP-3 increased with an increase in pressure, especially in critical and pseudocritical regions. Before reaching critical and pseudocritical points, the viscosity of RP-3 exhibited liquid-like properties where the viscosities of RP-3 decreased with an increase in temperature.

Two different methods were proposed for hydrocarbons online viscosity measurements at high temperatures and high pressures in a two-capillary viscometer based on the Hagen–Poiseuille theory [231]. The first method, called Referenced Flow Method, measures the pressure drop, mass flux and density ratios of the test and reference fluid in a two-capillary system, and then calculates the test viscosity from the ratio relations regardless of the tube parameters. In the second method, a thermal expansion method (TEM), the fluid viscosity is obtained in a two-capillary process by measuring the pressure drop ratio, density ratio, and thermal expansion of a capillary tube, such that mass flux and reference fluid are no longer required in TEM. Pure *n*-dodecane and a binary mixture of *n*-heptane and *n*-octane were selected to validate the reliability and accuracy of the two methods. Viscosities of two endothermic fuels were obtained using the two-capillary viscometer at temperatures from 303 to 673 K and pressures up to 5.00 MPa. Based on these data, a viscosity relation formula as a function of temperature for two fuels was developed within 4.2% deviation.



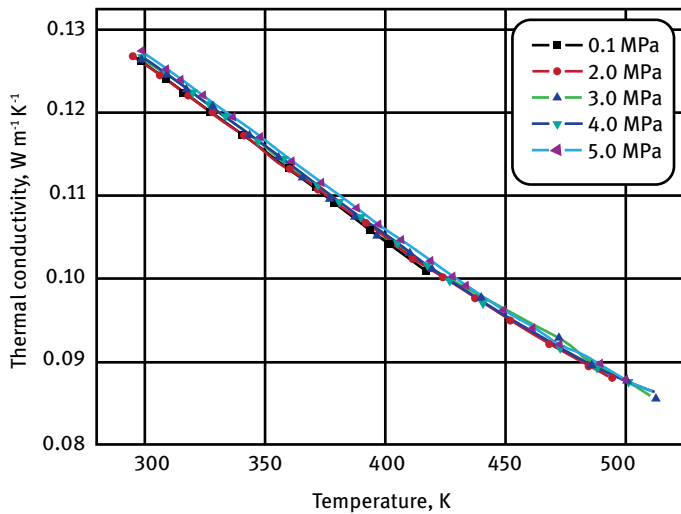
**Figure 29:** Dynamic viscosity of RP-3 versus temperature at supercritical pressures. (Reprinted and adapted from [230], with permission from ©2012 American Chemical Society; permission conveyed through RightsLink.)

### 5.1.3 Thermal Conductivity of RP-3

The thermal conductivity of a representative endothermic hydrocarbon aviation kerosene fuel RP-3 was measured using the classical transient hot-wire method at sub- and supercritical pressures [232]. The measured data cover a temperature range of 285 to 513 K and a pressure range of 0.1 to 5 MPa (Figure 30). The expanded uncertainty of the experiment was less than 3.0% based on an uncertainty analysis. The measured data were correlated using a polynomial equation to analyze the deviations; 97.6% of the measured data were within a 2% error band. The AAD and MAD of the fitted thermal-conductivity data were 0.209 and 2.31% for all values respectively.

### 5.1.4 Heat-Transfer Coefficient of RP-3

The convective heat-transfer characteristics of China RP-3 kerosene under supercritical pressure conditions were studied using the finite volume method and a two-equation turbulence model with enhanced wall treatment [233]. The heat transfer with different constant wall heat fluxes was analyzed, and a correlation of heat-transfer enhancement was obtained. The effect of mass flow rate on the convective heat transfer with a varying wall heat flux condition at the supercritical pressure was investigated. Because of the special thermophysical properties of the



**Figure 30:** Variations of the thermal conductivity of RP-3 with temperature at different pressures. (Reprinted and modified from [232], with permission by ©2015 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

kerosene at supercritical pressure, the Nusselt number can only be related to the Reynolds number after the heat transfer is enhanced. The simulation results were compared with empirical formulas in the literature.

The heat-transfer characteristics of RP-3 flowing through vertically downward capillary tubes (ID=1.8 mm) were experimentally investigated at supercritical pressure ( $P=5$  MPa,  $P_R=2.15$ ) at 373 to 800 K [234]. Test results indicated that in the initial heating region, wall temperatures increased dramatically from the initial heating point and then decreased rapidly at higher heat flux, but this phenomenon diminished when the inlet Reynolds number reached 10000. In addition, heat transfer deterioration occurred when the thermal acceleration parameter ( $K_v$ ) was less than  $1.5 \times 10^{-8}$  or the buoyancy factor ( $Bo^*$ ) was less than  $1.6 \times 10^{-10}$ . A new heat transfer correlation was developed based on the experimental data and that predicted the heat transfer for RP-3 with reasonable accuracy.

A surrogate fuel composed of 53% (mol-%) *n*-undecane, 18% 1-butylcyclohexane, and 29% 1,3,5-trimethyl-benzene was proposed to simulate a specific composition of aviation kerosene RP-3, based on the method of averaging molecular weight [235]. Taking advantage of the principle of extended corresponding states and fundamental thermodynamic relationships, thermophysical and transport properties of the surrogate fuel were calculated and verified by comparison with RP-3 experimental data. A numerical study was conducted aimed at RP-3 flow heat-transfer characteristics in a vertical tube, which revealed the typical heat exchange characteristics of RP-3 flow heat exchange at supercritical pressure, and which showed that heat transfer was sig-



nificantly enhanced owing to abrupt changes of physical property when the fluid temperature approached the pseudo-critical temperature. The effect of buoyancy and turbulent kinetic energy on heat transfer needed to be analyzed.

A 2D axisymmetric numerical study of supercritical heat transfer of RP-3 flowing inside the cooling channels of scramjet used a ten-species surrogate fuel to evaluate the viscosity of RP-3 at 3 MPa with NIST Supertrapp software [236]. Density, viscosity, heat capacity, and thermal conductivity at 300–800 K and 3 MPa were available in the literature from experimental data and shown in four graphs. In addition, viscosity was computed from a commercial code with a ten-species surrogate. A study of the effects of heat flux, mass flow rate, and inlet temperature on supercritical heat-transfer processes indicated that when the wall temperature rose above the pseudocritical temperature of RP-3, the heat-transfer coefficient decreased as a result of a drastic decrease in the specific heat. The conventional heat-transfer correlations were no longer appropriate for the supercritical heat transfer of RP-3. Other formulas, which were proposed for supercritical CO<sub>2</sub> and water, gave a good prediction except when the wall temperature was near or higher than the pseudocritical temperature.

The flow patterns of two-phase flow inside the cooling channels of a scramjet have a great influence on the heat-transfer characteristics. Phase transition processes of RP-3 kerosene flowing inside a square quartz-glass tube were experimentally investigated [237]. Three distinct phase transition phenomena (liquid-gas two-phase flow under sub-critical pressures, critical opalescence under critical pressure, and corrugation under supercritical pressures) were identified. The conventional flow patterns of liquid–gas two phase flow, namely bubble flow, slug flow, churn flow, and annular flow, were observed under sub-critical pressures. Dense bubble flow and dispersed flow were observed when the pressure was increased toward the critical pressure whereas slug flow, churn flow, and annular flow disappeared. Under critical pressure conditions, the opalescence phenomenon was observed. Under supercritical pressures, no conventional phase transition characteristics, such as bubbles, could be seen. However, some kind of corrugation appeared when RP-3 transferred from liquid to supercritical conditions. The refraction index variation caused by a sharp density gradient near the critical temperature is thought to be responsible for this corrugation.

Two-dimensional coupled heat transfer of RP-3 in a tube was modeled and computed [238]. Effects of thermal conductivity on coupled heat transfer and influences of radial property variation, buoyancy, and acceleration on heat-transfer deterioration were investigated. Results indicated that solid thermal conductivity had almost no effect on the convective heat transfer, but high wall metal thermal conductivity reduced radial temperature gradients inside the wall. Acceleration effect on heat transfer could be neglected under the typical operating conditions of scramjet engines. Buoyancy caused heat-transfer deterioration for upward flow at relatively small values of the specific mass flow rate. When the value of the specific mass flow rate was relatively large, radial property variation caused heat-transfer deterioration. Heat-transfer de-

terioration appeared when the ratio of heat flux to specific mass flow rate was larger than  $410 \text{ J/kg}$  at  $4.5 \text{ MPa}$ .

A three-dimensional Navier–Stokes code was used to investigate the heat-transfer characteristics and flow resistance of kerosene RP-3 under supercritical pressure in a tube [239]. For the numerical simulation, the thermophysical and transport properties of a surrogate fuel, which consisted of 53% (mol-%) *n*-undecane, 18% 1-butylcyclohexane, and 29% 1,3,5-trimethyl-benzene, were calculated and verified by comparison with RP-3 experimental data. The length and diameter of the stainless tube were 300 and 1.8 mm respectively. The inlet temperatures varied from 370 to 770 K, and the operating pressures were 3, 4 and 5 MPa. The mass flows were 2, 3 and 4 g/s, with different heat-flow densities of 300, 400, 500, and  $550 \text{ kW/m}^2$ . The research results showed that the calculated pressure drops agreed well with the experimental data when the temperature was lower than 720 K. The discrepancy between numerical and experimental data became gradually more distinct after the temperature rose to higher than 720 K. When the bulk temperature was lower than the critical temperature, the pressure drops under different operating pressures were almost the same. Although the bulk temperature was higher than the critical temperature, the diversion of pressure drop under different operating pressures became gradually more noticeable. The local Nusselt number first increased and then suddenly decreased at a certain position. The heat-transfer deterioration was caused by intensive variations of thermo-physical properties of the fuel under supercritical pressures. The sudden decrease shift appeared earlier when the heat flux was larger.

An updated correlation for heat transfer to RP-3 in vertical tubes under supercritical pressure was based on the literature database of RP-3, which contained 1722 experimental data points compiled from six published papers [240]. It had a MAD of 11.0%, predicting 83.7% of the entire database within  $\pm 20\%$ , whereas the best existing model available in the literature prior to that time only had an MAD of 24.1%, predicting 58.4% of the entire database within  $\pm 20\%$ . The new model improved the prediction accuracy of RP-3 heat transfer under supercritical pressure remarkably.

The mixed convection heat transfer to supercritical RP-3 in vertical tubes and the effects of buoyancy and thermophysical properties on convection were investigated [241]. The wall heat fluxes ( $200\text{--}500 \text{ kW/m}^2$ ), inlet pressures (3–5 MPa) and inlet Reynolds numbers (5000–10500) were maintained constant in the experiments. The study showed that heat-transfer impairment occurred in the inlet region for all upward flow conditions due to buoyancy effects, which was not observed in the downward flow tests. The heat-transfer coefficient increased as the fluid bulk temperature increased as a result of comprehensive effects of thermophysical properties. At a lower inlet Reynolds number (5700), the radial velocity profile changed in downward flow conditions leading to heat-transfer enhancement due to buoyancy effects. The buoyancy effects were also significant for higher inlet Reynolds numbers (10500).

The heat transfer to supercritical pressure RP-3 in vertical miniature round tubes and the influence of heat flux, fluid inlet temperature, flow orientation and pressures on the heat transfer of RP-3 were measured [242]. The heat transfer of supercritical pressure kerosene RP-3 flowing through a vertical pipe with an inner diameter of 1.8 mm was investigated for inlet pressures of 3–5 MPa, which is beyond the critical pressure (2.33 MPa), and an inlet Reynolds number of 5000. Heat-transfer deterioration occurred only for upward flow at the entrance section owing to wall shear forces weakened by buoyancy forces. In heated downward flow, heat transfer was enhanced with high buoyancy effects. In contrast, heat transfer in heated upward flow increased monotonically with increasing buoyancy. The existing criteria for evaluating the buoyancy effects are invalid for supercritical hydrocarbon fuel. Periodic thermoacoustic oscillation (0.125–0.25 Hz) was detected in the case of low inlet temperatures under high heat flux. Probably, some micro bubbles may be generated near the tube wall under high undercooling condition. Owing to the high solubility of supercritical pressure fluids, these micro bubbles rapidly vanish into the mainstream, resulting in a sharp local fluid bulk temperature decrease.

Heat transfer to RP-3 at supercritical pressures in vertical capillary tubes with inner diameters of 0.538, 1.09, and 1.82 mm under heating conditions and the effects of system pressure, heat flux, mass flow rate, and flow direction were experimented with and analyzed for a wide range of supercritical conditions [243]. The effect of capillary tube inner diameter on heat transfer was compared at otherwise identical conditions. The results indicated that sharp variations of thermal properties with temperature were the key factor in influencing heat transfer. Normal, deterioration, and enhancement heat-transfer phenomena generally occurred along the  $X/L$  dimensionless position along the tube. Nusselt number variation showed good agreement as long as the temperature ratio  $T_b/T_{pc}$  was lower than 0.80 and  $Bo^* = 1.0 \times 10^{-8}$  would be the critical point for evaluating buoyancy influence. Two empirical correlations of Nusselt numbers were proposed for downward and upward flow heat transfer in 1.09-mm tubes.

Convective heat-transfer characteristics of RP-3 at supercritical pressures flowing through U-shaped tubes with an inner diameter of 1.82 mm and bending radius of 20, 30, and 40 mm were experimentally investigated [244]. Inner wall temperature and heat-transfer coefficient variations were analyzed under different conditions including heat flux, system pressure, tube bending radius, and flow direction. Test results indicated that centrifugal force strengthens the flow mixing at the bending section and the heat-transfer coefficient was enhanced to 140 to 200% compared with a straight tube. Heat-transfer coefficient values increased with a decrease in bend diameter.

Experimental investigations into heat transfer of RP-3 at supercritical pressure in a horizontal capillary round tube examined the influence of buoyancy on heat transfer of RP-3 [245]. Buoyancy-induced deviations are significant in horizontal flows, and may lead to non-uniform temperature distributions in cross sections of the test section even for narrow round tubes. The buoyancy effects of heat transfer can be evaluated

by the ratio of the Grashof numbers, the non-dimensional parameter  $Gr_q/Gr_{th}$  developed by Petukhov [246]. This criterion was tested for the horizontal flow in narrow round tubes under supercritical pressure conditions, leading to a correlation of Nusselt numbers for supercritical pressure fuels in horizontal tubes.

Convective heat-transfer characteristics of RP-3 at supercritical pressure ( $P = 5$  MPa) in vertical helical tubes were experimentally studied [247]. The helical tube had an inner diameter of 1.82 mm, a helical diameter of 20 mm, and pitch of 10 mm. Circumferential temperatures were measured during both upward and downward flow experiments and the results indicated that:

1. The secondary flow induced by centrifugal force moves outward of the cross section and the inside temperature was larger than the outside temperature. The outside heat-transfer coefficient was about 31% larger than the inside heat-transfer coefficient.
2. Heat-transfer enhancement leading by centrifugal secondary flow was the key factor when the Richardson ratio was larger than 10.
3. Two correlations of Nusselt numbers were developed to predict heat transfer of RP-3 in helical tubes based on experimental data at supercritical pressure.

A CFD model was applied to study flow dynamics and heat transfer of the aviation kerosene RP-3 in a horizontal square cooling channel under asymmetric heating and buoyancy effects at various supercritical pressures [248]. The turbulent fluid flows were described by the standard  $k-\varepsilon$  turbulence model with an enhanced wall treatment, and the strong thermophysical property variations were calculated using the extended corresponding state approaches and a four-component surrogate model of RP-3. The effects of secondary flows and heat flux redistribution induced by buoyancy on supercritical-pressure heat transfer were analyzed. Results indicated that drastic variations of the fuel density with temperature at a supercritical pressure of 3 MPa induced a strong buoyancy effect on heat transfer. As the operating pressure increased from 3 to 5 MPa, the density variation of RP-3 decreased, consequently leading to a weakened buoyancy effect.

Thermo-acoustic instability accompanied by abnormal sounds was observed for supercritical RP-3 flowing in a heated small-scale channel [249]. The instability appeared when the applied heating power exceeded a threshold value. The threshold power can be affected by three operating parameters: fuel mass flow rate, channel inlet temperature, and channel operating pressure. A series of experiments were designed to study the effect of these three parameters on the threshold power. It was found that the threshold power changed monotonously with fuel mass flow rate, whereas there was no simple linear effect of inlet temperature and operating pressure on the threshold power. Two dimensionless parameters, namely, sub-pseudo-critical number and true trans-pseudo-critical number were used to study the boundary of the thermo-acoustic instability. The result revealed that the system stability was significantly enhanced by increasing operating pressure, whereas the effect

of mass flow rate on the system stability was strongly coupled with inlet fluid temperature. The heat transfer was obviously enhanced when thermo-acoustic instability occurred. To understand the relationship between the enhancement on heat transfer and thermo-acoustic instability, the characteristics of thermo-acoustic instability were further investigated [250]. The pressure drop fluctuations were used to represent the characteristics of thermo-acoustic instability. Two main characteristics of thermo-acoustic instability are amplitude and phase duration of the pressure oscillations. These characteristics could be affected by three operating parameters: fuel mass flow rate, channel inlet temperature, and channel operating pressure. A series of experiments were designed to study the effect of these three parameters on the characteristics. It was found that the amplitude increased with increasing mass flow rate, whereas the duration reached the maximum value when mass flow rate was a certain value; the effects of operating pressure on the characteristics of thermo-acoustic instability were strongly dependent on the threshold power.

During experimental investigations into the flow and heat-transfer instabilities of RP-3 under supercritical pressures in a vertical tube with an inner diameter of 2 mm, the flow changed from laminar to the transition regime as the fuel was heated, which resulted from a decrease in fluid density and increase in velocity [251]. A 13-component surrogate model of RP-3 was used to calculate the thermophysical properties of fuel. Under large wall heat flux conditions, instabilities in flow and heat transfer are observed when the inner wall temperature and outlet fluid temperature approached the pseudo-critical temperature respectively. The former was accompanied by enhancement in heat transfer and could be explained by the pseudo-boiling mechanisms. Thermally induced pressure oscillations due to drastic density variation was found to be the reason for the latter case. During a study of the effects of inlet pressure, wall heat flux, and inlet Reynolds number on flow and heat-transfer instabilities, it was found that higher inlet pressures and heat fluxes can weaken the flow instabilities. The influence of inlet Reynolds number was more complicated. Different types of flow instabilities could be observed with the increase in inlet Reynolds number.

#### 5.1.5 Thermodynamic Properties of RP-3

The isobaric specific heat capacity of RP-3 was measured using a vacuum flow-calorimeter in the near-critical and supercritical regions [252]. During these experiments, the temperature was changed from 292 to 824 K, and the operation pressure was changed from 2.40 to 5.98 MPa. The operating pressure, fuel inlet and outlet bulk temperatures, mass flow rate, and heat power were measured using a pressure gauge transducer, K-type sheathed thermocouples, a Coriolis force flow meter, and current and voltage meters respectively. The estimated uncertainty of the measurement was lower than 2.1%. The expanded accuracy of the measured method for the low-temperature region was verified by comparing with water at a pressure of 3 MPa;

the high-temperature region was verified by comparing the temperatures calculated from  $C_p$  integrating enthalpy with the temperatures measured in the experiments.

The isobaric specific heat capacity of RP-3 at high temperature and high pressure was measured with a flow calorimeter [253]. Based on the energy conservation principle, the formula for heat capacity was derived and its measurement was performed by the convective mixing method between the hot and cold fuel. Taking the precision of the instrument and the error transfer into account, the relative expanded uncertainty of this method was about  $\pm 6.38\%$  (coverage factor  $k = 2$ ). Meanwhile, the accuracy and reliability were verified by comparing with the well-known data for water and *n*-decane. Within the temperature range 296–719 K and under the pressure range 2.4–4.0 MPa, the measurement for the kerosene RP-3 was carried out and the experimental observations agreed well with published data.

### 5.1.6 Critical Point Properties of RP-3

A short residence time flow equipment for the measurement of the critical temperature and pressure of fluids was developed to determine the critical properties of endothermic hydrocarbon fuels [254]. The short residence time (about 10 to 50 s) at an elevated temperature minimized the decomposition and other reactions of fuels. Taking *n*-pentane, *n*-hexane, and cyclohexane as standard reagents, the reliability of the apparatus was checked. The critical properties of endothermic hydrocarbon fuels Simulated JP-7 and RP-3 were determined. Four estimation methods based on the volume average boiling point and relative density were also used to estimate the critical properties of these fuels. The comparisons between the experimental and predicted values indicated that the correlations suggested by the API and Riazi Daubert were reliable for predicting the critical properties of fuels.

The critical pressure and temperature of RP-3 were determined by flow visualization [255]. The flow pattern images of RP-3 at different pressures and temperatures were recorded and the critical pressure was identified by disappearance of the phase boundary, whereas the critical temperature was determined by appearance of the opalescence phenomenon under the critical pressure. The opalescence phenomenon is unique to the critical point. The critical pressure and temperature of RP-3 were determined to be 2.3 MPa and 646 K respectively. The density of RP-3 at the critical point was identified as  $221.18 \text{ kg/m}^3$  [228].

## 5.2 Chemical Properties of RP-3

### 5.2.1 Composition of RP-3

RP-3 consists of 52.44% alkanes, 7.64% alkenes, 18.53% benzenes, 15.54% cycloalkanes, 4.39% naphthalene, and 1.46% other hydrocarbons. A more detailed analysis

showed 45 different hydrocarbons ranging all the way from *n*-hexane to 2-methylnaphthalene [223].

### 5.2.2 Thermal Stability of RP-3

#### 5.2.2.1 Coke Deposition in Stressed RP-3

Solid depositions from thermal stressing of an RP-3 jet fuel model compound, *n*-dodecane, was studied in the presence of three initiator additives, 1-nitropropane, triethylamine, or 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane, to show the role of initiators in the carbon deposition by thermal cracking of jet fuels [256]. It was found that the thermal cracking rate of *n*-dodecane is enhanced by the initiators in the following order: 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane > 1-nitropropane > triethylamine, and that 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane and triethylamine remarkably inhibit the formation of pyrolytic deposit by 30–50% at a similar conversion level. Temperature-programmed oxidation of deposits indicated that reactive deposition is improved slightly by 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane and triethylamine, but the less reactive deposits were reduced because of possible radical scavenging or the hydrogen donation effect, resulting from the decomposition of 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane and triethylamine. Scanning electron microscopy showed that triethylamine and 1-nitropropane also have a significant effect on the deposit morphologies. Those results were also observed in the thermal stressing of Chinese RP-3 jet fuel with initiators.

Flowing RP-3 was stressed to 5 MPa and heated up to 700 K (427 °C) in a stainless steel 1Cr18Ni9Ti tube (inner diameter 1.8 mm, outer diameter 2.2 mm) with constant heat flux [257]. The inlet temperature was controlled at 353, 373, 400, and 423 K (80, 100, 127, and 150 °C). The amount of surface coke deposition was weighed. The results showed that, as RP-3 inlet temperature increased, coke deposition peaks shifted upstream and grew slightly. The total amount of coke deposition increased initially and then remained at a certain value after inlet temperature reached 400 K (127 °C).

The influence of pressure on the surface coke deposition of RP-3 was studied by experiments where the flowing RP-3 was heated up to supercritical state in a single-pass stainless steel tube measuring 2 m long (inner diameter 2.2 × 0.2 mm wall thickness, 1Cr18Ni9Ti alloy) with constant heat flux and mass flow of 4 g/s [258]. The amount of surface coke deposition was obtained by a weighting method. The influences of pressure on RP-3 surface coke deposition rate were investigated by changing the pressure. The result showed that high pressure can suppress coke deposition to a certain extent. The location of the coking peak value tended to move backward along the experimental segment with increased pressure, but the shapes of surface coke deposition distribution curves under different pressures were the same.

The effect of surface coke deposition on the heat transfer of RP-3 under supercritical pressure was studied by flowing RP-3 kerosene at 5 MPa, and heated up to 403 to 623 K (130 to 450 °C) in a stainless tube (inner diameter 1.8 mm, outer diameter

2.2 mm, 1Cr18Ni9Ti) with a constant heat flux and a mass flow rate of 3 g/s [259]. The working fluids flowed downward through a tube measuring 1800 mm long. The experimental results indicated that insoluble products deposited onto a metal surface have a significant impact on flow resistance and heat transfer. The effect of coke deposition on the heat-transfer coefficient can be divided into four regimes: a) onset heat-transfer enhancement zone; b) transition zone; c) heat-transfer impairment zone; d) heat-transfer stabilizing zone.

An improved methodology was proposed to experimentally obtain detailed information on the local composition and temperature along the microchannels of a heat exchanger in an electrically heated capillary tube (inner diameter 1 mm) [260]. This method used a variable reactor tube length to carry out thermal cracking of supercritical hydrocarbon aviation fuels while the electric current heating was maintained constant. A series of experimental data on detailed local chemical compositions of cracked hydrocarbon fuel along the cooling microchannels were reported under supercritical conditions (5 MPa, 953–973 K, 680–700 °C), and the calculated thermodynamic properties, flow velocity, and residence times along the tube were reported. A modified molecular reaction model consisting of 18 species and 24 reactions was developed to predict thermal cracking of hydrocarbon aviation fuels within a wide range of cracking conversion fractions (up to 86%) and compared with experimental results.

A series of electrically heated circular tube experiments were conducted to investigate the influences of physical factors on supercritical RP-3 thermal oxidation coking [261]. The flowing RP-3 kerosene was stressed from 3 to 7 MPa and heated to different bulk temperatures below 723 K (450 °C) in a stainless steel tube (inner diameter 1.8 mm and outer diameter 2.2 mm, 1Cr18Ni9Ti) with various heat fluxes. Tube surface coke deposits and liquid-space coke were both collected and weighed using different methods to evaluate the coking characteristics. Some test tube coke compositions were analyzed for the investigation of chemical reactions. The experimental results showed that the fuel temperature is a generated dominant influence factor for RP-3 coking, and its influence is greater than that of the wall temperature. The system pressure had no obvious effect for RP-3 with a high distillation range ( $C_9$ – $C_{12}$ ). The wall coke deposit quantity gradually increased with the mass velocity. The average coking rate was proportional to  $Re_{in}$ . The inlet temperature had little effect on the liquid-space coking, and the coke particles basically posed no threat to the fuel path and nozzle.

Kerosene RP-3 was pyrolyzed in an electrically heated horizontal channel with an internal diameter of 4.0 mm at temperatures up to 913 K (640 °C) and at a pressure of 3 MPa [262]. The dynamic behavior of the coking process due to fuel pyrolysis was experimentally investigated. The coke deposition process was considered to be the net result of two simultaneous sub-processes: a deposition process and a removal process. Results indicated that coking was an unsteady and dynamic process with randomness. During the entire duration of coking runs, the pressure drop across the test channel and the fuel outlet temperature oscillated somewhat. The wall temperature and the



pressure drop variation within a wide range became unpredictable, owing to the random coke build-up and removal in a short time. However, repeated experiments were carried out to get reliable results of some regular patterns of coking. The pressure drop exponentially increased and the wall temperature rapidly changed at the initial stage of a coking run. The pressure drop increased linearly, but the wall temperature nearly achieved steady state at the following stages. Surprisingly, and opposite to the general assumption that coke is a thermal resistance layer that reduces heat transfer, surface deposition enhanced the heat transfer during pyrolysis of RP-3 under the given test conditions.

A numerical simulation of the pressure effect on thermal cracking of RP-3 under supercritical conditions has been conducted based on a complete set of conservation equations [263]. A four-species surrogate for RP-3 was selected to calculate the thermophysical properties. The modified Kumar–Kunzru chemical kinetics model consisting of one primary reaction and 23 secondary reactions was adopted to simulate the cracking process. Detailed variations of the thermophysical property, thermal cracking behavior, and flow and heat-transfer processes of the fuel were investigated. Simulation results indicated that the conversion of RP-3 is proportional to the pressure. Increasing pressure would enhance the heat transfer when the fuel temperature is below 830 K, and a reversed trend was observed as the fuel temperature further increased. The heat transfer is reduced when the fuel temperature approaches a critical value if the pressure is lower than 7 MPa.

A mathematical model was developed for studying fluid dynamics and heat-transfer characteristics of RP-3 at supercritical pressures [264]. The model accommodated a detailed pyrolytic chemical reaction mechanism, which consisted of 18 species and 24 elementary reactions similar to [260]. Accurate calculations of thermophysical properties at supercritical pressures were incorporated. After rigorous model validations, numerical studies of turbulent heat transfer of RP-3 in a micro cooling tube at a supercritical pressure of 5 MPa were conducted under operating conditions of both constant wall heat flux and constant surface temperature to obtain a fundamental understanding of the complex physicochemical processes. Results indicated that endothermic fuel pyrolysis, which prevails once the bulk fluid temperature rises above 750 K, dictates the fluid flow and heat-transfer process in the high fluid temperature region. Significant variations of the fluid thermophysical properties have strong impacts on other processes. Two scenarios of heat-transfer enhancement resulting from property variations under the tested conditions were analyzed.

Surface coke deposition mechanisms of supercritical RP-3 were studied under stable and pressure oscillation heat-transfer conditions [265]. The flowing RP-3 kerosene was pressurized to 5 MPa and heated from 400 to 723 K in a stainless tube (inner diameter 1.8 mm; outer diameter 2.2 mm; length 1800 mm) with a constant heat flux. The experimental downward mass flow rate was fixed at 3 g/s ( $1180 \text{ kg m}^{-2} \text{ s}^{-1}$ ). Constricted flow experiments were performed with 1-h duration with a stable flow, 1 h with 600 Hz

induced vibration, and long duration with 566 Hz vibration. The two vibration frequencies were close to the main frequencies of combustion chamber pressure oscillation under actual working conditions. Flow resistance, heat-transfer characteristics, coking amount, and component analysis were compared between stable and vibration conditions. The results indicated that vibration can affect the coking distribution to become much more uniform and extend the tube working time. Vibration inhibited the exponential growth of flow resistance by changing coke formation compared with the stable condition. Three obvious regions for heat transfer were considered during the long-duration vibration experiments. For coking element analysis, trace amounts of Cu have catalytic effects under vibration conditions.

The thermal oxidation deposition characteristics of RP-3 have been experimentally studied in a vertical tube at supercritical pressure [266]. Thermal stressing of the fuel was carried out in a heated tube made from stainless steel 321 (SS321, 1Cr18Ni9Ti), as-received, pre-oxidized, and electrolytically passivated for 1 h. All of the experiments were conducted under a constant pressure of 5 MPa, at fixed inlet and outlet fuel temperatures of 400 and 723 K respectively, and under the same heat flux and mass flow rate conditions. Deposition of coke on the different segments of the tube was analyzed using a weighing method to quantify the deposition profile along the length of the test section. The morphology and components of the surface deposition were examined along each tube, with different surface treatments, to investigate the surface thermal deposit mechanisms. It was found that the pre-oxidized and electrolytically passivated treatments could reduce the total coke deposition by about 35.83 and 58.33% respectively, as a result of the formed passivation layer and reduced surface roughness in the treated progress in contrast to the as-received CRES-321 tube. On the basis of SEM images and component analysis of the surface deposit, the deposit on the treated tube surface could be attributed to the adhered deposit formed in the liquid fuel rather than the surface catalytic filamentous deposition on the untreated tubes.

Controllable hydrocarbon cracking with greatly reduced coke deposits has been realized by the addition of a little ethanol over a bifunctional coating [267]. The coating, consisting of perovskite and phosphotungstic acid, was prepared in a nickel-based super alloy tube reactor (inner diameter 3 mm  $\times$  width 0.5 mm  $\times$  length 1000 mm) by the wash-coating method. SEM, EDS, and X-ray diffraction were used to characterize the morphology and phase composition of the coating and deposited cokes. The results showed that  $\text{BaWO}_4$ ,  $\text{BaCeO}_3$ ,  $\text{SiO}_2$ , and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  coexisted of the 4.2  $\mu\text{m}$  thick coating with a uniform distribution. The anti-coking tests were conducted during the supercritical thermal cracking of RP-3 with a flow rate of 1 g/s for 30 min at 973 K (700  $^\circ\text{C}$ ) and 4 MPa. The results showed that the efficiency of coke inhibition reached up to 96%, and the durability (i.e., pressure drop of tube reactor and cooler) of the system was improved. The deposited cokes were characterized by temperature-programmed oxidation and using SEM. The pyrolysis products, including gas and liquid, were analyzed. The results indicated that the strategy based on ethanol and a bifunctional coating not only can eliminate the coke deposits on the reactor tube

walls but can also reduce the amount of typical coke precursors related to the aromatic condensation cokes. A possible mechanism for the process has been proposed. In general, phosphotungstic acid in the coating is capable of catalyzing the dehydration of ethanol for the production of water. The perovskite structures can remove coke deposits on the coating through carbon-steam gasification reaction.

In order to study the mechanism of thermal decomposition coking of RP-3 at a supercritical pressure of 5 MPa in helical tubes, the bulk temperature of the fuel was varied from 400 to 723 K, and the mass flux was varied from  $393 \text{ kg m}^{-2} \text{ s}^{-1}$  to  $1178 \text{ kg m}^{-2} \text{ s}^{-1}$  [268]. Four types of helical tubes with different helical diameters were bent and tested for a maximum duration of 5 h. The total coking amount and distribution were analyzed using a weighing method. The results indicated that coking distribution in a coiled tube was more uniform than in the case of a straight tube, and that there was no prominent local coking peak because of the effect of centrifugal forces. The maximum total coking amount among all the experiments decreased by approximately 69.5% compared with that in a straight tube. Three main types of coking morphologies were observed under the SEM: thin coking layers, dense clumps, and crystalline particles.

#### 5.2.2.2 Effect of Additives on Cracking of RP-3 Fuel

Solid coke deposits from thermal stressing of a jet fuel model compound, *n*-dodecane, was studied in the presence of three initiator additives, 1-nitropropane (NP), triethylamine (TEA) or 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TEMPO), to show the role of initiators in the carbon deposition during the thermal cracking of jet fuels [256]. It was found that the thermal cracking rate of *n*-dodecane was enhanced by the initiators in the following order: TEMPO > NP > TEA and that TEMPO and TEA remarkably inhibited the formation of pyrolytic deposits by 30–50% at a similar conversion level. Temperature-programmed oxidation of deposits indicated that reactive deposition can be reduced slightly by TEMPO and TEA, but the less reactive deposits are reduced because of possible radical scavenging or the hydrogen donation effect, resulting from the decomposition of TEMPO and TEA. SEM showed that TEA and NP also have a significant effect on the deposit morphologies. Those same results were also observed in the thermal stressing of Chinese RP-3 fuel with initiators.

Various additives were tested in the hope that they would prevent the formation of carbonaceous deposits during thermal stressing of hydrocarbons at high temperatures ( $> 773 \text{ K} = > 500^\circ \text{C}$ ) [269]. Three hydrogen donors, tetralin (THN),  $\alpha$ -tetralone (THNone), and benzyl alcohol (BzOH), as well as two organic selenides, diphenyl selenide ( $\text{Ph}_2\text{Se}$ ) and diphenyl diselenide ( $\text{Ph}_2\text{Se}_2$ ), in addition to their mixtures, were selected as thermally stable additives to inhibit the deposition from the thermal stressing of *n*-dodecane and Chinese RP-3 (No. 3 jet fuel). It was found that the amount of solid deposits from thermal stressing of RP-3 was reduced by 77.0% with the additive of  $\text{Ph}_2\text{Se}_2/\text{THN}/\text{THNone}$ . It was found that hydrogen donor THN/THNone and organic selenides possibly reduce the carbon deposits through retarding the thermal crack-

ing rate, blocking surface catalysis, and depressing the reactivity of sulfur with the surface metals, as well as their synergistic effect. The morphologies of deposits also dramatically changed after adding organic selenides or hydrogen donors.

### 5.2.2.3 Catalytic Cracking of RP-3 Fuel

Catalytic cracking of Chinese RP-3 can be enhanced by Cu/ZSM-5 (CZ) zeolite and Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (PCA) composite catalysts [270]. The PCA, PCA + CZ, and CZ catalysts had been prepared using an impregnation method. It was found that PCA + CZ had better catalytic cracking activities than the other catalysts, but they had poor stabilities at high temperatures. The addition of CZ onto PCA to form a composite catalyst may be an effective approach to maintaining both catalytic activity and thermal stability (>923 K = >650 °C).

Catalytic cracking of RP-3 over wall-coated Pt/ZrO<sub>2</sub>-TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts with different Al<sub>2</sub>O<sub>3</sub> ratios was investigated under high temperature and pressure conditions [271]. It was found that the gas yield and heat sink of catalytic cracking of RP-3 were improved compared with thermal cracking.

A series of WO<sub>3</sub>-ZrO<sub>2</sub> composite oxides were prepared by co-precipitation and their catalytic performances for RP-3 kerosene cracking were investigated [272]. The amount of gas evolution as the result of catalytic cracking over Pt/WO<sub>3</sub> (4 mass-%)-ZrO<sub>2</sub> catalyst within the temperature region 923–973 K (650–700 °C) was about 1.5 times higher than that of thermal cracking. After the composite oxides were calcined at 1073 K (800 °C) for 3 h, they almost lost their catalytic activities.

## 6 Other Foreign Grades of Kerosenes

### 6.1 Russian Grades of Kerosenes

At the beginning of the rocket age in the US, RP-1 was a low sulfur, low aromatics kerosene distillate fuel (MIL-P-25576, 1956). Parallel development efforts in the USSR in the 1950s produced a similar, slightly denser propellant later known in the US as RG-1 and known in Russia as

## НАФТИЛ

A comparative evaluation of Russian kerosene and US RP-1 was performed to support integration of Russian propulsion elements into the US space program [85]. A two-prong approach was followed to provide a better understanding of the differences. First, analysis provided insight into chemical and physical properties and the theoretical performance difference between the two fuels. Second, hot fire testing provided performance and engine operational data with the two fuels. Analysis of the

data showed three major differences: Russian kerosene was more dense than RP-1. It had a lower sulfur content, and temperature rise with Russian kerosene while passing through the cooling jacket was lower. No significant difference in the characteristic exhaust velocity was found. The data generated during this study were to be used in two major ways. First, initial assessments could be made to identify advantages and disadvantages of using Russian kerosene in US vehicles. Second, impacts of using RP-1 with Russian engines could be evaluated. A limited quantity of Russian kerosene used on the RD-180 engine was acquired from Energomash. A portable test stand approach with a small engine was a low-resource, time-effective method of getting hot-fire engine data. Work at NASA MSFC started in 1994 and was completed in 1995.

Over the years, the Russians have developed and used several forms of natural kerosenes and synthetic hydrocarbons as rocket engine fuels. As with the US, the Russians initially used kerosenes for military air-breathing applications and later used them as rocket fuels.

## 6.2 T-1

The Russian kerosene with a designation of T-1 (aka TS-1) kerosene appears to be the first version of kerosene-based hydrocarbon rocket fuel used by the Soviets immediately following WWII. The evolution of this fuel is not known, though it appears to have been used more commonly in military applications, most notably the early versions of the Scud missile and its variants. Its interchangeability with RG-1 is not known, but it was reportedly used in some Soyuz launches. It may have been a forerunner to RG-1.

## 6.3 T-6

The Russian kerosene T-6 may have been initially developed to power the Mikoyan MIG-25 jet aircraft. T-6 is a hydrogenated naphthenic kerosene that is processed to have low volatility, a low freezing point, low aromaticity, high thermal stability, and good relight capability. There is no equivalent to this fuel available in the US, although in the 1980s the USAF demonstrated the production of fuels similar to T-6. In fighter aircraft, as in any volume-limited operations, the higher density of the kerosene fuel translates into wider range. It was generally believed that this fuel, like T-1 and RG-1, was produced from the kerosene fraction of naphthenic crude oil. T-6 is also used as a substitute for RG-1 in engine tests because of its similar physical properties and increased availability. The RD-180 engines were acceptance tested in Russia using T-6 and then shipped to the US, where they were launched using RP-1 [1, 3].

## 6.4 RG-1

The type of kerosene typically used in the Russian space program, RG-1 is also known as “naphthyl” and its specification is defined in Russian state specification TU 38.001244. Like RP-1, it is a low-volatility kerosene fuel, but there are some critical differences, most notably the higher density and lower sulfur content. The higher density results from the chemical hydrocarbon types in RG-1 and T-6. The kerosene fraction of naphthenic crude oil contains 2-ringed (fused decalins) and 3-ringed paraffins, which are denser than the single-ringed paraffins. The density can be even further increased by chilling the fuel prior to loading onto the vehicle, which is a common practice that has been performed on previous (e.g., N-1, ENERGIYA) and is performed on current (e.g., SOYUZ) launch systems. Its high thermal stability and performance are supported by a high fraction of fused naphthenes (decalins). It is handled in metal containers under a humidity-controlled nitrogen gas barrier to prevent the infiltration of oxygen or water into the fuel. The freezing point for RG-1 has been reportedly specified to be less than 208 K (−85°F) in order to support launch operations in Siberia, but this has not been verified in any of the sources reviewed [273].

## 6.5 TM-185

The liquid hydrocarbon fuel TM-185 is used in several battlefield and ICBM missile systems, such as the R-12 SANDAL. It reportedly consists of 80–92% kerosene (probably T-1) diluted with gasoline. Its simplicity and ease of production has resulted in its being adopted for use in several emerging third-world missile systems (e.g., the North Korean TAEPO-DONG 2 and HWASONG 5, the Iranian SHAHAB-6). TM-185 may have been used as the fuel in both stages of the Iranian SAFIR satellite launch vehicle, although the NIAS report errs in describing AK-271/TM-185 as a hypergolic combination [274].

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# Metals of the 2<sup>nd</sup> and 3<sup>rd</sup> Row and their Hydrides

## Metals of the 2<sup>nd</sup> and 3<sup>rd</sup> Row and their Hydrides

This chapter on metals of the second and third row of the periodic table of elements and their hydrides may be misplaced in an *Encyclopedia of Liquid Fuels*, because these are all solid compounds. We anticipate that such materials would be used as finely divided powders or nanometals suspended in liquid fuels.

### 1 Rare Gases (“Noble Gases”) as Rocket Propellants

For a book on the chemistry of rocket propellants, it would have been best to arrange the sequence of chapters by the sequence of elements in the periodic table of elements. Instead, for an encyclopedia, the chapters were arranged in alphabetical order. If we had arranged the chapters in the order of the periodic table of elements, as we did in the past, the next propellant to be discussed after hydrogen would have been helium; however, helium is used mostly as a pressurant for propellants and coolant for infrared optics and not as a propellant by itself. It requires a source of energy to heat it up and use it for propulsion. The energy can be supplied externally (electrothermal thrusters) or from chemical reactions in contact with helium. Helium can be used as a diluent for gaseous oxygen/hydrogen mixtures and thus allow the formation of non-detonable, non-self-propagating mixtures that can be ignited like a monopropellant over a catalyst. It has been attempted to prepare chemical compounds from “noble” gases and this attempt has been successful in the case of the rare gas fluorides and oxyfluorides of krypton through xenon, but not for helium or neon; however, no rare gas hydrides have been found.

Experimenters have demonstrated the ability to create metastable helium and store it as a Bose-Einstein condensate. The conversion of metastable helium to normal helium would enable a specific impulse of 2825 s.

A metastable version of helium (often designated as He\*) may be storable to some degree. He\* is an He atom with one electron promoted outside of its normal shell location, and in a reversed spin state. He\* atoms can be produced by running electrical current through helium gas. He\* can be produced by a helium-neon laser at better than 10% efficiency. Normally this atom is very unstable. In the presence of opposite spin He\* (or other matter), collisions will return He\* to its normal state (gaseous He) with an impressive release of energy (about 20 eV per atom, or 480 MJ/kg) that can be used for propulsion. Xenon and krypton are used as working fluids in ion and Hall thrusters.

## 1.1 Metals of the Second and Third Row of the Periodic Table of Elements

The following sections discuss the metals and metalloids of the second and third row and the first, second, third and fourth column of the periodic table of the elements. These metals and metalloids are rarely used as fuels by themselves but are most often used as additives to other propellants to increase the heat of combustion and also increase the specific impulse. All metals that leave metal oxides or metal fluorides as condensable species in the exhaust actually cause some performance loss due to two-phase flow. Slag depositions on critical orifices and in the nozzle throat also may cause operational problems with rocket engines that have to be used more than once.

## 1.2 Metal Hydrides

Metal hydrides will be presented in section “Metal Hydrides” immediately following the sections on metals. Boron does not count as a metal, but it is a non-metal, a metalloid, and it was assigned to its own chapter in this volume, the *Encyclopedia of Liquid Fuels* (although it is not a liquid). Boron hydrides are discussed in a separate chapter “Boranes.”

## 2 Lithium Metal

After helium, the next element in line in the periodic table of elements is lithium, starting the second row of the system. Lithium is a metal in the group of alkali metals and forms many salts with acids. It forms oxides and nitrides with oxygen and nitrogen. It forms a hydride with hydrogen which is not a covalent hydride but a saline hydride in which lithium is a positive ion and hydrogen is a negative ion.

### 2.1 Lithium and Lithium Compounds

Lithium is a potential rocket propellant both in its form as a metal as well as in the form of saline hydrides, such as lithium hydride LiH or complex hydrides such as lithium boron hydride (lithium borohydride) LiBH<sub>4</sub>. The low atomic mass of lithium, 6.941 g/g-atom, maintains the low average molecular mass of the exhaust products and allows the achievement of high specific impulses. Lithium perchlorate is a promising oxidizer since it contains a high percentage of useable oxygen (60.15 mass-% oxygen in LiClO<sub>4</sub>). There are many summary publications that describe the properties and application of lithium and lithium compounds [1–4].

Lithium compounds are used for batteries, air conditioners/chillers, lightweight alloys, construction materials, medicines, fine chemicals, glass and ceramics, lithium

greases and lubricants, also in the form of lithium hypochlorite for swimming pool water “shock” treatment, and polymerization catalysts. In addition to its potential use as a propellant, lithium in the form of lithium-aluminum alloys or lithium-magnesium alloys has recently found widespread applications as lightweight alloys for rocket propellant tanks and structural elements where lightweight structures are at a premium to increase the useful payloads.

Until 1940 lithium compounds were only used for medicinal purposes. When industry started using lithium soaps as high-temperature lubricants, the demand for lithium increased substantially. Lithium-ion batteries have high cell voltage and good long-term storage properties (slow self-discharge) and initially were often used in emergency locating beacons of aircraft and marine vessels. In the meantime, lithium-ion batteries are now widely used in electric automobiles, but the transportation of lithium-ion batteries in aircraft has been outlawed after several incidents of fires in cargo holds.

Lithium deuteride  ${}^6\text{Li}^2\text{H}$  or lithium tritide  ${}^6\text{Li}^3\text{H}$  can be used in thermonuclear fusion weapons and fusion reactors. Lithium deuteride is a potential fuel for controlled fusion nuclear reactors.

## 2.2 Occurrence of Lithium

Lithium occurs naturally in the form of lithium ores but never as the free metal. Lithium ores are in the form of lepidolith, a lithium-potassium-aluminum silicate containing 2–7 mass-% Li, often accompanied by spodumene containing 3–7.6% Li and petalite, a lithium aluminum phyllosilicate mineral,  $\text{LiAlSi}_4\text{O}_{10}$ , containing 2.27% Li. Lithium demand has skyrocketed in the early 2000s due to increased demand for lithium-ion batteries in portable electronic devices and electric cars or even passenger airplanes [5]. Further expansion of electric cars and airplanes with lithium batteries may be delayed by the limited availability of lithium.

There is some disagreement on whether the supply of lithium is adequate to support a future global fleet of electric vehicles. A comprehensive supply analysis of the global lithium resources and a comparison to global lithium demand from 2010 to 2100 assumed rapid and widespread adoption of electric vehicles but estimates of global lithium resources have reached very different conclusions [6]. Some investigators concluded that even with a rapid and widespread adoption of electric vehicles powered by lithium-ion batteries, lithium resources should be sufficient to support demand until at least the end of this century [7]. In the future, diverting any amount of lithium to use it as a high-energy rocket propellant on a larger scale would only aggravate the supply situation.

Hardrock mining of pegmatites has been the traditional source for lithium products, in particular from open-pit mines in North Carolina in the USA, Bikita in Zimbabwe, Manitoba, Canada, and in Western Australia; however, the North Carolina

spodumene mines are being abandoned in favor of South American sources. The two North Carolina pegmatite operations closed with the development of lower cost sources in Chile but could be reactivated, should a massive demand materialize and prices rise as a result. Cyprus Foote Minerals closed its spodumene mine in 1986 to concentrate its efforts on brines of the Salar de Atacama in Chile together with its existing brine operation at Silver Peak, Nevada. Sociedad Quimica y Minera (SQM) is a major producer of nitrates and iodine in Chile and produces potassium and lithium salts as by-products. Lithium Corporation of America operated a pegmatite mine in Bessemer City, Gaston Co., North Carolina, USA until the late 1990s. It was located about 6 miles northeast of the Foote mine. There have been many changes in the lithium exploration and mining business during the past years. Lithium mines that were dormant for a while are now re-opened because there is a high demand of lithium for batteries.

### 2.3 Production of Lithium Metal

There are several leading industrial international and national companies in the field of lithium compounds. The most common form of lithium in the as-processed and enriched form from ores is lithium carbonate. Lithium metal is made from a melt of lithium chloride by electrolysis.

### 2.4 Physical Properties of Lithium Metal

Lithium is the lightest metal in the periodic table of elements. Its density is so low that it even floats on water (but not for long because it will react with water forming lithium hydroxide and hydrogen gas). The physical properties of lithium metal are summarized in Table 1. See also [8].

**Table 1:** Physical properties of lithium metal.

| Property               | SI Units                                  | Other Units                                  |
|------------------------|-------------------------------------------|----------------------------------------------|
| Atomic mass            | 6.941 Atomic mass units                   | 144.07 g-atom/kg                             |
| Melting point          | 453.69 K                                  | 180.54 °C                                    |
| Boiling point          | 1620 K                                    | 1347 °C                                      |
| Density at 298 K       | 0.534 g/cm <sup>3</sup>                   | —                                            |
| Heat capacity at 298 K | 24.63 J mol <sup>-1</sup> K <sup>-1</sup> | 5.887 cal mol <sup>-1</sup> °C <sup>-1</sup> |
| Heat of fusion         | 3.00 kJ/mol                               | 0.7171 kcal/mol                              |
| Heat of evaporation    | 147.1 kJ/mol                              | 35.16 kcal/mol                               |

### 2.4.1 Vapor Pressure of Lithium

The vapor pressure of molten lithium can be calculated from an Antoine equation

$$\log_{10}(P) = A - [B/(T + C)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in K. The constants  $A$ ,  $B$ , and  $C$  are listed in Table 2 for two different temperature ranges. See also [9].

**Table 2:** Antoine equation constants for lithium.

| Temperature range, K | A       | B        | C        |
|----------------------|---------|----------|----------|
| 298–1600             | 4.98831 | 7918.984 | −9.52    |
| 1204–1353            | 1.58992 | 1603.966 | −711.088 |

Data source: [10]; Coefficients calculated by NIST from author's data.

### 2.4.2 Viscosity of Lithium

Molten lithium has been considered as a coolant for nuclear reactors. Molten lithium would be a key ingredient for  $F_2/H_2/Li$  tripropellant combinations that would give the highest specific impulse achievable with any chemical propellant. Rocket engines have been operated on molten lithium as a fuel. The viscosity of molten lithium has been measured [11, 12].

### 2.4.3 Surface Tension of Lithium

The effects of oxygen and nitrogen contamination on surface tension and contact angle of molten lithium were measured at 479–836 K (206–563 °C) [13]. The maximum bubble pressure method was used for measuring the surface tension.

### 2.4.4 Heat Capacity of Lithium

The heat capacity of lithium as a function of temperature can be calculated from the following polynomial Shomate equation:

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + E/\tau^2$$

where  $C_p$  is the molar heat capacity in  $J\ mol^{-1}\ K^{-1}$ ,  $\tau$  is the temperature in kelvin divided by 1000 and  $A$ ,  $B$ ,  $C$ ,  $D$ , and  $E$  are constants listed in Table 3 for three different physical states and four different temperature ranges.



**Table 3:** Thermodynamic property polynomial equation coefficients for lithium.

| Physical state | Solid     | Liquid     |           | Gas       |
|----------------|-----------|------------|-----------|-----------|
| Temperature, K | 298–453   | 453.69–700 | 700–1620  | 1620–6000 |
| A              | 169.5520  | 32.46972   | 26.00896  | 23.33408  |
| B              | –882.7110 | –2.635975  | 5.632375  | –2.772423 |
| C              | 1977.438  | –6.327128  | –4.013227 | 0.767421  |
| D              | –1487.312 | 4.230359   | 0.873686  | –0.003595 |
| E              | –1.609635 | 0.005686   | 0.344150  | –0.035246 |

Data source: [10]

Molten lithium and lithium alloys have been evaluated as both coolant, heat transfer fluid, and neutron moderator in nuclear reactors (SP-100 space nuclear power supply), and its thermodynamic properties for that application have been thoroughly evaluated [14]. Compilations of properties including density, vapor pressure, viscosity, surface tension, electrical conductivity, thermal conductivity, thermal diffusivity, heat capacity, and enthalpy were provided for temperatures between the melting point and boiling point of lithium and other alkali metals [15, 16]. It is unlikely that anyone will be able again to pump liquid lithium as a rocket propellant in tripropellant or pentaplex propellant combinations, but just in case, the transport properties of liquid lithium are available [17].

## 2.5 Chemical Properties of Lithium Metal

Lithium, Li, CAS RN [7439-93-2], is a soft, metallic-shiny metal that is stable in dry air. Freshly cut surfaces will quickly discolor to a dull gray due to interaction of the metal with moisture in the air. Once ignited, lithium burns in air with a pink-red flame. Lithium cannot be melted under a nitrogen “inert gas” atmosphere because molten lithium reacts with nitrogen to form the nitride  $\text{Li}_3\text{N}$ . If a chunk of lithium gets thrown on water, it will float and develop hydrogen gas, but the metal will not melt like sodium and potassium usually do. Lithium bar or lithium extruded wire is usually stored under oil to protect it from the moisture of the air.

Lithium forms salts with many acids. Lithium ions in salts are always in the oxidation state of 1+ as the lithium  $\text{Li}^+$  cation. Lithium salts are colorless unless the anion originates from a colored acid, like  $\text{HCrO}_4$ . Most lithium salts are water-soluble, but many have limited solubility and they are more similar to those of magnesium due to a diagonal relationship in the periodic table of elements (“Schräganalogie” in German). For instance, lithium carbonate or lithium phosphate is not very soluble in water and in this respect resembles magnesium carbonate or magnesium phosphate.

## 2.6 Handling of Lithium

Lithium must be stored under dry conditions and preferably under a protective atmosphere of argon. Molten lithium reacts with oxygen **and** nitrogen. Lithium metal bars are often stored under a heavy hydrocarbon oil to protect them from the atmosphere. Lithium fires can be extinguished by smothering them with carbon dust [18].

## 2.7 Toxicity Properties of Lithium

Overdoses of lithium salts cause vomiting, tremors, kidney damage, unconsciousness and cardiac arrest. Small doses of lithium salts are used as antidepressants.

## 2.8 Use of Lithium as a Rocket Propellant

It has been attempted to use molten lithium as a liquid rocket propellant (see future volume *Encyclopedia of Hypergolic Bipropellant Combinations*), but the melting, feeding and injection of molten lithium into a rocket engine is a very difficult task. The metal may solidify in places where it was not supposed to and may clog lines and injector orifices. There is experience with pumping of molten alkali metals in cooling circuits of nuclear reactors. The other use of lithium as a rocket propellant would use lithium in combination with a binder as a solid in hybrid rocket engines or in tribrid or pentaplex rocket engines. Another potential use of lithium metal as a rocket fuel would be in the form of a solution in liquid ammonia (see chapter “Ammonia”). It is very unusual that a metal dissolves in a solvent without a chemical reaction. The lithium metal shares some of its electrons with the liquid ammonia solvent, causing the liquid to assume a deep blue color. At very high concentrations, the surface of the solutions has a copper-colored metallic sheen.

## 3 Beryllium and Beryllium Compounds

Beryllium and beryllium compounds in combination with hydrogen-rich fuels will theoretically enable the rocket propellant chemist to achieve the ultimate high in chemical propellant specific impulse; however, the extreme toxicity of beryllium exhaust prevents the widespread use of beryllium propellant combinations, at least for earthbound applications. Besides that, beryllium is available only in limited quantities.

### 3.1 Production of Beryllium and Beryllium Compounds

There have been many changes in the beryllium mining, processing, and forming industries. Beryllium Manufacturing Corp. was founded in 1974. The company's line of business includes the manufacturing of aircraft parts and equipment. Brush Wellman Inc. is the world's leading producer of pure beryllium and beryllium products [19]. Brush Wellman Beryllium Products is an integrated global producer of beryllium-based metals and metal matrix composites. The Brush Wellman Beryllium Products industrial plant in the remote Sevier Desert of western Utah is one of the only sources of concentrated beryllium in the world. The plant is a mill and finishing facility for beryllium, the high-strength, lightweight metal used in military, aerospace and medical industries. The ore for the plant comes from Brush Wellman's mine, located in the Topaz-Spor Mountains, 50 miles west, which is North America's only developed source for the metal. The facility is located here due to the remoteness of the area, as beryllium dust is highly toxic, and the proximity of a source of power, the Intermountain Power Project, a coal-fired power plant located a few miles away.

American Beryllia Inc. is a manufacturer and distributor of beryllium oxide ceramic (BeO) heat sinks, crucibles, rods, washers, thermocouple tubing and custom-made substrates for a diverse range of aerospace, defense, electronic, and commercial applications [20]. Beryllium oxide, commonly called beryllia, is a ceramic material that offers a combination of desirable properties not found in any other ceramic material. Distinguished by excellent thermal conductivity, BeO ceramic retains dielectric constant, loss factor, and dielectric strength in the range of most electrical insulators. Along with good mechanical strength and stiffness to weight ratios, this unique combination of properties provides designers with a material that can reduce the size of heat generating circuitry while retaining essential high-power capability and improved thermal stability. Typical applications of BeO ceramics include heat sinks in high power electronics and semiconductors and use as a heat dissipation medium in a wide range of miniaturized circuitry applications in the defense, aerospace, and commercial markets.

Pure beryllium metal is used in the manufacture of aircraft disc brakes, nuclear weapons and reactors, missile parts, heat shields, X-ray machine parts, mirrors, and spacecraft. In addition to its controversial use as a consumable rocket propellant, beryllium metal also has found applications as lightweight alloy in spacecraft structures. For instance, the engine mounting bracket on Magellan Venus Orbiter reaction control monopropellant thruster modules was made from a beryllium alloy to allow improved thermal management while in orbit around Venus.

Brake drums that must take high heat loads, such as those once flown on Space Shuttle, have been made from beryllium alloys. Beryllium/copper alloys are used in non-sparking tools.

The use of beryllium as a rocket propellant for outer-space applications where specific impulse is at a premium and toxicity is not a concern is still hampered by its high price (\$ 231/lb as of 2016) and limited availability.

### 3.2 Occurrence of Beryllium

Beryllium occurs in the form of beryl mineral containing ~14% BeO corresponding to 3.4–5% Be. Beryl occurs in many places, usually accompanied by pegmatite. For a long time the separation of the ore from the tailings was done by hand. The United States has very little beryl resources that can be economically hand sorted from pegmatite deposits. Large beryl deposits were found in Brazil and Argentina. The Spor Mountain area in Utah, an epithermal ore deposit, contains a large bertrandite resource which is being mined. Many fly ashes from coal-fired power plants contain 0.1–1% BeO which is a toxicity concern.

### 3.3 Processing of Beryllium Ores into Beryllium Metal

Beryllium ores are first processed to BeO or BeF<sub>2</sub> from which the metal can be obtained by reduction with molten sodium or by electrolysis of molten beryllium salts. The main beryllium producer in the US as of 2010 was Brush Wellman in Utah. The US beryllium metal production in 2016 was 190 metric tons.

For using beryllium as a rocket propellant, it is important to have it in the form of small particles that burn completely without being encrusted with an oxide layer which results in incomplete combustion. Beryllium powder can be made by an amalgam method [21, 22], or by electrolysis of a beryllium chloride-sodium chloride molten eutectic mixture with a mercury cathode and beryllium anode [23, 24].

### 3.4 Physical Properties of Beryllium

Beryllium, CAS RN [7440-41-7], is a lightweight metal with remarkable strength, also when used as an alloying metal with other metals. The physical properties of beryllium are summarized in Table 4.

The heat capacity of beryllium as a function of temperature can be calculated from the following polynomial Shomate equation:

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + E/\tau^2$$

where  $C_p$  is the molar heat capacity in J mol<sup>-1</sup> K<sup>-1</sup>,  $\tau$  is the temperature in kelvin divided by 1000 and A, B, C, D, and E are constants listed in Table 5 for four different temperature ranges.

**Table 4:** Physical properties of beryllium.

| Property                      | SI Units                                  | Other units                                                  |
|-------------------------------|-------------------------------------------|--------------------------------------------------------------|
| Atomic mass                   | 9.013 Atomic mass units                   |                                                              |
| Melting point                 | 1556 K                                    | 1283 °C                                                      |
| Boiling point                 | 2757 K                                    | 2484 °C                                                      |
| Density at 293 K              | 1.84 g/cm <sup>3</sup>                    | —                                                            |
| Heat capacity at 298 K        | 16.45 J mol <sup>-1</sup> K <sup>-1</sup> | 3.932 cal mol <sup>-1</sup> °C <sup>-1</sup>                 |
| Heat of fusion                | 11.7 ± 2.1 kJ/mol                         | 2.8 ± 0.5 kcal/mol                                           |
| Heat of sublimation           | 327 kJ/mol                                | 78.254 kcal/mol                                              |
| Heat of combustion            | 565 kJ/mol                                | 135 kcal/mol                                                 |
| Thermal conductivity at 273 K | 1.6096 W cm <sup>-1</sup> K <sup>-1</sup> | 0.3847 cal cm <sup>-1</sup> s <sup>-1</sup> °C <sup>-1</sup> |

**Table 5:** Thermodynamic property polynomial equation coefficients for beryllium.

| Physical state       | Solid     |           | Liquid    | Gas       |
|----------------------|-----------|-----------|-----------|-----------|
| Temperature range, K | 298–1527  | 1527–1560 | 1560–2741 | 2741–6000 |
| A                    | 21.20694  | 30.00037  | 25.42516  | 28.57195  |
| B                    | 5.688190  | –0.000396 | 2.157952  | –5.384682 |
| C                    | 0.968019  | 0.000169  | –0.002573 | 1.038152  |
| D                    | –0.001749 | –0.000026 | 0.000287  | –0.012100 |
| E                    | –0.587526 | –0.000105 | 0.003958  | –4.261321 |

Data source: [10]

### 3.5 Chemical Properties of Beryllium

Summaries on the chemistry of beryllium and beryllium compounds were published in [25–28]. There are numerous books devoted to beryllium that can serve as the source of additional information [29].

#### 3.5.1 Analysis of Beryllium

The analysis of beryllium content in the air at places of employment is an important part of the precautions taken against the accidental poisoning by airborne beryllium. The methods used for grab samples (air filters, wipes, biological specimens) are emission spectrography [30, 31], or gas chromatography [32] or wet spectrophotometric methods; [33–35].

### 3.5.1.1 Monitoring of Workplace Beryllium Concentrations

Workplace concentrations of beryllium need to be measured regularly to show compliance with government regulations and to catch any sloppy housekeeping that may develop after workers become used to the hazard. Workplace concentrations are measured both in air samples and in wipe samples. Wipe samples are taken with moist filter paper on floors, shelves and on top of cabinets in work areas. The beryllium concentration in wipe samples should not exceed  $2\mu\text{g}/\text{m}^2$ . Clothing of employees leaving the plant should be inspected periodically for beryllium contamination.

Concentration of airborne particulate beryllium is measured by passing a known volume of air through a micro-pore filter and leaching the filter with acid to extract all acid-soluble compounds. It would make most sense to place the intake of the air sampler at the nose level of the personnel we are trying to protect.

### 3.5.1.2 Direct Reading Beryllium Contamination Monitors

There are no off-the-shelf direct-reading analyzers on the market which give a direct readout of the beryllium concentration in the air at levels near the recommended TLV-MAC. It has been attempted to develop continuously operating direct-reading emission spectrometers which aspirate air and pass it through an electric discharge between two electrodes [36] or by atomic absorption spectrometry in a nitrous oxide/acetylene flame [37]. Sensitivity is about  $0.5\mu\text{g}/\text{m}^3$  beryllium. Another direct-reading method is laser-induced-breakdown spectroscopy [38]. The limit of detection for beryllium in air was  $0.5\text{ ng/g}$ , which is one third of the Occupational Safety and Health Administration (OSHA) limit for the 8-h average exposure to beryllium. Another direct-reading continuous analysis method is by microwave-induced plasma spectroscopy [39].

### 3.5.2 Reactions of Beryllium

Beryllium metal burns in atmospheres of oxygen or carbon dioxide, it would thus burn in the atmosphere on Mars. The rates of oxidation are dependent on the moisture content of the atmosphere [40–43]. Oxide layers retard the combustion of beryllium [44–46].

### 3.5.3 Applications of Beryllium in Rocket Propellants

Beryllium metal can be used as a high-energy additive to solid rocket propellants or as a component in hybrid, tribrid, and pentaplex propellants [47]. The first major solid propellant beryllium program was operated by the US Air Force. Another method of using beryllium as a small-particle size powder is to suspend it in gelled hydrocarbon fuel slurries, thus substantially increasing the heat of combustion.

### 3.6 Toxic Properties of Beryllium and Beryllium Compounds

Beryllium was known for many years as “glucinium,” a name based on its sugary taste. Obviously, nobody would want to repeat this taste experiment! Although it is unlikely that beryllium will again be evaluated as a rocket propellant, we have included a chapter on beryllium toxicity because beryllium is continued to be used in other lightweight components of spacecraft. Summaries recommended for further study on toxicity of beryllium and beryllium compounds are in [48, 49].

#### 3.6.1 History of Beryllium Toxicity and Epidemiology

Prior to 1933 it was not known that beryllium compounds are toxic and can cause severe acute and chronic fatal poisonings in workers exposed to the metal, beryllium-containing minerals and other compounds.

In the 1930s, workers in a beryllium-processing factory in Germany fell ill with symptoms similar to chlorine or phosgene poisonings. In addition, they developed skin eczema, mostly on unprotected parts of the skin in the face and on the hands. A total of 17 cases were reported between 1933 and 1942, including 3 fatalities. Initially the problems were blamed on beryllium fluoride which was a common thread in the exposure history of all cases, but soon thereafter cases developed where workers had been exposed to other beryllium compounds that had been considered harmless up to that time.

The German experience was either insufficiently documented or had not entered the international medical literature, because in the years after WW-II a group of 38 workers out of a cohort of 170 workers in a US ore processing plant came down with lung sickness and 5 of them perished. It was not until 1948 that occupational hygiene supervisory agencies issued guidelines for avoiding the exposure to beryllium and the number of further poisonings decreased (See Section 3.6.8). Berylliosis, or chronic beryllium disease (CBD), is a chronic allergic-type lung response and chronic lung disease caused by exposure to beryllium and its compounds, a form of beryllium poisoning. The condition is incurable but symptoms can be treated.

In 1952 a “Beryllium Case Registry” (BCR) was founded at Massachusetts General Hospital in Boston which maintained a database about victims and their exposure history [50–54]. Anybody who was promoting the use of beryllium-containing rocket propellants in the 1950s and 1960s should have been aware of the toxicity hazards of this chemical. Additional surveys on beryllium toxicity are [55, 56].

#### 3.6.2 Types of Beryllium Poisoning

There are at least three types of beryllium poisoning to worry about: acute toxicity, chronic toxicity, and skin irritation. Acute beryllium poisoning is the result of brief inhalation of high concentrations of volatile beryllium compounds (e.g., BeF<sub>2</sub>, BeSO<sub>4</sub>), occasionally also caused by inhalation of dust. Symptoms are dry cough, pneumoni-

tis, and a permanent alteration of the lung structure which can be recognized in X-ray shadowgraphs. The symptoms will appear soon, usually within 1 week, after the exposure and can end either fatally or allow seemingly complete recovery; however, as of 1965, the BCR contained 22 cases in which an acute beryllium poisoning led to subsequent chronic poisoning symptoms. See also [57].

### 3.6.3 Symptoms of Beryllium Poisoning

The autopsy of victims of acute beryllium poisoning revealed drastically altered lung tissue, enlarged lungs with the vesicles filled completely or partially with fluid. Chronic berylliosis symptoms are similar to idiopathic sarcoidosis. Differences were recognized only after the epidemic disease occurrence in the fluorescent light bulb industry due to widely used beryllium-containing phosphors was revealed. As of 1983, of a cohort of 23000 potentially exposed workers in the fluorescent light bulb industry, 207 developed chronic beryllium disease.

Symptoms of victims of chronic beryllium poisonings are not quite distinct. There were several cases where not workers, but neighbors to the factory living downwind of the installation came down with cases of berylliosis. The symptoms were sudden weight loss, loss of appetite, cough, shortness of breath, and changes in the lung structure similar to those observed as the result of acute poisoning. Chronic beryllium poisoning often leads to long-lasting lingering illness and high mortality [58–61].

Chronic beryllium disease is predominantly a pulmonary granulomatosis where symptoms usually include dyspnea and cough [62]. Fever, anorexia and weight loss are common. Skin lesions are the most common extrathoracic manifestation. Granulomatous hepatitis, hypercalcemia, and kidney stones can also occur. Radiographic and physiologic abnormalities are similar to those in sarcoidosis but are characterized by well-formed granuloma.

Beryllium continues to have a wide range of industrial applications. Exposure to beryllium can lead to beryllium sensitization (BeS) and chronic beryllium disease (CBD). The beryllium lymphocyte proliferation test is used for both medical surveillance and the diagnosis of BeS and CBD [63]. A confirmed abnormal beryllium lymphocyte proliferation test without evidence of lung disease is diagnostic of BeS. BeS with evidence of a granulomatous inflammatory response in the lung is diagnostic of CBD. The determinants of progression from BeS to CBD are uncertain, but higher exposures and the presence of a genetic variant in the HLA-DP  $\beta$  chain appear to increase the inherited risk. Periodic evaluation of affected individuals can detect disease progression (from BeS to CBD, or from mild CBD to more severe CBD). Corticosteroid treatment is typically administered when a patient with CBD exhibits evidence of significant lung function abnormality or decline. Medical surveillance in workplaces that use beryllium-containing materials can identify individuals with BeS and at-risk groups of workers, which can help prioritize efforts to reduce inhalational and dermal exposures.



In order to help determine the steps necessary to protect its workforce from the adverse effects of exposure to beryllium used in military aerospace applications, the US Air Force requested that the US National Research Council Committee on Toxicology conduct an independent evaluation of the scientific literature on beryllium, provide risk estimates for cancer and non-cancer health end points, and make recommendations about specific tests for surveillance and biomonitoring of workers [64]. The request specified that two reports be produced to accomplish those tasks. The first was to provide a review of the scientific literature on beryllium, and the second to expand more critically on the review in considering the maximum chronic inhalation exposure levels that are unlikely to produce adverse health effects, in estimating carcinogenic risks, and in providing guidance on testing methods for surveillance and monitoring of worker populations and other specific issues detailed in the statement of task. The first report identified the available toxicologic, epidemiologic and other literature on beryllium that is most relevant for addressing the problem, focusing primarily on BeS, CBD, and cancer.

#### **3.6.4 Epidemiological Studies of Prevalence of Beryllium Disease**

Epidemiological studies of workers at beryllium processing plants were eventually expanded to their family members and people living near a beryllium processing plant, but not working there [65].

In order to describe relative hazards in sectors of the beryllium industry, risk factors of beryllium disease and sensitization related to work processes were sought in a beryllium manufacturing plant producing pure metal, oxide, alloys, and ceramics [66]. All 646 active employees were interviewed. Beryllium sensitization was ascertained with the beryllium lymphocyte proliferation blood test on 627 employees. Clinical evaluation and bronchoscopy were offered to people with abnormal test results. Industrial hygiene measurements related to work processes taken in 1984–1993 were reviewed: 59 employees (9.4%) had abnormal blood tests, 47 of whom underwent bronchoscopy, 24 new cases of beryllium disease were identified, resulting in a beryllium disease prevalence of 4.6%, including 5 known cases (29/632). Employees who had worked in ceramics had the highest prevalence of beryllium disease (9.0%). Employees in the pebble plant (producing beryllium metal) who had been employed after 1983 also had increased risk, with a prevalence of beryllium disease of 6.4%, compared with 1.3% of other workers hired in the same period, and a prevalence of abnormal blood tests of 19.2%. Logistic regression modelling confirmed these two risk factors for beryllium disease related to work processes and the dependence on duration of exposure at the pebble plant. The pebble plant was not associated with the highest gravimetric dust measurements reported since 1984.

### 3.6.5 Animal Exposure Tests with Beryllium

Numerous animal exposure tests to different forms of beryllium and under different routes of administration have been conducted in order to have a better understanding of the effects of this poison in humans. Two beagle dogs were exposed by the natural respiratory route to rocket exhaust fumes containing beryllium oxide, beryllium fluoride, and beryllium chloride [67]. After a 3-year post-exposure observation period, the lung tissue was examined electron microscopically. Beryllium particles and small agglomerates less than  $1\mu$  in size were deposited in lysosomes in the cytoplasm of histiocytes in the interstitium of the septa. They were closely associated with collagen bundles several microns wide and with increases in numbers of septal capillaries. The lesions were more typical of the classical reaction to a foreign body than immunologic in character and represented an early form of chronic beryllium disease.

Groups of rats were exposed once by nose only for 50 min to a mean concentration of  $800\mu\text{g}/\text{m}^3$  of beryllium metal (initial lung burden,  $625\mu\text{g}$ ) to characterize the acute toxic effects within the lungs and histological changes within the lungs and enzyme changes within bronchoalveolar lavage fluid were evaluated at 3, 7, 10, 14, 31, 59, 115, and 171 **days post-exposure (dpe)** [68]. Beryllium metal-exposed rats developed acute, necrotizing, hemorrhagic, exudative pneumonitis and intra-alveolar fibrosis that peaked at 14 dpe. By 31 dpe, inflammatory lesions were replaced by minimal interstitial and intra-alveolar fibrosis. Necrotizing inflammation was observed again at 59 dpe which progressed to chronic-active inflammation by 115 dpe. This inflammation worsened progressively, as did alveolar macrophage and epithelial hyperplasia, becoming severe at 171 dpe. Results indicated that inhalation of beryllium metal by rats resulted in severe, acute chemical pneumonitis that was followed by a quiescent period of minimal inflammation and mild fibrosis. Progressive, chronic-active, fibrosing pneumonitis was observed later. Chronic beryllium lung disease in man is an immunologically mediated granulomatous lung disease, whereas beryllium-induced lung lesions in rats appeared to be due to direct chemical toxicity and foreign body type reactions.

### 3.6.6 Threshold Concentrations

Based on the cases observed in the US, the threshold concentration for acute poisonings was assumed to be above  $0.1\text{mg Be}/\text{m}^3$  for an 8-h work shift. In 3 cases of acute accidental exposure of only 20 min at a concentration of  $0.45\text{--}0.6\text{mg Be}/\text{m}^3$ , the first symptoms were observed within 72h of the incident.

The OSHA has set a limit of  $2\mu\text{g beryllium}/\text{m}^3$  of workroom air for an 8-h work shift. The National Institute of Occupational Safety and Health (NIOSH) recommends a standard for occupational exposure of  $0.5\mu\text{g beryllium}/\text{m}^3$  of workroom air during an 8-h shift to protect workers from the increased cancer risk associated with beryllium exposure [69]. The EPA restricts the amount of beryllium released into the

air to 0.01 µg beryllium/m<sup>3</sup> of air, averaged over a 30-day period. The EPA has set a maximum allowable amount of 0.004 mg/L beryllium in drinking water.

The susceptibility of workers to beryllium poisoning is quite different. Some workers had been unknowingly exposed for more than 10 years and survived, whereas others fell ill soon after they started working in the factory. As of 1965, there were 42 known cases (with 50% of these with fatal endings) of persons who had lived within 1.2 km of a beryllium factory and had never worked there. The downwind concentrations were probably of the order of 0.01 – 0.1 µg Be/m<sup>3</sup>.

### 3.6.7 Skin Effects

Beryllium compounds can cause contact dermatitis within a few days after exposure, evidenced by dermatitis and conjunctivitis. The lesions will heal soon after the exposure has been discontinued [70].

There are various references to sensitization to beryllium in the literature. Since introducing a patch test for patients with suspected sensitization to metals, three cases of sensitization to beryllium were found [71]. Of these three cases, the first two were regarded as relevant sensitization. Occupational chronic beryllium disease includes cutaneous irritation and skin exposure may cause the disease [72].

### 3.6.8 Government Regulations and Recommendations

The US Atomic Energy Commission formed a “Beryllium Advisory Committee” in 1948 which issued the following recommendations:

1. The airborne concentration of beryllium in workspaces shall not exceed 2 µg/m<sup>3</sup>, averaged over an 8-h shift.
2. The concentration shall not exceed 25 µg/m<sup>3</sup> at any time.
3. If the average concentration during 3 months exceeds 2 µg/m<sup>3</sup> but remains below 5 µg/m<sup>3</sup>, or if a single sample exceeds 25 µg/m<sup>3</sup>, work may be continued while corrective steps are taken to reduce the airborne concentration, but all workers must wear respiratory protection.
4. For exposure of the general public, the concentration shall not exceed 0.01 µg/m<sup>3</sup> at any time.

Since the introduction of these regulations (recommendations??) there were no further beryllium poisoning incidents at AEC facilities [73].

The following is a condensed version of information taken from the [www.chemicalindustryarchives.com/](http://www.chemicalindustryarchives.com/) and [www.chemicalindustryarchives.com/dirtysecrets/beryllium/1.asp](http://www.chemicalindustryarchives.com/dirtysecrets/beryllium/1.asp) web sites and provides some revealing background information on the efforts to establish safe beryllium exposure limits. It appears that sometimes the needs for national security in support of the atomic weapons program have taken priority over occupational safety concerns.

Brush Wellman began researching beryllium in 1921, opened its first commercial facility to produce the metal in 1931 and continues to operate to this day. The primary consumer of beryllium – it was the top consumer until a recent surge in commercial uses – has been the US government, which first used the metal to build better atomic weapons. Workers were not educated about the dangers of beryllium dust, nor were they aware that the government and industry knew of workers dying from on the job exposure. Over 40 cases of chronic beryllium disease, including 7 deaths and about 500 cases of acute disease, including nearly a dozen deaths, had been reported in the US by September 1947.

In 1948, additional cases of beryllium disease, including cases among non-worker residents living near the beryllium plants, became known. The Atomic Energy Commission, which was the largest consumer of beryllium at the time, worked out a deal with Brush, agreeing to contract with the company to build and operate a government-owned beryllium plant. At the same time, the AEC also contracted with the Beryllium Corporation of America (Berylco), Brush's main competitor, and those two companies promised to provide all of the government's beryllium needs. While the contract included a clause limiting airborne levels of beryllium to a maximum of 2.0 micrograms of beryllium per cubic meter of air ( $\mu\text{g}/\text{m}^3$ ), this standard was never enforced by the AEC [74]. Brush and the AEC were aware that even the  $2.0\mu\text{g}/\text{m}^3$  standard was not necessarily safe. One of the reports stated: "It is believed that the two microgram figure has not been proven with any degree of technical rigidity to be an absolute safe maximum concentration." Despite this knowledge, neither Brush nor the AEC ever enforced the questionable  $2.0\mu\text{g}/\text{m}^3$  standard.

When the OSHA proposed a tightening of the standard for airborne beryllium concentrations in the 1970s, Brush Wellman went on the offensive. Brush urged the Department of Energy (DOE) and Department of Defense (DOD) to drop the proposed OSHA standard, threatening to quit the business if the tighter standard was promulgated. The complaints compelled the Secretary of Energy to write to the Secretary of Labor declaring that the proposed regulations would threaten national security. He insisted that beryllium was vital to the development of nuclear weapons and that its continued production could not be compromised. The Secretary of Labor agreed, writing in his response that "the Department [of Labor] has no intention of significantly or adversely affecting key national defense programs."

The  $2.0\mu\text{g}/\text{m}^3$  standard is still the law for workplace exposures [See 29 C.F.R. 1910.1000 (2001)], even though many scientists dispute the safety of this standard. As for those who contract beryllium disease, it appears that about one third die from it, another third are disabled, and the rest appear to live relatively healthy lives. Doctors still are not exactly sure how to explain the different reactions or why some are more susceptible to the disease than others. For victims of the disease, the symptoms can be treated with powerful steroids, although beryllium disease itself remains incurable to this day.

### 3.6.9 Atmospheric Diffusion of Beryllium Exhaust Clouds

The US Air Force conducted atmospheric diffusion of beryllium exhaust clouds in remote areas by releasing clouds under carefully controlled and highly instrumented conditions. The project was called by the code name Project ADOBE for **A**tmospheric **D**iffusion of **B**eryllium [75–77]: 57 sets of field data were collected from 250–350 air samplers per test using solid rocket motors containing from 45–1812 kg (100–4000 lb) of propellant containing beryllium. Surveys covered a 25 square mile sector, covered with an array of 492 air samplers (250–350 samplers per test) located from 600 to 9600 m from the source. Analysis of exhaust samples showed that beryllium oxide is essentially insoluble and of low toxicity [78].

## 3.7 Handling and Processing of Beryllium and Beryllium Compounds

The main concern during the processing of beryllium and beryllium compounds is the avoidance of dust. Solid rocket propellant preparation with beryllium powder and static firing of rocket motors with beryllium-containing propellants required special safety precautions [79].

### 3.7.1 Marking of Designated Beryllium Workspaces

It is recommended to restrict work with beryllium to a designated beryllium work zone with precautions that prevent the spread of contamination throughout the building. The entry to the potentially beryllium-contaminated area should go through air locks where operators can change their work clothes and take showers before they leave work. Change rooms have a clearly marked “clean” and a “potentially contaminated” entrance.

### 3.7.2 Storage of Beryllium and Beryllium Compounds

Beryllium and beryllium compounds should be stored away from other chemicals and only in fire-proof cabinets.

### 3.7.3 Design of Workplaces for Handling Beryllium

Workplaces for beryllium and beryllium compounds should have unidirectional ventilation like in a laminar flow bench [80]. Some beryllium compounds are so toxic or sensitive to air and moisture that they need to be handled only in glove boxes under an inert atmosphere. The process most likely to cause toxicity problems is the weighing and packaging of fine powders.

### 3.7.4 Control of Beryllium Fires

As part of the SNAP-10A (Space Nuclear Auxiliary Power) project, beryllium hazards were measured in four controlled fires. Over 125 air samples and swipe samples were taken during the tests. Only eight samples showed concentrations of Be above the minimum detectable level [81]. Beryllium fires can be extinguished by smothering them with carbon dust [18].

## 3.8 Applications of Beryllium as Rocket Propellant

The addition of beryllium to solid or liquid propellants results in substantial increases in the theoretical specific impulse. There are several surveys investigating the potential benefits of beryllium addition to rocket propellants, mostly solid rocket propellants. Applications of beryllium in solid propellants will be discussed in more detail in future volumes on solid propellants. Applications of beryllium powder as a slurry suspended in liquid propellant fuels will be discussed in more detail in the future volume on non-hypergolic bipropellant combinations.

## 4 Magnesium Metal

Magnesium is used mostly in pyrotechnic formulations and not so much in rocket propellants. The main application of magnesium is in military illumination and signaling flares and in display fireworks. The use of flash powder for photography is part of a bygone era, but it saw a lot of magnesium powder burned to create some light for family portraits or newspaper reporting. The photographer held a pan covered with magnesium chips on a broomstick and lit it with a long fuse. People had to sit or stand still while the fuse burned. That is history.

Magnesium has been evaluated as a slurry in kerosene fuels in combination with liquid oxygen (LOX) and storable oxidizers. It has no advantage over aluminum, which is more widely used for the same purpose. Finely powdered spherical magnesium can be prepared by evaporating magnesium in a stream of helium and flash cooling it in a vertical tower [82]. Similar methods can be used for the preparation of other finely divided metal powders.

## 5 Aluminum Metal

Aluminum, Al, aluminium, CAS RN [7429-90-5], is the second most abundant metal in the universe after iron. By mass, aluminum makes up about 8% of the Earth's crust. It is the third most abundant element after oxygen and silicon and the most abundant metal in the crust, although it is less common in the mantle below. Aluminum metal

is so chemically reactive that it occurs only very rarely as native metal in the metallic state in nature. Instead, it forms part of over 270 different minerals, mostly mixed oxides. The main mineral from which aluminum is made is bauxite.

Pure aluminum is relatively soft and weak, but it forms many strong alloys. It has high thermal and electrical conductivity. Aluminum's adherent passivating surface oxide film makes it corrosion resistant. It resists attack by most acids, but alkaline solutions dissolve the oxide film and cause rapid corrosion.

The current section deals only with the physical and chemical properties of aluminum. There are several other chapters in this book that deal with specific applications of aluminum as fuel in solid and liquid rocket propellants. A future set in an encyclopedia of solid propellants will deal with aluminum in solid propellants, also combustion of nanomaterials, including nanoaluminum in various oxidizing environments. In the area of liquid propellants, kerosols are gelled suspensions of aluminum in kerosene and these have been tested extensively ever since 1933 in combination with LOX and other oxidizers.

The performance of many explosives can be enhanced by adding a few percent aluminum powder. Aluminum/air dust explosions are used in thermobaric explosives. Summaries of all kinds of properties of aluminum and its reactivity are published in [83, 84].

## 5.1 Production of Aluminum Metal

The production of aluminum metal by electrolysis of molten potassium hexafluoroaluminate (cryolite) is a well-established industry. The small percentage of aluminum used as rocket propellant has no significant impact on the availability of aluminum.

### 5.1.1 Production of Aluminum Powder

Most of the aluminum powder is used as pigment in paint ("silver" paint) in the form of flakes that have good light reflecting properties. A small portion is used in thermites for pyrotechnic incendiary and thermite iron-welding applications. For rocket propellant and explosive applications, spherical as opposed to flake-shaped particles are preferred. Prior to the advent of nanoaluminum, micron-size spherical aluminum powders were produced by a vapor condensation process. Suppliers for micron-size ("atomized") spherical aluminum powders include(d) Valley Metallurgical Processing Company (Haskell, NJ) and Argonide (Sanford, FL). Micron-sized H-5 aluminum may be passivated by treatment with potassium dichromate.

Valley Metallurgical H-3 (3 micron), and Alcan MDX-65 (6 micron) spherical aluminum powders have been produced by Valley Metallurgical Processing Company and can be used for rocket propellants.

Nanoaluminum can be made by the process of electro-explosion of metal wires, which was first developed in Russia in 1975 for the production of nanometer-sized metal powder (See section “Production of Nanoaluminum”). One of the brand names for nanoaluminum made by this process is Alex<sup>®</sup>. Particles of Alex<sup>®</sup> are typically spherical with diameters in the range of 100–200 nm and Brunauer–Emmett–Teller (BET) surface areas of 12 m<sup>2</sup>/g. For the first several years, Alex<sup>®</sup> was produced in Russia and sourced out by Argonide Corporation.

### 5.1.2 Particle Size of Aluminum

The particle size of aluminum powder is an important criterion that will affect the burning rate of solid propellants. The particle size of nanoaluminum may change with time due to agglomeration of small particles.

Thermogravimetric analysis (TGA) was used to study the reactivity of aluminum powders in air, oxygen, and nitrogen. In addition, the data were to characterize active Al content, Al oxide content, volatile impurity content, particle size, and particle size distribution [85]. Weight gains from complete oxidation of the Al were used to calculate average particle sizes in the range of 30–500 nm. These particle sizes correlated well with particle sizes derived from surface area measurements. Particle size was also examined by SEM and compared with crystallite size determined by X-ray diffraction (XRD). Particle size distributions were derived from TGA analysis data based on a model for uniform oxidation of Al from the exterior to the interior of the particle. The method is well-suited for analyzing samples with broad particle size distributions, and in particular, for monitoring the presence of 500–5000 nm particles within nominally nanosized samples. Nitridation of Al powders was studied for extended times at 873 K (600 °C). Surprisingly, 2 μm powder was nearly completely nitrided in 1 h, indicating that the nitride coating has little inhibiting effect on the reaction.

## 5.2 Physical Properties of Aluminum

The heat of combustion of aluminum is 7420 cal/g. Physical properties of aluminum are summarized in Table 6.

### 5.2.1 Vapor Pressure of Aluminum

The vapor pressure of molten aluminum in the temperature range 1557–2329 K can be calculated from an Antoine equation

$$\log_{10}(P) = 5.73623 - [13204.109 / (T - 24.306)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in K. The enthalpy of formation of aluminum vapor at 298 K is  $330.0 \pm 4.0$  kJ/mol. The enthalpy of formation of liquid aluminum is 10.56 kJ/mol.



**Table 6:** Physical properties of aluminum.

| Property                         | SI Units                                | Other units                               |
|----------------------------------|-----------------------------------------|-------------------------------------------|
| Atomic mass                      | 26.9815386 g/g-atom                     | 37.0623 g-atom/kg                         |
| Melting point                    | 933.45 K                                | 660.3 °C                                  |
| Boiling point                    | 2793 K                                  | 2520 °C                                   |
| Density at 293 K                 | 2.6989 g/cm <sup>3</sup>                | —                                         |
| Heat capacity at 298 K           | 0.90 J g <sup>-1</sup> K <sup>-1</sup>  | 0.21 cal g <sup>-1</sup> °C <sup>-1</sup> |
| Heat of fusion at 933 K = 660 °C | 10.56 kJ/g-atom                         | 2.56 kcal/g-atom = 94.5 cal/g             |
| Heat of sublimation              | 326 kJ/g-atom                           | 78.0 kcal/g-atom                          |
| Heat of combustion               | 837 kJ/g-atom                           | 200 kcal/g-atom                           |
| Thermal conductivity at 300 K    | 2.47 W cm <sup>-1</sup> K <sup>-1</sup> | —                                         |

### 5.2.2 Heat Capacity of Aluminum

The solid, liquid and gas phase heat capacities of aluminum as a function of temperature can be calculated from the following polynomial Shomate equation:

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + E/\tau^2$$

where  $C_p$  is the molar heat capacity in J mol<sup>-1</sup> K<sup>-1</sup>,  $\tau$  is the temperature in kelvin divided by 1000 and A, B, C, D, and E are constants listed in Table 7 for three different temperature ranges.

**Table 7:** Thermodynamic property polynomial equation coefficients for aluminum.

| Physical state       | Solid     | Liquid                     | Gas       |
|----------------------|-----------|----------------------------|-----------|
| Temperature range, K | 298–933   | 933–2790                   | 2790–6000 |
| A                    | 28.08920  | 31.75104                   | 20.37692  |
| B                    | –5.414849 | $3.935826 \times 10^{-8}$  | 0.660817  |
| C                    | 8.560423  | $-1.786515 \times 10^{-8}$ | –0.313631 |
| D                    | 3.427370  | $2.694171 \times 10^{-9}$  | 0.045106  |
| E                    | –0.277375 | $5.480037 \times 10^{-9}$  | 0.078173  |

Data source: [10]

## 5.3 Chemical Properties of Aluminum

### 5.3.1 Reactions of Aluminum

Aluminum is a very reactive metal and that is why it is used as an ingredient in rocket propellants. The main reaction we are concerned with here is the oxidation of aluminum by oxidizers leading to ignition and combustion. The reactivity depends on the particle size and possible passivating coatings of the particles. Coarse aluminum has to melt before it can burn. It is well known that aluminum will corrode rapidly

in alkaline solutions but will resist many acidic environments. The reaction of aluminum with sodium hydroxide solutions, a popular method for making hydrogen gas, will have active atomic hydrogen at its surface, that under certain conditions can temporarily form a thin layer of aluminum hydride [86]. It was concluded that  $\text{AlH}_3$  forms continuously during dissolution by reaction of cathodically generated hydrogen with the Al metal and is oxidized to aluminate ions in the accompanying anodic process.

### 5.3.2 Ignition of Aluminum Powders in Air

Aluminum powders, in particular nanoaluminum powders, may ignite spontaneously in air under unfavorable conditions (moisture, electrostatic sparks). Before studying the ignition of aluminum particles in air, the particle size had to be known. A comparison of different experimental techniques for metallic particle size evaluation including light diffraction, scanning electron microscope analysis and nitrogen adsorption was made in preparation of ignition tests, including nitrogen adsorption method for particle size evaluation. Chemical reactivity of micron and submicron aluminum powders in air was measured using TGA/DTA [87]. Three types of Al powders were analyzed: S-400 (Reynolds Co.), Alex (Argonide Corp.), and WARP-1 (Ceramic and Materials Processing, Inc.). Based on TGA/DTA analysis, S-400 (specific surface area =  $0.3 \text{ m}^2/\text{g}$ ) did not react below the melting point of Al (2% conversion). Alex powder (specific surface area =  $12.0 \text{ m}^2/\text{g}$ ) started reacting at around 713 K ( $440^\circ\text{C}$ ) and 16% had reacted before the melting point temperature was reached. WARP-1 samples (specific surface area between 16.0 and  $26.5 \text{ m}^2/\text{g}$ ) already reacted at 473 K ( $200^\circ\text{C}$ ) and 25 mass-% of aluminum was oxidized below melting point temperature. Differential thermal analysis did not discover any “stored” energy in S-400 or Alex materials; however, WARP-1 samples released thermal energy already at 403 and 503 K ( $130$  and  $230^\circ\text{C}$ ), which was assigned to “stored energy.”

The minimum ignition temperature of aluminum dust clouds was investigated in a heated furnace and compared to predictions from a theoretical model of aluminium dust cloud ignition in the hot zone of a heated furnace [88]. The model was developed based on two-phase flow, heat transfer, and chemical reaction kinetics. The kinetic parameters of  $E_a$  and A in the model were calculated from the dependence of ignition delay on temperature. The theoretical model could predict the minimum ignition temperature under different conditions exceptionally well.

Minimum ignition temperatures and explosion characteristics of micron-sized aluminum powders were examined in a 20-L near-spherical dust explosion chamber with different ignition energies, dust particle sizes, and dust cloud concentration values [89]. It was found that under similar dust-cloud concentrations and with dust particle size increasing from 42.89 to  $141.70 \mu\text{m}$ , the minimum ignition temperatures of aluminum powder also increased.

### 5.3.3 Specifications for Aluminum

The procurement of aluminum powder is covered by the following MIL-SPECs:

- MIL-A-512 and amendments 1-4, Military Specification: Aluminum Powder, Flaked, Grained, and Atomized (20 May 1961) [Superseding JAN-A-289] [S/S by MIL-DTL-512B]
- MIL-A-23950A, Military Specification: Aluminum Powder, Spherical (1-Sep-1966) [S/S by MIL-PRF-23905B]; MIL-A-23950A (1966) shows three different grades of spherical aluminum powders.
- MIL-A-81335, Aluminum Powder, Spherical (8-Nov-1965) [No S/S document]
- JAN-A-667, National Military Establishment Specification: Aluminum Powder, Superfine (20-Aug-1948)

### 5.3.4 Analysis of Aluminum

The analysis of aluminum in propellant mixtures is a fairly easy process and there are many methods available. The main step is sample preparation to make sure the sample is no longer combustible or explosive while it is digested to extract the aluminum and convert it to a water-soluble form. Another important analytical method would be to determine the amount of unburnt aluminum in propellant exhaust because aluminum particles do not always burn to completion this is a waste of energy that could have been used to deliver propulsion.

A permanganatometric variant of the titrimetric method was found to be suitable for measuring metallic/unburned aluminum in propellant or exhaust [90]. The determination of aluminum nitride in combustion products using a combination of wet chemical and XRD methods was illustrated by results obtained from condensed combustion products of propellant formulations containing highly active ultrafine aluminum powder. Even for this formulation the content of aluminum nitride in the final condensed combustion products was found to be negligibly small, independently of the nature of the gas (argon or nitrogen) used for bomb pressurization.

## 6 Nanoaluminum

Much to-do has been made about nanometals and their potential for increasing the performance of propellants and explosives. Since this is only a change of physical properties and has little to do with chemistry, we have not attempted to keep track of the many publications on nanometals and other nanomaterials. Just a few publications are referenced here to serve as a superficial sampling of the type of information that is available in the literature. Nanoaluminum has unique properties and has been extensively evaluated as a rocket propellant ingredient but no commercial flight applications are known [91–94].

Different conditions of nanoaluminum synthesis by the exploding wire method and powder passivation were used to optimize the process: syntheses under low-pressure gases (Ar, N<sub>2</sub>, CO<sub>2</sub>) and passivation in atmospheric pressure gases (air, N<sub>2</sub>, CO<sub>2</sub>) [95, 96]. Particle sizes and morphology were measured with a transmission electron microscope (TEM). Particle shapes were predominately spherical. The specific surface area determined by the BET method was 15–40 m<sup>2</sup>/g. The composition and surface properties of nanopowders produced under various conditions were studied by mass-spectroscopy.

Nanoaluminum can be made by the process of electro-explosion of metal wires, which was first developed in Russia in 1975 for the production of nanometer-sized metal powder. One particular brand of nanoaluminum is known under the trade name Alex<sup>®</sup> manufactured by the exploding wire method. Particles of Alex<sup>®</sup> are typically spherical with diameters in the range of 100–200 nm and BET surface areas of 12 m<sup>2</sup>/g. For the first several years, Alex<sup>®</sup> was initially produced in Russia and sourced out by Argonide Corporation.

When conducting literature searches for nanoaluminum, it is advisable to search for both spellings: in one word and in two words as nano aluminum and also connected by a hyphen. It appears that the two-word spelling is more popular in the literature, but we preferred the one-word spelling for the document at hand. In addition, the European spelling of aluminium needs to be included in the search. Nanoaluminum may also be called “activated aluminum.” A popular abbreviation is nAl.

## 6.1 Production of Nanoaluminum

Nanometals like nanoaluminum are produced by electro-explosion (plasma-explosion process) of metal wires in an inert gas atmosphere at 2–3 atm pressure [97–99]. The electrical discharge instantly vaporizes the metal, briefly maintains a plasma of metal vapor which is then carried away by the purge gas. The metal vapor condenses in the form of nanometer-size metal particles of about 50–100 nm in diameter. The nanometal is separated from the purge gas in a cyclone separator or a sedimentation chamber and stored under an inert hydrocarbon oil or under argon. Once passivated in dry air, the high surface area powder contains 5–8% of adsorbed air. A similar process heats and vaporizes the metal by a pulsed laser instead of a plasma discharge. Al nanopowders with diameters ranging from 20 to 50 nm can also be produced by two different evaporation routes: induction heating evaporation (IHE) and laser-induction complex heating evaporation (LCHE).

Several production processing parameters affect the physical, thermal and combustion properties of plasma-synthesized aluminum nanopowders [100, 101]. It was shown that feed rate and quench rate had the largest effect on particle size. All synthesized powders were characterized by TGA/DTA, field emission SEM, BET surface area, and bomb calorimetry.

Another mechanical process for comminuting metal particles is ball milling of aluminum in gaseous atmospheres of ammonia and monomethylamine (MMA) which can produce particles in the 100 nm size range [102]. A combination of mass spectrometry, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis with mass spectrometric product analysis (TGA-MS), SEM, IR spectroscopy, and dynamic light scattering (DLS) was used to study the particles and the chemical interactions responsible for particle production. Both  $\text{NH}_3$  and MMA react with aluminum under milling conditions, producing  $\text{H}_2$  and other gaseous products, and leaving the surfaces functionalized. The surface functionalization enhances size reduction by reducing the surface free energy and the tendency toward mechanochemical coalescence. For both  $\text{NH}_3$  and MMA, the particle cores are metallic aluminum, but the surface chemical properties are quite different. The ammonia-milled particles are coated by an  $\text{AlN}_x\text{O}_y\text{H}_z$  layer ~10 nm thick, which passivates the particles. The MMA-milled particles are coated with a thinner passivating layer, such that they are pyrophoric in air and react with  $\text{N}_2$  at elevated temperatures. A similar process used either vapor-phase or liquid-phase acetonitrile as the ball-milling fluid [103]. The Materials Research Society which conducts periodic symposia on energetic materials, has devoted an entire conference series to the discussion of the synthesis, characterization and properties of energetic/reactive nanomaterials [104].

A mathematical model of nanoparticles formation by condensation from the vapor phase process was developed and applied to the manufacture of alumina-coated aluminum nanoparticles [105]. This process involves conversion of gaseous aluminum in the presence of helium carrier gas to solid aluminum nanoparticles. The mathematical model is useful to study the trends on the dependence of the nanoparticle size distribution on the operating parameters such as pressure and temperature profile in the reactor.

Nanoaluminum particles can form by the corrosive attack of caustic solutions on aluminum foil [106]. The as-prepared aluminum particles were composed of several aluminum microcrystals. Their size depends on the concentration of  $\text{OH}^-$  in the caustic solution. See also [107].

## 6.2 Protective Coatings for Nanoaluminum

Instead of using the term “coated nanoaluminum,” sometimes researchers also use the term “capped nanoaluminum.” Encapsulation also describes the coating process. Using all three terms in a literature search may improve the results of the search.

Nanosize aluminum (Alex<sup>®</sup>), an organic coated variant (L-Alex<sup>®</sup>), and a 17  $\mu\text{m}$  aluminum powder (Cap45a) were aged under accelerated conditions of elevated temperature and humidity [108]. Fourier transform infrared (FTIR) and mass spectrometry analyses identified the passivation coating on L-Alex as palmitic acid and showed it to be chemically bound to the aluminum surface via a carboxylate linkage. This coat-

ing was shown to form an effective barrier to hydrolysis and oxidation, with only minor degradation of the metal seen after 40 days of accelerated aging. The coating was retained on the metal surface and provided excellent protection against oxidation.

Nanoaluminum particles are covered by an amorphous oxide layer, which is typically 0.5–4 nm thick. For example, a 38-nm diameter aluminum particle has ~47.5 mass-% oxide which detracts from its value as a rocket fuel. The specific thickness of the oxide layer depends on the temperature of the particle and the duration of exposure to the oxidizing environment. When the particle is exposed to the oxidizing gas for a sufficient period, the oxide layer thickness saturates at a value of 4 nm<sup>3</sup>. The oxide layer protects the particle from further attack by the oxidizer. Aluminum particles with diameters greater than 100  $\mu\text{m}$  ignite only upon melting of the oxide layer at 2350 K. This results in a long ignition delay and a slow rate of energy release. It is thus desirable to reduce the ignition temperature of micrometer-sized aluminum particles. The formation of the oxide layer on aluminum particles can be significantly inhibited by applying transition metal coatings which have higher melting points than the aluminum.

A considerable amount of effort has been directed towards making nanomaterials safer and easier to handle. One approach toward achieving this goal is to passivate the nanomaterials by functionalizing their surfaces. The disadvantage of nanoaluminum is that if it is kept in air, it will be covered by a thick oxide layer, which reduces its energy content. This happens if it is not passivated sufficiently to prevent further oxidation during storage. The kinetics of the interaction of Al nanopowders with N<sub>2</sub>, air, and moisture were investigated by DTA-TGA and by volumetric analysis [109]. If nanopowders are coated with passivating agents, they often retain large amounts of solvents from which the coating was precipitated. Organic coatings (oleic acid) protect the surface against further oxidation more effectively than oxide coatings. The surface of electro-exploded aluminum nanopowders can be passivated by nitrocellulose, oleic acid (C<sub>17</sub>H<sub>33</sub>COOH) and stearic acid (C<sub>17</sub>H<sub>35</sub>COOH), suspended in kerosene and ethanol [110–112].

Coated and uncoated nanoaluminum can react with nitrogen and become nitrated at higher temperatures [113]. Aluminum nanopowders with a protected surface had increased stability to oxidation in air during storage and higher reactivity by heating [114].

Coating nanoaluminum with hydroxyl-terminated polybutadiene (HTPB) would serve two purposes: it would protect the metal particles from oxidation and it would improve the bonding between particles and HTPB binder in a solid propellant formulation [115]. The reactivity and 2-year storage stability of HTPB-coated Al nanopowders outperformed Al<sub>2</sub>O<sub>3</sub>-passivated Al nanopowders.

Fluorocarbon polymer powders added to monopropellants containing aluminum are known to improve burning rates and achieve more complete combustion of aluminum. The same mechanism helps to improve burning rates and protection against air oxidation of nanoaluminum coated with fluorocarboxylic acid functional coatings

[116]. The fluorocarboxylic acid functional coating was 1–2 nm thick, and TGA analysis confirmed an 80% active fuel content, an increase of 17% from untreated product.

Protective coatings evaluated for nanoaluminum include nickel [117], carbon [118–122], cyclooctane [123–125], polystyrene [126, 127], fluorocarbon polymers and long-chained perfluorinated carboxylic acids [128–130], and other coating materials [131]. Carbon-coated nanoaluminum is more resistant to moisture than uncoated nanoaluminum [132].

Coating nanoaluminum with HTPB improved storability, processability of formulations prepared with nano-Al and adhesion to binders in composite solid propellants [133]. Gaseous, liquid, and solid passivating reagents were investigated [134]. The advantages of non-oxide passivation are the potentially higher combustion heat of the powders covered by organic passivating layers and a lower particle size for such aluminum nanopowders in comparison with the commercially produced powder Alex<sup>®</sup>.

Nanoaluminum coated with hydrocarbons or fluorocarbons is more resistant to oxidation in air than uncoated nanoaluminum [135]. It was found that while fatty acids have a weak effect on the non-isothermal oxidation behavior, fluoroelastomers shift the oxidation onset of nanoaluminum to higher temperatures by ~20 °C for the first oxidation stage and by ~100 °C for the second oxidation stage.

The reactivity of passivated aluminum nanopowders was studied and it was shown that organic coatings enhance the resistance of aluminum nanoparticles to the effect of water vapor and cause changes in the parameters of the non-isothermal oxidation by air oxygen [136]. Passivation of aluminum nanopowders has been established to increase the temperature of oxidation onset and the heat release rate.

Nanoaluminum was modified with three different functional organic silanes and the effect of organic coatings on reducing oxidation of n-Al was measured via accelerated aging tests [137]. This study showed that all three types of organosilane-modified nanoaluminum have much better resistance to aging than the pristine uncoated nanoaluminum. See also [138, 139].

### 6.3 Physical Properties of Nanoaluminum

Pressed pellets of nanoaluminum had an unusually high electrical resistance, indicating that the particles are surrounded by an oxide layer which may behave like a semiconductor with electron defect conduction. Scanning electron microscope images showed the nanoparticles to change shape and coalesce into spheres if the electron beam energy was too high, a sort of unintentional electron beam welding.

In order to obtain more reproducible results with different batches of nanoaluminum, the nanoparticles need to be better characterized. A variety of standard particle characterization techniques were applied to 15 different types of particles [140]. The parameters measured were average particle diameter, specific surface area, amount of active content, and oxide layer thickness. Trends in propulsion performance measured

using a parameter of great interest to the hybrid rocket community (fuel mass burning rate) in general matched trends in particle characteristics (i.e. active content, surface area), but there were some noticeable exceptions. Other parameters that need to be examined include particle size distribution, degree of agglomeration, reactivity and thermal effects. See also [141].

### 6.3.1 Melting Behavior of Nanoaluminum

Nanocrystalline aluminum powders have been synthesized by mechanical attrition under different atmospheres or by gas condensation. The crystal refinement and the development of the microstructure were investigated by XRD, DSC, TEM, and electron energy loss spectrometry. Both preparation techniques lead to powders with comparable grain sizes. There is a drastic reduction of the melting point with decreasing grain size, in comparison to the bulk melting point value [142]. Subsequent remelting does not recover the bulk melting point. This is due to the microstructure of the nanocrystalline powders, the contribution of the stored enthalpy of cold work, and the nucleation of disorder/melting at grain boundaries/particle interfaces.

A nanocomposite material has been prepared by consolidation of gas-phase condensation nanocrystalline aluminum particles, which had been passivated with an alumina overlayer prior to the compaction step and it was characterized by XPS, DSC, TEM, and atomic force microscopy (AFM) [143]. The consolidated material, although showing a metallic shine and an ohmic electrical resistivity, presents a microstructure constituted of Al grains interconnected by a very thin alumina network, which prevents the material from falling apart when heated at temperatures above the melting point of aluminum.

The melting point of nanoaluminum decreased with decreasing particle size and the heat of fusion decreased. The effect of the oxide coating on the particles is to apply a compressive force to the aluminum core, thereby increasing the observed melting point and the heat of fusion. The melting point depression, both corrected and uncorrected for the effects of the oxide shell, is linear with the reciprocal of particle radius [144]. The size-dependent heat of fusion was significantly smaller than that predicted by the effects of the surface tension indicating that the solid nanoparticle is at a higher energy than expected, presumably due to the presence of defects or irregularities in the crystal structure at or emanating from the surface.

### 6.3.2 “Stored Energy” in Nanoaluminum?

The process of electro-explosion of metal wires, which has been known for more than 200 years, has been adapted to the preparation of activated aluminum, called Alex. The process produces metallic particles of approximately 50–100 nanometers in size. The most unusual characteristic of this aluminum is the “stored energy” that is released upon reaching a threshold temperature. While this heat generation has been confirmed by other researchers, no one has a proven theory for the source of this en-



ergy. It was postulated that during the very rapid cooling of an individual droplet of aluminum, the outer region of the particle would cool faster than the inner region and if an outer shell solidifies and shrinks as it cools, it may compress the molten liquid in the inner region. This process may work on the liquid region and store energy in the particle [145, 146].

A critical re-evaluation of stored energy in ultrafine aluminum powder produced by plasma explosion concluded that the postulated stored energy mechanism results in measurable stored energy for only unrealistically high cooling rates [147]. The objective of this study was to determine whether measurable energy can in fact be stored in an Alex particle during the rapid solidification process because of the compression of the inner liquid region by the shrinking outer solid shell or crust. It was concluded that although the postulated mechanism could store energy, the amount of energy stored is negligible. This theoretical finding was in agreement with experiments that showed no observable stored energy in Alex particles.

Mixtures of Alex with various oxidizers yielded burning rates many times higher than those of mixtures with ordinary aluminum powder. This enhanced burning rate phenomenon of Alex was confirmed for several solid propellants with hydroxyl-terminated polybutadiene (HTPB) as the binder [148].

However, the cause for this burning rate increase has not yet been definitively identified. Using TGA and DTA of Alex, Ivanov and Tepper noted that an exotherm occurred at 723 K (450 °C) and peaked at 823 K (550 °C) in the absence of air, without oxidation. From this result, it was suggested that the unique burning characteristics of Alex might be due to a stored internal energy, which is released on reaching a threshold temperature. Ivanov estimated this stored energy to be 400 cal/g (or  $1.67 \times 10^6$  J/kg). This claim of stored energy has been refuted by several research teams. TGA and DTA experiments with Alex, observed no release of internal energy [149]. Laboratory experiments using DSC and DTA arrived at the same conclusion [150, 151].

Before the publication of these findings, a study commenced with the intent of investigating the possibility that the rapid solidification of aluminum droplets during the plasma explosion process might impart stored internal energy to Alex showed that, in principle, a highly disordered crystal may contain higher internal energy than the same material in a more ordered crystal structure. Therefore, the recrystallization process could be exothermic. According to Ivanov and Tepper, the energy released by recrystallization is too small to produce the unique behavior of Alex, and an alternative source of internal stored energy was considered.

### 6.3.3 Crystal Structure of Nanoaluminum

Aluminum nanopowders with diameters ranging from 20 to 50 nm passivated by Al<sub>2</sub>O<sub>3</sub> coatings can be produced by two different evaporation routes: Induction heating evaporation (IHE) and laser-induction complex heating evaporation (LCHE). Thermal and crystal structure properties of these nanopowders were investigated

by DTA in a dry oxygen environment [152]. The results showed that Al nanopowders produced by LCHE had an oxidation enthalpy change ( $\Delta H$ ) of 3.54 kJ/g, while the  $\Delta H$  of Al produced by IHE was only 1.18 kJ/g. The phase constitution and microstructures of these nanopowders were revealed using XRD, TEM, and high-resolution transmission electronic microscopy (HRTEM). The results showed that the two powders had the same composition and mean particle size, as well as the same thickness of  $\text{Al}_2\text{O}_3$  coatings (3–5 nm). Defects were observed on the surfaces of the particles by LCHE; however, the defects were not detected by HRTEM on the surfaces of the particles by IHE. The results indicated that there exists excessive stored energy in Al nanopowders by LCHE because of the non-equilibrium condition brought by the laser and the defects are the storage location of the excessive stored strain energy. Propellants containing Al nanopowders made by LCHE showed higher specific impulse than those made by IHE.

## 6.4 Chemical Properties of Nanoaluminum

Many nanometals in the freshly prepared state are pyrophoric and have to be handled under an inert atmosphere to prevent autoignition. Some may even autoignite with nitrogen. Passivated nanoaluminum has very sharp exotherms when heated in oxygen or nitrogen. The exotherm starts well below the melting point of Al, while coarse, micron-size Al does not ignite in air until about 1273 K (1000 °C). The metals can be passivated by slow controlled exposure to dry oxygen in an argon atmosphere and can be protected by a hydrophobic coating (e.g. palmitic acid) or a water-impervious plastic film (polytetrafluoroethylene). In passivated and coated nanoaluminum the useful Al content is only 88–90 mass-%. If a layer of nanoaluminum powder is spread on a ceramic plate and ignited, a dark-glow exothermic reaction propagates through the powder before it ignites. The process of self-heating and self-sintering of the powder is faster than the oxidation reaction [145]. When one edge of a pressed pellet of nanoaluminum is pressed against a hot plate, there is a visible light-emitting hot zone traveling through the pellet. The source of this stored energy has not yet been totally explained.

### 6.4.1 Reactions of Nanoaluminum

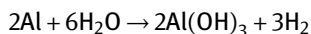
There is concern that nanoaluminum particles may sinter together and coalesce during storage and they may have only a limited shelf life. The activities of different aluminum powders were studied by means of a gasometric method [153]. The results showed that the activity of spherical nanoaluminum powder is 76.1%, and the activity of common flake aluminum powder is 43.0%. Particle sizes had significant effects on the activities of aluminum powders. The shelf life prediction of nanoaluminum was studied by an accelerated test and a Berthelot method. If one assumes that the co-

alescence change values of nanoaluminum powder are 10, 20 or 30% as expiration limits, then the shelf lives of nanoaluminum powder are predicted to be 4.73, 9.77, and 14.80 years at 298 K (25 °C).

With its large surface area, nanoaluminum can adsorb many species, some adversely affecting its stability, others providing a protective coating. The composition of adsorbed species can be determined by temperature-programmed desorption with mass spectrometric analysis of the off-gassing. Water adsorption and desorption is a particular concern, since the aging reaction of Al nanopowders may be related to the water adsorbed on its surface. The thermodesorption of adsorbed gases on nanometer-sized aluminum powders was investigated using TGA and TGA-FTIR-MS [154]. The results showed that the Al nanopowder studied contained 12 mass-% of adsorbed gases. Desorption of water and carbon dioxide was observed by FTIR and MS. The kinetic parameters for the desorption of the adsorbed gases were determined using variable heating rate and isothermal studies giving numbers for the activation energies of desorption.

#### 6.4.1.1 Reactions of Nanoaluminum with Liquid Water

Nanoaluminum reacts rapidly with water:



The reaction begins at 323 K (50 °C) and accelerates to explosive strength at 353 K (80 °C) [155]. A gelled propellant consisting of Alex in cold water gelled with 3% polyacrylamide is stable for only a short time. Its burning rate in 1 cm diameter × 3 cm length quartz tubes in an argon-filled Crawford bomb was measured as a function of pressure and the burning rate can be expressed by the equation

$$r = 0.183(P/P_0)^{0.4}$$

where  $r$  is the linear burning rate in cm/s,  $P$  is the pressure in atm and  $P_0$  is the pressure of 1 atm [146]. Nanoaluminum ignited by a hot wire in a nitrogen-filled Crawford bomb burned vigorously at 20–60 atm, forming AlN containing a little (3%) unreacted Al. Mixtures of nanoaluminum with lead nitrate or barium nitrate and ignited by a hot wire under heavy confinement formed AlN instead of  $\text{Al}_2\text{O}_3$ . It appears that under the conditions of this experiment, the formation of AlN is favored over the formation of  $\text{Al}_2\text{O}_3$ , contrary to what thermodynamics would predict.

A suspension of nanoAl/gelled water slurry was prepared by adding 0.1 mass-% polyacrylamide and mixed with 15 mass-% nanoAl powder (mean particle size 50 nm) [156]. The single droplets were suspended on the tip of a quartz fiber and ignited using a hot nichrome wire or an electric arc in air or argon atmosphere. The experiments showed that the droplets can ignite and burn in air or argon with a stable spherical flame. Successful experiments in the inert atmosphere confirmed that the combustion occurs due to the reactions between Al and  $\text{H}_2\text{O}$ . Replacement of nanoAl with coarser

Al powder (6  $\mu\text{m}$ ) dramatically increased the ignition delay time in air and made the ignition in argon impossible.

In a study of the self-deflagration of nanoAl and liquid water without the use of any additional gelling agents, steady-state burning rates were obtained at room temperature using a windowed chamber for a pressure range of 0.1–4.2 MPa in an argon atmosphere, particle diameters of 38–130 nm, and overall mixture equivalence ratios ( $\phi$ ) from 0.5 to 1.25 [157, 158]. At the highest pressure studied, the linear burning rate was found to be  $8.6 \pm 0.4 \text{ cm/s}$ , corresponding to a mass-burning rate per unit area of  $6.1 \text{ g cm}^{-2} \text{ s}^{-1}$ . The pressure exponent at room temperature was 0.47, which was independent of the overall mixture equivalence ratio for all of the cases considered. The mass-burning rate per unit area increased from  $\sim 1.0$  to  $5.8 \text{ g cm}^{-2} \text{ s}^{-1}$  for an equivalence ratio range of  $\phi = 0.5$ –1.25. It varied inversely to particle diameter, increasing by 157% when the particle diameter was decreased from 130 to 50 nm at  $\phi = 1.0$ .

The suspensions of aluminum in water would have to be gelled to prevent settling of the particles during standing [159, 160]. Using liquid hydrogen peroxide in place of water would give even more energetic propellants [161–163].

The reaction of suspensions of nanoaluminum in liquid or frozen water can be discussed here in the chapter on reactions of metals or in future volumes on mono-propellants, gelled propellants, and solid propellants. Some of the more academic studies, short of actually launching a rocket with these propellants, are already described here in the current and the following section. There may be some overlap of the information presented in different volumes.

The reaction of nanoaluminum with water for the production of hydrogen can be initiated by a trace of LiOH and the hydrogen gas can be used in fuel cells or other devices [164].

The strand-burning rate of nanoaluminum/water mixtures was studied for particles in the size range of 38–130 nm and over a pressure range of 1–10 MPa in a constant volume high-pressure chamber [165]. The burning rate as a function of pressure and particle size could be expressed by the equation

$$r_b = 98.8P^{0.32}d_p^{-1}$$

where  $r_b$  is the burning rate in cm/s,  $P$  is the pressure in MPa and  $d_p$  is the particle diameter in nm. The flame zone thickness increased with increasing particle size and decreasing pressure. The rate of combustion of aluminum/water mixtures was controlled by mass diffusion across the inevitable oxide layers coating the particles.

#### 6.4.1.2 Reactions of Nanoaluminum with Frozen Water

The theoretical specific impulse of the Al/H<sub>2</sub>O propellant is about 300 s. The propellant combination of aluminum and ice (frozen water) has become known under the name *Allce*. Similar combinations have been called *refrigerated solid propellants* or *cryogenic solid propellants*. Allce propellants are simple to prepare, water is likely to

be found near extraterrestrial landing sites, and Allce propellants are good candidates for propulsion using **In-Situ Resource Utilization (ISRU)** methods. A rocket propellant has been tested consisting of nanoaluminum embedded in a matrix of frozen water. This cryopropellant must be kept below freezing all the time [166].

Nanometer sized aluminum particles, when combined with water to self-propagate, reacted to form high-temperature molecular hydrogen and condensed phase aluminum oxide. Freezing these mixtures produced a storable solid propellant having potential applications to hydrogen storage. Generally, the particles used had a nominal diameter of 80 nm and an active aluminum content of 74.5 mass-% Al. Experimental analysis of burning of frozen compositions was conducted using a constant pressure strand burner, constant volume cell and a series of scaled rocket motors [167].

The combustion of alane and aluminum powder with water in its frozen state was studied experimentally and theoretically using both nano-sized and micron-sized particles over a wide range of chamber pressures [168]. The linear strand burning rate and chemical efficiency were obtained using a constant-pressure strand burner or a constant-volume chamber, respectively. The 80-nm Al particles had spherical shapes in contrast to the rhombohedral-shaped alane. The effect of replacing nano-Al particles by micron-sized Al or alane particles was examined systematically for additive mass fractions up to 25%. The equivalence ratio was fixed at 0.943. The pressure dependence of the burning rate followed the power law,

$$r_b = aP^n$$

with  $n$  ranging from 0.41 to 0.51 for all the materials considered. For the Allce without any additive the burning rate equation was

$$r_b = 0.992P^{0.405}$$

where  $r_b$  is the burning rate in cm/s, and  $P$  is the pressure in MPa. The burning rate decreased with increasing alane concentrations, whereas it remained approximately constant with cases containing only Al particles. The chemical conversion efficiency ranged from 32 to 83%, depending on the mixture composition and pressure, too low for many of the intended applications.

The combustion of aluminum with ice was studied using various mixtures of nano-sized and micrometer-sized aluminum particles as a means to generate high-temperature hydrogen at fast rates for propulsion and power applications [169, 170]. Bimodal particle size distributions gave better mixture packing densities. The burning rate can be tailored by introducing various particle sizes. The effects of the bimodal particle size distributions and equivalence ratio on ignition, combustion rates, and combustion efficiency were investigated in strand burner experiments at constant pressure and in small laboratory scale (1.91 cm = 0.75 in. diameter) static fired rocket-motor combustion chambers with center-perforated propellant grains. The substitution of micron-size aluminum for nanometer aluminum had little effect on the linear burning rates of Allce mixtures for low-mass substitutions. The effects

of bimodal aluminum compositions on motor performance were minor, although the experimental results suggested that longer  $L^*$  chambers and combustion times are necessary for complete combustion.

Strand burning tests provided information on propellant linear and mass burning rates with respect to pressure and composition which were correlated using a Saint Roberts Law fit. Figure 1 is a comparison of linear strand burning rates of 80-nm nanoaluminum with frozen or liquid water, also using data from [171]. The black line is the result of a burning rate equation of stoichiometric ( $\phi = 1.0$ ) liquid  $H_2O/Al$

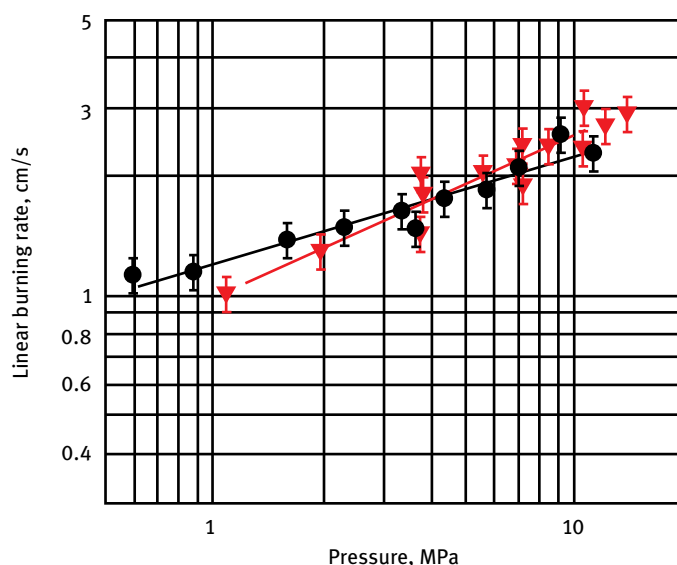
$$r_b = 1.2P^{0.27}$$

where  $r_b$  is the burning rate in cm/s and  $P$  is the pressure in MPa. In comparison, the burning rate of slightly under-oxidized ( $\phi = 0.943$ ) nanoaluminum/ice shown as the red dashed line has a burning rate equation of

$$r_b = 0.992P^{0.405}$$

where  $r_b$  is the burning rate in cm/s and  $P$  is the pressure in MPa. Graphs like Figure 1 actually belong in *Encyclopedia of Monopropellants*, but this information is shown here to illustrate the reactivity of nanoaluminum with water.

All ice mixtures were fired in strand burners and static-firing motors, instrumented with pressure and force transducers, to determine the propulsive performance of several propellant formulations. Additional formulations were tested with added ammonia borane, aluminum hydride or hydrogen peroxide. See also [161, 172–178].



**Figure 1:** Comparison of linear strand burning rates of nanoaluminum with frozen (in red) or liquid (in black) water. (Reproduced and modified from [167].)

AllIce mixtures were tested in strand burners and fired in static-firing heavy-duty motors, in preparation for a free-flight demonstration [179]. The burning rate equation for AllIce mixtures with an equivalence ratio of 0.71 was

$$r_b = 0.70274P^{0.57019}$$

where  $r_b$  is the burning rate in cm/s and  $P$  is the pressure in MPa. After several static firings in a heavy-duty motor casing, the AllIce propellant was installed in a 10-cm (4-in. O.D.), 2.5 m (8 ft 6 in.) tall sounding rocket and ignited by a solid propellant charge and launched in a free-flight demonstration. The rocket coasted upwards after the grain was depleted and reached a peak altitude of ~394 m.

Strand burning rates of aluminum/water ice (AllIce) mixtures over a pressure range of 1–10 MPa were studied using both a monomodal distribution of nanoaluminum particle sizes and a bimodal distribution of nano-sized and micron-sized aluminum particle sizes [180]. The burning rate of the 80 nm AllIce mixture increased from 1.22 to 2.5 cm/s as the pressure increased from 1 to 10 MPa. For stoichiometric AllIce mixtures with 80 nm particles, the burning rate showed a pressure dependence of

$$r_b = 1.18P^{0.33}$$

where  $r_b$  is the burning rate in cm/s and  $P$  is the pressure in MPa. If a portion of 80 nm particles was replaced with 5 and 20  $\mu\text{m}$  particles, the burning rate was not significantly affected for loading densities up to 15–25% but decreased significantly beyond this value. The pressure exponent decreased with the addition of 20  $\mu\text{m}$  Al particles. The flame thickness of a bimodal particle mixture was greater than its counterpart of a monodispersed particle mixture.

Using frozen hydrogen peroxide in place of water ice would give even more energetic propellants.

The energy and the high-pressure gases released in the aluminum-water reaction can also be used for underwater propulsion and of course there would be plenty of water surrounding the vehicle to draw from [181, 182]. A similar underwater propellant is the exothermic reaction of aluminum hydride with water [183].

#### 6.4.1.3 Oxidation of Nanoaluminum

Nanostructured aluminum is much easier oxidized than ordinary aluminum. Differential scanning calorimetry measurements showed that when heated in air, the Alex material is partly oxidized resulting in a large exotherm starting at around 723 K (450 °C) [184]. With an ordinary aluminum powder a much smaller exotherm is obtained. Microcalorimetry measurements, carried out at 338 and 318 K (65 and 45 °C), showed that Alex has good stability in dry air but that it reacts quickly, although not vigorously, at high relative humidity, releasing much heat. The BET surface area of Alex was about 12 m<sup>2</sup>/g. It was estimated that active aluminum content of micron-size aluminum is

99.5% or better, while the active aluminum content of passivated nanoaluminum typically ranges from 50 to 95%.

Experimental size-dependent reactivity measurements of aluminum nanoparticles using a single particle mass spectrometer (SPMS) indicated that the reactivity of aluminum nanoparticles increased with decreasing primary particle size as well as decreasing particle mobility size [185, 186]. A phenomenological model has been described which highlights the difference in the mechanism of oxidation of aluminum nanoparticles as compared to micron-sized particles. This model also showed the significance of physical phenomena that are important at the nanoscale, such as a pressure gradient present inside the particles, and may impact the oxidation process.

It had been suggested that very low melting temperatures should be expected for nano-sized aluminum powders and that such low melting temperatures could accelerate oxidation and trigger ignition much earlier than for regular, micron-sized aluminum powders. The melting and oxidation behavior of nano-sized aluminum powders, powder samples with three different nominal sizes of 44, 80, and 121 nm was studied by DSC where the powders were heated from room temperature to 1023 K (750 °C) in an argon environment [187]. TGA was used to measure the mass increase indicative of oxidation while the powders were heated in an oxygen-argon gas mixture. Characteristic stepwise oxidation was observed for all studied nanopowders. The observed oxidation behavior was well interpreted using published kinetics of oxidation of micron-sized aluminum powders. No correlation was found between the onset of melting and oxidation of aluminum nanopowders.

The particle structure of aluminum nanopowders oxidized at different temperatures, was modeled via geometrical considerations that enabled the calculation of the variation of specific surface area during oxidation [188]. A two-step oxidation scenario was proposed. In the early oxidation stage for temperatures up to 923 K (650 °C), where a pseudoplateau was reached, the oxidation occurred by diffusion of oxygen or aluminum through the alumina layer and resulted in a core-shell structure. At higher temperatures above the melting point of aluminum, outward diffusion of aluminum through the oxide shell was controlling the reaction rate. The reaction interface was then located at the external surface and voids were formed inside the particles. The migration of aluminum toward the surface of the particles was faster than the oxidation.

#### 6.4.2 Ignition of Nanoaluminum

Depending on the preparation history of nanoaluminum, freshly prepared, non-passivated nanoaluminum is pyrophoric in air. Aluminum particles with diameters less than about 68 nm were predicted to be pyrophoric, e.g., ignite in air without appreciable initial preheating [189, 190]. Oxidation of a nanoaluminum particle occurs in a few microseconds [191].



The oxidation and ignition of aluminum nanoparticles with a mean diameter of 150 nm was investigated with the help of simultaneous thermal analysis, XRD, EDAX, SEM, and TEM at heating rates of 2–30 K/min [192]. A unique early ignition reaction was observed when the heating rate was  $\geq 8$  K/min.

A study of the thermal and hazard properties of various uncoated and coated aluminum nanopowders and their effects on the thermal stability, out-gassing behavior and electrostatic discharge sensitivity of various energetic materials showed that these aluminum nanopowders had a mean particle size of 20–120 nm [193]. The coated samples had a layer of 7–25% of polymer. The thermal behavior of the aluminum nanopowders in air and the effects of the particle size and the coating on the reactivity of aluminum nanopowders was determined. Aluminum nanopowders are very reactive in the presence of water, resulting in aging problems. The coating with a polymer had only a minor effect on the reactivity of aluminum nanopowders with water. On the other hand, the results from an aging study showed that the coated aluminum nanopowder was more stable than the uncoated nanopowder in humid atmospheres. The addition of uncoated aluminum nanopowders has previously been shown to increase the electrostatic discharge sensitivity of both ammonium dinitramide and ammonium perchlorate to very low electrostatic ignition energies that can easily be carried by a human body. In contrast, the coated aluminum nanopowders did not appear to sensitize ammonium dinitramide and ammonium perchlorate toward electrostatic discharge, which suggested that coatings can effectively prevent the sensitization effect.

The ignition and combustion of aluminum particles of various sizes, mostly coarser than nanoaluminum, will be discussed in future volumes on solid propellants, because it affects the burning rate and performance of metallized solid propellants. That section also includes combustion of aluminum dust aerosols in air or other oxidizer atmospheres. A good review of combustion of nanoaluminum is available in [194]. Combustion of metallized liquid monopropellants containing nanoaluminum will be discussed in *Encyclopedia of Monopropellants*.

#### 6.4.3 Aging of Nanoaluminum

Small particles of any kind, not just nanoaluminum, have a tendency to agglomerate and fuse into larger particles, a process that minimizes surface area and entropy. This limits the storage life of unprocessed nanoaluminum [108]. Once formulated into solid propellants or gelled liquid propellants, the particles are separated by the continuous phase and no longer in direct contact with each other, which would prevent or delay particle growth.

## 6.5 Applications of Nanoaluminum

Besides its applications in liquid and solid rocket propellants, nanoaluminum has been evaluated as fuel in thermites used as igniters or heat sources and in explosives. These non-propulsive applications are not included in this book. Some of the studies cover a very wide range of applications, including the use of nano engineered energetic materials (NEEMs) [195]. This is a very good status report on applications of nanomaterials. See also [93, 196–202].

## 7 Metal Hydrides

Another group of rocket fuel compounds discussed here following the same sequence as the one used for getting the metals into a systematic order is the group of hydrides of these metals, in particular hydrides of light metals, such as lithium, beryllium, boron, and aluminum. These constitute quite promising rocket fuels and additives to rocket fuels. This includes simple and complex hydrides. Complex and saline hydrides combine hydrides of more than one metal in a molecule and are usually in crystalline solid form, with the exception of aluminum borohydride (aluminum boranate), which is a liquid.

Hydrides can be divided into three (four) categories, depending on the type of chemical bonds holding the hydrogen atom to its partner:

1. Covalent hydrides contain covalent bonds, such as those in hydrocarbons and hydronitrogens.
2. Saline or ionic hydrides contain hydrogen in the form of a negatively charged hydride ion  $H^-$ , such as in lithium hydride or sodium hydride. These are the types of hydrides discussed here.
3. Metallic hydrides are formed by absorption of hydrogen into the electron cloud surrounding atoms in metals. The compounds are electrical conductors and are non-stoichiometric, allowing a wide variation of hydrogen contents. Many metals become embrittled as the result of inadvertent hydrogen absorption. Reversible intermetallic hydrides such as those of iron-titanium alloys are being tested as methods for compressed hydrogen storage in vehicles. Nickel-hydrogen batteries have replaced nickel-cadmium batteries in satellites and many earth-bound applications.
4. Hydrogen bonding in diborane allows this compound to exist as a dimer of  $BH_3$ . Boranes will be discussed in the chapter “Boranes.”

The ionic hydrides are formed by the strongly electropositive alkali and alkaline earth metals. Beryllium hydride  $BeH_2$ , which is rather covalent in character, is an exception. The alkali metal hydrides are sensitive to air and humidity, and alkali metal hydride powders react violently with water. In contrast, the sensitivity of alkaline-earth metal

hydrides to air and water strongly depends on their preparation and storage. Fresh, finely divided powders may be very reactive, or even pyrophoric, but commercial  $\text{MgH}_2$  and  $\text{CaH}_2$  powders are often passivated and can then be safely handled in air.

Solid hydrides, e.g., lithium hydride, can be used as fuels in hybrid or tribrid engines. Liquid hydrides, e.g. pentaborane have been considered as liquid rocket fuels or as fuels in air-breathing engines. Boron hydrides and organic boron compounds are discussed in this book in a chapter outside the metal hydride domain because they have different hydride bonds and they have at one time assumed a more important role than all other metal hydrides combined.

Chemical rocket propellant performance can be improved by using metal hydrides that store high volumes of hydrogen at ambient conditions that can be released during combustion. A theoretical investigation of hydrides as additives in hybrid fuels and solid propellants started to look at aluminum hydride, but aluminum hydride is not commercially available. As a consequence, attention was focused on other simple and complex hydrides that are readily available [203]. A comparative analysis of theoretical mass-specific and volume-specific impulses, propellant average density, adiabatic flame features, and preliminary estimates of exhaust products was conducted. Eight different hydrides, potentially applicable as replacements for metallic aluminum currently used in solid propellants and hybrid rocket systems, were considered.

Predictive methods for calculation of enthalpies of formation of metal hydrides include Born-Haber cycles and density functional theory methods [204]. Other bibliographies and reviews on hydrides were published, such as [205]. Comprehensive reviews of metal hydrides are in [206–208]. Table 8 is a summary of physical properties of metal hydrides.

**Table 8:** Physical properties of metal hydrides.

| Hydride          | Molecular mass<br>g/mol | CAS Registry number | Hydrogen content<br>mass-% H | Density<br>g/cm <sup>3</sup> | Enthalpy of formation<br>kJ/mol |
|------------------|-------------------------|---------------------|------------------------------|------------------------------|---------------------------------|
| LiH              | 7.95                    | [7580-67-8]         | 12.68                        | 0.775                        | −90.7                           |
| NaH              | 24                      | [7646-69-7]         | 4.2                          | 1.363                        | −56.5                           |
| KH               | 40.11                   | [7693-26-7]         | 2.51                         | 1.43                         | −57.9                           |
| RbH              | 86.48                   | [13446-75-8]        | 1.17                         | 2.595                        | −47.4                           |
| CsH              | 133.91                  | [13772-47-91]       | 0.75                         | 3.41                         | −49.9                           |
| BeH <sub>2</sub> | 11.03                   | [13597-97-2]        | 18.28                        | 0.65                         | −19.3                           |
| MgH <sub>2</sub> | 26.32                   | [7693-27-8]         | 7.66                         | 1.45                         | −75.4                           |
| CaH <sub>2</sub> | 42.1                    | [7789-78-8]         | 4.79                         | 1.902                        | −186.3                          |
| SrH <sub>2</sub> | 89.64                   | [13598-33-91]       | 2.25                         | 3.269                        | −180.5                          |
| BaH <sub>2</sub> | 139.36                  | [13477-09-3]        | 1.45                         | 4.156                        | −171.2                          |
| AlH <sub>3</sub> | 30.00536                | [7784-21-6]         | 10.08                        | 1.43                         | −11.55                          |

Data source: [208]

Beryllium hydride and aluminum hydride are solids. For many rocket applications, liquid fuels would be preferred. A search was started for liquid metal hydrides with fuel performance properties similar to  $\text{BeH}_2$  or  $\text{AlH}_3$  [209]. The objectives of the liquid metal hydride research programs have been to demonstrate the feasibility of forming liquid beryllium fuels from known energetic beryllium compounds unencumbered by ligands of low energy, to prepare liquid beryllium compounds of good fluidity and thermal stability, and which have a theoretical  $I_{sp}$  performance goal of at least 330 s with 100%  $\text{H}_2\text{O}_2$ , to tailor the physical properties of these energetic fuels by the substitution of appropriate groups, and to provide compatible and thermally stable vehicles for the formulation of heterogeneous gelled fuels containing suspended solid  $\text{BeH}_2$ . Several approaches to liquid beryllium fuels were pursued: Depolymerization of alkylberyllium hydrides,  $(\text{CH}_3\text{BeH})_x$ , by  $\text{B}_2\text{H}_6$  and  $(\text{CH}_3\text{BeBH}_4)_2$  to form liquids, generation of  $\text{BeH}_2$  *in situ* by hydriding of organoberyllium derivative, dissolution of reactive boron alkyl-terminated  $\text{BeH}_2$  in preformed beryllium liquids and dissolution of  $\text{BeH}_2$  in  $\text{Al}(\text{CH}_3)_3$ . It was demonstrated that liquids containing the components of  $(\text{BeH}_2)_n$  and other beryllium polymers can be prepared when segments of such polymers are suitably terminated with borane (BTBH) or alane (ATBH) groups. An example for the first group of BTBH is  $\text{H}_2\text{BH}_2\text{BeH}_2\text{BeH}_2\text{BH}_2$ , which is still a solid with an enthalpy of formation of  $-131 \text{ kJ/mol}$  ( $-31.4 \text{ kcal/mol}$ ), but its melting point can be lowered by including some methyl groups, such as in  $(\text{CH}_3\text{BeBH}_4)[\text{Be}(\text{CH}_3)_2]_n(\text{BH}_4\text{BeCH}_3)$ . The overall concepts of termination liquefaction and tailoring to achieve good physical properties were exemplified by a sequence including some general physical properties of each compound. In addition to the borane-terminated liquids, alane-terminated liquids have been investigated and found to be suitable media for the formulation of heterogeneous propellants, e.g.,  $(\text{BeH}_2)_n$  gels. The overall objective of these programs is a family of homogeneous and heterogeneous propellants in the 330–360 s  $I_{sp}$  range. Some homogeneous liquid BTBH fuels are reaching the edge of the range and heterogeneous fuels composed of  $(\text{BeH}_2)_n$  gels in ATBH liquids are well within it.

## Binary Metal Hydrides

### 8 Alkali Metal Hydrides

#### 8.1 Lithium Hydride

Pure lithium hydride,  $\text{LiH}$ , CAS RN [7580-67-8], is a white powder and forms colorless, cubic crystals. Commercial grades of lithium hydride are often gray as a result of containing some unreacted elemental lithium.

### 8.1.1 Preparation of Lithium Hydride

Lithium hydride is normally prepared by the action of hydrogen on molten lithium metal at about 973 K (700 °C). This is an exothermic reaction that needs to be controlled by adjusting the hydrogen feed rate. The heavier lithium hydride sinks to the bottom of the reaction vessel as a fluid melt which crystallizes on cooling below the melting point of 961 K (688 °C). Commercial grades of lithium hydride are colored due to the photosensitivity of clear white crystals, and due to impurities caused by incomplete hydrogen absorption. The blueish tint is similar to that of F-centers in irradiated potassium bromide.

Protective coatings have been evaluated for lithium hydride to protect it from the effects of moisture and carbon dioxide in air. Fourteen organic coating materials for protecting lithium hydride from normal atmospheric water vapor were evaluated and weight changes of unprotected and protected specimens were measured as a function of time of exposure [210].

### 8.1.2 Physical Properties of Lithium Hydride

Physical properties of lithium hydride are listed in Table 9. Other summaries of the properties of lithium hydride are published in [211–214].

**Table 9:** Physical properties of lithium hydride.

|                               | SI units                | Other units          |
|-------------------------------|-------------------------|----------------------|
| Molecular mass                | 7.949 g/mol             | 125.8 mol/kg         |
| Melting point                 | 953 K                   | 680 °C               |
| Boiling point                 | Decomposition           | —                    |
| Density at 293 K (20 °C)      | 0.82 g/cm <sup>3</sup>  | —                    |
| Density at 298 K (25 °C)      | 0.775 g/cm <sup>3</sup> | —                    |
| Enthalpy of formation, solid  | –116 kJ/mol             | –27.7 kcal/mol       |
|                               | –90.63 kJ/mol           | –21.66 kcal/mol      |
| Enthalpy of formation, liquid | –77.71 kJ/mol           | –18.57 kcal/mol      |
| Heat of fusion at 961 K       | 25.65 ± 0.50 kJ/mol     | 6.37 ± 0.12 kcal/mol |

#### 8.1.2.1 Density of Lithium Hydride

The density of lithium hydride at 298 K (25 °C) is 0.775 g/cm<sup>3</sup> and the lattice constant of the cubical crystal structure is 4.083 Å. The coefficient of thermal expansion at temperatures from 298 to 798 K (25–525 °C) as measured by XRD may be expressed by the equation:

$$a_t = a_0(\text{at } 25^\circ\text{C}) \left[ 1 + 4.2 \times 10^{-5}(t - 25) + 1.9 \times 10^{-8}(t - 25)^2 \right]$$

where  $a_0$  is the coefficient of thermal expansion at 298 K (25°C) and  $t$  is the temperature in °C. This gives a linear coefficient of expansion of  $4.2 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$  at 298 K (25°C), or a cubical coefficient of expansion of  $1.26 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ . The density of pressed lithium hydride grains as a function of compacting pressure can be derived from an empirical formula [215, 216].

### 8.1.2.2 Thermal Conductivity of Lithium Hydride

The development of a regression law for lithium hydride grains in hybrid rockets for sizing hybrid engines for different thrust levels depends on accurate data for the thermal conductivity of the fuel grain. The thermal conductivity of pressed lithium hydride grains with a density of  $0.69 \text{ g/cm}^3$  at 673 K (400°C) is  $0.040705 \text{ W cm}^{-1} \text{ K}^{-1} = 3.5 \text{ kcal m}^{-1} \text{ h}^{-1} \text{ }^\circ\text{C}^{-1}$  [217, 218].

The effective thermal conductivity of cast lithium hydride was evaluated as a function of temperature as influenced by non-homogeneous (cracked) distribution, various gases in cracks and voids [219]. The overall effective thermal conductivity of lithium hydride between the outer surface of its container and the surface of an enclosed cooling tube can be established at  $0.1055$  and  $0.05189 \text{ W cm}^{-1} \text{ K}^{-1}$  at 394 and 755 K (6.1 and 3.0  $\text{BTU h}^{-1} \text{ ft}^{-1} \text{ }^\circ\text{F}^{-1}$  at 250 and 900°F), respectively, with a helium internal atmosphere. The thermal conductivity of LiH compacts with 0.7% void increased from 2 to  $100 \text{ W m}^{-1} \text{ K}^{-1}$  between 10 and 70 K, maximized at 50–71 K, and then decreased to  $20 \text{ W m}^{-1} \text{ K}^{-1}$  at room temperature [220].

The thermal conductivity of lithium hydride was measured because it was intended to be used as a nuclear radiation (neutron) shield around nuclear reactors [221]. A large disc of molten lithium hydride, 2.18 m (86 in.) in diameter and weighing 770 kg (1700 lb.) was cast to be used as a radiation shield for a SNAP in-space nuclear reactor. Thermal conductivity data of lithium hydride are listed in Table 10.

Thermal conductivity of solid lithium hydride over the temperature interval 333–783 K (60–510°C) was measured by a stationary radial heat-flux method [222]. The test

**Table 10:** Thermal conductivity of solid lithium hydride.

| Temperature |     | Thermal conductivity             |                                                                 |
|-------------|-----|----------------------------------|-----------------------------------------------------------------|
| K           | °C  | $\text{W m}^{-1} \text{ K}^{-1}$ | $\text{kcal m}^{-1} \text{ h}^{-1} \text{ }^\circ\text{C}^{-1}$ |
| 323         | 50  | 7.79                             | 6.7                                                             |
| 373         | 100 | 6.98                             | 6.01                                                            |
| 423         | 150 | 6.32                             | 5.44                                                            |
| 473         | 200 | 5.74                             | 4.94                                                            |
| 523         | 250 | 5.35                             | 4.6                                                             |
| 573         | 300 | 4.77                             | 4.1                                                             |
| 623         | 350 | 4.39                             | 3.78                                                            |
| 673         | 400 | 4.25                             | 3.66                                                            |

sample was a cylinder constructed from 1.2 to 2.5 cm thick, hollow disks with 1 cm inner diameter and 7 cm outer diameter in a helium atmosphere. The heat flux from the internal heater was measured by means of potential leads and the temperature differential in the range of 15–25 °C was measured with thermocouples placed along the inner and outer surfaces of the disk to be studied. The thermal conductivity of lithium hydride measured by Fieldhouse is given in Table 11. These data are very similar to those in Table 10.

**Table 11:** Thermal conductivity of solid lithium hydride.

| Temperature |     | Thermal conductivity              |                                                       |
|-------------|-----|-----------------------------------|-------------------------------------------------------|
| K           | °C  | W m <sup>-1</sup> K <sup>-1</sup> | kcal m <sup>-1</sup> h <sup>-1</sup> °C <sup>-1</sup> |
| 335         | 62  | 7.28                              | 6.26                                                  |
| 374         | 101 | 6.49                              | 5.58                                                  |
| 445         | 172 | 5.92                              | 5.09                                                  |
| 509         | 236 | 5.56                              | 4.78                                                  |
| 539         | 266 | 5.36                              | 4.61                                                  |
| 613         | 340 | 5.07                              | 4.36                                                  |
| 680         | 407 | 4.50                              | 3.87                                                  |
| 723         | 450 | 4.36                              | 3.75                                                  |
| 786         | 513 | 4.08                              | 3.51                                                  |

Data source: [222]

The thermal conductivity of lithium hydride was measured using crystal samples placed in various media [213, 223]. One set of measurements was carried out in an inert gas by a relative method involving axial heat flux. The rest of the data (Table 12) were obtained by a method in which the heat flux was determined by measuring the rise in the temperature of gas that passed through a tube inside the lithium hydride test sample (the calorimetric method).

The thermal conductivity of molten lithium hydride can be expressed by the linear equation

$$\lambda = 3.72 \times 10^{-3} T - 2.37$$

where  $\lambda$  is the thermal conductivity in W m<sup>-1</sup> K<sup>-1</sup> and  $T$  is the temperature in kelvin. See also [224].

Lithium hydride cannot be melted unless one operates under hydrogen pressure. The viscosity of molten lithium hydride has been measured in the temperature range 951–1132 K (1252–1578 °F) [225]. A closed system utilizing a Brookfield viscometer was designed for measuring the viscosity of LiH at 951–1132 K. The system was operated under hydrogen at 138 kPa (20 psig) with provisions for external control of the furnace and viscometer. The viscosity varied little and appeared to be described by a straight

**Table 12:** Thermal conductivity of solid lithium hydride obtained by the calorimetric method.

| Temperature |     | Thermal conductivity            |             |              |              |                                                   |             |              |              |
|-------------|-----|---------------------------------|-------------|--------------|--------------|---------------------------------------------------|-------------|--------------|--------------|
|             |     | In<br>hydrogen                  | In<br>argon | In<br>vacuum | In<br>helium | In<br>hydrogen                                    | In<br>argon | In<br>vacuum | In<br>helium |
| K           | °C  | $\text{W m}^{-1} \text{K}^{-1}$ |             |              |              | $\text{kcal m}^{-1} \text{h}^{-1} \text{°C}^{-1}$ |             |              |              |
| 366         | 93  | 9.01                            | —           | 6.57         | —            | 7.75                                              | —           | 5.65         | —            |
| 394         | 121 | 9.01                            | —           | —            | 8.75         | 7.75                                              | —           | —            | 7.53         |
| 422         | 149 | 8.19                            | 5.69        | 5.89         | 8.11         | 7.05                                              | 4.90        | 5.07         | 6.98         |
| 477         | 204 | 7.28                            | 5.10        | 5.10         | 6.90         | 6.26                                              | 4.39        | 4.39         | 5.94         |
| 533         | 260 | 6.39                            | 4.70        | 4.52         | 5.89         | 5.50                                              | 4.04        | 3.89         | 5.07         |
| 588         | 315 | 5.81                            | 4.30        | 3.86         | 5.02         | 5.00                                              | 3.70        | 3.32         | 4.32         |
| 644         | 371 | 5.36                            | 3.97        | 3.39         | 4.39         | 4.61                                              | 3.42        | 2.92         | 3.78         |
| 699         | 426 | 5.02                            | 3.72        | 2.85         | 3.97         | 4.32                                              | 3.20        | 2.45         | 3.42         |
| 727         | 454 | —                               | 3.56        | 2.51         | 3.81         | —                                                 | 3.06        | 2.16         | 3.28         |
| 755         | 482 | 4.85                            | —           | —            | —            | 4.17                                              | —           | —            | —            |

Data source: [213]

line between 0.37 cPs at 951 K and 0.24 cPs at 1128 K. The LiH evidently melted at approximately 951 K, which is 5.5° lower than the reported value.

### 8.1.2.3 Crystal Structure of Lithium Hydride

The crystal structures of the alkali metal hydrides are the same as that of rock salt (NaCl) or zinc sulfide (ZnS). The lattice constant of the cubical crystal structure is 4.083 Å. Single crystals of optical quality LiH can be prepared by slow crystallization of the melt under hydrogen gas at moderate pressure [226]. Measured and reported values of the physical, thermal, chemical, and optical properties of LiH and LiD were compared to those of LiF and NaCl. These properties bear out the predominantly ionic nature of the crystalline LiH structure. The optical properties of LiH differed from those expected by a comparison with the properties of the alkali metal halides or the other alkali metal hydrides. This difference is assumed to be related to distortion and polarization effects on the hydride ion in the LiH crystal lattice. The Li—H bonds may be somewhat covalent which may contribute to the binding energy of crystalline LiH, and this also may be responsible for its somewhat anomalous behavior.

The optical properties of blue color centers involving trapped electrons or ions in LiH showed that properties of the crystalline media other than the lattice parameter are important in relation to the energy of the optical absorption bands [227].

### 8.1.2.4 Thermodynamic Properties of Lithium Hydride

The heat capacity of solid lithium hydride at 293 K (20 °C) is  $C_p = 34.21 \text{ J mol}^{-1} \text{K}^{-1}$  or  $4.305 \text{ J g}^{-1} \text{K}^{-1}$  ( $8.177 \text{ cal mol}^{-1} \text{°C}^{-1}$  or  $c_p = 1.029 \text{ cal g}^{-1} \text{°C}^{-1}$ ). The heat capacity of solid



and liquid lithium hydride as a function of temperature can be calculated from the Shomate equation

$$C_p^\circ = A + B\tau + C\tau^2 + D\tau^3 + E/\tau^2$$

where  $C_p$  is the heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$ , A, B, C, D, and E are constants and  $\tau$  is the absolute temperature in kelvin divided by 1000. The constants A through E for two phase states are listed in Table 13.

**Table 13:** Coefficients for heat capacity of lithium hydride.

| State                | Solid     | Liquid     |
|----------------------|-----------|------------|
| Temperature range, K | 298–961.8 | 961.8–2000 |
| A                    | 15.45842  | 62.34202   |
| B                    | 52.93220  | 0.00       |
| C                    | −0.099970 | 0.00       |
| D                    | 0.029244  | 0.00       |
| E                    | −0.291667 | 0.00       |

Data source: [10]

The specific heat of LiH between 3.7 and 295 K and entropy and enthalpy at 298 K were obtained from calorimetric measurements [228, 229]. The heat capacities of polycrystalline LiH and LiD were measured by differential scanning calorimeter in the temperature range from 125 to 800 K [230]. The smoothed values of heat capacities were used to calculate various thermodynamic functions for LiH and LiD from 0 to 800 K. The isotopic effect on heat capacity of LiH and LiD was predominant at higher temperatures (> 80 K), whereas below 80 K the isotopic effect was negligible. See also [231].

### 8.1.3 Chemical Properties of Lithium Hydride

#### 8.1.3.1 Hydrolysis of Lithium Hydride

Lithium hydride is resistant to oxygen in dry air, but in moist air it will gradually degrade and turn into useless lithium oxide and lithium hydroxide. While hydrolysis of lithium hydride is very undesirable where it is used as a rocket fuel, this reaction is important where lithium hydride/water reactions are used as a source of hydrogen. The reaction of lithium hydride with sea water can be used to expel ballast water from deep ocean probes and create buoyancy to bring the probe back to the surface [232]. Lithium hydride reacts with water very vigorously developing hydrogen gas. This reaction is a potential hydrogen source for fuel cell applications, although it is not easily reversible. The kinetics of hydrolysis of lithium hydride have been investigated mostly for its use as a source of hydrogen, but the information listed here will now help in assessing potential damage to lithium hydride-containing rocket propellants during

storage in ambient air. The effect of carbon dioxide in ambient air also needs to be considered.

Reactions and reaction products that are formed during reactions of LiH with H<sub>2</sub>O and the reaction kinetics involved were categorized as reactions in low and higher concentration regimes as well as reactions between LiH hydrolysis products [233]. Both LiH and H<sub>2</sub>O can contain various impurities, all of which may affect products and kinetics.

Polycrystalline LiH was reacted with decarbonated H<sub>2</sub>O to determine reaction products, rates, mechanisms, and the effects of experimental parameters [234]. X-ray analyses showed that product oxygen species growth rates had an initial steep rise and then increased linearly with H<sub>2</sub>O exposure time. Increasing H<sub>2</sub>O concentrations increased O growth rate while both increasing temperature and pressure decreased O growth rates. A thin-layer, diffusion-controlled reaction rate was suggested to explain the results, and a growth process for LiOH was illustrated. Micrographs of polycrystalline LiH sections showed a two-phase bulk material and a surface hydrolysis layer with cracks.

The corrosion kinetics of commercial LiH powder (~100 μm, Alfa Aesar) by water vapor in a humidified nitrogen stream was found to be constant in time and first order in gas phase water (<1% relative humidity, RH) [235]. Data obtained using a customized microbalance system equipped with a precision water saturator, dew point analyzer and magnetic sectoring mass spectrometer were used to derive a rough empirical rate expression for the corrosion of the powder by water at low (0.1–0.9%) RH values. These data were consistent with two models: **(1)** a three-layer model and **(2)** rate control by diffusion through a barrier layer.

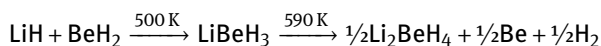
Hydrolysis of LiH at room temperature and under low RH conditions (RH < 2%) was studied by manometry working with heavy water either in closed (variable water vapor pressure) or open (constant water vapor pressure) systems [236]. Products of the reaction were characterized by XRD and FTIR. It was shown that the hydrolysis reaction occurs in two steps: first water is adsorbed onto the LiH surface and then the hydrolysis reaction starts. In an open system, for relative humidity lower than 0.04% only the formation of Li<sub>2</sub>O was observed while for higher moisture the reaction continued with the production of LiOD. The reaction rate was extremely slow and only a very small amount of LiH was transformed. The kinetics depend on diffusion through the layer of Li<sub>2</sub>O and/or LiOD surrounding the LiH particles. For practical application, it was concluded that if LiH is stored under controlled humidity lower than 0.04% (40 ppm) there is no major risk to form LiOH in significant amounts.

A mechanism describing the hydrolysis of lithium hydride under moist atmosphere involved the formation of lithium oxide (Li<sub>2</sub>O) at low vapor pressure and both Li<sub>2</sub>O and LiOH at higher vapor pressures, with diffusion of water in these layers [237]. A numerical model based on this mechanism was implemented to simulate the hydrolysis of LiH particles in an open system (constant water vapor pressure).

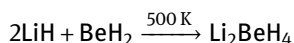
Kinetic parameters in the model such as rate constants of reactions and diffusion coefficients of water in Li<sub>2</sub>O and LiOH were fitted against experimental data. The best agreements were obtained when the diffusion coefficient of water was 10 times higher in LiOH than in Li<sub>2</sub>O. The resulting model accurately predicted the hydrolysis rates experimentally measured for a wide range of water vapor pressures (0.3–17 Pa). The thickness of the Li<sub>2</sub>O layer did not depend much on the water vapor pressure whereas that of LiOH increased drastically at high water vapor pressures.

### 8.1.3.2 Reactions of Lithium Hydride with Other Hydrides

Using simultaneous DTA and TGA and powder XRD, it was determined that the reactions of equimolar amounts of lithium hydride and beryllium hydride follow the pathway



and for reaction mixtures containing  $\geq 66.6$  mol-% LiH or more it follows:



LiBeH<sub>3</sub> melted at 430 K. Li<sub>2</sub>BeH<sub>4</sub> had two thermal transitions at 550 and 660 K; the first may be intramolecular rearrangement and the second may be fusion. The two products were indistinguishable by powder XRD [238, 239].

### 8.1.3.3 Decomposition of Lithium Hydride

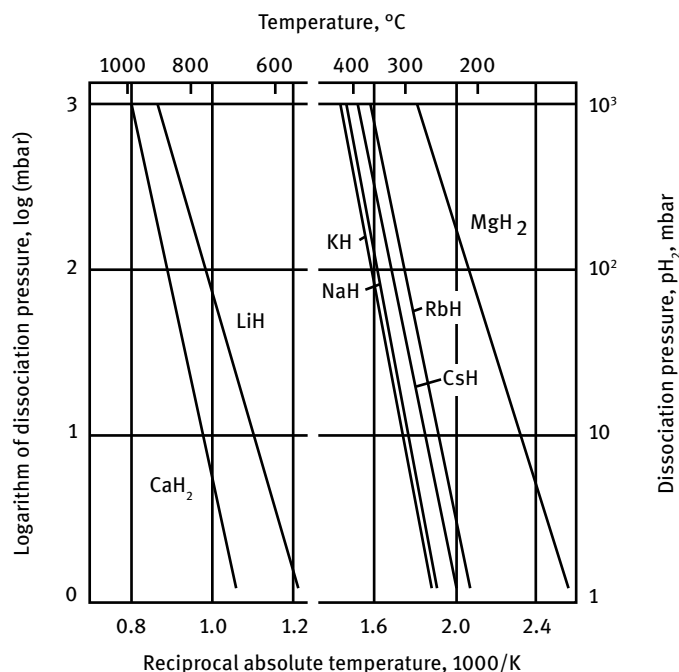
All metal hydrides dissociate into the elements at higher temperatures. The dissociation pressures of lithium hydride and other alkali metal hydrides and some alkaline earth metal hydrides are illustrated in Figure 2. Lithium hydride decomposes at  $> 970\text{ K} = > 700^\circ\text{C}$ . Lithium hydride is the second most stable hydride among the group of hydrides shown. Lithium hydride is the only metal hydride known to dissociate reversibly at pressures less than one atmosphere.

The equilibrium dissociation pressures and thermodynamic properties of lithium hydride and lithium deuteride have been determined from 723 to 1023 K (450 to 750 °C) [240]. The dissociation pressure as a function of temperature followed the equation

$$\log_{10} P = B - A/T$$

where  $P$  is the pressure in Pa and  $T$  is the temperature in kelvin. The constants  $A$  and  $B$  differed for solid and molten LiH: solid  $A = 10355 \pm 18$ ,  $B = 14.243 \pm 0.022$ ; liquid  $A = 7675 \pm 30$ ,  $B = 11.456 \pm 0.031$ . The latent heat of fusion was  $25.65 \pm 0.50\text{ kJ/mol}$ . The melting point was 961.8 K. Similar data were obtained for lithium deuteride. See also [241, 242].

The endothermic decomposition of lithium hydride was evaluated as an internal coolant for reentry bodies subjected to intense aerodynamic heating on entering the atmosphere [243, 244]. The dissociation of lithium hydride absorbs 0.75 times as much heat as the vaporization of an equal weight of lithium metal, four times as much as



**Figure 2:** Dissociation pressures of alkali metal hydrides and alkaline earth metal hydrides (republished and modified from [208], with permission of ©2016 John Wiley & Sons; permission conveyed through RightsLink)

sodium metal, and 6.9 times as much as water at a pressure of one atmosphere. The instability temperature  $T_e$  of lithium hydride was found to lie above the observed melting point, in accordance with computer simulation results [245].

#### 8.1.3.4 Photolysis of Lithium Hydride

When clean (colorless) lithium hydride is exposed to intense daylight at room temperature, it can be observed to slowly change in color from white to rose, brown, and finally to gray-blue. Ultraviolet light produces the blue color more rapidly. The coloration lasts indefinitely at room temperature but disappears on heating to 343 K (70 °C). Ionic radiation bombardment at room temperature also produced the blue color (F centers).

#### 8.1.4 Lithium Hydride Fuel Grains

Lithium hydride has been evaluated as a fuel for hybrid rocket engines, in particular with fluorine as the oxidizer [246]. There are at least three different methods to convert LiH powder to solid fuel grains: melt-casting, pressing, and bonding with organic polymers. Lithium hydride can be melted and cast into cylindrical shapes only under

a protective atmosphere of hydrogen, because otherwise it would decompose into the elements [247].

Lithium powder can be pressed into grains with low void content in a die in a hydraulic press without pelletizing aids [215]. The density of grains pressed at very high pressures approached that of single crystals.

### 8.1.5 Applications of Lithium Hydride

Lithium hydride has been proposed as a rocket propellant fuel, as fuel for fusion reactors, as neutron-absorbing radiation shield for nuclear reactors, and as endothermic heat sink for reentry vehicles. Lithium hydride is used in the synthesis of many other metal hydrides, some of which can be used as rocket propellants.

Encapsulated lithium hydride was evaluated as a phase change material for solar-thermal power plants in satellites to maintain operations while in the shade of Earth and as a peak heat load absorbent for pulsed power plants in directed energy beam space weapons, allowing for the design of smaller radiators. The containment of molten lithium hydride at high temperatures and high pressures requires special precautions due to the corrosiveness of the melt and permeation of hydrogen through metals [247].

## 8.2 Sodium Hydride

Sodium hydride, NaH, CAS RN [7646-69-7], has rarely been used as rocket propellant. Its main application is in the synthesis of other hydrides. Its standard enthalpy of formation is  $-56.44$  kJ/mol.

Sodium hydride is usually sold as a dispersion in inert hydrocarbons (kerosene) which may contain up to 25% NaH. The sodium hydride has a higher density than the hydrocarbon and will settle when allowed to stand in a quiet place. Sodium hydride suspensions in kerosene are hypergolic with white fuming nitric acid (WFNA) or red fuming nitric acid (RFNA). Only very small concentrations of NaH are required to hypergolize this very economical combination.

## 9 Alkaline Earth Metal Hydrides

The crystal structures of the alkaline-earth metal hydrides are of the  $\text{PbCl}_2$  type, and only  $\text{MgH}_2$  has the rutile ( $\text{TiO}_2$ ) crystal structure.

## 9.1 Beryllium Hydride

Beryllium hydride, beryllium dihydride,  $\text{BeH}_2$ , CAS RN [7787-52-2], has received a significant amount of attention as a potential rocket propellant. Much of the early work in the US in the 1960s and 1970s was classified confidential. Much of it remains under a limited distribution status, although most of it is obsolete and of less strategic value by now. During the time when much of the beryllium hydride work was classified, beryllium hydride was often referred to under its code name, Light Metal Hydride 2, LMH-2. The number of publications on beryllium hydride climaxed in the 1960s and then dropped off sharply as the interest in  $\text{BeH}_2$  waned. Beryllium hydride is a colorless, amorphous solid that is insoluble in solvents that do not decompose it. See also [248, 249].

### 9.1.1 Preparation of Beryllium Hydride

Different manufacturing methods were sought for light metal hydrides that would provide a solvate-free, high-density product. Much of the early work on beryllium hydride in the mid-1960s was performed by Ethyl Corp. [250]. This resulted in a method for preparing beryllium hydride in high purity (better than 90 mass-%) and in a method for converting the amorphous product to a crystalline high-density form.

#### 9.1.1.1 Preparation of Beryllium Hydride from the Elements

While lithium hydride with an enthalpy of formation of  $-90 \text{ kJ/mol}$  can be directly formed from the elements under pressure, the formation of beryllium hydride with an enthalpy of formation of  $-19 \text{ kJ/mol}$  from the elements is much less likely. The first synthesis of  $\text{BeH}_2$  directly from the elements was reported in 1933 by Pietsch et al. [251], but later questioned on closer examination.

The direct synthesis of beryllium hydride from the elements was attempted, but in vain, in equipment designed to grind beryllium metal powder while subjected to heat and hydrogen pressure [252]. The ability of the equipment to grind metals satisfactorily was demonstrated in test runs, in which magnesium hydride was synthesized from the elements; however, beryllium hydride was not prepared by this method, even when catalytic additives were used. There were no indications even of partial hydriding.

#### 9.1.1.2 Preparation of Beryllium Hydride by Hydride Substitution

Subsequent  $\text{BeH}_2$  syntheses were not directly from the elements, but by reduction of dimethylberyllium with lithium aluminum hydride (lithium alanate)  $\text{LiAlH}_4$  in ether [253, 254]. Another method was the reduction of beryllium chloride  $\text{BeCl}_2$  with lithium hydride, which led to a mixture of  $\text{BeH}_2$ ,  $\text{LiH}$ , and  $\text{LiCl}$  [255], but there are serious doubts about the purity of the first preparations of this compound. Later authors [256] had difficulties repeating the synthesis methods reported by the early investigators. It appears that most of the early preparations contained varying amounts of ether as

an adduct which was difficult to remove. Some  $\text{BeH}_2$  products decomposed at the attempt to remove the ether. The reaction between  $\text{LiAlH}_4$  and  $\text{Be}(\text{CH}_3)_2$  in  $\text{Et}_2\text{O}$  gives a product with ~60 mass-%  $\text{BeH}_2$ .

There are a number of patents covering various methods for preparation of beryllium hydride, but not all of them deliver what they promise. Processes patented include preparing beryllium hydride by the direct reaction of beryllium borohydride and aluminum hydride trimethylamine adduct [257]; reacting anhydrous beryllium chloride with sodium triethyl borohydride [258]; reacting a tetraalkyldiborane of the general formula  $\text{R}_2\text{BH}_2\text{BR}_2$  with a dialkyl beryllium compound of the general formula  $\text{R}_2\text{Be}$  [259]; reacting dialkyl aluminum hydride/trialkyl aluminum with beryllium halides or beryllium alkoxides [260]; reaction of beryllium borohydride etherate with triphenylphosphine, followed by extraction with benzene [261]; reduction of beryllium alkyls with hydrogen under pressure (2000–10000 psi) [262]. Looking at the time elapsed between filing date and publishing date, it appears that many of these patents were under a secrecy order for several years and they were only published in 1973–1975 after some of the restrictions were relaxed.

#### 9.1.1.3 Preparation of Beryllium Hydride by Pyrolysis of Alkylberyllium Compounds

Properties of alkylberyllium compounds are described in *Encyclopedia of Liquid Fuels*, chapter “Organometallic Compounds.” Alkylberyllium compounds are of interest as intermediates in the production of beryllium hydride. Beryllium hydride obtained by pyrolysis of di-*tert*-butylberyllium was more stable [263, 264]. Di-*tert*-butylberyllium decomposed rapidly above 373 K to give mainly beryllium hydride and isobutene. This process has been used for a long time to make amorphous beryllium hydride, which has a relatively low density. Diisopropylberyllium and diethylberyllium have dimer structures and the boiling points are relatively high (553 and 467 K = 280 and 194 °C) for a single metal alkyl molecule. Diisopropylberyllium is thermally more stable than di-*tert*-butylberyllium.

Beryllium hydride can be prepared by the pyrolysis of both pure di-*tert*-butylberyllium and its etherate [265]. Pure di-*tert*-butylberyllium is a clear, colorless, mobile liquid with a density of 0.65 g/cm<sup>3</sup> and a freezing point of 257 K (–16 °C). When freshly prepared, it had a vapor pressure of about 4.7 kPa at 298 K (35 mm Hg at 25 °C). On standing it undergoes slow decomposition at room temperature with the evolution of isobutene. Beryllium hydride prepared by pyrolysis of di-*tert*-butylberyllium had a density of about 0.57 g/cm<sup>3</sup>, evolved hydrogen slowly at 463–473 K (190–200 °C) and rapidly at 493 K (220 °C), was relatively inert to laboratory air, and reacted slowly with water but rapidly with acid. It decomposed only above 523 K (250 °C).

The “Beane” material that was supplied during the early 1960s for propellant evaluation was essentially an amorphous form of undetermined structure with a maximum density of about 0.67 g/cm<sup>3</sup>. In addition to the amorphous form, at least three crystalline polymorphs of beryllium hydride had been identified. The crystal structures of two polymorphs had been determined, one of which had a theoretical

density of  $0.82 \text{ g/cm}^3$ . Crystal structure and theoretical density of the third polymorph were uncertain.

Crystalline as opposed to amorphous beryllium hydride was occasionally encountered in samples prepared by metathetical reduction reactions rather than pyrolysis of beryllium alkyls; however, the degree of crystallinity obtained was quite variable with little or no apparent correlation with processing variables.

Beryllium hydride can be produced in purities of 90–98 mass-% by the controlled pyrolysis of di-*tert*-butylberyllium etherate in hot oil [266]. It was obtained as an amorphous solid, remarkably stable at elevated temperatures and resistant to attack by water and common organic solvents. The source of residual impurities was shown by deuterium labeling to be derived largely from incomplete pyrolysis and ether cleavage. A series of alternate alkylberyllium homologs was subjected to the pyrolysis reaction. Of these di-*tert*-butylberyllium etherate gave the highest purity  $\text{BeH}_2$ . The preparation of crystalline beryllium hydride (average density  $0.78\text{--}0.80 \text{ g/cm}^3$ ) requires the incorporation of lithium hydride and crystallization at elevated temperature and pressure. In practice, instead of adding lithium hydride later, *n*-butyllithium is added to the beryllium alkyl and the resultant solution pyrolyzed to a mixture of amorphous beryllium hydride containing 1.5–2 mass-% lithium hydride.

Studies of the  $\text{Be}(\text{BH}_4)_2/\text{AlR}_3$  reaction system led to the discovery of new forms of beryllium hydride, the borane-terminated beryllium hydrides,  $(\text{BeH}_2)_x(\text{BH}_3)_2$  [267]. These materials had good physical and chemical stability and were essentially equivalent to pure  $\text{BeH}_2$  in theoretical rocket propellant performance. They were, like  $\text{BeH}_2$ , amorphous and of low density, and studies aimed at inducing  $(\text{BeH}_2)_x(\text{BH}_3)_2$  crystallization met with very limited success. Beane (Ethyl Corporation  $\text{BeH}_2$ ) was shown to dissolve smoothly in  $\text{Al}(\text{CH}_3)_3$ , forming a liquid complex; however,  $\text{Al}(\text{CH}_3)_3$  was known to form strong bonds with  $\text{BeH}_2$ , and no attempt was made to recover  $\text{BeH}_2$  from the dissolved complex. During pressure studies of Beane crystallization at pressures up to 150 kilobars (2.2 million psi) it was found that the most important factors in crystallization were the time for which samples were held at given pressure-temperature (*P-T*) conditions, and the rate at which they were quenched back to ambient conditions.

There are a number of patents covering various methods for preparation of beryllium hydride, but not all of them deliver what they promise. Patented processes include pyrolysis of di-*t*-alkyl beryllium etherate at 373–473 K (100–200 °C) [268]; pyrolysis of di-*t*-butyl beryllium etherate with agitation [269]; low-pressure pyrolysis of dialkylberyllium compounds in absence of a solvent [270].

#### 9.1.1.4 Preparation of Beryllium Hydride by Disproportionation

Direct synthesis of dense  $\text{BeH}_2$  was attempted by thermal and chemical dissociation of complexes of  $\text{BeH}_2$  with alkyl derivatives of boron or aluminum [271]. Although  $\text{BeH}_2$  was produced in purities of 93 mass-%, only the low density, amorphous form was obtained. Neutral tertiary amine complexes of  $\text{BeH}_2$  were prepared by heating



pyrolytic BeH<sub>2</sub> with amines. Alkyl, cyclic and aromatic monoamines and diamines of suitable base strength and steric requirements formed Lewis adduct complexes in high yield. The monoamine adducts were white, crystalline solids, soluble in aromatic hydrocarbons and amines. They exist as dimeric species in solution. The diamine complexes were polymeric and were insoluble in aromatic solvents and amines. The weak BeH<sub>2</sub>•amine complexes can be thermally dissociated to high purity BeH<sub>2</sub>, though not crystalline but only amorphous BeH<sub>2</sub>. They represent attractive intermediates in the direct crystallization of BeH<sub>2</sub>. The trimethylamine adduct of BeH<sub>2</sub> was prepared by dissociation of Be(Et<sub>3</sub>AlH)<sub>2</sub> with trimethylamine. The preparation of the intermediate Be(Et<sub>3</sub>AlH)<sub>2</sub> was accomplished in high yield.

Beryllium chloride hydride ClBeH and its etherate which were tested as precursors for the synthesis of BeH<sub>2</sub> can be made in 95% yield from beryllium chloride-etherate and sodium hydride. Disproportionation of the ClBeH intermediate was demonstrated to give beryllium hydride in purities up to 85 mass-% BeH<sub>2</sub> [272]. The disproportionation was retarded in ether as the solvent. A solvent was sought to extract BeCl<sub>2</sub> from the reaction mixture. Although BeCl<sub>2</sub> etherate was extracted by benzene, some Be—Cl bonds retained in the solid. This indicated that some residual Be—Cl bonds were either physically occluded in the solid or chemically bound in the structure. The product was amorphous with residual Be—Cl bonds, retained ether, and Be—O bonds as the major contaminants. The atomic ratio of active hydride to residual chloride in some samples of the final product reached up to 137:1, corresponding to an impurity content of 5 mass-% BeCl<sub>2</sub>. Disproportionation of beryllium chloride hydride under vacuum gave beryllium hydride with purities of up to 88 mass-% and, conversions of up to 87% based on initial ClBeH amount [273]. Lithium aluminum hydride treatment of the final product reduced chloride and ether contaminants to tolerable levels.

#### 9.1.1.5 Crystallization of Beryllium Hydride

Amorphous beryllium hydride has a low density and has widely varying properties. There are only few solvents that would dissolve beryllium hydride and allow it to be recrystallized in a higher density modification. Most solvents will tenaciously adhere as solvates to the recrystallized product.

The crystallization of BeH<sub>2</sub> via compaction-fusion of amorphous pyrolytic material (Beane product) with various metal fluorides as co-additives with lithium hydride, drastically reduced the pressure required to crystallize Beane product in short times [274]. At 2–3 mass-% concentration of the metal fluoride, the pressure requirement was reduced by about 50%. Crystalline BeH<sub>2</sub> used as seed crystals in large concentrations was effective for crystallizing Li-doped BeH<sub>2</sub> at room temperature under high pressure; however, the effectiveness became progressively less with repeated cycling. Be metal, formed *in situ* also was an active crystallization catalyst at lower pressures. Gross crystallization was obtained without use of an extended temperature quench. Attempts to crystallize beryllium hydride via dissociation of tertiary amine complexes

were unsuccessful. The triethylamine and *N*-methylmorpholine complexes of  $\text{BeH}_2$  were successfully prepared for the first time.

Attempts to prepare dense, crystalline beryllium hydride,  $\text{BeH}_2$ , at near atmospheric pressure were largely unsuccessful. Vapor pyrolysis of ether-free di-*tert*-butylberyllium produced  $\text{BeH}_2$  with purities as high as 98 mass-% and without any residual alkyl groups; however, all products were amorphous and of low density. The density of the clear glassy deposit obtained by vapor deposition and growth on the walls of the pyrolysis vessel was  $0.70 \text{ g/cm}^3$ . Attempts to deposit crystalline  $\text{BeH}_2$  by growth from the vapor on various crystalline substrates produced only amorphous material. Solution pyrolysis of dioctylberyllium and dihexylberyllium produced impure, amorphous  $\text{BeH}_2$ . The best product was obtained using dihexylberyllium; however, product purity was only 60–85 mol-%. Thermal dissociation of the  $\text{BeH}_2$  triethylamine complex from a toluene solution in the presence of a seed bed of crystalline  $\text{BeH}_2$  indicated that a small amount of crystalline deposit was formed. The quantity of deposit obtained was too small to obtain unequivocal proof for the feasibility of this method, even though the disassociation was continued for as long as 104 h. Long-term digestion of lithium-doped amorphous  $\text{BeH}_2$  in the presence of such Lewis bases as amines and ethers containing crystalline  $\text{BeH}_2$  as seed also gave inconclusive evidence that partial crystallization was obtained. Extended grinding of mixtures of amorphous and crystalline  $\text{BeH}_2$  in the presence of an inert solvent caused reversion of crystalline material to the amorphous form.

There have been numerous efforts to improve the beryllium hydride products by recrystallizing the amorphous product under pressure or using synthesis routes other than the pyrolysis of di-*tert*-butylberyllium [275–278]. In trying to densify  $\text{BeH}_2$  by crystallization in a suitable solvent, commercially available raw beryllium hydride (an Ethyl Corporation  $\text{BeH}_2$  product called “Beane”) was shown to dissolve smoothly in  $\text{Al}(\text{CH}_3)_3$ , forming a liquid complex; however,  $\text{Al}(\text{CH}_3)_3$  forms strong bonds with  $\text{BeH}_2$ , and no attempt was made to recover pure  $\text{BeH}_2$  from the complex [267]. Pressure studies of Beane crystallization up to 15 GPa (150 kilobars = 2.2 million psi) were carried out, and unadulterated Beane was crystallized for the first time. The most important factors in crystallization proved to be the duration of time for which samples were held at given *P-T* conditions, and the rate at which they were quenched back to ambient conditions. Lithium-doped  $\text{BeH}_2$  was crystallized using a hydrothermal pressure apparatus and this process was planned to be scaled up.

The amorphous  $\text{BeH}_2$  product can be converted to crystalline  $\text{BeH}_2$  by compaction-fusion at an ultrahigh pressure of 1.38 GPa (200000 psi) and 473 K (200 °C). These methods are uneconomical and time-consuming and thus impractical for large-scale production of crystalline  $\text{BeH}_2$ . A sustained effort was directed at the densification of LMH-2 by crystallization under high pressure [279, 280].

The study of  $\text{BeH}_2$  crystallization process parameters has provided a partial phase diagram for the *P-T* regime of 393–523 K (120–250 °C) and 275–965 MPa (40–140 kpsi)

[281]. It showed that both the product density and distribution of crystalline polymorphs are simple functions of the applied pressure and temperature. Hydrostatic compaction time does not appear to be a critical variable. A pressure of at least 275 MPa (40 kpsi) (at about 473 K = 200 °C) and temperature of at least 403 K (130 °C) (with pressures above 620 MPa = 90 kpsi) appear necessary for crystallization. Other reports stated that temperatures of at least 393–408 K (120–135 °C) and pressures greater than 275 MPa (40 kpsi) are required for crystallization. The more thermally stable phase evidently has a higher density (0.77–0.78 g/cm<sup>3</sup>) than the other phase (0.73–0.74 g/cm<sup>3</sup>). A high-density phase is formed preferentially at higher pressures, requiring about 758–827 MPa (110–120 kpsi) for production in its pure form. Small changes in the concentration of the Li dopant or Be metal content did not noticeably affect crystallization or polymorph distribution. Undoped BeH<sub>2</sub> was not crystallized under conditions of 965 MPa (140 kpsi) at 478 K (205 °C) even after 4 h; however, the density was increased to 0.70 g/cm<sup>3</sup>. Encapsulation of BeH<sub>2</sub> appears necessary for successful crystallization by hydrostatic compaction. Various types of metal thimbles and closures were tested as capsules for pre-compaction and crystallization steps.

An effective, practical technique was found for pre-compacting and encapsulating Li-doped BeH<sub>2</sub> prior to crystallization by hydrostatic compaction at elevated temperature [282]. The technique employed seamless aluminum capsules fitted with solid metal plug closures and sealed with Viton O-rings. The powdered feed was pre-compacted within the capsules by use of a piston-mold unit in a platen press. The finely divided BeH<sub>2</sub> feed is easily pre-compacted within the capsule by means of a piston-mold unit operated at the moderate pressure of 48 MPa (7000 psi). The technique was successfully tested in a series of 30 crystallization experiments. No significant change in optimum crystallization conditions or polymorph distribution was observed with this new technique. The feasibility of a ‘slurry’ process for crystallization of BeH<sub>2</sub> by hydrostatic compaction was also demonstrated. Hydrocarbon-wet Li-doped BeH<sub>2</sub> was completely crystallized at temperatures ranging from 478 to 503 K (205–230 °C) and pressures of 482–965 MPa (70–140 kpsi). Two process alternatives, namely dry encapsulation and slurry processes were tested successfully [283]. Temperature quench rate had no effect on extent of crystallization or preferred polymorph. With the slurry process, hydrocarbon-wet BeH<sub>2</sub> was crystallized at pressures of 482–965 MPa (70–140 kpsi) and 478–503 K (205–230 °C); however, concentrations of high-density phase in the product were much lower than those obtained by the dry process under similar operating conditions.

### 9.1.2 Physical Properties of Beryllium Hydride

The physical properties of beryllium hydride (Table 14) are not as clear-cut as the properties of many other rocket propellants. First, the reported properties were for impure preparations, which often contained solvated ether molecules. Then, as much of the research was for military purposes, the results were shrouded for a long time by se-

crecy restrictions. The exact composition and properties of the synthesis products depended on the method of preparation. Beryllium hydride has a melting point of 523 K (250 °C) with decomposition. See also [284].

**Table 14:** Physical properties of beryllium hydride.

|                              | SI Units                                            | Other Units                | References |
|------------------------------|-----------------------------------------------------|----------------------------|------------|
| Molecular mass               | 11.02806 g/mol                                      | 90.678 mol/kg              | [10]       |
| Density, at 173 K            | $0.57 \pm 0.02$ g/cm <sup>3</sup> , amorphous       | —                          | [265]      |
| Density, at 298 K            | $0.77\text{--}0.78$ g/cm <sup>3</sup> , crystalline | —                          | [285]      |
|                              | 0.70 g/cm <sup>3</sup>                              | 0.0242 lb/in. <sup>3</sup> | [286]      |
| Enthalpy of formation, solid | $-4.1 \pm 20.9$ kJ/mol                              | $-1 \pm 5$ kcal/mol        | [287]      |
|                              | -19.3 kJ/mol                                        | -4.6 kcal/mol              | [208]      |
|                              | -20.9 kJ/mol                                        | -5.0 kcal/mol              | [288]      |
|                              | -18.4 kJ/mol                                        | -399 cal/g                 | [286]      |
|                              |                                                     | = -4.4 kcal/mol            |            |
|                              | -20.9 kJ/mol                                        | -5.0 kcal/mol              | [289]      |
| Enthalpy of formation, vapor | +125.52 kJ/mol                                      | +30 kcal/mol               | [10]       |

### 9.1.2.1 Molecular Structure of Beryllium Hydride

Unlike the ionically bonded hydrides of the heavier Group 2 elements, beryllium hydride is covalently bonded (two or more beryllium atoms linked by three-center two-electron hydrogen bonds). The synthesis of LMH-2 has been plagued by the low density of the product. In an effort to determine the theoretical density of LMH-2, attempts have been made to index X-ray powder photographs of the material. These attempts have been frustrated by low symmetry and lack of purity of phase and composition. Microscopic studies of reported polymorphic transitions were investigated and found to be inconclusive [290]. An early powder diffraction pattern of BeH<sub>2</sub> has been shown to be indexed incorrectly. A radial distribution analysis of the glassy phase of LMH-2 was carried out using XRD methods. The results of the analysis confirmed the theoretical tetrahedral four-fold coordination proposed for the cation.

Beryllium hydride is usually formed as an amorphous white solid, but a hexagonal crystalline form with a higher density was reported, prepared by heating amorphous BeH<sub>2</sub> under pressure. Crystalline BeH<sub>2</sub> was prepared by high-pressure compaction-fusion of amorphous BeH<sub>2</sub> catalyzed by 0.9–2.5 mol % lithium [285], added in the form of lithium hydride or lithium aluminum hydride [291, 292]. Pressures of at least 2.75 kbar (at 473 K = 200 °C) as well as temperatures exceeding 403 K = 130 °C (at 6.2 kbar) were required for the transformation. This was accompanied by an increase in density from  $0.62\text{--}0.65$  g/cm<sup>3</sup> for amorphous BeH<sub>2</sub> to  $0.77\text{--}0.78$  g/cm<sup>3</sup>. Two separate crystalline phases were identified. XRD patterns of the phase were indexed for a hexagonal unit cell with dimensions  $a = 4.20$  Å and  $c = 6.76$  Å with a theoretical XRD density of  $0.82$  g/cm<sup>3</sup>. Because the identification of various amorphous or

polymorphic forms of BeH<sub>2</sub> was not always standardized and uniform among the scientific community, early versions of crystalline BeH<sub>2</sub> were sometimes identified by the two strongest lines in the XRD diffraction pattern instead of Greek letters. For instance, the crystalline hexagonal form phase 338–208 reverted to amorphous BeH<sub>2</sub> after heating to 433 K (160 °C) for several hours.

The crystal and molecular structure of BeH<sub>2</sub> has been determined from high-resolution powder diffraction data obtained at a synchrotron radiation source [293]. The unit cell parameters of the body-centered orthorhombic crystals were  $a = 9.082(4)$  Å,  $b = 4.160(2)$  Å,  $c = 7.707(3)$  Å,  $V = 291.2$  Å<sup>3</sup>, corresponding to space groups, *Ibam* or *Iba2*. The crystal structure is based on a network of corner-sharing BeH<sub>4</sub> tetrahedra rather than flat infinite chains containing hydrogen bridges as previously assumed. The Be–H bond distances were 1.38(2) Å around Be(1) and 1.41(2) Å around Be(2). The H–Be–H tetrahedral bond angles ranged from 107 to 113° and the <Be–H–Be bond angle was approximately 128°. The space group is *Ibam*, and there are 12 BeH<sub>2</sub> molecules in the unit cell. The XRD theoretical density was 0.755 g/cm<sup>3</sup>.

The lattice dynamics of crystalline BeH<sub>2</sub> were studied using a Born-von Karman model [294]. The zone-center frequencies, isotopic shifts and the phonon density of states were calculated. The symmetries of the zone-center modes were determined and the types of ion oscillations were identified.

Crystalline beryllium hydride may undergo an irreversible thermally induced solid-state phase change, with the product being amorphous or glassy beryllium hydride [295]. The phase change was observed using simultaneous DTA/TGA and XRD. The phase change took place at 485–550 K, just below the thermal decomposition temperature of 570 K. There was slight decomposition of the beryllium hydride during the phase change of about  $5 \pm 2\%$ . The enthalpy change associated with the phase transition was  $2.3 \pm 0.7$  kJ/mol.

The crystal structure, mechanical properties and electronic structure of ground state BeH<sub>2</sub> were calculated employing the first-principles methods based on density functional theory [296]. The calculated structural parameters at equilibrium volume were consistent with experimental results. The bulk modulus *B*, shear modulus *G*, Young's modulus *E* and Poisson's ratio  $\nu$  were deduced from the elastic constants. The bonding nature in BeH<sub>2</sub> was fully interpreted by combining characteristics in band structure, density of states, and charge distribution. The ionicity in the Be–H bond is mainly featured by charge transfer from Be 2s to H 1s atomic orbitals while its covalency is dominated by the hybridization of H 1s and Be 2p states. An analysis of BeH<sub>2</sub> described the ionic/covalent character quantitatively and it was found that about 1.6 electrons transfer from each Be atom to H atoms.

The theory of electronic and structural properties, ionization potential (IP), electron affinity (EA), polarizability ( $\alpha$ ), chemical potential ( $\mu$ ), hardness ( $\eta$ ), softness (*S*), band gap and spectral characteristics of beryllium hydride oligomers were analyzed by quantum chemical calculations [297]. The discrepancies in the calculated reactive descriptors of molecules were presumably due to variations in electron distribu-

tion and spin pairing near Fermi level. The molecules  $\text{BeH}_2$ ,  $\text{Be}_3\text{H}_5$ ,  $\text{Be}_5\text{H}_{10}$ ,  $\text{Be}_7\text{H}_{14}$ , and  $\text{Be}_9\text{H}_{18}$  were predicted to be more stable than  $\text{Be}_2\text{H}_4$ ,  $\text{Be}_4\text{H}_8$ ,  $\text{Be}_6\text{H}_{12}$ ,  $\text{Be}_8\text{H}_{16}$ , and  $\text{Be}_{10}\text{H}_{20}$ . Ultra-soft pseudopotentials for electron-nuclei interactions with local density approximation and generalized gradient approximation have been used to interpret the nature of bonding in crystalline beryllium hydride. The observed band gap value of crystalline  $\text{BeH}_2$  is comparable with the band gap value of beryllium hydride oligomers.

### 9.1.2.2 Optical Properties of Beryllium Hydride

Laser-ablated beryllium atoms react with  $\text{H}_2$  upon co-condensation in excess frozen hydrogen and neon to form  $\text{BeH}_2$  and  $(\text{BeH}_2)_2$ , which were identified through isotopic substitution as supported by DFT calculations [298]. Unreacted Be atoms isolated in solid neon or solid hydrogen are atoms in excited states and react further with  $\text{H}_2$  to enhance the  $\text{BeH}_2$  and  $(\text{BeH}_2)_2$  concentrations and produce  $(\text{BeH}_2)_n$  polymers.  $\text{BeH}_2$  molecules associate upon diffusion in solid hydrogen to form one-dimensional  $(\text{BeH}_2)_n$  polymers. The series of strong IR-active parallel Be—H—Be bridge-bond stretching modes observed for  $(\text{BeH}_2)_n$  polymers suggested one-dimensional structures, and this conclusion was supported by DFT calculations. The computed polymerization energy per  $\text{BeH}_2$  unit was about 138 kJ/mol (33 kcal/mol).

The vibrational density of states of amorphous beryllium hydride ( $\alpha\text{-BeH}_2$ ) and lithium beryllium hydrides were studied using inelastic neutron scattering, IR, and Raman spectroscopy [299]. The positions of the symmetrical (120–180 meV) and anti-symmetrical (200–260 meV) Be—H stretching modes and those of the H—Be—H bending mode (50–120 meV) were determined and the results were compared with theoretical calculations. The addition of lithium to the beryllium hydride network shifted the vibrational bands to lower energies, indicating a less rigid network.

### 9.1.3 Chemical Properties of Beryllium Hydride

Beryllium hydride is inert against oxygen in dry atmospheric air. It hydrolyzes in water only slowly at room temperature. Dilute mineral acids will destroy and dissolve it. Beryllium hydride is insoluble in all ordinary solvents. Beryllium hydride reacts with and dissolves in complexing solvents, such as tertiary amines,  $\text{AlR}_3$  or  $\text{BeR}_2$ . Raw beryllium hydride contains several percent of alkyl groups. Almost half the residual alkyl groups are ethyl groups. This indicates that ether cleavage is one of the more important sources of impurities in the product. Total oxygen content of typical Beane product, as determined by neutron activation analysis, averages about 1–3 mass-%. It is present as oxide, hydroxide, and alkoxide groups.

#### 9.1.3.1 Reactions of Beryllium Hydride

The crystalline form of  $\text{BeH}_2$  was slightly more reactive with protonic solvents than amorphous  $\text{BeH}_2$ . Passivation treatment was required for use with usual binders and

plasticizers. Part of this increased reactivity was due to the lithium hydride that was added as a crystallization aid.

#### 9.1.3.2 Reactions with Other Metal Hydrides

Lithium hydride and beryllium hydride powder have been mixed and heated. In the hydride reaction, 1 atom of hydrogen was released at 500–600 K and almost 2 atoms were released at 675 K. XRD showed the formation of  $\text{Li}_2\text{BeH}_4$  plus an unknown lithium-beryllium hydride at temperatures as low as 343 K [300]. The yield of these compounds decreased with increasing temperature and was as high as 60–100% at 350–400 K. Identical behavior was seen with crystalline and non-crystalline  $\text{BeH}_2$ . The  $\text{LiH-BeH}_2$  reaction is thought to create enough heat to temporarily melt the products. Released hydrogen gas or organic vapors then push the material into a foam at 440–470 K. The addition reactions with lithium hydride where the hydride ion is the Lewis base, form sequentially  $\text{LiBeH}_3$  and  $\text{Li}_2\text{BeH}_4$ .

#### 9.1.3.3 Hydrolysis of Beryllium Hydride

Beryllium hydride reacts slowly with water but is rapidly hydrolyzed by acids, such as hydrogen chloride to form beryllium chloride.

#### 9.1.3.4 Reactions of Beryllium Hydride with Lewis Bases

Beryllium hydride reacts with trimethylamine,  $\text{N}(\text{CH}_3)_3$  to form a dimeric adduct, with bridging hydrides [301]; however, with dimethylamine,  $\text{HN}(\text{CH}_3)_2$ , it forms a trimeric beryllium diamide,  $[\text{Be}(\text{N}(\text{CH}_3)_2)_2]_3$  and loses its hydride hydrogen. The addition reactions with lithium hydride where the hydride ion is the Lewis base, form sequentially two different compounds,  $\text{LiBeH}_3$  and  $\text{Li}_2\text{BeH}_4$ . Several tertiary amine complexes of beryllium hydride have been synthesized by three different preparative routes. In the first, trimethylamine allowed to react with the liquid adduct diethylberyllium-diethylaluminum hydride produced a crystalline beryllium complex. The other two procedures involved direct reaction between the amine and polymeric beryllium hydride either by (1) heating the mixture in a sealed system, or (2) ball-milling the reactants together. The complexes were characterized by chemical analysis, IR and NMR spectra, and XRD. These data, along with molecular weight determinations, indicated that the fundamental unit in every case is the hydrogen-bridged  $\text{BeH}_2$  dimer. Beryllium hydride reacts with ammonia or hydrazine under evolution of hydrogen but is stable when dispersed in UDMH.

#### 9.1.3.5 Thermal Decomposition of Beryllium Hydride

Both lithium hydride and beryllium hydride had been considered as materials for radiation shields (neutron shields) around nuclear reactors but the thermal stability of beryllium hydride was found to be insufficient for this task. An investigation of the thermal stability of  $\text{BeH}_2$  showed that after an induction period, the compound would decompose irreversibly.

The kinetics of decomposition and deflagration of a solid propellant containing beryllium hydride (LMH-2) was studied by flash pyrolysis combined with kinetic spectroscopy to determine the cause of low combustion efficiency [302]. The mechanism of deflagration and combustion of beryllium hydride above 2000 K showed the existence of BeH and  $\text{BeH}^+$ . In the temperature range 2200–2800 K, the species BeH appeared to be about three times as plentiful as the ion  $\text{BeH}^+$ . The  $\text{BeH}^+$  ion appears to be more stable at high temperatures than BeH, although it accounts for only a small fraction of the gaseous beryllium-containing decomposition product. The large amount of  $\text{BeH}^+$  found in the deflagration products of beryllium hydride may be responsible for the low combustion efficiency. Because of its low reactivity, this charged ion can pass through the combustion chamber and rocket nozzle without undergoing appreciable reaction with the  $\text{NH}_4\text{ClO}_4$  oxidizer or its decomposition products.

The flash-pyrolysis decomposition of  $\text{BeH}_2$  and  $\text{AlH}_3$  has been studied by kinetic spectroscopy at 2477 K. A combined flash heating-flash photolysis apparatus was used to study very fast reactions in the decomposition of metal hydrides. In this apparatus it was possible to study the chemistry of the gas-phase immediately above the flash-pyrolyzed solid. Additionally, the apparatus can be used for the more familiar technique of flash photolysis [303]. The first product seen in the flash pyrolysis of  $\text{BeH}_2$  was BeH. Within a few microseconds of the appearance, the BeH was seen to decrease in intensity. At 25  $\mu\text{s}$  after the photoflash the first bands of  $\text{BeH}^+$  were seen. From 60  $\mu\text{s}$  on, the  $\text{BeH}^+$  was the major beryllium-containing pyrolysis product. The flash-induced combustion of  $\text{BeH}_2$  in oxygen has been studied at 20 mm pressure of oxygen. The absorption spectra of OH, BeH,  $\text{BeH}^+$ , and BeO were observed, and the relative concentration of each was measured for 140  $\mu\text{s}$  following the initial photoflash. This was the basis of a proposed mechanism for the combustion of  $\text{BeH}_2$ .

#### 9.1.4 Applications of Beryllium Hydride in Rocket Propellants

During the 1960s, when much of the work on beryllium hydride was still classified “Confidential” or even “Secret,” this hydride was known under the code name “LMH-2” or the trade name “Beane.” Research grants adding up to several million dollars were issued to further the production and rocket propellant use of beryllium hydride, all driven by the desire to develop rocket propellants with higher specific impulse, but ultimately the concern about toxicity of the exhaust put an end to all that effort.

##### 9.1.4.1 Applications of Beryllium Hydride in Solid Rocket Propellants

Applications of beryllium hydride in solid propellants will be discussed in future volumes on solid propellants.



#### 9.1.4.2 Applications of Beryllium Hydride in Liquid Monopropellants

Generally metal hydrides like LiH or B<sub>2</sub>H<sub>6</sub> are quite sensitive to moisture but apparently one form of BeH<sub>2</sub> is not sensitive to moisture or H<sub>2</sub>O<sub>2</sub>. A metallized monopropellant has been patented consisting of 26 parts powdered BeH<sub>2</sub>, 5 parts 7–10 nm fumed silica as a gelling agent and 59 parts 98% H<sub>2</sub>O<sub>2</sub>, first mixed in a high-shear blender and later diluted with 59 parts of water and blended again to obtain a thixotropic gelled propellant with a specific impulse of 317 s [304]. Nothing was said about the storage stability of this propellant.

#### 9.1.4.3 Applications of Beryllium Hydride in Liquid Bipropellant Fuels

Beryllium hydride can be suspended in gelled liquid fuels and burned with a variety of liquid oxidizers. In some instances, beryllium hydride suspended in a non-hypergolic hydrocarbon or ether fuel may not only increase the specific impulse but may also make the combination hypergolic when previously it was not.

Beryllium hydride has been evaluated as an additive to both non-hypergolic and hypergolic fuels and the storage stability of BeH<sub>2</sub> in liquid carriers has been investigated. Long-term storage stability tests were made with slurries of beryllium hydride and organometallic liquid carriers at 305 K (90 °F) [305, 306]. Systems containing triethylaluminum, diethylaluminum hydride, diethylberyllium, and triethylborane at 23% ullage evolved gas at 0.6–0.006 cm<sup>3</sup> lb<sup>-1</sup> min<sup>-1</sup>. Systems containing trimethylaluminum and dimethylaluminum hydride produced gas at a rate of 8–19 cm<sup>3</sup> lb<sup>-1</sup> min<sup>-1</sup>. The complex Be(Et<sub>3</sub>AlH)<sub>2</sub> is completely stable but when slurried with beryllium hydride it developed gas at 0.00004 cm<sup>3</sup> lb<sup>-1</sup> min<sup>-1</sup>. The Be(Et<sub>2</sub>BH<sub>2</sub>)<sub>2</sub> complex either alone or mixed with beryllium hydride evolved hydrogen at a rate of about 0.00044 cm<sup>3</sup> lb<sup>-1</sup> min<sup>-1</sup>. The source of initial gassing was found to be gases (mostly nitrogen) adsorbed on the surface of the beryllium hydride. A vacuum bake at 403 K (130 °C) followed by treatment with helium largely eliminated initial gassing and improved the material handling properties.

The compatibility of pyrolytic beryllium hydride (Beane product) with various liquid organometallic compounds was evaluated by measuring the rate of pressure rise of slurries of beryllium hydride in these liquids in a closed system at 305 K (90 °F) [307]. Methyl and ethyl derivatives of beryllium, boron, and aluminum, and their complexes with beryllium hydride were tested for compatibility with beryllium hydride. All systems were characterized by an initial rapid pressure rise, followed by a levelling off until a constant rate of pressure increase was established. The initial large pressure rise has been attributed to desorption of gases (nitrogen) adsorbed on the beryllium hydride surface and can be minimized by baking the beryllium hydride *in vacuo* and storing it under helium. Of the liquids tested, the smallest pressure rise was obtained with diethylberyllium; however, the BeH<sub>2</sub>-Et<sub>2</sub>BeH slurry became completely solid during the course of the compatibility testing period. The standard heats of formation of the complexes, Be(Et<sub>3</sub>AlH)<sub>2</sub> and Be(Et<sub>2</sub>BH<sub>2</sub>)<sub>2</sub> were measured to be  $-282 \pm 43$  kJ/mol

( $-67.3 \pm 10.4$  kcal/mol) and  $-310 \pm 167$  kJ/mol ( $-74 \pm 40$  kcal/mol), respectively. The large errors arise from inaccuracies in the values for the heats of formation of diethylaluminum hydride and triethylborane.

#### 9.1.4.4 Beryllium Hydride Slurries in Hypergolic Bipropellant Fuels

The preferred hypergolic fuel where beryllium hydride would be suspended to increase performance is methylhydrazine (MMH). Several programs have evaluated the storability, ignition and combustion behavior of gelled  $\text{BeH}_2$ /MMH fuels [308]. The dispersion of high percentages of  $\text{BeH}_2$  in liquid fuels continues to be attractive because the resulting fluids when combined with all currently known oxidizers potentially provide storable liquid propellants with very high specific impulse. The calculated theoretical  $I_{sp}$  of  $\text{BeH}_2$  in thickened or gelled MMH would be 350 s with hydrogen peroxide for a 45 mass-% dispersion. Early work showed that fluid dispersions containing more than 20 mass-% of Beane in MMH could not be prepared unless the Beane particles were modified.

LMH-2 powders were treated with a variety of organic chemicals and water in order to find a gas or vapor that would adsorb permanently to the powders and produce surfaces that would not decompose in the presence of MMH [309]. The Lewis acids boron trifluoride and thionyl chloride chemisorbed to the LMH-2 powders and showed good potential for producing a permanently adsorbed film capable of stabilizing the LMH-2/MMH system. Preliminary rheological studies indicated that guar gum, carboxymethylcellulose, agar-agar, Carbopol 940, and Gantrez could thicken or gel MMH, but all reacted with MMH, liberating methane and other gases. Preliminary stability tests on LMH-2/MMH slurries revealed high gas evolution rates that were attributable primarily to hydride degradation. Heat treating the LMH-2 decreased the rate of decomposition.

## 9.2 Magnesium Hydride

Magnesium hydride, magnesium dihydride,  $\text{MgH}_2$ , CAS RN [7693-27-8], is a white powder. It could be used as a less toxic, low-cost replacement for beryllium hydride. Magnesium hydride can be prepared by reaction of magnesium halides with lithium borohydride. It forms also as a result of disproportionation of magnesium bromide hydride [310] or by pyrolysis of alkyl magnesium halide compounds [311]. Magnesium hydride can be prepared from the elements by direct hydrogenation of Mg metal at high pressures and temperatures (200 atm, 500 °C) with  $\text{MgI}_2$  catalyst.

### 9.2.1 Physical Properties of Magnesium Hydride

Physical properties of magnesium hydride are summarized in Table 15.

**Table 15:** Physical properties of magnesium hydride.

|                       | SI units                | Other units                  | References |
|-----------------------|-------------------------|------------------------------|------------|
| Molecular mass        | 26.3209 g/mol           | 37.993 mol/kg                | [10]       |
| Density at 293 K      | 1.45 g/cm <sup>3</sup>  | —                            | [312]      |
|                       | 1.419 g/cm <sup>3</sup> | —                            | [313]      |
|                       | 1.45 g/cm <sup>3</sup>  | 0.0524 lb/in. <sup>3</sup>   | [286]      |
|                       | 523 K decomp.           | 250 °C decomp.               | —          |
| Melting point         | 523 K decomp.           | 250 °C decomp.               | —          |
|                       | —71.03 kJ/mol           | −645 cal/g = −16.98 kcal/mol | [286]      |
|                       | −90.8 kJ/mol            | −21.71 kcal/mol              | [313]      |
|                       | −75.4 kJ/mol            | −18.02 kcal/mol              | [208]      |
|                       | −74.9 kJ/mol            | −17.9 kcal/mol               | [287]      |
| Enthalpy of formation | −76.15 kJ/mol           | −18.20 kcal/mol              | [10]       |
|                       | —                       | —                            | —          |
|                       | —                       | —                            | —          |
|                       | —                       | —                            | —          |
|                       | —                       | —                            | —          |

The heat capacity of magnesium hydride as a function of temperature can be calculated from the following polynomial Shomate equation which was obtained from NIST Chemistry WebBook:

$$C_p^\circ = A + B \times \tau + C \times \tau^2 + D \times \tau^3 + E/\tau^2$$

where  $C_p$  is the molar heat capacity in  $\text{J mol}^{-1} \text{K}^{-1}$ ,  $\tau$  is the temperature in kelvin divided by 1000 and A, B, C, D, and E are constants listed in Table 16. One must note that  $\text{MgH}_2$  is unstable at temperatures above 600 K and the column for the higher temperature range 600–2000 K is only of academic interest.

**Table 16:** Thermodynamic property polynomial equation coefficients for magnesium hydride.

| Temperature range, K | 298–2000  |
|----------------------|-----------|
| A                    | 13.30646  |
| B                    | 103.1607  |
| C                    | −60.36801 |
| D                    | 12.17967  |
| E                    | −0.332913 |
| F                    | −85.32850 |
| H                    | −76.14922 |

Data source: [10]

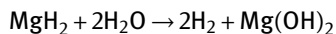
The enthalpy of formation of magnesium hydride as a function of temperature can be calculated from the following polynomial equation:

$$H^\circ - H_{298.15}^\circ = A \times \tau + B \times \tau^2/2 + C \times \tau^3/3 + D \times \tau^4/4 - E/\tau + F - H$$

where  $H^\circ - H_{298.15}^\circ$  is the excess enthalpy in kJ/mol,  $\tau$  is the temperature in kelvin divided by 1000 and A, B, C, D, E, F, and H are constants listed in Table 16.

### 9.2.2 Chemical Properties of Magnesium Hydride

Magnesium hydride readily and irreversibly reacts with water to form hydrogen gas:



The controlled hydrolysis of magnesium hydride is a candidate method for hydrogen storage as a supply of hydrogen for fuel cells. The hydrolysis of  $\text{MgH}_2$  is very slow unless it is carried out in acidic or alkaline solutions [314, 315] or in the presence of ammonium salts [316]. At 560 K (287 °C) magnesium hydride decomposes to produce  $\text{H}_2$  gas at 100 kPa pressure, but the high temperature required is seen as a limitation in the use of  $\text{MgH}_2$  as a reversible hydrogen storage medium.

## 10 Trivalent Metal Hydrides

### 10.1 Boron Hydrides

Logically, boron hydrides (boranes) should be discussed at this location along with other trivalent hydrides between beryllium hydride and the higher metal hydrides; however, the chemistry of boranes is so complex and involves so much information that this topic has been moved to a chapter of its own: “Boranes.” Complex boron hydrides (“boranates”) will be discussed at the end of the section on the binary hydrides.

### 10.2 Aluminum Hydride

Aluminum hydride,  $\text{AlH}_3$ , alane, aluminum trihydride, alumane, CAS RN [7784-21-6], is a white powder that at room temperature usually exists in a polymeric form. It is very sensitive to air and moisture. Aluminum hydride has a good chance to be used as a rocket propellant, because it is not as toxic and as expensive to produce as beryllium hydride. Anhydrous aluminum chloride as the starting material for aluminum hydride production is readily available in large quantities. During the 1960s, when some of the work on aluminum hydride was still classified as “Confidential,” this hydride was known under the code name “LMH-1.”

Although aluminum hydride has been investigated as a rocket propellant repeatedly and for a very long time since the first examinations became public [317, 318], there has been little progress and it has not yet been widely used as a solid propellant ingredient. Quality, solvate contamination and reproducibility were ongoing and lasting problems since day one when this compound was first proposed as a rocket propellant. The viability of further research on aluminum hydride as a rocket propellant ingredient has been critically reviewed. In the final analysis, it was determined that alane in typical solid propellants offered potentially very high  $I_{sp}$ , but this was traded against the resultant low density relative to use of aluminum alone. The most signif-

icant hurdle, however, was the apparent thermal instability of the material since the decomposition is autocatalytic. This led to an impractical shelf life for the developed formulations and ultimately, to the abandonment of alane as an energetic material in the United States in the 1990s. The interest in alane was revived when a higher quality of crystallized alane became available from foreign sources in 2001.

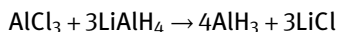
This chapter on aluminum hydride would be a very short chapter were it not for its ability to serve as a storage medium for hydrogen gas that is intended as an energy carrier for automobile and other vehicle propulsion [319]. The volumetric hydrogen storage capacity of  $\text{AlH}_3$  is 0.148 g/mL, which is twice as much as the density of liquid hydrogen (0.070 g/mL). The recent hydrogen storage work has revived the interest in aluminum hydride and it may eventually become available in commercial quantities for that application. Its eventual application as a rocket propellant would then benefit from the  $\text{AlH}_3$  production capacity established in the hydrogen storage industry, which would greatly exceed the amount of aluminum hydride consumed as a rocket propellant, another example of synergy and down-to-earth benefits derived from space technology.

### 10.2.1 Literature Summaries on Aluminum Hydride

Since aluminum hydride has been known for a long time, there are numerous literature summaries that are far more detailed than what we can offer here in this book [320–323].

### 10.2.2 Preparation of Aluminum Hydride

Aluminum hydride was first reported as an impure solid or as an etherate or as an amine adduct. Aluminum hydride can be prepared by reduction of anhydrous aluminum chloride with lithium aluminum hydride in ether [254, 324].



This reaction yields an unstable solution because the solvated aluminum hydride precipitates after a while. The delay of precipitation is dependent on concentration and temperature. This instability of the solution was assumed to be due to polymerization of  $\text{AlH}_3$ , but this could not be confirmed by molecular mass measurements. The solvated ether could not be removed without decomposition of aluminum hydride to its elements.

It is difficult to recrystallize  $\text{AlH}_3$  to create crystals suitable for XRD structure determination without occlusion of solvent molecules [325]. The solubility of aluminum hydride in various solvents was measured for that purpose. Continuous, direct crystallization of aluminum hydride was studied and achieved in a draft tube baffle crystallizer. Four methods of thermally seeding the crystallizer were examined. Solution stability was a problem. Photomicrographs were taken of the nucleation and growth processes occurring during decomposition of aluminum hydride.

Magnesium has been incorporated as a stabilizer into  $\text{AlH}_3$  made by a continuous crystallization technique and improved thermal stability was achieved in products from a larger process unit [326]. The complex hydride  $\text{LiMg}(\text{AlH}_4)_3$  has been used as the Mg doping agent and magnesium concentrations of 1% were achieved. Flame photometry was used to determine the equivalence point of the  $\text{AlCl}_3 + \text{LiAlH}_4$  reaction for aluminum hydride synthesis in the presence of an excess of  $\text{LiAlH}_4$ . The optimum conditions for the nucleation of  $\alpha\text{-AlH}_3$  and growth of good crystals were very different. A continuous crystallizer would require a continuous feed of seed crystals. Macrocrystalline, Mg-doped and diphenylacetylene (DPA)-treated  $\text{AlH}_3$  showed no improvement in thermal stability after it was kept in a pressure bomb under 52 MPa (7500 psia) hydrogen at room temperature for 5 months. Double base propellant containing magnesium-doped, *in situ* DPA-treated  $\text{AlH}_3$  showed a twofold improvement in stability over standard hydride when stored at 298 or 313 K (25 or 40 °C). Magnesium-doped, *in situ* DPA-treated and magnesium-doped aged  $\text{AlH}_3$  were remarkably stable at 333 K (60 °C). Propellants containing aged magnesium-doped  $\text{AlH}_3$  decomposed only 0.74% after 243 days. Magnesium-doped, *in situ* DPA-treated  $\text{AlH}_3$  in a double base propellant suffered 1% decomposition in 173 days, while in a composite propellant it suffered 0.84% decomposition in 91 days.

Non-solvated aluminum hydride can be prepared from an alkali metal hydride with aluminum chloride in ether solution in the presence of lithium aluminum hydride [327]. Macrocrystalline unsolvated aluminum hydride can be obtained via a  $\text{NaAlH}_4 + \text{AlCl}_3$  route by a process which involves synthesis and further treatment in a 1:1 ether-toluene medium [328]. This process is considerably more economical and yields a superior product compared with the conventional  $\text{LiAlH}_4 + \text{AlCl}_3$  route. One of the solvents used to precipitate alane from its ether solutions is toluene [329, 330].

Six crystalline phases of non-solvated aluminum hydride were prepared by heating aluminum hydride etherate in the presence of a small excess of lithium aluminum hydride  $\text{LiAlH}_4$  [331]. The most stable  $\alpha\text{-AlH}_3$  was prepared from both the solid metastable phases and by crystallizing directly from a refluxing diethyl ether/benzene solution at 349 K (76 °C). Thermal stability and ease of preparation of  $\text{AlH}_3$  were highly dependent on its purity. A product of high purity  $\alpha\text{-AlH}_3$  in the shape of hexagonal macrocrystals was obtained by refluxing  $\text{AlH}_3(n\text{-Pr})_2\text{O}$  with a diethyl ether-benzene solution [332].

Interactions in the  $\text{LiAlH}_4/\text{AlH}_3/\text{Et}_2\text{O}$ ,  $\text{LiBH}_4/\text{AlH}_3/\text{Et}_2\text{O}$ ,  $\text{Mg}(\text{AlH}_4)_2/\text{AlH}_3/\text{Et}_2\text{O}$ , and  $\text{Li}_2\text{Mg}(\text{AlH}_4)_4/\text{AlH}_3/\text{Et}_2\text{O}$  systems leading to formation of unsolvated  $\text{AlH}_3$  were studied by chemical analysis and IR-spectroscopy [333, 334]. Complexes of the compositions  $\text{LiAlH}_4 \bullet 4\text{AlH}_3 \bullet 4\text{Et}_2\text{O}$  (**1**) and  $2\text{LiAlH}_4 \bullet \text{AlH}_3 \bullet 4\text{Et}_2\text{O}$  (**2**) were extracted from the first system and complexes  $\text{LiBH}_4 \bullet \text{AlH}_3 \bullet 2\text{Et}_2\text{O}$  (**3**) and  $\text{LiBH}_4 \bullet 2\text{AlH}_3 \bullet 3\text{Et}_2\text{O}$  (**4**) from the second one. Systems on the basis of magnesium alumohydride are the systems of the eutonic type. Controlled decomposition of crystal compounds (**1**) and (**2**) and their solutions in ether-toluene media leads to formation of  $\text{LiAlH}_4$  with  $\alpha$ -,  $\alpha'$ -, and

$\gamma$ -AlH<sub>3</sub> mixtures, and the decomposition of crystal compound **(4)** leads to formation of LiBH<sub>4</sub>•AlH<sub>3</sub>•0.33Et<sub>2</sub>O. Pure  $\alpha$ -modification of unsolvated aluminum hydride is thus formed by the combined presence of complexes **(1)** and **(4)**. Under those conditions, apparently only the  $\alpha$ -alane form is observed. Other syntheses of aluminum hydride start with sodium hydride and aluminum trichloride in diethyl ether [335] or calcium hydride and aluminum chloride in diethyl ether [336].

$\alpha$ -AlH<sub>3</sub> was also named LMH-1451 [337]. At one time, high-purity material was produced at a production rate of 1000 lb/day via a continuous process. While pure, the quality of the crystals was lacking. The crystals suffered from poor morphology (porous, lower overall density  $\rho = 1.474 \text{ g/cm}^3$ ), and poor long-term stability. In 2001 a sample of Russian (FSU) AlH<sub>3</sub> was obtained in the US and compared to a domestic product from ATK. The Russian AlH<sub>3</sub> was of superior quality with very uniform crystal shapes and narrow particle size distribution range centered at 22  $\mu\text{m}$ . In the hydrogen generation stability test at 316 and 330 K (43 and 57 °C), the ATK material behaved similarly to FSU material at elevated temperatures. In developing a scalable AlH<sub>3</sub> production process, it was noted that several alane polymorphs would survive work-up and can contaminate the  $\alpha$ -phase product. Multiple polymorph combinations were occasionally observed. Finding a scaleable, reproducible process has proven very challenging.

During a study of the crystallization of non-solvated aluminum hydride from a diethyl ether/benzene mixed solvent it was found that the desolvation of AlH<sub>3</sub>•(Et<sub>2</sub>O)<sub>x</sub> etherate in solution and the crystallization of  $\alpha$ -AlH<sub>3</sub> during polythermal heating of the solution occur only in the presence of ~10 mass-% LiAlH<sub>4</sub> [338]. The process is multi-stage, and the crystallization begins with the formation of the AlH<sub>3</sub>•0.25Et<sub>2</sub>O solvate, which recrystallizes in the solid phase into  $\gamma$ -AlH<sub>3</sub> and then  $\alpha$ -AlH<sub>3</sub>. Four crystalline modifications of aluminum hydride were characterized by XRD and electron microscopy. See also [339].

Aluminum hydride has been proposed as a hydrogen storage medium and synthesized electrochemically, providing a synthetic route which closes a reversible cycle for regeneration of the material [340]. The electrolysis of NaAlH<sub>4</sub> in THF gives sodium metal and AlH<sub>3</sub>. For hydrogen storage, AlH<sub>3</sub> would be an excellent candidate if it could be cheaply produced. It has a density of 1.48 g/cm<sup>3</sup>, a volumetric hydrogen storage capacity of 0.148 g/cm<sup>3</sup>, i.e. greater than that of liquid hydrogen (0.070 g/cm<sup>3</sup>) and a hydrogen mass capacity exceeding 10 mass-%.

Aluminum hydride is typically synthesized in ether solution. The ether clings tenaciously to the solid product. The residual ether content of AlH<sub>3</sub> can be determined by gas chromatography [341].

Crystalline aluminum hydride can be prepared using an organometallic synthesis method with changed heat treatment conditions and crystallization conditions in toluene. Crystalline alane samples were characterized using Raman spectroscopy, XRD, and TGA-DTA [342]. It seems to be difficult to obtain pure  $\alpha$ -AlH<sub>3</sub> by heat

treatment of  $\alpha$ -AlH<sub>3</sub> etherate. Treating samples mostly containing the crystalline  $\alpha$  form of alane with dilute acid induced a better thermal stability. Aluminum hydride has a volumetric hydrogen capacity (0.148 g/mL) greater than that of liquid hydrogen (0.070 g/mL) and a hydrogen mass storage capacity slightly exceeding 10 mass-%. The enthalpy of formation of AlH<sub>3</sub> is negative (−11.4 kJ/mol), but due to a positive entropy (30.04 J mol<sup>−1</sup> K<sup>−1</sup>), the equilibrium hydrogen pressure is 270 kbar at 298 K. The metastability of alane is generally attributed to a surface oxide layer that acts as a kinetic barrier to decomposition and protects the alane from the environment. There are at least seven AlH<sub>3</sub> polymorphic crystalline forms reported in the literature and except for the  $\alpha$  (the most stable), and  $\gamma$  phases, the crystal structures for the other phases remain unknown or are subject of dispute among the experts. Experiments showed that the thermal stability and ease of preparation of alane are strongly dependent upon purity of the reactants and reaction conditions. The presence of impurities or moisture affects strongly the thermal stability.

In order to obtain  $\alpha$ -AlH<sub>3</sub> with high purity, solid AlH<sub>3</sub>-etherate was synthesized and separated from the reaction mixture of LiAlH<sub>4</sub> and AlCl<sub>3</sub> in diethyl ether [343]. Then  $\alpha$ -AlH<sub>3</sub> with a purity of 99.5% was prepared via desolvation of the solid AlH<sub>3</sub>-etherate in toluene at 363 K (90 °C) for 2 h with the yield of 96.4%. The product was characterized by XRD, IR, elemental analysis, TGA/DSC, and SEM. The results indicated that the product had uniform crystallization, high purity, and good stability.

There are two possibilities to transform the etherate into the solid dry phase: **(1)** by heat treatment under vacuum or **(2)** by precipitation in an organic solvent [344]. With the heat treatment method at different temperatures, one obtains pure  $\gamma$ -AlH<sub>3</sub> and small crystallite  $\alpha$ -AlH<sub>3</sub> plus a small amount of  $\gamma$ -AlH<sub>3</sub> and traces of aluminum. With the solvent method at different crystallization temperatures, one obtains polymeric crystalline  $\alpha$ -AlH<sub>3</sub> plus  $\gamma'$ -AlH<sub>3</sub> (not identified) and traces of  $\epsilon$ -AlH<sub>3</sub>, polymeric crystalline  $\alpha$ -AlH<sub>3</sub> plus traces of  $\gamma'$ -AlH<sub>3</sub> (not identified) and traces of  $\epsilon$ -AlH<sub>3</sub> and a little pure polymeric crystalline  $\alpha$ -AlH<sub>3</sub>.

In analogy to the problems with obtaining an ether-free product with beryllium hydride, it is equally difficult to obtain a completely ether-free aluminum hydride. It has been attempted to improve the stability of AlH<sub>3</sub> by doping it with magnesium or magnesium hydride or lithium borohydride [345].  $\alpha$ -AlH<sub>3</sub> was synthesized in an inert solvent by desolvation of solid AlH<sub>3</sub>-etherate, which was obtained from the reaction of LiAlH<sub>4</sub> and AlCl<sub>3</sub> in ether. The effects of LiBH<sub>4</sub> addition, temperature and time, solvent, crystallizing agent in desolvation on the product were discussed. The optimum process conditions were as follows: the molar ratio of LiAlH<sub>4</sub> and AlCl<sub>3</sub> was 4:1, the solid AlH<sub>3</sub>-etherate was obtained by solvent removal in vacuum; the desolvation was conducted in toluene at 363 K (90 °C) for 2 h in the presence of crystallizing agent. In this process,  $\alpha$ -AlH<sub>3</sub> with cubic crystal shape and high stability was prepared with a purity of 96% and yield of 96.4%.



Aluminum hydride etherate has the molecular formula of  $\text{AlH}_3 \cdot 0.22\text{Et}_2\text{O}$ .  $\text{AlH}_3$ -etherate is first desolvated to  $\gamma\text{-AlH}_3$ , which immediately transforms into the  $\alpha$ -phase during the heating process. Excess  $\text{LiAlH}_4$  is essential to remove ether in the desolvation process. Three aluminum hydride polymorphs ( $\alpha\text{-AlH}_3$ ,  $\beta\text{-AlH}_3$ , and  $\gamma\text{-AlH}_3$ ) were prepared through the desolvation of  $\text{AlH}_3$ -etherate using the organometallic synthesis method and the structure and morphology of the samples were characterized using FTIR, SEM, and XRD [346]. The thermal properties of  $\text{AlH}_3$  polymorphs were experimentally investigated under transient heating and isothermal processes. The results suggested that the  $\alpha$ -polymorph is the most stable of the three polymorphs, and the decomposition of the less stable polymorphs,  $\beta\text{-AlH}_3$  and  $\gamma\text{-AlH}_3$ , typically occurs via an exothermic transformation to the  $\alpha$ -phase ( $\geq 100^\circ\text{C}$ ) followed by the decomposition of  $\alpha\text{-AlH}_3$  phase into Al and  $\text{H}_2$ ; however, a fraction of  $\gamma$  and  $\beta$ -polymorphs may decompose directly to Al and  $\text{H}_2$  at low temperatures ( $< 100^\circ\text{C}$ ). The direct decomposition of the  $\gamma$  and  $\beta$  phases is faster than that of the  $\alpha$  phase due to the lower total formation enthalpy.

Instead of ether as a solvent, the reaction can be carried out in aliphatic amines, leading to Lewis adducts of  $\text{AlH}_3$  as intermediates. This method can use the more economical lithium hydride instead of lithium aluminum hydride as a starting material [347]. At first, the dimethylethylamine-alane (DMEAA) was synthesized by reaction of LiH and  $\text{AlCl}_3$  with the participation of dimethylethylamine (DMEA). Then DMEAA and an excess of triethylamine (TEA) were transaminated giving triethylaminealane (TEAA). Finally,  $\text{AlH}_3$  was obtained by vacuum heating of TEAA. All intermediate and ultimate products were characterized by FT-IR, XRD, and TGA. The cost of  $\text{AlH}_3$  preparation could be reduced through switching to the economical LiH instead of  $\text{LiAlH}_4$ .

The electrolysis of sodium aluminum hydride in a nonpolar solvent gives aluminum hydride at the anode [348]. The anolyte solution slurry is then filtered to remove the alane.

To better understand the desorption properties of hydrogen in alane, thermodynamically stable  $\alpha\text{-AlH}_3$  was synthesized by employing an ether-solvent reaction method [349]. The dependence of pathways on phase formation and the properties of hydrogen evolution were investigated, and the results were compared with the ones for  $\gamma\text{-AlH}_3$ .  $\alpha\text{-AlH}_3$  was formed when the residue of the process, i.e.,  $(4\text{AlH}_3n[(\text{C}_2\text{H}_5)_2\text{O}] + \text{LiAlH}_4 + \text{LiBH}_4)$ , was heated at 353–363 K ( $80\text{--}90^\circ\text{C}$ ) for 4 h, while  $\gamma\text{-AlH}_3$  was obtained when the residue was heated at 333–343 K ( $60\text{--}70^\circ\text{C}$ ) for 3 h.

$\alpha$ -Alane can be made by reacting lithium aluminum hydride and aluminum chloride in a solvent to produce alane etherate, filtering alane etherate from the reactant, combining the filtered alane etherate with a lithium borohydride solution to produce microcrystalline alane etherate, removing remaining solvent from the solids, creating a slurry from the solids and an aromatic solvent, and heating the slurry to convert the microcrystalline alane etherate to microcrystalline alpha alane [350].

A method for forming an alane-etherate complex and  $\alpha$ -alane from the alane-etherate complex includes reacting an alkyl halide (*n*-butyl bromide) with a metal alanate (sodium aluminum hydride or lithium aluminum hydride) in a solvent (diethyl ether) [351]. A tertiary amine (trialkyl amine) may also be added to the reaction. The alane is collected after removal of the solvent and/or the tertiary amine.

It was attempted to produce a stable alane structure through a wet chemical synthesis process [352]. Initial dissolution of starting reactants in ether produced a consistent crystal structure (cubic shape) and elemental compositions analogous to the theoretical composition. The chemical structure, when examined by XRD, matched well with the standard reference  $\alpha$ -type alane, and the resulting particle size of the precipitated  $\alpha$ -type alane ranged from 7 to 13  $\mu\text{m}$ . A pivotal step in the alane synthesis was selective crystallization from the liquid phase alane-etherate  $\text{AlH}_3 \cdot (\text{Et}_2\text{O})_n$ , followed by acid treatment of the precipitated particulate alanes using an appropriately mixed solution. See also [353–355].

#### 10.2.2.1 Preparation of Aluminum Hydride without the Use of Solvents

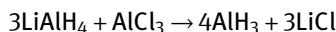
The problem with ether as a solvent and solvate tenaciously adhering to  $\text{AlH}_3$  can be circumvented by solid-state ball-milling the two reactants anhydrous aluminum chloride with a metal hydride in the dry state under a hydrogen atmosphere. Many of the publications on this process fail to report the hydrogen pressure under which the reaction was carried out.

Alane can be synthesized by cryomilling alkali metal or alkaline earth metal alanates and aluminum halides [356]. The yield of alane has been found to be increased using  $3\text{NaAlH}_4 + \text{AlCl}_3$ . Furthermore, the relative amount of  $\alpha'$ - $\text{AlH}_3$  over  $\alpha$ - $\text{AlH}_3$  was increased from 0.63–0.67 to 1.05 by adding small amounts of  $\text{FeF}_3$  to  $3\text{LiAlH}_4 + \text{AlCl}_3$ . When synthesized from  $3\text{NaAlH}_4 + \text{AlCl}_3$  the ratio  $\alpha'/\alpha$  was increased to 1.04.  $\alpha'$ - $\text{AlH}_3$  was confirmed to be less thermally stable than  $\alpha$ - $\text{AlH}_3$ . The maximum amount of synthesized alane was obtained by using  $\text{NaAlH}_4$  as a starting material instead of  $\text{LiAlH}_4$ ; however, the synthesis route from  $\text{NaAlH}_4$  produced alane with less thermal stability than the synthesis from  $\text{LiAlH}_4$ . The use of  $\text{Na}_3\text{AlH}_6$ ,  $\text{LiH}$  or  $\text{TiCl}_3$  resulted in no alane formation.

A mechanochemical dry grinding synthesis process has been used to synthesize alane nanoparticles [357]. The alane was synthesized via a dry chemical reaction between lithium alanate ( $\text{LiAlH}_4$ ) and aluminum chloride ( $\text{AlCl}_3$ ) at room temperature within a ball mill and also at 77 K within a cryogenic mill. The reaction product formed consisted of alane nanoparticles embedded within a lithium chloride by-product phase. The  $\text{LiCl}$  was then washed with a solvent resulting in alane nanoparticles, which were separated from the by-product phase but are kinetically stabilized by an amorphous particle surface layer. The synthesis of a particular alane structural phase is largely dependent on the milling conditions and two major phases ( $\alpha$ ,  $\alpha'$ ) as well as two minor phases ( $\beta$ ,  $\gamma$ ) have been identified. Excessive ball-milling at room

temperature can provide enough energy to allow alane to release hydrogen gas and form aluminum metal nanoparticles, which is undesirable. A comparison between XRD and hydrogen desorption results suggested that a non-crystalline  $\text{AlH}_3$  phase may be present in the synthesized samples.

The problem with ether as a solvent and solvate tenaciously adhering to  $\text{AlH}_3$  is avoided by ball-milling the two reactants anhydrous aluminum chloride with lithium aluminum hydride in the dry state under a hydrogen atmosphere [358, 359]. The synthesis of  $\text{AlH}_3$  from  $\text{LiAlH}_4$  and  $\text{AlCl}_3$  can be performed by ball-milling solid phase chemical reaction under a hydrogen atmosphere, thus avoiding the use of solvents which might cling to the product. The effects of different milling times (4–20 h) on the solid-state chemical reaction and dehydrogenation properties of the milled mixture were investigated comprehensively using XRD, TGA-DSC, MS, SEM, and dehydrogenation measurements. The reaction



was almost complete after milling for 20 h and amorphous  $\text{AlH}_3$  was formed.

Many of the current synthesis methods for aluminum hydride involve reacting  $\text{AlCl}_3$  and  $\text{LiAlH}_4$  in solvents. The reaction requires the formation of an alane adduct such as  $\text{AlH}_3 \cdot [(\text{C}_2\text{H}_5)_2\text{O}]$  prior to obtaining crystallized stable  $\alpha\text{-AlH}_3$ . This process requires several hours of pumping in a vacuum system to remove the ether and convert the alane etherate into stable  $\alpha$ -alane. This crystallization process is both costly and hazardous because a large amount of highly flammable material (e.g. ether) is removed by vacuum pumps over several hours. A different method to synthesize adduct-free alane involved mixing  $\text{AlCl}_3$  and  $\text{LiAlH}_4$  in the solid state, heating to 348 K (75 °C) and only solvate-free  $\alpha\text{-AlH}_3$  was obtained [360]. The  $\alpha\text{-AlH}_3$  product can be washed with ether-free solvents leading to zero formation of alane adducts. In addition, the unwanted LiCl by-product can also be removed during the solvent wash, resulting in halide-free  $\alpha$ -alane. Although simply mixing and heating the powdered reactants led to a 40% yield of alane, having the reactants pre-compacted and mechanically pressed while heating increased the yield to 60% of crystalline  $\alpha\text{-AlH}_3$ .

Nearly quantitative mechanochemical synthesis of non-solvated  $\text{AlH}_3$  from lithium aluminum hydride ( $\text{LiAlH}_4$ ) and aluminum chloride ( $\text{AlCl}_3$ ) has been achieved at room temperature under reasonably low pressure of hydrogen (210 bar) or inert gas (125 bar for He or 90 bar for Ar) [361, 362]. XRD, solid-state  $^{27}\text{Al}$  NMR spectroscopy, and temperature programmed desorption (TPD) analyses of as-milled materials revealed a nearly complete conversion of a 3:1 (molar) mixture of  $\text{LiAlH}_4$  and  $\text{AlCl}_3$  to a 4:3 (molar) mixture of  $\text{AlH}_3$  and LiCl in ca. 30 min. By applying pressure of 210 bar or less (depending on the gas: hydrogen, helium or argon), competing reactions leading to formation of metallic aluminum can be completely suppressed. XRD and NMR analyses of products extracted at various stages of the mechanochemical reaction between  $\text{LiAlH}_4$  and  $\text{AlCl}_3$  revealed that the solid-state transformation proceeds with  $\text{LiAlCl}_4$  as an intermediate. Evidently, the critical

pressure required to suppress the formation of metallic aluminum depends on the rate at which mechanical energy is supplied during milling. For example, the critical pressure is reduced from 210 to 1 bar of hydrogen when the milling speed of a standard planetary mill is reduced from 300 to 150 rpm, although at the expense of sluggish kinetics and much longer reaction time.

A mechanochemical, solid-state reaction process for the synthesis of alane ( $\text{AlH}_3$ ) starting with lithium hydride and anhydrous aluminum chloride at room temperature and the underlying reaction pathway have been studied [363]. In contrast to a conventional process using the same two reactants dissolved in diethyl ether, this approach enables a solvent-free synthesis, thereby directly leading to adduct-free alane. The method is quick and efficient, resulting in the quantitative conversion of all aluminum in the starting mixture to alane. Both the intermediate compounds formed during the reaction and the final products have been characterized by powder XRD, solid-state  $^{27}\text{Al}$  NMR spectroscopy and temperature programmed desorption analysis of the as-milled mixtures. An excess of LiH in the starting mixture (with an optimal ratio of 9 LiH:1  $\text{AlCl}_3$ ) is essential for the formation and stability of Al–H bonds, initially in the form of alanates and, eventually, as alane. Further processing of this mixture, gradually adding  $\text{AlCl}_3$  to reach the ideal 3 LiH:1  $\text{AlCl}_3$  stoichiometry, appears to restrict the local accumulation of  $\text{AlCl}_3$  during the ball-milling process, thereby preventing the formation of unstable intermediates that decompose to metallic Al and molecular hydrogen. Under the milling conditions used, a hydrogen pressure of ca. 300 bar is required to suppress competing reactions that lead to the formation of metallic Al at room temperature.

Aluminum hydride has a high gravimetric hydrogen capacity (10.1 mass-%) and has attracted considerable attention due to its potential application for hydrogen storage. Most of the routes developed for the synthesis of  $\text{AlH}_3$  and regeneration of the aluminum metal residue are energy-consuming and economically impractical for mass production. Solid state reactive milling methods to synthesize  $\text{AlH}_3$  using aluminum chloride and cheap metal hydrides as starting reagents, such as LiH/ $\text{AlCl}_3$ ,  $\text{MgH}_2/\text{AlCl}_3$  or  $\text{CaH}_2/\text{AlCl}_3$  reaction systems are more promising. In addition to LiH, NaH,  $\text{LiAlH}_4$ , and  $\text{NaAlH}_4$ , also  $\text{MgH}_2$  can be used as the starting hydride for making  $\text{AlH}_3$  by a solid state reactive milling reaction [364, 365]. Based on SEM, TEM, and NMR analyses, an amorphous intermediate  $(\text{AlH}_6)_n$  was preferentially formed during the solid state reaction between  $\text{MgH}_2$  and  $\text{AlCl}_3$  and recrystallized as a  $\gamma$ -phase  $\text{AlH}_3$  at the final stage of the reaction. The reaction progress and products during reactive milling were characterized by XRD and  $^{27}\text{Al}$  NMR, and the morphology as well as the microstructure of the as-milled samples by SEM and TEM, respectively [366]. It was found that nano-sized  $\gamma$ - $\text{AlH}_3$  could be synthesized by reactive milling with commercial  $\text{AlCl}_3$  and nanocrystalline  $\text{MgH}_2$  as reagents.

Solid-state mechanochemical synthesis of alane starting from sodium hydride (NaH) and aluminum chloride at room temperature was achieved by a stepwise addition of  $\text{AlCl}_3$  to the initial reaction mixture that contained sodium hydride in excess

of stoichiometric amount [362, 367]. As in the case of previously investigated LiH-AlCl<sub>3</sub> system, complete selectivity was achieved whereby formation of unwanted elemental aluminum was fully suppressed, and AlH<sub>3</sub> was obtained in quantitative yield. Reaction progress during each step was investigated by means of solid-state NMR and powder XRD, which revealed that the overall reaction proceeds through a series of intermediate alانات that may be partially chlorinated. The NaH/AlCl<sub>3</sub> system presented some subtle differences compared to LiH/AlCl<sub>3</sub> system particularly with respect to optimal concentrations needed during one of the reaction stages. High local concentrations of NaH may stabilize chlorine-containing derivatives and prevent premature decomposition of AlH<sub>3</sub> into elemental aluminum with hydrogen evolution. Complete conversion with quantitative yield of alane was confirmed by both NMR and hydrogen desorption analysis.

Aluminum hydride can be prepared by thermal decomposition of triethylaluminum under mild hydrogen pressures (10 MPa) with the use of surfactants [368]. With tetraoctylammonium bromide, the synthesis led to the formation of nanosized AlH<sub>3</sub> with the known  $\alpha$ -phase, and these nanoparticles released hydrogen from 313 K (40 °C) and above instead of the 398 K (125 °C) observed with bulk  $\alpha$ -AlH<sub>3</sub>.

#### 10.2.2.2 Preparation of Aluminum Hydride by Direct Synthesis from the Elements

Aluminum hydride forms from the elements only under extreme pressure conditions. This is not an economic method for making aluminum hydride. The PT diagram for aluminum hydride at 0.5–6.5 GPa and 373–1073 K (100–700 °C) indicated that the decomposition of AlH<sub>3</sub> is reversed at high pressures [369]. The compound can be prepared from the elements at pressures above 2.5 GPa; however, synthesis of AlH<sub>3</sub> via the solid-state exchange reactions of LiAlH<sub>4</sub> or LiH with AlCl<sub>3</sub> under quasi-hydrostatic conditions with excess hydrogen is more advantageous. The synthetic PT condition diagram is limited by two straight lines that correspond to the decomposition of AlH<sub>3</sub> into elements and the phase transition  $\alpha$ -LiAlH<sub>4</sub>  $\rightarrow$   $\beta$ -LiAlH<sub>4</sub>. The reaction of AlCl<sub>3</sub> with LiH to give AlH<sub>3</sub> proceeds only at  $P > 5.6$  GPa and  $T > 823$  K ( $> 550$  °C). Only the most compact  $\alpha$  modification of AlH<sub>3</sub> is formed under these PT conditions.

The decomposition of solid aluminum hydride was carried out at 423 and 413 K (150 and 140 °C) and under high pressure of gaseous hydrogen [370]. Pressure plateaus were observed indicating an equilibrium between the hydride and gaseous hydrogen. The AlH<sub>3</sub> dissociation equilibrium kinetics were measured by recording the hydrogen pressure increase as a function of time.

The formation of aluminum hydride by bombarding a thin film of solid aluminum chloride with active (atomic) hydrogen from a plasma discharge can be catalyzed by finely divided palladium black [371]. This is not a reaction that would be economically feasible. It is only of academic interest.

The PT diagram of the hydrogen-aluminum system was determined for a pressure range of 0–10 GPa and a temperature range of 300–1073 K (27–800 °C) by *in situ* XRD

[372, 373]. Pristine aluminum was hydrogenated to trihydride at 8.9 GPa and 873 K (600 °C). The cyclic formation and decomposition of the hydride resulted in a more active porous material and lowering of the hydrogenation conditions down to 4.9 GPa and 603 K (330 °C). Transparent single crystals were recovered at ambient conditions after cooling and depressurization.

The direct synthesis of aluminum hydride from the elements would be a promising approach to make aluminum hydride more readily available but it is still far removed from industrialization [374]. Aluminum hydride can be prepared by direct hydrogenation of an aluminum/gallium alloy at pressures up to 103 MPa (15 kpsi) [375]. The mixture of aluminum hydride and gallium hydride is heated to decompose the thermally less stable gallium hydride, leaving the thermally more stable aluminum hydride behind, and the gallium metal is recycled.

Alane is difficult to synthesize directly from its elements. Using density functional theory, the defect-mediated formation of alane monomers on Al(111) single crystal metal surfaces in a two-step process was examined by computations: **(1)** dissociative adsorption of  $H_2$  and **(2)** alane formation, which are both endothermic on a clean surface [376]. Only with Ti dopant to facilitate  $H_2$  dissociation and vacancies to provide Al adatoms, both processes become exothermic. In agreement, *in situ* scanning tunneling microscopy showed that during  $H_2$  exposure, alane monomers and clusters form primarily in the vicinity of Al vacancies and Ti atoms. Moreover, ball-milling of the Al samples with Ti (providing necessary defects) showed a 10% conversion of Al into  $AlH_3$  or closely related species at 344 bar  $H_2$ , indicating that the predicted pathway may lead to the direct synthesis of alane from elements at pressures much lower than the 104 bar expected from bulk thermodynamics.

### 10.2.2.3 Stabilization of Aluminum Hydride

The rate of thermal decomposition and reactivity of aluminum hydride in air and with other propellant ingredients can be decreased by passivating or coating the freshly prepared hydride. Aging of magnesium-doped  $AlH_3$  has resulted in an approximate sevenfold improvement in hydride stability. The increased stability due to aging was found to increase as the magnesium concentration was increased [377].

Treatment for 5 days in *n*-butylamine (NBA) containing 2% water was recommended as the best procedure at that time for magnesium-doped aluminum hydride [378]. This treatment produced a material with good thermal stability (15–25 days to 0.1% decomposition at 333 K = 60 °C), a low oxygen content (0.1%), and it had a proven compatibility with high energy propellant ingredients. Scanning electron photomicrographs revealed the surface characteristics of aluminum hydride crystals and showed a thin coating, probably  $Al(OH)_3$ , generated by hydrolysis treatment. The coating thickness depended on the type of treatment, length of treatment, water content in the organic solvent, and original stability of the material. Treatment for 5 days in ethanol containing 2% water at 353 K (80 °C) produced aluminum hydride

with better thermal stability than the NBA method. The best samples required 35–40 days to reach 0.1% decomposition at 333 K (60 °C). Compatibility with TVOPA was worse and the increase in oxygen content was greater than for NBA-treated samples. Aluminum hydride hydrolyzes slowly in water buffered at pH 7. After drying, the hydride had an improved thermal stability and excellent compatibility with TVOPA and TEGDN. For a given amount of hydrolysis (measured by oxygen uptake during treatment), the increase in thermal stability at 333 or 353 K (60 or 80 °C) was poorer than the NBA or EtOH treatments. Aluminum hydride treated for 3 days in a pH 7 solution and followed by a 5-day treatment in ethanol containing 2% water at 353 K (80 °C) had a thermal stability comparable to the NBA-treated material. It has better compatibility with TVOPA than the latter, but oxygen uptake during the treatment was almost double (2 vs. 1%). The water which is in the solvents used for treatment is necessary for an improvement in thermal stability. Treatment in solvents with low water contents (<0.1%) resulted in a loss of stability or an exothermic reaction of the hydride with the organic solvent.

Soaking Mg-doped unsolvated  $\text{AlH}_3$  in a buffered solution of  $\text{KH}_2\text{PO}_4$  and NaOH at pH 6.8 for 15 min and drying under vacuum was supposed to result in a thermally more stable hydride [379].  $\text{AlH}_3$  can be stabilized by soaking it in an aqueous solution containing amines or hydrazine [380] or by doping it with magnesium from a solution of  $\text{MgCl}_2$  in an ether/benzene mixture [381].

Storing non-solvated crystalline  $\text{AlH}_3$  or Mg-doped  $\text{AlH}_3$  for at least 4 months under an inert atmosphere at low temperatures in the range of 258–73 K (–15 to –200 °C) was supposed to improve the thermal and storage stability of the hydride after it is brought back to room temperature [382]. In one example, samples of Mg-doped  $\text{AlH}_3$  with 2.1% Mg were held at 258 K for 75 days and 1.5 years. After thawing, samples heated to 333 K (60 °C) took 75 and 93 days, respectively, to reach 1% decomposition, while an untreated reference sample reached 1% decomposition in only 13 days. Adsorbing of up to 1% nitric oxide at  $10^{-5}$  mm Hg pressure for 16 h onto the surface of  $\text{AlH}_3$  was supposed to improve thermal stability and compatibility with other propellants [383]. The treated sample, when heated to 373 K (100 °C) for 4 or 7 h, decomposed to an extent of 0.1 and 0.2%, respectively, while an untreated sample was 0.6 and 5.6% decomposed under the same conditions.

In a method for preparing non-solvated alane, alane-etherate may be desolvated in the presence of a small amount of lithium aluminum hydride [330, 384]. The combination of  $\text{LiBH}_4/\text{LiAlH}_4$  enables use of a lower processing temperature, and  $\alpha$ -alane is the final product after heating at 338 K (65 °C) under vacuum.

Alane can be stabilized by treating  $\alpha$ - $\text{AlH}_3$  with an acidic solution that contains a stabilizing agent such as an electron donor, an electron acceptor, or a compound such as 8-hydroxyquinoline which coordinates the  $\text{Al}^{3+}$  ion [385–388].

A crystallization additive (e.g., squalene, norbornylene, norbornadiene, dimethyl anisole) added to an alane-ether complex solution or to an aqueous ether/alane-ether

complex solution may result in more uniform crystals of  $\alpha$ -AlH<sub>3</sub> [389, 390]. Ether is then removed from the crystallization solution to crystallize the stabilized  $\alpha$ -alane. See also [391].

#### 10.2.2.4 Coatings for Aluminum Hydride

The main disadvantage for the application of AlH<sub>3</sub> as an ingredient in propellants is its sensitivity towards oxidation, and hydrolysis. Stabilization by additives or coatings is required to ensure the safe handling of AlH<sub>3</sub>.

Coatings with alkyl cyanides such as acrylonitrile or propionitrile make aluminum hydride more compatible with other rocket propellant ingredients [392]. Acrylonitrile-coated AlH<sub>3</sub> had a much better compatibility with trimethylolethane trinitrate as indicated by sharply reduced gas evolution of the mix during storage. Coating with stearic acid offers some protection of  $\alpha$ -AlH<sub>3</sub> particles [393]. Coating aluminum hydride with nitrocellulose (NC) has the advantage that the nitrocellulose contributes to the performance of solid rocket propellants using these NC-coated AlH<sub>3</sub> particles [394].

A detailed characterization of a stabilized sample of aluminum hydride was performed and different stabilization concepts were tested [395]. An effective stabilization mechanism was achieved by a protective coating with aluminum hydroxide clusters.

Liquid carbon dioxide can be used as an anti-solvent, dispersant, drying medium and inert fluid for coating aluminum hydride [396]. Alane samples coated from a suspension in liquid carbon dioxide were characterized by SEM, XPS, XRD, and FT-IR. The coating agent was uniformly applied on the surface of alane and the crystalline phase remained unchanged. The thermal stability of alane before and after coating was analyzed by DSC, indicating improved thermal stability. The lower electric spark sensitivity of the coated alane improved safety, serviceability and stability of this material.

Once it is exposed to air, the surface of alane is widely believed to consist of an aluminum oxide layer, which is expected to exhibit different reactivity toward organic polymer coating molecules than the native aluminum hydride surface. Microscale  $\alpha$ -AlH<sub>3</sub> particles were passivated by nanometer Al<sub>2</sub>O<sub>3</sub> layers via atomic layer deposition [397]. Conformal amorphous Al<sub>2</sub>O<sub>3</sub> films were coated around the crystalline  $\alpha$ -AlH<sub>3</sub> particles, serving as physical barriers to prevent reactions with air or moisture. If used as a hydrogen storage medium, the dehydrogenation speed of passivated AlH<sub>3</sub> particles was about the same as that of untreated samples.

#### 10.2.3 Physical Properties of Aluminum Hydride

It is difficult to obtain a complete, consistent set of physical properties for aluminum hydride, because the material is often contaminated with solvents and may exist in several polymorphic modifications. Physical properties of aluminum hydride are summarized in Table 17. See also [398, 399].



**Table 17:** Physical properties of  $\alpha$ -aluminum hydride.

| Property              | SI units               | Other units                | References |
|-----------------------|------------------------|----------------------------|------------|
| Molecular mass        | 30.00536 g/mol         | 33.33 mol/kg               | [10]       |
| Density               | 1.43 g/cm <sup>3</sup> | —                          | [208]      |
|                       | 1.43 g/cm <sup>3</sup> | 0.0516 lb/in. <sup>3</sup> | [286]      |
| Enthalpy of formation | −11.55 kJ/mol          | −92 cal/g = −2.76 kcal/mol | [286]      |
|                       | −11.42 kJ/mol          | −2.73 kcal/mol             | [313]      |

### 10.2.3.1 Molecular Structure of Aluminum Hydride

Alane is a polymer structure with hydrogen bridges and its formula should be written  $(\text{AlH}_3)_n$ . There are at least seven different  $\text{AlH}_3$  solid phases described in the literature but only the most stable  $\alpha$ - $\text{AlH}_3$  polymorph with an enthalpy of formation of  $\Delta H_f^\circ = -11.4 \text{ kJ/mol}$  can be a candidate for propellant utilization. Aluminum hydride exists in several polymorphs, which are named  $\alpha$ -alane,  $\alpha'$ -alane,  $\beta$ -alane,  $\delta$ -alane,  $\varepsilon$ -alane,  $\theta$ -alane, and  $\gamma$ -alane.  $\alpha$ -Alane has a cubic or rhombohedral crystal morphology, whereas  $\alpha'$ -alane forms needle-like crystals and  $\gamma$ -alane forms a bundle of fused needles. Alane is soluble in THF and diethyl ether.

The structure of  $\alpha$ -alane consists of aluminum atoms which are surrounded by six hydrogen atoms that bridge to six other aluminum atoms. Alane phases have been prepared by desolvating the alane etherate and several solid-state NMR techniques have been used to characterize various  $\text{AlH}_3$  samples. NMR spectra for the  $^1\text{H}$  and  $^{27}\text{Al}$  nuclei have been obtained on a variety of  $\text{AlH}_3$  samples that include the  $\beta$ - and  $\gamma$ -phases as well as the most stable  $\alpha$ -phase [400, 401]. Direct decomposition of the  $\gamma$ - $\text{AlH}_3$  to aluminum metal at room temperature was unambiguously confirmed by these NMR studies.

Aluminum hydride has been evaluated as a hydrogen storage medium. The thermodynamic and spectroscopic properties of  $\text{AlH}_3$ , were measured, in particular those of the  $\alpha$ ,  $\alpha'$ , and  $\gamma$  polymorphs, of which  $\alpha'$ - $\text{AlH}_3$  is characterized in more detail, and free from traces of other polymorphs or side products [402, 403]. All three polymorphs were investigated by  $^1\text{H}$  magic-angle spinning (MAS)-NMR spectroscopy, and their  $^{27}\text{Al}$  MAS-NMR spectra were measured and compared with literature data. The etherate  $\text{AlH}_3 \cdot n\text{Et}_2\text{O}$  was studied by  $^1\text{H}$  and  $^{27}\text{Al}$  MAS-NMR spectroscopy and DSC and TGA methods, and an accurate decomposition pathway has been established for this adduct.

While the dominant components in these NMR spectra correspond to the aluminum hydride phases, other species were found that include Al metal, molecular dihydrogen ( $\text{H}_2$ ), as well as peaks that can be assigned to Al-O species in different configurations. The occurrence and concentration of these extraneous components are dependent upon the initial  $\text{AlH}_3$  phase composition and preparation procedures. Both the  $\beta$ - $\text{AlH}_3$  and  $\gamma$ - $\text{AlH}_3$  phases were found to generate substantial amounts of Al

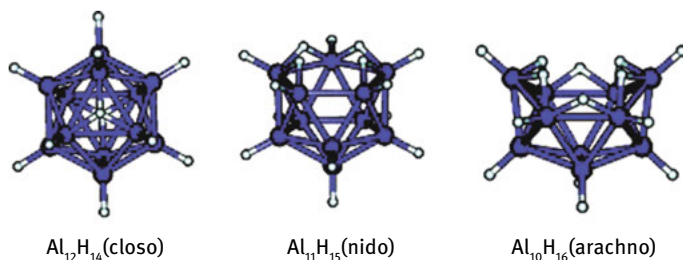
metal when the materials were stored at room temperature while the  $\alpha$ -phase materials do not exhibit these changes.

Alane has been subjected to Raman studies under static compression to see if there were any phase changes [404]. The Raman spectra showed four modes, which increased in frequency as pressure was increased from ambient to 6.6 GPa. From the pressure dependence, the pressure coefficient for each mode has been estimated and used to evaluate the Grueneisen parameters. Infrared spectra were also collected under ambient pressure condition for alane polymorphs.

Alane, crystallizing in the  $\gamma$ - $\text{AlH}_3$  polymorphic modification, was synthesized and then structurally characterized by means of synchrotron X-ray powder diffraction [405].  $\gamma$ - $\text{AlH}_3$  crystallized with an orthorhombic unit cell (space group  $Pnmm$ ,  $a = 5.3806(1) \text{ \AA}$ ,  $b = 7.3555(2) \text{ \AA}$ ,  $c = 5.77509(5) \text{ \AA}$ ). The crystal structure of  $\gamma$ - $\text{AlH}_3$  contains two types of  $\text{AlH}_6$  octahedra as the building blocks. The Al–H bond distances in the structure vary in the range of 1.66–1.79  $\text{\AA}$ . A prominent feature of the crystal structure is the formation of the bifurcated double-bridge bonds,  $\text{Al}\cdots 2\text{H}\cdots\text{Al}$ , in addition to the normal bridge bonds,  $\text{Al}-\text{H}-\text{Al}$ . The geometry of the double-bridge bond showed formation of short Al–Al (2.606  $\text{\AA}$ ) and Al–H (1.68–1.70  $\text{\AA}$ ) bonds compared to the Al–Al distances in Al metal (2.86  $\text{\AA}$ ) and Al–H distances for Al atoms involved in the formation of normal bridge bonds (1.769–1.784  $\text{\AA}$ ). The crystal structure of  $\gamma$ - $\text{AlH}_3$  contains large cavities between the  $\text{AlH}_6$  octahedra. As a consequence, the density is 11% less than for  $\alpha$ - $\text{AlH}_3$ .

Although a multitude of boron hydrides are known, the aluminum hydride chemistry is limited to very few examples such as  $\text{AlH}_3$ , its dimer and its polymeric form. In view of experimental studies on the possible existence of higher aluminum hydrides, a systematic theoretical study of the electronic structure and properties of these aluminum hydrides studied different classes of hydrides, viz., closo ( $\text{Al}_n\text{H}_{n+2}$ ), nido ( $\text{Al}_n\text{H}_{n+4}$ ), and arachno ( $\text{Al}_n\text{H}_{n+6}$ ) (Figure 3), similar to the boranes [406]. All the aluminum hydrides were predicted to have exceptionally large highest-occupied molecular orbital lowest-unoccupied molecular orbital gaps, low electron affinities, large ionization potentials, high symmetries and also large enthalpy and free energy of atomization. These exceptional properties can be indicative of the pronounced stability, and hence, it was expected that other aluminum hydride complexes can indeed be observed experimentally at some time in the future.

In order to resolve a contradiction between early theoretical prediction and experiments concerning the  $\gamma \rightarrow \alpha$  phase transition of aluminum hydride, computer models of Li-doped  $\text{AlH}_3$  were constructed and investigated theoretically [407]. Thermodynamic calculations showed that the  $\gamma \rightarrow \alpha$  transition of pure  $\text{AlH}_3$  absorbs energy, and the changes in Gibbs free energy are in the range of 1.74–1.99 kJ/mol at 298–380 K. These are opposite to the experimental fact that the  $\gamma$ - to  $\alpha$ -phase transition takes place at 380 K; however, the changes in enthalpy and Gibbs free energy in the  $\gamma \rightarrow \alpha$  phase transition of Li-doped  $\text{AlH}_3$  are negative. The doping of Li decreases the activation energy of the  $\gamma \rightarrow \alpha$  transition and introduces more metastable states between them.

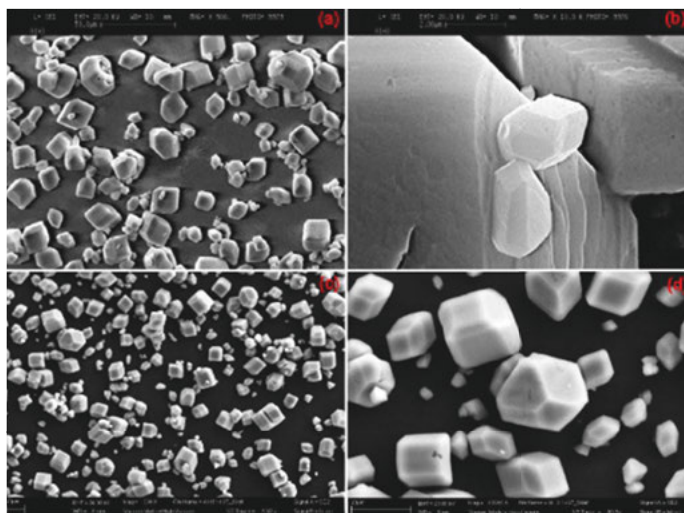


**Figure 3:** Theoretical molecular structure of higher aluminum hydrides (reprinted from [406], with permission from ©2010 American Chemical Society; permission conveyed through RightsLink.)

### 10.2.3.2 Crystal Structure of Aluminum Hydride

SEM micrographs of  $\text{AlH}_3$  crystals taken at various laboratories show mainly monocrystalline particles in the size range 1–20  $\mu\text{m}$ , with irregular structure having crystalline edges ([408]; Figure 4). Structural analyses revealed the presence of a unique crystalline phase ( $\alpha\text{-AlH}_3$ ) with very large crystalline domains of 730 nm. The high purity and quality of these crystals seems the key factor for the overall excellent properties shown by the tested material.

The most stable structure of aluminum hydride is believed to be a hexagonal symmetry. Density functional theory calculations have identified two additional stable structures for  $\text{AlH}_3$  with cubic and orthorhombic symmetries [409]. Based on



**Figure 4:** SEM micrographs of  $\text{AlH}_3$  crystals (reprinted from [408] with permission from Dr. L. T. DeLuca 9 May 2021)

Legend: Magnification (a) 500X; (b) 10000X; (c) 300X; (d) 1000X

the quasi-harmonic approximation, the cubic and orthorhombic  $\text{AlH}_3$  are almost degenerate when the zero-point energies are included. The geometric and electronic structures, the phonon, and the thermodynamic properties for the hexagonal, cubic, and orthorhombic  $\text{AlH}_3$  have been studied by means of density functional theory and direct *ab initio* force constant approaches. The calculated electronic structures, phonon density of states, and thermodynamic functions for the three hydrides were similar. The results showed that these three hydrides have negative enthalpies of formation, but positive free energies of formation. The thermodynamic properties indicate that the orthorhombic and cubic  $\text{AlH}_3$  should be more difficult to dissociate than the hexagonal  $\text{AlH}_3$ .

X-ray diffraction confirmed the hexagonal unit cell and lattice parameters  $a = 4.447 \text{ \AA}$ ,  $c = 1.81 \text{ \AA}$  at 433 K immediately before decomposition [410]. X-ray and neutron powder diffraction data for aluminum hydride,  $\text{AlH}_3$ , and aluminum deuteride,  $\text{AlD}_3$ , were used to resolve these structures [411]. Both compounds crystallize in the trigonal space group  $R\bar{3}c$  with six molecules in a hexagonal unit cell of dimensions  $a = 4.449 \text{ \AA}$  and  $c = 11.804 \text{ \AA}$  for the hydride and  $a = 4.431 \text{ \AA}$  and  $c = 11.774 \text{ \AA}$  for the deuteride. Columns of Al atoms and spirals of H atoms are parallel with the  $c$  axis and are packed so that the Al has octahedral coordination symmetry. The closest  $\text{Al}\cdots\text{Al}$  distance is  $3.24 \text{ \AA}$ . The alternating planes of Al and H atoms perpendicular to the  $c$  axis, result in a stable structure which is a three-dimensional network of  $\text{Al}\cdots\text{H}\cdots\text{Al}$  bridges and is consistent with the observed high density of the crystal. The structure of  $\alpha\text{-AlH}_3$  shows that the corners of the hexagonal unit cell are formed of  $\text{AlH}_6$  octahedra, whereas hydrogen bridges connect two octahedra to each other. The unit cell of  $\text{AlH}_3$  is composed of atoms of aluminum (Al) and hydrogen (H) linked by single bonds of different distances:  $1.715 \text{ \AA}$  ( $\text{Al-H}$ ),  $2.418 \text{ \AA}$  ( $\text{H}\cdots\text{H}$ ) and  $3.236 \text{ \AA}$  ( $\text{Al}\cdots\text{Al}$ ) and a unit cell volume of  $33.5 \text{ \AA}^3$  per  $\text{AlH}_3$  unit cell.

In situ isothermal high-pressure synchrotron XRD and optical Raman spectroscopy were used to examine the structural properties, equation of state and vibrational dynamics of  $\alpha$ -aluminum hydride [412]. The X-ray measurements showed that the pressure-volume relations remain smooth up to pressures near 50 GPa. Although there was no evidence for a first-order phase transition, the unit cell axial ratio ( $c/a$ ) was anomalous near 2.5 GPa, which corresponded to the onset of a monoclinic structural distortion. Infrared measurements conducted within a similar pressure range showed a distinct discontinuity in the frequencies of the  $\text{Al-H}$  lattice modes. The combined data provided evidence for a monoclinic structural distortion beginning near 2.5 GPa. All structural changes were reversible upon pressure release.

### 10.2.3.3 Dimers and Polymers of Aluminum Hydride

Looking at the tendency of borane  $\text{BH}_3$  to form dimers like diborane  $\text{H}_2\text{BH}_2\text{BH}_2$ , one wonders if the same dimer-forming behavior and hydrogen bridging can be found with its higher analog,  $\text{AlH}_3$  [413]. The binding energy of dialane,  $\text{Al}_2\text{H}_6$ , has been measured

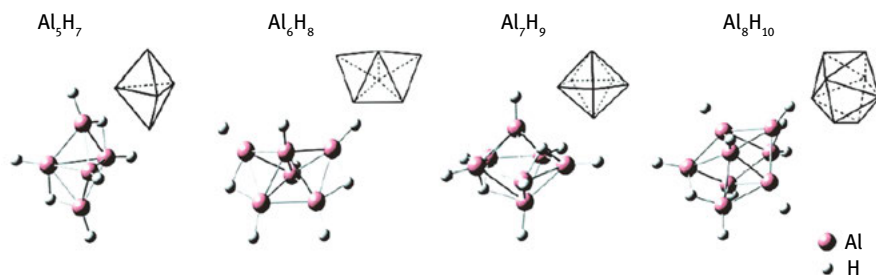
using mass spectrometric techniques to be  $138 \pm 21$  kJ/mol ( $33 \pm 5$  kcal/mol) [414]. This represented the first measurement of the thermochemical properties of dialane, which has only been observed in low-temperature matrices. High-level quantum mechanical calculations gave a binding energy in agreement with the measured value. Experimental and quantum mechanical calculations showed that dialane,  $\text{Al}_2\text{H}_6$ , is chemically similar to diborane,  $\text{B}_2\text{H}_6$ , even though the bonding for these two systems shows significant differences. Calculations revealed that the  $\text{Al}_6\text{H}_{18}$  cluster, with its hexa-coordination of the Al atoms, resembles the unit-cell of  $\gamma\text{-AlH}_3$ , thus  $\text{Al}_6\text{H}_{18}$  is a building block from which  $\gamma\text{-AlH}_3$  is formed [415].

Although many volatile binary boron hydride compounds are known, binary aluminum hydride chemistry is limited to the polymeric  $(\text{AlH}_3)_n$  solid. The reaction of laser-ablated aluminum atoms and pure  $\text{H}_2$  during co-deposition at 3.5 K, followed by UV irradiation and annealing to 6.5 K, allows dimerization of the intermediate  $\text{AlH}_3$  product to form  $\text{Al}_2\text{H}_6$  in a matrix of frozen hydrogen [416]. The  $\text{Al}_2\text{H}_6$  molecule was identified by seven new IR absorptions that were accurately predicted by quantum chemical calculations for dibridged  $\text{Al}_2\text{H}_6$ , a molecule that is isostructural with diborane.

Seven new absorptions for  $\text{Al}_2\text{H}_6$  were found in the IR spectrum of the solid hydrogen matrix sample [417]. These frequencies included terminal  $\text{Al-H}_2$  and bridge  $\text{Al-H-Al}$  stretching and  $\text{AlH}_2$  bending modes, which were accurately predicted by quantum chemical calculations for dibridged  $\text{Al}_2\text{H}_6$ , a molecule isostructural with diborane. Annealing these samples to remove the  $\text{H}_2$  matrix decreased the sharp  $\text{AlH}_3$  and  $\text{Al}_2\text{H}_6$  absorptions and formed broad  $1720 \pm 20$  and  $720 \pm 20$   $\text{cm}^{-1}$  bands, which are due to solid  $(\text{AlH}_3)_n$ . New absorptions were assigned to the  $\text{Al}_2\text{H}_5$  radical with a dibridged structure [418].

While boron forms many different hydrides, aluminum has been able to form only a few. A combined anion photoelectron and density functional theory computational study of the  $\text{Al}_4\text{H}_6^-$  anion and its corresponding neutral molecule,  $\text{Al}_4\text{H}_6$ , suggested that it may be a borane analog [419]. The data supported an  $\text{Al}_4\text{H}_6$  structure with a distorted tetrahedral aluminum atom framework, four terminal  $\text{Al-H}$  bonds, and two sets of counter-positioned  $\text{Al}\cdots\text{H}\cdots\text{Al}$  bridging bonds. The large gap between the highest occupied and the lowest unoccupied molecular orbitals found for  $\text{Al}_4\text{H}_6$ , together with its exceptionally high heat of combustion, further suggested that  $\text{Al}_4\text{H}_6$  may be an important energetic material **if** it can be prepared in bulk.

Aluminum hydride anion clusters,  $\text{Al}_n\text{H}_m^-$  ( $4 \leq n \leq 8$ ;  $0 \leq m \leq 10$ ) were studied by anion photoelectron spectroscopy and density functional theory [420] (Figure 5). Photoelectron spectra revealed that  $\text{Al}_4\text{H}_4$ ,  $\text{Al}_4\text{H}_6$ , and a family of species with general formula  $\text{Al}_n\text{H}_{n+2}$  ( $5 \leq n \leq 8$ ) have small adiabatic electron affinities and large HOMO-LUMO gaps (ranging from 0.5 to 1.9 eV) relative to those of their stoichiometric neighbors, possibly giving hope for their enhanced stabilities. DFT calculations showed that the  $\text{Al}_n\text{H}_{n+2}$  ( $5 \leq n \leq 8$ ) family adopts  $n$ -vertex polyhedral closo-structures with two extra hydrogen atoms occupying opposite bridging positions in agreement with Wade's



**Figure 5:** Molecular structure of theoretical higher aluminum hydrides (reprinted from [420], with permission from ©2007 American Chemical Society; permission conveyed through RightsLink.)

rule. These can be viewed as aluminum analog versions of hypothetical diprotonated closo-borane dianions ( $B_nH_n^{2-} + 2H^+$ ).  $Al_4H_4$  assumes a closo-tetrahedral geometry, while  $Al_4H_6$  takes on a distorted tetrahedral ( $D_{2d}$ ) structure with two counterpositioned bridging hydrogen atoms and had the largest HOMO-LUMO gap (1.9 eV) of all the alanes studied. All these studies on higher aluminum hydrides may be interesting from an academic point of view, but they will unfortunately not immediately lead to improved rocket propellants.

#### 10.2.3.4 Thermodynamic Properties of Aluminum Hydride

The enthalpy of formation and absolute entropy of solid  $AlH_3$  at 298 K have been measured as  $-11.4 \pm 0.8$  kJ/mol ( $-2.73 \pm 0.20$  kcal/mol) and  $30.0 \pm 0.4$  J mol $^{-1}$  K $^{-1}$  ( $7.18 \pm 0.10$  cal mol $^{-1}$  °C $^{-1}$ ), respectively [421]. The derived Gibbs energy of formation at 298 K of  $46.5 \pm 1.0$  kJ/mol ( $11.11 \pm 0.23$  kcal/mol) indicated that  $AlH_3$  is unstable at room temperature with respect to decomposition into its elements.

The phase change thermodynamics and molecular structures of the  $\alpha$ ,  $\beta$ , and  $\gamma$  polymorphs of  $AlH_3$  were determined using DSC and *ex situ* XRD [422]. The results demonstrated that at around 373 K (100 °C) the decomposition of the  $\beta$  and  $\gamma$  polymorphs occurred by an initial phase transition to the  $\alpha$  polymorph, followed by decomposition of the  $\alpha$  phase. The total heat evolved during the  $\beta \rightarrow \alpha$  transition was  $1.5 \pm 0.4$  kJ/mol and  $2.8 \pm 0.4$  kJ/mol during the  $\gamma \rightarrow \alpha$  transition. The transformation to the  $\alpha$ -phase is exothermic and is therefore likely to occur spontaneously at room temperature. A formation enthalpy of approximately  $-10$  kJ/mol was measured for  $\alpha$ - $AlH_3$ , which was in good agreement with previous experimental and calculated results.

Several polymorphs of  $AlH_3$  were prepared by organometallic synthesis and subjected to controlled decomposition to evaluate them as hydrogen storage media [423, 424]. It was shown that freshly synthesized, non-solvated  $AlH_3$  releases approximately 10 mass-%  $H_2$  at desorption temperatures less than 373 K (100 °C). The decomposition kinetics, measured by isothermal hydrogen desorption between 303 and 413 K (30 and 140 °C), suggested that the rate of  $H_2$  evolution is limited by nucleation and growth of

the aluminum phase. The decomposition thermodynamics were measured using DSC and ex situ XRD. The decomposition of the less stable polymorph,  $\gamma$ - $\text{AlH}_3$ , occurred by an exothermic transformation to the  $\alpha$  phase ( $\sim 100^\circ\text{C}$ ) followed by the decomposition of  $\alpha$ - $\text{AlH}_3$ . The enthalpy of formation of approximately  $-10\text{ kJ/mol}$  of  $\alpha$ - $\text{AlH}_3$  was confirmed, in good agreement with previously reported values.

## 10.2.4 Chemical Properties of Aluminum Hydride

### 10.2.4.1 Thermal Stability and Decomposition of Aluminum Hydride

Quite often, attempts to isolate the non-solvated form of alane from the ether solution result in the decomposition of the complex to aluminum and hydrogen [425]. Six of the seven known polymorphs of solid aluminum hydride will dehydrogenate on their own at room temperature over a period of hours or days. Only  $\alpha$ - $\text{AlH}_3$  is stable enough at room temperature to be considered as a rocket propellant ingredient.

The flash-pyrolytic decomposition of  $\text{AlH}_3$  has been studied by kinetic spectroscopy at  $2477 \pm 20\text{ K}$  [303]. The major dissociation product seen in the flash pyrolysis of  $\text{AlH}_3$  was  $\text{AlH}$ . The existence of a subhydride  $\text{AlH}_2$  was postulated, and its role in the pyrolytic decomposition of  $\text{AlH}_3$  was correlated to the already observed species  $\text{AlH}$ .

Metallographic studies showed that decomposition of  $\text{AlH}_3$  occurs throughout the crystal, particularly at discontinuities, such as voids, cracks, and grain boundaries [378]. Ion probe mass spectrometry showed a higher lithium content near the surface than in the interior of the crystals. Lithium aluminum hydride was extracted from  $\text{AlH}_3$  and is believed to be responsible for nucleation sites which result in the decomposition of  $\text{AlH}_3$ .

The thermal stability of three different samples of  $\text{AlH}_3$  was tested at 298, 313, 333 or 353 K (25, 40, 60 or  $80^\circ\text{C}$ ) [318]. Three different samples were studied: Lot 07035 (untreated), Lot 11236 (Mg-doped) and Lot 11177B (Mg-doped, DPA-treated and hydrolyzed, pH 7). There was a distinct difference in thermal stability between the three samples, with Lot 11177B being significantly better than either of the others. Hydrogen was observed from Lot 11177B only at 353 K ( $80^\circ\text{C}$ ) after 15 days. These samples showed no detectable decomposition after 30 days at 333 K ( $60^\circ\text{C}$ ) and about 3% decomposition after 72 days at 333 K ( $60^\circ\text{C}$ ). Investigators at Dow observed approximately 1% decomposition of  $\text{AlH}_3$  (Lot 11177B) in 30 days at 333 K ( $60^\circ\text{C}$ ). It is generally agreed that  $\text{AlH}_3$  decomposes autocatalytically. The induction period associated with the decomposition was observed by Dow to vary significantly from sample to sample. A combination of the autocatalytic process, the poorly defined induction period and sample to sample variations all contributed to variations in these results reported by different laboratories. Based on these results, all compatibility studies were conducted using Lot 11177B. When the sample was heated from ambient to 413 K ( $140^\circ\text{C}$ ), hydrogen constituted approximately 90% of the evolved gases. See also [425].

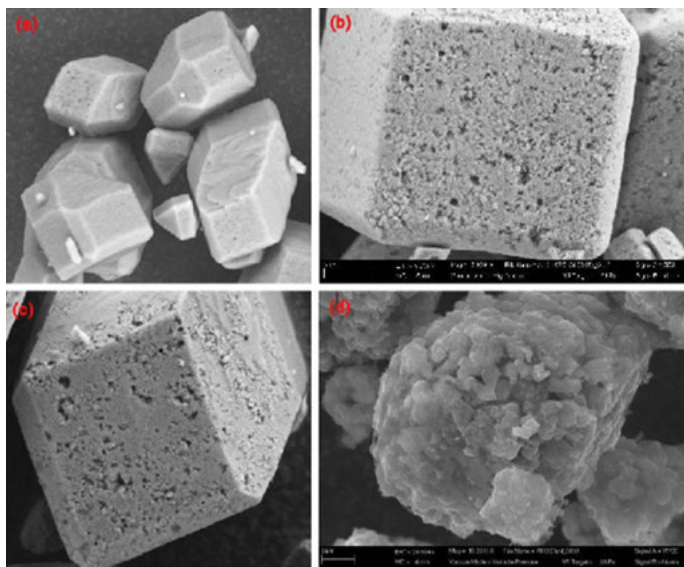
The temperature-dependent rate constants of aluminum hydride decomposition were determined by measuring the rate of isothermal hydrogen evolution between 333 and 413 K (60 and 140 °C) [426]. If aluminum hydride is intended as a reversible hydrogen storage medium for automobiles, it would be important to accelerate the decomposition and hydrogen release reaction. Particle size control and doping of  $\text{AlH}_3$  with small levels of alkali-metal hydrides (e.g.  $\text{LiH}$ ) results in accelerated desorption rates [427].

Decomposition kinetics of aluminum hydride were determined from gravimetric TGA data and volumetric vacuum thermal stability (VTS) results [428–430]. Chemical analysis showed the fresh samples had 88.30% (by mass) aluminum and 9.96% hydrogen. The average density, as measured by helium pycnometry, was  $1.486 \text{ g/cm}^3$ . Scanning electron microscopy showed that the particles were mostly composed of sharp-edged crystallographic polyhedra such as simple cubes, cubic octahedrons and hexagonal prisms. The decomposition kinetics of alane in argon atmosphere were examined by TGA to shed light on the mechanism of alane decomposition. Two kinetic models were successfully developed and used to propose a mechanism for the complete decomposition of alane and to predict its shelf life during storage. Alane decomposes in two steps: The slowest (rate-determining) step is solely controlled by solid-state nucleation of aluminum crystals. The fastest step is due to growth of the crystals. Thus, during decomposition, hydrogen gas is liberated and the initial polyhedral  $\text{AlH}_3$  crystals yield a final mix of amorphous aluminum and aluminum crystals. After establishing the kinetic model, prediction calculations indicated that alane can be stored in inert atmosphere at temperatures below 263 K (10 °C) for long periods of time (e.g., 15 years) without significant decomposition. After 15 years of storage, the kinetic model predicts ~0.1% decomposition, but storage at higher temperatures (e.g. 303 K = 30 °C) is not recommended.

The intrinsic and mechanically modified (ball-milled) thermal stabilities of the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases of  $\text{AlH}_3$  have been experimentally determined [431]. The TGA profiles of the  $\alpha$  and  $\gamma$  phases exhibited dehydriding reactions in the temperature range of 370–450 K. The amounts of hydrogen released were nearly 9 mass-%. The profile of the  $\beta$  phase showed continuous dehydriding reactions, which differed from the other two phases. The values of the enthalpy of dehydriding reactions  $\Delta H_{\text{dehyd}}$  were determined to be  $6.0 \pm 1.5$ ,  $-3$  to  $-5$ , and  $1.0 \pm 0.5 \text{ kJ/mol H}_2$  for the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases, respectively. The milling time dependences of the powder XRD measurement and thermal analyses indicated the occurrence of dehydriding reactions both in the  $\alpha$  and  $\gamma$  phases during ball-milling, but there was no drastic change in the  $\beta$  phase.

Alane splits completely into hydrogen and aluminum on heating at temperatures between 433 and 533 K depending on the heating rate. This reaction is of interest for hydrogen storage methods [432]. This endothermic process was observed with DSC and TGA, *in situ* XRD under argon and the residual crystallites were imaged by SEM (Figure 6). On dehydrogenation a nanostructured porous Al material emerges with





**Figure 6:** Decomposition of aluminum hydride (reprinted from [408] with permission of Dr. L. T. DeLuca 9-May-2021)

Legend: (a)  $\text{AlH}_3$  crystals before pyrolysis test at ICT; (b) porous structure after decomposition at 200 °C; (c) porous structure after decomposition at 400 °C; (d) amorphous Al in a pyrolysis furnace

specific surfaces up to 15–20 m<sup>2</sup>/g. The cuboid particles maintain their external shape while porosity develops in their internal shape [433, 434]. Similar tests then studied the oxidation of dehydrided particles in air [410, 435]. A thermal explosion risk may arise from a subsequent sudden Al oxidation of nanostructured, pyrophoric porous aluminum bodies as soon as they are exposed to air. If  $\text{AlH}_3$  is ever used as a hydrogen storage medium and the dehydrided porous Al, such as in the tank of an air/ $\text{H}_2$  fuel-cell powered automobile, is accidentally exposed to air, a fire hazard may result [436]. On dehydrogenation of  $\text{AlH}_3$ , a nanostructured pyrophoric Al material emerges with specific surfaces up to 15–20 m<sup>2</sup>/g. The surface areas depend on the heating rate because of a temperature-dependent crystallite growth. The resulting Al oxidizes up to 20–25% weight on air access forming an alumina passivation layer of 3–4 nm thickness on all exposed surfaces. The heat released from this Al oxidation induces a high risk to this type of hydrogen storage if the containment vessel might be accidentally destroyed. The kinetics of the dehydrogenation and the subsequent oxidation were investigated by thermal analysis. A reaction scheme was confirmed which consisted of a starting Avrami–Erofeev mechanism followed by formal 1st order oxidation on unlimited air access. The kinetic parameters, activation energies and pre-exponentials were evaluated and can be used to calculate the reaction progress and heat release rate.

Dehydrogenation precedes the burning of aluminum hydride in solid or hybrid rocket propellants at elevated pressures [437, 438]. The decomposition rate of aluminum hydride powder was measured at slightly elevated temperatures (400–500 K) using the pressure rise due to the released hydrogen [439]. The information is useful for understanding the combustion behavior of aluminum hydride when used in solid or hybrid rocket propellants. The thermolysis measurements fit well to an Arrhenius-type exponential fit, with a pre-exponential of  $3.29 \times 10^9 \text{ s}^{-1}$  and an activation energy of 97.6 kJ/mol.

The thermal decomposition of two polymorphs,  $\alpha\text{-AlH}_3$  and  $\gamma\text{-AlH}_3$ , was investigated by synchrotron XRD and thermal desorption spectroscopy (TDS) [440]. Activation energies, anisotropic volume expansions, and phase transformation paths were followed. The crystal structure data, including structure of hydrogen sublattice, and small charge transfer from the aluminum towards the hydrogen sites were observed during this high-resolution XRD study of  $\alpha\text{-AlH}_3$ .

$\alpha\text{-AlH}_3$  that was synthesized from  $\text{LiAlH}_4$  and  $\text{AlCl}_3$  was characterized by XRD and SEM and the thermal decomposition was investigated by TGA/DTG-DSC [441]. The kinetic parameters of the major decomposition reaction were calculated. The decomposition reaction kinetics of  $\alpha\text{-AlH}_3$  agreed with a nuclei production and nuclei growth model. The apparent activation energy, pre-exponential factor and mechanism function of the decomposition reaction of  $\alpha\text{-AlH}_3$  were  $E_a = 110.89 \text{ kJ/mol}$ ,  $\ln A = 26.94 \text{ s}^{-1}$ ,  $f(\alpha) = -\ln(1-\alpha)^{1/4}$ , respectively. The kinetic equation of the decomposition process can be expressed as

$$d\alpha/dT = (2.004 \times 10^{11}/\beta) \exp(-1.33378 \times 10^4/T)(1-\alpha)[- \ln(1-\alpha)]^{3/4}$$

To better understand the desorption properties of hydrogen in alane, thermodynamically stable  $\alpha\text{-AlH}_3$  was synthesized [349]. The dependence of phase formation on synthesis pathways and the effect on rates of hydrogen evolution were investigated, and the results were compared with those for  $\gamma\text{-AlH}_3$ . For desorption, all hydrogen atoms of alane evolved under an isothermal condition at 411 K (138 °C) in less than 1 h, and the sample completely transformed to pure aluminum. The results showed that the total amount of desorbed hydrogen from  $\alpha\text{-AlH}_3$  exceeded 9.05 mass-%.

The presence of elemental Al contamination had no impact on the friction sensitivity or impact sensitivity of pure  $\alpha\text{-AlH}_3$  [442]. However, the presence of Al increased the decomposition rate of  $\alpha\text{-AlH}_3$ . In the DSC, the onset temperature of  $\text{Al}/\alpha\text{-AlH}_3$  was lower than that of pure  $\alpha\text{-AlH}_3$ . The dehydrogenation endotherm of  $\alpha\text{-AlH}_3$  had a maximum at 449 K (176 °C).

#### 10.2.4.2 Long-Term Storage Stability of Aluminum Hydride

The storage stability of various samples of aluminum hydride including unstabilized macrocrystalline, magnesium-doped and magnesium-doped, diphenylacetylene (DPA)-treated  $\alpha\text{-AlH}_3$  was monitored under a surveillance program [443]. These samples were tested by themselves at 258, 298, and 313 K (–15, 25, and 40 °C), and in

propellant at 298, 313, and 333 K (25, 40, and 60 °C). Results of surveillance of neat aluminum hydride continue to indicate greater improvement in 298 K (25 °C) stability than was achieved with these samples at 333 K (60 °C). Two samples which previously had suffered 1% decomposition in 18.8 and 25.5 days at 333 K (60 °C) had decomposed by only 0.05 and 0.019%, respectively, after 1 year at 298 K (25 °C). Results of surveillance of aluminum hydride propellant showed decreasing gas generation rates with time. At 298 K (25 °C), a double base propellant containing unstabilized microcrystalline hydride decomposed approximately 0.28 and 0.09% during the first and second year, respectively, and samples containing stabilized aluminum hydride, decomposed only approximately 0.10% during the first year. Small amounts of water in the environment which the aluminum hydride was subjected to have been found to prevent the typical autocatalytic shaped decomposition curve. Instead, an initial gassing period is observed followed by excellent stability. Treatments utilizing small amounts of controlled hydrolysis to improve stability were then recommended. One sample of magnesium-doped aluminum hydride had decomposed only 0.055% after 2 years [444]. Many samples which demonstrated much better 333 K (60 °C) stability were being studied. Correlating aluminum hydride decomposition data using the Avrami–Erofeev equation gave an average activation energy of 96 kJ/mol (23 kcal/mol). High stability magnesium-doped samples have shown even higher activation energies. The equations used for correlating the decomposition data can also be used for predicting the 298 K (25 °C) storage stability from the decomposition data at a higher temperature. The weakest part of this correlation is in the assumption of a particular activation energy. An *n*-butylamine treated sample studied in the neat surveillance program was expected to require 1–3 years to decompose 0.03% based on 2 possible activation energy values.

Once aluminum hydride is embedded in solid propellants, its shelf life may be limited by interactions with other propellant ingredients. For *n*-butylamine passivated Mg-doped aluminum hydride decomposing at the rate of approximately 0.04% per year at 295 K (22 °C), a shelf life of a 1-m (40-in.) web was predicted to be less than 6 months. In the absence of any scavenging or *in situ* stabilizing processes, therefore, at least a fivefold stability/compatibility improvement would be required, i.e., <0.008% decomposition per year, to achieve the desired propellant shelf life [445–447].

#### 10.2.4.3 Reactions of Aluminum Hydride

AlH<sub>3</sub> showed good compatibility with HAP and AP after 70 days at 313 K (40 °C) [318]. The difluoroamino-compound poly-[1,2-bis(difluoroamino)-2,3-propylene oxide] (P-BEP) binder prepolymer was also reasonably compatible with AlH<sub>3</sub> at 313 K (40 °C), but all three NF plasticizers promoted the decomposition of AlH<sub>3</sub> at 353 K (80 °C). No increase in the amount of hydrogen evolved was observed at 333 K (60 °C) and lower, over the time interval studied. Acrylate binder prepolymers posed no serious compatibility problems with AlH<sub>3</sub> and may in fact improve its thermal stability.

Neither HAP or AP appeared to promote the evolution of gaseous decomposition products at 298, 313 or 333 K (25, 40, or 60 °C) for time periods up to 70 days. After 70 days at 353 K (80 °C), the amount of hydrogen evolved from the AP/AlH<sub>3</sub> mixture was the same, within the limits of reproducibility, as that expected from pure AlH<sub>3</sub>. For the HAP mixture, at the same time interval and temperature, the hydrogen evolution was three to four times greater than would be expected from neat hydride.

### Reactions of Aluminum Hydride with Lewis Bases

Adducts of aluminum hydride with Lewis bases are thermally more stable than aluminum hydride itself and can be used as hypergolic fuels. The preferred Lewis base would be ammonia or trimethylamine.

Reaction of aluminum hydride with an excess of trimethylamine gives a white, solid residue of AlH<sub>3</sub>•2N(CH<sub>3</sub>)<sub>3</sub> which sublimes undecomposed in vacuum at 30–40 °C and melts at 368 K (95 °C) [413]. The adduct is a monomer readily soluble in ether, benzene or THF. If one used only a 1:1 molar ratio of AlH<sub>3</sub> and NMe<sub>3</sub>, a more reactive hydride is formed that reacts with air.

The molecular structure of trimethylamine alane, H<sub>3</sub>AlN(CH<sub>3</sub>)<sub>3</sub> was determined by gas phase electron diffraction [448]. The Al–N bond distance in this complex is significantly shorter than the Al–N bond distance in (H<sub>3</sub>C)<sub>3</sub>AlN(CH<sub>3</sub>)<sub>3</sub> and significantly longer than the Al–N bond distances in (H<sub>4</sub>B)<sub>3</sub>AlN(CH<sub>3</sub>)<sub>3</sub> and Cl<sub>3</sub>AlN(CH<sub>3</sub>)<sub>3</sub>.

Tertiary amine-aluminum hydride complexes have gained interest due to their application as chemical reducing agents and in aluminum thin-film deposition. Various alane amine complexes have been made and studied previously, but these compounds were not formed directly using pressurized hydrogen. The direct reaction of catalyzed aluminum, a tertiary amine, and hydrogen in a common solvent proceeded to form an alane amine adduct at moderate pressures and temperatures [449]. A complex of aluminum hydride was formed with dimethylethylamine by this technique. A vibrational analysis of the product of these reactions by Raman and IR clarified the molecular and vibrational structure of alane amine complexes formed by direct hydrogenation. A new method for the formation of alane triethylamine used the direct hydrogenation of dimethylethylamine and catalyzed aluminum followed by transamination with triethylamine. This may lead to a new low-energy method to regenerate AlH<sub>3</sub> from catalyzed recycled aluminum and hydrogen gas and thus close the hydrogen storage cycle.

AlH<sub>3</sub>-amine and Al(CH<sub>3</sub>)<sub>3</sub>-amine adducts were investigated as potential additives for rocket propellant formulations [450]. The investigation included the calculation of property predictions for a variety of known and notional adducts. Property predictions were based on results from quantum chemistry calculational methods. Gas-phase property predictions included Al–N bond dissociation energies (BDEs) and enthalpies of formation at 298 K [ $\Delta H_f(G)(298)$ ]. Condensed-phase property predictions included enthalpies of sublimation [ $\Delta H_s(298)$ ], enthalpies of formation at 298 K [ $\Delta H_f(cond)(298)$ ], and densities ( $\rho$ ). Values derived from measured data or

higher level computational methods were obtained for these properties from open literature sources. These values were employed both to develop and to validate the estimation methods. Assessments of the thermal and/or air stabilities of some adducts were also identified in the course of the literature search, and an attempt was made to correlate the assessments with Al—N BDEs. The  $[\Delta H_f(\text{cond})(298)]$  estimates were employed as input for thermochemical code-based predictions for the specific impulse these adducts could potentially generate when combined with inhibited red fuming nitric acid (IRFNA) as the oxidizer in a rocket engine. Results from the study indicated that several of these adducts warrant further investigation as additives for liquid/gel or solid (hybrid) rocket motor fuels.

The structures adopted by a range of aluminum hydride complexes  $\text{AlH}_3 \bullet n\text{L}$ , ( $n = 1$  or  $2$ ), have been explored in detail to identify the factors that determine the value of  $n$ , and whether a monomeric or dimeric arrangement is preferred for the 1 : 1 complexes [451]. Single-crystal XRD, vibrational, and NMR spectroscopies, and thermal analysis data have been collected. DFT calculations have been performed for  $\text{AlH}_3 \bullet n\text{L}$  species, and  $\text{p}K_a$  values have been collated for a series of amine and phosphine ligands (L). The  $\text{p}K_a$  of the ligand L exerts an important influence on the type of complex formed: as the basicity of L increases, a monomeric structure is favored over a dimeric arrangement. Dimeric amine complexes form if  $\text{p}K_a < 9.76$ , while monomeric complexes are preferred when  $\text{p}K_a > 9.99$ . The steric requirements of L also influence the structural preference: bulky ligands with large cone angles ( $> 163^\circ$ ) tend to favor formation of monomers, while smaller cone angles ( $< 125^\circ$ ) encourage the formation of dimeric or 1 : 2 adducts. Raman spectroscopy and DFT calculations have been particularly helpful in elucidating the stoichiometric preferences and structures of complexes that have been contentious. These included  $\text{AlH}_3 \bullet \text{NMe}_2\text{Et}$ ,  $\text{AlH}_3 \bullet \text{NMe}_3$ , and  $\text{AlH}_3 \bullet n\text{Et}_2\text{O}$ .

One of the thermally most stable  $\text{AlH}_3$  adducts was with tetramethylethylenediamine (2,5-dimethyl-2,5-diazahexane). This compound could be heated to 406 K (133 °C) for long periods without decomposition [452].

### Oxidation of Aluminum Hydride

The oxygen sensitivity of aluminum hydride is dependent on its purity. Generally, all aluminum hydride processes are conducted under an inert gas. The autoxidation of fresh aluminum hydride may lead to accidental ignition in air. Once the particles are passivated, the ignition hazard is reduced. The oxidation of aluminum hydride particles is similar to the oxidation of nanoaluminum, at first a passivation layer forms, and subsequent oxidation is controlled by diffusion of oxygen through the passivation layer. In this second diffusion-controlled conversion step, the diffusion of oxygen occurs from the hole or pore surface of the particle to the bulk metal or the metal to the surface [410]. The oxidation of aluminum hydride is sometimes preceded by or accompanied by loss of hydrogen. A passivation layer forms on aluminum hydride in air, and a similar passivation layer forms in moist air or in water vapor, protecting particles from further reaction.

The combustion of aluminum hydride in air leads to combustion products that contain  $\approx 50\%$  aluminum nitride (by weight) [453]. The formation mechanism of the final combustion products of aluminum hydride is similar to that of ultradisperse metallic aluminum powder burning in air.

#### 10.2.4.4 Ignition of Aluminum Hydride

The ignition of aluminum hydride precedes combustion. Combustion of aluminum hydride will be dealt with in more detail in future sets “Solid Propellants” and “Hybrid Propellants.” Ignition of aluminum hydride may be accidental, such as during the preparation or storage or processing of aluminum hydride, or intentional, such as when it is used as an ingredient in solid rocket propellants.

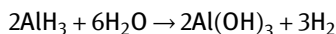
An experimental investigation on the ignition behavior of  $\alpha\text{-AlH}_3$  used two separate modified T-jump experiments [454]. In each experiment, a small amount of material was placed onto a platinum wire, which was heated rapidly through resistive heating. As a result, both ignition and hydrogen release temperatures were studied for heating rates ranging from  $10^4$  to  $10^5$  K/s. The ignition temperature was studied at ambient pressure in air,  $\text{CO}_2$ , and mixtures of argon with oxygen. Both the hydrogen release and ignition temperature increased as the heating rate increased. Hydrogen release temperatures ranged from approximately 650 to 1200 K. For conditions in which the particles would ignite, the environment did not play a significant role in the ignition temperature, beyond a critical oxygen mol fraction of  $\chi_{\text{O}_2} > 0.05$ . Sample average burning times decreased by a factor of about 3 when the oxygen mol fraction was increased from 0.1 to 0.5. Within experimental uncertainty, there was no difference in the ignition temperature in air or  $\text{CO}_2$ . In both cases the ignition temperature increased as the heating rate increased starting from just below the melting temperature of aluminum (933 K), at the lowest heating rate, to about 1500 K at the highest heating rate.

In order to determine the high-pressure ignition characteristics of  $\alpha$ -aluminum hydride, to quantify the ignition temperature and to observe the ignition process, aluminum hydride particles were heated on a platinum filament at heating rates of approximately  $1 \times 10^5$  K/s in a pressure vessel for pressures ranging up to about 7 MPa [455]. Experiments were conducted in air, argon, and nitrogen as the pressurizing environment. The dehydrogenation of aluminum hydride was not a function of pressure under the conditions tested. In addition, ignition temperatures were found to be approximately linearly related to pressure until pressures exceeded about 0.4 MPa, at which point they remained constant through the remaining highest pressures tested. High-speed imaging of the ignition process showed a dramatic change in the ignition behavior for pressures above 0.4 MPa, corresponding to what is assumed to be a threshold for  $\text{H}_2$ /air autoignition or perhaps even an explosion limit. The combustion behavior of aluminum hydride particles shared many traits with aluminum particles, including a diffusion flame surrounding the particle, spinning, jetting and explosions/fragmentation. Quenched particles showed clear evidence of gas phase com-

bustion with parent particles containing nanofeatures, which had condensed from the gas phase. The results of this study provide additional understanding of the ignition and combustion process of aluminum hydride at extreme conditions, which may be useful in modeling efforts or in the development of solid propellants.

#### 10.2.4.5 Hydrolysis of Aluminum Hydride

Aluminum hydride reacts with water only slowly because the particles are quickly coated with a passivating layer of impermeable  $\text{Al}(\text{OH})_3$  deposits:



This reaction would be a good source of storable hydrogen, but it is not reversible and it would be more difficult to regenerate  $\text{AlH}_3$  from  $\text{Al}(\text{OH})_3$  than from metallic Al.

The exothermic reaction between aluminum hydride and water was studied using a microcalorimeter [456]. The results showed that the standard enthalpy of formation and standard molar heat capacity of  $\text{AlH}_3$  obtained by an extrapolation method were  $-11.49 \text{ kJ/mol}$  and  $45.22 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The values of activation energy  $E$ , pre-exponential factor  $A$  and the reaction order  $n$  for the reaction of  $\text{AlH}_3$  and water over the temperature range from 313 to 328 K were  $69.41 \text{ kJ/mol}$ ,  $108.46 \text{ s}^{-1}$ , and about 1.033, respectively. Aluminum hydride is relatively reactive and may be incompatible with many other propellant ingredients it comes in contact with.

#### 10.2.4.6 Analysis of Aluminum Hydride

Analysis of three different aluminum hydride samples by mass spectrometry with a spark ion source showed that all three samples had contamination from lithium and boron (most likely introduced with lithium borohydride used in the synthesis of  $\text{AlH}_3$ ) and magnesium (a contaminant in the  $\text{AlCl}_3$  used in the synthesis of  $\text{AlH}_3$ ) [457]. The apparatus was able to detect contaminants down to 10 ppm.

### 10.2.5 Other Applications of Aluminum Hydride

#### 10.2.5.1 Gelled Hydrazine with Aluminum Hydride Suspensions

Aluminum hydride has been suspended in gelled hydrazine to be used as a fuel in bipropellant engines or maybe even as a monopropellant by itself. The objective of the study was to find gelling agents that are compatible not only with hydrazine, but also with the  $\text{AlH}_3$  suspended in it [458]. The off-gas generation rate of these formulations was very nearly the same as the off-gas generation rate of an equivalent amount of neat LMH-1 by itself [459]. The presence of water in the hydrazine substantially increased the initial off-gas generation rate of LMH-1/hydrazine formulations, presumably due to reaction of the water with LMH-1. Gelling agents such as lightly cross-linked ammonium polyacrylates have been selected for formulations into LMH-1 heterogeneous systems on the basis of polymeric structure and compatibility. Heterogeneous gels with acrylamide/acrylic acid copolymers have been especially promising due to

their good physical integrity and cohesiveness. Work with ammonium polyacrylate gellants showed that a certain chemical structure is advantageous in obtaining desirable gel characteristics [460]. When pretreated LMH-1 was combined with hydrazine, the amount of gas generated in the initial reaction was reduced and the long-term gas generation rate decelerated in comparison to untreated LMH-1 in hydrazine [461]. The polyacrylamide gelling agent slightly increased the amount of initial gassing of the gelled LMH-1/hydrazine propellant, but the long-term stability equaled the stability of ungelled LMH-1/hydrazine. Fifty pounds of LMH-1/hydrazine heterogeneous propellant was prepared and sent to AFRPL for performance evaluation [462].

#### 10.2.5.2 Aluminum Hydride as a Hydrogen Storage Medium

Aluminum hydride has been evaluated extensively as a hydrogen storage (ideally, a reversible hydrogen storage) material. If alane is to be used as a hydrogen storage medium new and novel methods of regenerating alane from spent aluminum must be found. This application is responsible for the majority of publications on aluminum hydride during the past decades. If aluminum hydride comes to be used as a hydrogen storage medium in automobiles, the expanded availability of aluminum hydride and a better understanding of its properties might benefit its use as a rocket propellant and *vice versa*.

An entire chapter in the book on hydrogen storage [463] is devoted to aluminum hydride and provides a good summary of its properties [464]. With a high gravimetric  $H_2$  storage capacity of 10.1 mass-% H and a hydrogen storage density of  $1.48 \text{ g/cm}^3$ ,  $AlH_3$  makes a good hydrogen storage medium. Aluminum hydride decomposes to its elements above 333 K ( $60^\circ\text{C}$ ) with no side reactions. The properties of  $AlH_3$  were explored in depth, in particular the  $\alpha$ ,  $\alpha'$  and  $\gamma$  polymorphs, of which  $\alpha'$ - $AlH_3$  was reported for the first time, free from traces of other polymorphs [402]. Thermal analysis of  $\alpha$ ,  $\alpha'$  and  $\gamma$ - $AlH_3$  was conducted using DSC, TGA, and pressure composition temperature (PCT) methods, and the results obtained were compared with each other and with literature data. The thermal decomposition of  $AlH_3 \cdot nEt_2O$  was followed by TEM imaging, enabling the pathway and mechanism of decomposition to be identified. Low-level hydrogenation of Al using  $H_2$  gas has been achieved in supercritical fluid reaction media. PCT measurements of hydrogenated samples of Ti-doped Al indicated that 0.33 mass-% H was absorbed in supercritical  $Me_2O$ , while 0.27 mass-% H was absorbed in supercritical  $CO_2$ . The hydrogenation appears to be limited to the surface of the Al particles. See also [465, 466].



## Ternary Metal Hydrides

### 11 Complex Metal Hydrides

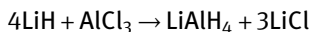
While the simple binary metal hydrides of the  $\text{MeH}_n$  type are more likely to be used as rocket propellants, they are not always easy to make. Some of the complex hydrides of the  $\text{Me}^1\text{Me}^2\text{H}_n$  type are more readily available from commercial sources but there is very little experience in using them as rocket propellants. A chapter on complex metal hydrides could fill a book in its own right but we have not attempted to compile a complete review of complex metal hydrides as rocket propellants in this book. Several complex metal hydrides have been tested as ingredients in solid gas generants for generating hydrogen or deuterium gas at short notice, such as for use in a chemical laser for military applications. A mere sampling and incomplete collection of randomly selected references is assembled here in this section, including some review publications on complex hydrides and their potential application as rocket propellants [467, 468]. Many of the complex metal hydrides that were once considered as rocket fuels are now being evaluated as hydrogen storage media, but it is not easy to design a reversible and easily regenerable hydrogen storage cycle based on complex metal hydrides [469]. A book on hydrogen storage contains an entire chapter on complex metal hydrides as hydrogen storage media for fuel cell and other energy storage and conversion applications [470].

Metal borohydrides (also called metal boranates), although they would fit nicely into this current chapter on complex metal hydrides, will be discussed in the chapter “Boranes.” That leaves only the complex magnesium and aluminum hydrides to be discussed in the current chapter.

#### 11.1 Lithium Aluminum Hydride

Aluminum hydride forms complex hydrides (called alanates) with many alkali metal and alkaline earth metal hydrides and also with boranes. The most important example is lithium aluminum hydride, lithium alanate, lithium aluminum tetrahydride, lithium tetrahydridoaluminate,  $\text{LiAlH}_4$ , CAS RN [16853-85-3], which is widely used in the synthesis of other metal hydrides and in the selective reduction of organic unsaturated compounds. Lithium aluminum hydride has been used in the synthesis of aluminum hydride. Lithium aluminum hydride suspensions have been tested for the hypergolization of hydrocarbon fuels but have not found actual flight applications. Lithium aluminum hydride has been considered as a hydrogen storage material because it contains 18.5 mass-% hydrogen but it requires a high decomposition temper-

ature and is too difficult to regenerate [470]. Lithium aluminum hydride can be made by reaction of aluminum chloride with an excess of lithium hydride



Lithium aluminum hydride and other alkali metal aluminum hydrides can be made by direct reaction from the elements in tetrahydrofuran at 423 K (150 °C) under 13.8 MPa (2000 psi) hydrogen pressure [471].

### 11.1.1 Physical Properties of Lithium Aluminum Hydride

Physical properties of lithium aluminum hydride are summarized in Table 18.

**Table 18:** Physical properties of lithium aluminum hydride.

| Property                                | SI units               | Other units                  | References |
|-----------------------------------------|------------------------|------------------------------|------------|
| Molecular mass                          | 37.954 g/mol           | 26.35 mol/kg                 | [10]       |
| Melting point                           | 398 K                  | 125 °C                       | —          |
| Density                                 | 0.92 g/cm <sup>3</sup> | 0.917 g/cm <sup>3</sup>      | —          |
| Standard enthalpy of formation at 298 K | −119 kJ/mol            | −28.4 kcal/mol               | [472]      |
|                                         | −109.6 kJ/mol          | −690 cal/g = −26.19 kcal/mol | [286]      |
|                                         | −117.15 kJ/mol         | −28.0 kcal/mol               | [10]       |
|                                         | −103.2 ± 9.2 kJ/mol    | −24.67 ± 2.21 kcal/mol       | [473]      |
|                                         | −100.8 kJ/mol          | −24.1 kcal/mol               | —          |
|                                         | −117 kJ/mol            | −28 kcal/mol                 | —          |

### 11.1.2 Chemical Properties of Lithium Aluminum Hydride

Lithium aluminum hydride is stable in dry air but reacts with explosive force with water, often with spontaneous ignition. It reacts instantly and hypergolically with hydrogen peroxide, nitric acid, or fluorine.

### 11.1.3 Decomposition of Lithium Aluminum Hydride

The thermal decomposition of  $\text{LiAlH}_4$  as a source of hydrogen has been investigated using isothermal kinetics, DTA, and TGA [474]. The DTA confirmed that the decomposition occurs in four stages. The first stage accounted for only a small percentage of the evolved  $\text{H}_2$  and on occasion exhibited properties of an explosion. Contrary to prior work, the kinetics of the second stage were shown to follow a modified Prout-Tompkins relation. The isothermally determined activation energy of 99.6 kJ/mol (23.8 kcal/mol) for this stage was the same at temperatures both above and below a phase change seen in the DTA; however, the pre-exponential factors

differed in the two regions. The third stage, corresponding to the stoichiometric equation



was found to follow first-order kinetics, with an activation of 196 kJ/mol (46.9 kcal/mol).

The slow pyrolysis of lithium aluminum hydride proceeds by a successive dehydrogenation of the fuel in three stages over a temperature range between 483 and 533 K (210 and 460 °C) [475, 476]. The combustion of lithium aluminum hydride follows a similar multi-stage process in which the pyrolytic dehydrogenation is followed by an afterburning of the metal substrate. Experimental studies were performed to determine the delay times between successive stages for solid mixtures of lithium aluminum hydride with selected oxidizers. Time-resolved spectrographic techniques were used to determine the duration of these stages. Studies were performed using  $\text{Li}_2\text{O}_2$  and  $\text{NH}_4\text{NO}_3$  oxidizers over a particle size range between 75 and 300  $\mu\text{m}$  and O/F mixture ratios of between 0.5 and 3.0. Ignition delay times for the initial reaction were found to vary between 5 and 40 ms for the first stage and 10–120 ms for the second stages.

#### 11.1.4 Applications of Lithium Aluminum Hydride

Lithium aluminum hydride is widely used for the synthesis of other hydrides and for reduction of organic compounds. A solution of lithium aluminum hydride in ether, THF or dioxane and turpentine was patented as a hypergolic fuel in combination with nitric acid [477].

### 11.2 Sodium Aluminum Hydride

Sodium aluminum hydride, sodium alanate,  $\text{NaAlH}_4$ , CAS RN [13770-96-2],  $M = 54.00 \text{ g/mol}$ , is a useful reagent in the preparation of other metal hydrides but is not likely to be used as a rocket fuel. In contrast to sodium borohydride, sodium aluminum hydride is very sensitive to moisture and there are few solvents for it. Sodium aluminum hydride has been considered as a reversible hydrogen storage material but the kinetics of dehydrogenation as well as of rehydrogenation are too slow for any practical application unless it is doped with a suitable catalyst such as  $\text{TiCl}_3$ . There is also a similar sodium aluminum hydride with the formula  $\text{Na}_3\text{AlH}_6$ .

#### 11.2.1 Physical Properties of Sodium Aluminum Hydride

Physical properties of sodium aluminum hydride  $\text{NaAlH}_4$  are listed in Table 19.

**Table 19:** Physical properties of sodium aluminum hydride.

| Property                                | SI units               | Other units        |
|-----------------------------------------|------------------------|--------------------|
| Molecular mass                          | 54.00 g/mol            | 18.52 mol/kg       |
| Melting point                           | 451 K                  | 178 °C             |
| Density at 298 K                        | 1.28 g/cm <sup>3</sup> | —                  |
| Standard enthalpy of formation at 298 K | −115 ± 4 kJ/mol        | −27.5 ± 1 kcal/mol |

### 11.2.2 Decomposition of Sodium Aluminum Hydride

If sodium aluminum hydride were to be used as a reversible hydrogen storage medium for automotive propulsion, the controlled decomposition at the point of end use could be accelerated by titanium catalysts [478].

### 11.3 Magnesium Aluminum Hydride

Magnesium aluminum hydride, magnesium alanate,  $\text{Mg}(\text{AlH}_4)_2$ , CAS RN [17300-62-8],  $M = 86.33 \text{ g/mol}$ , is a lesser known complex hydride. There are no known applications or evaluations of magnesium aluminum hydride as a rocket propellant. Magnesium aluminum hydride has been added to  $\text{AlH}_3$  as a stabilizer. Magnesium aluminum hydride can be prepared by a metathesis reaction of magnesium chloride and sodium alanate followed by purification.

Magnesium alanate has been considered as a material for reversible hydrogen storage. It has a density of  $1.046 \text{ g/cm}^3$ , an enthalpy of formation of  $-152.7 \text{ kJ/mol}$  ( $-36.5 \text{ kcal/mol}$ ) and decomposes at 413 K (130 °C). If it should ever be used on a wider scale for that application, it might become more readily available to be used in rocket propellants. Magnesium alanate was investigated by XRD and TGA and mass spectrometry (MS) of the evolved gas [479]. Thermal analysis showed a decomposition with a release of hydrogen proceeding in two major steps. Measured in vacuum, the peak decomposition temperature of the first step was 436 K (163 °C) and the residue at 473 K (200 °C) consisted of  $\text{MgH}_2$  and Al which continues to release hydrogen and transforms into an  $\text{Al}_3\text{Mg}_2/\text{Al}$  mixture at higher temperatures. In the first decomposition step only 6.6 mass-% of hydrogen was released.

Magnesium aluminum hydride can be made by reactions of lithium and sodium aluminum hydrides with magnesium halides in ether solvents [480, 481]. The ability of these reactions to produce magnesium aluminum hydride depended on the nature of the alkali metal, the halide, the solvent, and the solubility of the alkali metal halide by-product. Contrary to previous reports,  $\text{Mg}(\text{AlH}_4)_2$  could not be prepared by the reaction of  $\text{LiAlH}_4$  and  $\text{MgBr}_2$  in diethyl ether. Magnesium aluminum hydride was prepared in a pure form as the ether solvate by the reactions of  $\text{NaAlH}_4$  and  $\text{MgCl}_2$  in THF or  $\text{NaAlH}_4$  and  $\text{MgBr}_2$  in diethyl ether. Magnesium aluminum hydride is insoluble in diethyl ether

and tetrahydrofuran; thus, it was separated from the NaCl and NaBr by-products by Soxhlet extraction. See also [482, 483].

Magnesium aluminum hydride  $\text{Mg}(\text{AlH}_4)_2$  and calcium aluminum hydride  $\text{CaAlH}_5$  can be synthesized by direct ball-milling of  $\text{AlH}_3$  and  $\text{MgH}_2$  or  $\text{AlH}_3$  and  $\text{CaH}_2$  hydrides [484]. The XRD profiles indicated crystalline compounds.

Magnesium aluminum hydride melts at  $413\text{ K} = 140^\circ\text{C}$  under decomposition and its standard enthalpy of formation is  $-96.6\text{ kJ/mol} = -23.1\text{ kcal/mol}$ . PEPCODED.DAT lists properties of magnesium aluminum hydride as  $\Delta H_f^{298} = -131.8\text{ kJ/mol} = -365\text{ cal/g} = -31.5\text{ kcal/mol}$  and a density of  $\rho = 1.046\text{ g/cm}^3 = 0.0378\text{ lb/in.}^3$  [286]. Other sources list an enthalpy of formation of  $-152.7\text{ kJ/mol}$  ( $-36.5\text{ kcal/mol}$ ).

## 12 Silicon Hydrides (Silanes)

Although silicon and hydrogen are two of the most common elements of the cosmos, their combination, silicon hydrides, are not occurring naturally due to their reactivity with oxygen, immediately combusting to water and silicon dioxide, both combustion products with highly negative enthalpies of formation, thus driving the combustion reaction in the direction of the most stable products.

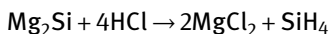
Silanes have been considered as fuels mostly for air-breathing propulsion, and not so much for rocket propulsion. They can also be used as hypergolic slug igniter fluids with conventional, non-hypergolic fuels.

The main disadvantage of using silanes as rocket propellants is the formation of silicon dioxide slag which is likely to clog the nozzle throat and injector orifices with a glassy coating. In most cases that would mean that the rocket can be started only once; however, at one time, silicone oil has been deliberately added to Agena fuels to provide for a protective coating of silicon dioxide in regeneratively cooled rocket engines. In that case the silicon dioxide film deposition was considered advantageous instead of troublesome, but the Agena engines had to fly only once.

It has been speculated that on distant planets where no carbon can be found in the soil, but somehow water or another source of hydrogen is available, the abundant silicon in minerals could be used to synthesize *in situ* resource utilization (ISRU) silanes as fuels for the trip home.

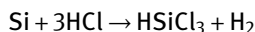
### 12.1 Preparation of Silicon Hydrides (Silanes)

Silane can be prepared by the reaction of hydrogen chloride with magnesium silicide:



This process gives a mixture of silanes, so-called crude silane (in analogy to crude oil), consisting of about 40%  $\text{SiH}_4$ , 30%  $\text{SiH}_2$ , 15%  $\text{Si}_3\text{H}_8$ , 10%  $\text{Si}_4\text{H}_{10}$ , and 7% higher

silanes [485]. Monosilane can also be prepared from metallurgical grade silicon in a two-step process. First, silicon is treated with hydrogen chloride at about 573 K (300 °C) to produce trichlorosilane,  $\text{HSiCl}_3$ , along with hydrogen gas:



The trichlorosilane is then converted to a mixture of silane and silicon tetrachloride by a disproportionation (redistribution) reaction which requires a Lewis acid catalyst:



Another, more expensive route to silane is the reduction of  $\text{SiCl}_4$  with lithium aluminum hydride  $\text{LiAlH}_4$ .

## 12.2 Physical Properties of Silicon Hydrides (Silanes)

Silane, silicon tetrahydride, tetrahydridosilicon, monosilane,  $\text{SiH}_4$ , CAS RN [7803-62-5] is a structural analog to methane. Its homologue, disilane,  $\text{Si}_2\text{H}_6$ , is a colorless gas. Physical properties of silanes are summarized in Table 20.

**Table 20:** Physical properties of silanes.

| Property                                           | SI units                                 | Other units         | References |
|----------------------------------------------------|------------------------------------------|---------------------|------------|
| <b>Silane <math>\text{SiH}_4</math></b>            |                                          |                     |            |
| Molecular mass                                     | 32.1173 g/mol                            | 31.136 mol/kg       | [10]       |
| Freezing point                                     | 88.1 K                                   | −185 °C = −301 °F   | [312]      |
| Boiling point                                      | 161 K                                    | −111.8 °C = −170 °F |            |
| Liquid density at 188 K                            | 0.68 g/cm <sup>3</sup>                   | —                   |            |
| Viscosity, vapor, at 298 K                         | 115.66 μPs                               | 115.66 μPs          | [486]      |
| Viscosity, liquid, at 100 K                        | —                                        | 0.48 cPs            | [486]      |
| Thermal conductivity, vapor, at 298 K              | 0.0228 W m <sup>−1</sup> K <sup>−1</sup> | —                   | [486]      |
| Enthalpy of formation, gas                         | +34.31 kJ/mol                            | +8.2 kcal/mol       | [10]       |
|                                                    | +30.5 kJ/mol                             | +7.3 kcal/mol       | [487]      |
| <b>Disilane <math>\text{Si}_2\text{H}_6</math></b> |                                          |                     |            |
| Molecular mass                                     | 62.2186 g/mol                            | 16.07 mol/kg        | [10]       |
| Freezing point                                     | 141 K                                    | −132.5 °C = −206 °F | [312]      |
| Boiling point                                      | 259 K                                    | −14.5 °C = 7 °F     |            |
| Liquid density at 253 K                            | 0.686 g/cm <sup>3</sup>                  | —                   |            |
| Viscosity, liquid, at 298 K                        | —                                        | 0.148 cPs           | [486]      |
| Viscosity, gas, at 298 K                           | —                                        | 97.6 μPs            | [486]      |

The standard enthalpy of formation of silane gas is +34.31 kJ/mol (+8.2 kcal/mol). With a positive enthalpy of formation, silane can decompose spontaneously into its ele-

ments if heated suddenly, as in a shock tube. The vapor pressure of silane in the temperature range 93.8–161.7 K can be calculated from the Antoine equation [10]

$$\log_{10}(P) = 4.22228 - [703.987/(T + 5.352)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin.

Silanes have higher densities than hydrocarbons, due to their much higher molecular masses when compared to their relatives in structure, the hydrocarbons. Also, their liquid temperature range is wider, which is a benefit for non-cryogenic liquid rocket propellants.

The most striking difference of silanes when compared to the alkanes are their heats of formation. While for linear silicon hydrides with the general formula  $\text{Si}_n\text{H}_{2n+2}$ , where  $n$  denotes the chain length, i.e. the number of Si atoms contained in each species, the heats of formation increase by about +40 kJ/mol per  $\text{SiH}_2$  group, the heats of formation of the corresponding alkanes decrease by about 20 kJ/mol per  $\text{CH}_2$  group. Cyclic silanes have even higher enthalpies of formation due to the strain in the rings. Therefore, the decomposition of cyclic silanes in a combustion chamber releases additional energy which may be converted into additional thrust for propulsion.

First-principle computations were performed on the  $n$ -silane series ( $\text{Si}_n\text{H}_{2n+2}$ ,  $n = 1 - 10$ ) [488]. The enthalpy of formation ( $\Delta H_f$ ), Gibbs free energy of formation ( $\Delta G_f$ ), bond length, and bond dissociation energy (BDE) for both the Si–Si and Si–H bonds were predicted from computations. The computed values of  $\Delta H_f$  and  $\Delta G_f$  for lower silanes ( $n \leq 5$ ) were compared to experimental values and used as benchmarks. The increments of the  $\Delta H_f$  and  $\Delta G_f$  values with each increasing  $\text{SiH}_2$  unit for  $n$ -silanes were 40.39 and 58.93 kJ/mol on average, respectively. The length of Si–Si bond increased slightly as the series number increased and then tended to remain constant for higher silanes. The BDE for both the Si–Si and Si–H bonds initially decreased for lower silanes and then approached a constant for higher silanes. The BDE of the Si–Si bonds were smaller than those of Si–H bonds. The higher silanes are more unstable than the lower silanes. The average BDE of Si–Si bond was ca. 302 kJ/mol, which is only half the experimental BDE value of the C–C bond (618 kJ/mol).

## 12.3 Chemical Properties of Silicon Hydrides (Silanes)

### 12.3.1 Silane Reactions

Silane and disilane (a common contaminant in silane) are both pyrophoric in air. The presence of traces of disilane is responsible for the spontaneous flammability of silane produced by acid hydrolysis of magnesium silicide. Even a highly diluted 1% mixture of silane in nitrogen easily ignites when exposed to air. Silane has been used in supersonic combustion ramjets to initiate combustion in the compressed air stream. Silanes have been proposed as combustion enhancer additives to hydrocarbons. Lower molec-

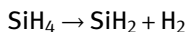
ular mass silanes are soluble in liquid hydrocarbons and can enhance their combustion [485, 489].

### 12.3.2 Decomposition of Silane

The decomposition of silanes to elemental silicon is of practical interest in the production of semiconductor and photovoltaic cell devices by chemical vapor deposition (CVD). The decomposition of silane may precede its combustion. Because silane has a positive enthalpy of formation, it can decompose when heated suddenly. Premature decomposition of silane during storage would prevent its use as an ignition material.

A detailed analytical and kinetic study of the thermal decomposition of monosilane in the temperature range 648–703 K (375–430 °C) and the initial pressure range 4.7–30.6 kPa (35–230 mm Hg) found that the gaseous products in the very early stages of the reaction are hydrogen, disilane, and trisilane [490]. Later in the reaction a solid silicon hydride was formed, its composition varying as the reaction progressed. The reaction is accelerated by the addition of certain foreign gases but is unaffected by packing of the reaction vessel. A tentative mechanism involving the intermediate species silylene,  $\text{SiH}_2$ , was proposed. Similar observations were made when starting with disilane instead of monosilane.

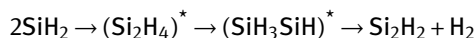
The homogeneous gas-phase decomposition kinetics of silane has been investigated using the single-pulse shock tube comparative rate technique ( $T = 1035 - 1184$  K,  $P_{\text{total}} \approx 533$  kPa  $\approx 4000$  mm Hg) [491]. The initial reaction of the decomposition



is a unimolecular process in its pressure fall-off regime with experimental Arrhenius parameters of:

$$\log k_1 = 13.33 \pm 0.28 - 52700 \pm 1400 / 2.303RT \text{ s}^{-1}$$

The decomposition has also been studied at lower temperatures by conventional methods. The results confirmed the total pressure effect, indicating a small but not negligible extent of induced reaction, and showed that the decomposition was first order in silane at constant total pressures. Good agreement with all the data was obtained with a model whose high-pressure parameters were  $\log A_1 = 15.5 \text{ s}^{-1}$ ,  $E_{1(\infty)} = 238 \text{ kJ} = 56.9 \text{ kcal}$ , and  $\Delta E^0_0 = 234 \text{ kJ} = 55.9 \text{ kcal}$ . When examining the mechanism of the decomposition, it was concluded that hydrogen atoms are not involved. It was suggested that silylene in the pure silane pyrolysis ultimately reacts with itself to give hydrogen:

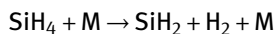


Kinetic data for static system silane pyrolysis at 640–703 K and 8–53 kPa = 60–400 mm Hg and conversions from 3–30% followed first-order kinetics, with silane loss rates equal to half the hydrogen formation rates [492]. At conversions greater



than 40%, rate inhibition attributable to the back reaction of hydrogen with silylene occurs. Overall reaction rates were not surface sensitive, but disilane and trisilane yield maxima under some conditions were dependent on surface:volume ratios. A non-chain mechanism capable of describing quantitatively all stages of the silane pyrolysis was proposed. After the 1.0% initiation phase, the reaction was both homogeneous (gas phase) and heterogeneous (on the walls), and reaction intermediates were silylenes and disilenes. Free radicals were not involved at any stage of the reaction. The dominant sink reaction for silylene intermediates is 1,2-H<sub>2</sub> elimination from disilane (followed by Si<sub>2</sub>H<sub>4</sub> polymerization and wall deposition).

The thermal decomposition of silane highly diluted in argon was observed behind reflected shock waves over the temperature range from 1060 to 1730 K and pressures between 61 and 506 kPa (0.6 and 5.0 atm) [493]. Silane and silylene time histories were monitored using the infrared emission of SiH<sub>4</sub> near 4.7 μm and laser absorption of a SiH<sub>2</sub> transition near 579 nm. Reaction rate coefficients for the first-order and second-order forms of the decomposition reaction



were determined from the species measurements for M = Ar. The bimolecular rate constant over the pressure range considered was determined to be

$$k_{1a} = 7.2 \times 10^{15} \exp(-E/RT)$$

where  $k_{1a}$  is the rate constant in cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and  $E$  is the activation energy  $E = 188.7 \pm 5.0$  kJ/mol =  $45.1 \pm 1.2$  kcal/mol. This second-order rate coefficient described the silane decomposition reaction over the entire range of temperatures and pressures and showed good agreement with the results of previous studies at similar temperatures as well as those at lower pressures and at temperatures above and below the values referenced above. The implication of the second-order reaction rate is that even at total mixture pressures as high as 5 atm, the silane decomposition is still in the low-pressure limit. A pressure-dependent rate equation is therefore not needed for SiH<sub>4</sub> decomposition over a wide range of conditions of practical interest when the reaction is simply expressed in the bimolecular form.

#### 12.4 Toxicity of Silane

Unlike methane, silane is very toxic. The lethal concentration in air for rats (LC50) is 0.96% (9600 ppm) over a 4-h exposure. The NIOSH has set a recommended maximum allowable exposure limit of 5 ppm (7 mg/m<sup>3</sup>) over an 8-h time-weighted average.

## 12.5 Handling of Silane

The handling of silanes requires safety precautions to prevent accidental leakage and ignition [494–496].

## 12.6 Combustion of Silicon Hydrides (Silanes)

The ignition and combustion of silane is mostly of interest for air-breathing engines, but also for the hypergolic start of non-hypergolic fuels in rocket engines. The addition of silanes to hydrocarbon fuels will enhance their ignition, increase heat of combustion and accelerate the burning velocities. While experiments with silanes in current combustion engines will be discussed in future volumes on bipropellant combinations, the current sections summarize only the studies of more academic interest, where many of the experiments could be conducted in glass apparatus.

Self-ignition and flame propagation properties of silane combustion have been studied through computer simulations using a database of kinetic and thermodynamic information that was consistent with current understanding of the elementary processes, including the mechanism for chain branching through the  $\text{SiH}_3$  radical, rate constants for the reactions of  $\text{HO}_2$  with silane and its breakdown products, and the reaction of  $\text{SiO}$  with oxygen [497]. Over the entire temperature range, the simulations showed two distinct mechanisms. At low temperatures, the kinetics of  $\text{SiH}_3$  is controlling, whereas at high temperatures,  $\text{SiH}_2$  chemistry is of key importance. The upper explosion limit and ignition at room temperature and 1 bar can be described by the same set of reactions. For very lean flames, the maximum reaction rate occurs at the lower temperature region of the flame zone.

### 12.6.1 Limits of Flammability of Silicon Hydrides

There have been several accidents caused by silane leaks in the semiconductor and photovoltaic cell processing industry [498]. Accident investigations have concentrated on the limits of flammability in air and on the conditions leading to autoignition and explosions when silane leaks out into air. Research was carried out to develop improved protection guidelines for silane handling systems through enhanced understanding of the behavior of releases of this pyrophoric gas. The approach involved addressing various aspects of the problem: The autoignition behavior of silane; the reactivity characteristics of quiescent silane/air mixtures; and the rates of reaction of silane leaked into enclosures with and without explosion venting, in the presence of ventilation air flow.

When measuring the explosivity of monosilane-air mixtures, the limiting oxygen concentration at which monosilane will not self-ignite in a nitrogen-oxygen atmosphere was 0.7–3%, depending on the humidity of the medium [499]. Monosilane

autoignition was observed at very low temperatures. Reducing the temperature of the nitrogen-oxygen medium only slightly raised the oxygen autoignition limit. Methyl iodide effectively inhibited the ignition of monosilane in air for near-stoichiometric mixtures.

Contrary to previous information, the ventilation flow has no measurable effect on the prompt ignition of a silane release. From experiments in a 5.1-L (311-in.<sup>3</sup>) sphere it was found that silane/air mixtures of concentrations between 1.4 and 4.1% (by volume) are explosive but stable [500]. In this case, piloted ignition tests yielded laminar burning velocities up to 5 m/s (1000 ft/min). Mixtures between 4.5 and 38% (the maximum reached in the tests) were found to be metastable, and would undergo spontaneous ignition after a delay ranging from 15 to 120 s, with the shorter values corresponding to higher silane concentrations. Experiments were also performed in a 0.645 m<sup>3</sup> (22.8 ft<sup>3</sup>) vessel both with and without explosion venting, to measure the rates of energy release associated with impulsively started silane leaking from 1/8 and 1/4-in. (3.2 and 6.4 mm) lines. A method for the prediction of the venting requirements of partial-volume deflagrations was developed to quantify the pressure rise from ignition of silane leaks in enclosures.

### 12.6.2 Autoignition of Silane in Air

While silane is a pyrophoric gas with a wide range of flammability, releases into the air may not always ignite immediately or sometimes not at all. The spontaneous ignition of pre-mixed silane-oxygen-nitrogen mixtures has been investigated under a variety of conditions. Silane when released at high velocities may not immediately ignite. The smaller the diameter of the release tube is, the lower is the pressure at which no ignition would occur. It was found that the autoignition temperatures were lower than room temperature even if the oxygen concentration was extremely low [501]. The spontaneous ignition of silane takes place in extremely oxygen-lean mixtures, like those which are instantaneously produced when silane or silane mixtures are vented into the air, as in an accidental leak.

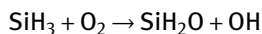
Spontaneous ignition limits of silane have been investigated at relatively low concentrations [502]. For silane, the spontaneous ignition occurred if the mixture concentrations were such that the silane/oxygen ratio was higher than a certain threshold limit value. The mixture was not stable if the ratio was higher than a certain value. It was concluded that the spontaneous ignition of silane occurs as a result of a competition of both chain branching and chain breaking reactions, in a way that is qualitatively similar to that in hydrogen oxidation.

A mechanism of low temperature silane combustion has been proposed based on the assumption that a trace amount of water facilitates spontaneous ignition of silane in air at room temperature [503]. This assumption has been made based on the fact that the combustion product of silane positively influences the occurrence of spontaneous ignition. Energetic calculation of the reaction pathway for low temperature

silane combustion also supported this assumption. A numerical model was developed which could interpret the spontaneous ignition limit at room temperature, the ignition delay times and the second explosion limit of silane mixtures.

The concentration of silane in fuel required to achieve ignition was investigated using a practical, non-premixed, oxygen-methane, swirled-stabilized burner in a laboratory [504]. The effects of fuel and oxidizer injection timing, flow rates, injector configuration, silane gas temperature (273–325 K), and combustion system geometry were investigated. In each case the minimum silane concentration in methane necessary for prompt, repeatable ignition was recorded. The role of methane as a diluent in low-temperature silane autoignition for a methane-oxygen combustion system was examined to serve in the design of a flight engine.

A chemical kinetic reaction mechanism for the oxidation of silane/hydrogen mixtures was based on shock-tube ignition delay time data [505]. Good agreement between experimental results and the results predicted by the mechanism was obtained by adjusting the rate coefficient for the reaction of the silyl radical



The reaction mechanism was used to theoretically investigate the ignition characteristics of silane/hydrogen mixtures in air. The results revealed that over the entire range of temperature examined (800–1200 K), substantial reduction in ignition delay times can be obtained when silane is added to hydrogen. Silane is a pyrophoric gas commonly used in semiconductor and photovoltaic cell manufacturing and has also been considered as a fuel additive to improve flame stabilization in scramjet engines.

Calculations have been made to demonstrate the use of silane/methane liquid mixtures as an ignition promoter and flame stabilizer in hydrogen (or other) fueled scramjet applications [506]. The calculations showed that initially non-flammable mixtures undergo rapid methane evaporation to produce droplets capable of spontaneous inflammation. This technique may be expanded to other spontaneously flammable materials. It was assumed that the liquid silane/methane mixture was sprayed into the combustion chamber upstream of the main fuel injectors. Droplet size, flow velocity, temperature and initial liquid fuel mixture composition were varied.

A chemical kinetic mechanism was proposed for the combustion of oxygen-silane-hydrogen-nitrogen mixtures in the initial temperature range from 800 to 1250 K and pressure range from 51 to 137 kPa (0.5–1.35 atm) [507]. Predicted ignition results agreed with published ignition delay times obtained from shock-tube experiments. Comparisons between the results obtained using the proposed mechanism and that of an alternative mechanism revealed that the former predicts appreciably shorter ignition delay times, but a flame blow-out envelope which was shifted so as to decrease the stable flame region. Over much of the thermodynamic range examined, the mechanism predicted long reaction times. A three-step global mechanism was proposed which closely modeled the ignition phase of air/SiH<sub>4</sub>/H<sub>2</sub> combustion; however, the

initial reaction phase was less well reproduced by the global model, which could not be confirmed without additional experimental data.

The products of oxygen (air) + silane mixture combustion and explosions vary with mixture composition [508]. For O<sub>2</sub>-rich mixtures (> 70% O<sub>2</sub>), the products are H<sub>2</sub>O and SiO<sub>2</sub>. As the mixtures become richer in silane, H<sub>2</sub> replaces H<sub>2</sub>O as a final product. For very SiH<sub>4</sub>-rich mixtures (> 70% SiH<sub>4</sub>), the products are H<sub>2</sub>, SiO<sub>x</sub>, and Si. The fact that silane is totally consumed in silane-rich mixtures (70–90% silane) demonstrates that solid particle formation (SiO<sub>2</sub>, SiO, and Si) occurs very rapidly and that the accompanying heat release is essential to drive the reactions to completion. It is also clear that the explosion of silane-rich mixtures is primarily a thermal explosion of silane by itself, which does not depend on the presence of an oxidizer.

A shock tube was used to measure the ignition delay time of stoichiometric O<sub>2</sub>/H<sub>2</sub> mixtures with and without addition of 25% silane to the hydrogen fuel [509]. The shock-tube conditions were 880–1600 K and 172–517 kPa (1.7–5.1 atm). The ignition augmenting effects of silane were more pronounced at lower temperatures (880–1300 K) than at high temperatures. The slope of the ignition delay time versus reciprocal temperature was different at low temperatures than at high temperatures.

If silane is to be used as an ignition fluid, it is important to know how fast it ignites and how the ignition delay is affected by O/F ratio, diluents, and pressure. Ignition studies were performed behind shock waves in a shock tube using SiH<sub>4</sub>, O<sub>2</sub>/SiH<sub>4</sub>, O<sub>2</sub>/H<sub>2</sub>, O<sub>2</sub>/SiH<sub>4</sub>/H<sub>2</sub>, O<sub>2</sub>/CH<sub>4</sub>, and O<sub>2</sub>/SiH<sub>4</sub>/CH<sub>4</sub> highly diluted in argon [510]. Reflected-shock temperatures ranged from 1050–2250 K at pressures near 101 kPa (1 atm). Reaction progress was monitored by observing the time concentration histories of several species, including OH\*, SiH<sub>4</sub>, SiH<sub>2</sub>, and CH\* using emission and laser absorption techniques. The oxidation and ignition data were reported in the form of species concentration profiles and plots of characteristic delay times as a function of temperature. The species concentration time histories exhibited a dual oxidation behavior for most of the fuel/O<sub>2</sub>/SiH<sub>4</sub> experiments, indicating that silane reacts first, followed by reaction of the fuel with the remaining oxygen. As expected, the presence of silane in the O<sub>2</sub>/fuel mixtures markedly reduced the ignition delay time, usually by a factor of two or more even at molar SiH<sub>4</sub> concentrations as low as 1% of the fuel concentration. The shock-tube kinetic data can be used to validate chemical kinetics models of high temperature silane oxidation for propulsion and materials processing applications.

Several dilute mixtures of varying concentrations and equivalence ratios ( $\Phi = 0.5, 1.0$ ) of O<sub>2</sub>/Ar/C<sub>2</sub>H<sub>4</sub>/SiH<sub>4</sub> were studied between 1115–1900 K and 91–334 kPa (0.9–3.3 atm) [511]. Argon dilution ranged from 96–98% with total concentrations between 0.67 and  $3.2 \times 10^{-5}$  mol/cm<sup>3</sup>. Reaction was monitored using chemiluminescence emission from the hydroxyl radical near 307 nm. For SiH<sub>4</sub> concentrations less than those of ethylene in the mixture (by volume), the ignition delay time was reduced by ~30 to >50%. The addition of SiH<sub>4</sub> had a small effect on ignition activation energy, indicating the chain branching mechanism for C<sub>2</sub>H<sub>4</sub> ignition was speeded up but not altered greatly by the silane at higher temperatures. After

adding an appropriate  $\text{OH}^\bullet$  free radical submechanism, several kinetics mechanisms containing high-temperature ethylene chemistry were compared to the data without  $\text{SiH}_4$ . Most of the mechanisms predicted the ignition activation energy quite well. The basic formation and quenching characteristics of the  $\text{OH}^\bullet$  profiles were reproduced by most mechanisms, but each required some adjustment to match all features.

Silane is a pyrophoric gas which normally ignites upon contact with air; however, a silane release from a pressure source may not always lead to prompt ignition and frequently the ignition occurs only shortly after the release is shut off. In a confined space, significant quantities of unburnt silane can accumulate prior to autoignition, leading to an explosion, potentially causing significant damage. A series of tests was aimed at a better understanding of the precise conditions for pure silane ignition and explosion upon release into air [512, 513]. Tests were performed for releases at controlled and steady flow velocities. With careful control of test conditions, the critical exit flow velocity for prompt ignition of steady silane releases was found for different vent diameters. If the releases were reduced to below the critical exit velocity, prompt ignition of silane release was observed. Above this critical exit velocity, silane can be released indefinitely into air without any ignition. The critical exit velocity was found to vary with the vent diameter. The most reactive ignition kernel occurred in the range when the ratio of volumetric flow rate of entrained air to the silane flow reached  $0.322 \pm 0.076$ , which was equivalent to the most reactive silane concentration of 75.6% in air.

Ignition of pure silane upon release into air always occurred in a well-defined mixture fraction called the most reactive mixture fraction. The critical exit velocity and the most reactive mixture fraction suggest that silane release without prompt ignition is most likely caused by flow strains or by scalar dissipations, which prevent chemical reactions of silane oxidation [514].

The critical velocity for delayed ignition was determined for different silane temperatures and moisture contents in ambient air [515]. The logarithm of the critical exit velocity was found to be inversely proportional to silane temperature. Moisture in air had a strong inhibiting effect on silane autoignition in air. Prompt ignition of silane was favored in a high-temperature and low-humidity environment.

During field experiments on unconfined explosions of silane-air mixtures in a cubic frame covered with a thin vinyl film, ignition from the tube exit located at the center of cubic frame was initiated by shutting off the silane flow [516]. Silane/hydrogen mixtures are used during elemental silicon production and semiconductor processing but constitute an acute ignition and explosion risk if accidentally released into ambient air [517, 518]. Additional information on ignition and combustion of silanes in ramjet and rocket engines will be contained in a future volume on hypergolic bipropellant combinations.

### 12.6.3 Flame Speeds of Silicon Hydride Combustion

Addition of silanes to hydrocarbon fuels may raise the flame speeds sufficiently such that these fuels can be used in pulsed detonation engines or rotating detonation engines. One of the fuels already tested in these engines is ethylene. Adding silane to ethylene enhances its ignition and combustion in compact combustors with limited chamber volumes.

The burning velocities of lean pre-mixed silane-oxygen-nitrogen flames were measured in the silane and oxygen concentration ranges from 1.6 to 2.9% and from 4 to 24%, respectively [519]. The burning velocity of a silane-air flame was ~55 cm/s at a silane concentration of 2%. For lean mixtures, when the oxygen concentration was reduced, dependence of burning velocity on silane concentration decreased but did not significantly affect the flame temperature. For extremely lean flames, the degree of hydrogen production increased with decreasing silane concentration and silane was almost completely consumed. On the other hand, if the silane concentration exceeded the stoichiometric point, the burning velocity increased gradually with increasing silane concentration. In that case, silane as well as oxygen were completely consumed and, at the same time, hydrogen rather than water production became dominant. The burning velocity of silane in 21% O<sub>2</sub>/balanced N<sub>2</sub> increased from zero near the lower limit of flammability (1.5% SiH<sub>4</sub>) to 3 m/s at 4.5% SiH<sub>4</sub>.

Exposure of the reactor walls to the products of the low-pressure silane-oxygen flame at a temperature of 523–773 K (350–500 °C) activates the wall as a catalyst of heterogeneous chain initiation [520]. It was shown that new lattice structures saturated with crystal lattice defects are formed, whose number on the wall increases continuously during condensation of the reaction products, together with adsorption of silicon-containing free radicals.

The combustion mechanism of air/silane flames was studied through a computer simulation employing a detailed chemical kinetic scheme [521]. Two different pathways for the consumption of silane were found: SiH<sub>4</sub> → SiH<sub>3</sub> → SiH<sub>2</sub>O → HSiO, which proceeds in low-temperature regions, and SiH<sub>4</sub> → SiH<sub>2</sub> → HSiO, occurring at high temperatures. This observation supported results previously reported in the literature. It was also found that some reactions occurred over wide ranges of temperature and that the governing step for the whole silane combustion is the reaction of silane with hydroxyl radicals. A least-square fitting to the burning velocities and adiabatic flame temperatures obtained for the four investigated mixtures, with equivalence ratios of  $\Phi = 2.0, 1.43, 1.0$ , and  $0.5$ , indicated that a mixture with equivalence ratio of about 1.2 would have the fastest burning velocity and the highest flame temperature. The simulation of silane-air flat pre-mixed flames using a detailed reaction scheme with 45 reactions and the analyses of the obtained results led to the following conclusions: **(1)** in the flames with equivalence ratio around 1.0 the combustion reactions take place very intensely, and consequently are confined within thin areas of the flame about 0.05 mm thick. The burning velocity of the stoichiometric flame was 2.2 m/s, which is a little slower than that of the hydrogen flame. **(2)** Two mechanisms were provided for

the reaction from  $\text{SiH}_4$  to  $\text{HSiO}$ : one proceeds along  $\text{SiH}_2\text{O} + \text{HSiO}$  and the other along  $\text{SiH}_4 + \text{SiH}_2 + \text{HSiO}$ . These pathways are activated in different temperature ranges. The former starts even at low temperatures because it progresses as chain reactions having hydroxyl radicals as chain carriers, which are produced in a large amount even at low temperatures. The latter is activated at high temperatures because the initiation reaction of this route has a large activation temperature. The second mechanism is also accelerated under rich conditions since it starts with dissociation of silane.

A detailed chemical reaction scheme and a full set of governing equations for fluid dynamics were used to demonstrate the chemical and physical phenomena involved in an air/silane counterflow diffusion flame, where the fuel and air issue from a lower and an upper nozzle [522]. It was found that a stagnation surface, where the axial velocities decrease to zero, is kept in a position slightly shifted to the upper side, dividing the system into two zones: the upper air side and the lower fuel side. After leaving the nozzle silane begins to dissociate into  $\text{SiH}_2$  and  $\text{H}_2$  when it reaches the region of rising temperature. Oxygen penetrates into the fuel side by diffusion and reacts with  $\text{H}_2$  forming OH radicals and H atoms. The  $\text{SiH}_2$  intermediate is further dehydrogenated to  $\text{SiO}$  via  $\text{HSiO}$ . When compared to pre-mixed flames, the diffusion flames have large local equivalence ratios, so that the combustion reactions in the latter flames proceed through a different mechanism.

## 12.7 Applications of Silicon Hydrides

It is unlikely that silanes would ever be used as the main fuels in bipropellant rocket engines [523]. They could be used as ignition aid for a hypergolic slug start prior to switching to the main fuel which is only non-hypergolic without addition of silane [524]. Silane has been used in supersonic combustion ramjets to initiate combustion in the compressed air stream. Monosilane was successfully used in the hypersonic NASA X-43A scramjet flights as an ignition aid [525, 526]. Silanes have been proposed as combustion enhancer additives to hydrocarbons [489].

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# Methylhydrazine

## Methylhydrazine

*Encyclopedia of Liquid Fuels* contains four chapters dealing with hydrazines: Chapter “Hydrazine” dealing with the parent compound, the inorganic compound hydrazine, chapter “Alkylhydrazines” dealing with alkylhydrazines other than methylhydrazine or dimethylhydrazine, chapter “Dimethylhydrazines,” and finally, chapter “Methylhydrazine,” the chapter at hand.

Methylhydrazine, also known as monomethylhydrazine, hydrazinomethane,  $\text{H}_2\text{NNHCH}_3$ ,  $\text{C}_1\text{N}_2\text{H}_6$ , MMH, Chemical Abstracts Service Registry Number CAS RN [60-34-4], is the simplest alkylhydrazine and widely used as a hypergolic rocket fuel. Methylhydrazine is usually erroneously called *monomethylhydrazine* (often abbreviated as MMH). As the corresponding amine is called methylamine and not monomethylamine, and as there are no structural isomers depending on which nitrogen atom the methyl group is attached to (as long as they are both  $^{14}\text{N}$ ), the prefix *mono* is considered an unnecessary waste of print space.

## 1 Production of MMH

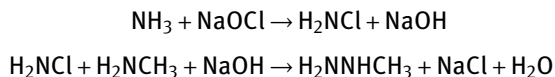
At a cursory glance, one might assume that the simplest way of preparing MMH would be to methylate hydrazine (Section 1.2.3). This is not the case. Even if the direct methylation of anhydrous hydrazine did lead to the desired product, the MMH would be much more expensive than the anhydrous hydrazine used as a starting compound if it had to be made this way. Methylhydrazine can be produced more economically using a modified Raschig process by substituting methylamine in the second step of the reaction [1] (see Section 1.1). The reaction can be carried out in aqueous solution or in excess amine [2].

It appears that so far, most of the MMH used as rocket propellant has been produced in the US, and other countries such as Russia (former USSR), France, China, or India have used more unsymmetrical dimethylhydrazine (UDMH) than MMH, but these countries have also maintained the ability to make smaller quantities of MMH.

In an effort to become independent of MMH imports, France developed its autonomous MMH manufacturing capability, and in doing so, evaluated several MMH and UDMH manufacturing processes. The most promising route chosen for the national production of MMH in France was a modified Raschig process. Supporting studies were documented in a series of doctoral theses and reports published by the University of Lyon [3, 4]. An explosion at the neighboring AZF chemical plant in Toulouse in September 2001 interrupted MMH and UDMH production at SNPE for 3 years.

### 1.1 Preparation of Methylhydrazine Using a Modified Raschig Process

Methylhydrazine can be prepared by a variation of the basic Raschig synthesis in which chloramine is first formed in the conventional manner, but the ammonia in the second-stage reaction is replaced by methylamine:



A similar method using dimethylamine instead of methylamine can be used for the production of UDMH. Substantial effort has gone into optimizing the reaction conditions to maximize the MMH yield in a small (30 g MMH/h) pilot plant, in particular to define the optimal pH, chloramine:methylamine mixture ratio, operating temperature, and dwell time. Kinetic equations were derived for all major process steps. The MMH was isolated from the primary reaction product mixture using a four-step process: **(1)** stripping of the unreacted volatiles ( $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ), **(2)** distillation of an azeotropic mixture, **(3)** breaking the azeotrope by the addition of NaOH, and **(4)** distillation of the MMH-rich phase. The phase diagrams of MMH in a mixture with water, NaCl, and NaOH have been extensively investigated as they determine the amount of sodium hydroxide needed and the mass of waste generated that needs to be disposed of at a substantial cost. The studies included ternary MMH/water/NaOH [5] as well as quaternary MMH/water/NaOH/NaCl systems [6]. Isotherms at 288, 298, and 313 K were measured and the liquid–liquid miscibility gap was pretty well bracketed from both sides. It was shown that the concentration of MMH in the lighter phase increased with decreasing temperature.

In all modifications of the Raschig process for making MMH, UDMH, or hydrazine, it is important to have an efficient way of making chloramine without losing too much active chlorine during the first step. The chloramine yield depends on the pH of the ammonia or ammonium chloride solution reacting with sodium hypochlorite and needs to be optimized [7].

Instead of generating the chloramine by reaction of ammonia and hypochlorite, chloramine can be synthesized electrochemically by electrolysis of a solution of ammonia and ammonium chloride, with subsequent extraction of the chloramine [8, 9]. The electrolysis conditions were optimized using a three-electrode cell. The electrochemical yield was close to 70%. A similar study using ammonium bromide to generate bromamine gave  $\text{NH}_2\text{Br}$  with 100% yield. A suitable immiscible solvent for extraction of chloramine is methyl-*tert*-butyl ether, which until recently was widely used as a gasoline additive. The extracted chloramine can be reacted with methylamine at 288 K instead of 343 K (as was common for the aqueous-phase reaction), leading to fewer by-products and MMH yields up to 78% [10, 11]. In order to find a way of preparing MMH using Raschig synthesis in a biphasic medium with methyl-*tert*-butyl ether

(MTBE) as the organic phase, the solid/liquid/vapor quaternary system  $\text{CH}_3\text{NH}_2/\text{H}_2\text{O}/(\text{CH}_3)_3\text{COCH}_3/\text{NaOH}$  has been investigated at 288 K [12]. By the addition of NaOH to a mixture of  $\text{CH}_3\text{NH}_2/\text{H}_2\text{O}/(\text{CH}_3)_3\text{COCH}_3$  three liquid phases were observed in a first step, and an isothermal–isobaric four-phase invariant equilibrium may be obtained (three liquids and one vapor). This procedure can be carried out as a continuous process, as was demonstrated using a pilot-scale unit in the laboratory. The by-products resulting from degradation remained in the organic phase.

The production of MMH or UDMH by the modified Raschig process may form small amounts of hydrazine as a by-product. Although the presence of a little hydrazine does not interfere when MMH or UDMH is used as a rocket fuel, it may lead to undesirable side reactions when MMH or UDMH is intended to be used for the synthesis of pharmaceutical or agrochemical products. Traces of hydrazine can be selectively removed from a MMH or UDMH solution by heating it in contact with catalysts that do not destroy any alkylhydrazines (nickel supported on silica/alumina, nickel–nickel oxide mixture supported on silica/alumina, or rhodium supported on carbon at a temperature between 333 and 393 K = 60 and 120 °C) [13].

### 1.1.1 Reaction Kinetics and Mechanisms

The mechanism of the reaction between chloramine and methylamine is almost identical to that of the Raschig synthesis. The  $\text{S}_\text{N}2$  mechanism was studied [14], and it supported conclusions drawn earlier about the nucleophilic type of attack on the chloramine. Similar reactions occur with secondary amines in place of primary amines, leading to unsymmetrical dialkylhydrazines. The rate of MMH formation can be expressed by the equation:

$$V = \frac{d[\text{CH}_3\text{NHNH}_2]}{dt} = k_1[\text{NH}_2\text{Cl}]^\alpha[\text{CH}_3\text{NH}_2]^\beta - ck_2[\text{NH}_2\text{Cl}]^\gamma[\text{CH}_3\text{NHNH}_2]^\delta$$

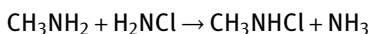
where  $k_1$  is the rate constant of the MMH-forming reaction and  $k_2$  is the rate constant of an undesirable side reaction in which MMH is destroyed. The exponents  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  determine the order with which reactants enter into the reaction. These orders and the rate constants of unit reactions can be determined by working with a large excess of one of the reactants, in this case typically methylamine, and monitoring the rate of disappearance of the other reactant (chloramine) and the rate of appearance of the desired product (MMH). Measurements have shown that the exponents  $\alpha$  and  $\beta$  are equal to 1 [15, 16]. The MMH formation reaction is thus first order in both reactants. The first step of the MMH-forming reaction is independent of pH, but the second is accelerated by increasing the pH. For an initial methylamine: chloramine ratio of 10, the optimal MMH yield is achieved at a pH of 13.5. Increasing methyl substitution (the methyl group is an electron donor) on the ammonia molecule makes the molecule more reactive in an  $\text{S}_\text{N}2$ -type mechanism, as summarized in Table 1.

**Table 1:** Rate constants of chloramine reactions with amines.

| Number of methyl groups | Amine                              | Hydrazine formed                                 | Constant $\lambda$ , L mol <sup>-1</sup> s <sup>-1</sup> |
|-------------------------|------------------------------------|--------------------------------------------------|----------------------------------------------------------|
| 0                       | NH <sub>3</sub>                    | N <sub>2</sub> H <sub>4</sub>                    | $1.04 \times 10^{-4}$                                    |
| 1                       | CH <sub>3</sub> NH <sub>2</sub>    | CH <sub>3</sub> NHNH <sub>2</sub>                | $48.7 \times 10^{-4}$                                    |
| 2                       | (CH <sub>3</sub> ) <sub>2</sub> NH | (CH <sub>3</sub> ) <sub>2</sub> NNH <sub>2</sub> | $899.5 \times 10^{-4}$                                   |

Data source: [15]

The MMH yield is limited by several unwanted reactions, in particular, the chlorine transfer from chloramine to methylamine [17–19]:



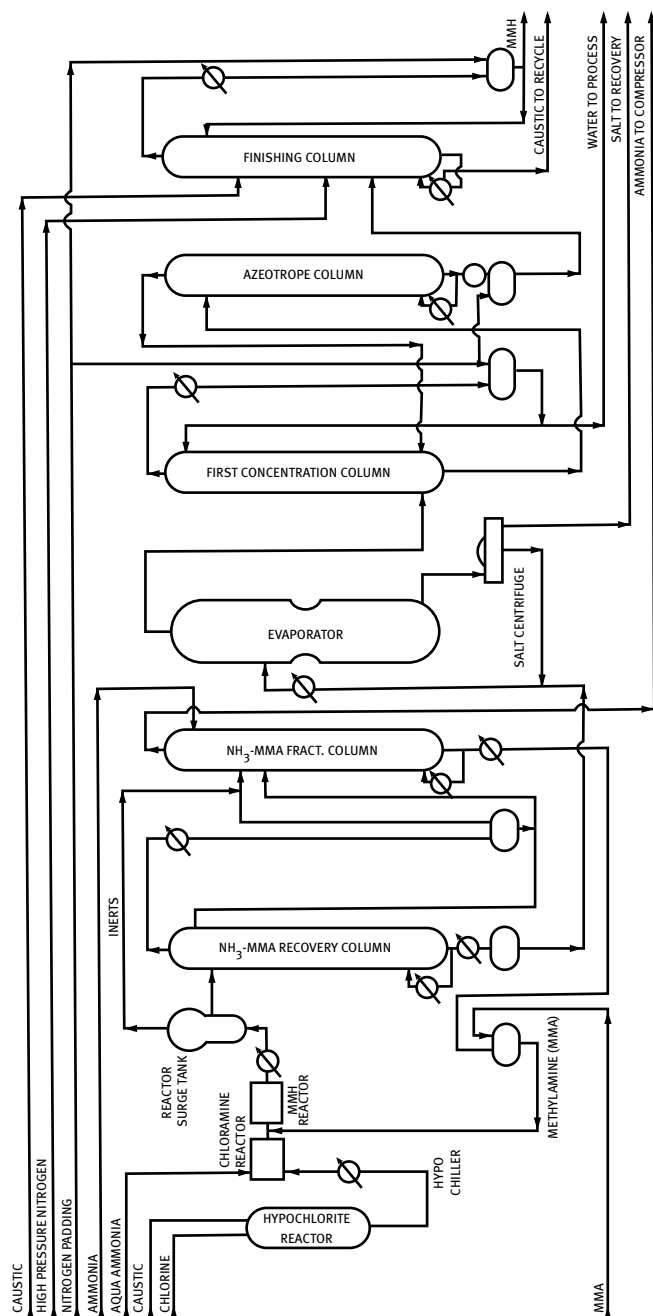
and the oxidation of MMH by chloramine [20]. Chlorine transfer is maximum at a pH of 10 and decreases to a constant value above pH 12.8. MMH oxidation by chloramine is the result of two competitive reactions, the first one being pH independent, and the second one being accelerated by decreasing pH. The optimal pH for MMH formation would be above the range where chlorine transfer and MMH oxidation can take place. MMH oxidation by chloramine leads to a mixture of unwanted by-products, including methanol, methyl chloride, and formaldehyde methylhydrazone  $\text{CH}_3\text{NHN}=\text{CH}_2$ .

Chloramine for the production of MMH by the Raschig process can be synthesized under stoichiometric conditions, which leads to a more economical process because it avoids the additional steps of extraction due to the presence of excess reagents [21]. However, chloramine is not very stable and, therefore, it was important to study its stability. Differential scanning calorimetry (DSC) analyses of stoichiometric chloramine solutions revealed a risk of decomposition above 309 K (36 °C). Limiting the temperature rise requires efficient cooling in the synthesis reactor or synthesis at a low temperature, in order to avoid any sudden decomposition of the synthesis solution.

### 1.1.2 Industrial MMH Plant Designs and Flowcharts

The process flow chart of an MMH production facility designed by Olin Mathieson (then Olin Chemicals, later Arch Chemicals, Lonza, now Arxada) is illustrated in Figure 1.

In the Olin process, liquid chlorine and precooled dilute (12%) caustic soda are mixed to form fresh sodium hypochlorite solution. An excess of aqua ammonia (5%) is reacted with the hypochlorite solution to form a solution of chloramine. Up to this step everything is similar to the production of hydrazine itself. The major difference is in the next step, where chloramine is reacted with anhydrous methylamine in a specially designed reactor to form MMH. The effluent from the reactor is a very dilute aqueous solution of MMH. Excess unreacted methylamine and ammonia are present as impurities, sodium chloride as a reaction by-product. The purification and concentration



**Figure 1:** Process flow chart of methylhydrazine production. (Republished from [22], with permission from Wiley Interscience New York.)



of the product requires five process steps. Ammonia and methylamine are recovered in distillation columns and recycled. The nitrogen, a product of undesirable side reactions that limit the MMH yield, is recovered and used to blanket the concentration columns where explosive vapor concentrations could exist. The bottom of the ammonia-methylamine recovery columns contains only water along with sodium chloride and MMH. The sodium chloride is crystallized in an evaporator and removed by centrifuging. The dilute MMH solution is then concentrated in a three-step train of distillation columns. The first concentration column yields as overheads distilled water that is used for process dilution. The partially concentrated MMH solution from the bottom of the first column is fed to the second column, called the azeotrope column, which yields an MMH/water azeotrope (35% MMH). In the finishing columns, the azeotrope is broken with a very concentrated solution of sodium hydroxide. The ability of sodium hydroxide to lower the vapor pressure of water selectively allows the production of at least 98% pure MMH.

Whereas at least one mol of NaOH per mol of water is needed to break the hydrazine/water azeotrope (see Section 2.3), very little NaOH is required to break the MMH/water azeotrope. Azomethane (a potentially hazardous contaminant that has been the cause of an explosion [23]) and unreacted methylamine form a constant boiling azeotropic mixture that can be readily removed by fractional distillation of the first overhead stream of the reaction product of chloramine and excess methylamine in aqueous solution [24]. The methylamine is recycled to the process. The MMH is obtained with the water phase that is the bottom of the first column. The azeotrope contains approximately 90 mol-% methylamine and boils at 275–280 K. In order to prevent the accumulation of azomethane (AM), which is explosive, steam is sprayed into the condenser. By open steam heating of the second stage of the distillation column, AM and ammonia depart overhead, whereas aqueous methylamine is recovered as a second bottom and recycled [25]. Dangerous by-products formed by the reaction of chloramine and methylamine in the presence of base can be destroyed by adding an extra heating stage to remove by-products, mostly methylazine before work-up of the reaction product solution [26]. In this example, MMH is produced by reaction of chloramine with a one-mol excess of  $\text{MeNH}_2$  for a time  $T_1$  in an oxygen-free atmosphere in the presence of a strong base, preferably NaOH, and working up the mixture of MMH and volatile by-products by stripping followed by distillation, to give a concentrated aqueous solution of MMH. The novelty is that, before the reaction mixture is worked up, it is first heated to 343–373 K (70–100 °C) for a time  $T_2$  such that  $T_2/T_1$  is greater than 10 (pref. 50–100), in the absence of oxygen and keeping the pH above 13.5, so that the unwanted by-products are partly or completely removed.

A comparison of the traditional Raschig process with the rarely cited Thiele method for production of MMH showed that with a modern method of benzalazine preparation the Thiele method may be more suitable than the Raschig process for pilot plants with production of more than 1000 kg MMH/year [27].

## 1.2 Other Methods for Alkylhydrazine Production

Methyl-, ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, isobutyl-, and *tert*-butyl-hydrazine have been obtained in good yields (55–71%) by reaction of chloramine with the corresponding primary amines [28]. The reaction products were isolated and identified as their sulfates. The addition of gelatin to the reacting mixture was essential in obtaining good yields just as with the fundamental Raschig reaction. The minimum amount required for a good MMH yield was determined in a series of experiments and found to be 0.3 g/200 mL of 0.16-M chloramine solution. The reaction was generally carried out with an excess of methylamine, and a  $\text{CH}_3\text{NH}_2:\text{H}_2\text{NCl}$  ratio of at least 8 was required for a 64% yield. Increasing the ratio above 8 did not improve the MMH yield significantly.

Monoalkylhydrazines with a functionalized alkyl group, for instance, allylhydrazine, can be obtained from chloramine, alkali, and an excess of primary amine in a stirred, two-phase continuous flow reactor [29].

### 1.2.1 Preparation of MMH Using the Urea Process

The urea process for the preparation of hydrazine can also be modified for MMH synthesis: *N*-methylurea and sodium hydroxide dissolved in water and reacted with 5% sodium hypochlorite solution at 278 K give MMH in a 70% yield [30].

The formation of alkylhydrazines from substituted urea proceeds via two different mechanisms: **(1)** a mechanism analogous to Hofmann carboxamide conversion and **(2)** via an intramolecular aminating reaction, which passes through a diaziridinone as an intermediate [31].

The methylurea process gained renewed attention when the US Air Force sponsored a series of programs to identify new production processes that would yield both MMH and UDMH from one and the same plant, but would not use poisonous *N*-nitrosamines [32]. The first step of the urea process involves the preparation of monomethylurea or dimethylurea, which is then converted to the corresponding hydrazine by a reaction with sodium hypochlorite. Several processes to obtain the methylated ureas needed as starting materials have been described: reaction of amines (primary or secondary for MMH or UDMH) with phosgene, urethane, or cyanate will eventually provide the methylureas. A more economical route is substitution of one amino group in urea with methylamine or dimethylamine. This can be done in either anhydrous medium or in aqueous solution. A process design analysis and preliminary plant layout for a plant producing 454 metric tons/year (1 million lb/year) of MMH and UDMH each was conducted for the aqueous urea/amine process, but no additional work was carried out because the capital cost of the urea process was greater than for any of the other candidate processes [33].

*N*-Methyl-*N*-methoxyurea or *N*-methyl-*N*-hydroxyurea hydrolyze with concentrated alkali and yield MMH [31]. Following a different route, if urea is chlorinated to dichlorourea and reacted with ethylamine, at first 1,6-diethylbiurea will be obtained, which can then be converted to alkylhydrazines [34].

Chlorination of methylurea with *tert*-butyl hypochlorite gives *N*-methyl-*N*-chlorourea, which melts at 350 K. If this compound is slowly added to 50% aqueous sodium hydroxide in an ice bath, a 26% yield of MMH is obtained [35]. The reaction between *N*-methyl-*N*-chlorourea and NaOH may even proceed in the dry state by pyrolysis at 473 K, but the yields are rarely better than 26% [36].

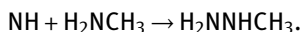
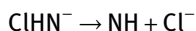
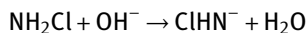
The reaction of chloramine with monomethylurea has been shown to yield MMH and several side products, including formaldehyde monomethylhydrazone, 1,1-dimethylhydrazine, 1-methyl-3-methylene-1-triazene, methanol, and 1-methyl-triazene,  $\text{CH}_3\text{NHNHNH}_2$ , originating from the further oxidation of monomethylhydrazine with chloramine [37]. Reaction of chloramine with the sodium salts of aliphatic carboxamides such as *N*-methylacetamide gives the corresponding acethydrazide, which can be hydrolyzed to give MMH [38].

### 1.2.2 Preparation of MMH in Non-Aqueous Systems

Production of MMH or UDMH in aqueous systems requires multi-step separations of products from the reaction mixtures and the water solvent. In order to avoid the energy-intensive distillation process for separating water and MMH, processes in non-aqueous solvents have been examined as alternate processes. The Sisler process, using chloramine in non-aqueous systems, is attractive, but has not yet been used on an industrial scale. If chloramine is allowed to react with undiluted liquid ammonia or amines, a large ratio of amine to chloramine (typically 400:1) must be maintained to obtain a profitable yield of hydrazines [39]. Instead of using extreme mixture ratios, dilution with inert solvents can possibly lead to more economical operations. Reactions were carried out with either KOH or potassium methylate dissolved in methanol or in the presence of a fixed base.

In non-aqueous solvents (ether, xylene, methanol, diglyme), chloramine does not react with methylamine, in contrast to the ready chloramination of ammonia, dimethylamine, or MMH [40, 41]. However, when chloramine was fed into a solution of methylamine in methanol in the presence of a “fixed” base, such as KOH or  $\text{CH}_3\text{ONa}$ , the formation of some MMH could be observed, although the yield in laboratory experiments was very poor. The poor MMH yield was caused by the preferential reaction of chloramine with MMH rather than methylamine. Three different mechanisms for the reaction of chloramine with ammonia or amines have been proposed. Hydroxylamine as an intermediate is unlikely because it has not been detected during hydrolysis of chloramine and because no MMH results from mixing hydroxylamine and methylamine [42]. A bimolecular displacement of chlorine from

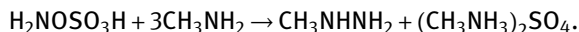
chloramine by amine or ammonia [43] should not be dependent on the presence of a fixed base. Although this mechanism may work for ammonia or dimethylamine chloramination, the reaction of methylamine and chloramine in the presence of fixed bases proceeds most likely by the formation of imide radicals, as proposed by Audrieth and co-workers [44]:



If chloramine is fed into a mixture of methylamine and MMH in a non-aqueous solvent without a strong base, the MMH is destroyed and the methylamine survives unchanged. Similarly, when bubbling chloramine gas through liquid methylamine without a solvent or fixed base, MMH is obtained in a yield of only 49% [45]. However, in the presence of alkali, chloramine reacts preferentially with the fixed base, thus not only allowing the survival of MMH but even resulting in the synthesis of additional MMH from methylamine and an intermediate. The yield of MMH or other monoalkylhydrazines prepared by the anhydrous Sisler process [46–48] can be improved if a tertiary amine such as triethylamine is used to tie up the hydrogen chloride formed in the reaction [49].

By-products from the MMH or UDMH production by reaction of chloramine with methylamine or dimethylamine have been analyzed using a gas chromatography-mass spectrometry (GC-MS) system with a 6-ft column packed with Carbowax 20M or Carbowax B [50]. Peaks identified in the MMH product mix are unreacted methylamine,  $\text{H}_3\text{CN}=\text{NH}$  or  $\text{H}_2\text{C}=\text{N}-\text{NH}_2$ , MMH, UDMH, AM, and  $(\text{CH}_3)_2\text{N}-\text{N}=\text{CH}_2$ . Similarly, the UDMH reaction products contained unreacted dimethylamine, UDMH, AM, and two unidentified peaks,  $\text{C}_4\text{H}_{10}\text{N}_2$  and  $\text{C}_2\text{H}_7\text{N}_3$  (all listed in sequence of retention times).

Instead of chloramine, hydroxylamine-*O*-sulfonic acid also gives MMH by reaction with methylamine and similarly gives UDMH on reaction with dimethylamine [51]. The reaction with methylamine may be written as:



Besides MMH and methylammonium sulfate, some water and methanol are formed as by-products. The reaction is best carried out in diglyme as a solvent. Typical MMH yields are 55%, based on the amount of  $\text{H}_2\text{NOSO}_3\text{H}$  used. In the latter case, when reacting hydroxylamine-*O*-sulfonic acid with dimethylamine to make UDMH, water and 1,1,4,4-tetramethyl-2-tetrazene were formed as by-products, presumably by oxidation of UDMH. This presumption was confirmed by reacting UDMH with excess  $\text{H}_2\text{NOSO}_3\text{H}$  under the conditions of UDMH synthesis.

### 1.2.3 Preparation of MMH by Direct Alkylation of Hydrazine

It was stated in the introduction to this section that direct methylation of hydrazine is not economical. It is still true that the methylation is uneconomical, but it is not impossible. On special occasions, such as the synthesis of isotope-labeled methylhydrazines, the direct methylation (using  $\text{CD}_3\text{I}$ ) may still be a preferred method [52]. Separation of the reaction mixture by preparative chromatography gave 56.1%  $\text{CD}_3\text{NHNH}_2$ , 42.4%  $(\text{CD}_3)_2\text{NNH}_2$ , and 1.5%  $\text{CD}_3\text{NHNHCD}_3$ .

Methylation of hydrazinium(1+) chloride or hydrazinium(2+) chloride in methanol with methyl chloride in an autoclave at 393 K, 1200 kPa for 2 h can lead to MMH chloride in a yield of 99% [53–55]. Hydrazine hydrate can be used as the base to free the MMH and the resulting hydrazinium chloride solution can be used as starting material for continued methylation [56]. Methanol instead of methyl chloride can be used as the methylating agent if 85% phosphoric acid in concentrated hydrochloric acid is used as the catalyst [57]. The reaction conditions were rather severe (4 h in an autoclave at 403 to 408 K). The MMH yield was 32.6% with 95% selectivity. Addition of hydrazine hydrate to higher alkyl bromides under stirring gives monoalkylhydrazines in yields up to 93% [58], but this method does not work well for methylhydrazine and the MMH yield is only in the vicinity of 26%.

Direct alkylation of hydrazine or hydrazinium sulfate with dimethyl sulfate gives only a mixture of methylhydrazines that need to be separated by distillation if the mixture can be used as a hypergolic fuel [59]. A laboratory method was used for the preparation of MMH and UDMH by direct methylation of hydrazine with dimethyl sulfate [60]. The relative quantities of MMH and UDMH obtained can be varied by altering the molar ratios of dimethyl sulfate to hydrazine. Small amounts of symmetrical dimethylhydrazine and trimethylhydrazine can also be formed as byproducts in this reaction. The methylation procedure was employed to manufacture several hundred pounds of MMH and UDMH for distribution to various agencies for their test programs in the 1950s.

Methylhydrazine can be prepared by methylating hydrazine or hydrazinium(1+) chloride or hydrazinium(2+) chloride with methyl chloride and/or methanol/hydrochloric acid mixture under pressure. This is done by reacting the mixture resulting from the methylation with an organic base having a  $\text{p}K_{\text{a}}$  value of greater than 7 and a boiling point above 393 K (120 °C), and separating by distillation MMH in a high boiling fraction from the reaction mixture. The high boiling fraction is optionally subjected to further distillation and the amine can be recycled [61–63].

### 1.2.4 Preparation of MMH by Indirect Alkylation of Hydrazine

According to a patent [64], hydrazine and acetone are reacted first to form the acetone hydrazone  $(\text{CH}_3)_2\text{C}=\text{N}-\text{NH}_2$  in a 94% yield. The hydrazone boils at 406–408 K (271–275 °F) and is distilled for purification, then alkylated with dimethyl sulfate to give MMH sulfate in a 72% yield, which melts at 414 K when recrystallized from ethanol. The

sulfate can then be decomposed with diethylenetriamine (which is a stronger base) to give an MMH yield of 67%.

### 1.3 Removal of Water in MMH Manufacturing

Anhydrous MMH can be obtained by continuous distillation of aqueous solutions to which seven parts of a less volatile amine such as hydrazine or ethylene diamine for each part of water have been added. In this azeotropic system, MMH of 99.8% purity will come off at the top of the column [65]. The auxiliary fluid (with all the water in it) is withdrawn from the bottom of the column and must be fractionated in a separate setup.

The separation of MMH (as well as UDMH) from water by selective permeation through membranes and pervaporation has been investigated, but it is not known if it has been used already for the production of any of these fuels. Measurements of diffusion and sorption coefficients of MMH and water in ethyl cellulose membranes were made from the reduced sorption curves to determine the overall selectivity of the membrane [66]. Desorption of MMH hydrate from ethyl cellulose has been attributed to polymer relaxation phenomena. These studies showed that the ethyl cellulose membrane can be used for prolonged periods in MMH and, as such, is suitable for the separation of MMH/water solutions.

Ethyl cellulose membranes have been selected for the separation of hydrazine and MMH solutions by pervaporation based on an extensive study of the overall mass transfer resistance experienced by the permeants [67]. The resistance values were quantitatively estimated by changing the membrane thickness and calculating the corresponding flux. Owing to its lower sorption and fewer interactions, the membrane showed least desorption resistance toward water and thus it is permselective with respect to water. Results of pervaporation selectivity obtained in the separation of water/hydrazine and water/MMH mixtures at azeotropic compositions have been correlated. Higher sorption of MMH and hydrazine did not result in preferential separation, in spite of lower membrane resistance. Experimental results clearly showed that desorption resistance and diffusivity were predominant over the respective solubilities. To confirm the reasons for these phenomena, Fourier transform infrared (FTIR) spectra and DSC thermograms of membranes soaked in pure hydrazine, MMH, water, or hydrazine hydrate were compared.

The desalted reaction aqueous liquor of MMH from a typical Raschig process contains only ~2 mass-% MMH, which also forms an azeotrope with water at an MMH concentration of 35 mass-%. Removal of water to obtain pure MMH using conventional separation methods such as distillation is hazard prone and requires much steam. The potential of membrane-based pervaporation techniques has been investigated for enriching aqueous solutions of MMH [68]. Ethyl cellulose membranes gave promising

results and were resistant to chemical attack by MMH. The effect of operating parameters such as feed concentration and membrane thickness on flux and selectivity were evaluated and aging studies have been carried out to determine the useful life of the membrane in the MMH solution. Polyphenylene oxide membranes were synthesized for dehydration of MMH and UDMH and the effect of feed concentration, membrane thickness, and permeate pressure on permselectivity was investigated [69].

The existence of an azeotrope in the binary system MMH/H<sub>2</sub>O prevents the separation by simple distillation and limits the separation possibilities [70]. An alternative, suitable for continuous flow production units, would be distillations in overpressure or under reduced pressure. Unfortunately, the definition and the development of such processes imply knowledge of experimental data, which are very often lacking. The modeling of the vapor phase compositions represents an advantageous alternative as it allows the selection of the additives and an optimization of the conditions of extraction. Auxiliary fluids were sought that facilitate the separation of MMH and water, and ethylenediamine (EDA) was one such candidate auxiliary fluid. A quasi-ideal model was applied to the predictive calculation of liquid/vapor equilibria of the system H<sub>2</sub>O/EDA [71]. The phase diagram was described by the existence of an azeotrope that disappeared under pressure. A perfect correlation was observed between the calculated results and those of the experiment for the five pressures of the binary system H<sub>2</sub>O/EDA studied. There was a limiting pressure, of 180 kPa, above which the azeotrope phenomenon was no longer observed. Next, the liquid–vapor equilibria of the ternary system H<sub>2</sub>O/EDA/MMH were calculated. The phase diagram was characterized by the existence of a diazotrophic spindle whose projection in the compositions plane separated the system into two distinct distillation fields. This is favorable for the extraction of anhydrous MMH from its azeotropic aqueous solution. Indeed, the continuous distillation of a mixture with a well-defined composition leads to anhydrous MMH at the head of the column and azeotrope H<sub>2</sub>O/EDA at the column bottom. EDA can be dehydrated by distillation under pressure and the anhydrous amine can be recycled continuously.

#### 1.4 Regeneration of Out-of-Specification MMH

At one time during the height of the Space Shuttle program, the White Sands Test Facility (WSTF) had more than 3000 gallons of MMH with a non-volatile residue (NVR) concentration in excess of the specification limit in storage. The MMH had been collected in tanks for several years for future disposition. Rather than dispose of unusable MMH, the feasibility of decontaminating and regenerating the propellant was studied as a cost-effective and environmentally friendly alternative [72]. The NVR was analyzed by FTIR and the spectrum showed that the NVR is a mixture of organic compounds with nitrogen–hydrogen and carbon–hydrogen bonds. After evaluation of several sep-

aration techniques (filtration, adsorption, distillation), distillation was selected as the separation technique. Scaling up from a bench-top distillation unit to a pilot-plant scale distillation unit required careful planning and repeated analysis of the purified MMH [73]. The bench-top distillation unit was able to reduce NVR contamination levels of 12 to 25 mg/L to a level of 0.1 to 0.2 mg/L.

### 1.5 Nitrosation Methods for the Preparation of MMH

The nitrosation of amines leading to the nitrosamine intermediate, followed by reduction with hydrogen, is normally practiced for secondary amines on the way to unsymmetrical dialkylhydrazines only (see the following section). Nitrosation of primary amines is possible if one amine hydrogen is first protected by acetylation, preparing *N*-methylacetamide (AcNHMe) as an intermediate, which is then nitrosated with sodium nitrite and acid. The nitrosamine can be reduced electrolytically in acid solution. The acetylmethylhydrazine is then hydrolyzed and MMH can be recovered by extractive distillation. Recovery of MMH of 69% based on a AcNHMe starting reactant has been reported [74]. Methylhydrazine was obtained in a 25.8% yield by the reduction of *N*-nitrosomethylamine with hydrogen gas over Pd-C catalyst at 2.06 MPa [75]. The need for an increased supply of MMH arose only after the hydrazine (UDMH) industry in the US had already learned its lessons from the production of UDMH via the troublesome nitrosamine process. Consequently, MMH production by way of nitrosamines was never developed to the pilot-plant or even industrial-scale production process level owing to the concern about the toxicity of the nitrosamine intermediates.

### 1.6 Natural Occurrence of Methylhydrazine

Methylhydrazine occurs naturally as a hydrolysis product of a mushroom glucoside gyromitrin, which has been the cause of numerous mushroom poisoning incidents [76–78].

## 2 Physical Properties of MMH

Physical properties of MMH are summarized in Table 2. Additional sources of physical properties of MMH are in the USAF Propellant Handbook, Hydrazine Fuels [79] (from which much information was extracted and was used in the compilation of this section), manufacturer's product data sheets [80], and material safety data sheets.



**Table 2:** Physical properties of methylhydrazine.

| Property                                     | SI units                                   | Other units                                                                     |            |
|----------------------------------------------|--------------------------------------------|---------------------------------------------------------------------------------|------------|
| Molecular mass                               | 46.0724 g/mol                              | 21.705 mol/kg                                                                   |            |
| Melting point                                | 220.78 K                                   | -52.37 °C                                                                       | -62.27 °F  |
| Boiling point                                | 360.80 K                                   | 87.65 °C                                                                        | 189.77 °F  |
| Vapor pressure                               | 6.6 kPa                                    | 49.47 mm Hg                                                                     | 0.957 psia |
| Density, liquid                              | 0.8702 g/cm <sup>3</sup>                   | 54.32 lb/ft <sup>3</sup>                                                        | —          |
| Viscosity, liquid                            | 0.775 cPs                                  | —                                                                               | —          |
| Surface tension                              | 0.3383 mN/cm = dyn/cm × 10 <sup>2</sup>    | —                                                                               | —          |
| Thermal conductivity, liquid                 | 0.248 W m <sup>-1</sup> K <sup>-1</sup>    | 5.92<br>× 10 <sup>-4</sup> cal cm <sup>-1</sup> K <sup>-1</sup> s <sup>-1</sup> | —          |
| Heat capacity, liquid                        | 2.9296 J g <sup>-1</sup> K <sup>-1</sup>   | 0.7002 cal g <sup>-1</sup> °C <sup>-1</sup>                                     | —          |
| Enthalpy of formation, liquid                | +54.835 kJ/mol                             | +13.106 kcal/mol                                                                | —          |
| Heat of fusion, solid                        | 10.420 kJ/mol                              | 2.4905 kcal/mol                                                                 | —          |
| Heat of evaporation, at normal boiling point | 37.212 kJ/mol                              | 8.894 kcal/mol                                                                  | —          |
| Standard entropy, liquid                     | 165.93 J mol <sup>-1</sup> K <sup>-1</sup> | 39.66 cal mol <sup>-1</sup> °C <sup>-1</sup>                                    | —          |
| Standard entropy, vapor                      | 301.3 J mol <sup>-1</sup> K <sup>-1</sup>  | 72.02 cal mol <sup>-1</sup> °C <sup>-1</sup>                                    | —          |
| Dielectric constant, liquid                  | 19                                         | —                                                                               | —          |
| Dipole moment, liquid,                       | 1.68 Debye units                           | —                                                                               | —          |
| Index of refraction n <sub>D</sub>           | 1.4284                                     | —                                                                               | —          |

Note: Physical properties are listed at 298 K unless otherwise stated

Data sources: [22, 81, 82]

## 2.1 Vapor Pressure of MMH

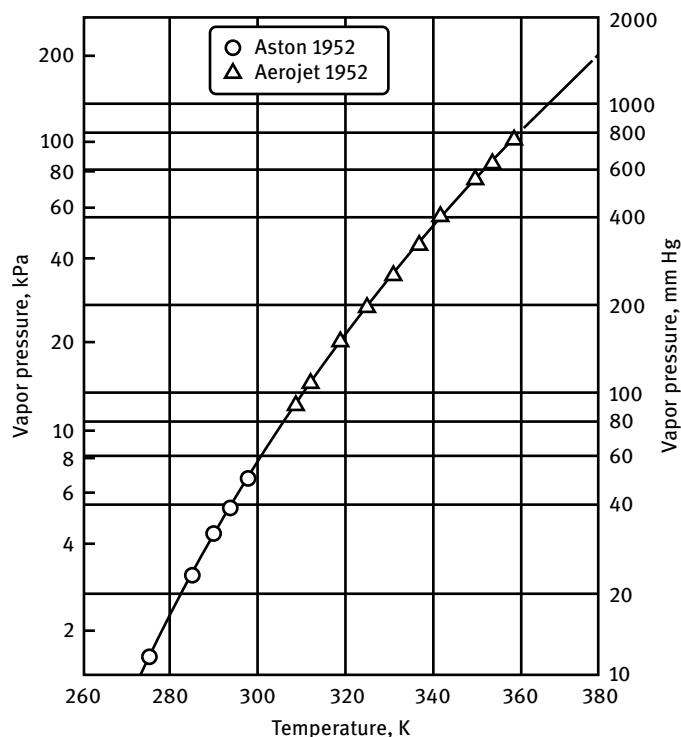
Vapor pressure data for MMH as a function of temperature were compared and graphed in Figure 2 for a moderate temperature range. Vapor pressure of MMH as a function of higher temperature ranges is shown Figure 3, where the curve was forced through the normal boiling point.

The vapor pressure of MMH based on data from Aerojet General Corp [83], and Aston et al. [81] can be described by the following curve-fitted equation:

$$\log p = 7.11158 - \frac{1104.5711}{T} - \frac{152227.7}{T^2}$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. This equation is valid between 265 and 360 K. It would indicate a standard MMH boiling point of 360.8 K (189.8 °F). Another reported boiling point is 360.6 K (189.5 °F) [84]. A more recent source [85] determined the vapor pressure of MMH as:

$$\ln p = 16.749949 - \frac{2776.4399}{T} - \frac{314983.3}{T^2}$$

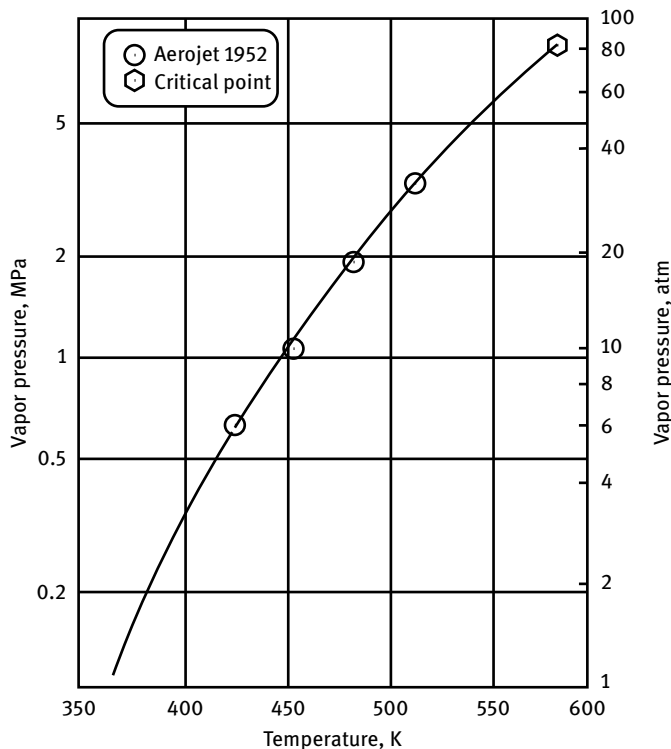


**Figure 2:** Vapor pressure of methylhydrazine as a function of temperature, moderate temperature range. (Reproduced and modified from [79].)

where  $p$  is the vapor pressure in mmHg and  $T$  is the temperature in kelvin. The vapor–liquid equilibria of the binary system  $\text{CH}_3\text{NHNH}_2/\text{H}_2\text{O}$  were investigated from 27 to 108 kPa using a Swietoslawski-type ebulliometer [86]. From the results obtained, the modeling, in terms of associations, of the Gibbs free energy of mixing at 101.35 kPa for the liquid phase of this system enabled one to explain the observed non-ideality of the solution and to give a picture of the strong interactions existing in the mixtures, considered to be chemical associations by hydrogen bonds. This information is needed to explain some physical properties of the liquid phase, such as molar volumes, viscosity, static permittivity, and dielectric relaxation times over the whole concentration range.

Vapor pressure between the boiling point and the critical point can be represented by the following equation [79, 83]:

$$\log P = 4.5106 - \frac{1355.07}{T} - \frac{98237.8}{T^2}$$



**Figure 3:** Vapor pressure of methylhydrazine as a function of temperature, high temperature range. (Reproduced and modified from [79])

where  $P$  is the pressure in atm and  $T$  is the temperature in kelvin. In SI units ( $P$  in kPa), these equations convert to (for 273–360 K) [87–90]:

$$\log P = 6.2638 - \frac{1104.57}{T} - \frac{152227.06}{T^2}$$

where  $P$  is the pressure in kPa and  $T$  is the temperature in kelvin. And for the higher temperature range of 360–580 K the following equation can be used:

$$\log P = 6.5163 - \frac{1355.07}{T} - \frac{98237.8}{T^2}$$

Vapor pressure and sublimation pressure measurements of MMH were extended to low temperatures below the freezing point [91]. The data between 207 and 350 K can

be represented by:

$$\log P = 9.181621 - \frac{1065.025088}{T} - \frac{158905.5445}{T^2}$$

where  $P$  is the vapor pressure in pascal and  $T$  is the temperature in kelvin.

The vapor pressure data from Aston et al. 1951 for the range 275.11–298.32 K can be expressed by an Antoine equation:

$$\log_{10}(P) = 3.96787 - [1115.19/(T - 81.502)]$$

where  $P$  is the pressure in bar and  $T$  is the temperature in kelvin.

Vapor pressure measurements below 383 K could be expressed by the curve-fitted equation [92]:

$$\ln P = 19.153 - 5516.3/T + 103742.19/T^2$$

where  $P$  is the pressure in kPa and  $T$  is the temperature in kelvin. The maximum deviation of this curve from literature data was 7%. The heat of vaporization derived from the slope of this vapor pressure curve was 40.9 kJ/mol, similar to the 40.36 kJ/mol reported by Aston [81].

## 2.2 Equation of State of MMH

The accurate knowledge of the vapor pressure of MMH and other propellants is important for the assessment of flammability, explosion, and toxicity hazards at rocket test sites and in spacecraft. In an effort similar to previous/parallel calculations with various equations of state for anhydrous hydrazine, the Peng–Robinson and Soave–Redlich–Kwong (SRK) equations of state (EOS) for MMH were tested for thermodynamic consistency and the property data (critical properties, fugacity coefficients, and vapor pressure values) [89, 93]. In a side-by-side comparison, both the Peng–Robinson and the SRK EOS were then used to calculate vapor pressure values that were compared with published experimental data and vapor pressure correlation values. The Peng–Robinson EOS gave a better fit for hydrazine, and the SRK EOS gave a better fit for MMH. It was not stated which vapor pressure data from which source were used for this exercise. Equations of state, critical properties, and vapor–pressure correlations for hydrazine and MMH were used to show the importance of utilizing the most accurate vapor pressure values, and a safety analysis was performed on a hypothetical hazardous fluids test cell that needed to be purged to remove toxic vapors. The analysis showed the effect that a  $\pm 5\%$  difference in the initial vapor pressure can have on determining the length of time it takes a cell to be flushed out with air in order to meet the toxicity limits permissible for personnel to re-enter the contaminated area.

In another example, the SRK EOS was used to calculate real fluid isentropic (near adiabatic) compression temperature for the fuel/ullage gas mixtures. The isentropic final temperature  $T_2$  after compressing an ideal gas sample from  $P_1$  to  $P_2$  is:

$$T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

where  $\gamma = C_p/C_v$ . For real gases and MMH vapors,  $C_p$  and  $\gamma$  vary with temperature. The EOS was inserted to calculate compression temperature as a function of compression ratio. Starting with MMH vapor at its room temperature vapor pressure, compression ratios near 150 would be required to heat the vapor to the autodecomposition temperature of MMH in nitrogen (about 530 K). Similar calculations were made for helium, nitrogen, and mixtures of carbon monoxide, carbon dioxide, and water vapor in contact with MMH. It is assumed that the mixture of carbon monoxide, carbon dioxide, and water vapor was supposed to simulate the exhaust gas of a pyrotechnic charge in a pyrovalve blow-by situation.

In continuing to try to find the best-fitting EOS for MMH under rapid compression situations, the SRK EOS was again used for computing isentropic compression temperatures of MMH vapor [94]. It was shown that there can be a significant difference between treating MMH as a real fluid and as an ideal gas. Using the SRK EOS, a table of thermodynamic properties was computed for MMH, both saturated liquid and saturated vapor, and applied to isentropic compression or expansion of two-phase mixtures, e.g., liquid–vapor, of MMH. The use of an EOS to calculate vapor pressure reversed the previous application of the equation which required equality of the fugacity coefficients. For a given temperature, the pressure was adjusted until the computed liquid and vapor fugacity coefficients were equal. Application of the SRK EOS to the low temperature regime for MMH resulted in a consistent set of data. By comparing liquid and vapor phase fugacity coefficients, using the SRK EOS, which was previously determined to be a good representation of the phase behavior of MMH, it was possible to adjust low pressure vapor pressure data to achieve thermodynamic consistency. Using the adjusted vapor pressure data, a pseudo-Mollier diagram,  $S$  vs.  $\ln T$ , was constructed for MMH using an orthobaric calculation and applied to calculations of isentropic compression or expansion of MMH. The shape of the liquid–vapor coexistence envelope curve was thermodynamically consistent. Future work would need to perform a closer examination of the behavior of MMH near the critical point, including scaling law considerations.

To calculate the vapor pressure during the vaporization of MMH at very high pressures, such as in a rocket combustion chamber, requires a different set of equations [95]. Under these conditions, MMH transitions from evaporation to decomposition.

### 2.3 Vapor-Phase Composition of MMH/H<sub>2</sub>O Mixtures

The vapor-phase composition and partial pressure above dilute solutions of hydrazine or MMH in water is of practical interest for several reasons: **(1)** for the recovery of hydrazines from dilute solutions by distillation, **(2)** for predicting the downwind hazard from evaporating hydrazine spills, and **(3)** for designing water spray scrubbers for the removal of MMH vapors from depressurizing storage tanks vent gases or tank purge gases. Henry's law constants were determined for hydrazine and MMH in water as part of a vapor scrubber design study [96]. Measurements were performed at 283, 293, and 303 K on 1, 0.5, 0.25, and 0.1% solutions, buffered at pH 7 and unbuffered. The effect of 1 and 2% added sodium chloride was also evaluated. The addition of salt reduces the constant  $k$  slightly. Henry's law states that the partial pressure of constituent  $A$  above a mixture is proportional to the molar fraction  $X$  of the ingredient  $A$  in the liquid phase:

$$p_A = kXA.$$

The values of  $k$  were found to be relatively independent of concentration (Table 3). A plot of  $\log k$  versus  $1/T$  (reciprocal absolute temperature) gave the following heats of vaporization in kJ/mol (kcal/mol):

|           | Buffered at pH 7         | Unbuffered               |
|-----------|--------------------------|--------------------------|
| Hydrazine | 36 kJ/mol (8.6 kcal/mol) | 39 kJ/mol (9.3 kcal/mol) |
| MMH       | 25 kJ/mol (5.9 kcal/mol) | 31 kJ/mol (7.4 kcal/mol) |

The  $k$  values for hydrazine or MMH are only 5% of what would be expected from ideal mixtures based on Raoult's law. This indicates that there is strong solvent-solute interaction for both hydrazines that reduces their concentrations in the vapor phase. MMH and water form an azeotrope containing 42% MMH.

**Table 3:** Henry's law constants for aqueous solutions of methylhydrazine.

| Temperature<br>K | Henry's law constant $k \times 10^4$ ,<br>buffered pH 7<br>Concentration, mass-% |     |     | Henry's law constant $k \times 10^4$ ,<br>unbuffered<br>Concentration, mass-% |     |     |
|------------------|----------------------------------------------------------------------------------|-----|-----|-------------------------------------------------------------------------------|-----|-----|
|                  | 1.0                                                                              | 0.5 | 0.1 | 1.0                                                                           | 0.5 | 0.1 |
| 283              | 1.4                                                                              | 1.6 | 1.6 | 13                                                                            | 15  | 15  |
| 293              | 1.4                                                                              | 1.7 | 1.8 | 26                                                                            | 25  | 29  |
| 303              | 3.0                                                                              | 3.1 | 3.4 | 33                                                                            | 33  | 34  |

Data source: [96]

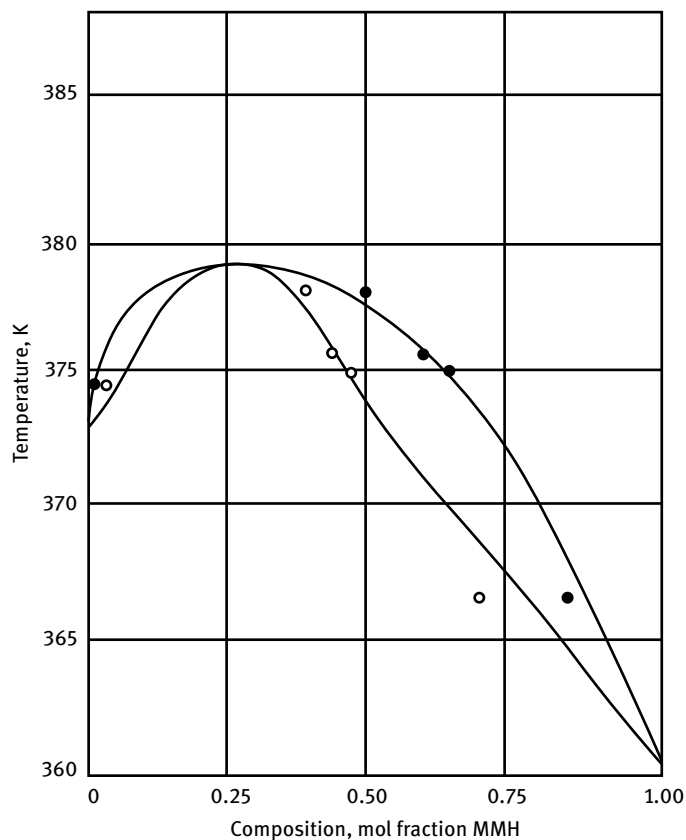
There is a pinch point at the azeotrope concentration, making further concentration difficult. Using a longer distillation column results in only a small improvement of product concentration [32]. For sizing an azeotrope distillation column that takes in a 2% MMH solution and delivers a 42% MMH solution, model distillations were performed under laboratory conditions. A separation factor was calculated from the composition of the overhead and the reboiler. The relative volatility  $\alpha$  can then be calculated based on the number of theoretical plates in the column. The volatility  $\alpha$  and the optimal number of theoretical plates can be determined graphically. Once the 42% MMH intermediate is obtained, the remaining water has to be removed by the addition of concentrated caustic and an extractive distillation in the finishing column. An equation for the activity coefficient of MMH volatility in water mixtures takes the form:

$$\log y_c = \frac{-0.9172}{\left[1 + \frac{0.9172X_c}{0.3273(1 - X_c)}\right]^2}$$

where  $X_c$  is the MMH molar fraction in the liquid phase [97]. Measurements of the equilibrium liquid and vapor compositions vs. temperatures at 101 kPa (1 atm) total pressure for the non-ideal system MMH/H<sub>2</sub>O showed a rather large deviation from ideal liquid–vapor solution behavior [85]. The solution model attributes the non-ideality to the formation of chemical association species that obey Henry's law in terms of actual solution equilibrium molar fractions. The unassociated MMH and water are assumed to obey Raoult's law in terms of actual molar fraction composition. Similar measurements were performed for UDMH-containing systems. Figure 4 shows a maximum boiling azeotrope of MMH and water and shows the two lines, the liquid composition and the vapor composition, to be tangent to one another at 378.83 K (105.68 °C) and  $\chi_{\text{MMH}} = 0.2837$ . If one plots the excess Gibbs free energy of mixing, the curve shows a rather large negative free energy. For the H<sub>2</sub>O (= A)/MMH (= B) system, both A : B = 1 : 1 and 1 : 3 association clusters prevail in the mixture.

The Ferriol data illustrated in Figure 5 are better than those in Figure 4 because the graph in Figure 5 is based on eight data pairs instead of only five, as in Figure 4 (but the graph is more confusing because it contains additional data for three different pressures).

The water used in the process of MMH preparation and separation is critical for the quality of MMH. The vapor–liquid equilibrium of MMH/H<sub>2</sub>O binary system was measured at 101 kPa and the influence of MMH/H<sub>2</sub>O/electrolyte ternary systems was examined [98]. Electrolytes remarkably raised the volatility of MMH and changed the vapor–liquid equilibrium of the MMH/H<sub>2</sub>O binary system. The vapor–liquid equilibrium of MMH/H<sub>2</sub>O/NaCl and MMH/H<sub>2</sub>O/NaOH ternary systems were studied by experiments. Salt effects of electrolytes were correlated using a salt effect coefficient method and a solvation method. NaOH had a greater effect on the MMH/H<sub>2</sub>O binary system than NaCl. Salt effects of these two electrolytes were compared.



**Figure 4:** Equilibrium liquid and vapor compositions at 1atm total pressure vs. molar fraction methylhydrazine. (Republished and modified from [85], with permission from ©1987 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

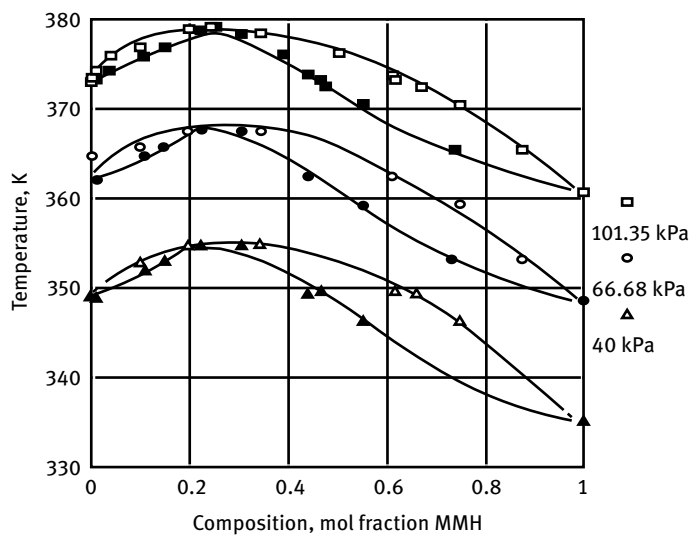
The vapor pressure of a mixture of 72mass-% MMH and 28% water can be calculated from the equation:

$$\log P = 7.8894 - \frac{1852}{T}$$

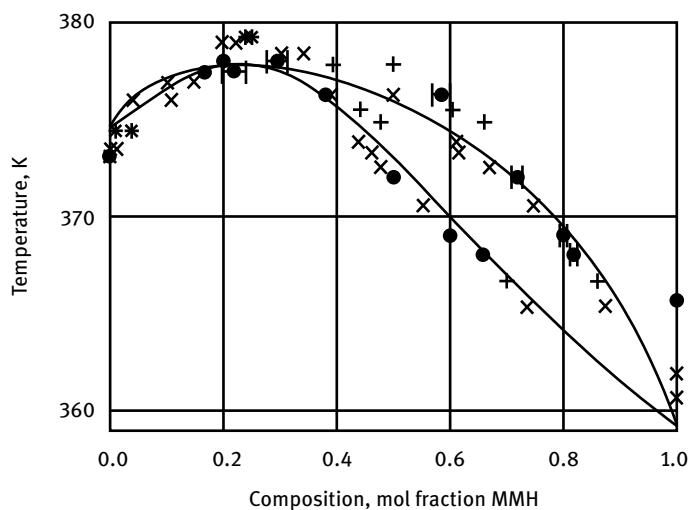
where  $P$  is the pressure in mm Hg and  $T$  is the absolute temperature [99].

Vapor-liquid equilibria of the MMH/water system can be predicted by computational chemistry. Predictions for MMH/water isobaric vapor-liquid equilibria and vapor phase compositions from quantum mechanical and Grand Equilibrium and force field model computational methods were compared with measured data from Ferriol et al. [86] or Cohen-Adad et al. [85] and were in moderately accurate agreement [100]. Figure 6 depicts the vapor-liquid equilibrium of MMH + water at ambient pressure. It





**Figure 5:** Vapor–liquid equilibrium of methylhydrazine/water mixtures at three different pressures. (Reproduced and modified from [86], with permission of ©1991 Elsevier; permission conveyed through RightsLink.)



**Figure 6:** Isobaric vapor–liquid phase diagram of MMH. (Republished and modified from [101], with permission of ©2012 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Legend: + water at 0.1013 MPa; (x) experimental data by Ferriol et al. [86]; (+) experimental data by Cohen-Adad et al. [85]; (•) Elts simulation data with  $\xi = 1.3$ ; solid line Peng–Robinson EOS with  $k_{ij} = -0.197$

can be seen that the experimental data by Ferriol et al. [86] and by Cohen-Adad et al. [85] are quite similar; however, they differ near the azeotropic region. Like aqueous hydrazine, this mixture is azeotropic, having a temperature maximum. In this case, the azeotropic point lies at an MMH molar fraction of  $\chi_{\text{MMH}} \approx 0.25$  mol/mol. The experimental data by Ferriol et al. [86] at 372.55 K and  $\chi_{\text{MMH}} = 0.476$  mol/mol were taken to adjust the binary parameter of the molecular model ( $\xi = 1.3$ ) and of the Peng–Robinson EOS ( $k_{ij} = -0.197$ ). In the water-rich region, to the left of the azeotropic point in Figure 6, vapor–liquid equilibrium computer simulations were not feasible because of sampling problems [101]. Considering the substantial experimental uncertainties, the data sets from all three approaches agreed very favorably.

If MMH is made by methylation of hydrazine or hydrazine hydrate, in the presence of an excess of hydrazine or hydrazine hydrate, the reaction mixture may consist of MMH, unreacted hydrazine (hydrate), and water. This ternary mixture forms an azeotrope that is difficult to separate by simple distillation [102].

Methylhydrazine vapor and water vapor associate in the vapor phase to form clusters in which the frequencies of hydrogen bond infrared (IR) bands are shifted. A theoretical study of the geometry and molecular parameters of the methylhydrazine–hydrate complex analyzed two geometries, considering the interaction between water in: **(1)** a lone nitrogen pair assisted by a  $\text{CH}_3$  group; and **(2)** the nitrogen of the  $\text{NH}_2$  group [103]. These geometries were examined by examining the formation of ( $\text{N}\cdots\text{H}$ ) hydrogen bonds, which were characterized using charge transfer, as well as topological parameters derived from Quantum Theory of Atoms in Molecules calculations. A trimolecular system may be formed by methylhydrazine and two attached water molecules.

## 2.4 Density of Methylhydrazine

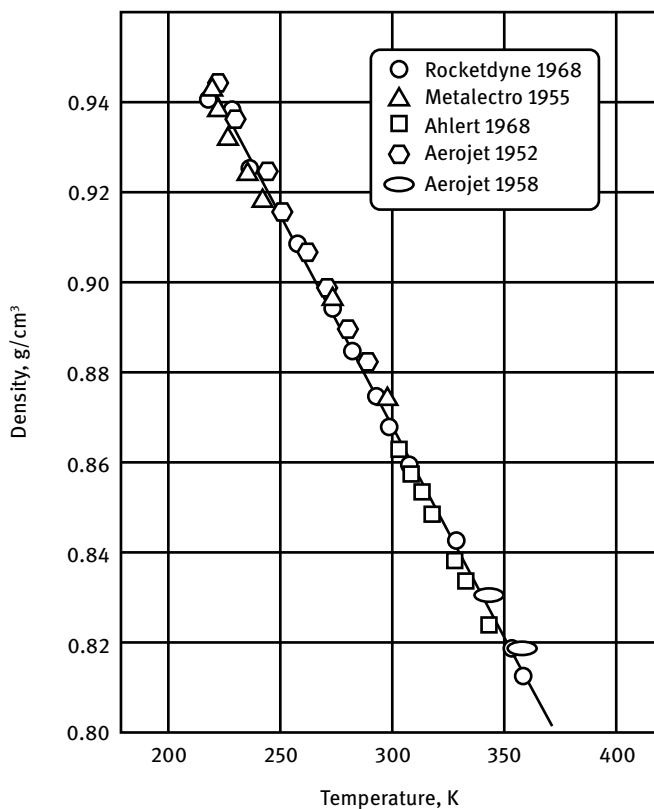
The density of methylhydrazines is generally below that of hydrazine itself. This is due to reduced association of the molecules in the liquid phase (less hydrogen bonding). The density of MMH has been measured by numerous authors and companies, including Horvitz and Osborg [104], Ahlert and Shimalla [105], Aerojet General Corp. [83], and Barger et al. [106]. The temperature dependence of the density of MMH can be reproduced by:

$$\rho = 1.15034 - 9.3949 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. Other authors obtained the following relationship, giving slightly higher densities [107]:

$$\rho = 0.7917 + 1.9396 \times 10^{-3} T - 5.564 \times 10^{-6} T^2$$

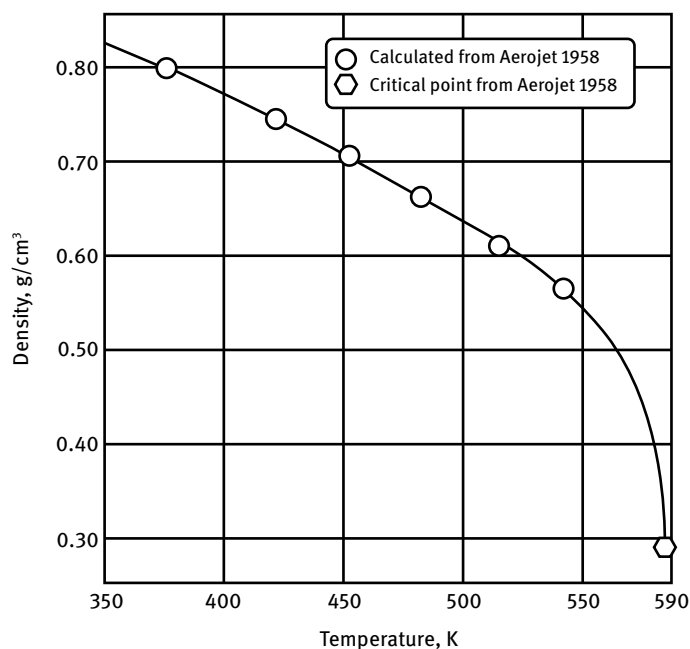
where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. Density data from several different sources at moderate temperatures are shown in Figure 7.



**Figure 7:** Density as a function of temperature, saturated liquid methylhydrazine; moderate temperature range. (Reproduced and modified from [79].)

The density of the saturated liquid at elevated temperatures above the normal boiling point has to take into consideration the compressibility of the liquid at higher pressures. Data reported for pressures other than the saturation pressure should thus be normalized to the saturation pressure. Normalized density data from Aerojet [83] and the Handbook [79] for the density of liquid MMH between the normal boiling point and the critical point are shown in Figure 8.

Attempts to predict density, EOS, second virial coefficients, and critical point properties of MMH from theoretical computations have not always produced accurate results [100, 101].



**Figure 8:** Density as a function of temperature, saturated liquid methylhydrazine; elevated temperature range. (Reproduced and modified from [79].)

## 2.4.1 Density of MMH Mixtures

### 2.4.1.1 Density of Mixtures of Methylhydrazine with Water

The density of MMH/H<sub>2</sub>O mixtures at 295 K increases linearly from 0.873 at 0% H<sub>2</sub>O to 0.955 g/cm<sup>3</sup> at 28% H<sub>2</sub>O. The rate of density increase is less steep for water concentrations above 28%. The density of the 28% water/MMH mix can be calculated from:

$$\rho = 0.975 - 0.00086 t$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $t$  is the temperature in °C. The density of the same mix as a function of temperature and pressure can be calculated from:

$$\rho = 0.975 - 8.6 \times 10^{-4} t + 3.3 \times 10^{-6} P$$

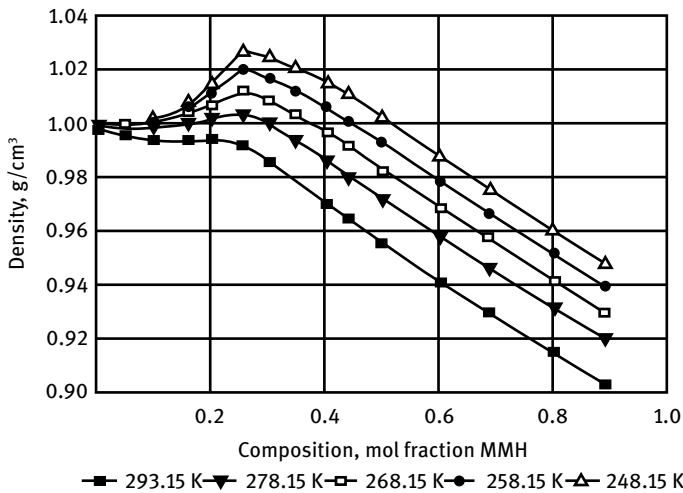
where  $\rho$  is the density in g/cm<sup>3</sup>,  $t$  is the temperature in °C, and  $P$  is the pressure in psia [99]. If one plots the results of this equation on graph paper, the curves are very close to each other and the pressure effect is not very pronounced (at least within this range in the order of hundreds instead of thousands of psia).

Density and viscosity of MMH/water mixtures were measured over the entire range of compositions and between 148 and 293 K [107], as summarized in Table 4 (density) and Table 6 (viscosity) and as illustrated in Figure 9 (density) and Figure 13

**Table 4:** Density of methylhydrazine/water mixtures.

| Temperature, K     | 293.15                     | 278.15 | 268.15 | 258.15 | 248.15 |
|--------------------|----------------------------|--------|--------|--------|--------|
| Molar fraction MMH | Density, g/cm <sup>3</sup> |        |        |        |        |
| 0.0000             | 0.9982                     | 0.9999 | 0.9993 | 0.9963 | —      |
| 0.0514             | 0.9955                     | 0.9985 | 0.9998 | —      | —      |
| 0.1003             | 0.9940                     | 0.9989 | 1.0012 | 1.0026 | —      |
| 0.1615             | 0.9940                     | 1.0000 | 1.0045 | 1.0064 | 1.0080 |
| 0.2017             | 0.9941                     | 1.0020 | 1.0071 | 1.0112 | 1.0146 |
| 0.2563             | 0.9916                     | 1.0038 | 1.0124 | 1.0205 | 1.0276 |
| 0.3030             | 0.9860                     | 1.0005 | 1.0090 | 1.0170 | 1.0250 |
| 0.3482             | 0.9760                     | 0.9942 | 1.0037 | 1.0120 | 1.0210 |
| 0.4048             | 0.9700                     | 0.9860 | 0.9970 | 1.0060 | 1.0152 |
| 0.4408             | 0.9650                     | 0.9800 | 0.9920 | 1.0010 | 1.0110 |
| 0.5008             | 0.9558                     | 0.9720 | 0.9830 | 0.9932 | 1.0028 |
| 0.6034             | 0.9410                     | 0.9580 | 0.9690 | 0.9780 | 0.9880 |
| 0.6873             | 0.9300                     | 0.9460 | 0.9580 | 0.9669 | 0.9760 |
| 0.8036             | 0.9150                     | 0.9320 | 0.9420 | 0.9520 | 0.9610 |
| 0.8917             | 0.9030                     | 0.9200 | 0.9300 | 0.9400 | 0.9480 |
| 1.0000             | 0.8835                     | 0.9010 | 0.9120 | 0.9213 | 0.9300 |

Data source: [107]



**Figure 9:** Density of methylhydrazine/water mixtures. (Graph created by Schmidt 2016, based on data from [107].)

(viscosity). Vapor pressure, density, and viscosity data applied to a chemical association model indicated that the solutions contain a MMH monohydrate, a trihydrate, and an MMH dimer [85, 107, 108].

#### 2.4.1.2 Density of Mixtures of Methylhydrazine with Hydrazine

Hydrazine/MMH blends containing 14, 35, 60, and 90% hydrazine were tested as rocket propellants and densities of the four blends were measured from 260 to 325 K [109]. The temperature dependence of the density of three selected hydrazine/MMH mixtures can be represented by the three equations in Table 5.

**Table 5:** Temperature dependence of the density of three selected hydrazine/methylhydrazine mixtures.

| Composition, mass-% $\text{N}_2\text{H}_4$ | Density $\rho$ in $\text{g}/\text{cm}^3$ , temperature $T$ in kelvin |
|--------------------------------------------|----------------------------------------------------------------------|
| 30.24                                      | $\rho = 1.1998117 - 0.000967625T$                                    |
| 56.15                                      | $\rho = 1.23459405 - 0.000965816T$                                   |
| 78.04                                      | $\rho = 1.24102194 - 0.00090115T$                                    |

Data source: [105]

More detailed data on density of MHF-3 as a function of temperature and pressure are presented in Section 13.2.1.1.

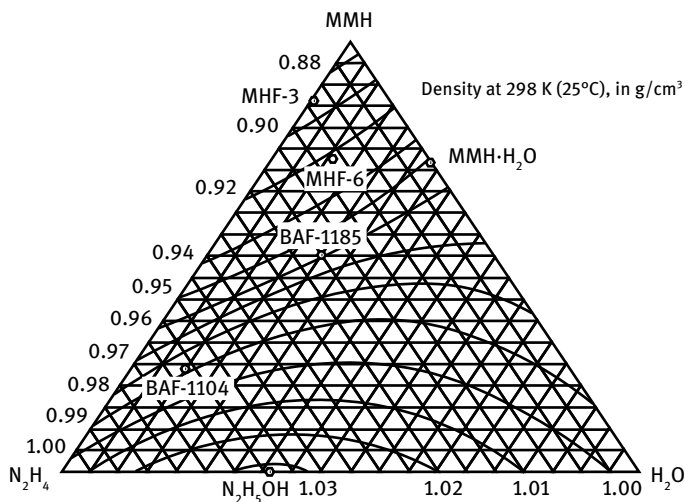
#### 2.4.1.3 Density of Ternary MMH/ $\text{N}_2\text{H}_4$ / $\text{H}_2\text{O}$ Mixtures

Mixtures of MMH, hydrazine, and water are of interest as monopropellants and as fuels. The densities of MMH, hydrazine, and water mixtures are illustrated in Figure 10. There is a maximum of density around the point that corresponds to hydrazine hydrate.

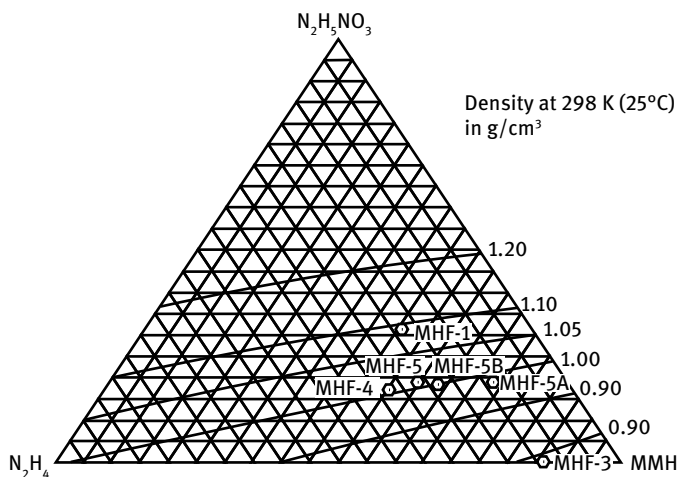
#### 2.4.1.4 Density of Ternary MMH/ $\text{N}_2\text{H}_4$ /HN Mixtures

Mixtures of MMH, hydrazine, and hydrazinium nitrate (HN) are of interest as monopropellants and as fuels. The density of MHF-5A, a monopropellant composed of 68% MMH, 13%  $\text{N}_2\text{H}_4$ , and 19% HN, is  $0.996 \text{ g}/\text{cm}^3$  ( $62.2 \text{ lb}/\text{ft}^3$ ) at 298 K (77°F) and  $0.968 \text{ g}/\text{cm}^3$  ( $60.4 \text{ lb}/\text{ft}^3$ ) at 328 K (130°F). The density of MHF-5B (58% MMH, 23%  $\text{N}_2\text{H}_4$ , 19% HN) at the same two temperatures is 1.002 and  $0.974 \text{ g}/\text{cm}^3$  respectively [110].

The densities of mixtures of MMH, hydrazine, and HN are illustrated in Figure 11. The lowest densities are in the MMH corner of the graph. Densities increase with increasing hydrazine and/or HN content.



**Figure 10:** Densities of methylhydrazine, hydrazine, and water mixtures. (Reproduced and modified from [79].)



**Figure 11:** Densities of ternary mixtures of methylhydrazine,  $\text{N}_2\text{H}_4$ , and hydrazinium nitrate. (Reproduced and modified from [79].)

## 2.5 Compressibility of Methylhydrazine

Sonochemistry is a new discipline in the study of chemical reactions. Transient temperatures up to 5000 K and pressures of 500 atm can occur during the adiabatic compression (collapse) of cavitating microcavities. Under these conditions, ther-

modynamically unstable substances such as hydrazine and MMH are susceptible to decomposition. Hydrazine in pure form or in dilute aqueous solution (100 ppm) decomposes smoothly to nitrogen and hydrogen when irradiated by a 600-W ultrasonic probe at 20 kHz [111]. Dilute solutions of MMH decompose at about the same rates as hydrazine; however, the products are more complex, yielding methyl amine, methyl alcohol, and ammonia.

For MMH, no direct measurements of isothermal compressibility have been reported, but isothermal compressibilities  $\beta_i$  can also be calculated from density data at different pressures:

$$\beta_i = \frac{1}{V} \frac{dV}{dP}$$

A set of MMH densities has been reported for temperatures from 340.6 to 543 K at two different pressures [83, 106]. From these data a compressibility–temperature dependence function of:

$$\begin{aligned}\beta_i \left( \frac{\text{cm}^2}{\text{kg}_f} \right) &= 2.133 \times 10^{-6} T - 6.727 \times 10^{-4} \\ \beta_i \left( \frac{\text{m}^2}{\text{N}} \right) &= 2.174 \times 10^{-11} T - 6.857 \times 10^{-9}\end{aligned}$$

can be calculated. However, as density was measured at only two pressures for each temperature, the equation is not very accurate.

Data compiled by Rocketdyne over a wider temperature range gave the following equation for the temperature dependence of the adiabatic compressibility for MMH (we are repeating the original equations in units of  $\text{cm}^2/\text{kg}_f$  in spite of their non-standard units):

$$\beta_a(\text{MMH}) \left( \frac{\text{cm}^2}{\text{kg}_f} \right) = 3.0413 \times 10^{-5} - 2.1258 \times 10^{-7} T + 9.194 \times 10^{-10} T^2$$

where  $T$  is the temperature in kelvin.

## 2.6 Velocity of Sound in Liquid Methylhydrazine

The velocity of sound in liquid MMH is 1548 m/s at 298 K and the velocity of sound in MMH vapor is 310.2 m/s at 361 K [90]. The velocity of sound in liquid MMH and its temperature dependence can be calculated by using the following equation:

$$c_{\text{MMH}} = 2711.6 - 3.903T$$

where  $c$  is the velocity of sound in m/s and  $T$  the temperature in kelvin.

It is planned to determine the density by the buoyancy of a floater and to determine the velocity of sound in MMH along the saturation curve at temperatures up to



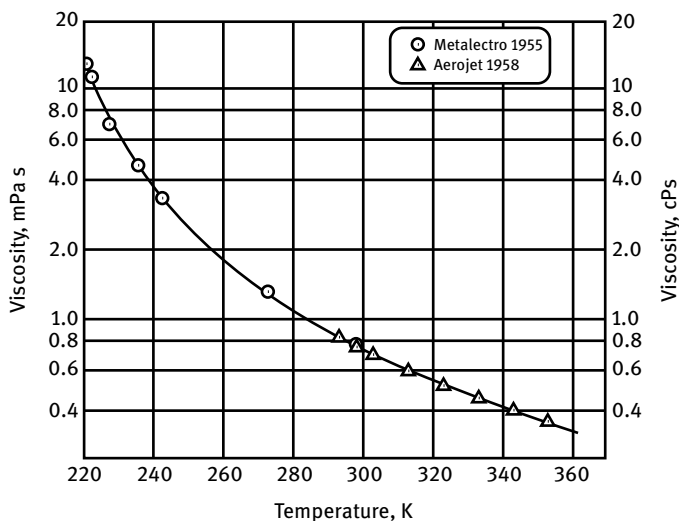
the critical point and pressures up to 200 bar by measuring the resonant frequency in a high-pressure bomb made of titanium with sapphire windows [112].

## 2.7 Viscosity of Methylhydrazine

The viscosity of MMH has been measured by numerous authors and companies, including Horvitz and Osborg [104], Barger et al. [106], Horvitz [113], and Horvitz et al. [114]. The data were obtained at different temperatures, but agreement within the overlapping range at 298 K is quite good. The curve in Figure 12 was calculated using the following formula, which is based on the combined data from multiple sources:

$$\log \mu = -7.9944 + \frac{6123.96}{T} - \frac{1.7458 \times 10^6}{T^2} - \frac{1.8509 \times 10^8}{T^3}$$

where  $\mu$  is the dynamic viscosity in cPs and  $T$  is the temperature in kelvin.



**Figure 12:** Dynamic viscosity versus temperature for liquid methylhydrazine. (Reproduced and modified from [79].)

### 2.7.1 Viscosity of MMH/H<sub>2</sub>O Mixtures

The viscosity of MMH/H<sub>2</sub>O mixtures passes through a maximum at 28 mass-% H<sub>2</sub>O. This mixture corresponds to a 1:1 molar ratio of MMH:H<sub>2</sub>O, indicating formation of a hydrate compound [99]. The viscosity of the MMH hydrate at 277.5 K (40 °F) is 8 cPs, much higher than that of water (2.5 cPs) or MMH (1.3 cPs). The viscosity of the MMH hydrate mix increases steeply as it approaches 255 K (0 °F). At that temperature the vis-

cosity is 35 cPs. Viscosity of MMH/water mixtures was measured over the entire range of compositions and between 148 and 293 K, as summarized in Table 6 and as illustrated in Figure 13 [107].

**Table 6:** Viscosity of methylhydrazine/water mixtures.

| Temperature, K     | 293.15         | 278.15 | 268.15 | 258.15 | 248.15 |
|--------------------|----------------|--------|--------|--------|--------|
| Molar fraction MMH | Viscosity, mPs |        |        |        |        |
| 0.0000             | 1.01           | 1.53   | 2.16   | 3.34   | 6.45   |
| 0.0514             | 1.53           | 2.55   | 3.67   | —      | —      |
| 0.1003             | 2.35           | 4.18   | 6.46   | 11.44  | —      |
| 0.1615             | 3.54           | 7.18   | 11.79  | 24.83  | 52.28  |
| 0.2017             | 4.51           | 9.30   | 16.16  | 37.62  | 84.39  |
| 0.2563             | 5.58           | 12.15  | 22.30  | 50.90  | 124.95 |
| 0.3030             | 6.00           | 13.52  | 26.47  | 58.85  | 165.14 |
| 0.3482             | 5.90           | 13.32  | 26.89  | 61.50  | 167.20 |
| 0.4048             | 5.50           | 12.28  | 24.33  | 54.67  | 140.14 |
| 0.4408             | 4.91           | 10.68  | 20.84  | 42.43  | 118.51 |
| 0.5008             | 4.07           | 7.88   | 14.95  | 30.62  | 78.79  |
| 0.6034             | 2.98           | 5.53   | 9.40   | 17.58  | 41.96  |
| 0.6873             | 2.16           | 3.48   | 5.80   | 10.15  | 23.36  |
| 0.8036             | 1.56           | 2.51   | 3.67   | 5.97   | 10.63  |
| 0.8917             | 1.22           | 1.66   | 2.34   | 2.88   | 5.27   |
| 1.0000             | 0.96           | 1.15   | 1.59   | 2.18   | 3.19   |

Data source: [107]

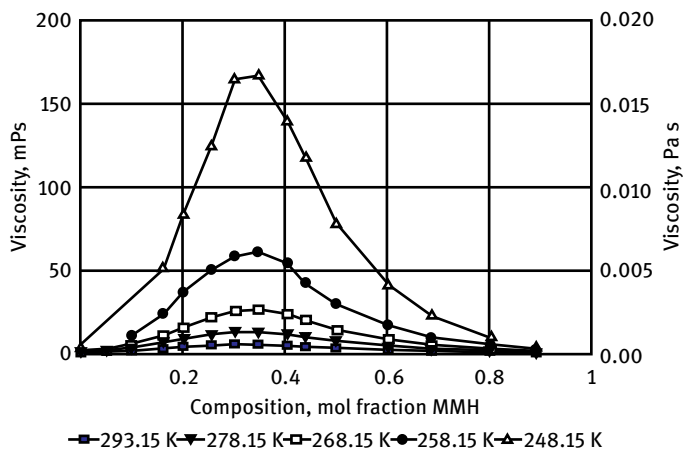
The viscosity of MMH/water mixtures peaks near an MMH molar fraction of 0.33. The peak is very pronounced at the lower temperatures. These data indicate that the solutions contain a MMH monohydrate, a trihydrate, and an MMH dimer. One mixture of 72% MMH and 28% water was of particular interest, as it was used as a fuel in the SURVEYOR space probes that soft-landed on the Moon [99]. The viscosity of this fuel blend as a function of temperature is tabulated in Table 7.

## 2.7.2 Viscosity of Methylhydrazine/Hydrazine Mixtures

The viscosity of MHF-3 is described in Section 13.2.1.4.

## 2.7.3 Viscosity of Ternary Mixtures with Methylhydrazine

The viscosity of MHF-5B, a monopropellant consisting of 58% MMH, 23%  $\text{N}_2\text{H}_4$ , and 19% HN at 233, 298, and 328 K, is 38, 1.98, and 1.1 cPs, respectively [110]. Additional properties of MHF-5B are listed in Section 13.3.1. The absolute viscosities of ternary mixtures of MMH,  $\text{N}_2\text{H}_4$ , and  $\text{N}_2\text{H}_5\text{NO}_3$  are illustrated in the triangular chart in Figure 14. The viscosities of these mixtures increase with increasing HN content.



**Figure 13:** Viscosity of methylhydrazine/water mixtures. (Chart created by Schmidt 2016, based on data from [107].)

**Table 7:** Kinematic viscosity of 72% methylhydrazine/28% water fuel blend.

| Temperature |       |       | Kinematic viscosity |
|-------------|-------|-------|---------------------|
| K           | °C    | °F    | cSt                 |
| 237.1       | −36.0 | −32.8 | 225.0               |
| 255.6       | −17.5 | 0.7   | 37.0                |
| 273.1       | 0.0   | 32.0  | 10.3                |
| 298.1       | 25.0  | 77.0  | 3.45                |
| 306.6       | 33.5  | 92.3  | 2.59                |

Data source: [99]

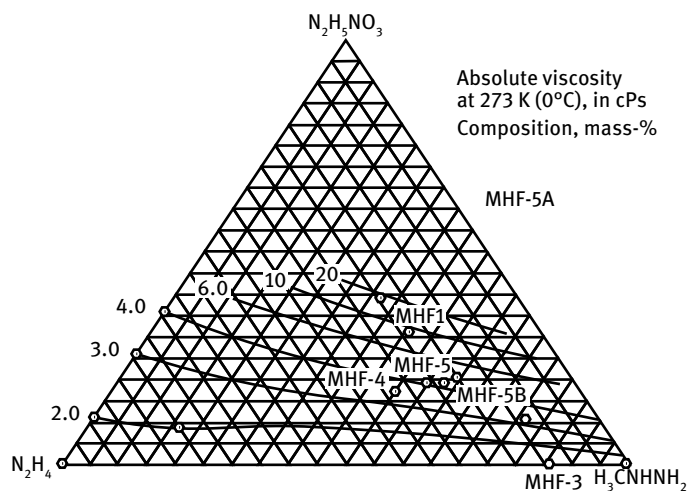
## 2.8 Surface Tension of Methylhydrazine

Knowledge of surface tension of methylhydrazine is of both theoretical and practical interest because (1) the surface tension can be used to derive parachor data and gain information on the molecular structure of these compounds and (2) the design of fuel tanks for retaining fluids by capillary forces in the weightlessness of outer space requires the knowledge of the surface tension and wetting angles.

The surface tension of MMH at 298 K is  $3.383 \times 10^{-4}$  N/m [90]. The surface tension of MMH as a function of temperature can be expressed by the following equations:

$$\sigma_{\text{MMH}} \left( \frac{\text{dyn}}{\text{cm}} \right) = 63.480 - 0.09944T$$

$$\sigma_{\text{MMH}} \left( \frac{\text{N}}{\text{m}} \right) = 0.06348 - 9.9944 \times 10^{-5}T.$$



**Figure 14:** Absolute viscosities of ternary mixtures of methylhydrazine,  $\text{N}_2\text{H}_4$ , and hydrazinium nitrate. (Reproduced and modified from [79].)

The surface tension data of MMH listed in Table 8 and illustrated in Figure 15 can be calculated by the analytical expression [115, 116]:

$$\gamma = 65.8 \times 10^{-3} \left( 1 - \frac{T}{606} \right)$$

where  $\gamma$  is the surface tension in N/m and  $T$  the temperature in kelvin. The denominator under  $T$  is the critical temperature of MMH in kelvin. The equation can also be expressed in logarithmic form:

$$\gamma = 65.2 \times 10^{-3} \left( 1 - \frac{T}{585.2} \right)^{0.937}$$

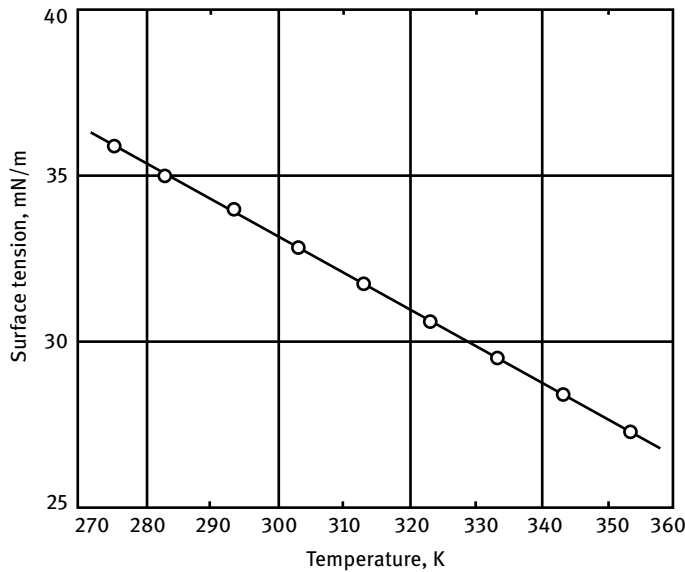
where  $\gamma$  is the surface tension in N/m and  $T$  the temperature in kelvin. Both the linear and the logarithmic expressions reproduce the experimental results equally well.

Whereas there are numerous data on MMH viscosity and surface tension, only very few data can be found on the angle of wetting of MMH in contact with various surfaces. Such wetting angle data are needed for the design of surface tension retention propellant management devices for propellant tanks for space use in zero-gravity environments (see Section 9.1). The wetting angle is very dependent not only on the chemical composition of the metal, but also on the method of surface treatment prior to the test and on surface changes that may occur with prolonged wetting by MMH or exposure to MMH vapor.

**Table 8:** Surface tension of methylhydrazine.

| Compound | Temperature |      | Surface tension       |        |
|----------|-------------|------|-----------------------|--------|
|          | K           | °C   | N/m × 10 <sup>3</sup> | dyn/cm |
| MMH      | 275.4       | 2.3  | 35.9                  | 35.9   |
| MMH      | 283.2       | 10.1 | 35.0                  | 35.0   |
| MMH      | 293.2       | 20.1 | 34.0                  | 34.0   |
| MMH      | 303.2       | 30.1 | 32.9                  | 32.9   |
| MMH      | 313.2       | 40.1 | 31.8                  | 31.8   |
| MMH      | 323.2       | 50.1 | 30.7                  | 30.7   |
| MMH      | 333.2       | 60.1 | 29.6                  | 29.6   |
| MMH      | 343.2       | 70.1 | 28.5                  | 28.5   |
| MMH      | 353.2       | 80.1 | 27.4                  | 27.4   |

Data source: [116]



**Figure 15:** Surface tension of methylhydrazine. (Reproduced and modified from [116].)

**2.9 Thermal Conductivity of Methylhydrazine**

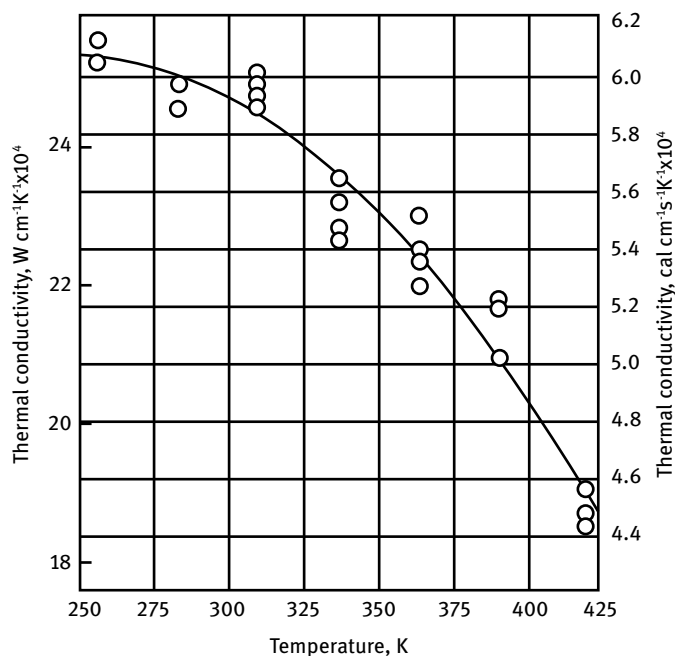
The thermal conductivity of liquid MMH as a function of temperature is represented by the following equations [117]:

$$\lambda = 3.4025 \times 10^{-4} + 2.200 \times 10^{-6}T - 4.545 \times 10^{-9}T^2$$

where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{K}^{-1} \text{s}^{-1}$  and  $T$  is the temperature in kelvin. The same data in SI units give the equation:

$$\lambda = 1.4236 \times 10^{-1} + 9.2048 \times 10^{-4} T - 1.9016 \times 10^{-6} T^2$$

where  $\lambda$  is the thermal conductivity in  $\text{W m}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. The accuracy of these equations was estimated to vary from  $\pm 1.5$  to  $\pm 4\%$  depending on where in the range 256–325 K the data are calculated. The scatter of data is evident if one looks at the data points in Figure 16.



**Figure 16:** Thermal conductivity of liquid methylhydrazine. (Reproduced and modified from [79].)

The MMH used in this study was of 99.2% purity and contained 0.7% water. Single-point data for the thermal conductivity of liquid MMH were reported as  $0.25 \text{ W m}^{-1} \text{K}^{-1}$  ( $1.72$  British thermal units [BTU]  $\text{in. ft}^{-2} \text{h}^{-1} \text{°F}^{-1}$ ) [90]. The thermal conductivity of MMH was calculated and estimated to be of the order of  $0.027 \text{ W m}^{-1} \text{K}^{-1}$ .

## 2.10 Heat-Transfer Coefficient of Methylhydrazine

Knowledge of heat-transfer characteristics of methylhydrazine is of importance in the design of injectors and cooling jackets for rocket engines and gas generators using this

propellant. An excellent summary of heat flux limits of storable rocket propellants, including hydrazine, MMH, UDMH, and their mixtures, is provided in [118]. More specifically, heat transfer and burnout flux studies were made in MMH and MHF-5 at subcritical and supercritical pressures [119–123]. Fifty-five heat transfer tests were conducted with electrically heated CRES-347 stainless steel and Inconel 718 tubes within the following ranges of conditions: 1.71 to 27.3 MPa (250 to 3960 psia) pressure, 5.38 to 62.3 m/s (17.7 to 205 ft/s) flow velocity, 232 to 426 K (–42 to 308 °F) bulk temperature, and heat fluxes up to 81 MW/m<sup>2</sup> (49.6 BTU in.<sup>–2</sup> s<sup>–1</sup>). Normal nucleate boiling was observed with MHF-5 and MMH at subcritical pressures and at wall temperatures slightly greater than the saturation temperature. Steady-state film boiling was also observed with MMH. The burnout heat flux, that is the heat flux where a transition from nucleate boiling to film boiling occurred, correlated with the product of velocity and subcooling. A reduction in burnout heat flux, attributed to viscous effects, was observed with MHF-5 and MMH at low bulk temperatures. This behavior was noted in previous investigations with other propellants and a fairly general correlation for predicting this phenomenon was established. Burnout-like conditions were observed with both propellants at supercritical pressures. It was found that the heat flux at which this condition developed, termed the ultimate heat flux, could be predicted reasonably well with conventional forced convection expressions in conjunction with a maximum wall temperature of 644 K (700 °F). Forced convection heat transfer with MMH and MHF-5 can be described using the Hines Correlation:

$$\text{Nu}_b = 0.005 \text{Re}_b^{0.95} \text{Pr}_b^{0.4}.$$

Heat transfer coefficients significantly higher than given by the Hines Correlation were measured at low bulk temperatures with both propellants at subcritical and supercritical pressures. These high coefficients were due to thermal entrance effects and correlated with a modified form of the Hines Correlation:

$$\text{Nu}_b = 0.005 \text{Re}_b^{0.95} \text{Pr}_b^{0.4} (F_{L/D})$$

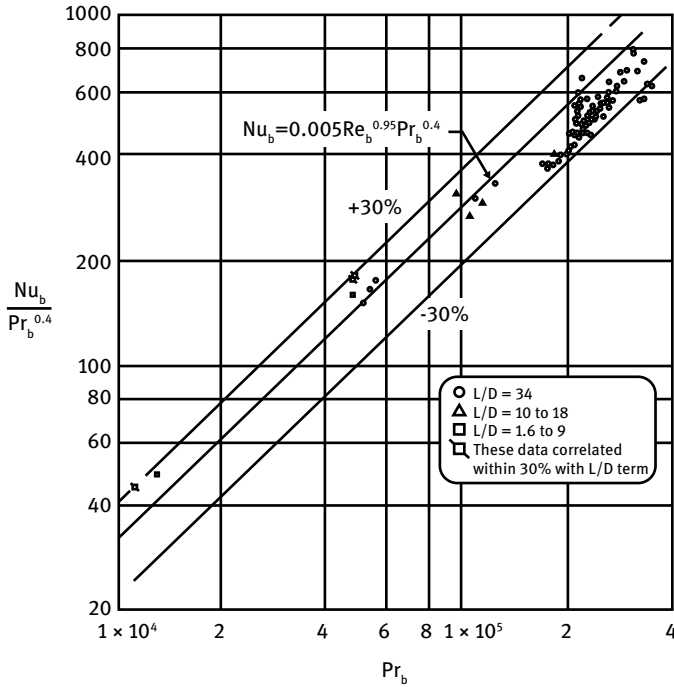
where

$$F_{L/D} = 1.0 + 0.018 \frac{\text{Pr}}{(L/D)^{\frac{1}{2}}}$$

for  $L/D \leq 10$  and  $3.8 \leq \text{Pr} \leq 141.3$ . Subcritical forced convection heat flux data for MMH are illustrated in Figure 17.

After previous futile – and in part disastrous – attempts to use anhydrous hydrazine as a cooling medium in regeneratively cooled rocket engines [124], nobody now seriously considers anhydrous hydrazine to be a suitable fuel in regeneratively fuel-cooled engines. MMH is thermally more stable than N<sub>2</sub>H<sub>4</sub> and proved to be a suitable regenerative coolant.

Two sets of data are available for the ultimate heat flux of MMH as a function of flow, pressure, and bulk and wall temperatures [118]. The ultimate heat flux  $q_{ul}$  ranged



**Figure 17:** Subcritical methylhydrazine forced convection data. (Reproduced and modified from [121, 122].)

from  $7.52 \times 10^6$  to  $1.60 \times 10^7$  W/m<sup>2</sup> (4.6–9.8 BTU in.<sup>-2</sup> s<sup>-1</sup>) at 1.5–2.2 MPa and fluid temperatures from 327 to 421 K. Development testing with MMH in the regeneratively fuel-cooled Surveyor thrust chamber revealed that decomposition of MMH under transient thrust extremes degraded the cooling characteristics of the engine [99]. Addition of 28% water to MMH improved the heat-transfer characteristics and cooling capability of the fuel and reduced flame temperature on the hot side of the combustion chamber wall.

Limitations of the upper heat flux and cooling capability of MMH are evident in small bipropellant rocket engines operating at high pressures. Heat transfer calculations showed that beyond a certain operating regime, MMH cooling is insufficient.

## 2.11 Critical Constants of Methylhydrazine

In some extreme cases of heat transfer to hydrazines at high pressures and high temperatures the conditions may approach the critical point and reach supercritical conditions where totally different physical laws govern fluid properties and heat transfer.



Although this regime is fairly well explored for water, liquid hydrogen, and other thermally stable fluids, very little information is available on hydrazines under supercritical conditions. The critical constants of hydrazine(s) are very difficult to determine because the liquid usually undergoes decomposition before the critical point is reached. Critical constants for methylhydrazine are summarized in Table 9. Most of these data are calculated from other physical and thermodynamic properties measured under non-critical conditions [125].

**Table 9:** Critical constants of methylhydrazines in comparison with those of hydrazine.

| Compound        | Critical temperature, K | Critical pressure, MPa | Critical density, g/cm <sup>3</sup> | References |
|-----------------|-------------------------|------------------------|-------------------------------------|------------|
| MMH             | 567                     | 8.1                    | 0.17                                | [1]        |
| MMH             | 585                     | 8.21                   | 0.29                                | [83]       |
| MMH             | 585                     | 8.21                   | 0.29                                | [90]       |
| MMH             | 530                     | 7.6                    | —                                   | [81]       |
| UDMH            | 522                     | 6.06                   | —                                   | [126]      |
| UDMH            | 523                     | 5.4                    | 0.275                               | [106]      |
| For comparison: |                         |                        |                                     |            |
| Hydrazine       | 653                     | 0.2307                 | —                                   | [127]      |
| Hydrazine       | 653                     | 1.469                  | —                                   | [128]      |

## 2.12 Solubility of Pressurant Gases in Methylhydrazine

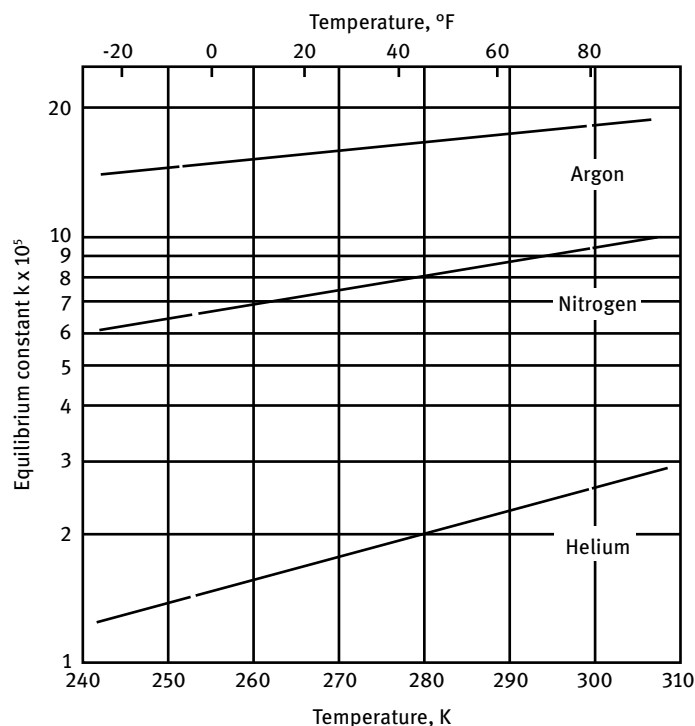
The solubility of gases in methylhydrazine(s) is of interest in the application of methylhydrazine(s) as rocket propellants. In many cases the propellants are fed into the decomposition or combustion chamber not by a pump, but by a pressurant gas, usually nitrogen or helium [129]. Unless a gas-tight, impermeable diaphragm is employed, the fuels become saturated with the pressurant gas. Heat-transfer characteristics of the gas-saturated liquids are significantly different from those of the pure liquid because dissolved gas bubbles are released prematurely, blocking effective heat transfer and sometimes causing the rocket chamber wall to burn out. Release of dissolved gasses and loss of thermal margin cause two-phase flow. Two-phase flow has a higher pressure drop than a clean single-phase flow. Solubility–pressure relationships are governed by Henry’s law:

$$\chi = KP$$

where  $\chi$  is the molar fraction of dissolved gas,  $P$  is the partial pressure of the gas, and  $K$  is the solubility constant. If the pressure is entered in units of atmospheres, then the unit of  $K$  is atm<sup>−1</sup>.

The solubility of common pressurant gases (nitrogen, argon, helium) in methylhydrazines has been determined by Chang, Gokcen, and Poston [130–132]. These data

have been reviewed and converted to other units published in solubility data reference works [133]. The values of  $K$  as a function of temperature can be read from Figure 18. The unit of  $K$  is  $\text{atm}^{-1}$ . These data were taken at relatively low pressures, much lower than typical rocket operating pressures. It would be inaccurate to extrapolate these data to higher pressures.



**Figure 18:** Gas solubility in liquid methylhydrazine as a function of temperature. (Reproduced and modified from [22] as adapted from [130].)

The equilibrium constant  $K_i$  for the pressurant gas equilibrium between the gas phase and the dissolved state is the molar fraction of solute  $i$  divided by its partial pressure  $P_i$  over the equilibrated solution. Its temperature dependence can be expressed by:

$$\log K_i = \frac{A}{T} + B$$

where  $A$  and  $B$  are constants and  $T$  is the absolute temperature in kelvin. Table 10 gives a summary of  $A$  and  $B$  constants for three different gases dissolved in MMH in comparison with other hydrazines.

Raw data for the solubility of nitrogen in liquid MMH are summarized in Table 11.

**Table 10:** Solubility of pressurant gases in methylhydrazine in comparison with other hydrazines.

| Gas             | Propellant                    | A    | B      | Solubility at 101 kPa, ppm by mass |       |
|-----------------|-------------------------------|------|--------|------------------------------------|-------|
|                 |                               |      |        | 273 K                              | 298 K |
| He              | MMH                           | −393 | 1.6586 | 1.6                                | 2.1   |
| N <sub>2</sub>  | MMH                           | −245 | 2.5691 | 47                                 | 56    |
| Ar              | MMH                           | −142 | 2.6664 | 140                                | 155   |
| For comparison: |                               |      |        |                                    |       |
| He              | N <sub>2</sub> H <sub>4</sub> | −275 | 0.7387 | 0.5                                | 0.6   |
| N <sub>2</sub>  | N <sub>2</sub> H <sub>4</sub> | −516 | 2.5322 | 4.4                                | 6.3   |
| Ar              | N <sub>2</sub> H <sub>4</sub> | −446 | 2.6841 | 11.3                               | 15.4  |
| He              | UDMH                          | −461 | 2.3410 | 4.5                                | 6.2   |
| N <sub>2</sub>  | UDMH                          | −175 | 2.8275 | 154                                | 174   |
| Ar              | UDMH                          | −52  | 2.8351 | 440                                | 456   |

Data source: [131]

**Table 11:** Gas solubility of nitrogen in methylhydrazine.

| Temperature |      | Nitrogen partial pressure |      | Experimental specific gas solubility, raw data | Calculated specific gas solubility         |                                            |
|-------------|------|---------------------------|------|------------------------------------------------|--------------------------------------------|--------------------------------------------|
| °F          | °C   | psia                      | atm  | cm <sup>3</sup> N <sub>2</sub> (STP)/g MMH     | cm <sup>3</sup> N <sub>2</sub> (STP)/g MMH | 10 <sup>−4</sup> lb N <sub>2</sub> /lb MMH |
| 95.4        | 35.2 | 279                       | 19.0 | 0.76                                           | 0.73                                       | 9.1                                        |
| 95.5        | 35.3 | 290                       | 19.7 | 0.73                                           | 0.76                                       | 9.5                                        |
| 95.4        | 35.2 | 576                       | 39.2 | 1.55                                           | 1.53                                       | 19.1                                       |
| 95.5        | 35.3 | 590                       | 40.1 | 1.55                                           | 1.57                                       | 19.6                                       |
| 95.5        | 35.3 | 893                       | 60.8 | 2.41                                           | 2.41                                       | 30.1                                       |

STP = standard temperature and pressure

Data source: [134]

From the data in this table, a solubility constant  $\alpha$  can be calculated from [134]:

$$\alpha = 2.582 \times 10^{-3}P + 1.3 \times 10^{-7}P^2$$

where  $\alpha$  is the solubility constant  $\alpha$  in terms of milliliters of nitrogen at STP dissolved in 1 g of MMH and  $P$  is the pressure in psia, or

$$\alpha = 17.80P + 6.18P^2$$

where  $\alpha$  is the solubility constant  $\alpha$  in terms of milliliters of nitrogen at STP dissolved in 1 g of MMH and  $P$  is the pressure in kPa.

It is often difficult to achieve reproducible pressurant gas saturation for development and qualification testing of rocket engines where release of pressurant gases is suspected to cause cavitation, premature transition to different boiling mechanisms in fuel-cooled rocket engines, loss of thermal margin, and burnout. Just pressurizing the run tank and waiting is often not an acceptable solution. Methods for accelerating pressurant gas saturation by sparging, recirculating the liquid, and actively pumping or stirring have been evaluated, but none is satisfactory. Dissolved gas measurements on propellant samples taken from large tanks never show the same amount of saturation as that that can be achieved in the laboratory using a glass apparatus. Table 12 is a comparison of helium saturation in MMH normalized to 1720 kPa (250 psig) and 298 K (77 °F) and shows a wide range of data reported in the literature.

**Table 12:** Comparison of helium saturation in methylhydrazine normalized to 1720 kPa (250 psig) and 298 K (77 °F).

| Solubility,<br>cm <sup>3</sup> STP g <sup>-1</sup> | Source                         | References                              |
|----------------------------------------------------|--------------------------------|-----------------------------------------|
| 0.21                                               | Aerospace Corp. (1968, 1969)   | Chang, Gokcen, and Poston cited in [79] |
| 0.18                                               | Marquardt (1967)               | —                                       |
| 0.13                                               | WSTF (1979)                    | [135]                                   |
| 0.13                                               | Aerojet (1966)                 | [136]                                   |
| 0.12                                               | JPL Viking                     | [137]                                   |
| 0.15 to 0.17                                       | JPL Galileo Alternate Thruster | [127]                                   |
| 0.16 to 0.19                                       | JPL Mars Observer              | [137]                                   |

WSTF = White Sands Test Facility; JPL = Jet Propulsion Laboratory

Data source: [137]

Computer models have been developed to predict the amount of pressure lost owing to pressurant gas solubility in MMH or dinitrogen tetroxide (NTO), also with respect to launch safety criteria on Space Shuttle Space Transportation System (STS) Orbit Maneuvering System (OMS) and Reaction Control System (RCS) propellant tanks [138]. Sometimes thin-walled tanks holding liquids have to be pressurized to a minimum pressure to have sufficient stiffness during launch acceleration and they would buckle if too much pressurant gas was absorbed because gas absorption was not figured into the launch preparations check list. Comparison of predicted and measured pressurant gas pressure decay during the prelaunch hold period due to gradual saturation of propellant showed acceptably good agreement [139, 140]. Unexpected pressure changes occur in bipropellant blowdown systems and may cause a shift in the oxidizer : fuel ratio and resultant performance losses or hotter-than-nominal operation with chamber burnouts [141, 142]. Some systems are pressurized immediately prior to launch. If some of the propellant is consumed right away shortly after launch, the effects of gas solubility will become less noticeable with a larger ullage. But with small ullages at

the beginning of the blowdown cycle, and if the system is not used right away, it may take weeks for saturation to be achieved and the tank pressures may be imbalanced. The same may apply to pairs of tanks of the same propellant connected by a manifold. If the two tanks are at different temperatures, propellant distribution may be uneven and cause unexpected shifts in the center of gravity of the upper stage rocket or the satellite (“thermal pumping”).

Dissolved pressurant gases and the degree of gas saturation may affect the performance (ignition delay, injector boiling, dribble volume expulsion) of bipropellant rocket engines [143]. Pressurant gas evolution during refueling transfer of helium-saturated propellants from supply vehicles to satellites in space may complicate metering the amount of propellant transferred under zero-g conditions [144, 145].

It was planned to accurately measure the pressure decay after pressurization of the ROSETTA MMH tank with helium, but the ullage warmed up significantly during pressurization, which accelerated helium absorption even before the pressurization process was completed [146]. The ROSETTA tanks had a relatively large ullage volume, compared with those in a previously tested smaller satellite, METEOSAT Second Generation (MSG), where pressure decay predictions using the Knowles method were more accurate. It was not possible to determine how much helium had dissolved already during the pressurization process in the ROSETTA tank. Pressure decay measurements are complicated by the fact that satellites and upper stages prior to launch are not in a thermostatted constant temperature environment and ambient temperature fluctuations result in pressure fluctuations. By knowing the speed of the pressure decay, it would be possible to compute the necessary initial elevated filling pressures that would then drop to the desired pressure at launch time. Measured pressure decay data from the ESA CLUSTER spacecraft and a number of American satellites were used to predict the pressure decay in MMH-propellant tanks of the ESA MSG and ROSETTA spacecraft [147].

The Japanese H-II Transfer Vehicle (HTV) has four main thrusters (500 N) used for orbit control, and 28 RCS thrusters (110 N) used for reaction control. HTV has multiple engine and long propellant supply lines that make its operation and surge pressure spikes dependent on propellant pressurant gas saturation level. A visual bubble point technique and GC were used to determine the helium saturation level prior to ground level testing of the propulsion system [148].

Owing to helium solubility in propellants (MMH and NTO), tank pressure may decrease for several days after initial tank pressurization on the ground prior to launch. A model is necessary to predict the pressure loss. Conventional models had been designed with the assumption that the tank was static. However, in the case of the Japanese HTV, propellant sloshing occurred by movement of the HTV between buildings on the ground prior to launch. Tank pressure loss in HTV tanks could not be predicted by the conventional model because of the sloshing. An improved numerical

solubility model expresses the influence of sloshing on helium solubility by solving the vertical distribution of helium concentration in the stratified tank contents [149].

## 2.13 Thermochemical Properties of Methylhydrazine

Thermochemical properties such as heat capacity, enthalpy of formation, heat of combustion, heat of vaporization, and other thermal characteristics are necessary for calculation of the useful energy derived from MMH in a number of industrial applications.

There are several summary publications dealing with thermochemistry and molecular structures of alkylhydrazines, also in their relation to azo and azoxy compounds derived by the oxidation of alkylhydrazines [150, 151]. See also [112, 152].

### 2.13.1 Heat Capacity of Methylhydrazine

Whereas heat capacity data for ideal vapors can be calculated from IR spectroscopic data, heat capacity determination of liquids and solids depends on calorimetric measurements, which are usually less accurate. Heat capacities are important for the calculation of temperature changes in hydrazines during industrial processes. They are also required for conversion of standard enthalpies and entropies of formation to other temperatures (other than 298 K).

Data on the heat capacity of solid and liquid MMH are available from [81, 117]. Combination of the two sets of data for MMH lead to the following equations:

$$c_p = 0.6528 - 1.7284 \times 10^{-5} T + 3.9142 \times 10^{-7} T^2$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. The same data in SI units give the equation:

$$c_p = 2.7313 - 7.2316 \times 10^{-5} T + 1.6377 \times 10^{-6} T^2$$

where  $c_p$  is the heat capacity in  $\text{J g}^{-1} \text{K}^{-1}$  and  $T$  is the temperature in kelvin. This equation may be used for liquid MMH up to 397 K (see also [153]). Other summary publications recommend the following equations for the heat capacity of liquid MMH [90]:

$$C_p(\text{J mol}^{-1} \text{K}^{-1}) = 125.6 - 3.3265 \times 10^{-3} T + 1.1383 \times 10^{-4} T^2, \quad T \text{ in K}$$

and for MMH vapor:

$$C_p(\text{J mol}^{-1} \text{K}^{-1}) = 9.4708 + 0.2495 T - 1.495 \times 10^{-4} T^2 + 3.537 \times 10^{-8} T^3, \quad T \text{ in K.}$$

Some of Aston's historical heat capacity data for MMH from [81] are summarized in Table 13.

Table 14 gives a comparison of the heat capacities of three liquid methylhydrazines.

**Table 13:** Heat capacity of solid, liquid, and vapor methylhydrazine.

| Temperature    |                                     |                                        | Temperature   |                                     |                                        |
|----------------|-------------------------------------|----------------------------------------|---------------|-------------------------------------|----------------------------------------|
| Heat capacity  |                                     |                                        | Heat capacity |                                     |                                        |
| K              | J mol <sup>-1</sup> K <sup>-1</sup> | cal mol <sup>-1</sup> °C <sup>-1</sup> | K             | J mol <sup>-1</sup> K <sup>-1</sup> | cal mol <sup>-1</sup> °C <sup>-1</sup> |
| <i>Crystal</i> |                                     |                                        | <i>Liquid</i> |                                     |                                        |
| 20             | 4.213                               | 1.007                                  | 220.79        | 130.8                               | 31.27                                  |
| 30             | 9.828                               | 2.349                                  | 230           | 131.4                               | 31.40                                  |
| 40             | 16.02                               | 3.830                                  | 240           | 131.9                               | 31.52                                  |
| 50             | 21.84                               | 5.220                                  | 250           | 132.4                               | 31.64                                  |
| 60             | 26.86                               | 6.420                                  | 260           | 132.9                               | 31.76                                  |
| 70             | 31.51                               | 7.531                                  | 270           | 133.4                               | 31.88                                  |
| 80             | 35.86                               | 8.570                                  | 280           | 133.9                               | 32.01                                  |
| 90             | 39.28                               | 9.389                                  | 290           | 134.5                               | 32.14                                  |
| 100            | 42.38                               | 10.13                                  | 298.16        | 134.9                               | 32.25                                  |
| 110            | 45.31                               | 10.83                                  | <i>Vapor</i>  |                                     |                                        |
| 120            | 48.20                               | 11.52                                  | 298.16        | 71.1                                | 17.0                                   |
| 130            | 51.09                               | 12.21                                  | 300           | 71.6                                | 17.11                                  |
| 140            | 53.72                               | 12.84                                  | 400           | 87.9                                | 21.0                                   |
| 150            | 56.65                               | 13.54                                  | 500           | 101.7                               | 24.3                                   |
| 160            | 61.38                               | 14.05                                  | 600           | 113.3                               | 27.1                                   |
| 170            | 61.38                               | 14.67                                  | 700           | 122.6                               | 29.3                                   |
| 180            | 64.18                               | 15.34                                  | 800           | 130.9                               | 31.3                                   |
| 190            | 66.86                               | 15.98 <sup>a</sup>                     | 900           | 138.5                               | 33.1                                   |
| 200            | 69.45                               | 16.60 <sup>a</sup>                     | 1000          | 144.8                               | 34.6                                   |
| 210            | 71.96                               | 17.20 <sup>a</sup>                     | 1200          | 155.2                               | 37.1                                   |
| 220            | 74.47                               | 17.80 <sup>a</sup>                     | 1500          | 166.5                               | 39.8                                   |
| 220.79         | 74.64                               | 17.84                                  |               |                                     |                                        |

<sup>a</sup> Extrapolated

Data source: [81]

**Table 14:** Heat capacity of methylhydrazines.

| Compound              | Formula                                            | Temperature | Heat capacity                        |                                   | References |
|-----------------------|----------------------------------------------------|-------------|--------------------------------------|-----------------------------------|------------|
|                       |                                                    | K           | cal g <sup>-1</sup> °C <sup>-1</sup> | J g <sup>-1</sup> K <sup>-1</sup> |            |
| Methylhydrazine       | CH <sub>3</sub> NNH <sub>2</sub>                   | 298         | 0.700                                | 2.929                             | [79]       |
| 1,1-Dimethylhydrazine | (CH <sub>3</sub> ) <sub>2</sub> NNH <sub>2</sub>   | 298         | 0.65                                 | 2.73                              | [154]      |
| Trimethylhydrazine    | H <sub>3</sub> CNHN(CH <sub>3</sub> ) <sub>2</sub> | 298         | 0.60                                 | 2.51                              | [154]      |

### 2.13.2 Enthalpy of Formation of Methylhydrazine

Exact knowledge of thermodynamic data, including enthalpy of formation, free energy of formation, and entropy is important for the calculation of the theoretical performance of alkylhydrazines in a number of practical applications, such as rocket engines. In addition to those from calorimetric determinations, these data are usually obtained from IR, Raman, or microwave spectroscopic observations and quantum mechanical or statistical thermodynamics calculations of the molecular vibrations. This requires knowledge of the structure of the molecules, which is discussed in more detail in Section 2.16.

The upper heat of combustion of MMH at 305.6 K (32.5°C) was measured as 1303 to 1305 kJ/mol (311.5 to 311.8 kcal/mol) in a calorimeter, after corrections for a contaminant assumed to be UDMH [155]. In the same apparatus, a heat of combustion of hydrazine was measured as 629.68 kJ/mol (150.497 kcal/mol). A later measurement in the same apparatus gave the heat of combustion of MMH as 1304.2 kJ/mol (311.711 kcal/mol) at 303 K [156].

The upper heat of combustion once reported by Cole and Gilbert in 1951 [157] actually was given to them by Aston and is the same as that reported by Aston in 1952 [81]. The enthalpy of formation of MMH calculated by Cole and Gilbert [157] based on the heat of combustion given to them by Aston was +54.14 kJ/mol (+12.94 kcal/mol) and this number was different than the generally accepted number published a few decades later.

The upper heat of combustion of MMH was measured at 303.15 K and found to be 1304 kJ/mol = 311.711 kcal/mol [158]. If this number is corrected to the heat of combustion at 298 K, a value of 1306 kJ/mol = 312.112 kcal/mol would be obtained. Using the known heats of formation of CO<sub>2</sub>(G) and (H<sub>2</sub>O)L, the standard enthalpy of formation of MMH can be calculated:  $(\Delta H)_f^{298} \text{MMH(L)} = +54.83 \text{ kJ/mol} = +13.106 \text{ kcal/mol}$ . Note that this is a positive number, indicating that MMH is capable of exothermic decomposition into its elements or lower molecule fragments such as ammonia and methane.

Enthalpies of formation of liquid methylhydrazines are derived mostly from calorimetric measurements of the heat of combustion, but literature data obtained by these methods are not always consistent. Thermochemical data for vapors of methylhydrazines can be derived from spectroscopic measurements or molecular orbital quantum chemical calculations. Because of the lack of consistency of the thermochemical data derived from calorimetric measurements and reported in the literature, a consistent set of data has been calculated at the G4 level for methylhydrazines in the vapor state, also in comparison with methylamines from which they are made [159]. The computed values from two different sources are compared with experimental values in Table 15 and show generally good agreement. When looking at the changes in enthalpy of formation caused by the introduction of a methyl group replacing a hydrogen atom, it is interesting to compare this effect as it applies to ammonia going to methylamines and hydrazine going to methylhydrazines.



**Table 15:** Computed and experimental values for enthalpies of formation of methylhydrazine vapors.

| Compound                                                          | Enthalpy of formation, kJ/mol |                  |                  |
|-------------------------------------------------------------------|-------------------------------|------------------|------------------|
|                                                                   | Method of obtaining data      |                  |                  |
|                                                                   | Experimental                  | Computational G3 | Computational G4 |
| Data source                                                       |                               | [160]            | [159]            |
| CH <sub>3</sub> NHNH <sub>2</sub>                                 | 94.7 ± 0.7                    | 90.7 ± 2.2       | 108.2            |
| (CH <sub>3</sub> ) <sub>2</sub> NNH <sub>2</sub>                  | 84.1 ± 3.3                    | 79.7 ± 2.2       | 83.4             |
| CH <sub>3</sub> NHNHCH <sub>3</sub>                               | 92.2 ± 4.3                    | 92.7 ± 2.4       | 95.8             |
| (CH <sub>3</sub> ) <sub>2</sub> NNHCH <sub>3</sub>                | 78.6 ± 2.3                    | 82.4             | —                |
| (CH <sub>3</sub> ) <sub>2</sub> NN(CH <sub>3</sub> ) <sub>2</sub> | 76.4 ± 2.3                    | 80.7             | —                |
| For comparison:                                                   |                               |                  |                  |
| NH <sub>3</sub>                                                   | −45.9                         | −45.9 ± 0.4      | −42.5            |
| CH <sub>3</sub> NH <sub>2</sub>                                   | −23.4 ± 1.0                   | −21.8 ± 1.5      | −19.6            |
| (CH <sub>3</sub> ) <sub>2</sub> NH                                | −18.8 ± 1.5                   | −18.8 ± 1.5      | −15.9            |
| (CH <sub>3</sub> ) <sub>3</sub> N                                 | −23.6 ± 1.3                   | −27.2 ± 2.0      | −25.4            |
| N <sub>2</sub> H <sub>4</sub>                                     | 95.4                          | 95.2 ± 0.5       | 100.8            |

Another set of computational estimations of the enthalpies of formation of hydrazine vapor and vapors of hydrazine derivatives gives a summary of literature and computed data for the enthalpies of formation and heats of vaporization of several methylhydrazines and three other alkylhydrazines [161], as shown in Table 16.

**Table 16:** Experimental and theoretical enthalpies of formation ( $\Delta H_f^{298}$ ) in both condensed and gaseous phases and enthalpies of evaporation ( $\Delta H_{\text{vap}}^{298}$ ) of alkylhydrazines.

| Compound                              | Enthalpy of formation ( $\Delta H_f^{298}$ ) | Enthalpy of evaporation ( $\Delta H_{\text{vap}}^{298}$ ) | Enthalpy of formation ( $\Delta H_f^{298}$ ) | Method <sup>a</sup>                                    |
|---------------------------------------|----------------------------------------------|-----------------------------------------------------------|----------------------------------------------|--------------------------------------------------------|
| Physical state                        | liquid                                       | liquid                                                    | vapor                                        |                                                        |
| SI unit                               | kJ/mol                                       | kJ/mol                                                    | kJ/mol                                       |                                                        |
| CH <sub>3</sub> NHNH <sub>2</sub> (L) | 54.1                                         | 40.4                                                      | 94.5                                         | experimental                                           |
|                                       |                                              |                                                           | 81.0                                         | calculated: B3LYP/6-311+G(3df,2pd)                     |
|                                       |                                              |                                                           | 96.0                                         | calculated: G2MP2                                      |
|                                       |                                              |                                                           | 107.0                                        | calculated: G3                                         |
|                                       |                                              |                                                           | 90.7 ± 2.2                                   | calculated: composite methods with isodesmic reactions |
|                                       |                                              |                                                           | 108.2                                        | calculated: G4                                         |
|                                       |                                              |                                                           | 99.5 ± 2.4                                   | calculated: average of CBS-QB3, CBS-APNO, G3, G4       |
|                                       |                                              |                                                           | 93.4 ± 3.0                                   | calculated: G4 with 20 reactions                       |

Table 16: (continued)

| Compound                                               | Enthalpy of formation<br>( $\Delta H_f^{298}$ ) | Enthalpy of evaporation<br>( $\Delta H_{\text{vap}}^{298}$ ) | Enthalpy of formation<br>( $\Delta H_f^{298}$ )                                      | Method <sup>a</sup>                                                                                                                                                                                                                                                        |
|--------------------------------------------------------|-------------------------------------------------|--------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Physical state                                         | liquid                                          | liquid                                                       | vapor                                                                                |                                                                                                                                                                                                                                                                            |
| SI unit                                                | kJ/mol                                          | kJ/mol                                                       | kJ/mol                                                                               |                                                                                                                                                                                                                                                                            |
| (CH <sub>3</sub> ) <sub>2</sub> NNH <sub>2</sub> (L)   | 48.3 ± 3.6                                      | 35.0 ± 0.2                                                   | 83.3 ± 3.6<br>77.0<br>77.0<br>94.0<br>79.7 ± 2.2<br>83.4<br>84.0 ± 3.1<br>82.3 ± 3.0 | experimental<br>calculated: B3LYP/6-311+G(3df,2pd)<br>calculated: G2MP2<br>calculated: G3<br>calculated: composite methods with isodesmic reactions<br>calculated: G4<br>calculated: average of CBS-QB3, CBS-APNO, G3, G4<br>calculated: G4 with 30 reactions              |
| CH <sub>3</sub> NHNHCH <sub>3</sub> (L)                | 52.8 ± 4.2                                      | 39.3 ± 0.1                                                   | 92.1 ± 4.3<br>84.0<br>89.0<br>103.3<br>90.0<br>92.7 ± 2.4<br>95.8<br>97.1            | experimental<br>calculated: B3LYP/6-311+G(3df,2pd)<br>calculated: G2MP2<br>calculated: G3MP2<br>calculated: G3MP2 with isodesmic reactions<br>calculated: composite methods with isodesmic reactions<br>calculated: G4<br>calculated: average of CBS-QB3, CBS-APNO, G3, G4 |
| CH <sub>3</sub> CH <sub>2</sub> NHNH <sub>2</sub> (L)  | 25.7 ± 4.0                                      | 40.0 ± 3.0                                                   | 65.7 ± 2.0<br>—                                                                      | calculated: G4 with 10 reactions<br>estimated                                                                                                                                                                                                                              |
| (CH <sub>3</sub> ) <sub>2</sub> NNHCH <sub>3</sub> (L) | 48.8                                            | 33.3 ± 0.11<br>(292 K)                                       | —<br>78.6 ± 2.3<br>82.4<br>83.2 ± 3.7<br>82.1 ± 3.0                                  | experimental<br>calculated: composite methods with isodesmic reactions<br>calculated: G4<br>calculated: average of CBS-QB3, CBS-APNO, G3, G4<br>calculated: G4 with 47 reactions                                                                                           |
| (CH <sub>3</sub> ) <sub>2</sub> CHNNH <sub>2</sub> (L) | -10.7 ± 5.0                                     | 42.0 ± 3.0                                                   | 31.3 ± 3.0<br>—                                                                      | estimated MEP                                                                                                                                                                                                                                                              |

Table 16: (continued)

| Compound                                                              | Enthalpy of formation<br>( $\Delta H_f^{298}$ ) | Enthalpy of evaporation<br>( $\Delta H_{\text{vap}}^{298}$ ) | Enthalpy of formation<br>( $\Delta H_f^{298}$ ) | Method <sup>a</sup>                                    |
|-----------------------------------------------------------------------|-------------------------------------------------|--------------------------------------------------------------|-------------------------------------------------|--------------------------------------------------------|
| Physical state                                                        | liquid                                          | liquid                                                       | vapor                                           |                                                        |
| SI unit                                                               | kJ/mol                                          | kJ/mol                                                       | kJ/mol                                          |                                                        |
| (CH <sub>3</sub> ) <sub>2</sub> NN(CH <sub>3</sub> ) <sub>2</sub> (L) | 47.9                                            | 32.9 (305 K)                                                 | —                                               | exp                                                    |
|                                                                       |                                                 |                                                              | 76.4 ± 2.3                                      | calculated: composite methods with isodesmic reactions |
|                                                                       |                                                 |                                                              | 80.7                                            | calculated: G4                                         |
|                                                                       |                                                 |                                                              | 81.3                                            | calculated: average of CBS-QB3, CBS-APNO, G3, G4       |
|                                                                       |                                                 |                                                              | 80.8 ± 4.0                                      | calculated: G4 with 45 reactions                       |
| (CH <sub>3</sub> ) <sub>3</sub> CNNH <sub>2</sub> (L)                 |                                                 |                                                              | −2.0 ± 3.0                                      | calculated: G4 with 15 reactions                       |
|                                                                       | −49.6 ± 5.0                                     | 47.6 ± 3.0                                                   | —                                               | estimated MEP                                          |

<sup>a</sup> Acronyms encountered in this table:

B3LYP Becke, 3-parameter, Lee–Yang–Parr

G Gaussian

G2MP2 modified version of G2

CBS-QB3 Complete Basis Set-QB3

CBS-APNO Complete Basis Set-A Pair Natural Orbital

MEP Molecular Electrostatic Potential

Data source: [161] and references listed therein

The standard enthalpy of formation of an equimolar mix of MMH and water containing 28 mass-% H<sub>2</sub>O is −239.7 kJ/mol (−57.3 kcal/mol) [99]. This is 4.33 kJ/mol below the mathematical sum of heats of formation of the ingredients. This fuel blend was used in the SURVEYOR lunar landers.

### 2.13.3 Enthalpy of Fusion of MMH

The heat of fusion of MMH, corrected for pre-melting was determined as 10.4202 ± 0.0012 kJ/mol (2.4905 ± 0.0003 kcal/mol) [81]. The decreasing molar heat of fusion of methylhydrazines with progressive methylation is an indication of reduced hydrogen bonding in the series N<sub>2</sub>H<sub>4</sub>, MMH, and UDMH.

### 2.13.4 Enthalpy of Evaporation of MMH

The heat of evaporation of MMH was not only derived from the vapor pressure curve, but also directly measured by Aston et al. 1951. The average of five determinations gave  $(\Delta H)^{298}_{\text{vap}} = 40.36 \text{ kJ/mol} = 9.648 \text{ kcal/mol}$ , compared with 40.693 kJ/mol = 9.726 kcal/mol calculated from the vapor pressure equation. The heat of vaporization

at the normal boiling point is of more practical importance. It has been calculated to be  $37.21 \text{ kJ/mol} = 8.894 \text{ kcal/mol}$  with a Trouton constant of 24.6. Other sources gave the heat of vaporization at 364 K as  $36.12 \text{ kJ/mol}$  [162]. The heat of vaporization derived from the slope of a vapor pressure curve was  $40.9 \text{ kJ/mol}$ , [92] similar to  $40.36 \text{ kJ/mol}$  reported by Aston [81]. Attempts to predict vapor pressure and enthalpy of vaporization of MMH from theoretical computations have not always produced accurate results [101].

### 2.13.5 Entropy of MMH

Entropy data for liquid and vapor MMH are summarized in Table 17. The entropy of vaporization at 298 K is  $135.39 \text{ J mol}^{-1} \text{ K}^{-1}$ . The entropy of fusion at 220.79 K is  $47.19 \text{ J mol}^{-1} \text{ K}^{-1}$ .

**Table 17:** Entropy data for liquid and vapor methylhydrazine at 298.16 K.

| State            | $\text{J mol}^{-1} \text{ K}^{-1}$ | $\text{cal mol}^{-1} \text{ }^{\circ}\text{C}^{-1}$ | References |
|------------------|------------------------------------|-----------------------------------------------------|------------|
| Liquid           | 165.9                              | 39.66                                               | [81]       |
| Liquid           | 165.94                             | 39.662                                              | [163]      |
| Vapor, ideal gas | 278.7                              | 66.61                                               | [81]       |
| Vapor, ideal gas | 278.7                              | 66.61                                               | [163]      |
| Vapor, ideal gas | 269.87                             | 64.50                                               | [153]      |
| Vapor, real gas  | 301.3                              | 72.02                                               | [81]       |
| Vapor, real gas  | 301.36                             | 72.028                                              | [163]      |
| Vapor, real gas  | 284.72                             | 68.050                                              | [164]      |

## 2.14 Optical Properties of MMH

This section deals with the interaction of methylhydrazines with electromagnetic radiation in the wavelength range from 100 nm to 20 cm. Correspondingly, this section is subdivided into ultraviolet (UV)/visible absorption, IR absorption, and microwave absorption. The spectra obtained in these spectral ranges are of particular interest in the clarification of the molecular structure of hydrazines and measurement of the energies of the atomic and intermolecular bonds in them. As the hydrazine N—N bond (as opposed to the azo bond N=N and its many azo dyes) is not a chromophore, there is nothing to report on light absorption of hydrazine derivatives within the visible range. The optical properties of MMH and other methylhydrazines are important for analytical applications, verifying the purity of the propellant before it is loaded into spacecraft or missiles, and detecting the presence of leaked MMH vapors in areas where it does not belong and constitutes a hazard to both equipment and personnel. Spectra of MMH enabled us to better understand the structure of this molecule and derive thermochemical properties that are important for its use as a rocket propellant.

### 2.14.1 Ultraviolet Spectra of MMH

Vacuum UV absorption coefficients for hydrazine, MMH, and UDMH were measured from 115 to 185 nm to determine interference of leaked propellants with UV sensors in space applications [165]. Vacuum UV absorption coefficients for  $\text{N}_2\text{H}_4$ ,  $\text{CH}_3\text{HNNH}_2$ , and  $(\text{CH}_3)_2\text{NNH}_2$  were measured for wavelengths between 115 and 185 nm with an estimated experimental error of  $\pm 15\%$ . The measurements were made in a hydrazine-compatible flow-cell apparatus at room temperature.

For the UV absorption of MMH at 213.9 nm a UV absorption cross-section of  $\sigma = 2489 \times 10^{-20} \text{ cm}^2/\text{mol}$  was assumed for hydrazine photolysis and autoxidation studies in the atmosphere [166, 167].

### 2.14.2 Infrared Spectra of MMH

It is common practice to describe spectra by giving wavenumbers and intensities of absorption bands. The following abbreviations are in use for describing peak heights: **vs**, very strong; **s**, strong; and **w**, weak. Wavenumbers (in  $\text{cm}^{-1}$ ) can be converted to wavelength (in  $\mu\text{m}$ ) by forming the reciprocal. A common unit for wavenumbers is reciprocal centimeters,  $\text{cm}^{-1} = \text{kayser}$ . This gives the number of wavelengths that fit into 1 cm. A chapter on IR spectroscopy could possibly also be subdivided by the experimental technique used, of which there are quite a few: transmission, reflectance, attenuated total reflectance, vapor absorption, liquid absorption, mulls, emulsions, solid films, solid matrix isolation, adsorbed state on solid surfaces, complexed state in ligand spheres, isotope substitution, Fourier transform enhanced, and many more. Almost all of these have been applied to measure IR spectra of MMH at one time or another. A separation that proved difficult was to discuss IR spectra without repeatedly referring to supporting Raman spectroscopy work, which was supposed to be summarized in a separate section, following the section on IR spectra. The two methods complement each other, and one would be well served to read both sections when looking for spectroscopic information on methylhydrazines.

The 21 normal vibrations of MMH are all expected to be IR active [168]. Apart from the three skeletal vibrations that absorb at low wavenumbers, the fundamentals listed in Table 18 are expected.

Infrared gas-phase spectra of MMH have been measured from 33 to  $4000 \text{ cm}^{-1}$  [153]. The IR and Raman spectra of MMH in the liquid state were also recorded. Absorption band assignments were made possible by isotope substitution and recording the IR and Raman spectra of  $\text{D}_2\text{NNDCH}_3$  and  $\text{D}_2\text{NNDCH}_3$ . A complete vibrational analysis based on band intensity, position, and isotopic shift could be obtained. By assuming that a symmetrical threefold cosine potential governs both rotors in MMH, rotational barriers of 15.3 and 15.6 kJ/mol (3.67 and 3.72 kcal/mol) were calculated for the methyl and amino group torsions respectively. Several of the frequencies are shifted as a result of hydrogen bonding, and the difference becomes apparent when comparing spectra obtained in the gas phase or in a frozen argon solid matrix. The monomeric

**Table 18:** Fundamental vibration modes and infrared spectra of methylhydrazine.

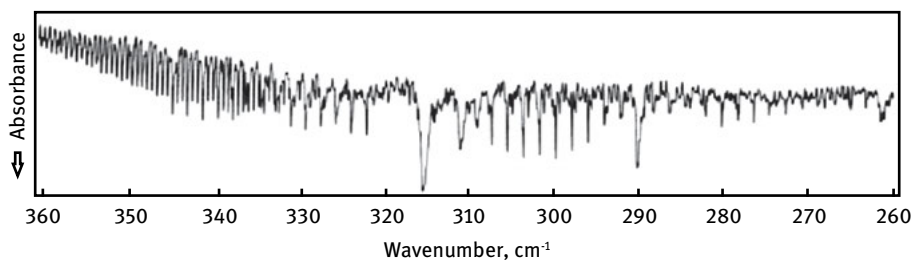
| Methylhydrazine                       |                              |
|---------------------------------------|------------------------------|
| Mode                                  | Wavenumber, $\text{cm}^{-1}$ |
| Skeletal bending                      | 443                          |
| Skeletal stretching                   | 816, 1103                    |
| $\text{NH}_2$ symmetrical deformation | 1587                         |
| $\text{NH}_2$ wagging and rocking     | 886, 1137                    |
| NH deformation                        | 770, 1122                    |
| $\text{CH}_3$ wagging                 | 969, 1197                    |
| $\text{CH}_3$ deformation             | 1412, 1441, 1474             |
| C—H stretching                        | 2865, 2933, 2965             |
| N—H stretching                        | 3177, 3245, 3317             |

Data source: [168]

argon matrix N—H stretching vibrations occur at 3366, 3358, and  $3314\text{ cm}^{-1}$ , but as a result of association, they are found in the Raman spectra of the liquid at lower frequencies, 3316, 3304, and  $3258\text{ cm}^{-1}$ . The intensity of the  $3182\text{-cm}^{-1}$  line of  $\text{NH}_2\text{NHCH}_3$  has been studied as a function of temperature. The  $\Delta H^\circ$  for hydrogen bond formation was found to be  $-1749\text{ J/mol}$  ( $-418\text{ cal/mol}$ ). MMH thermodynamic functions have been calculated for the temperature range 200–3000 K on the basis of a rigid rotator, harmonic oscillator model. These fundamental rotational–vibrational assignments superseded those of Axford, Janz, and Russell [168]. Slightly different assignments of group frequencies in MMH were made based on spectra of deuterium-substituted methylhydrazines,  $\text{D}_3\text{CNHNH}_2$  and  $\text{H}_3\text{CNDND}_2$  [52].

Although most investigators only measure the location of the absorption bands on the wavenumber scale, there are only very few measurements of the absorption coefficient of MMH in the vapor state. Such measurements are necessary to determine the MMH concentration by IR absorption of the vapor, for instance, in the pressurant gas vented from bipropellant systems and fed to a scrubber. The peak absorption coefficients for two near-IR absorptions of MMH at  $6560$  and  $9620\text{ cm}^{-1}$  were measured [169]. It was difficult to establish accurate partial pressures of MMH in the dry nitrogen purge system owing to adsorption of MMH on the walls of the tubing and FTIR absorption multiple reflection cells. Dynamic and static methods were tested, but none provided better than  $\pm 20\%$  accuracy in partial pressure. The dynamic method generated MMH-saturated nitrogen by bubbling dry  $\text{GN}_2$  through liquid MMH in a thermostatted bath. The static method injected MMH from a syringe into a known volume and relied on convection for complete mixing. The peak absorption coefficient at  $6560\text{ cm}^{-1}$  was  $3.1 \times 10^{-2}\text{ cm}^{-1}\text{ atm}^{-1}$  and at  $9620\text{ cm}^{-1}$  it was  $9.7 \times 10^{-4}\text{ cm}^{-1}\text{ atm}^{-1}$ . Absorption bands located at 6560, 6423, and  $6316\text{ cm}^{-1}$  were assigned to the  $\Delta\nu = 2$  overtones of the N—H stretching fundamentals at 3317, 3245, and  $3177\text{ cm}^{-1}$ .

The IR spectra of MMH and other methylhydrazines are contained in a catalog of IR spectra for qualitative analysis of gases [170]. The far-IR spectra of methylhydrazine ( $\text{CH}_3\text{NHNH}_2$ ), deuterated methylhydrazine- $\text{C-d}_3$  ( $\text{CD}_3\text{NHNH}_2$ ), and d-methylhydrazine- $\text{N,N'-d}_3$  ( $\text{CH}_3\text{NDND}_2$ ) in the gas phase have been recorded between 370 and  $100\text{ cm}^{-1}$  with a resolution of  $0.1\text{ cm}^{-1}$  [171] (Figure 19).



**Figure 19:** Far-infrared spectrum of methylhydrazine vapor. (Reprinted and adapted from [171], with permission from ©1989 American Chemical Society; permission conveyed through RightsLink.)

The amino torsional fundamentals and several hot bands have been observed and assigned on the basis of the presence of the inner and outer skew conformers. Rotational constants have been determined from the observed K-structure arising from the amino torsional mode of the inner conformer. A potential function for the amino torsion of MMH has been calculated by using three potential coefficients. The methyl torsions in  $\text{CH}_3\text{NDND}_2$  have been assigned to the frequency region between 280 and  $255\text{ cm}^{-1}$ .

A convenient source of IR radiation for various analytical applications is the diode laser. Absorption measurements of pure hydrazine and MMH were recorded in an optical absorption cell (3 passes,  $50\text{ cm/pass}$ ) at low pressure ( $0\text{--}35\text{ Torr}$ ) using a tunable external-cavity diode laser, operating within the range from  $6350$  to  $6650\text{ cm}^{-1}$  ( $1.49$  to  $1.58\text{ }\mu\text{m}$ ) [172, 173]. Peak absorption cross-section measurements of MMH, as determined from fixed wavelength absorption measurements recorded at various pressures, were found to be  $\alpha_e/\nu = 0.152 \pm 0.003\text{ cm}^{-1}\text{ atm}^{-1}$  at  $6560\text{ cm}^{-1}$  ( $\lambda = 1524.4\text{ nm}$ ). The measurements represented the first high-resolution survey spectra of these hydrazines in the near IR. These measurements were supporting the design of a diode-laser-based leak detection system for the STS Space Shuttle launchpad.

The injectors of bipropellant engines remain filled after the engine shuts down and their unreacted contents evaporate slowly into vacuum. Thin films of hydrazine or MMH or their decomposition products that may condense on cryocooled germanium optical windows of sensors on satellites in outer space might block IR transmittance. Therefore, IR absorption spectra of thin films of frozen MMH on cold germanium windows were measured and interpreted by Fourier transform analysis [174, 175]. Thin MMH films from  $0.25$  to  $9.0\text{ }\mu\text{m}$  thick were formed on a germanium substrate at  $20\text{ K}$  (cold helium gas) or  $80\text{ K}$  (liquid nitrogen) in vacuum, and the IR transmittances

were measured by using an FTIR spectrometer [176, 177]. A dual-angle laser interference technique was used to determine the thickness and the refractive index of the thin hydrazine films. In addition, a quartz crystal microbalance was used to weigh the amount and give the average loading density. Absorption spectra of frozen MMH films on germanium windows showed a relatively strong band at  $3164\text{ cm}^{-1}$ , whereas no such band was observed in liquid MMH. Also, a splitting at  $2934$  and  $2964\text{ cm}^{-1}$  was not visible in the liquid samples analyzed by other authors. Spectra continued to be recorded while the sample warmed up from 80 K. The most significant spectral change after warm-up was the appearance of a sharp, strong absorption band at  $3340\text{ cm}^{-1}$ . This is believed to be either the  $\nu_1$  or  $\nu_2$  fundamental.

Because of the need for a controlled environment, atmospheric studies of homogeneous autoxidation of hydrazines in air have to be conducted in laboratory chambers with non-reactive walls. It has been noted that much of the oxidation occurs heterogeneously on the walls of these chambers and it was difficult to eliminate wall effects. The IR spectra of adsorbed MMH on chamber materials (silica, silica-alumina, and alumina) were recorded in an effort to find inert chamber materials. Diffuse reflectance spectroscopy of hydrazines adsorbed on silica, silica-alumina or alumina indicated that the primary surface-MMH interaction is hydrogen bonding [178, 179]. In the adsorbed methylhydrazines, the C—H stretching and methyl deformation modes are shifted to higher frequencies by 10 to  $20\text{ cm}^{-1}$  as the result of electron density changes on the adjacent nitrogen atom.

### 2.14.3 Raman Spectra of MMH

Raman spectra often supplement IR spectra in a very useful manner. In many instances a complete assignment of absorption lines to fundamental vibrations can only be made by comparing the two types of spectra side-by-side.

The Raman spectra of MMH were recorded in the liquid state [153]. Absorption band assignments were made possible by isotope substitution and recording the IR and Raman spectra of  $\text{D}_2\text{NNDCH}_3$  and  $\text{D}_2\text{NND CD}_3$ . It is quite educational to look at some of the very first, quite ancient Raman spectra of MMH, UDMH, and symmetrical dimethylhydrazine (SDMH) published in 1938 [180].

Methylhydrazine forms a hydrate and dimers that have distinctly different properties from those of anhydrous and monomeric MMH. Water/MMH mixtures were investigated by means of Raman spectroscopy for the entire concentration range at room temperature and vs. temperature for some mixtures [181]. The Raman spectra of the liquid mixtures have shown that several species coexist in solution. Spectroscopic features have been assigned to MMH dimers and MMH  $n$ -hydrates. It was shown that solvation of MMH had a major influence on the C—N—N skeleton vibrations. For highly concentrated solutions in MMH, the presence of a high percentage of MMH dimers has been confirmed. A preliminary study of the effects of temperature on some water-MMH mixtures showed that the skeleton frequencies were perturbed by cooling.



When cooled to low temperatures, MMH hydrate does not crystallize readily, but forms a glass. Raman scattering investigations were carried out in the MMH/water molecular glass-former systems, revealing different species of molecular association through characteristic hydrogen-bonding interactions [182]. A relation between fragility and dilution was proposed based on low-frequency Raman data. The ability to form hydrogen bonds was analyzed versus dilution from the temperature dependence of the frequency of stretchings associated with hydrogen bonding, and discussed in the context of the glass formation. Unusual behavior of mixtures around the eutectic composition was noted and interpreted in relation to hydrogen-bond heterogeneities. See also [180].

#### 2.14.4 Index of Refraction of MMH

The index of refraction of MMH at 298 K is  $n_D^{25} = 1.4284$ .

### 2.15 Microwave Spectra of MMH

Microwave spectra extend the IR toward very long wavelengths of the order of millimeters instead of micrometers. Because of the lesser quantum energy, microwave spectra reveal details of low-energy molecular transitions, such as individual rotation energy states and their thawing temperatures. This helps to identify molecular structures and intermolecular forces leading to adducts and dimers.

In the microwave spectrum of MMH, two rotational isomers (“rotamers”) have been observed and their spectra assigned and interpreted [183]. The ground-state rotational constants of the inner skew isomer were  $A = 36704$  MHz,  $B = 9689.7$  MHz, and  $C = 8531.9$  MHz, whereas the values obtained for the outer skew rotamer were  $A - C = 29597.2$  MHz and  $\kappa = -0.925849$ . Strong evidence for the proposed conformational assignments was obtained from dipole moment components that differed for the two rotamers. Relative intensity measurements indicated that the inner rotamer is more stable than the outer rotamer by  $293 \pm 23$  cm<sup>-1</sup>. Spectral splitting by inversion and methyl “tunneling” have also been observed. Analysis of the latter effect indicated a barrier of  $1329$  cm<sup>-1</sup> for the inner rotamer. Hyperfine splitting caused by interaction with <sup>14</sup>N nuclei could be resolved, and the quadrupole coupling constants were  $\chi_{aa} = 4.09 \pm 0.03$  MHz,  $\chi_{bb} = 0.69 \pm 0.03$  MHz, and  $\chi_{cc} = -4.78 \pm 0.04$  MHz.

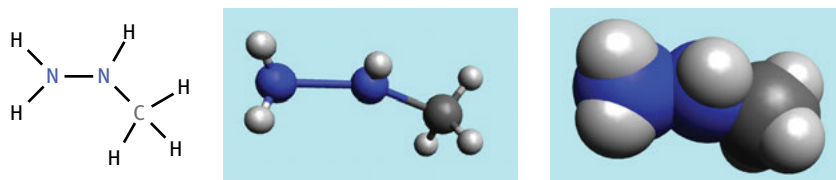
The microwave spectra of the inner and outer conformers of MMH have been measured [184]. The rotational constants and the <sup>14</sup>N nuclear quadrupole coupling constants (in MHz) for the outer conformer were determined as:  $A_0 = 38091.6(3)$ ,  $B_0 = 9591.93(6)$ ,  $C_0 = 8494.42(6)$ ,  $\chi_{aa1} = 3.7(3)$ ,  $\chi_{bb1} = 0.7(4)$ ,  $\chi_{aa2} = 3.2(3)$ , and  $\chi_{bb2} = -2.5(3)$ . The values in parentheses represent estimated limits of error, and suffixes 1 and 2 represent the N nuclei with and without the methyl group respectively. The inversion motion at the N1 nucleus is found to split the rotational levels; the barrier

heights of the inversion for the inner and outer conformers were estimated to be  $1960$  and  $2480\text{ cm}^{-1}$  respectively. Far-IR spectra have been measured for the normal and  $\text{CH}_3\text{NDND}_2$  species with a resolution of  $0.1\text{ cm}^{-1}$ . The observed absorption peaks were assigned to transitions related to the N—N and N—C torsional modes. The equilibrium dihedral angles for the N—N torsion were estimated to be  $93$  and  $268^\circ$  for the inner and outer conformers respectively.

Microwave spectral data on the inversion splittings in MMH were analyzed by the use of a generalized internal-axis method [185]. Inversion tunneling parameters reproducing the observed splittings were determined through a least-squares analysis for the inner and outer conformations.

## 2.16 Molecular Structure of MMH

The molecular structure of MMH is illustrated in Figure 20.



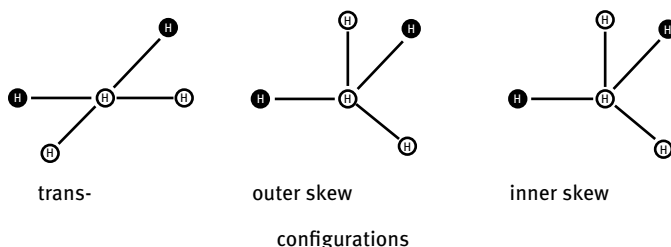
**Figure 20:** Molecular structure of methylhydrazine

The molecular structure of MMH was described by Aston, Rock, and Isserow [158]. The bond angles are assumed to be tetrahedral, and the bond lengths are as follows:

|     |                                 |
|-----|---------------------------------|
| N—N | $1.45 \times 10^{-10}\text{ m}$ |
| N—C | $1.47 \times 10^{-10}\text{ m}$ |
| N—H | $1.04 \times 10^{-10}\text{ m}$ |
| C—H | $1.09 \times 10^{-10}\text{ m}$ |

Three different configurations have been proposed for the molecular structure of MMH, a *trans*, an *outer-skew*, and an *inner-skew* configuration [163]. Looking at the possible configurations of the MMH molecule end-on in the same direction as the N—N axis gives the three different views illustrated in Figure 21, where the solid lines indicate the bonds to the two hydrogen atoms on the terminal nitrogen and the dashed lines indicate the bonds to the central nitrogen atom.

On the basis of spectroscopic data, it was concluded that MMH exists predominantly in the skew outer form with its methyl group farthest from the hydrogens of the  $\text{NH}_2$  group. This is also supported by photoelectron spectra of MMH [186]. See Section 2.17.



**Figure 21:** End-on views of three different methylhydrazine configurations

The *cis*-barrier height hindering the N–N torsional motion in MMH is  $36.2 \pm 3.6$  kJ/mol ( $8.66 \pm 0.86$  kcal/mol), with the maximum at a torsional angle of  $359^\circ$  [164]. The *trans* barrier is only  $15.0 \pm 0.3$  kJ/mol ( $3.58 \pm 0.07$  kcal/mol) and peaks at  $197^\circ$ . In addition to obstructed rotation around the N–N axis, the impeded rotation around the C–N axis also contributes to the varying degrees of freedom that are responsible for the specific heat of the molecule [171].

Another set of *ab initio* calculations using Pulay's force method and a new normal coordinate force relaxation procedure showed that in MMH the most stable conformation is the one in which the C–N bond can interact with the adjacent lone electron pair on nitrogen [187]. The optimized parameters for bond distances, bond angles, and total energies were in moderately close agreement with experimental data.

The electron diffraction intensity of methylhydrazine  $\text{CH}_3\text{NHNH}_2$  has been measured and analyzed jointly with the rotational constants of the conformers, inner and outer [188]. The optimized geometrical parameters and the force constants of the two conformers, derived from an Self-Consistent Field Molecular Orbital (SCF-MO) calculation with a 4-31G\* basis set, were utilized in the analysis. The following bond lengths ( $r_g$ ) and angles ( $r_z$ ) were measured:  $r(\text{C}–\text{H}) = 1.115(10)$  Å,  $r(\text{N}–\text{N})_{\text{i}} = 1.433(12)$  Å,  $r(\text{N}–\text{C})_{\text{i}} = 1.463(12)$  Å,  $\angle \text{CNN}_{\text{i}} = 113.47(21)^\circ$ ,  $r(\text{N}–\text{C})_{\text{o}} = 1.466(2)$  Å, and  $\angle \text{CNN}_{\text{o}} = 109.46(15)^\circ$ , where values in parentheses represent estimated limits of error ( $2.5\sigma$ ).  $r(\text{C}–\text{H})$  is a weighted average for the inner (i) and outer (o) conformers and the difference  $r(\text{N}–\text{C})_{\text{o}} - r(\text{N}–\text{N})_{\text{o}}$  is fixed to that predicted by the calculation, 0.0353 Å.

Various computational methods have been applied to model the MMH molecule, also in comparison with the parent molecule hydrazine, and in comparison with other methylhydrazines. The MMH molecule with its two rotational axes is a challenge for modeling computations. Not all computer models give accurate representations of physical properties. Computer models need experimental data for comparison and verification. Most models need to be tweaked to get their predictions to more closely match experimental data.

A few force field parameters and models have been published for hydrazine and alkylhydrazines and validated against experimental saturated densities, vapor pressure, heat of vaporization, isobaric heat capacity, and self-diffusion coefficients. Al-

though in one case this yielded satisfactory results for the liquid density and the heat of vaporization, the vapor pressure predicted for hydrazine and its derivatives deviated significantly from experimental data [189]. The model underestimated the experimental saturated liquid density of MMH from 2.8% at 273 K to 7.7% at 450 K and the vapor pressure of MMH was on average 4% below the experimental data.

Improved molecular models for hydrazine, MMH, and UDMH were developed to study the fluid phase behavior of these compounds [101]. A parameterization of classical molecular interaction models was carried out by using quantum chemical calculations and subsequent fitting to experimental vapor pressure and saturated liquid density data. Predicted critical temperature, 606.6 K, was 22 to 40° different than the literature data. Predicted critical density, 6.53 mol/L, was totally mismatched with literature data (3.69 mol/L). Predicted critical pressure (7.66 MPa) was in close agreement with the experimental value of 8.04 MPa. To validate the molecular models, vapor–liquid equilibria for the pure hydrazines and binary hydrazine mixtures with water or ammonia were calculated and compared with available experimental data. In addition, the Henry's law constant for the physical solubility of argon, nitrogen, and carbon monoxide in liquid MMH and UDMH was computed. In general, the simulation results were in good agreement with the experimental data.

Frozen MMH crystallizes in monoclinic crystals, space group  $P2_1/c$ , with unit cell parameters of  $a = 10.043 \text{ \AA}$ ,  $b = 3.925 \text{ \AA}$ ,  $c = 7.670 \text{ \AA}$ ,  $Z = 4$ ,  $\beta = 107.28^\circ$ ,  $V = 48.9 \text{ \AA}^3$ , and  $\rho = 1.06 \text{ g/cm}^3$  [190]. When cooled quickly, MMH supercools and forms a glassy solid instead of crystallizing.

## 2.17 Photoelectron and XPS Spectra of MMH

Electron spectroscopy for chemical analysis (ESCA, synonym: X-ray photoelectron spectroscopy, XPS) is a spectroscopic method that can be applied to vapors and solid surfaces. Depending on the objective of the analysis and the range of atomic weights to be scanned, resonance lines of noble gases in the vacuum UV or monochromatic X rays (magnesium or aluminum) are used to excite photoelectrons that are then passed through a monochromator, and their energy and intensity are measured. In solid materials, only a very thin surface layer is analyzed, usually only 5 nm deep. Photoelectron spectroscopy has developed into a very useful tool for conformational analysis, and ESCA spectra permit quantitative determination of the interaction of molecular orbitals by measuring the ionization energies of various molecular valence orbitals with high precision. Different conformations are characterized by different energy states and usually show up as separate or split peaks in the ESCA spectrum. Additional data on photoionization and ionization potentials of hydrazines can be found in Section 4.3. Ionization potentials of MMH in mass spectrometers are summarized in Section 4.5.

The ESCA spectra of aliphatic hydrazines allow a conformational analysis of substituted hydrazines with C—N—N linkages [191]. There is a correlation between the torsional angle between the two lonely pairs of electrons with the splitting of the two *n*-orbitals determined from the photoelectron spectrum [192]. See also [193, 194].

The He I photoelectron spectra of unsymmetrical hydrazines  $\text{CH}_3\text{HNNH}_2$  and  $(\text{CH}_3)_2\text{NNH}_2$  have been measured and CNDO/2 calculations have been carried out, in which *gauche* (outer- and inner-skew) forms and *trans* form were taken into account for  $\text{CH}_3\text{HNNH}_2$ . It was found that non-bonding splittings in the photoelectron spectra are well reproduced by CNDO/2 calculations with *gauche* forms. Based on orbital assignments of the photoelectron spectra it was concluded that: (1) The first and second bands are due to the methylated and unmethylated nitrogen lone pairs respectively; (2) the third bands are attributed to the N—N bonding orbitals; (3) the rest of the photoelectron spectra up to 18 eV can be explained in terms of other p-type orbitals (C—N bonding,  $\text{CH}_3$  pseudo  $\pi$ , and  $\text{NH}_2$  pseudo  $\pi$ ). The ESCA-XPS spectra have been used for conformational structural analysis of molecules of hydrazine derivatives [195].

The valence shell electronic structures of MMH, 1,1-dimethylhydrazine, and tetramethylhydrazine were examined by recording threshold and conventional (kinetic energy resolved) photoelectron spectra [196, 197]. In parallel, *ab initio* calculations were performed on the three methyl substituted hydrazines. The ionization energies of the valence molecular orbitals were calculated, allowing the photoelectron bands to be assigned to specific molecular orbitals. The ground-state adiabatic and vertical ionization energies, as determined from the threshold photoelectron spectra, were  $IE_a = 8.02 \pm 0.16 \text{ eV}$  and  $IE_v = 9.36 \pm 0.02 \text{ eV}$  for MMH,  $IE_a = 7.78 \pm 0.16 \text{ eV}$  and  $IE_v = 8.86 \pm 0.01 \text{ eV}$  for UDMH, and  $IE_a = 7.26 \pm 0.16 \text{ eV}$  and  $IE_v = 8.38 \pm 0.01 \text{ eV}$  for tetramethylhydrazine. Owing to the large geometry change that occurs upon ionization, these  $IE_a$  values were all higher than the true thresholds. New heats of formation ( $\Delta H_f^\circ$ ) were proposed for the three hydrazines in the vapor state on the basis of G3 calculations: 107, 94, and 95 kJ/mol for MMH, 1,1-dimethylhydrazine, and tetramethylhydrazine respectively. The previously reported  $\Delta H_f^\circ$  for tetramethylhydrazine was shown to be erroneous.

## 2.18 Bond Dissociation Energies of MMH

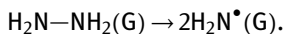
Like hydrazine itself, MMH readily decomposes under the influence of heat or energetic radiation. The most labile part of the molecule is the N—N bond. Various methods have been applied to measure the N—N bond energy and N—N bond dissociation energy in MMH and compare it with that of hydrazine or other methylhydrazines (Table 19). A common method is to observe the appearance potentials in a mass spectrometer. The knowledge of the bond dissociation energy of MMH and other hydrazine-

**Table 19:** Bond dissociation energies in methylhydrazines in comparison to hydrazine.

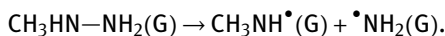
| Bond                                                                  | Dissociation energy |          |        | References |
|-----------------------------------------------------------------------|---------------------|----------|--------|------------|
|                                                                       | kJ/mol              | kcal/mol | eV     |            |
| <i>Methylhydrazine</i>                                                |                     |          |        |            |
| CH <sub>3</sub> NHNH—H                                                | 368                 | 88       | —      | [198, 199] |
| CH <sub>3</sub> NHNH—H                                                | 276 ± 21            | 66 ± 5   | —      | [200]      |
| HNN(CH <sub>3</sub> )—H                                               | 222 ± 25            | 53 ± 6   | —      | [200]      |
| H <sub>2</sub> NNH—CH <sub>3</sub>                                    | 347                 | 83       | —      | [198, 199] |
| H <sub>2</sub> N—NHCH <sub>3</sub>                                    | 280                 | 67       | —      | [198, 199] |
| H <sub>2</sub> NNHCH <sub>2</sub> —H                                  | 410                 | 98       | —      | [198, 199] |
| <i>1,1-Dimethylhydrazine</i>                                          |                     |          |        |            |
| (CH <sub>3</sub> ) <sub>2</sub> NNH—H                                 | 368                 | 88       | —      | [198, 199] |
| (CH <sub>3</sub> ) <sub>2</sub> NNH—H                                 | 356 ± 21            | 85 ± 5   | —      | [200]      |
| H <sub>2</sub> NN(CH <sub>3</sub> )—CH <sub>3</sub>                   | 377                 | 90       | —      | [198, 199] |
| H <sub>2</sub> N—N(CH <sub>3</sub> ) <sub>2</sub>                     | 156 ± 21            | 38 ± 5   | —      | [201]      |
| H <sub>2</sub> NN(CH <sub>3</sub> )CH <sub>2</sub> —H                 | 410                 | 98       | —      | [198, 199] |
| <i>Other Derivatives</i>                                              |                     |          |        |            |
| (CH <sub>3</sub> ) <sub>2</sub> N—N(CH <sub>3</sub> ) <sub>2</sub>    | 209 ± 21            | 50 ± 5   | —      | [201]      |
| (CH <sub>3</sub> ) <sub>2</sub> N—NN—N(CH <sub>3</sub> ) <sub>2</sub> | 69                  | 16.5     | —      | [201]      |
| For comparison:                                                       |                     |          |        |            |
| <i>Hydrazine</i>                                                      |                     |          |        |            |
| H—N <sub>2</sub> H <sub>3</sub>                                       | 318 ± 21            | 76 ± 2   | 33 ± 2 | [202]      |
| H <sub>2</sub> N—NH <sub>2</sub>                                      | 242 ± 38            | 58 ± 3   | 25 ± 4 | [202]      |
| H <sub>2</sub> N—NH <sub>2</sub>                                      | 226                 | 54       | 23     | [203, 204] |
| H <sub>2</sub> N—NH <sub>2</sub>                                      | 251                 | 60       | —      | [198, 199] |

based fuels is helpful when examining thermal stability, photolysis, autodecomposition temperature, and accidental explosions of these compounds.

A combined Density Functional Theory (DFT) theoretical study gave the following predicted bond dissociation enthalpies (BDEs) and vapor phase enthalpies of formation ( $H_f$ ) for hydrazine, MMH, UDMH, and SDMH: BDE in kJ/mol: N<sub>2</sub>H<sub>4</sub>, 278 ± 4; MMH, 272 ± 4; UDMH, 259 ± 12; SDMH, 272 ± 12.  $H_f$  in kJ/mol: N<sub>2</sub>H<sub>4</sub>, 95 ± 6; MMH, 94 ± 4; UDMH, 80 ± 4; SDMH, 91 ± 4 [205]. The BDEs for the cleavage of the N—N bond decreases in the order N<sub>2</sub>H<sub>4</sub> > MMH > UDMH > SDMH. For hydrazine, for example, the bond dissociation enthalpy is the enthalpy  $\Delta H$  of the following reaction forming two radicals H<sub>2</sub>N• in their equilibrium configuration:



The bond enthalpy (BE) for the N—N bond in hydrazine itself amounts to BE(N—N, H<sub>2</sub>N—NH<sub>2</sub>) = 159 ± 4 kJ/mol. For MMH, the bond dissociation equation is:



## 2.19 Computational Chemistry Calculations of MMH Molecular Structure

Force Field (FF) computations were performed for hydrazine and organic hydrazine derivatives, including MMH, UDMH, ethylhydrazine, and 2-hydroxyethylhydrazine [189]. The FF computations successfully reproduced a range of equilibrium properties, including vapor-liquid coexistence densities, vapor pressures, enthalpies of vaporization, and critical properties. Using this as a basis, a FF method was also developed for the protonated forms of these species, i.e., hydrazinium cations. Properties of 1:1 energetic salts formed by pairing these cations with the nitrate anion were computed and compared with a limited amount of experimental data.

## 2.20 Electrical Properties of MMH

### 2.20.1 Electrical Conductivity of MMH

Methylhydrazine as a non-aqueous solvent is not as good a conductor as its parent compound, hydrazine. The electrical conductance of propellant-grade MMH is lower by about a factor of 7 than that of  $\text{N}_2\text{H}_4$ . Propellant-grade MMH had a specific conductance of  $0.13 \times 10^{-4}$  mho/cm at 298 K [206]. Treatment with BaO removed some of the contaminants (most likely methylcarbamic acid) and lowered the specific conductance to  $0.03 \times 10^{-4}$  mho/cm. The specific resistance of MMH between 283 and 323 K can be expressed by the equation:

$$\Omega = 8.2 \times \exp[1135/(T - 273)]$$

where  $\Omega$  is the specific resistance in Ohm cm and  $T$  is the temperature in kelvin [207, 208]. The difference between the conductivities of two commercial samples of MMH was substantial, amounting to 25%.

### 2.20.2 Dielectric Constant and Dipole Moment of MMH

Measurements of the dielectric constant of MMH/water mixtures are not only useful for studying the internal structure of such liquids but can also serve in the rapid analysis of MMH/water mixtures. The dielectric constants of MMH (DC = 19) and water (DC = 80.1 at 293 K) are sufficiently apart that an instrument could be calibrated to give direct readouts. The dielectric constant of MMH is 19.2 at 288.7 K and 17.3 at 305.3 K [80]. Other sources gave a dielectric constant of MMH of 19.0 at 298 K [79].

Earlier attempts to analyze small quantities (<10%) of water in hydrazine or MMH had failed because the dielectric constants of the two liquids were too close to each other for the oscillometer instrument used [209]. In UDMH, the water content between 0.01 and 1 mass-% could be determined with an average error of 2.2%. The methylhydrazines are less polar liquids and the dielectric constants are correspondingly lower (e.g., 19 for MMH).

Liquid propellant level gauging in a rotating spacecraft can be achieved by capacitance measurements of the liquid-filled space between two concentric tubes serving as the electrodes of a capacitor. Dielectric properties (permittivity and specific conductivity) of MON-1 and MMH were measured as a function of temperature because these numbers were needed for calibrating the sensors [207, 208]. The permittivity of MMH between 283 and 323 K can be expressed by the following equation:

$$\varepsilon = 23.1 - 0.11 \times (T - 273)$$

where  $\varepsilon$  is the permittivity (a dimensionless number) and  $T$  is the temperature in kelvin.

The CNDO/2 calculations of dipole moments and charge distributions for hydrazine and nine substituted hydrazines gave satisfactory agreement between calculated and experimental values [210]. Calculated dipole moments (in Debye units) were  $\text{N}_2\text{H}_4$  2.37, MMH 2.49, UDMH 2.93, 1,2-dimethylhydrazine 0.06, *cis*-trimethylhydrazine 3.37, *trans*-trimethylhydrazine 0.18, and propionyl hydrazine 2.6. N–N bond enthalpies can also be calculated using this method.

The dipole moment calculated for the “outer” skew rotamer of MMH, 1.91 D, was closer to the measured moment of 1.68 D than a calculated moment of 1.13 D for the “inner” configuration [163, 211].

### 2.20.3 Electric Properties of MMH/ $\text{H}_2\text{O}$ Mixtures

The dielectric relaxation times and static permittivity of binary mixtures of MMH/water and UDMH/water were determined in supercooled conditions down to 150 K to study the association between MMH and water in the liquid and solid state [212]. For each system, these properties can be modeled using chemical associations of the type  $(\text{H}_2\text{O}) \bullet (\text{RR}'\text{NNH}_2)$ , and also self-associations for pure hydrazines. Permittivity  $\varepsilon'$  and dielectric loss factor  $\varepsilon''$  define the complex permittivity  $\varepsilon = \varepsilon' - i\varepsilon''$ . Capacitance and dielectric loss factor measurements were taken for eight frequencies – 2 MHz, 1 MHz, 400, 200, 100, 40, 20, and 10 kHz – on an automatic microprocessor-based LRC meter. As spontaneous crystallization occurred on cooling within a certain range of compositions, the relaxation phenomenon could be studied only for the following molar fractions  $\chi$  in alkylhydrazine:  $0.2 < \chi < 0.9$  for the MMH/water system. The maximum relaxation time was located near the molar fraction  $\chi = 0.30 - 0.35$  for the MMH–water mixtures. This behavior is closely related to that observed for viscosity [107].



## 2.21 Base Strength and Protonization of MMH

Alkylation of hydrazine reduces its base strength. Alkylhydrazines are less likely to form double-protonated salts. Table 20 is a comparison of the base strengths and heats of neutralization of methylhydrazines in comparison with hydrazine.

**Table 20:** Base strength, heat of neutralization, and heat of ionization of hydrazines.

| Gross formula  | Abbreviated compound structure | $pK_a$ at 298 K | Heat of neutralization |          | Heat of ionization |          | References |
|----------------|--------------------------------|-----------------|------------------------|----------|--------------------|----------|------------|
|                |                                |                 | kJ/mol                 | kcal/mol | kJ/mol             | kcal/mol |            |
| $H_4N_2$       | $H_2NNH_2$                     | 7.95            | 40.9                   | 9.78     | 40.7               | 9.73     | [213]      |
| $CH_6N_2$      | $MeHNNH_2$                     | 7.85            | 34.6                   | 8.27     | 34.6               | 8.26     | [213]      |
| $CH_6N_2$      | $MeHNNH_2$                     | 8.14            | —                      | —        | —                  | —        | [214]      |
| $CH_6N_2$      | $MeHNNH_2$                     | 7.87            | —                      | —        | —                  | —        | [215]      |
| $C_2H_8N_2$    | $Me_2NNH_2$                    | 7.09            | —                      | —        | —                  | —        | [216]      |
| $C_2H_8N_2$    | $Me_2NNH_2$                    | 7.12            | 24.0                   | 5.73     | 23.8               | 5.69     | [213]      |
| $C_2H_8N_2$    | $MeHNNMeH$                     | 7.49            | 29.3                   | 7.00     | 29.4               | 7.03     | [213]      |
| $C_2H_8N_2$    | $MeHNNMeH$                     | 7.52            | —                      | —        | —                  | —        | [215]      |
| $C_2H_8N_2$    | $Me_2NNH_2$                    | 7.21            | —                      | —        | —                  | —        | [215]      |
| $C_3H_{10}N_2$ | $Me_2NNMeH$                    | 6.78            | —                      | —        | —                  | —        | [217]      |
| $C_3H_{10}N_2$ | $Me_2NNMeH$                    | 6.58            | 18.5                   | 4.43     | 18.7               | 4.46     | [213]      |
| $C_4H_{12}N_2$ | $Me_2NNMe_2$                   | 6.10            | 10.2                   | 2.44     | 10.2               | 2.44     | [213]      |
| $C_4H_{12}N_2$ | $Me_2NNMe_2$                   | 6.30            | —                      | —        | —                  | —        | [215]      |

## 2.22 Nuclear Magnetic Resonance Spectra of Alkylhydrazines

Nuclear magnetic resonance spectra of alkylhydrazines, either from the nitrogen or carbon nuclei or the hydrogen nuclei (protons) are useful for determining the structure of alkylhydrazine molecules. NMR spectra of anhydrous substituted hydrazines were reported in [218].

## 3 Physical Properties of MMH Mixtures

### 3.1 Physical Properties of MMH/Hydrazine Mixtures

The most frequently used hydrazine/MMH mixture is the 14 mass-% hydrazine/86% MMH mixture (“M-86,” “MHF-3”) with a freezing point of 219 K (−65 °F). Another mixture of practical interest is Ae-76, a blend of 76% MMH and 24% hydrazine formulated by Aerojet to contain the same amount of carbon as Aerozine-50 and at one time intended as a replacement for Ae-50. It freezes at ~237 K (−33 °F). A third blend of interest

is M-20, containing 20% MMH in hydrazine, which freezes at  $\sim 269\text{K}$  ( $25^\circ\text{F}$ ), and it was proposed as a replacement for hydrazine in bipropellant rocket engines to reach lower storage temperatures.

### 3.2 Physical Properties of MMH/Water Mixtures

#### 3.2.1 Freezing Points of MMH/Water Mixtures

The freezing points of MMH/water mixtures are summarized in Table 21. Mixtures with 56% MMH became viscous between 253 and 233 K ( $-20$  and  $-40^\circ\text{C}$ ) and formed glassy solids at about 193 to 187 K ( $-80$  to  $-86^\circ\text{C}$ ). No crystallization could be induced.

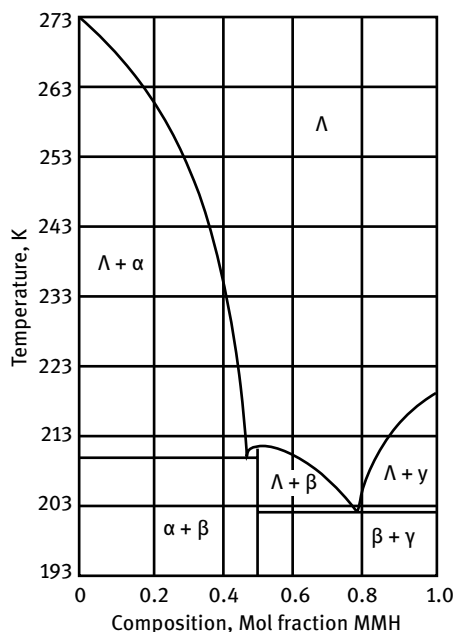
**Table 21:** Freezing points of methylhydrazine/water solutions.

| Methylhydrazine<br>Mass-% | Water<br>Mass-% | Liquidus<br>K | Solidus<br>K | Liquidus<br>$^\circ\text{C}$ | Solidus<br>$^\circ\text{C}$ |
|---------------------------|-----------------|---------------|--------------|------------------------------|-----------------------------|
| 29.8                      | 70.2            | 254.1         | 189.1        | $-19.0$                      | $-84.0$                     |
| 34.9                      | 65.1            | 248.1         | 187.1        | $-25.0$                      | $-86.0$                     |
| 40.2                      | 59.8            | 240.6         | 189.1        | $-32.5$                      | $-84.0$                     |
| 44.9                      | 55.1            | a             | a            | a                            | a                           |
| 49.6                      | 50.4            | a             | a            | a                            | a                           |
| 55.9                      | 44.1            | a             | a            | a                            | a                           |
| 60.2                      | 39.8            | a             | a            | a                            | a                           |
| 64.9                      | 35.1            | a             | a            | a                            | a                           |
| 70.0                      | 30.0            | a             | a            | a                            | a                           |
| 75.2                      | 24.8            | a             | a            | a                            | a                           |
| 80.6                      | 19.4            | a             | a            | a                            | a                           |
| 85.4                      | 14.6            | a             | a            | a                            | a                           |
| 88.2                      | 11.8            | a             | a            | a                            | a                           |
| 94.3                      | 5.7             | 213.1         | 195.1        | $-60.0$                      | $-78.0$                     |

<sup>a</sup> These solutions became viscous between 253 and 233 K ( $-20$  and  $-40^\circ\text{C}$ ) and formed glassy solids at about 193 to 187 K ( $-80$  to  $-86^\circ\text{C}$ ). No crystallization could be induced.

Data source: [60]

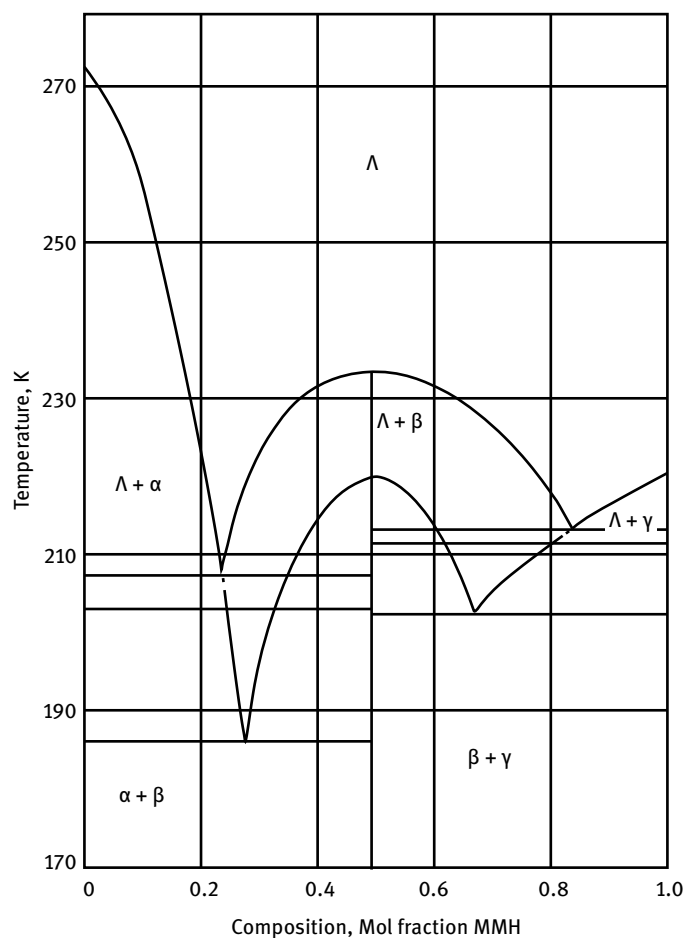
Freezing point data shown in Figure 22 indicate that MMH and water form a hydrate similar to what hydrazine does [99]. Similar conclusions can be drawn based on viscosity data. The composition of the hydrate is 28%  $\text{H}_2\text{O}$  and 72% MMH. It contains water and MMH in a 1:1 molar ratio and forms a congruent compound. A liquid with this composition has a sharp freezing point ( $213\text{K} = -78^\circ\text{F}$ ) and when cooled to this temperature and below freezes to a solid with the same composition. In Figure 22, the symbol  $\Lambda$  designates the liquid solution,  $\alpha$  is water ice,  $\beta$  is frozen MMH hydrate, and  $\gamma$  is frozen MMH.



**Figure 22:** Solid–liquid phase diagram for the methylhydrazine/H<sub>2</sub>O system. (Reproduced and modified from [22] as adapted from [99].)

Crystallization kinetics of MMH monohydrate were followed under adiabatic conditions and the measurements indicated that two solid phases, a metastable form and a stable form, exist between 186 and 223 K [219]. This method allows one to determine the temperature dependence of the growth process of the metastable solid in only one experiment. The spontaneous evolution of the system temperature with time during the crystallization process was modeled assuming a temperature dependence of the growth rate and using the Avrami–Kolmogorov assumption. The results suggested that the number of nuclei is constant during the growth process and that the crystallites grow with a constant shape in the undercooled liquid. Figure 23 shows that MMH and water form a monohydrate that exists in a metastable (dashed line) and a stable form (solid line) at temperatures between 186 and 223 K.

When cooling the MMH/H<sub>2</sub>O mixture, glass was readily formed at any cooling rate. The glass transition temperature was in the vicinity of 157 K. Crystallization then occurred during reheating of the sample. Depending on the heating rate, the hydrate crystallized in a metastable form that melted at about 219 K and (or) in a stable form that melted sharply at 234 K. The phase transformation was very slow and may take hours or days. The heat of transformation was measured in an adiabatic calorimeter similar to an accelerating rate calorimeter (ARC). In one example, the crystallization of the metastable phase was complete at 209.3 K and the melting of the metastable phase took place at 222 K. The energy released by the crystallization process increased the temperature of the system from 186 to 222.4 K.



**Figure 23:** Solid–liquid phase diagram for the methylhydrazine/H<sub>2</sub>O system. (Republished and modified from [219], with permission of ©1996 Elsevier, permission conveyed through RightsLink)

Phase transformations in the MMH monohydrate ( $\text{CH}_3\text{NHNH}_2 \cdot \text{H}_2\text{O}$ ) system were investigated using DSC over the temperature range 110–300 K [220, 221]. On cooling of the solution, glass was formed by quenching the liquid. Depending on the heating/cooling rate, two solid phases (metastable and/or stable) with slow-phase transformation kinetics were observed. The optimal temperature for nucleation and growth processes were determined for the two solid phases. The nucleation rate was at a maximum in the glass transition region ( $T_g \cong 160$  K) and the temperature-growth regions were estimated to be 188–202 K for the metastable solid phase and 212–228 K for the stable solid phase. The metastable and the stable solid phases melted at 220 and 234 K, respectively.

The molecular associations of MMH with water were analyzed over a wide range of mixture compositions using Raman and the bond lengths of N—H and O—H were measured as a function of the temperature of the liquid [222]. In addition to the hydrate, there were indications of MMH dimers. Deviations from normal solution behavior were due to hydrogen bonding, also evident from sudden changes of the heat capacity and viscosity of the liquid.

Two monohydrates of MMH were formed by annealing at a low temperature ( $T < 218.9\text{ K}$ ) of supercooled stoichiometric mixtures of MMH and water, and nucleation and crystallization temperature/composition regimes were investigated by DSC [223]. The results agreed with the data deduced from a light scattering method. The formation of each solid phase is controlled by two kinds of nuclei.

Solid-liquid equilibria of the system MMH/water were investigated by direct thermal analysis on heating [224, 225]. Three liquidus curves could be observed corresponding to ice, MMH, and a stable congruently melting MMH monohydrate. Another metastable form of monohydrate could be observed, its transformation into the stable form being monotropic. A model was deduced from the study of the water/alkylhydrazines vapor-liquid equilibria and representing strong interactions between molecules as chemical associations, which allowed one to reproduce all the liquidus curves correctly. This modeling was based on the evolution of Raman spectra of the liquid phase. The crystal structure of pure MMH, determined at 179 K by X-ray diffraction (XRD) on a single crystal, is favorable to the existence of strong interactions between MMH molecules. The model can also be used to reproduce the system UDMH/water.

### 3.2.2 Freezing Points of MMH/Hydrazine Mixtures

Methylhydrazine is a preferred additive to hydrazine to lower its freezing point without changing its specific impulse in bipropellant combinations. Freezing points of MMH/hydrazine mixtures are listed in Table 22 and illustrated in Figure 24. The most important MMH/N<sub>2</sub>H<sub>4</sub> mixture is MHF-3 with 86 mass-% MMH. MHF-3 has a freezing point of 219.26 K (−53.9°C).

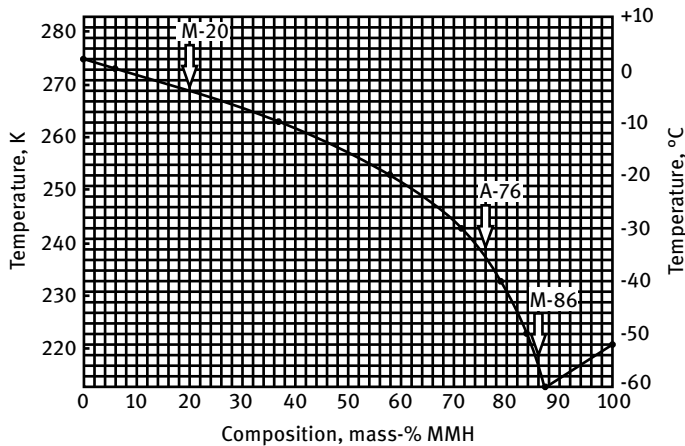
### 3.3 Physical Properties of Other MMH Mixtures

In search of a freezing point suppressant for MMH in bipropellant systems, five different organic additives and water were tested to measure freezing points, densities, vapor pressures, and to calculate the potential effect on bipropellant performance with NTO as the oxidizer [226]. The additives tested in quantities between 5 and 40% were: urea, acetamide, 1-methyl-1-phenylhydrazine, *N,N*-dimethylformamide, and formamide. Other than water, which would have lowered performance and caused corrosion, *N,N*-dimethylformamide was the best candidate additive for

**Table 22:** Binary system methylhydrazine–hydrazine freezing point data.

| Composition of mixture, mass-% |           | Freezing point |       |
|--------------------------------|-----------|----------------|-------|
| Methylhydrazine                | Hydrazine | K              | °C    |
| 0.0                            | 100.0     | 274.1          | +1.0  |
| 14.6                           | 85.4      | 270.6          | −2.5  |
| 33.1                           | 66.9      | 264.1          | −9.0  |
| 69.9                           | 30.1      | 244.1          | −29.0 |
| 84.3                           | 15.7      | 224.6          | −48.5 |
| 85.0                           | 15.0      | 222.6          | −50.5 |
| 86.5                           | 13.5      | 217.1          | −56.0 |
| 88.0                           | 12.0      | 213.6          | −59.5 |
| 88.5                           | 11.5      | 214.1          | −59.0 |
| 89.8                           | 10.2      | 214.1          | −59.0 |
| 92.6                           | 7.4       | 217.1          | −56.0 |
| 94.9                           | 5.1       | 219.1          | −54.0 |
| 96.8                           | 3.2       | 218.6          | −54.5 |
| 100.0                          | 0.0       | 220.6          | −52.5 |

Data source: [60]



**Figure 24:** Freezing/melting points of methylhydrazine/hydrazine mixtures. (Author’s laboratory data.)

lowering the freezing point without excessive loss of performance. Addition of 5% *N,N*-dimethylformamide lowered the freezing point to below 203 K (−70 °C), increased the density at 299 K (26.5 °C) to 0.875 g/cm<sup>3</sup>, and increased the boiling point to 362 K (91 °C). In the system MMH/UDMH, a eutectic freezing at 193 K (−80 °C = −112 °F), appeared at the composition: 39.8 mass-% MMH and 60.2% UDMH [60].

### 3.4 Freezing Points of Ternary MMH Mixtures

Ternary MMH mixtures may occasionally be selected to obtain blends with properties not otherwise achievable with binary mixtures.

#### 3.4.1 Freezing Points of MMH/N<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>O Mixtures

The MMH mixtures listed in Table 23 have been formulated to provide one oxygen for every carbon when these mixtures were used as monopropellants. The addition of water lowers the performance of MMH/N<sub>2</sub>H<sub>4</sub> mixtures as monopropellants and fuels, but it was hoped that the preferential formation of carbon monoxide would avoid the formation of soot in the monopropellant exhaust. At the lower temperatures, the mixtures exhibited extensive supercooling, and only a freezing range rather than a freezing point could be determined [227].

**Table 23:** Freezing ranges of ternary MMH/N<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>O mixtures.

| Composition, mass-% |                               |                  | Freezing range |            |
|---------------------|-------------------------------|------------------|----------------|------------|
| MMH                 | N <sub>2</sub> H <sub>4</sub> | H <sub>2</sub> O | K              | °C         |
| 47.9                | 33.3                          | 18.8             | 223–218        | –50 to –55 |
| 35.9                | 50.0                          | 14.1             | 238–236        | –35 to –33 |
| 25.6                | 64.4                          | 10.0             | 255–250        | –18 to –23 |

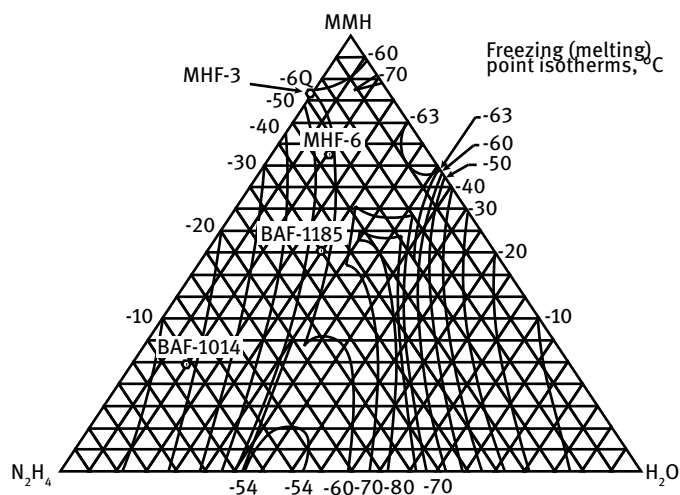
Data source: [227]

The freezing (melting) point isotherms of ternary MMH/N<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>O mixtures are illustrated in the triangular chart in Figure 25. Fuel mixtures of interest are marked on the chart as MHF-3, MHF-6, BAF-1014, and BAF-1185.

If one holds the MMH:H<sub>2</sub>O ratio constant at a molar ratio of 1:1 corresponding to MMH hydrate, then the freezing point as a function of added hydrazine is almost a linear function, as illustrated in Figure 26. Note that the abscissa scale is mol-%, not mass-% N<sub>2</sub>H<sub>4</sub>.

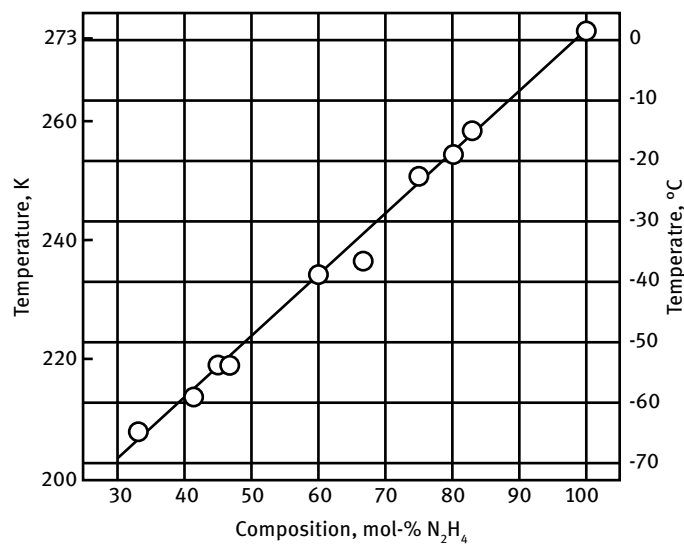
#### 3.4.2 Freezing Points of MMH/N<sub>2</sub>H<sub>4</sub>/HN Mixtures

Frequently, the desired low freezing point of hydrazine fuels could not be achieved by adding only one compound. Satisfactory freezing points and performances were achieved only with a number of ternary mixtures that also contained HN as an oxidizer. Mixtures of hydrazine/MMH/HN and also hydrazine/UDMH/HN have been investigated (see Table 24). A mixture with a nominal composition of 23.3% hydrazine, 45.3% MMH, and 31.4% HN freezes at 219.2 K (–65 °F) and has subsequently been named Mixed Hydrazine Fuel-1 (MHF-1). This mixture has been



**Figure 25:** Freezing (melting) points of ternary methylhydrazine/ $\text{N}_2\text{H}_4$ / $\text{H}_2\text{O}$  mixtures. (Reproduced and modified from [79].)

Note: broken lines indicate uncertainties due to supercooling



**Figure 26:** Freezing/melting points of methylhydrazine: $\text{H}_2\text{O} = 1:1/\text{N}_2\text{H}_4$  mixtures. (Reproduced and modified from [79].)



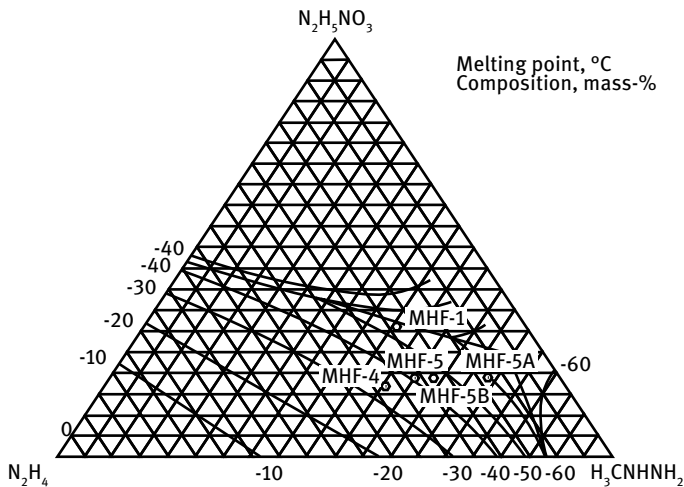
**Table 24:** Freezing points of MMH/hydrazine/hydrazinium nitrate (HN) mixtures.

| Composition, mass-% |                               |      | Freezing point |       |
|---------------------|-------------------------------|------|----------------|-------|
| MMH                 | N <sub>2</sub> H <sub>4</sub> | HN   | K              | °C    |
| 45.3                | 23.3                          | 31.4 | 219.3          | −53.8 |
| 40.6                | 31.3                          | 28.1 | 228.2          | −44.9 |
| 36.8                | 37.7                          | 25.5 | 237            | −36.1 |
| 31.0                | 47.6                          | 21.4 | 245.4          | −27.7 |

Data source: [227]

thoroughly characterized with regard to physical properties, performance, and material compatibility, but has not found widespread use. All mixtures listed in Table 24 were composed so as to provide sufficient oxygen for all carbon to react to carbon monoxide, thus avoiding carbon deposition when used as a monopropellant.

Freezing (melting) points of the ternary MMH/hydrazine/HN mixtures are illustrated in the triangular graph in Figure 27. The highest performance and lowest freezing point mixture in this graph is MHF-1, but for safety's sake the investigators selecting monopropellants for missile applications backed off and eventually chose MHF-5B for further development.



**Figure 27:** Freezing (melting) point isotherms of ternary methylhydrazine-hydrazine-hydrazine nitrate (HN) mixtures. (Reproduced and modified from [79].)

## 4 Chemical Properties of MMH

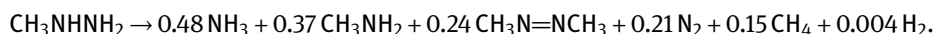
### 4.1 Thermal Decomposition of MMH

Thermal decomposition of MMH, similar to that of hydrazine, could occur accidentally or deliberately, as in a rocket engine or gas generator. The conditions leading to accidental decomposition of MMH must be known to prevent accidents.

Throughout the discussion of kinetics and thermodynamics of MMH decomposition it is very important to know the bond dissociation energies, for unless sufficient energy is pumped into the system to break at least one of the bonds, no decomposition would occur, at least not thermodynamically. Molecules are reluctant to dissociate if they have the same bond energy as carbon in diamond, which is a very sturdy material. The activation energy is a barrier to decomposition. In order for MMH to decompose on command, the most frequently used method is the lowering of the activation energy.

The main interest in the slow liquid-phase decomposition of MMH stems from practical concern about unwanted pressure buildup during storage and the effect of various materials it is in contact with on the rate of such buildup. Pressure buildup during storage was and still is an important design consideration. During a 10-year storage test in an all-glass apparatus, the rate of MMH decomposition at 316 K (110 °F) in the absence of metal surfaces and catalytic contaminants was 0.02–0.1%/year [228, 229].

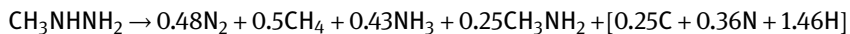
The major products of the thermal decomposition of liquid MMH at 473 K (200 °C) are ammonia, methylamine, azomethane, nitrogen, and methane, plus an unidentified species that has a retention time between those of water and MMH on a Quadrol GC column [206]. Hydrogen was found only in trace amounts and formaldehyde methylhydrazone and hydrogen cyanide (HCN) were not formed in measurable amounts. The stoichiometry based on the analysis of the gaseous products was:



The investigation showed that the decomposition rate of MMH in Pyrex glass is only one-tenth the rate observed with hydrazine. The rate of MMH decomposition in Pyrex at 473 K is 0.017%/h. The presence of a CRES-321 surface increased the decomposition rate of propellant-grade MMH by a factor of 5. Acid catalysis by addition of ammonium chloride accelerated decomposition 100%. BaO-treated  $\text{N}_2\text{H}_4$  was more stable in Pyrex than BaO-treated MMH by a factor of 5. MMH is thus more susceptible to decomposition by acid catalysis than hydrazine itself.

The influence of various substances (including metal salts) in specification-grade and refined-grade MMH was examined to provide an understanding of the factors influencing MMH decomposition [230, 231]. The MMH was purified by drying over  $\text{CaH}_2$  for several days, degassing the sample on a vacuum line, and distilling. The purified MMH contained less than 10 ppm water, ammonia, or methylamine. MMH heated in Pyrex tubes at 448 K (175 °C) yielded the products  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ , and  $(\text{CH}_3)_2\text{N}_2$ .

Only a trace of  $\text{H}_2$  was formed at temperatures below 403 K (130 °C). The composition of the products could be expressed by the following stoichiometric equation:



where the atoms in the brackets have not been assigned to specific compounds. Propellant-grade MMH (neat, without diluent) decomposed much faster than purified MMH. Although the rate decreased from 0.0095 to 0.0037%/h during the 673-h test at 448 K, the overall decomposition was 2.5%. Under the same conditions, the purified sample had decomposed only 0.8%, and the final rate was 0.0012%/h. Care was taken to exclude  $\text{CO}_2$  from all container tubes. Small amounts (0.003 M) of dissolved nickel and iron increased the decomposition rate of MMH by a factor of 10 at 373 K (100 °C.) Dissolved copper had no appreciable effect. The addition of 1% water to MMH had no effect on its decomposition rate at 448 K (175 °C).

The Aestus engine of the upper stage of ARIANE 5 is fed with MMH under a pressure of 16 bar. The propellant, initially at room temperature, is about 393 K when introduced into the combustion chamber, owing to heating up through the regenerative cooling jacket. As MMH is unstable above 373 K, it was necessary to check its thermal decomposition rate in a steel bomb at up to 500 K [92]. The pressure rise rates as a function of temperature are listed in Table 25. The activation energy derived from the Arrhenius equation was 83.8 kJ/mol.

**Table 25:** Liquid phase decomposition of methylhydrazine in a steel bomb.

| Temperature, K | Pressure rise rate, Pa/s |
|----------------|--------------------------|
| 413.4          | 9.2                      |
| 423.9          | 16.2                     |
| 434.2          | 25.5                     |
| 444.3          | 35.6                     |
| 455.7          | 42                       |
| 465.7          | 82                       |
| 476.2          | 175                      |
| 497.8          | 292                      |

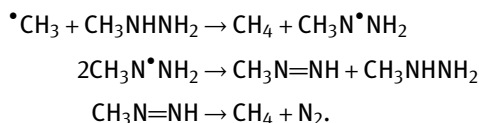
Data source: [92]

#### 4.1.1 Effect of Dissolved Contaminants on the Decomposition of MMH in a Liquid State

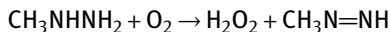
The effect of acid-forming materials on the decomposition of MMH is of key importance. The addition of acid-forming materials such as  $\text{NH}_4\text{Cl}$ ,  $\text{HCl}$ ,  $\text{NH}_4\text{NO}_3$ , or  $\text{CO}_2$  have been shown to strongly accelerate the decomposition of hydrazine  $\text{N}_2\text{H}_4$  in the presence of metals [232]. Although similar studies apparently have not been carried out with MMH, the investigation reported in Axworthy [232] found that the addition

of 1%  $\text{NH}_4\text{Cl}$  increased the rate of MMH decomposition at 473 K (200 °C) in Pyrex by a factor of 100 – a more pronounced effect than that observed with hydrazine. The effects of metal surfaces were not investigated. It appears probable, however, that acidic impurities or contaminants are detrimental to the stability of MMH in contact with some metal surfaces.

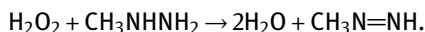
The unimolecular decomposition of MMH, UDMH, and tetramethylhydrazine vapor was studied at low pressures (0.13 Pa = 0.001 mm Hg) and at 873–1273 K (600–1000 °C), and was found to proceed through the elimination of  $\text{NH}_3$  and  $\text{H}_2$  [233]. The heats for formation of the radicals were  $\cdot\text{NH}_2$  (197 kJ/mol = 47.1 kcal/mol),  $\text{CH}_3\text{N}\cdot\text{H}$  (191 kJ/mol = 45.6 kcal/mol), and  $(\text{CH}_3)_2\text{N}\cdot$  (160 kJ/mol = 38.2 kcal/mol). Both  $(\text{CH}_3)_2\text{NNH}_2$  and  $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2$  decomposed via N–N scission. At higher pressures, on the order of one atmosphere, and sealed Pyrex tubes at 592 K (319 °C), the decomposition of MMH was more complex, yielding as major products  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{NH}_3$ , and  $\text{CH}_3\text{NH}_2$ . In gas-phase experiments at 592 K (319 °C), in which methyl radicals were generated in samples of MMH, no chain reaction was initiated. Instead, a stoichiometric reaction took place shown by these equations:



Methylhydrazine was found to react rapidly with oxygen at a pressure of a few millimeters of mercury and at room temperature. The presence of  $\text{CH}_3\text{N}=\text{NH}$  was confirmed by both IR and MS data, and a suggested reaction sequence is:



and



The condensed phase decomposition reactions of 0.1 M MMH at 592 K (319 °C) in hexadecane showed considerable scatter, which was attributed to the presence of trace amounts of some uncontrollable reaction-promoting material, probably oxygen. The major products were  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{NH}_3$ , and  $\text{CH}_3\text{NH}_2$  in the ratio 1:1:0.0:0.5. Hydrogen was a minor product. The rate of decomposition was highly erratic, and apparently some unknown, uncontrollable catalytic factor was operative. The range of rates corresponded to first-order half-lives spanning 6 to 300 h. In other experiments under the same conditions, ullage increases on the order of a factor of three and surface-to-volume increases on the order of a factor of 50 or higher caused minimal changes in both decomposition rate and product nature [234].

Experiments were performed in which soluble metal ions were introduced in solutions with MMH in the ratio MMH : ion = 90 : 1 [230, 235]. The decomposition of MMH in the presence of Fe(III), Fe(II), Cu(II), Ni(II), Zn(II), Mn(II), and Mg(II) is immeasurably

slow at room temperature. At 592 K (319 °C), however, MMH decomposition was total for the first four ions within 3 h. The iron and nickel ions were reduced to the native metals. The introduction of methyl radicals into a sample of MMH at 592 K (319 °C) did not initiate long chain reactions, but rather resulted in a stoichiometric 1:1 decomposition of the material.

Instead of using undiluted MMH and risking runaway decomposition reactions, diluted MMH solutions in hexadecane were used to study the sensitivity of MMH to the presence of transition metal salts [236]. In experiments at 473 K (200 °C) in which the ratio of MMH to metal was 90:1, MMH was completely destroyed within 5 min. when in the presence of Ni(II), Fe(II), or Fe(III). Cu(II), on the other hand, brought about decomposition at a considerably slower rate, only 72% destruction of MMH in 72 h. The product distributions in these experiments were dependent to some extent upon the metal salts present. The degree of MMH decomposition in an experiment with Ni(II) was independent of the presence of oxygen. Thus, there appears to be no synergistic effect operating on MMH destruction when MMH is decomposing in the presence of both O<sub>2</sub> and a transition metal salt.

Methylhydrazine solutions of 0.003 M Ni(II), Fe(II), and Cu(II) (about 200 ppm of metal) were heated to 373 K (100 °C) for periods up to 24 h [230, 237]. The Cu-doped solutions exhibited little if any increased decomposition over a sample without added metal, but the Ni- and Fe-doped solutions decomposed to the extent of 2.6 and 2.2% respectively over that period. The zero-valency metal powders precipitated in each case within 6 h, and although there was no certainty that the ions themselves were catalytic, it was evident that the deposited metals were active catalysts. These results are significant with regard to predicting the long-term storage of MMH fuels, as the metal salts form a sediment that may both foul lines and valves and catalyze MMH decomposition. The presence of both the nitrate and chloride salts of MMH in MMH greatly increased the rate of decomposition.

#### 4.1.2 Effect of Metal Surfaces on Decomposition of Liquid MMH

In an investigation of the compatibility of titanium, CRES-347, Al-2014-T6, A-2024, maraging steel A, and maraging steel B, with MMH at 343 K (70 °C) after 107 days, only the maraging steels gave any indication of instability [238]. The criterion of compatibility was the development of significant pressure in the test capsule compared with the pressure development of controls that contained no metal specimen. The maraging steels had the following compositions: maraging steel A: 18 Ni, 4 Mo, balance Fe; maraging steel B: 20 Ni, 1.5 Ti, balance Fe. In this case, the lack of compatibility may in part be attributed to the presence of molybdenum and high nickel in the alloys. Molybdenum, and possibly nickel, are known to effect decomposition of hydrazine-type fuels. One major product of the slow decomposition for all metals tested was N<sub>2</sub>. No CH<sub>4</sub> was reported and only a trace of H<sub>2</sub> and NH<sub>3</sub> in one test. Methyl amines and formaldehyde methylhydrazone were reported as

decomposition products remaining in the liquid phase. The apparent absence of methane in these studies is surprising in view of its ubiquity in other decomposition reactions reported in the literature. JPL reported on the decomposition of MMH stored in contact with 6Al-4V Ti, CRES-303, and CRES-304L at 316 K (43 °C) [239]. In contact with both Ti-6Al-4V and CRES-303, MMH decomposition amounted to only 0.18% of the propellant weight in 1368 days. A slightly smaller (0.15%) decomposition was noted in contact with CRES-304L for 150 days. Approximately equivalent amounts of N<sub>2</sub> and CH<sub>4</sub> were found in the volatile products of decomposition.

The surfaces of the metal alloys, aluminums 6061, 1100, 2014; stainless steels 347, 321, and 17-7PH; and Inconel X-750, showed little to no effect on the decomposition of neat MMH in runs at 373 K (100 °C) for 7 days [236]. Propellant-grade MMH was stored in contact with various metal surfaces at 373 K (100 °C) for 7 days, and the observed stability order was Al about equal to Ti about equal to Cr < Fe < Mo < Ni [240]. The degrees of decomposition due to the metal surface ranged from essentially zero for Al, Ti, and Cr to about 5% for Ni under these conditions. In an experiment conducted at 423 K (150 °C) for up to 356 h, propellant-grade MMH samples appeared to be as stable as samples of purified material. Thus, the impurities present in propellant-grade MMH seemed to have little effect on thermal stability. In studies carried out at 448 K (175 °C) on purified material in both the vapor and liquid phases and in which the amount of Pyrex surface was varied, the rate of MMH decomposition was found to be roughly first order in surface area and zero order in MMH itself. The surfaces of the metal alloys, aluminums 6061, 1100, 2014; stainless steels 347, 321, and 17-7PH; and Inconel X-750, showed no adverse effect on the decomposition of neat MMH in runs at 373 K (100 °C) for 7 days.

A vapor-phase exothermicity test (VPET) and a liquid-phase exothermicity test (LPET) were used at NASA WSTF to test the compatibility of MMH vapor or liquid with construction materials at an elevated temperature in inert atmospheres [241, 242]. The VPET apparatus itself, a 500-mL Pyrex test chamber, was inert to MMH at 473 K. An amount of 0.02 mL of MMH was squirted on flat-panel test samples in the chamber, and eventual temperature rises were recorded. After the MMH had evaporated and reacted with the sample, the vapor space was purged and the remaining MMH amount analyzed. If the metal sample was incompatible with MMH, as indicated by an exothermic event, only very little undecomposed MMH was remaining. Columbium 300 was one of the materials shown to be incompatible with MMH in these tests. The fuel in the test chamber was consumed in approximately 13 s at 473 K.

The LPET consisted of a smaller, 100-mL stainless-steel chamber. The chamber was made from CRES-304L. The liquid level was adjusted such that 112 cm<sup>2</sup> of the wall was wetted in each test. The bomb was then pressurized with helium or nitrogen to 2760 kPa (400 psig) to prevent the liquid from evaporating. It appears that early tests used helium, but later tests used nitrogen [243]. The system could be operated in the adiabatic (well-insulated) mode or with a heat sink attached to maintain isothermal conditions.

The parameter reported in the LPET test is the exothermic threshold temperature in the presence of the material under test, the initial temperature at which a runaway decomposition is first seen to occur. This temperature gives an indication of the relative catalytic activity/incompatibility and needs to be compared with the temperature at which the empty chamber by itself would cause hydrazine(s) to decompose. The absolute value of the LPET exo temperature is highly system dependent and should not be taken as applicable to all situations. In many cases, a temperature range instead of a specific temperature number was given to emphasize the inaccuracy of the data in Table 26.

Comparing the VPET and LPET energy release rates of MMH, the liquid phase produced more severe exothermic reactions than the vapor phase with any of the ten materials tested. In another early test series with MMH in the LPET, 5 out of 12 materials produced varying degrees of exothermic reactions [242]. In most cases, metallic materials that exhibited exothermicity in the liquid MMH/LPET would also react exothermically with MMH vapor in the VPET.

**Table 26:** Liquid-phase exothermicity test results for materials in contact with methylhydrazine or hydrazine in nitrogen.

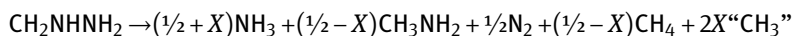
| Material                                          | Exothermic threshold temperature, K |                               |                      |
|---------------------------------------------------|-------------------------------------|-------------------------------|----------------------|
|                                                   | N <sub>2</sub> H <sub>4</sub>       | N <sub>2</sub> H <sub>4</sub> | MMH                  |
| Data source                                       | Benz and Pedley 1986                | Pedley et al. 1990            | Benz and Pedley 1986 |
| Kynar 460                                         | 366                                 | 367                           | 366                  |
| Kel-F 81                                          | —                                   | —                             | 414                  |
| Tefzel                                            | 422                                 | —                             | 450–464              |
| Hastelloy-X                                       | 469–489                             | —                             | 519–530              |
| CRES-316                                          | 477–489                             | —                             | 478–502              |
| Stainless steel 17-7 PH<br>precipitation hardened | 478                                 | 478                           | 448–508              |
| Teflon PFA                                        | 478                                 | —                             | 478                  |
| Teflon TFE                                        | —                                   | —                             | 478                  |
| Teflon TFE, glass-filled                          | —                                   | —                             | 478                  |
| Krytox 240AC                                      | —                                   | —                             | 478                  |
| CRES-304                                          | 479                                 | 480                           | 478                  |
| Al-6061-T6                                        | 483                                 | —                             | 469                  |
| Al-2014-T6                                        | 500                                 | —                             | 472                  |
| CRES-304L                                         | 505–511                             | 480                           | 505–508              |
| CRES-347                                          | 511                                 | 480                           | 448–508              |
| Haynes-25                                         | 525                                 | —                             | 497                  |
| CRES-321                                          | 525–530                             | 505                           | 478–511              |
| Inconel-X750                                      | 527–530                             | 430                           | 494–502              |

TFE = tetrafluoroethylene

Sorted by threshold temperature N<sub>2</sub>H<sub>4</sub> in the first column

Data source: [241, 243]

A comparison of the heating rates and onset of exothermicity of hydrazine, H-70, and MMH in titanium in an ARC showed that with hydrazine the onset was at 468 K, with H-70 it was at 483 K, and with MMH it was at 490 K [244]. The stepwise discontinuity (seen at the point where all liquid hydrazine was consumed) did not appear with H-70. With MMH, the step was seen at 510–513 K. The isokinetic temperatures for the three propellants were 523, 527, and 555 K respectively. Additional tests with MMH in the absence of any added catalysts showed that the thermal decomposition products were dinitrogen, ammonia, methane, methylamine, dimethyldiazene, and traces of ethane, propane, ethylene, acetylene, ethylamine, 1-methyl-2-ethyldiazene, dimethylamine, trimethylamine, UDMH, and SDMH [245]. Hydrogen was only present at less than 0.1%. This list of reaction products shows that the thermal decomposition of MMH is a very complex reaction. It was assumed that dimethyldiazene decomposes to diazomethane  $\text{CH}_2\text{N}_2$ , which is a very active methylating agent and is responsible for methylating some of the N–H and C–H bonds in the reaction mixture, leading to di- and tri-methylamines and polymethylhydrazines along with C–C compounds. It was difficult to determine the activation energy of MMH decomposition in the titanium bulb, as the rates varied substantially from test to test. The stoichiometry of the MMH decomposition can be approximated by the reaction sequence:



where  $X$  is a variable (typically  $X = 0.07$ ) and “ $\text{CH}_3$ ” groups all other organics and treats them as ethane.

The decomposition of MMH in contact with a wide variety of materials of construction was tested in an ARC in a titanium bulb [246]. The materials tested were used in powder form, or, where not available, in the form of fine turnings. In either case, the surface areas were measured first and used to normalize the reaction rates. The results, expressed in the form of relative reactivity of various materials normalized by the reactivity of the empty titanium bulb (activity arbitrarily set to 1.0) and at a common temperature of 353 K are summarized in Table 27, sorted in descending order of reactivity.

**Table 27:** Relative reactivity of materials of construction with methylhydrazine.

| Metal          | Relative reaction rate at 353 K | Metal    | Relative reaction rate at 353 K |
|----------------|---------------------------------|----------|---------------------------------|
| Nickel         | 750                             | Vanadium | 2.8                             |
| Tungsten       | 13                              | CRES-316 | 2.3                             |
| Rene nickel 41 | 8.9                             | CRES-304 | 1.7                             |
| E-Brite 29-4   | 7.3                             | Titanium | 1.0                             |
| Iron           | 6.7                             | CRES-301 | 0.41                            |
| Manganese      | 5.6                             | Tantalum | 0.026                           |
| CRES-321       | 4.2                             | Silver   | 0.020                           |
| Gold           | 3.9                             | Niobium  | 0.011                           |

Data source: [246]



There appears to be a correlation between metals that actively catalyze the decomposition of hydrazine and those that catalyze the decomposition of MMH. One is often tempted to list only the energy of activation of various reactions, such as the heterogeneous decomposition of MMH, as a measure of incompatibility. However, it is better to list the relative reaction rates, correlated for a common temperature point.

#### 4.1.3 Autodecomposition Temperature of MMH in the Absence of Air

Although only rare nowadays, a method that was at one time widely used method for determining the thermal stability of monopropellants and explosives was the Interagency Chemical Rocket Propulsion Group (later Joint Army Navy NASA Air Force) Liquid Propellant Test Method No. 6 [247]. It used a 2.5-mL bombulet holding a 0.5-mL sample immersed in a molten metal bath (Wood's metal) preheated to 460 K. The bath temperature and the differential temperature between the bath and the propellant sample are recorded in order to detect the onset of exotherms. The results of thermal stability tests with hydrazine, MMH, MHF-5, and MHF-7 are summarized in Table 28.

Only the lowest temperature at which exotherms occurred or burst disks ruptured are listed. (The original source showed a range of temperatures.) There is a distinct dependence of the exotherm and disk rupture temperatures on the material from which the bombulets were made. The heating rate was 5.5 K/min. The stability was best in Inconel-X or CRES-321 and worst in aluminum. With MMH, the stability was best in Hastelloy-X and worst in aluminum. In comparative tests where hydrazine or MMH vapors only were contained in the bombulets the burst disks ruptured at lower temperatures than in the liquid tests. Rupture occurred at temperatures 55 K below those measured in the liquid tests, and MHF-5 was much less stable than any of the other propellants.

Until the 1980s, exothermicity tests had to be conducted in fairly large experimental setups to obtain measurable heat flows. Such large tests could not be conducted in a normal chemistry laboratory and had to be relegated to remotely located hazardous test facilities with concrete walls. This situation changed when first DSCs and then ARCs and microcalorimeters became commercially available. These instruments are now found in most energetic materials laboratories and enable the investigators to conduct rocket propellant exothermicity tests in the comfort of a laboratory. The current section deals mostly with the thermal stability of liquids as they affect their safety and hazard properties. Kinetics of hydrazine decomposition reactions are discussed in Section 4.1.4. More hazardous, uncontrolled decomposition reactions are those occurring in cook-off and bonfire tests. Before elaborately setting up an expensive and potentially catastrophic cook-off test, it would be advisable to totally characterize the propellant using DSC and ARC tests. These tests can be conducted in the laboratory and consume less sample. They are standardized by the American Society for Testing and Materials (ASTM) E-698-79 *Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials*. With MMH, the onset of exothermicity in

**Table 28:** Interagency Chemical Rocket Propulsion Group thermal stability test results for methylhydrazine (MMH) and mixed hydrazine fuels (MHF) blends (Sorted by fuel and materials name).

| Fuel                          | Material    | Exotherm |     | Disk rupture |                     |
|-------------------------------|-------------|----------|-----|--------------|---------------------|
|                               |             | K        | °F  | K            | °F                  |
| MMH                           | 17-7PH      | 508      | 455 | 555          | 540                 |
| MMH                           | Al-2014-T6  | 472      | 390 | 550          | 530                 |
| MMH                           | Al-6061-T6  | 469      | 385 | 505          | 450                 |
| MMH                           | CRES-304L   | 505      | 450 | 553          | 535                 |
| MMH                           | CRES-316    | 497      | 435 | 555          | 540                 |
| MMH                           | CRES-321    | 497      | 435 | 547          | 525                 |
| MMH                           | CRES-347    | 505      | 450 | 550          | 530                 |
| MMH                           | Hastelloy-X | 519      | 475 | 547          | 525                 |
| MMH                           | Haynes-25   | 497      | 435 | 544          | 520                 |
| MMH                           | Inconel-X   | 494      | 430 | 533          | 500                 |
| MHF-5                         | 17-7PH      | 452      | 355 | 499          | 440                 |
| MHF-5                         | Al-6061-T6  | 463      | 375 | 478          | 400                 |
| MHF-5                         | CRES-304L   | 452      | 355 | 491          | 425                 |
| MHF-5                         | CRES-316    | 422      | 300 | 519          | 475                 |
| MHF-5                         | CRES-321    | 444      | 340 | 491          | 425                 |
| MHF-5                         | CRES-347    | 452      | 355 | 505          | 450                 |
| MHF-5                         | Hastelloy-X | 449      | 350 | 511          | 460                 |
| MHF-5                         | Haynes-25   | 435      | 325 | 497          | 435                 |
| MHF-5                         | Inconel-X   | 416      | 290 | 508          | 455                 |
| MHF-7                         | 17-7PH      | 505      | 450 | 563          | 555 (max. exotherm) |
| MHF-7                         | Al-2014-T6  | 464      | 375 | 524          | 484 (max. exotherm) |
| MHF-7                         | CRES-304L   | 503      | 445 | 553          | 535                 |
| MHF-7                         | CRES-316    | 530      | 495 | 591          | 605                 |
| MHF-7                         | CRES-321    | 528      | 490 | 583          | 590                 |
| MHF-7                         | CRES-347    | 505      | 450 | 555          | 540                 |
| MHF-7                         | Hastelloy-X | 547      | 525 | 544          | 520                 |
| MHF-7                         | Haynes-25   | 505      | 450 | 547          | 525                 |
| MHF-7                         | Inconel-X   | 483      | 410 | 527          | 490                 |
| For comparison:               |             |          |     |              |                     |
| N <sub>2</sub> H <sub>4</sub> | 17-7PH      | 514      | 465 | 553          | 535                 |
| N <sub>2</sub> H <sub>4</sub> | Al-1100-0   | —        | —   | 533          | 500, detonation     |
| N <sub>2</sub> H <sub>4</sub> | Al-2014-T6  | 500      | 440 | 547          | 525                 |
| N <sub>2</sub> H <sub>4</sub> | Al-6061-T6  | 483      | 410 | 534          | 502                 |
| N <sub>2</sub> H <sub>4</sub> | CRES-304L   | 505      | 450 | 544          | 520                 |
| N <sub>2</sub> H <sub>4</sub> | CRES-316    | 478      | 400 | 572          | 570                 |
| N <sub>2</sub> H <sub>4</sub> | CRES-321    | 525      | 485 | 550          | 530                 |
| N <sub>2</sub> H <sub>4</sub> | CRES-347    | 511      | 460 | 550          | 530                 |
| N <sub>2</sub> H <sub>4</sub> | Hastelloy-X | 469      | 385 | 539          | 510                 |
| N <sub>2</sub> H <sub>4</sub> | Haynes-25   | 525      | 485 | 550          | 530                 |
| N <sub>2</sub> H <sub>4</sub> | Inconel-X   | 511      | 490 | 553          | 535                 |

Data source: [247]

a titanium bulb in the ARC in the absence of other metals was at 490 K [244, 245]. Nitrogen, ammonia, methylamine, methane, and ethane were the major decomposition products. Dimethylamine, 1,2-dimethyldiazene, and traces of nine other nitrogenous compounds or hydrocarbons were observed in the decomposition product mixture. The Arrhenius parameters for the decomposition reaction were compensated and linearly related by the relationship:

$$\ln A = \frac{E_a}{R\theta} + \ln k_0$$

with a compensation temperature  $\theta$  of 478 K. The isokinetic temperature was 475 K. Activation energies were found to be within the range 71.8–114.8 kJ/mol.

Prior to the availability of ARC, it was attempted to obtain thermal stability, kinetic rate and activation energy data by testing MMH in a DSC [248]. The difficulty encountered with all testing of liquid samples in a DSC is the pressure buildup first due to evaporation and then to decomposition products, which causes conventional sample holders (crimped metal pans, glass vials, capillaries, sometimes called “crucibles” although they are no longer crucible-shaped) to bulge, leak, and rupture. Puncturing the lid with a pinhole allows some of the pressure to vent, but also results in sample loss. ASTM Methods E557 (DTA) and E698 (Arrhenius kinetics) deal with these problems insufficiently, and little progress has been made for DSC of hydrazine or MMH. The internal pressure in the crucibles can be compensated for by enclosing the sample cell and the reference cell in a pressurized enclosure and/or using pressure-resistant crucibles. The increased thermal mass of heavier walls reduces the sensitivity of the method. The first exotherm of MMH began to appear at 390 K. The addition of gold powder to MMH caused another secondary exotherm at 500 K.

#### 4.1.4 Kinetics of MMH Vapor Decomposition

When comparing the ease of decomposition of hydrazine and methylhydrazines, one seeming contradiction is the fact that the rate constant for UDMH at a given temperature is higher than that of MMH or hydrazine, although in other parts of this book it was stated that the thermal stability of hydrazine increases in the order hydrazine, MMH, and UDMH. Apparently, additional factors become important in the decomposition of hydrazine at higher concentrations than those studied in the Princeton reactor. A comparison of rates of decomposition in the Princeton flow reactor was shown in *Encyclopedia of Liquid Fuels*, chapter “Hydrazine,” Figure 40, which showed the rate constants of thermal decomposition of hydrazine and its methyl derivatives as a function of reciprocal absolute temperature. The activation energy could be derived from the slope of these lines.

The thermal decomposition of MMH has been investigated using the toluene carrier method previously used for hydrazine [249]. The rate constants were calculated from the total amount of MMH decomposed and the amounts of nitrogen and ammo-

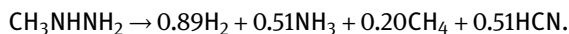
nia formed. The rate constant did not change when the surface: volume ratio of the reactor was varied. It remained fairly constant in the range 26–159 Pa (0.2–1.2 mm Hg) reactant pressure, 1.33–4 kPa (10–30 mm Hg) toluene pressure, and contact times in the order of 0.5–1.5 s. The Arrhenius plot for MMH decomposition can be represented by the equation:

$$\log k = 13.19 \frac{51900}{2.3RT} \quad \text{s}^{-1}.$$

The decomposition of MMH in the Princeton adiabatic flow reactor showed that the reaction is of first order, and based on their data the rate constant can be expressed as:

$$k = 10^{13.4} e^{\frac{-47000}{RT}} \quad \text{s}^{-1}.$$

This is very similar to the equation presented by Kerr et al. [249]. The stoichiometry based on gas analysis was represented by the following equation:



It is surprising to note that more hydrogen and considerably more HCN is formed than in the case of UDMH decomposition. The mechanism outlined in Table 29 was proposed for this reaction. This mechanism is more complex than that of hydrazine decomposition but less complex than that for UDMH decomposition. Several assump-

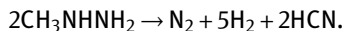
**Table 29:** Mechanism and rate constants of methylhydrazine decomposition.

| Reaction number        | Reaction                                                                                                    | Rate constant                                                                         |
|------------------------|-------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| <i>Initiation</i>      |                                                                                                             |                                                                                       |
| (1)                    | $\text{H}_3\text{CHNNH}_2 + \text{X}^* \rightarrow \text{H}_3\text{CN}^*\text{H} + \text{NH}_2 + \text{X}$  | $k_1 = 10^{22} e^{(-67000/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$          |
| (2)                    | $\text{H}_3\text{CHNNH}_2 + \text{X}^* \rightarrow \text{H}_3\text{CN} + \text{NH}_3 + \text{X}$            | $k_2 = 5 \times 10^{21} e^{(-67000/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
| <i>Branching</i>       |                                                                                                             |                                                                                       |
| (3)                    | $\text{H}_3\text{CN}^*\text{H} + \text{X} \rightarrow \text{CH}_3 + \text{NH} + \text{X}$                   | $k_3 = 10^{14} e^{(-18000/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$          |
| (4)                    | $\text{H}_3\text{CHNNH}_2 + \text{NH} \rightarrow \text{NH}_2 + \text{H}_3\text{CN}-\text{NH}_2$            | $k_4 = 10^{13} e^{(-7000/RT)} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$           |
| <i>Propagation</i>     |                                                                                                             |                                                                                       |
| (5)                    | $\text{H}_3\text{CN}-\text{NH}_2 + \text{X} \rightarrow \text{H}_2 + \text{N}_2 + \text{CH}_3 + \text{X}^*$ | $k_5 = 10^{14} e^{(-18000/RT)}$                                                       |
| (6)                    | $\text{H}_3\text{CHNNH}_2 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{H}_3\text{CN}^*-\text{NH}_2$        | $k_6 = 10^{13} e^{(-7000/RT)}$                                                        |
| (7)                    | $\text{H}_3\text{CHNNH}_2 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{H}_3\text{CN}^*-\text{NH}_2$        | $k_7 = 10^{13} e^{(-7000/RT)}$                                                        |
| <i>Termination</i>     |                                                                                                             |                                                                                       |
| (8)                    | $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$                                                | $k_8 = 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$                          |
| (9)                    | $\text{H}_3\text{CN}^* \rightarrow \text{HCN} + \text{H}_2$                                                 | $k_9 = 10^{14} e^{(-10000/RT)} \text{ s}^{-1}$                                        |
| <i>Global Reaction</i> |                                                                                                             |                                                                                       |
| (10)                   | —                                                                                                           | $k_r = 10^{8.84} e^{(-26700/RT)} \text{ s}^{-1}$                                      |

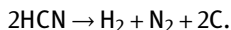
Data source: [198]

tions, such as using heats of reaction in place of activation energies, had to be made in suggesting rate constants listed in Table 29. Insufficient data were available on individual steps of the reaction.

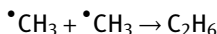
Decomposition of MMH in a quartz chamber heated to up to 1273 K preceding a time-of-flight mass spectrometer showed that significant decomposition occurred only above 800 K [250]. The relative intensity of 12 mass peaks of MMH and MMH decomposition products was plotted over the entire range 273–1273 K, with and without the presence of Shell 405 catalyst in the decomposition chamber. Under these conditions, MMH decomposition proceeded by way of the following equation:



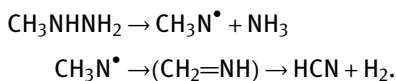
The HCN concentration peaked at 900 K and diminished at higher temperatures because HCN in turn decomposed to the elements in a subsequent reaction:



The maximum HCN abundance was very sharp and HCN decomposition above 900 K was more complete if an iridium catalyst was added to the decomposition chamber. The peak at a mass: charge ratio  $m/e$  of 30 was assigned to methylimine  $\text{CH}_3\text{NH}$  instead of ethane. Although ethane formation by methyl radical recombination has been proposed by Eberstein:



the occurrence of methylimine as an intermediate is more likely:



The rate constants for overall MMH decomposition were determined by very low-pressure pyrolysis (VLPP) [251]. The pyrolysis of a flowing gas in a reactor at a very low pressure where the molecular flow region is attained can be described by the Rice–Ramsperger–Kassel–Marcus theory. The product peaks at  $17m/e$  ( $= \text{NH}_3$ ) and  $2m/e$  ( $= \text{H}_2$ ) were used to compute rate constants for the formation of  $\text{NH}_3$  and  $\text{H}_2$  respectively. When  $\text{NO}_2$  was added as a radical scavenger, the rate of  $\text{H}_2$  and  $\text{NH}_3$  production decreased only insignificantly, suggesting that both were being formed by non-radical pathways. The investigators suggested that under the conditions of their experiment, MMH decomposed to ammonia through a four-center deamination reaction. If the MMH decomposition occurred through N–N homolysis, a higher activation energy would have to be expected. Table 30 gives a summary of calculated versus observed Arrhenius parameters for the VLPP decomposition of MMH and related methylhydrazines.

At 870–1270 K and 0.13 Pa, MMH decomposes through elimination of ammonia and hydrogen. Both MMH and UDMH are believed to decompose by way of N–N scis-

**Table 30:** Arrhenius parameters for pyrolysis of methylhydrazines.

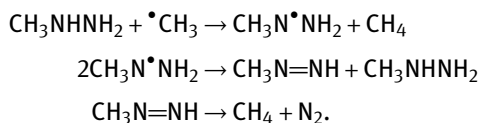
| Molecule        | Process                        | log [(A/298) s <sup>-1</sup> ] | Activation energy E <sub>298</sub> |          | Remarks                  |
|-----------------|--------------------------------|--------------------------------|------------------------------------|----------|--------------------------|
|                 |                                |                                | kJ/mol                             | kcal/mol |                          |
| MMH             | N—N homolysis                  | 16.9                           | 294                                | 70.3     | Not observed             |
| MMH             | → NH <sub>3</sub> <sup>a</sup> | 13.1                           | 225                                | 53.8     | Observed                 |
| MMH             | → H <sub>2</sub> <sup>a</sup>  | 13.0                           | 234                                | 56.0     | Observed                 |
| For comparison: |                                |                                |                                    |          |                          |
| UDMH            | N—N homolysis                  | 17.0                           | 259                                | 61.9     | Observed                 |
| UDMH            | → NH <sub>3</sub>              | 13.1                           | 213                                | 50.8     | Possible, but not proven |
| TMH             | N—N homolysis                  | 17.4                           | 223                                | 53.3     | Observed                 |
| TMH             | → NH <sub>3</sub>              | 13.4                           | 179                                | 42.8     | Possible, but not proven |

MMH = methylhydrazine; UDMH = unsymmetrical dimethylhydrazine; TMH = tetramethylhydrazine

<sup>a</sup> Refers to a four-center elimination of NH<sub>3</sub> or H<sub>2</sub>

Data source: [251]

sion. At higher pressures (near atmospheric) and temperatures (592K) in sealed Pyrex ampoules, the decomposition mechanism was more complex. Decomposition of MMH is initiated by methyl radicals and leads to methane and nitrogen:

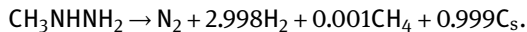


This does not seem to be a chain reaction. MMH vapor at higher pressures or 0.1M MMH solutions in hexadecane solvent decompose under formation of CH<sub>4</sub>, N<sub>2</sub>, NH<sub>3</sub>, and CH<sub>3</sub>NH<sub>2</sub> [230, 234].

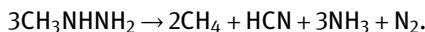
The rate constant ( $k_{\text{uni}}$ ) for the first-order disappearance of MMH in a static reactor has been determined under very low-pressure pyrolysis conditions [252]. The  $k_{\text{uni}}$  are not the rate constants of ultimate interest as they reflect the fact that energy transfer competes with the chemical decomposition. Theory allows the determination of the high-pressure rate constants ( $k_a$ ), if the mode of decomposition is known. The heats of formation of the radicals  $\cdot\text{NH}_2$ ,  $\text{CH}_3\text{N}\cdot\text{H}$ , and  $(\text{CH}_3)_2\text{N}\cdot$  are known. These values should be usable for prediction of the activation energy for N—N bond homolysis in the hydrazines. Measured rate constants for UDMH and tetramethylhydrazine bore this out, but the rate constant for MMH did not. This and other evidence led to the conclusion that MMH decomposes via molecular concerted elimination of NH<sub>3</sub> and H<sub>2</sub> and not by N—N bond scission. The activation energy of liquid MMH decomposing in a steel bomb, derived from pressure rise rates as a function of temperature and the Arrhenius equation was 83.8 kJ/mol [92].

If MMH is used in a gas generator for tank pressurization or turbine power, the actual composition of the exhaust gases depends on the operating conditions of the

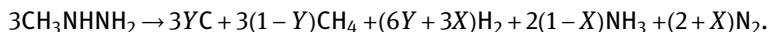
thermal bed reactor. On the basis of equilibrium calculations, one would expect complete dissociation of ammonia and nearly complete dissociation of methane:



This ideal case would give maximum pressurization efficiency but is never achieved. The worst case would be a reaction that leads to all carbon chemically bound:

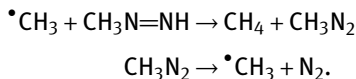


Fortunately, this does not happen either. The actual gas composition is somewhere in between. The degree of ammonia and methane dissociation can be expressed by two auxiliary parameters  $X$  and  $Y$ :



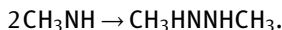
In reactor experiments,  $X$  was approximately 0.5 and  $Y$  was approximately 0.33.

Methyldiazene (methyldiimine) is a potential intermediate in the decomposition of MMH. Methyldiazene is the simplest of a number of monoalkyl diazenes that have been prepared [253, 254]. Pure methyldiazene has a melting point of 151 K ( $-122^\circ\text{C}$ ) and boils near 268 K ( $-5^\circ\text{C}$ ). Like diazene itself, the monoalkyl diazenes are more stable than was initially expected. The thermal and photolytic decomposition of methyldiazene in the gas phase leads to methane and nitrogen through a chain reaction propagated by the methyl radical [255]. The question remains whether similar free radical reactions take place during the decomposition of MMH:



If MMH is oxidized or decomposed, methylamino or aminomethyl radicals are expected as intermediates, which may lose another hydrogen atom to form methylene imine. Methylene imine  $\text{H}_2\text{C}=\text{NH}$  is an analog to diazene  $\text{HN}=\text{NH}$ .

One hypothesized mechanism would suggest that SDMH, a compound more carcinogenic than MMH, should also form according to:

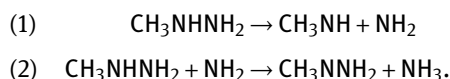


#### 4.1.5 Decomposition of MMH in Shock Tubes

The thermal decomposition of MMH vapor was studied by recording MMH absorption at 220 nm of the reacting gas behind a reflected shock wave at temperatures of 900–1370 K, pressures of 140–450 kPa, and in mixtures containing 97.5–99 mol-% argon [256, 257]. Based on previous work [258], a kinetic mechanism was developed over extended temperature and pressure ranges to model these experimental data. Specifically, the temperature and pressure dependence of the unimolecular rate coefficients

on the dissociation of MMH and the associated radicals were calculated by a master equation analysis at temperatures of 300–2000 K and pressures of 1–100 atm based on published thermochemical and kinetic parameters. They were then fitted and incorporated into the kinetic model. This unadjusted model was then used to predict the MMH decomposition profiles at different temperatures and pressures for seven groups of MMH/Ar mixtures and the half-life decomposition times from shock tube experiments. Good agreement was observed below 940 K and above 1150 K for the diluted MMH/Ar mixtures. The model predictions further showed that the overall MMH decomposition rate follows first-order kinetics, and that the N–N bond scission is the most sensitive reaction path for the modeling of the homogeneous decomposition of MMH at elevated pressures. However, the model predictions deviated from the experimental data with the incubation period of approximately 100  $\mu$ s observed in the 1030–1090 K temperature range, and it also predicted longer ignition delays for highly concentrated MMH/Ar mixtures. The discrepancy between the model predictions and experimental data under these special conditions of MMH decomposition was analyzed but is not yet resolved.

Measurements of  $\bullet\text{NH}_2$  and  $\text{NH}_3$  time-histories in MMH pyrolysis with MMH initial concentrations of  $\sim 1\%$  in Ar over the temperature range 941–1252 K at pressures near 202 kPa (2 atm) were performed behind reflected shock waves in a shock tube, using laser absorption techniques and an improved measurement of MMH using IR laser absorption [259].  $\bullet\text{NH}_2$  concentration was measured at the peak of the overlapping doublet lines at  $16739.90\text{ cm}^{-1}$  (597.4 nm).  $\text{NH}_3$  and MMH were measured using direct absorption of  $\text{CO}_2$  laser lines at 9.22 and 10.22  $\mu\text{m}$ . These measurements were then compared with a comprehensive MMH pyrolysis mechanism based on the work of Sun et al. [256] and Zhang et al. [260]. Based on the measurements of  $\bullet\text{NH}_2$  and  $\text{NH}_3$ , it was possible to measure rate coefficients for two key reactions in the MMH pyrolysis system:



These rates combined with the measured overall MMH decomposition rate strongly implied that Reaction (1) is the dominant MMH decomposition channel. The following rate coefficients (202 kPa, 900–1300 K) were determined:

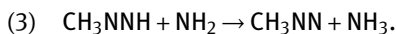
$$\begin{aligned} k_1 &= 1.50 \times 10^{58} \times T^{-12.84} \exp(-39580/T) \text{ s}^{-1} \\ k_2 &= 3.7 \times 10^{14} \exp(-2620/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}. \end{aligned}$$

Based on the MMH measurements, the contribution of the  $\text{CH}_3$  decomposition channel was 0–20% of the  $\text{NH}_2$  channel, and a value of:

$$1.64 \times 10^{58} \times T^{-12.84} \exp(-39580/T) \text{ s}^{-1}.$$



was recommended for the overall unimolecular decomposition of MMH. Further analysis of the  $\text{NH}_2$  measurements indicated that the rate of the following reaction used in the Princeton mechanism should also be significantly increased:



The changes to the MMH pyrolysis mechanism resulted in greatly improved agreement between measured and modeled  $\text{NH}_2$ ,  $\text{NH}_3$ , and MMH time-histories over the entire range of the study.

Pyrolysis of MMH was studied behind reflected shock waves using a laser absorption method [261, 262].  $\text{NH}_2$  concentration time-histories in MMH/argon mixtures were measured over the temperature range 1100–1400 K and pressures of 0.3–5 atm. The MMH pyrolysis mechanism developed by Sun et al. [256], with the update by Cook et al. [259], was used to simulate the  $\text{NH}_2$  time-histories and to compare computations with the experimental results. The rate constant of the reaction  $\text{CH}_3\text{NHNH}_2 \rightarrow \text{CH}_3\text{NH} + \text{NH}_2$  was determined based on the  $\text{NH}_2$  time-history measurements. Pressure dependence of  $k_{1a}$  was observed at 0.3–5 atm. The measured reaction rate constants followed a pressure dependence trend close to the theoretical results by Zhang et al. [260] based on transition state theory master equation analysis, and reducing their theoretical results by a ~40% lead to a close match with the measured data. With the experimentally determined  $k_{1a}$ , the simulation results matched closely with the measured  $\text{NH}_2$  time-histories at early times. Utilizing the later times of the  $\text{NH}_2$  time-histories, a good fit was achieved with the reaction rate constant of:

$$k_2 = 1.5 \times 10^{14} \exp\left(\frac{-755}{T}\right) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

for the reaction  $\text{NHNH}_2 + \text{H} \rightarrow \text{NH}_2 + \text{NH}_2$ . Simulation results using the modified mechanism, with the updated  $k_{1a}$  and  $k_2$ , agreed well with the measured  $\text{NH}_2$  time-histories.

The thermal decomposition of MMH diluted by more than 97% with argon was followed by absorption spectrophotometry at 220 nm within a temperature range between 770 and 1370 K and pressure of between 140 and 455 kPa [263]. This study served as a basis for the validation of a detailed kinetic model with 99 equilibrium reactions and 39 species. Using susceptibility criteria, the mechanism was reduced to 14 reactions and 15 species. Explosive decompositions of MMH diluted between 70 and 80% by argon have been observed. The study of the self-ignition times of  $\text{O}_2/\text{MMH}/\text{Ar}$  mixtures was carried out in a shock tube behind a reflected shock wave. The ignition delay as a function of temperature and initial concentrations and the effect of additives has been studied. It was shown in this study that  $\text{O}_2/\text{MMH}/(\text{diluent})$  mixtures are likely to detonate behind a shock wave. Experimental detonation velocities have been compared with the theoretical Chapman–Jouguet (C-J) velocities. The three-dimensional structure of the detonation waves has been studied using the

soot deposition technique. Criteria of limits of detonability have been proposed by considering the model and the structure of the detonation wave.

Ignition delays have been investigated for mixtures of  $O_2 + MMH + Ar$  at high temperatures (850–1440 K) within the pressure range 160–400 kPa, for equivalence ratios of 1–4.3 and in the Ar dilution range 82–96 mol-% [264]. The replacement of argon by nitrogen led to a twofold increase in the delay. The addition of 0.88–2.4 mol-% hydrogen to the  $O_2 + MMH + Ar$  mixture showed that hydrogen has, globally, a promoting effect on the ignition in  $O_2 + MMH + (Ar)$ . A kinetic model predicted that the addition of MMH should promote hydrogen oxidation within the temperature range 900–1000 K by forming free radicals during its oxidative decomposition.

Gas-phase thermochemical properties of more than 50 compounds expected to play a role in the decomposition and oxidation chemistry of MMH were obtained from high-level *ab initio* quantum chemical calculations [265]. Groups of these compounds were discussed in terms of the conditions under which they were expected to be of potential importance in building a kinetic model of the reaction.

Depending on the amount added, methylhydrazine added in relatively small amounts (up to 10% with respect to hydrogen) can be an inhibitor or a promoter to the reaction of hydrogen and oxygen (diluted with argon) in a shock tube [266, 267]. The efficiency of ignition promotion or inhibition for  $O_2/H_2/Ar$  mixtures was investigated by computations performed with a detailed kinetic model and then validated with experimental ignition delays obtained behind a reflected shock wave in mixtures of  $O_2/MMH/Ar$ ,  $O_2/MMH/H_2/Ar$ , and  $O_2/H_2/Ar$ . Good agreement was obtained between experimental and computed ignition delays with the mixtures of  $O_2/MMH/H_2/Ar$  at high temperatures (900–1170 K) and within the pressure range 225–414 kPa.

Ignition delays of mixtures of  $O_2 + MMH + CH_4 + Ar$  at high temperatures (907–1360 K) within the pressure range 246–412 kPa have been measured in the reflected-shock region of a shock tube [268]. Reaction progress was monitored via piezoelectric pressure transducers and UV absorption by MMH. In the composition range studied, the ignition delays can be correlated by the expression:

$$t(\mu s) = 2.042 \times 10^{-2} [MMH] - 0.87 [O_2] - 2.09 [CH_4] + 0.68 [Ar] 1.24 \exp\left(\frac{8503}{T}\right)$$

where the concentrations are expressed in mol/m<sup>3</sup>. This study showed unambiguously that  $CH_4$  inhibits  $O_2 + MMH (+Ar)$  ignition. This inhibiting effect depends on the mixture composition (equivalence ratio in MMH,  $[MMH]/[CH_4]$  ratio, etc.), on the temperature, and on the pressure. From a mechanistic point of view, methane is supposed to compete with MMH decomposition products for reaction with oxygen. The comparison between the  $O_2/CH_4/Ar$  and  $O_2/CH_4/MMH/Ar$  ignition delays led to the conclusion that MMH can be used as an ignition promoter in  $O_2/CH_4$  mixtures.

#### 4.1.6 Computational Chemistry Calculations of MMH Decomposition Kinetics

The reaction kinetics for the thermal decomposition of MMH were studied using quantum mechanical theory [258]. Thermochemical properties were determined by *ab initio* and DFT calculations. The entropies  $S^\circ$  and heat capacities  $C_p^\circ$  from vibrational, translational, and external rotational contributions were calculated using statistical mechanics based on the vibrational frequencies and structures obtained from the density functional study. Potential barriers for internal rotations were calculated, and hindered rotational contributions to  $S^\circ$  and  $C_p^\circ$  were calculated by solving the Schrödinger equation with free rotor wave functions, and the partition coefficients were treated by direct integration over energy levels of the internal rotation potentials. Enthalpies of formation  $\Delta H_f^\circ$  for the parent  $\text{CH}_3\text{NHNH}_2$  molecule and its corresponding radicals  $\text{CH}_3\text{N}^\bullet\text{NH}_2$ ,  $\text{CH}_3\text{NHN}^\bullet\text{H}$ , and  $^\bullet\text{CH}_2\text{NHNH}_2$  were determined to be 90.4, 203, 214, and 263 kJ/mol (21.6, 48.5, 51.1, and 62.8 kcal/mol) by use of isodesmic reaction analysis and various *ab initio* methods. A kinetic analysis of the thermal decomposition, abstraction, and substitution reactions of MMH was performed, with those of N—N and C—N bond scissions determined by high-level calculations. Rate constants of thermally activated MMH going to dissociation products were calculated as functions of pressure and temperature. An elementary reaction mechanism based on the calculated rate constants, thermochemical properties, and literature data was developed to model the experimental data on the overall MMH thermal decomposition rate. The reactions of N—N and C—N bond scission were found to be the major reaction paths for the modeling of MMH homogeneous decomposition under atmospheric pressure conditions.

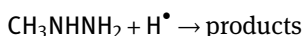
The decomposition kinetics of MMH were studied with *ab initio* transition state theory-based master equation analyses [269]. The simple N—N and C—N bond fissions to produce the radicals  $\text{CH}_3\text{N}^\bullet\text{H} + ^\bullet\text{NH}_2$  or  $^\bullet\text{CH}_3 + ^\bullet\text{NHNH}_2$  were expected to dominate the decomposition kinetics. The transition states for these two bond fissions were studied using variable reaction coordinate transition state theory employing directly determined interaction energies. The transition state theory analysis provided high pressure dissociation and recombination rate coefficients. Predictions for the pressure dependence and product branching in the dissociation of MMH were obtained by solving the master equation.

Methylamine radicals ( $\text{CH}_3\text{N}^\bullet\text{H}$ ) and amino radicals ( $^\bullet\text{NH}_2$ ) are the major products in the early ignition/pyrolysis of MMH. The kinetics of the thermal decomposition of  $\text{CH}_3\text{N}^\bullet\text{H}$  radicals were analyzed using master equation analysis [270]. It was found that  $\beta$ -scission of the methyl H atom from  $\text{CH}_3\text{N}^\bullet\text{H}$  radicals is dominant and fast enough to induce subsequent H-abstraction reactions to trigger ignition. The gas-phase kinetics of H-abstraction reactions from  $\text{CH}_3\text{NHNH}_2$  by H atoms was further investigated by *ab initio* second-order multi-reference perturbation theory and quadratic configuration interaction calculations. The rate coefficients for each of the abstraction channels were quantified by micro-canonical transition state theory, and the associated branching ratios determined. It was found that the total rate coefficient determined from

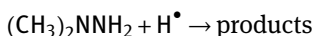
*ab initio* kinetics theories was in excellent agreement with the experimental value observed at room temperature. Thus, the theoretical rate coefficients from this work should be reliable over a wide temperature range and are essential parameters in the development of reaction mechanisms for the kinetics modeling of ignition involving MMH.

The thermal decomposition of the  $\text{CH}_3\text{N}^\bullet\text{NH}_2$ , *cis*- $\text{CH}_3\text{NHN}^\bullet\text{H}$ , *trans*- $\text{CH}_3\text{NHN}^\bullet\text{H}$ , and  $\text{C}^\bullet\text{H}_2\text{NNH}_2$  radicals, which are the four radical products from the H-abstraction reactions of MMH, were theoretically studied by using *ab initio* transition-state theory and master equation analysis [271]. Various decomposition pathways were identified by using various quantum chemistry methods. The study revealed that the  $\beta$ -scission of  $\text{NH}_2$  to form methylene imine is the predominant channel for the decomposition of the  $\text{C}^\bullet\text{H}_2\text{NNH}_2$  radical owing to its small energy barrier of 57.7 kJ/mol (13.8 kcal/mol). The calculated rate coefficients associated with updated thermochemical property data are essential components in the development of kinetic mechanisms for the pyrolysis and oxidation of MMH and its derivatives.

The mechanisms of multi-channel reactions between methylhydrazines and atomic hydrogen:



and



have been investigated by computational chemistry, and the dynamic properties were studied using a dual-level direct dynamics method [272]. The electronic structures and energies of the stationary points were calculated by the combination of various methods and basis sets. The rate constants of reactions in a temperature range of 200–2000 K were evaluated by using the canonical variational transition state theory with a small-curvature tunneling correction. The effect of treating torsional anharmonicity with different models on the rate constants was compared. Theoretical and experimental studies indicated that substitution of H by  $-\text{CH}_3$  groups on  $\text{H}_2\text{NNH}_2$  leads to a significant increase in rate coefficients. The kinetic isotope effects were studied for both the methylhydrazine(s) with hydrogen/deuterium and the MMH/deuterated MMH with hydrogen atom.

Mass spectrometric observations in a very-low-pressure pyrolysis study [252] of the decomposition of MMH had already indicated a dominant role for the molecular channels producing  $\text{NH}_3$  and  $\text{H}_2$  and their coproducts. In contrast, an *ab initio* transition state theory-based master equation theoretical study [269] predicted that simple N–N and C–N bond fissions would dominate the kinetics. The possible role of molecular decomposition channels in MMH was explored further through additional investigations of the potential energy surface [260]. These investigations considered the role of triplet channels, of roaming radical channels, and of some previously unexplored pathways for molecular decomposition. New *ab initio* transition state theory-based

master equation calculations provided revised predictions for the temperature and pressure dependence of the MMH decomposition kinetics that were in full agreement with shock tube measurements [261]. These calculations suggested only a very limited contribution from the molecular elimination channels. A roaming pathway was suggested to provide the dominant route for direct formation of ammonia. There is a possible role of secondary abstraction reactions in the very-low-pressure pyrolysis experiments.

## 4.2 Catalytic Decomposition of Liquid MMH

If excess liquid MMH is allowed to contact hydrazine decomposition catalysts at room temperature, a slow reaction with gas evolution ensues, but spontaneous ignition does not take place as in the case of hydrazine. The composition of the gases is essentially independent of the type of catalyst (Girdler G-22, Engelhard MFSA-4A, or Shell 405), consisting of (all numbers in mol-%) 0.2 H<sub>2</sub>, 39–43 CH<sub>4</sub>, 52–60 N<sub>2</sub>, and 0.4–3 C<sub>2</sub>H<sub>6</sub> [206].

## 4.3 Photolysis of MMH

In order to study the environmental fate of MMH vapors that have escaped into the air, it is necessary to know the conditions that will lead to photolysis of MMH, what the half-life time of MMH vapor is in intense sunlight, and what its photolysis products are. The same photolysis mechanism, sometimes in combination with ozonization, can be used with advantage in treatment of waste waters from rocket test sites and decontamination of propellant spills.

The gas-phase photochemistry of MMH photolysis has been studied in UV at 298 K [167]. Relative UV absorbance spectra of dilute mixtures of MMH in He buffer gas were recorded in the region 140–310 nm with an instrument resolution of 0.25 nm. These absorbance spectra were converted to absolute absorption cross-section profiles by scaling the data with absolute 253.65-nm cross-section values of  $\sigma_{253.65} = (8.022 \pm 0.481) \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  for MMH. Both MMH and UDMH exhibit continuous diffuse absorption bands in UV that correspond to electronic transitions to dissociative singlet excited states. Laser photodissociation product measurements revealed the absolute H atom primary quantum yields to be  $\Phi_{248} = 1.07 \pm 0.02$ ,  $\Phi_{222} = 0.99 \pm 0.01$ , and  $\Phi_{193} = 0.94 \pm 0.07$  for MMH photolysis at 248, 222, and 193 nm respectively. Kinetic measurements gave the absolute second-order H atom rate coefficients to be  $k = (7.60 \pm 1.14) \times 10^{-13}$  for reactions with MMH at 298 K diluted in 26.0 mm Hg of He.

#### 4.4 Radiolysis of MMH

Methylhydrazine fuel in satellites and space probes is subjected to intense cosmic radiation. Long-term radiolysis by hard gamma rays that can penetrate propellant tank walls would result in deterioration of MMH fuel quality and may result in undesirable pressure buildup in hermetically sealed tanks. Solar cosmic rays have a high-energy proton component. Satellites in the van Allen belt around Earth and in the radiation belt around Jupiter are subjected to intense radiation that may cause propellants to decompose. On long-term deep-space missions, Radioisotope Thermal Generators (RTGs) provide electric power from the heat generated by the decomposition of radioactive isotopes. Although RTGs are shielded and placed on extendable booms away from the spacecraft core, some radiation penetrates the shielding. Propellant tanks in the vicinity of RTGs are still subjected to nuclear radiation. Because oxidizers are less sensitive to radiation damage than fuels, it would be best to design the spacecraft such that the oxidizer tank is between the radiation source and the fuel tank.

Both the US and the former USSR have flown satellites with nuclear fission reactors such as SNAP-8 as powerplants. Some of these satellites may have used NTO/MMH thrusters for attitude control, orbit adjustment, and controlled de-orbit. The propellant tanks may not have been shielded from the nuclear reactors.

In an atomic war battle field situation, missiles with MMH fuel tanks may be subjected to intense neutron radiation that would alter propellant properties or cause premature decomposition. For all these reasons, radiolysis of MMH has been studied extensively in the past.

A radiation test was conducted on 98.7% MMH/1.3% H<sub>2</sub>O to evaluate the effects of reactor radiation on (1) the hypergolicity of this material with dinitrogen tetroxide as the oxidizer, and (2) the off-gas evolution leading to pressure buildup in the tank [273]. In addition, the effects of radiation on viscosity, density, melting point, and MMH assay were also measured. Samples of MMH were exposed to an integrated flux of approximately  $5 \times 10^{15}$  nvt ( $E > 0.5$  MeV) =  $5 \times 10^{15}$  n/cm<sup>2</sup> fast neutrons at a flux rate of  $2 \times 10^{10}$  n cm<sup>-2</sup> s<sup>-1</sup>, and a total dose of  $1 \times 10^8$  r. Based on measurements of ignition time delay, this exposure produced no significant effect on the hypergolicity of MMH when injected with NTO. However, a significant off-gas pressure developed that was a linear function of the radiation exposure above  $10^6$  r. After exposure to  $1 \times 10^8$  r, the off-gas volume (at 1 atm, and 298 K = 77 °F) was 21 mL gas per milliliter of liquid. The chromatographic analysis of the off-gas showed it to be a mixture of approximately 28 mol-% hydrogen, 41 mol-% nitrogen, and 31 mol-% methane with minor amounts of oxygen, ammonia, and monomethyl hydrazine vapor. The irradiated liquid material exhibited a 4.5% decrease in MMH assay, a 5.5% increase in viscosity, and a 0.9% increase in density. The melting point was unaffected by radiation.

Investigations were made of the possibility of suppressing the generation of non-condensable gases when MMH was subjected to ionizing radiation from cobalt-60 with and without free-radical scavengers [274, 275]. MMH produced more than twice its vol-

ume of gas (measured at 298 K = 25 °C and 101 kPa = 1 atm) consisting of hydrogen, nitrogen, and methane when irradiated to nearly  $10^7$  r with gamma rays. An attempt at gas suppression was made with chemical additives that could scavenge free radicals by reacting with them. Free radical scavengers had no effect on decomposition, indicating a molecular or ionic decomposition reaction rather than a free-radical mechanism. Two normally efficient olefinic additives (free-radical scavengers such as methyl methacrylate or pentadiene-1,3) failed to suppress gas evolution, thereby demonstrating that MMH does not decompose radiolytically via free-radical intermediates. Instead, MMH decomposes via a molecular or ionic process. The addition of carbon tetrachloride as a potential, gas suppressing additive actually increased gas evolution enormously, and this can be explained on the basis that it initiates a chemical chain reaction. The storability of MMH with respect to solar, cosmic, van Allen belt, and nuclear fission reactor radiation cannot be improved by the addition of free-radical scavengers as the scavengers fail to suppress the generation of off-gases in MMH by the radiation. Accordingly, the radiolytic decomposition of MMH proceeds via a molecular or ionic reaction rather than a diffusion-controlled, free-radical reaction. Gamma radiolysis of a 100-mL specimen of MMH to  $8.5 \times 10^6$  r produced 227 mL of off-gas (at 298 K and 101 kPa), which was nearly an equimolar mixture of hydrogen (38.7%), nitrogen (33.5%), and methane (27.8%). The average radiation yields (molecules/100 eV) of these gases were 4.7, 4.0, and 3.4 respectively.

Similar radiolysis measurements were made for UDMH [276] and Aerozine-50. See also [277, 278]. A summary was given of propellant radiation damage as a function of source type and mission. It was concluded that  $\alpha$ -heat sources such as  $^{238}\text{Pu}$  or  $^{244}\text{Cm}$  probably would not require additional shielding to protect the propellants, even with large power sources.  $\beta$ - and  $\gamma$ -radioisotope sources and nuclear reactor sources will most likely require propellant-shielding on long missions.

#### 4.5 Electron Bombardment Decomposition of MMH

The most common place for electron bombardment (electron impact) decomposition of MMH to take place is in the inlet to mass spectrometers, where the neutral molecules are ionized so that they can be separated by mass and electric charge in crossed electric and magnetic fields in the mass spectrometer.

Electron bombardment ionization thresholds give information on the ionization energy and bond dissociation energies of molecules. An alternate way of achieving ionization would be by UV radiation photolysis with light of different wavelengths. Dissociative ionization cross-sections, fragment appearance potentials, and fragment kinetic energies were measured for electron-impact excitation of jet-cooled MMH over an energy range of 10–270 eV and the data were entered into a data base containing 35 parent and fragment ions [279, 280]. All measurements were made in a crossed electron-molecular beam apparatus using pulsed extraction and time-of-flight mass de-

tection to ensure field-free excitation and high collection efficiency for energetic ions. The measured MMH cross-sections for total ionization at 70 eV were  $4.20 \text{ \AA}^2$ . High-resolution mass spectra were recorded for MMH in order to distinguish different fragment ions of the same unit mass. Substantial rearrangement was evident for  $\text{N}_2\text{H}_4$  and MMH dissociative ionization based on the appearance of ions such as  $\text{NH}_3^+$  and  $\text{NH}_4^+$ .

The dissociation of methylated hydrazine ions was observed to undergo extensive fragmentation and rearrangement leading to many fragments that have the same nominal mass, but differ in chemical composition by an N versus  $\text{CH}_2$  moiety. Previously, absolute ionization cross-sections were measured for hydrazine and MMH dissociative ionization using a high throughput time-of-flight mass spectrometer that had excellent detectability of high kinetic energy ions, but only moderate mass resolution (0.1 amu). Improved high-resolution quadrupole detection (0.005 amu) allowed one to distinguish ion fragments of the same nominal mass for MMH and UDMH [281]. The ratios of these close-lying fragment masses were measured for different electron impact energies and explained in terms of thermochemical thresholds and fragmentation mechanisms. The methyl groups account for complex reaction mechanisms. A high yield was observed for NH dissociation induced by a 1,2 sigmatropic hydride shift and for  $\text{CH}_4$  dissociation formed by a 1,2 elimination. Some fragmentation reactions involved large activation energies or unusual mechanisms.

## 4.6 Reactions of MMH

Methylhydrazine is one of the more reactive rocket fuels, and a complete account of all reactions it can enter into would fill a book in its own right. The following sections summarize reactions that relate to storability, contamination, explosion hazards, and safety properties of MMH.

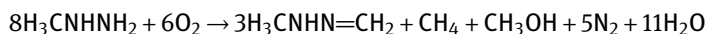
### 4.6.1 Reactions of MMH with Inorganic Compounds

#### 4.6.1.1 Reactions of MMH with Oxygen

Oxygen is everywhere on Earth where MMH may be handled. Typically, one avoids contact between MMH and oxygen in air by keeping a nitrogen pad at a slightly positive pressure above MMH stored in shipping containers and storage tanks. Often, facility nitrogen that is plumbed in at rocket test sites contains traces of oxygen contamination. Even ppm levels of oxygen react with MMH. Kinetics of gas-phase reactions of MMH with  $\text{O}_2$  were already discussed in Section 4.1.5 in conjunction with shock tube studies of MMH vapor decomposition. Here, we discuss reactions of oxygen with MMH at low partial pressures, autoxidation conditions that do not lead to ignition. Ignition of MMH in air or oxygen is discussed in Section 10.2. Rocket engines operating on LOX and MMH will be discussed in a future set *Encyclopedia of Non-Hypergolic Bipropellant Combinations*. Atmospheric decay of MMH is discussed in Section 12.3.



The autoxidation of MMH was studied in a 300-mL and a 12-L Pyrex flask, at a partial pressure of 5 mm Hg in a 44-cm path length IR spectrophotometer cell, and in a long path reaction cell constructed from a  $0.152 \times 3.05$ -m section of Pyrex pipe [282]. The half-life of MMH was 2–7 h depending on reaction vessel surface area and activity. Possible mechanisms were difficult to postulate, but the overall reaction was:



with the formaldehyde methylhydrazone condensing out as a polymer oil. Similar tests were conducted using hydrazine and UDMH vapors.

#### 4.6.1.2 Reactions of Methylhydrazines with Atomic Oxygen

Collision cross-sections were measured for MMH reactions with  $\text{O}^+$ ,  $\text{CO}^+$ ,  $\text{CO}_2^+$ , and  $\text{NO}^+$  at suprathermal collision energies ranging between 1 and 20 eV (center of mass) in an octopole guided-ion-beam apparatus [283]. Dissociative charge transfer occurred in each reaction, similar to reactions involving hydrazine. The total reaction cross-section was on the order of  $50\text{--}100 \text{ \AA}^2$ , and the amount of  $\text{CH}_3\text{NHNH}_2^+$  fragmentation in each case depended upon both the exothermicity of the charge transfer and the availability of internal degrees of freedom in the incident primary ion.

In low Earth orbit, atomic oxygen collides with plume/exhaust species with a relative velocity around 8 km/s. The several electron volts of kinetic energy in the collision can transfer energy into IR-emitting states of the plume species and can open chemical reaction pathways that are not available under thermal conditions.

Emissions of  $\text{CHA} \rightarrow \text{X}$ ,  $\text{CNB} \rightarrow \text{X}$ , and  $\text{NHA} \rightarrow \text{X}$  transitions within the range 325–440 nm caused by the reaction of fast  $\text{O}(^3\text{P})$  atoms with hydrazine, MMH, or UDMH in gas-phase collisions were observed using a crossed-beam molecular beam apparatus [284]. Many experiments have been plagued by uncertainties about the quality of the atomic oxygen stream used, which may have contained excited oxygen or molecular dinitrogen instead of pure atomic oxygen in the ground state. The  $\text{O}(^3\text{P})$  resonance fluorescence technique unambiguously provides a stream of atomic oxygen in the ground state by using a pulsed  $\text{F}_2$  laser emitting at 157 nm to photolyze the  $\text{O}_2$ . The reaction rates can be measured accurately by the decay of 131 nm  $\text{O}(^3\text{S} \rightarrow ^3\text{P})$  resonance fluorescence under both high pressure (6.6 kPa) and low pressure (133–350 Pa) conditions [285, 286]. The measured rate constants are summarized in Table 31.

The ratio of the rate constants is close to that of the number of hydrogen atoms in these three molecules. It cannot be proven that the mechanism is one of hydrogen abstraction, but it looks that way.

The gas-phase kinetics of  $\text{O}(^3\text{P})$  and OH reactions with MMH or UDMH were studied in a discharge flow-tube apparatus [287, 288]. The reactions were studied in 267 Pa (2 mm Hg) of He dilution under pseudo-first-order conditions in the transient species concentration with a known excess of hydrazine concentration. The steady-state concentration temporal profiles of the transient species were directly monitored using flu-

**Table 31:** Rate constants of reactions of atomic oxygen with hydrazines at 296 K.

| Fuel      | Rate constant, $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | Ratio (normalized by $\text{N}_2\text{H}_4$ rate) | Ratio of number of hydrogen atoms | Number of hydrogen atoms |
|-----------|-------------------------------------------------------------------|---------------------------------------------------|-----------------------------------|--------------------------|
| Hydrazine | $0.99 (\pm 0.12) \times 10^{-11}$                                 | 1.0                                               | 1.0                               | 4                        |
| MMH       | $1.6 (\pm 0.34) \times 10^{-11}$                                  | 1.6                                               | 1.5                               | 6                        |
| UDMH      | $2.3 (\pm 0.34) \times 10^{-11}$                                  | 2.3                                               | 2.0                               | 8                        |

Data source: [285, 286]

orescence techniques to deduce the absolute second-order reaction rate coefficients. The Arrhenius expression:

$$(2.71 \pm 0.04) \times 10^{-11} \exp(190 \pm 50)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

within the temperature range 252–640 K was obtained for reactions of  $\text{O}(^3\text{P})$  with MMH. The corresponding expression:

$$(2.88 \pm 0.04) \times 10^{-11} \exp(210 \pm 55)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

within the range 232–374 K was determined for the  $\bullet\text{OH}$  reaction with MMH. Alkylation in the hydrazine molecule allows direct H-abstraction mechanisms to operate in these reaction systems.

In a later study [288] with direct laser-induced fluorescence monitoring of the  $[\text{OH}]$  temporal profiles in a known excess of MMH yielded the following absolute second-order OH rate coefficient expression:

$$k_1 = (4.59 \pm 0.83) \times 10^{-11} \exp(85 \pm 35)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

for reactions with MMH within the temperature range 232–637 K.

The gas-phase reaction kinetics of O atoms with MMH was studied in a discharge flow-tube apparatus under pseudo-first-order conditions in  $[\text{O atom}]$  [289, 290]. Direct VUV CW-resonance fluorescence monitoring of the  $[\text{O atom}]$  temporal profiles in a known excess of MMH yielded the following absolute second-order O atom rate coefficient expression within the temperature range 232–644 K and under He pressure of 2.0 Torr:

$$k_1 = (2.29 \pm 0.40) \times 10^{-11} \exp(-145 \pm 40)/T \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

The modeling of UV radiation from high-altitude plumes containing MMH or UDMH was compared with observed data from the MIR space station [291].

#### 4.6.1.3 Shock Tube Studies of MMH Combustion and Detonation Kinetics

The ignition delays  $\tau$  of MMH decomposition products were measured behind a reflected shock wave at 900–1440 K, 160–350 kPa, fuel:oxidizer equivalence ratios from 1 to 2.27, and argon diluent molar fractions from 0.82 to 0.96 [292]. The MMH absorption at 220 nm was taken as an indication of MMH concentration in the

reacting mixture. A kinetic model/computer program was developed that included 300 individual reactions and that reproduced the experimental results quite well ( $\pm 35\%$ ) within the ranges 1070 to 1260 K and 190 to 290 kPa. Plotting an ignition delay function (a logarithm of  $\tau$ ) vs.  $1/T$  allowed the determination of the activation energy (it was of the order of  $99 \pm 3$  kJ/mol). If the ignition delay is sufficiently reduced by approaching stoichiometric ratios or applying less diluent, then a detonation wave can be initiated behind the incident shock. Detonation velocity of ternary  $O_2$ /MMH/ $N_2$  mixtures was measured both by equally spaced, directly inserted pressure probes and by measuring the cell size on smoked witness tubes. The critical conditions for a self-sustained detonation were bracketed by a series of experiments. The detonation velocity of 52.4 mol%  $O_2$ /47.6% MMH (equivalence ratio  $\phi = 2.27 =$  fuel rich) at an initial pressure of 2 kPa was 2400 m/s once the initiating shock wave from a bursting diaphragm in a helium-filled donor section (He fill pressure varied from 0.4 to 0.7 MPa) was energetic enough. This value was below that predicted from C-J calculations for this mix. Surprisingly, cell size vs. pressure plots showed that stoichiometric  $O_2$ /MMH mixtures were less detonable than  $O_2$ /UDMH or  $O_2$ / $N_2H_4$  mixtures. It was not possible to establish a simple correlation between the detonation cell size and the induction distance for the explosive oxidation calculated from ignition delay data.

The fundamental gas-dynamic characteristics of the detonation, instantaneous combustion (explosion) in constant volume, combustion at constant pressure, and deflagration for hydrazine, MMH, UDMH, SDMH, or trimethylhydrazine in mixtures with oxygen or air that are diluted with argon at varied initial pressure and temperature values were examined [293, 294]. Spray detonation is also potentially relevant to the study of pulse detonation engines and other hypersonic propulsion systems exploiting detonative reactions. The main parameters of these processes were analyzed both for the case of a gaseous propellant and for the case of a heterogeneous propellant where the propellant is a highly disperse, sprayed aerosol cloud in an oxidant medium. Calculations were performed by means of the computer code SAFETY. Calculation results were in agreement with experimental data. For MMH vapor, detonation wave velocity was predicted to be  $D_0 = 1941$  m/s. For a stoichiometric mixture of MMH vapor with oxygen the detonation wave velocity was predicted to be  $D_0 = 2476$  m/s. For a stoichiometric mixture of MMH vapor with air the detonation wave velocity was predicted to be  $D_0 = 1894$  m/s. A poorly dispersed spray of liquid MMH aerosol in a stoichiometric proportion to oxygen was predicted to detonate with  $D_0 = 1848$  m/s.

Ignition delay times for MMH/ $O_2$ /Ar gaseous mixtures have been modeled by a reaction scheme containing 70 species and 373 equilibrated elementary reactions [267]. For many reactions, the rate constants had to be estimated or adjusted because rate constants were available for only a few reactions. Results of measurements of ignition delay times behind reflected shock waves performed over a range of temperatures, pressures, and compositions were compared with computed predictions. Good agreement between measured and calculated ignition delay times was obtained,

but only for lean and less dilute mixtures. The reaction most likely begins with the scission of the N—N bond in MMH, but elimination reactions from MMH also have to be considered, especially at a high initial temperature. The  $\text{NH}_2$  radicals formed can react with MMH to give  $\text{CH}_3\text{NNH}_2$  radicals and products. These radicals react with  $\text{O}_2$  to produce methyldiazene ( $\text{CH}_3\text{N}=\text{NH}$ ) and  $\text{HO}_2$  radicals.  $\text{HO}_2$  radicals react with MMH to give  $\text{CH}_3\text{NNH}_2$  radicals and  $\text{H}_2\text{O}_2$ , which plays a major role through its thermal decomposition, which produces more hydroxyl radicals.

#### 4.6.1.4 Slow Autoxidation of MMH Vapors in the Atmosphere

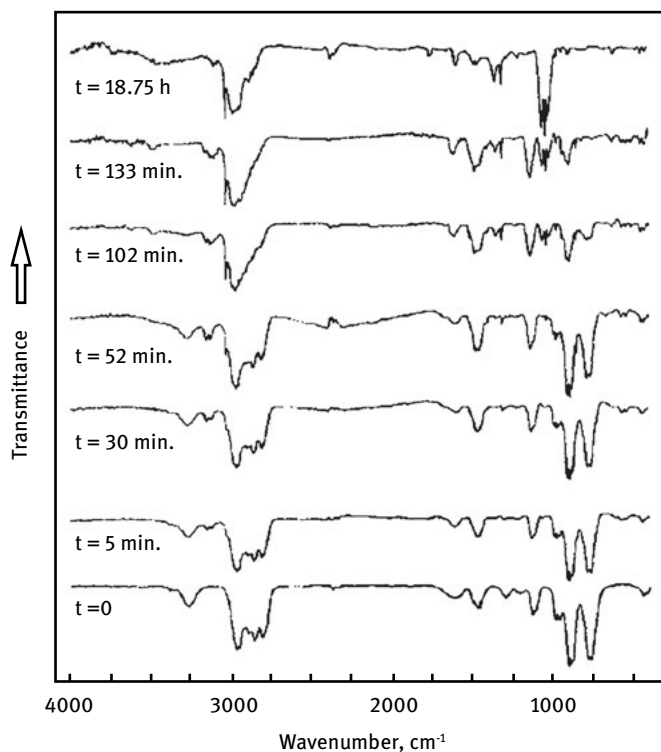
Exposure of MMH to air may be difficult to avoid during propellant transfer, in particular when venting the source tank after the transfer is complete. The slow reaction of MMH with oxygen was noticeably exothermic. Gas chromatographic analysis of the liquid reaction product after 24 h showed the presence of ten components, including methanol, MMH, *sym*-hexahydro-1,4-dimethyltetrazine, and water. The cytostatic action of MMH derivatives has been linked to the formation of peroxides or even free OH radicals during the biological oxidation of these compounds in cancer tissue [295]. The oxidation is catalyzed by  $\text{Cu}^{2+}$  ion and inhibited by complexing of Cu with EDTA, DNA, or pyrophosphate.

The reactions between MMH and molecular oxygen in the gas phase have been studied in three separate experiments [230, 235]. The results indicated that at room temperature the reaction is stoichiometric and that methyldiazene  $\text{CH}_3\text{N}=\text{NH}$  is the initial product. The reaction was complete in a matter of minutes. At 592 K (319 °C), in an experiment in which the initial  $\text{O}_2$  : MMH ratio was 1 : 6, all of the MMH disappeared with a surprisingly large quantity of hydrogen as a product. A chain-type process, possibly explosive, was implicated.

The level of trace organic impurities in MMH is a function of the handling history of the MMH sample. Atmospheric oxygen was responsible for the changes, and methane (<100 ppm), ethane (<50 ppm), and AM (<50 ppm) were found to be oxygen-generated [234]. SDMh was a possible but unconfirmed impurity.

In studying the autoxidation of MMH at room temperature in the gas phase, the objective was to characterize the lifetime of MMH mixed with  $\text{O}_2$ , both reactants in the gas phase, at 295 K in a 10-L spherical Pyrex vessel with a surface-to-volume ratio of  $22.4\text{ m}^{-1}$  and two different oxygen : MMH molar ratios of 2.52 (equivalence ratio = 0.99) and 6.4 (equivalence ratio = 0.39) [296]. The reaction was followed principally by IR spectroscopy over the mid-IR region ( $4000$  to  $500\text{ cm}^{-1}$ ) at  $4\text{ cm}^{-1}$  resolution. Figure 28 shows the changes in the IR spectrum with time for the experiment with an oxygen : MMH ratio of 6.4.

The spectrum at  $t = 0$  is that of pure gaseous MMH. The disappearance of MMH was obvious as some MMH bands disappeared and some new IR features became evident. The  $\text{O}_2$  : MMH equivalence ratio had no effect on the changes. The MMH bands that clearly disappeared were those centered at  $779\text{ cm}^{-1}$  (NH bending at  $777\text{ cm}^{-1}$ ), and those centered at  $900\text{ cm}^{-1}$  ( $\text{NH}_2$  rocking at  $888\text{ cm}^{-1}$ ), indicating that the  $-\text{NHNH}_2$



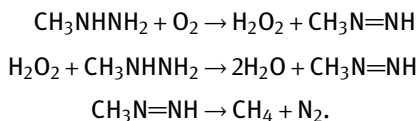
**Figure 28:** Progressive changes in the infrared spectrum of methylhydrazine vapor during autoxidation. (Reprinted and modified from [296], with permission by ©2000 Springer Nature; permission conveyed through Copyright Clearance Center Inc.)

structure as encountered in MMH no longer existed. The new IR features indicate the formation of methane ( $3016$  and  $1304\text{ cm}^{-1}$ ). Some other features were attributed to methanol ( $2960$ ,  $1477$ ,  $1345$ , and  $1033\text{ cm}^{-1}$ ). The formation of methyldiazene was not obvious when comparing the IR spectrum of this molecule with the spectra of the reaction products. Mass spectra of the reaction products did not clearly identify any of the products because many peaks overlapped with  $m/e$  of  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ .

A detailed kinetic model has been built to allow a numerical study of the slow homogeneous MMH/ $\text{O}_2$  reactivity. A kinetic model of this type is also useful for modeling the faster oxygen/MMH reaction leading to ignition and for explaining the ignition delay if such mixtures are rapidly heated in a shock tube. The ignition of oxygen or air mixtures with MMH vapors is discussed in a future *Encyclopedia of Non-Hypergolic Bipropellant Combinations*. This property also affects the flash point or auto-ignition temperature of MMH in air (Section 10.1).

The autoxidation of 4.6% MMH vapor in air in 320-mL glass or polyethylene flasks led to nitrogen and methane [297, 298]. In glass, the half-life time was 34 min.

In polyethylene the reaction was much faster and was complete in 10 min, indicating a surface catalytic effect. The reaction was designated as first order in MMH and zero order in oxygen despite the non-linearity of the  $\ln([MMH]/[MMH]_0)$  vs. time plot at long reaction times. The authors should have spent a little more time explaining this non-linearity. Exposure of MMH liquid to air for only brief periods changed the amounts of trace impurities (methane, AM, SDMH). With monitoring of the MMH/O<sub>2</sub> reaction in an IR spectrometer, the major MMH peaks at 11.2 and 12.9  $\mu\text{m}$  diminished steadily throughout the first several scans and almost disappeared after 10 min [230]. An intermediate peak at 11.8  $\mu\text{m}$  has been assigned to methyldiazene. It peaked after 10 min and then gave way to an increasing methane peak at 7.6  $\mu\text{m}$ . The following mechanism has been proposed:

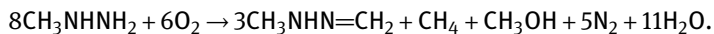


Subsequently, CH<sub>3</sub>N=NH has also been discovered as a peak at  $m/e = 44$  when extracting a sample from a reacting mixture of 4-kPa (30-mm-Hg) MMH and 2-kPa (15-mm-Hg) O<sub>2</sub> directly into a quadrupole mass spectrometer. This technique also confirmed the slow increase of SDMH at  $m/e = 60$ . It is possible that SDMH is a daughter product of methyldiazene decomposition. With additional oxygen, SDMH then becomes oxidized to AM. When adding AM to MMH in sealed tubes in molar ratios of AM : MMH = 1 : 5 and 1 : 25, each AM molecule destroyed only one MMH molecule in a stoichiometric reaction. Although AM is a radical source for the initiation of radical chain reactions (e.g., polymerizations), the decomposition of MMH does not appear to be a chain reaction.

Studying the autoxidation of MMH or other hydrazines in confined atmosphere chambers is difficult. MMH and oxygen may diffuse through thin plastic walls. Metal walls may catalyze autoxidation [299].

Air and oxygen oxidation studies of 1 mL of MMH injected and vaporized into a 300-mL Pyrex flask at 81-kPa (610-Torr) helium/13.3-kPa (100-Torr) oxygen pressure showed that all oxygen is consumed within 100 min. Nitrogen and methane are found as reaction products [282]. Tests with a larger (12-L) Pyrex vessel gave identical results. Reaction IR spectroscopy in a 44-cm pathlength cell gave even more detailed kinetic data. A number of changes in spectral features are apparent while the reaction is in progress. The N—H stretching band at 3260  $\text{cm}^{-1}$  decreased after 6 h and disappeared entirely after 23 h. A new band at 3080  $\text{cm}^{-1}$  became visible after 6 h and was very strong at 23 h. Similar tests with a 2.75-m-long 55-L cell with a multiple reflection (pathlength 200 m) even allowed the early detection of trace quantities of short-lived intermediates and oxidation products. One transient intermediate absorbing at 846  $\text{cm}^{-1}$  was not identified. MMH oxidation in synthetic air proceeds with a half-life of 2–7 h depending on vessel surface area and material. Heterogeneous processes are

probably dominant, in particular at higher concentrations. The stoichiometry can be approximated by:



The formaldehyde methylhydrazone condenses out as a polymer oil. Additional FTIR studies in a 60-L cell consisting of a 6-in by 10-ft section of Pyrex pipe with an effective pathlength of 200 m showed that the autoxidation of 25 ppm MMH in 80% helium/20% oxygen leads to intermediate production of methane, methanol, and methyldiazene [300]. After 74 h, only methane and some unidentified contaminants remained. The half-life time for MMH under these conditions was approximately 250 min.

It was difficult to study the autoxidation of hydrazines in Teflon-lined chambers because diffusion of MMH vapors through the Teflon foil and intrusion of ambient air oxygen through the Teflon foil interfered with the autoxidation measurements [301].

Methylhydrazine–air autoxidation studies on materials of construction in powder form in a tubular reactor at 328 K resulted in methanol, methyldiazene, methane, and, occasionally, traces of ammonia [302–304]. The overall reactivity order of the catalysts for the air oxidation of MMH was  $\text{Fe} > \text{Al}_2\text{O}_3 > \text{Ti} > \text{Zn} > \text{CRES-316} > \text{Cr} > \text{Ni} > \text{Al} > \text{CRES-304}$ . In this apparatus, di-, tri-, and tetra-methylhydrazines were much less reactive than hydrazine or MMH.

The autoxidation of MMH in the gas phase was studied in a strictly single-phase gaseous medium, in a reconstituted synthetic atmosphere [305]. The reaction kinetics was studied at 323 K (50 °C) to avoid condensation of the water formed and for  $\text{O}_2$ /MMH molar ratios between 1 and 4. Under these conditions, the partial pressures of  $\text{O}_2$  were between 0.05 and 0.18 bar (4% MMH per volume). The main reaction products were monitored through time and identified by GC-MS. The products were:  $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{H}_3\text{CNH}-\text{N}=\text{CH}_2$  (formaldehyde monomethylhydrazone),  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , and  $\text{H}_2\text{C}=\text{N}-\text{N}=\text{N}-\text{CH}_3$  (2,3,4-triazapenta-1,3-diene). The formation of nitrosamines was not observed under these experimental conditions. The rate laws related to the disappearance of the reactants were clearly established and could be described by two consecutive parallel reactions of second order whose rate constants were:  $k_1 = 7.57 \times 10^{-2} \text{ bar}^{-1} \text{ min}^{-1}$  and  $k_2 = 0.5 \text{ bar}^{-1} \text{ min}^{-1}$ . Analysis of the products permitted an approximated balance of the global reaction to be established.

#### 4.6.1.5 Autoxidation of MMH in the Liquid State

When dry oxygen was bubbled through liquid MMH for 21 days, the condensate in a 193-K cold trap contained methyl azide, ammonia, and methylamine [306]. Methyl azide formation has also been observed during the autoxidation of UDMH [307]. In a similar test, ambient air was bubbled through MMH to create artificially aged MMH and the NVR was analyzed [308].

#### 4.6.1.6 Autoxidation of MMH in Solution

The autoxidation of MMH by dissolved air in aqueous solution is an important process if one has to determine the longevity of MMH spills in clean surface waters without soil contact or suspended sediments. This information is needed for the design of wastewater treatment plants for waste water drained from rocket test sites.

The rate of oxidation of hydrazines (hydrazines spilled into surface water) was measured by pouring a measured amount of hydrazine, MMH, or UDMH into 2 L of distilled air-saturated water in a glass flask and measuring pH and dissolved oxygen as a function of time [309]. The starting concentration of dissolved oxygen was typically above 7.5 ppm. MMH concentrations from 220 to 880 mg/L and UDMH at concentrations from 200 to 800 mg/L were studied for rate of oxidation. In some experiments, controlled amounts (0.125, 0.25, 0.5, and 1.0 mg/L) of copper  $\text{Cu}^{2+}$  ion were added to test its effectiveness as a catalyst. In the sample containing the highest  $\text{Cu}^{2+}$  addition, dissolved oxygen dropped from 7 to 0.3 ppm in less than 1 min. No effort was made to exclude ambient air during the experiment, but as the experiments were short, reabsorption of oxygen from the air could be neglected. Besides, in free nature, additional oxygen from the air would also be available to aid degradation of hydrazines in the water. The data giving the rate of disappearance of oxygen and hydrazine were curve-fitted to a kinetic model with empirical constants of the type:

$$\frac{d(\text{DO})}{dt} = -\frac{k}{V}(\text{DO})^n$$

where DO is dissolved oxygen,  $k/V$  is an average rate constant, and  $n$  is the average order of the reaction. Results for hydrazine, MMH, and UDMH are shown in Table 32.

**Table 32:** Autoxidation of hydrazines (in the absence of copper ions).

| Propellant | Average order $n$ | Average rate constant, L/min |
|------------|-------------------|------------------------------|
| Hydrazine  | 0.985             | 4.0245                       |
| MMH        | 1.025             | 3.3296                       |
| UDMH       | 0.540             | 1.6895                       |

Data source: [309]

In a study of the rate of oxidation of MMH or UDMH as affected by pH and  $\text{Cu}^{2+}$  concentration, the authors concluded that for most real-life spill surface water conditions, neither UDMH nor MMH would persist for longer than a day or two in the absence of highly acidic conditions [310]. The kinetics of oxidation of MMH by dissolved oxygen in water has been measured at various acidities as a function of catalyst (cupric ion) concentration. In dilute solutions the oxidation occurs through a cupric ion catalyzed process as well as by an uncatalyzed step. Some formaldehyde was also detected during MMH autoxidation.



Glassware used for an environmental degradation study of hydrazines in seawater, pond water, and pure water was carefully washed with 50% nitric acid prior to use. This rigorous cleaning was necessary to achieve reproducible results [311, 312]. Before the environmental degradation tests in soil were started, it was necessary to know the rate of degradation in surface waters without the effect of soil. In the absence of soil or catalysts, aqueous half-lives were ~13 days for MMH and 6–13 days for UDMH. Additional half-life data are summarized in Table 33.

**Table 33:** Half-life of methylhydrazine in natural waters.

| Fuel            | Initial concentration, mM | Pond water, days | Sea water, days |
|-----------------|---------------------------|------------------|-----------------|
| MMH             | 19.0                      | $13.1 \pm 1.1$   | $13.1 \pm 2.2$  |
| MMH             | 9.5                       | $18.0 \pm 2.3$   | $24.1 \pm 8.8$  |
| For comparison: |                           |                  |                 |
| UDMH            | 13.1                      | $22.2 \pm 6.9$   | $12.6 \pm 2.8$  |
| UDMH            | 6.5                       | $16.3 \pm 6.9$   | $12.6 \pm 1.1$  |
| UDMH            | 0.9                       | $7.3 \pm 1.0$    | —               |
| Hydrazine       | 1.8                       | $8.3 \pm 0.6$    | —               |

Data source: [311, 312]

For a wastewater aeration basin with a common hydraulic detention time of 9 h, the efficiency of organics removal was seriously hampered when the MMH or UDMH concentration exceeded 5 or 8 mg/L, respectively [313]. As far as organics removal is concerned, the “no effect level” would be approximately 2mg MMH or UDMH/L. However, even at this low level, nitrogen speciation (ammonia conversion to nitrate) was severely impeded. Inhibition of nitrification occurred at concentrations above 0.5mg MMH/L and above 1mg/L for the other fuels. Both MMH and UDMH were still detectable under the same conditions, and their efficiency of removal was only 89 and 96%, respectively.

The degradation of MMH by dissolved oxygen in water was carried out in a variable volume and airtight reactor, which made it possible to continuously determine the oxygen and MMH (0–300 ppm) content by successive samplings, while remaining monophasic all-liquid [314]. The oxidation of the MMH was then studied in a strictly gaseous medium by means of an experimental setup designed to ensure a good vacuum resistance (10 Pa) up to a temperature of 473 K (200 °C). This installation made it possible to scan all the O<sub>2</sub>/MMH ratios, to follow the evolution of the gas mixture with the progress of the reaction, and to carry out an overall analysis of the reaction medium by GC. The identification of the different products was carried out using GC-MS and cross-checking their retention time. The results obtained in normal gaseous atmospheres showed that the O<sub>2</sub>/MMH system is a system of complex reaction chains owing to the high probability of interactions between free

molecules such as hydrazones and tautomeric forms of methyldiazene. The kinetic and thermodynamic parameters of activation energy have been determined and a reaction sequence was proposed.

The kinetics of the oxidation of MMH by dioxygen was studied in reducing medium (excess of MMH) as a function of the concentrations ( $[O_2] \leq 4 \times 10^{-4}$  mol/L,  $[MMH] \leq 6 \times 10^{-3}$  mol/L), pH (11 to 14), and temperature (298 to 318 K = 25 to 45 °C) [315]. The measurements were carried out in strictly monophasic medium in an isothermal, isobaric reactor with variable volume. The reaction is first order with respect to each of the reactants. The reaction orders and the stoichiometry were independent of the pH and within the range studied, and the variation of the rate constant was insignificant to be interpreted in terms of acid–base catalysis. The major product of the reaction was methanol. No compounds with chromophoric groups were observed. The isobaric isothermal reactor consists of a compensating piston that allows reagent injection and sample withdrawal without the appearance of a gaseous phase [316, 317].

#### 4.6.1.7 Reactions of MMH with Ozone

Ozone ( $O_3$ ) constitutes a more active form of oxygen and releases atomic oxygen during its decomposition. Ozonization is a clean method of decontamination of hydrazine(s) in rinse waters from propulsion systems. A parametric study of the ozonization of hydrazine, MMH, and UDMH investigated the effects of reactant concentration, pH, UV catalysis, and ultrasonic agitation on the rates of hydrazine(s) destruction [318, 319]. Two types of gas-sparging constant-volume stirred reactors were used, a 35-L UV reactor and a 5-L reactor with an ultrasonic agitator. The gas flow rate was typically 30 scfm. Ozonized air contained approximately 1% by weight ozone. Higher ozone concentrations (2% by weight) were possible with ozonized dry oxygen. The reaction rate increased with increasing pH. Ultraviolet light acted as a catalyst and decreased the half-life further. UV had some beneficial effect with MMH and UDMH. Kinetic analysis of the MMH concentrations showed that the data fit a zeroth-order and UDMH data fit a half-order relationship. Autodecomposition of dissolved ozone also followed a zeroth-order relationship. Even with very high initial hydrazine concentrations, the rate of hydrazine destruction followed a zeroth-order relationship after 15 min of bubbling ozone through the solution. The half-lives of the hydrazines in contact with ozone are summarized in Table 34.

In addition to the rate of hydrazine(s) disappearance, reaction products (nitrate, organics) were analyzed using spectrophotometric and GC-MS methods. Residual nitrate is undesirable and would make it more difficult to discharge the reactor effluents to surface waters. In the case of MMH ozonization, methanol was a by-product (predominantly at low-pH operation) that had secondary ozone requirements beyond the point where all MMH had disappeared. Methanol becomes oxidized/ozonized much more slowly than MMH. Again, measurable residual methanol

**Table 34:** Reaction of ozone with hydrazine, methylhydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH).

| Reaction conditions |                          | Half-life time, minutes |                               |                        |
|---------------------|--------------------------|-------------------------|-------------------------------|------------------------|
| pH                  | Catalyst                 | Hydrazine               | MMH                           | UDMH                   |
| 9.1                 | None                     | 20.7 to 21.3            | 20.8 to 26.2                  | 19.9 to 26.2           |
| 3.1 to 3.8          | None                     | 89.8                    | 38.4                          | 42.4                   |
| 9.1                 | UV                       | 20.7                    | 19.2                          | 19.2                   |
| 9.2                 | Ultrasound               | No effect               | —                             | 84 on effective        |
| 9.1                 | Air sparging, no UV      | 19% removed/<br>60 min  | No effect/20 min <sup>a</sup> | 5% removed/<br>60 min  |
| 9.1                 | Air sparging, with UV    | 35% removed/<br>60 min  | —                             | 14% removed/<br>60 min |
| 9.1                 | Oxygen sparging, no UV   | —                       | No effect/20 min              | —                      |
| 9.1                 | Oxygen sparging, with UV | —                       | 20                            | —                      |

UV = ultraviolet

<sup>a</sup> Different apparatus

Data source: [318]

concentrations would make it difficult to find a location where the ozonized MMH waste can be safely discharged to surface waters. In addition to methanol, there were four unidentified GC peaks. In the case of UDMH, the main reaction by-products were *N*-nitrosodimethylamine (NDMA) and dimethylformamide, in addition to 13 other unidentified peaks. UV spectra indicated formaldehyde dimethylhydrazone and tetramethyltetrazene.

The oxidation of MMH and UDMH by ozone is not complete but leads to organic products that may also be toxic [320–322]. Ozonization alone is not completely effective in decontaminating MMH- or UDMH-contaminated wastewater.

Reaction rates of hydrazines with ozone would be similar to reaction rates with atomic oxygen and hydroxyl free radicals, which are expected if MMH vapors are released into the atmosphere and exposed to direct sunlight. The reaction of atomic oxygen with MMH may excite fluorescent emissions at characteristic wavelengths within the UV and visible range.

The gas-phase reaction of MMH with ozone was investigated in a flow tube at atmospheric pressure and a temperature of  $295 \pm 2$  K using  $N_2/O_2$  mixtures (3–30 vol-%  $O_2$ ) as the carrier gas [323]. Proton transfer reaction-mass spectrometry and long-path FTIR spectroscopy served as the main diagnostic techniques. The kinetics of the reaction were investigated using a relative rate technique yielding:

$$k_{\text{MMH} + \text{O}_3} = (4.3 \pm 1.0) \times 10^{-15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

Methyldiazene was identified as the main intermediate product in this reaction system. The reactivity of methyldiazene toward ozone was estimated relative to the reac-

tion of MMH with ozone, resulting in:

$$k_{\text{HN=NCH}_3 + \text{O}_3} = (2.7 \pm 1.6) \times 10^{-15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

Increasing OH radical yields with increasing MMH conversion have been observed, pointing to the importance of secondary processes for OH radical generation. The results of this study did not support the mechanism of OH radical formation from the reaction of MMH with ozone as proposed in the literature, a reaction that was known to take place between hydrazine  $\text{N}_2\text{H}_4$  and ozone.

#### 4.6.1.8 Reactions of MMH with Nitrogen Dioxide

The hypergolic reaction of MMH with dinitrogen tetroxide is the main reason why that much MMH has been produced in the first place. Applications of the NTO/MMH propellant combination in rocket engines will be presented in a future *Encyclopedia of Hypergolic Bipropellant Combinations*.

Slow reactions of MMH with  $\text{NO}_2$  in the gas phase might occur in the vicinity of propellant storage areas where propellant has leaked, or in a rocket combustion chamber after the engine has shut down and the dribble volume slowly empties itself without a combustion reaction. These reactions also have to be anticipated if a bipropellant engine is fired for a very, very short pulse and fails to ignite.

The slow reaction of  $\text{N}_2\text{O}_4$  and MMH vapor diluted in high-pressure helium (15 MPa = 250 psia) was studied in 1989, but unfortunately the lessons learned were not applied to the design of the propellant pressurization system of the Mars Observer space probe, where oxidizer and fuel shared a common pressurant tank, leading to the loss of the spacecraft in 1993 [324]. In this test, helium saturated with  $\text{NO}_2$  ( $\text{N}_2\text{O}_4$ ) and helium saturated with MMH at 293 K (70 °F) were rapidly injected into an instrumented test section with 65 mL (4 in<sup>3</sup>) internal volume consisting of CRES-304 tubing with an outer diameter (O.D.) of 9.5 mm (3/8-in). There were no observable pressure or temperature spikes as a result of the mixing. The vapor mixing caused a number of complex reactions, resulting in accumulation of solid, yellow residues. Gas-phase analysis showed the presence of nitrous oxide, methyl nitrite, methyl nitrate, methanol, dimethyldiazene, methyl formate, acetonitrile, traces of diazomethane, 2-propanol (cleaning solvent contaminant), and its reaction products acetone and 2-propyl nitrite. Analysis of rinse water showed MMH nitrate and surprisingly high levels of sulfate and phosphate as contaminants (probable residues from aqueous industrial cleaners). Additional tests were performed with hydrazine instead of MMH (because some dual-mode systems, e.g., CASSINI, NEAR, Mars Climate Orbiter, use hydrazine as the fuel and may share a pressurant tank). These tests did not result in explosions.

In the slow, vapor phase reaction of  $\text{N}_2\text{H}_4$  with  $\text{NO}_2$  an intermediate nitrosamine  $\text{ONNH}_2$  has been postulated, but in the case of hydrazine itself, nitrosamine could not be detected because it is very unstable. However, nitrosamines are stable if

hydrogen in hydrazine is substituted by one or two methyl groups. The reaction of MMH with NTO leads to methylamine, dimethylamine, *N*-nitrosomethylamine, *N*-methylformamide, methanol, MMHN, water, nitric oxide, nitrous oxide, nitrogen, and carbon dioxide [325].

Residues from NTO/MMH engines firing in vacuum chambers at steady-state or pulse mode were collected from cryopanel and analyzed [326, 327]. IR spectra of the residues matched those of MMHN (see Section 5.2.1). When introducing gaseous NO<sub>2</sub> into a vacuum chamber containing liquid or solid N<sub>2</sub>H<sub>4</sub>, MMH, Aerozine-50, or UDMH at pressures below 13.3 kPa (100 mm of Hg) and a temperature of 262 K (−11 °C), a flameless reaction took place with a noticeable deposition of a viscous condensed phase. Oily residues thus obtained were identified by IR analyses as nitrate salts of the fuel. The buildup of non-volatile, partially combusted products occurred under these low-pressure conditions where only a flameless reaction takes place, and would lead to pressure spikes next time the engine ignites.

A detailed kinetic model of the gas-phase hypergolic ignition of NTO–MMH mixtures below 298 K and their combustion above 1000 K consisted of 403 reactions among 82 species [328]. The predictions of this mechanism were compared with theoretical data available in the literature and the agreement between theory and predictions was good. Important reactions for ignition at low initial temperature and pressure have been identified through sensitivity analyses. Two competing pathways can explain hypergolic ignition at low temperature. The formation of molecular preignition products was shown to promote the ignition. This conclusion was unexpected, as the formation of these products was generally considered to inhibit the ignition by reactant consumption. Some reactions are important both for low-temperature ignition and combustion, whereas others are important either for ignition only or combustion only.

Previous studies showed the formation of products, appearing as a white-yellow fog, when NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> and MMH vapor come into contact without ignition. This product formation is visible to the naked eye and appears almost instantaneously. Based on UV spectrophotometry measurements, this formation seems to be complete in less than 100 ms. This product formation seems to be unavoidable and is observed even if the two gases are both highly diluted (up to 97 mol-% He). High-speed imagery revealed what happens when a jet of NTO is introduced into a spherical metallic bomb that contains MMH vapor. The formation of product species occurred on a time scale of tens of milliseconds. Kinetic models derived for the NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> and MMH vapor reaction were confirmed by measuring the ignition boundaries of NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> and MMH vapor as a function of helium dilution, mixture ratio, and pressure at room temperature [329].

Reactive collisions between CH<sub>3</sub>NNH<sub>2</sub> + NO<sub>2</sub> and CH<sub>3</sub>NHNH + NO<sub>2</sub> vapors were simulated via direct molecular dynamics simulations [330]. A number of different H-atom abstraction paths were observed, with four isomeric (CH<sub>4</sub>N<sub>2</sub>) products being formed: CH<sub>3</sub>NNH, CH<sub>3</sub>NHN, H<sub>2</sub>CNNH<sub>2</sub>, and CH<sub>2</sub>NHNH. All abstractions were

barrierless, including those from the methyl group. The results suggested that finite rate chemical kinetics mechanisms for MMH/NTO and MMH/red fuming nitric acid (RFNA) systems should include steps for the production and decomposition of  $\text{CH}_3\text{NHNH}$ ,  $\text{H}_2\text{CNNH}_2$ ,  $\text{CH}_2\text{NHNH}$ , and  $\text{CH}_3\text{NHN}$  in addition to those for  $\text{CH}_3\text{NNH}_2$  and  $\text{CH}_3\text{NNH}$  [331]. Five transition states connecting  $\text{CH}_3\text{NHNH}_2 + \text{NO}_2$  complexes were identified. Transition states that connect  $\text{MMH} + \text{HNO}_2$  complexes to each other via H atom exchange and/or hindered internal rotation were also identified. The high point in the minimum energy path from the  $\text{CH}_3\text{NHNH}_2 + \text{NO}_2$  reactant asymptote to the manifold of nitrous acid (HONO)-containing product states was a transition state 36 kJ/mol (8.6 kcal/mol) above the reactant asymptote. From a kinetics standpoint, this value was considerably higher than the 24.7 kJ/mol (5.9 kcal/mol) value that was estimated for it based on theoretical results for H atom abstraction from  $\text{NH}_3$  by  $\text{NO}_2$ . The practical, real-world value of such esoteric calculations remains to be demonstrated.

An examination of the early reaction chemistry of hypergolic reactions between MMH and  $\text{NO}_2$  vapor at room temperature and 1 atm  $\text{N}_2$  used a gold-coated chamber reactor and a FTIR spectrometer [332]. The IR-active species identified in the early reactions include HONO, methylhydrazinium nitrite ( $\text{MMH} \cdot \text{HONO}$ ), methyl diazene ( $\text{CH}_3\text{N}=\text{NH}$ ), methyl nitrate ( $\text{CH}_3\text{ONO}_2$ ), methyl nitrite ( $\text{CH}_3\text{ONO}$ ), nitromethane ( $\text{CH}_3\text{NO}_2$ ), methyl azide ( $\text{CH}_3\text{N}_3$ ),  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}$ . Based on quantum mechanical studies, it was proposed that the oxidation of MMH in an atmosphere of  $\text{NO}_2$  occurs via two mechanisms: **(1)** sequential H-abstraction and HONO formation, and **(2)** reaction of MMH with asymmetric  $\text{ONONO}_2$ , leading to formation of methyl nitrate. These mechanisms successfully explain all intermediates observed experimentally. It was theorized that the formation of asymmetric  $\text{ONONO}_2$  is assisted by an aerosol formed by HONO and MMH that provides a large surface area for  $\text{ONONO}_2$  to condense, leading to the generation of methyl nitrate. It was proposed that the overall pre-ignition process involves both gas-phase and aerosol-phase reactions. Quantum mechanics calculations were supposed to expose the possible mechanisms by which these products were formed. These studies proposed that the intermediates found within the condensate play a fundamental role in the ignition event. Regarding  $\text{MMH}-\text{NO}_2$  liquid-phase reactions, it was not possible to find rate constants or activation energies in open literature. For the  $\text{MMH} + \text{NO}_2 \rightarrow \text{HONO} + \text{methylhydrazyl}$  radical reaction, Catoire et al. estimated an activation energy value of 24.7 kJ/mol (5.9 kcal/mol) based on comparisons with reactions between  $\text{NH}_3$  and  $\text{NO}_2$ . As both reactions involve hydrogen atom abstraction, the comparison was thought to be valid.

In addition to ignition delay measurements and high-speed camera recordings of NTO/MMH and RFNA/MMH droplet reactions, time-resolved UV/vis emission spectra of NTO/MMH and RFNA/MMH ignition flames were recorded with a streak camera coupled with a spectrometer for species emitting wavelengths from 250 to 950 nm

within a point of interest above the reaction zone measuring 1 mm in diameter [333]. NTO/MMH consistently produced brighter flames than RFNA/MMH and as such generally generated higher intensity signals for a given spectrometer setting. Both propellant combinations revealed conclusive evidence for OH and NH radicals and probable evidence of CN and/or CH radicals. In most tests OH yielded the highest intensity signals with both RFNA and NTO. NTO/MMH revealed greater NH intensity than RFNA/MMH.

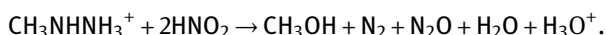
#### 4.6.1.9 Reaction Kinetics of N<sub>2</sub>O<sub>4</sub>/MMH Reactions

A substantial amount of information is available on liquid–liquid interaction of N<sub>2</sub>O<sub>4</sub> and MMH, leading to hypergolic ignition and use of this propellant combination in thousands of rocket engines. Very rarely does the need arise to look at the vapor-phase reaction of N<sub>2</sub>O<sub>4</sub> and MMH under conditions that do not immediately lead to ignition.

Potential problem areas in the design of storable bipropellant systems are the pressurization systems if they share a pressurant tank. Under ordinary conditions, propellant vapors would not back up into the helium as they are separated by a series of enable valves, check valves, and pressure regulators. During long interplanetary cruise phases, while the system is idle, it is possible for propellant vapors to permeate through the Teflon seat material of the valves and condense on the other side if that is the coldest part of the system. The reaction of N<sub>2</sub>O<sub>4</sub> and MMH diluted in high-pressure helium (15 MPa = 250 psia) was studied already in 1989, a study that would later help to explain the loss of the Mars Observer space probe in 1993 [334]. In this test, helium saturated with N<sub>2</sub>O<sub>4</sub> and helium saturated with MMH were rapidly injected into an instrumented test section with 65 m (4 in<sup>3</sup>) volume consisting of CRES-304 tubing with an O.D. of 9.5 mm (3/8-in). There were no observable pressure or temperature spikes as a result of the mixing.

#### 4.6.1.10 Reaction of MMH with Nitrous Acid Nitrosation of Methylhydrazines

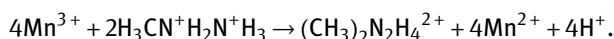
Although it is not possible to isolate the nitrosohydrazine as an intermediate in the NO<sub>2</sub>–hydrazine reaction, the nitroso derivatives of MMH and UDMH are stable enough to be isolated as intermediates. The nitrosation of MMH and UDMH proceeds through their conjugate acids and can be achieved with nitrous acid, nitrosonium ion, or nitrosyl halides as an electrophilic agent. For MMH, the product distribution shows that sizeable proportions of both possible protonated methylhydrazines must exist in solution. In the presence of an excess of nitrous acid, a secondary reaction can lead to the destruction of nitrosomethylhydrazine. The possible involvement of a dinitroso intermediate cannot be excluded. Reaction products are methanol, dinitrogen, and dinitrogen oxide:



#### 4.6.1.11 Mechanism and Kinetics of the Oxidation of MMH in Solution

The products of monoalkyl hydrazine oxidation depend on the type of oxidant used. Oxidation by air or oxygen or nitrogen dioxide was already discussed above. For other types of oxidizers, for example, when MMH is oxidized by hexacyanoferrate(III) or periodate in alkaline solution, it is converted to methane. Other monoalkylhydrazines are likewise converted to the corresponding alkanes. Surprisingly, oxidation of alkylhydrazines by iodine in non-aqueous or aqueous media gives alkyl iodides in good yields, better than 70% [335]. A little alkane is usually formed as a by-product by reduction of the alkyl iodide. In aqueous media, some alkanols are formed as well.

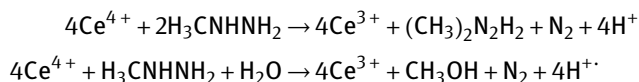
When studying the stoichiometry and kinetics of MMH oxidation by manganese(III), it was found that Mn(III) oxidizes MMH according to the following equation without formation of nitrogen [336]:



When using cerium(IV) in acid solution in place of manganese(III), a rate expression:

$$-d[\text{Ce(IV)}]/dt = K_H[\text{Ce(IV)}][\text{CH}_3\text{N}_2\text{H}_4^+]$$

was found that was identical in form to that found for Mn(III), but construed a different mechanism because nitrogen gas was evolved [337]. The  $k_H$  value was found to be pH dependent. When the molar ratio MMH:Ce(IV) was higher than 4, the molar ratio of  $\text{N}_2$  evolved to Ce(IV) consumed was 1:4. The observed stoichiometry can be explained by either one of the following two equations:



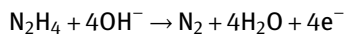
Radical cations of MMH and UDMH were generated by reaction of MMH or UDMH with cerium(IV) in sulfuric acid solutions in a fast-flow mixing chamber, and the electron spin resonance (ESR) spectra of these short-lived intermediates were recorded and experimental nitrogen and proton coupling constants determined [338]. Molecular orbital calculations for molecules were performed and the implications for reaction mechanisms for the oxidation of the hydrazines were explained.

#### 4.6.1.12 Electro-Oxidation of MMH in Solution

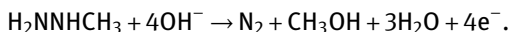
The electrochemical oxidation of hydrazine or MMH forms the basis of a rocket propellant vapor-sensing device used to monitor the space shuttle launch pad [339]. In alkaline electrolytes, such as 23% KOH, both hydrazine and MMH were electro-oxidized on gold electrodes at all potentials. It was possible to minimize interference by maintaining the sensing electrode potential at 1.1 V, where CO and NO are unreactive and where the signal caused by  $\text{NO}_2$  is weak. Of course, in a flow-through instrument, not all the contaminants are oxidized at high flow rates, whereas at low flow rates,



all the hydrazines are oxidized. If one plots the number  $z$  of electrons consumed per unit reaction as a function of gas flow rate, the curve intersects the ordinate at  $z = 4$  for flow rates approaching zero. This can be explained if one assumes that the overall electrochemical oxidation of hydrazine at 1.1 V on gold proceeds as:

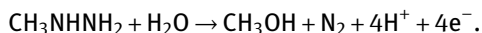


and likewise for MMH:



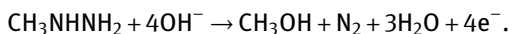
In analogy to the studies on hydrazine, the electro-oxidation of MMH, UDMH, and SDMH at a platinum electrode has been investigated using chronopotentiometry, coulometry, and product analysis [340]. Controlled potential coulometric oxidation of the MMH experiments were performed in a gas-tight cell designed for gas volume measurements and product analysis. Because of the strong dependence on such factors as the nature of the electrode surface and spontaneous catalytic decomposition of the methylhydrazines at the electrode surface, the reproducibility of the data was only fair. The results of this study bear certain significance for the attempted polarographic analysis of these compounds. The results showed that MMH is oxidized in a four-electron (gross) reaction to nitrogen and methanol. The measurements were done with an experimental setup that can collect, measure, and analyze gaseous electrolysis products of alkylhydrazines [341].

Three different methods were used to study the anodic oxidation of MMH and UDMH: cyclic voltammetry, controlled potential electrolysis, and potentiostatic step measurements [342]. The oxidation was achieved on smooth platinum electrodes in 1 M sulfuric acid or 2 M perchloric acid. The oxidation of MMH liberates four electrons according to:

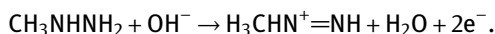


Methyldiazene (= methyldiimine)  $\text{CH}_3\text{N}=\text{NH}$  is a very likely intermediate oxidation product that had already been postulated by previous investigators.

The electro-oxidation of MMH in alkaline solutions has been studied on a mercury electrode [343]. Polarography and cyclic voltammetry were used to determine the parameters of the oxidation process. A mechanism that fits the experimental results was proposed in which the rate-determining step consists of the reaction of an adsorbed OH radical with an MMH molecule. The electro-oxidation of MMH on a gold electrode in  $\text{H}_2\text{SO}_4$  has been studied by linear sweep, steady-state, and quasi steady-state methods [344]. The oxidation process mechanism involves two fast de-electronation reactions and the rate-determining step is an activated desorption step. The following reaction has been proposed:



The rate-determining step involves a diazenium cation:



Although the overall reaction yields four electrons, the kinetics are determined by a one-electron step. The shape of the current-potential curve was dependent on the anion present (sulfate or perchlorate). This may be caused by the different oxygen density on the anode, an effect that may be superimposed on the true electrochemical MMH oxidation. The peak in the polarogram may be caused by both modes of oxidation.

#### 4.6.1.13 Complex-Forming Reactions of Alkylhydrazines

Just like its parent molecule, hydrazine, MMH can serve as a bidentate or unidentate ligand in complexes with transition metal cations [345]. Some of such complexes may be found among the corrosion products of contaminated MMH that was stored in metal tanks. The aqueous solution reactions between cobalt(II) chloride and MMH or UDMH lead only to precipitation of cobalt (II) hydroxide owing to the greater basic strengths of these ligands. The addition of MMH to a solution of cobalt(II)chloride hexahydrate in alcohol gave a pale violet precipitate of  $\text{CoCl}_2 \cdot 2\text{MMH}$  [346]. In the absence of a solvent, a compound  $\text{CoCl}_2 \cdot 6\text{MMH}$  is obtained, which is unstable in moist air and insoluble in MMH. In UDMH,  $\text{CoCl}_2$  gives an intensely blue solution, from which deep blue tetrahedral  $\text{CoCl}_2 \cdot 2\text{UDMH}$  crystals can be crystallized. This complex most likely has a tetrahedral structure with UDMH serving as a unidentate ligand. An octahedral complex could not be obtained, which may be due to steric hindrance of the methyl group(s). In the cationic complex  $[\text{Co}(\text{MeNHNH}_2)_6]\text{Cl}_2$ , the ligands are unidentate but in  $\text{CoCl}_2 \cdot (\text{MeNHNH}_2)_2$  the crystals are polymeric, with bridging and bidentate hydrazines. This pale violet precipitate of  $\text{CoCl}_2 \cdot (\text{MeNHNH}_2)_2$ , like the hydrazine analog, is insoluble in solvents with which it does not react. Similar complexes are formed with cobalt salts where the anion is bromide, iodide or isothiocyanate instead of chloride and two or six ligands are tied to the central cobalt atom [347].

The IR spectra and magnetic properties of eight complexes of nickel(II) chloride with hydrazine, MMH, or UDMH were measured [348]. In complex structures similar to the hydrazine-bridged complex  $\text{Ni}(\text{N}_2\text{H}_4)_2\text{Cl}_2$ , nickel(II) chloride forms  $\text{Ni}(\text{N}_2\text{H}_4)_3\text{Cl}_2$  in which the nickel atom is surrounded by six nitrogen atoms as nearest neighbors. In a similar vein, MMH forms  $\text{Ni}(\text{MeNHNH}_2)_2\text{Cl}_2$  and  $\text{Ni}(\text{MeNHNH}_2)_6\text{Cl}_2$  whereas 1,1-dimethylhydrazine forms  $\text{NiCl}_2 \cdot 4\text{UDMH}$ ,  $\text{NiCl}_2 \cdot 2\text{UDMH}$ , and  $\text{NiCl}_2 \cdot \text{UDMH}$ . The spectra and magnetic moments of all the complexes were consistent with octahedral (or tetragonal) stereochemistry.

A full normal coordinate analysis has been carried out on MMH, *N*-deuterated MMH, and the bidentate nickel complex  $\text{NiCl}_2 \cdot (\text{NH}_2\text{NHCH}_3)_2$  [349]. The  $C_{3v}$  symmetry of the methyl group is lost in MMH. Nevertheless, the concept of specific methyl group modes is still valuable. The N—N stretching mode is relatively pure, enabling it to be used as a criterion of coordination in complexes with transition metals. Interest-

ing changes were observed for the wagging and twisting modes of the  $\text{NH}_2$  group on coordination in a complex.

Methylhydrazine and methylhydrazinium chloride complexes of copper in various oxidation states (1+, 2+) have been prepared and characterized by elemental analyses and magnetic data [350]. The thermal decomposition of these complexes was studied by simultaneous DTA, TGA, and DTG. The complex  $\text{Cu(II)Cl}_2 \cdot (\text{NH}_3\text{NHCH}_3\text{Cl})$  decomposed on heating with reduction to  $\text{Cu(I)Cl}$ . Significantly, the mixed valence complex  $\text{Cu}_3(\text{2I, II})\text{Cl}_6(\text{NH}_3\text{NHCH}_3)_2$  on heating disproportionated as follows:  $3\text{Cu} \rightarrow 2\text{Cu(I)} + \text{Cu(II)}$ .

#### 4.6.1.14 Reaction of MMH with Carbon Dioxide

Methylhydrazine absorbs  $\text{CO}_2$  rapidly from the air, with a more than eleven-fold increase in  $\text{CO}_2$  content during the first 10 min. of an open-air experiment with 20 mL MMH in a 50-mL beaker [351]. After 60 min., the  $\text{CO}_2$  concentration had increased to 1600 ppm. Typical propellant samples taken from drums and flight systems contained 25 to 224 ppm  $\text{CO}_2$ . Carbon dioxide in MMH exists in the form of methylcarbamic acid, which forms salts and complexes with many metals. Methylhydrazine and  $\text{CO}_2$  give the thermally unstable salt  $[\text{CH}_3\text{NHNH}^+\text{H}_3]=[\text{CH}_3\text{NHNHCOO}^-]$ , which can react with  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  in ethanol to give  $[\text{Cr}^{\text{III}}(\text{H}_3\text{CNHNHCOO})_3] \cdot \text{H}_2\text{O}$  [352].

The stability of MMH is greatly affected by the presence of impurities. Six new metal complexes containing methylhydrazinecarboxylate and 1,1-dimethylhydrazinecarboxylate were prepared and the effects of these complexes on the homogeneous decomposition rates of the propellants were investigated. It was concluded that the  $\text{Mn(II)}$  methylhydrazinecarboxylate complex has a greater effect than either the  $\text{Cr(III)}$  or the  $\text{Ni(II)}$  complexes on the stability of MMH [353]. It was concluded that impurity profiles and stability are greatly affected by the manufacturing method.

Methylhydrazine, hydrazine, or ethylenediamine react readily and reversibly with carbon dioxide to form methylhydrazinium carboxylate, hydrazinium carboxylate, or ammonium carbamate adducts, respectively [354]. These adducts act as low-molecular-weight gelators, which self-assemble and in doing so trap unreacted hydrazines or diamine. The properties and molecular structures of the gels were investigated by means of elemental analysis, DSC-TGA, heteronuclear NMR ( $^1\text{H}$ ,  $^{15}\text{N}$ , and  $^{13}\text{C}$ ), diffusion-ordered NMR spectroscopy, and cryo-immobilized high-resolution scanning electron microscopy (SEM), providing a pictorial representation of the bulk gel structures on the molecular level.

#### 4.6.2 Reactions of MMH with Organic Compounds

Reactions of acyl chlorides and anhydrides with MMH lead to methylhydrazides of the carbonic acids. Reactions of MMH with carbonyl compounds are sometimes per-

formed as an intermediate step in the synthesis of heterocycles. Reaction of MMH or hydrazine with formaldehyde and methylamine led to cyclic 1,2,4- or 1,3,5-triazine derivatives.

Before getting too involved in the complex area of hydrazine reactions with carbonyl compounds, it may help to clarify the nomenclature here:

|                 |           |
|-----------------|-----------|
| $R-CH=N-NH_2$   | aldazone  |
| $R-CH=N-N=CH-R$ | aldazine  |
| $R_2C=N-NH_2$   | hydrazone |
| $R_2C=N-N=CR_2$ | ketazine  |

## 4.7 Analysis of MMH

The analysis of MMH is of importance in the production, quality control, application, occupational hygiene, and environmental control of this propellant. For the most part, the analysis methods will have to be quantitative. Many excellent monographs and survey articles appeared several decades ago, which makes a separate chapter on hydrazine(s) analysis almost unnecessary. A useful reference on this subject is a book on the determination of hydrazino-hydrazide groups [355]. The same author also published several chapters on hydrazines in a book on the analysis of rocket propellants [356] and did a thesis on the analysis of hydrazine compounds [357].

Most of the methods of analysis of MMH can also be used for the determination of hydrazine and/or UDMH. It is unavoidable that several of the references in this section will appear more than once. In some instances, if two or more hydrazines are present, it may be difficult to separate them from each other to obtain individual quantity assessment.

Most analytical procedures are performed in the convenience of a chemistry laboratory, but in the case of rocket propellants, it will also be necessary to have portable instruments that operate under rugged conditions at launch sites, in the battle field, or at sites of suspected environmental pollution.

### 4.7.1 Qualitative Analysis of MMH

Qualitative analyses of MMH and other hydrazines give only a “yes” or “no” answer and alert the analyst to a potential source of pollution or hazardous conditions for propellant handling personnel. In most cases, a surprise positive qualitative test will require a follow-up using a calibrated quantitative analysis method.

### 4.7.2 Assay and Specification Analysis of MMH

Propellant that has been off-loaded from reusable spacecraft such as the Space Shuttle has to be discarded or recycled, regenerated, and re-qualified before it can be loaded

into a spacecraft or launch vehicle again. A NASA specification describes the recommended handling, sampling, and analysis methods for hydrazine-based fuels such that it can be decided if the material should be reprocessed, returned to the manufacturer for reprocessing, or discarded [358]. A bench-top distillation unit was able to reduce NVR contamination levels in off-loaded MMH of 12 to 25 mg/L to a level of 0.1 to 0.2 mg/L so it would again meet military (MIL) and NASA specs [72]. This testing was done in preparation for the installation of a larger distillation unit.

#### 4.7.3 Gas Chromatographic Analysis Methods for MMH

Gas chromatography is the most versatile method for both quantitative and qualitative (quality control) analysis of alkylhydrazines. Most alkylhydrazines are of sufficient volatility to allow separation from each other and from other constituents by GC. However, the tendency of most alkylhydrazines to undergo thermal or catalytic decomposition severely limits the operating temperatures and the choice of materials in the GC system. Gas chromatography is also used for the analysis of gaseous decomposition products of alkylhydrazines. Most of the GC applications use a liquid stationary phase, and the exact abbreviation would be GLC. Suffice it here to say that GC and GLC are intended to serve as abbreviations for the same analytical methods.

Methylhydrazine, water, and hydrazine were nicely separated at 383 K on a column measuring 1/4-in. in diameter  $\times$  6 ft long filled with 10% Dowfax 9N9 on 60–80-mesh Teflon-6 [359, 360]. The fractogram also revealed traces of nitrogen and ammonia. For calibration purposes, response factors for water in hydrazine or MMH were determined by analyzing calibration mixtures of known composition. The reciprocal response ratio for water in MMH remained constant (1.15–1.20) for mixtures with 16–72% H<sub>2</sub>O in MMH. The column did not give satisfactory separation of UDMH from water in any of these mixtures. The column showed no loss of separating power after 200 injections. The addition of 1% sodium hydroxide to the stationary phase did not improve hydrazine separation, and better results were achieved in columns without NaOH.

##### 4.7.3.1 Gas Chromatographic Analysis of Impurities in MMH

Propellant-grade MMH analyzed on a 12-ft  $\times$  1/4-in. column packed with 4% Quadrol on Chromosorb T showed ammonia, AM, methylamine, water, and hydrazine, plus six unidentified peaks as contaminants [206]. Some of the unknowns could possibly be methanol, formaldehyde methylhydrazone, and cyanogen derivatives. Several of these unknown peaks increased in size if the MMH was analyzed after heating it to 473 K for 21 h.

In a similar study, MMH was analyzed on a 6-ft  $\times$  0.125-in. column packed with 100–120-mesh Chromosorb 103 [230]. Propellant-grade MMH samples typically contained 100 ppm methanol, 50 ppm ethane, 50 ppm AM, 50 ppm SDMH, and 50 ppm UDMH. Most of the contaminants were thought to be the result of air oxidation.

The analysis methods specified in earlier Military Specifications for hydrazines and hydrazine mixtures used packed GC columns, which usually resulted in broad, poorly resolved peaks. Increased component information and analysis speed can be achieved with capillary gas chromatography. Two capillary column methods of hydrazine analyses were developed at NASA WSTF and shared with round-robin participants. A round-robin analysis campaign was conducted with seven participating laboratories to gather multiple laboratory precision data for analysis of hydrazines using capillary GC [361]. Acceptable data were received from six of the laboratories. The fuels were analyzed for water, aniline, and other volatile carbonaceous material such as isopropyl alcohol. Statistical analysis of the results suggested that increased analyst experience with these capillary GC methods should significantly reduce inter-laboratory differences in the future.

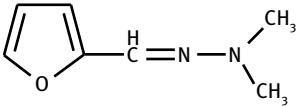
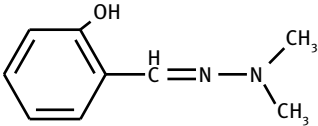
Only a few methods that combine GC with means of identifying the eluting peaks other than by retention volume give completely satisfactory results. GC-MS gives the  $m/e$  of the fragments of the eluting hydrazine and alkylhydrazines, but in the presence of organic contaminants, many CH compounds have fragment peaks at the same  $m/e$  ratios as NH compounds. GC-IR has attempted to avoid this problem by using IR absorption lines specifically for hydrazines [362]. The effluent from the GC was passed through a gold-plated optical waveguide with multiple reflections where IR absorption took place. The spectra were processed in an FTIR computer for compound identification.

The stability of MMH is greatly affected by the presence of impurities. Most organic impurities are present in the propellant from manufacture. In order to assess the likely range of impurities a review of manufacturing methods for propellant hydrazines was undertaken. This was followed by a stability assessment and impurity survey (using GC-MS) on samples of MMH and UDMH from four different sources [353]. It was concluded that impurity profiles and stability are greatly affected by the manufacturing method.

#### 4.7.3.2 Gas Chromatography of MMH Following Derivatization

The detection limit for toxic or otherwise troublesome contaminants by GC has generally been improved by several orders of magnitude through the introduction of the Flame Ionization Detector (FID) as the detector at the exit of the GC column. However, the FID is “blind” to hydrazine that combusts only to nitrogen and water. Alkylhydrazines give only a weak signal because they contain very little carbon. The sensitivity for detection of hydrazine(s) by GC-FID can be improved by converting hydrazine(s) to volatile, thermally stable organic derivatives with high carbon (or even some halogen or silicon) content, such as hydrazones or azines. Similarly, the electron capture detector is very sensitive to halogen, and halogen-containing derivatizing agents improve the detection limit dramatically. Derivatives formed between alkylhydrazines and aldehydes or ketones are shown in Table 35.

**Table 35:** Derivatives formed with methylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH).

| Reagent used                | Type of hydrazine analyzed | Derivative formed                                                                  |
|-----------------------------|----------------------------|------------------------------------------------------------------------------------|
| Acetone                     | MMH                        | $\text{CH}_3\text{NH}-\text{N}=\text{C}(\text{CH}_3)_2$                            |
| Acetone                     | UDMH                       | $(\text{CH}_3)_2\text{N}-\text{N}=\text{C}(\text{CH}_3)_2$                         |
| 2,4-Dinitrobenzaldehyde     | MMH                        | $\text{CH}_3\text{NH}-\text{N}=\text{CHC}_6\text{H}_3(\text{NO}_2)_2$              |
| 2,4-Dinitrobenzaldehyde     | UDMH                       | $(\text{CH}_3)_2\text{N}-\text{N}=\text{CHC}_6\text{H}_3(\text{NO}_2)_2$           |
| Furaldehyde                 | UDMH                       |  |
| 2-Nitrobenzaldehyde         | UDMH, daminozide           | $(\text{NO}_2)\text{C}_6\text{H}_4\text{CH}=\text{N}-\text{N}(\text{CH}_3)_2$      |
| Pentane-2,4-dione           | MMH                        |                                                                                    |
| Pentane-2,4-dione           | UDMH                       | $\text{H}_3\text{CCOCH}_2\text{C}(\text{CH}_3)=\text{N}-\text{N}(\text{CH}_3)_2$   |
| Pentafluorobenzoyl chloride | UDMH                       | $(\text{C}_6\text{F}_5\text{CO})_2\text{N}-\text{N}(\text{CH}_3)_2$                |
| Salicylaldehyde             | UDMH                       |  |

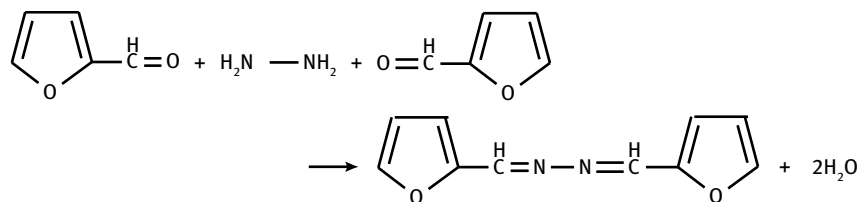
One disadvantage of derivatization with 2,4-pentanedione is that this method needs an excess of derivatizing agent for the analysis of mixtures containing UDMH and cannot be used for SDMH in addition to hydrazine or MMH. An alternative derivatization method has been developed using an excess of acetone forming the respective hydrazones of hydrazine, MMH, or UDMH [32]. The hydrazones are then extracted into dichloromethane and separated by GC-FID on a 60-m glass capillary column. In the extract, as little as 0.5 µg/mL UDMH or MMH and 0.2 µg/mL hydrazine could be detected as the hydrazones. The peak area/response factors were determined for synthetic mixtures containing known amounts of the three hydrazines. The recoveries for hydrazine, MMH, and UDMH were 96.2, 98.3, and 97.7% respectively. The turnaround time for this method is very fast, only 20 min for a trained operator. Benzaldehyde and cyclohexanone have been tested as derivatizing agents [363].

**Acetone.** If MMH or UDMH vapors are directly trapped into micro-impingers containing chilled acetone, they are immobilized and derivatized at the same time. The contents of the impingers can be injected without additional sample preparation and the two hydrazones and acetone azine are easily separated by GC using nitrogen-specific thermionic or Thermal Energy Analyzer detectors. This method is much faster

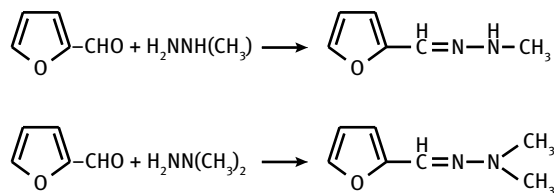
than conventional collection/derivatization methods and is sensitive down to 20 ppb [364, 365]. This procedure used a chilled acetone collection medium that quantitatively trapped the hydrazines and converted them to stable derivatives in a single step. The acetone solution was then assayed directly for the derivatives by using a gas chromatograph with a nitrogen-specific detector. The results obtained from this procedure were in excellent agreement with results obtained using independent analytical techniques, and the overall precision of the method was better than 5% (relative standard deviation) for 90 ppb hydrazine. The minimum detectable concentration was estimated to be approximately 4 ppb. The overall precision was better than 6% for 143 ppb MMH in air. The derivatives formed within minutes in the impinger and were stable in solution for a month. The acetone derivative of MMH was sensitive to light.

A gas chromatographic-mass spectrometric method was developed for analyzing trace levels of MMH in an experimental drug substance [366]. The method used acetone as a dissolving solvent for the drug substance and a derivatizing agent for MMH in the meantime, thus eliminating the need for post-derivatization sample clean-up prior to analysis. The gas chromatographic (direct injection) conditions provided good separation for the acetone-MMH derivative (acetone methylhydrazone) from matrix interference, and mass spectrometric detection (selected ion monitoring mode,  $m/z$  86) enabled detection of 1 part per million (by mass) MMH relative to the drug substance.

**2-Furaldehyde** has been used as a derivatizing agent for all three hydrazines [367, 368]. The method uses sampling tubes containing silica gel or firebrick granules coated with sulfuric acid to analyze for hydrazines in air [369, 370]. After drawing a known volume of workroom air through the tube, the hydrazines as sulfates are extracted from the sorbent with water, liberated with sodium acetate, and reacted with 2-furaldehyde to form azines:



or hydrazones:





The hydrazones and/or azines are extracted using ethyl acetate and quantified by GC after calibration with known standards. A Silicone OV-7 glass column in a gas chromatograph with FID detector gave good separation of the derivatives of all three hydrazines ( $N_2H_4$ , MMH, and UDMH) when the column oven temperature was raised by linear programming.

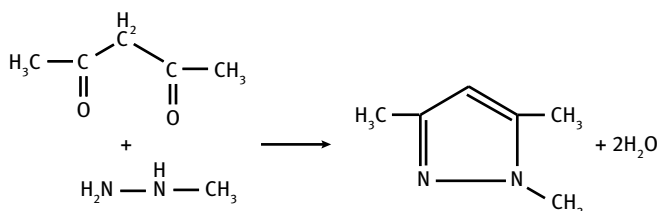
Firebrick is preferred as an absorbent, because it is geometrically stable in moist environments, and is better than silica gel for this application [371, 372]. The firebrick method was evaluated under field conditions and found to be superior in handling convenience to the previously used liquid acid impingers.

In addition to the analysis of air samples, furaldehyde derivatization has also been successfully used for the analysis of contamination in ground water [373], but this method is not applicable to MMH, because of incomplete derivatization and instability of the derivative. Instead, MMH in the same matrix has to be derivatized with 2,4-pentadione and analyzed as the pyrazole (see below).

***p*-Chlorobenzaldehyde.** Hydrazine or MMH in urine or blood can be derivatized with *p*-chlorobenzaldehyde, extracted with dichloromethane, and separated by GLC in glass columns with FID [374]. *o*-Chlorobenzaldehyde serves the same purpose for GC analysis with an electron capture detector.

A modification of the method by Timbrell et al. [375] can be used to analyze rat urine for MMH and MMH metabolites containing the  $-NH_2$  group. The modification involved the reaction of *p*-chlorobenzaldehyde (PCBA) to form hydrazones and *p*-chlorobenzaldehyde azine, which were recovered by extraction with dichloromethane. In order to collect the samples, a solution of 25 mg of PCBA in 0.1 mL of methanol was added to each milliliter of freshly voided urine. The derivatized metabolites were extracted using dichloromethane, dried over sodium sulfate, filtered, and concentrated by distilling off the solvent in a rotary evaporator. Prior to analysis by GC, the samples were redissolved in ethyl acetate for injection into the GC with FID. Individual derivative fractions were identified by GC-MS.

**2,4-Pentanedione.** A GC analysis method for trace amounts of hydrazine and/or MMH in water in concentrations of 0.1–50 ppm was based on conversion of hydrazine(s) to the corresponding pyrazole by reaction with pentanedione-2,4 [376]:

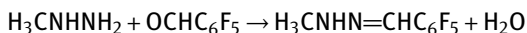


The stationary phase was a mixture of 16.7% Amine 220 (Applied Science) and 83.3% Apiezon L (Analabs) on Anakrom ABS. The method was not disturbed by the

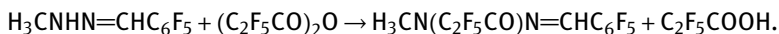
presence of UDMH, urea, or alanine, which caused high readings with use of the *p*-dimethylaminobenzaldehyde (PDAB) spectrophotometric method. Interference by  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ion can be reduced by the addition of  $\text{Na}_2\text{EDTA}$ . Once formed, the pyrazole solutions in water were very stable, and no change in concentration was noted over several months. This method was found to be useful for analysis of trace hydrazine ( $\text{N}_2\text{H}_4$ ) in environmental degradation studies [377]. In these studies it was shown that hydrazine degrades in the presence of atmospheric oxygen ( $t_{1/2}$  approximately 6 h) and in oxygenated aqueous solutions ( $t_{1/2}$  approximately 5 days).

In addition to the analysis of air samples, pentanedione derivatization has also been successfully used for the analysis of MMH contamination in ground water [373]. Separation was on Tenax-packed glass columns and detection was with the use of an FID detector. The detection limit was approximately 1.5 ppm MMH. When soil samples were amended with known amounts of MMH, constant amounts of MMH were not recoverable by acid extraction with 0.9 *N* sulfuric acid owing to irreversible reactions in the soil [378]. The filtered sulfuric acid soil extracts (~200 mL) were immediately derivatized by adding 5 mL pentanedione and adjusting the pH to 9 using 50% NaOH solution. The solution was then diluted to 500 mL with water and immediately analyzed by GC using a Carbowax 20M capillary column, temperature programming, and a thermionic ionization detector. The minimum detectable concentrations in the soil were 0.2 ppm MMH.

**Pentafluorobenzaldehyde.** A quantitative electron-capture gas chromatographic assay procedure was developed for the analysis of monoalkylhydrazines in biological samples [379]. In a further modification of this method, several monoalkylhydrazines including MMH in blood samples were derivatized not only with pentafluorobenzaldehyde to form a hydrazone:



but the remaining N—H hydrogen atom on the hydrazone was also substituted with a pentafluoropropionyl group by reaction with pentafluoropropionic anhydride, further increasing the fluorine content and the detectability of the derivative:



Gas chromatography analysis was then performed on a 30-m fused silica capillary column temperature programmed from 353 to 573 K and an electron capture detector with  $^{63}\text{Ni}$  isotope. Benzylhydrazine was used as an internal standard. Four monoalkylhydrazines were analyzed in whole blood by reaction with pentafluorobenzaldehyde to form stable hydrazone derivatives that were extracted and subsequently reacted with pentafluoropropionic anhydride to give products that were very sensitive to electron-capture detection when analyzed by GC. MMH yielded a single derivative with this procedure, suggesting that the analytical procedure has a broad application to the analysis of other monoalkylated hydrazines.

**Pentafluorobenzoyl chloride.** Traces of MMH found in the mushroom toxin gyromitrin can be analyzed by GC-MS following derivatization with pentafluorobenzoyl chloride [380]. The minimum detectable concentration of MMH by this method was estimated to be approximately 12 pg/ $\mu$ L.

**Pentafluoropropionic anhydride.** MMH in blood can be analyzed following derivatization with pentafluoropropionic anhydride and separation by GC with electron-capture detection [379].

**Chemiluminescence detection.** A Thermedics TEA-510 *N*-nitrosamine detector was interfaced with a modified GC for the specific detection of airborne hydrazine rocket propellant vapors [381]. The analysis involved an *in situ* derivatization followed by GC with chemiluminescence detection. The apparatus consisted of GC equipped with a sample inlet line, a derivatization chamber, delivery systems for the derivatizing agent and reaction catalyst, the TEA-510 chemiluminescence detector, and a PC to process data and control automatic sampling and analysis. Environmental air samples were aspirated into a chamber where trace levels of hydrazines could be extracted and concentrated from air samples for analysis. Derivatization was followed by a separation step utilizing capillary GC. Individual components were then quantified by the chemiluminescent reaction of nitric oxide and ozone. Preliminary results indicated that the system can detect 10 ppb of MMH, with a sampling time of 5 s and a total analysis turnaround time of 27 s. It should be possible to reduce detection limits further by increasing the sampling time.

#### 4.7.3.3 Reaction Gas Chromatography of MMH

The oxidation of MMH with sodium hypochlorite leads to nitrogen, methane, carbon monoxide, and traces of alkyl chlorides. The amount of methane formed is proportional to the amount of MMH present and can form the basis of an indirect GC method for the determination of MMH [382]. The methane produced represented only 25% of theoretical if it is assumed that 1 mol of methane is formed for each mol of MMH reacted. The MMH concentration in the reacting aqueous solution should not exceed 5%, and the lower limit of detectability is 0.3% MMH. The ratio of methane to nitrogen has been used to determine the MMH. This eliminated the day-to-day variation of integrator counts with detector current and effects of equipment aging. It is best to keep the reacting liquid nearly saturated with KCl to minimize solubility of methane in the liquid phase.

Hydrazine/MMH and hydrazine/UDMH mixtures can be analyzed by reactive column GC [383]. Linearity of methane production with sample size could be demonstrated if decomposition occurred on a copper oxide catalyst heated to 573 K. Nitrogen and methane were then analyzed on a 1.8-m  $\times$  6-mm column packed with 30–60 mesh molecular sieve 5A. The methyl substituted component was determined by comparison of the methane peak area with a calibration curve obtained from synthetic blends of the two components. Whereas the hydrazine/MMH mixtures gave a linear methane peak area response between 20 and 80% MMH, the point for pure MMH was not on

the line, and the practically more important 86% MMH mixture was not run, leaving some questions as to the suitability of this method for MHF-3 analysis. In repetitive analysis of 50:50  $\text{N}_2\text{H}_4$ /MMH mixtures, a coefficient of variation of 1.7% (for MMH) was obtained, corresponding to a standard deviation of  $\pm 0.9\%$  relative.

#### 4.7.4 Thin Layer Chromatography of Methylhydrazines

Hydrazine, MMH, SDMH, and UDMH as their dichloride salts can be separated by Thin Layer Chromatography (TLC) on cellulose powder on glass plates, using 2-propanol/water/concentrated HCl in a volume ratio of 130:40:30 as the eluent [384]. Folin–Ciocalteu reagent was used to develop the plates and formed distinct blue spots equally well with all four hydrazines, whereas PDAB did not react with SDMH. Using 366 nm UV light to stimulate fluorescence, hydrazine could be detected at the nanogram level after reaction with fluorescamine and isomeric phthalaldehydes [385]. Two nanograms of MMH from the hydrolysis of gyromitrin in mushrooms was determined by derivatization with PDAB, separation on a glass plate coated with cellulose powder, *n*-butanol/ethanol/water 4/1/2 eluent, and spectrofluorimetric analysis [386].

#### 4.7.5 High-Performance Liquid Chromatographic Analysis Methods for MMH Mixtures

##### 4.7.5.1 High-Performance Liquid Chromatographic Analysis of MMH Without Prior Derivatization

Hydrazine, MMH, UDMH, and SDMH can be separated and determined by ion-exchange high performance liquid chromatography (HPLC) using an electrochemical detector with glassy carbon working and auxiliary electrodes [387]. The hydrazines do not require derivatization and urine or blood plasma samples suspected of containing these compounds may be analyzed directly without previous work-up.

A liquid chromatography-tandem mass spectrometry method for the simultaneous determination of MMH, UDMH, and UDMH decay products used an isocratic mode on an analytical column with a Nucleosil-100-5SA sulfo-cation-exchanger [388]. The mobile phase composition was optimized in order to achieve effective separation of all analytes and provide high sensitivity of mass spectrometric detection. An ammonium acetate buffer solution (50 mM, pH 5.4) containing 25% methanol was used. Detection was performed in the positive electrospray ionization mode with multiple reaction monitoring. The parameters of ion source, ion optics, the inlet potentials of the quadrupoles and the collision energy for the detection of the product ions were optimized. Calibration curves for all compounds were linear in wide concentration ranges, covering 3–4 orders of magnitude. The detection limit was 18 ng/mL for MMH.

A hydrophilic interaction liquid chromatography method for the simultaneous determination of hydrazine, MMH, and UDMH in natural waters and soils was based on a combination of HPLC chromatographic separation on a zwitterionic sulfobetaine

stationary phase with amperometric detection and used a mixture of 78 vol. parts of acetonitrile with 22 parts of an aqueous phosphate buffer solution of pH 2.5 with an ionic strength of 20 mM as the mobile phase [389]. Detection in the direct current mode was performed at a working electrode potential of 1.1 V. The advantages of the method are the high efficiency of separation, speed, high sensitivity, and a wide dynamic range of analyte concentrations, covering four orders of magnitude. The limits of detection were within the range 0.07–0.13 µg/L, which was two orders of magnitude lower than those achievable in previously used methods of ion chromatography with electrochemical or mass spectrometric detection. The method was validated on samples of natural waters of different origin with added internal standards. The error of analysis did not exceed 10% for river and ground waters but increased to 20–30% for peat bog swamp waters. The utility of the method was demonstrated with samples of peat bog soils collected from places polluted by UDMH from the impact of the first stages of space launch rockets.

#### 4.7.5.2 High-Performance Liquid Chromatographic Analysis of MMH With Prior Derivatization

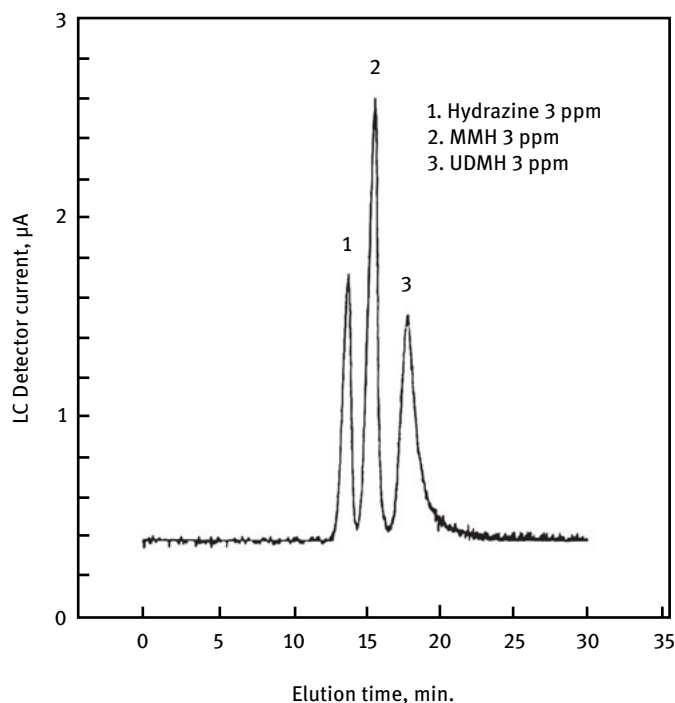
Just as with GC, derivatization of MMH stabilizes it as a derivative for the subsequent separation and analysis by liquid chromatographic methods. Most of the derivatizing agents described for hydrazine in *Encyclopedia of Liquid Fuels*, chapter “Hydrazine” have also been tried for analysis of MMH. Several of the derivatizing agents, for instance, 2-nitrobenzaldehyde, have been shown to work equally well for all three hydrazines,  $N_2H_4$ , MMH, and UDMH [390]. The lower limits of quantitation of MMH and UDMH were 10 ng/mL and that of hydrazine was 1 ng/mL.

MMH, UDMH, and hydrazine can be separated and analyzed after derivatization with naphthalene-2,3-dialdehyde and the separation of the derivatives on a Zorbax Eclipse AAA column in a single HPLC run under acidic conditions (pH 2.4) [391]. Hydrazine and MMH derivatives were found to be strongly fluorescent at  $\lambda_{ex} = 273$  nm,  $\lambda_{em} = 500$  nm. Limits of detection were 0.05 µg/L for MMH or hydrazine for an injection volume of 100 µL.

#### 4.7.6 Ion Chromatography for Analysis of Methylhydrazines

Analysis by ion chromatography uses equipment similar to HPLC. Ion chromatography is often performed in the same equipment as HPLC, just using ion-exchange resins instead of solid sorbents as the stationary phase. Ion chromatography can use cation-exchange resins or anion-exchange resins. A major drawback of the commonly used derivatizing agents for either GC or HPLC is that they rarely allow analysis of all three propellant hydrazines in one shot. It was therefore of interest when it was found that all three hydrazines, underivatized but in the state of their cations, could be separated by HPLC on a cation-exchange resin column using an acidic potassium phosphate buffer as the eluent [392]. DC amperometry of the eluent at a platinum elec-

trode is specific for hydrazines as they are easily electro-oxidized. Detection limits of  $1\text{ }\mu\text{g/L}$  were achieved in clean waste water samples. The only sample preparation was filtering, a substantial saving of labor over competing derivatizing/extracting methods. Similar results are possible with a gold electrode [393]. This method gave three cleanly resolved peaks for the three hydrazines within the concentration range 3 ppm each (Figure 29). The operating conditions were: Column:  $250 \times 4.1\text{ mm}$  Hamilton PRP-X200, Mobile phase: 5-M  $\text{KH}_2\text{PO}_4$ , 6% acetonitrile, Injection:  $25\text{ }\mu\text{l}$ , Flow:  $1.0\text{ mL/min}$ , Detection: Pulsed amperometric detection, gold electrode.



**Figure 29:** Ion chromatogram of hydrazine, methylhydrazine, and unsymmetrical dimethylhydrazine. (Reproduced and modified from [393].)

Hydrazine and hydroxylamine in aqueous solution may be determined using a Nucleosil 10SA cation-exchange column with 2mM citrate and 2mM ethylenediamine at pH 4.5 as eluent with a copper electrode [394]. Detection limits were within the range 2–10 nmol for the species examined.

Ion chromatography with amperometric detection was applied for direct determination of hydrazine, MMH, UDMH, and SDMH in water [395]. Selectivity of two column materials: **(1)** reversed phase silica modified by dodecylbenzenesulfonic acid and **(2)** silica with chemically bonded sulfonic acid groups was investigated using con-

ductivity detection. Retention of hydrazines was found to be similar to that for alkylamines with the same structure. Hydrazines have to be completely protonated in the mobile phase; therefore, an eluent buffer solution with pH less than 7.0 should be chosen. Mobile phase composition (buffer type, pH) and applied potential used for amperometric detection were optimized from the viewpoint of separation selectivity and detection sensitivity. The application of a phosphate buffer with pH about 7 and potential +1.0 V were recommended for the best results. An example for separation of the four hydrazines is shown in an ion chromatogram image in the UDMH section of the chapter “Dimethylhydrazines” in the present set *Encyclopedia of Liquid Fuels*. Detection limits with a 0.5-mL sample injection for hydrazine, MMH, UDMH, and SDMH were 0.4, 0.6, 2.0, and 1.0 ppb respectively.

The ion-exchange constants for ion-chromatographic retention of 16 aliphatic amines and hydrazines on Diasorb-130-Sulfo and Nucleosil 5 SA were calculated and the selectivities of the retention of these compounds were compared. The optimal conditions of detection were then determined [396]. MS detection was used for compound identification after the chromatography separation and the characteristics of the mass spectra of the aliphatic amines and hydrazines were discussed.

There are several methods for the direct determination of hydrazines in water, including ion, ion-pair, ion-exclusion, and hydrophilic interaction chromatography [397]. The separation selectivity and sensitivity of detection for each method depends on the type of samples. Direct methods are simpler than those requiring prior derivatization of the samples, as was demonstrated with examples of hydrazine(s) determinations in real samples.

#### 4.7.7 Capillary Electrophoresis Chromatography of Methylhydrazines

Another modern analysis procedure suitable for the analysis of ionized compounds is capillary electrophoresis (CE). This CE method in combination with electrochemical detection (called “CEEC”) allows the simultaneous determination of hydrazine and MMH in one injection without prior derivatization [398]. Detection of hydrazines in the eluent was achieved with a palladium-modified carbon fiber micro-disk array electrode. The detection limits for hydrazine or MMH were 1.2 and 2.1 pg respectively. This is several orders of magnitude more sensitive than other chromatographic methods. Hydrazine and methylhydrazines could be separated and detected at 1 millimol/L concentrations in a borate buffer at pH 7.18 [399].

Poly(methyl methacrylate) microchip electrophoresis separations with contactless conductivity detection, which integrates all separation and detection components in a compact portable device, enables the separation of hydrazine, MMH, and UDMH within <30 s at a separation voltage of 3.8 kV using a L(–)-histidine/2-(N-morpholino)-ethanesulfonic acid buffer (25:50 mM, pH 5.87) [400]. The contactless conductivity detection enabled detection limits for hydrazine, MMH, and UDMH of 11.9, 35.5, and 337.8 ng/mL respectively, with linear concentration dependence up to 10 µg/mL. In complex matrices such as soil samples or river water, interferences were eliminated

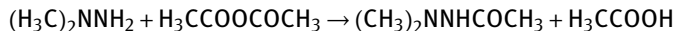
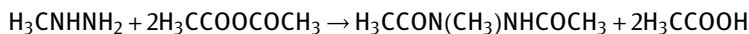
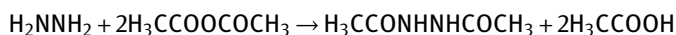
by implementing ultrasound-assisted headspace single-drop microextraction under strongly alkaline conditions, which led to improved limits of detection for hydrazine, MMH, and UDMH of 6.5, 15.3, and 11.4 ng/mL respectively.

#### 4.7.8 Volumetric Analysis Methods for MMH

Volumetric, titrimetric analysis methods have traditionally been the daily chore of the analytical chemist before wet chemistry was eventually replaced by automated titrators and instrumental methods of analysis where one does not have to wash dishes afterward. As they are listed here, volumetric analysis methods only differ by the type of reaction and endpoint indication.

##### 4.7.8.1 Acidimetric Titrations of Methylhydrazines

An analytical method for determining mixtures of either hydrazine and 1,1-dimethylhydrazine ( $\text{N}_2\text{H}_4$ /UDMH) or MMH and 1,1-dimethylhydrazine (MMH/UDMH) was based on the difference in reaction rates for acetylating hydrazines with acetic anhydride [355]. Both  $\text{N}_2\text{H}_4$  and MMH reacted immediately, whereas the acetylation of UDMH proceeded only slowly. The UDMH was slow to react even when a considerable excess of acetic anhydride was added:



The reactions were conducted in an acetonitrile-acetic acid medium. Two titrations are required: one measured the total basicity of the hydrazine mixtures by titration with perchloric acid in acetic acid and quinaldine red as the indicator and the other titration measured UDMH after the  $\text{N}_2\text{H}_4$  or MMH has reacted with  $\text{Ac}_2\text{O}$ . Increasing the water content (1 to 7.8%) did not interfere with the titration. Both the potentiometric and visual quinaldine red indicator endpoints were evaluated.

An investigation of the salicylaldehyde derivatization/acidimetric titration method showed that the species actually titrated in the mixture of hydrazine and methylhydrazines are the free MMH and the free UDMH and that low recovery rates are the result of incomplete hydrolysis of any hydrazone present during the titration [401]. When an excess of perchloric acid was included in the salicylaldehyde reaction mixture, hydrolysis was complete, and even MMH could be determined. For the analysis of hydrazine/MMH mixtures, the sample (~0.4 g) is added to 35 mL of chilled glacial acetic acid in a 50-mL volumetric flask. After equilibration to room temperature, the sample is diluted to the mark with more acetic acid. An aliquot is then added to 50 mL of acetic acid, an excess of 0.1N perchloric acid is added, and the excess is back-titrated with 0.1N sodium acetate in acetic acid, using potentiometric endpoint indication. The first titration gives total alkalinity, whereas subsequent titration on another aliquot after the addition of 2 mL of salicylaldehyde



titrates MMH only. The procedure was tested by analyzing synthetic mixtures of hydrazine and MMH over a wide range of compositions from 0 to 100% MMH. The error rarely exceeded 1% absolute. If the reaction products with salicylaldehyde were left standing too long in the acetic acid/perchloric acid mixture prior to the titration with sodium acetate, even the azine would eventually hydrolyze. After 24 h, 80% of the azine was hydrolyzed to hydrazone and salicylaldehyde, as indicated by UV spectra taken of monomethylhydrazone of MMH and azine of hydrazine before and after addition of perchloric acid.

Hydrazine and its methylated derivatives can be differentiated not only by reaction with acetylating agents or azine-forming reagents but also by acidimetric titration before and after reaction of the sample with isocyanates [357, 402]. The reaction of hydrazines with alkyl or aryl isocyanates leads to semicarbazides, which are weaker bases than the parent hydrazines. In alcoholic solution, hydrazine, MMH, and UDMH react with isocyanates at approximately the same rate to form semicarbazides. In contrast, in anhydrous acetic acid, hydrazine and MMH react rapidly, but UDMH reacts hardly at all. Suitable isocyanates for masking hydrazine or MMH are phenyl isocyanate or naphthyl isocyanate.  $\text{N}_2\text{H}_4/\text{UDMH}$  and  $\text{N}_2\text{H}_4/\text{MMH}$  mixtures were titrated by this method, and the error very rarely exceeded 0.5% absolute.

#### 4.7.8.2 Redox Titrations of Methylhydrazines

Because of the multitude of oxidizers that have been more or less successfully tried as oxidants for the redox titrations of alkylhydrazines, a systematic approach should be followed in discussing these analysis methods. The following discussion covers redox titrations in the sequence of groups in the periodic table of elements, arranged by the active atom that changes its state of oxidation.

Hydrazine nitrogen in monosubstituted organic hydrazine derivatives can be determined by potentiometric titration with potassium iodate, which may go to different states of reduction of iodine(V), depending on the pH [403].

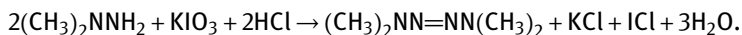
In evaluating several different methods for analysis of hydrazine and its methyl derivatives by redox titrations, both iodate and bromate titrations were conducted for hydrazine, MMH, UDMH, and SDMH [404]. In the iodate titration using a layer of chloroform and extraction as a visual endpoint indicator, hydrazine reacted on a 1:1 molar basis, but UDMH reacted on an iodate:UDMH = 1:2 and SDMH on a 3:2 basis. As an alternative, the four hydrazines can be titrated potentiometrically with 0.016 M  $\text{KBrO}_3$  when the samples are dissolved in 20 mL of concentrated HCl containing 2 g of KBr.

Methylhydrazine can be titrated with potassium iodate by titration with iodate in acidic medium [405]. The reaction of MMH is assumed to proceed by way of



Methanol does not become oxidized under these conditions and methanolic/aqueous iodate solutions gave the same results as titrations in pure water. Mixtures of hydrazine and MMH are analyzed by a first titration, which gives the total of hydrazine and MMH equivalents. Then, in a second sample, following reaction of hydrazine with

salicylaldehyde and removal of the precipitate, the remaining MMH is titrated with  $\text{KIO}_3$  [406]. The same method can also be used for hydrazine–UDMH mixtures. In this case the reaction goes to tetramethyltetrazene:



The method can even be applied to ternary mixtures of hydrazine, MMH, and UDMH. In this case, three aliquots are required. The sum of the hydrazines is determined with potassium iodate. The sum of MMH and UDMH is found after selective removal of hydrazine by reaction with salicylaldehyde. Finally, the UDMH content is obtained by acidimetric titration with  $0.1\text{N HClO}_4$  in acetic acid after acetylation of hydrazine and MMH with acetic anhydride in dioxane.

Attempts to apply iodine or iodate redox titration methods (which worked satisfactorily with hydrazine  $\text{N}_2\text{H}_4$ ) to the analysis of MMH or UDMH have not always been successful at the first attempt [355]. Acidity, sample size, temperature, amount of mercury catalyst, and time spent to reach the endpoint must be carefully controlled, with acidity maintained at above  $2\text{N HCl}$ . The endpoint can be detected by the blue color formed by starch with the first free iodine formed from excess iodate and iodide. Potentiometric endpoint indication is also possible.

Mixtures of hydrazine and MMH can be titrated next to each other using a differential method [407]. For this method, three standard reagents, together with several other additives and buffer, were required. First, an aliquot of the mixture is reacted with excess chloramine-T solution to determine the sum of the two hydrazines. In this step, MMH consumes four electrons, just like hydrazine itself. Excess oxidant is back-titrated with sodium thiosulfate. A second aliquot is then reacted with excess sodium hypochlorite in the presence of potassium bromide and a phosphate buffer. In this case, excess oxidant is also back-titrated with thiosulfate. Whereas chloramine-T is a moderately strong oxidant, sodium hypochlorite/hypobromite is a more vigorous oxidant, and the oxidation of MMH with this oxidizer consumes eight electrons. Both hydrazines involved a four-electron change with chloramine-T. With sodium hypochlorite,  $\text{N}_2\text{H}_4$  involved a four-electron change and MMH an eight-electron change. The difference between the two titrations allows one to calculate the amount of MMH present in the mixture:

$$mM\{\text{MMH}\} = \frac{\text{meq}[\text{OCl}^-] - \text{meq}[\text{CT}]}{4}$$

where CT is chloramine-T. Likewise, the amount of hydrazine is:

$$mM\{\text{N}_2\text{H}_4\} = \frac{2\text{meq}[\text{CT}] - \text{meq}[\text{OCl}^-]}{4}.$$

Clark and Smith failed to detect methane in the reaction products of MMH and hypochlorite, but it was later shown that non-stoichiometric amounts of methane are formed in this reaction [382]. Later investigators also reported problems with consistently high and otherwise erratic results with this method [401].

Oxidizer titrants that give clear-cut reactions with hydrazine may not always give unequivocal answers when used for the titration of MMH or UDMH, because of the involvement of the methyl groups that can be oxidized to different levels. Potassium iodate, ferric salts, potassium permanganate, periodic acid, and iodine were investigated as oxidizing agents for the quantitative determination of UDMH [408]. Titrations with potassium iodate were made to the iodine monochloride equivalence point in hydrochloric acid, to the iodine equivalence point in sulfuric acid, and to the iodide equivalence point in the presence of mercuric salts.

#### 4.7.9 Electrochemical Analysis Methods for MMH

Electrochemical analysis methods are becoming increasingly popular because they can be automated and would eventually interface with digital data acquisition and data reduction.

##### 4.7.9.1 Coulometric Analysis Methods for MMH

A rapid and automatic coulometric titration procedure for the determination of hydrazine and monosubstituted hydrazines with electrolytically generated bromine had a standard deviation of approximately  $\pm 1\%$  and was based on the use of the Faraday constant as a standard [409]. Samples in the 3–5-mg range could be analyzed. The use of anodically generated chlorine in place of bromine did not result in any improvements. An acetic acid/water/methanol/mercury(II)acetate/potassium bromide solvent was used for most of the compounds titrated. Other solvents tested were aqueous 0.3M hydrochloric acid with 0.1M potassium bromide and 80% acetic acid/20% water 1.0M in hydrochloric acid with potassium bromide. The choice of solvent depends on the type of hydrazine to be titrated. Hydrazine or MMH consumed close to four equivalents of bromine, and the reaction was rapid.

Improved accuracy for monitoring the air in places of employment, and a very wide dynamic range, is possible by analyzing impinger samples by coulometry with electrogenerated bromine in sulfuric acid. For MMH vapor collected in 40 mL of 0.1N  $\text{H}_2\text{SO}_4$  in an impinger by passing 10 L of air, the detection limit was an astounding 2 ppb corresponding to 25 ng of MMH [410]. This method constituted an improvement of the Olson [409] method. The dynamic range of the improved method extended from 25 to 2500 ng MMH. This method has also been used for the analysis of scrubber liquid from large citric acid-filled scrubbers through which vented nitrogen gas was passed after transferring fuel into the space shuttle and depressurizing the transfer tanks [411]. Ammonia was found to be a potential negative interferent. The higher the ammonia in the sample stream, the lower was the amount of the analyte detected in the scrubbed solutions, i.e., 25 and 58% average detection loss at 50 and 588 ppm levels of ammonia respectively.

Direct coulometric titration of hydrazine, MMH, or acetylhydrazine with electrically generated bromine in acetic acid gave reproducible results [412]. It was shown

that 0.9M  $\text{CH}_3\text{COONa}$  or  $\text{CH}_3\text{COOK}$  dissolved in glacial acetic acid provided a good anode electrolyte. Contamination by no more than 4% water could be tolerated, but none by acetanhydride.

#### 4.7.9.2 Potentiometric Analysis Methods for MMH

An electrochemical cell capable of detecting threshold limit values (TLVs) of hydrazine, MMH, or UDMH in air was coupled with a dynamic air-sampling system and electronic control and amplification circuitry to provide a direct-reading portable analyzer [413]. Although most of the reported data were specifically for MMH vapor analysis, qualitatively similar results can be obtained when using this instrument for hydrazine or UDMH measurements.

#### 4.7.9.3 Polarographic Analysis Methods for Alkylhydrazines

A measurement of the half-wave potentials of hydrazine, six alkylhydrazines and phenylhydrazine in 0.1M NaOH showed that the half-wave potential was shifted to more negative voltages with increasing length of the carbon skeleton in the alkyl group [414].

The half-wave potential of monosubstituted alkylhydrazines depends linearly on the length of the hydrocarbon chain [415]. Polarography in 2N  $\text{H}_2\text{SO}_4$  and in sodium pyrophosphate at pH = 6–7 on a platinum electrode showed that the potential decreased 60 mV per carbon atom in acidic and 48 mV per carbon atom in neutral solution. In methylhydrazines with progressive methyl substitution, the potential changed +20 mV per added methyl group in acidic and +80 mV per methyl group in neutral solution. All methylhydrazines were oxidized with the loss of four electrons, except SDMH in both media and UDMH in neutral solution, where the oxidation was only a two-electron transfer.

Using more advanced equipment, a hanging mercury electrode, and a commercial voltammetric analyzer with a stationary glassy-carbon disk anode, it was shown that the simultaneous addition of formaldehyde and catalytic amounts of platinum salts give sensitive and specific cyclic voltamperograms for all three propellant hydrazines (singly, not in admixture) at concentrations down to  $10^{-6}$  M [416].

Hydrazines can be determined by voltammetry, based on their hydrogen catalytic wave in formaldehyde–platinum–sulfuric acid media [417]. Adsorption of the platinum–formazone complex on the hanging mercury drop electrode enhanced the sensitivity, allowing convenient measurement of micromolar and submillimolar concentrations of simple hydrazines. The selectivity was better than that of conventional (anodic) measurements of hydrazine(s), as oxidizable compounds did not interfere. The sensitivity was also greatly improved. The hydrazine(s) response was evaluated with respect to preconcentration time, concentration dependence, platinum and formaldehyde concentrations, reproducibility, and other variables. The relative standard deviation (at  $2 \times 10^{-5}$  M) was 1.6%.

#### 4.7.9.4 Amperometric Analysis Methods for MMH

Mesoporous silica that was prepared by a sol-gel process was used as the electrolyte for the amperometric determination of vapor-phase MMH [418]. Three detection strategies were tested, namely cyclic voltammetry at a Pt working electrode with the oxidation mediated by  $\text{Fe}^{\text{II,III}}$  that was hosted by the silica, pulsed electrochemical detection with a gold working electrode, and potentiostatic oxidation at a mixed-valence ruthenium oxide film that was deposited on a Pt working electrode. The sensitivities (and linear dynamic ranges) for the three methods were determined. A cell design that provided a three-phase boundary at a mixed-valence ruthenium, oxide-modified electrode yielded a swift response of 90% of the steady-state current within 11 s.

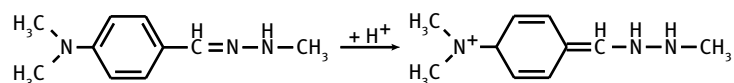
#### 4.7.10 Spectrophotometric Analysis Methods for MMH

##### 4.7.10.1 UV/Visible Spectrophotometric Analysis Methods for MMH

Many of the spectrophotometric methods operating within the visible range have the advantage of being easy to perform, are specific for hydrazines, and do not require very costly equipment. Therefore, for analysis of trace quantities of MMH in air or water, spectrophotometric methods are frequently used, either for routine analysis or to calibrate electronic direct-reading instruments that are based on non-spectroscopic principles. They typically involve the reaction of a sample in water or dilute acid with a color-forming reagent that is more or less specifically for MMH. Hydrazines and amines (only in the state of the free base, not their salts) form intensely colored adducts ("Meisenheimer complexes") with aromatic nitro compounds that may be suitable for qualitative detection of MMH or UDMH [419].

The spectrophotometric determination of hydrazine with *p*-dimethylaminobenzaldehyde (PDAB for short, sometimes also abbreviated to PDBA) is without any doubt the most widely used spectrophotometric analysis method for the determination of small quantities of hydrazine in air or water [420] and can also be used for determination of MMH. The PDAB method was applied to the analysis of microgram quantities of MMH in the blood serum of rats [421, 422]. Calibration curves covered the range 0.5–10  $\mu\text{g}$  of MMH. Minimum detectable dosage in blood serum was 3 mg/kg of MMH administered intraperitoneally. Blood specimens were collected at intervals of 1, 2, 4, and 6 h after injection. There was no interference by protein, urea, or uric acid.

The PDAB spectrophotometric method can also be used for the determination of MMH [405]. The yellow compound is believed to have a *p*-quinone-type structure similar to the highly colored hydrazine–PDAB compound, except with only one benzene (quinone) ring in the molecule:



The measurements were carried out at 458 nm, and determination errors of 1.6% relative were encountered. MMH stored in the form of the sulfate salt had to be recrystallized prior to preparing the standards, because yellow impurities accumulated on the outside of the crystals, most likely from air oxidation.

Methylhydrazine in blood or plasma samples can be analyzed by using the PDAB reagent and an automated analyzer such as the Technicon Autoanalyzer [423]. Such instruments are frequently used in clinical laboratories for routine analysis. The absorption at 480 nm was used for quantitation. The method was found to be accurate and reproducible in biological samples within the range 1–40 µg per sample. The apparatus was capable of automatically analyzing 40 samples per hour. The PDAB reagent concentration was 8%, dissolved in ethanol (instead of methanol, which gives lower sensitivity). Color development and stabilization was achieved by adding glacial acetic acid. Reliable analysis of blood MMH required prompt centrifugation to stop conversion of hemoglobin to methemoglobin. Immediately after centrifugation, the serum was removed and stored in a capped vial. Stored in this manner, the sample was stable for several days in the refrigerator. The catalytic activity of freshly washed red blood cells (RBCs) was demonstrated by incubation with MMH solution. Fifty percent of the MMH was destroyed in the first 10 min.

5-Nitro-2-furaldehyde was introduced as a derivatizing agent for the spectrophotometric determination of hydrazine, MMH, and UDMH [424]. It is characterized by high solubility in water and by a substantial difference in the positions of absorption bands of the three colored derivatives formed. The kinetics of the reaction of analyte derivatization were studied in order to optimize reaction conditions (pH 5, concentration of derivatizing agent 2 mM, 333 K = 60 °C, color development duration 40 min). The limits of detection were 5, 3, and 1.5 µg/L for hydrazine, MMH, and UDMH respectively.

#### 4.7.10.2 IR/Raman Spectrophotometric Analysis Methods for MMH

Water obeys Beer's law in liquid hydrazine hydrate, MMH, or UDMH. Using the 1.9-µm absorption band of water, an IR-spectrophotometric analysis method has been developed that is applicable to mixtures containing 0.1–15% water [425]. Dimethylamine or nitrosodimethylamine do not interfere, but methanol or ethanol would interfere if they were present in concentrations greater than 1%. One-centimeter quartz cells were used for these tests. The results can be expressed by  $P = a + bA$ , where  $P$  represents weight percent of water in the mixture,  $A$  is 100 times the absorbance, and  $a$  and  $b$  are constants as follows (all data for 1-cm path length):

|                               |               |                |
|-------------------------------|---------------|----------------|
| N <sub>2</sub> H <sub>4</sub> | $a = -0.053$  | $b = 0.1057;$  |
| MMH                           | $a = -0.0062$ | $b = 0.01958;$ |
| UDMH                          | $a = 0.019$   | $b = 0.01994.$ |

If the sample temperature differed by less than 2 K from that used during calibration, only minor deviations (<1%) were encountered. Oxygen must be excluded from the

solutions to prevent autoxidation and formation of additional water. A similar method used IR spectrophotometry for both water at 1.9  $\mu\text{m}$  and aniline at 6.66  $\mu\text{m}$  [426].

As far as the analysis of trace MMH and other hydrazine vapors in air by remote sensing IR methods is concerned, some of these methods are based on a tunable laser as the source of the IR radiation. The  $^{12}\text{C}^{16}\text{O}_2$  laser can produce over 100 different discrete wavelengths between 9.1 and 11  $\mu\text{m}$ , where there is very little interference from atmospheric water or carbon dioxide. Hydrazine, MMH, and UDMH have characteristic absorption bands in this regime [427]. The absorption spectra of three hydrazines and four of their air-oxidation products were measured in the 9–12- $\mu\text{m}$  spectral region with an FTIR spectrometer with a  $0.05\text{-cm}^{-1}$  resolution to determine absorption coefficients at  $\text{CO}_2$  and tunable diode laser wavelengths. The measurements agreed well with published  $\text{CO}_2$  laser determinations for many of the absorption coefficients, except where the published values were thought to be in error. The coefficients were then used to estimate the sensitivity for remote detection of these vapors using  $\text{CO}_2$  and tunable diode lasers in long-path differential absorption measurements.

Trace MMH and other hydrazine vapors in air can be detected by laser absorption or even by remote sensing techniques using Light Detection and Ranging (LIDAR) [428, 429]. Absorption cross-section data were measured for hydrazine, MMH, and UDMH vapors, as well as for their selected air oxidation products dimethylamine, trimethylamine, and methanol at up to 78  $\text{CO}_2$  laser wavelengths each [430]. These data are important for the assessment of the capability of  $\text{CO}_2$  laser-based spectroscopic techniques for monitoring low levels of hydrazine(s) fuel vapors in ambient air. Interference-free detection sensitivities of <30 ppb have been demonstrated for UDMH using a laboratory photoacoustic detection system.

The high-resolution laser radiation absorption cross-sections of hydrazine, MMH, UDMH, and their oxidation products were determined first in order to assess the value of the laser techniques [431]. In addition to IR absorption or LIDAR fluorescence, photoacoustic detection of hydrazines has been studied by pumping modulated energy into selected wavelengths of vapors in a cell with a microphone [432] (see Section 4.7.13). Absorption of energy by the vapor in question causes a temporary pressure pulse (=sound), which can be picked up by the microphone [433]. With a laser output at 1 W/line, the photo-acoustically detectable levels are 0.2, 0.3, and 0.3 ppb for hydrazine, MMH, and UDMH respectively. In comparison, for simple long-path-length (100-m cell) absorption, the sensitivities would be “only” 70, 140, and 130 ppb respectively. For LIDAR, remote sensing detection limits for the three hydrazines vary between 20 and 90 ppb. With polluted urban air as a background, detection limits would be significantly worse. Most laser methods would suffer one to two orders of magnitude in sensitivity if hydrazines had to be detected against a background of urban atmospheric pollutants. Another IR method (so far used mostly for detection of chemical warfare agents) relies on the blackbody radiation of buildings, rocks, or soil in the background of a radiometer-scanned area to provide

a source of radiation. A hydrazine vapor cloud drifting between the background horizon and the observation site can be detected by its IR absorption [434].

A laboratory prototype dual He-Ne laser system that was so far only used for the detection of methane leaks from underground pipelines and solid-waste landfill sites using differential absorption of radiation backscattered from topographic targets can also be used for detection of hydrazine fuel vapors and sense the presence of a vapor coming from a nearby source [435–437].

#### 4.7.10.3 Spectrofluorescence Analysis Methods for MMH

Fluorescence of solid or liquid samples excited with light of shorter wavelength can be very specific for certain hydrazine derivatives and is suitable for detection of trace quantities, such as hydrazine derivatives on a thin-layer chromatography plate.

2,3-Naphthalenedicarboxaldehyde forms derivatives with hydrazine that fluoresce intensely and give linear response within the range 50 to 500  $\mu\text{g}$  hydrazine [438–440]. In combination with a liquid absorbent/air concurrent contactor this allows real-time measurement of hydrazine(s) concentrations of less than 10 ppb in air. Three aromatic 2,3-dicarboxaldehydes were tested for the fluorescence of their hydrazine derivatives, *o*-phthalaldehyde (OPA), 2,3-naphthalenedicarboxaldehyde (NDA), and 2,3-anthracenedicarboxaldehyde (ADA). Incorporating MMH into the aromatic framework of benzene, naphthalene, or anthracene and adding another fused heterocyclic ring give highly efficient fluorophores (analog to chromophores). The derivatization of MMH with OPA, NDA, or ADA creates an efficient fluorophore the emission wavelength of which is red-shifted from the original reagent. The fluorescence emission for each of the different derivatizing reagents (OPA, NDA, and ADA), is minimal and nearly within the noise of the background. The hydrazine derivatives, on the other hand, are intensely fluorescent and characterized by a broad fluorescence emission centered at 376 nm for OPA, 500 nm for NDA, and 549 nm for ADA. By careful control of the pH and the aromatic dicarbaldehyde chosen, it is possible to differentiate quantitatively among the hydrazine, MMH, and UDMH levels present in mixed samples. The detection limits for MMH and UDMH using the NDA reagent are 120 ng/L and 40  $\mu\text{g}$ /L respectively [441, 442].

#### 4.7.11 Mass and Ion Mobility Spectrometric Analysis of MMH

Mass spectrometric analysis of alkylhydrazines is used extensively for trace detection, for the study of decomposition or oxidation kinetic mechanisms, or for the determination of molecular structure data. The simultaneous detection of MMH and NTO by MS is complicated by the fact that both propellants have the same molecular mass (46). The ionization and appearance potentials of several molecule fragments are summarized in Table 36 and 37. This will be an aid to future investigators in the identification of *m/e* peaks [443]. Some of the appearance potentials were determined by photoelectron ionization methods.



**Table 36:** Summary of ionization potentials of alkylhydrazines.

| Fragment                           | Ionization potential, eV | References |
|------------------------------------|--------------------------|------------|
| HN=NH                              | $9.85 \pm 0.1$           | [444]      |
| HNNCH <sub>3</sub>                 | $9.28 \pm 0.1$           | [200]      |
| HNNHCH <sub>3</sub>                | $7.3 \pm 0.2$            |            |
| HNN(CH <sub>3</sub> ) <sub>2</sub> | $6.4 \pm 0.2$            |            |
| HNN(CH <sub>3</sub> ) <sub>2</sub> | $6.6 \pm 0.3$            |            |
| N(CH <sub>3</sub> ) <sub>2</sub>   | $9.42 \pm 0.1$           | [445, 446] |

**Table 37:** Summary of appearance potentials of hydrazine and methylhydrazines.

| Species                                           | Parent compound               | Appearance potential, eV | References |
|---------------------------------------------------|-------------------------------|--------------------------|------------|
| N <sub>2</sub> H <sub>4</sub> <sup>+</sup>        | N <sub>2</sub> H <sub>4</sub> | 10.07                    |            |
| N <sub>2</sub> H <sub>4</sub> <sup>+</sup> (2B)   | N <sub>2</sub> H <sub>4</sub> | 10.64                    | [447]      |
| N <sub>2</sub> H <sub>4</sub> <sup>+</sup> (2A)   | N <sub>2</sub> H <sub>4</sub> | 15.61                    |            |
| N <sub>2</sub> H <sub>4</sub> <sup>+</sup> (2B2A) | N <sub>2</sub> H <sub>4</sub> | 16.66                    |            |
| N <sub>2</sub> H <sub>4</sub> <sup>++</sup>       | N <sub>2</sub> H <sub>4</sub> | 24.5                     | [448]      |
| N <sub>2</sub> H <sub>4</sub> <sup>+++</sup>      | N <sub>2</sub> H <sub>4</sub> | 30.0                     |            |
| HNNCH <sub>3</sub> <sup>+</sup>                   | MMH                           | $9.92 \pm 0.1$           | [200]      |
| HNNCH <sub>3</sub> <sup>+</sup>                   | MMH                           | $10.4 \pm 0.2$           | [449]      |
| HNNCH <sub>3</sub> <sup>+</sup>                   | MMH                           | $9.8 \pm 0.1$            | [450]      |
| HNNHCH <sub>3</sub> <sup>+</sup>                  | MMH                           | $10.18 \pm 0.1$          | [200]      |
| HNNHCH <sub>3</sub> <sup>+</sup>                  | MMH                           | $10.2 \pm 0.1$           | [449]      |
| HNNHCH <sub>3</sub> <sup>+</sup>                  | MMH                           | $9.8 \pm 0.2$            | [450]      |
| HNN(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>   | UDMH                          | $10.08 \pm 0.1$          | [200]      |
| HNN(CH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>   | UDMH                          | $10.2 \pm 0.2$           | [449]      |

In many instances not only is the hydrazine molecule dissociated but the ion is also left in a state of excitation from which a photon may be emitted. The state of excitation is indicated either by letters in parentheses or by an asterisk\* following the formula of the ion. The calculated ionization potential of N<sub>2</sub>H<sub>4</sub> is 7.54 eV, in agreement with experimental data.

Although the mass spectrometry of hydrazine itself seems to be a fairly straightforward approach, mass spectra of organic hydrazines can be very complex. High-resolution mass spectra of MMH were recorded in order to distinguish between different fragment ions of the same unit mass [279, 280]. Another objective of these tests was to obtain the effective cross-sections of hydrazine molecules in the electron beam ionizer section of a mass spectrometer [451].

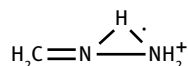
The main pathway of electron-impact decomposition of 40 different monoalkylhydrazines tested was not N–N cleavage but β-cleavage [452, 453]. When secondary or tertiary alkyl groups were present, α-cleavage was sometimes accompanied by hy-

drogen migration. Di- and trialkylhydrazines were studied in a similar fashion with similar results.

Fragmentation of triaryl hydrazines under electron impact was described as a retro-addition process that leads to a diazenium cation and an olefin [454]. Another fragmentation mode involved the breaking of the N—N bond.

Mass spectra of methyl-, ethyl-, propyl-, and other monoalkylhydrazines ionized in a strong electric field showed C—N cleavage with retention of the charge on both fragments,  $\text{N}_2\text{H}_4^+$  formation by way of intramolecular rearrangement, and no simple N—N cleavage [455]. The mass spectra of substituted hydrazines showed lines of fragments corresponding to cleavage of C—C bonds with simultaneous migration of a hydrogen atom from one fragment to another. In saturated alkylhydrazines, cleavage of the  $\alpha$  C—C bonds takes place with migration of a hydrogen atom from the nitrogen-containing fragment to the paraffinic fragment.

Formaldehyde hydrazone  $\text{H}_2\text{C}=\text{NNH}_3^+$  and its isomeric  $\text{C}_1\text{H}_5\text{N}_2$  monocations and hydrazyl radicals are intermediates in the decomposition and oxidation of MMH [456]. Isomeric  $\text{CH}_5\text{N}_2^+$  cations, radicals, and dication radicals have been studied by a variety of mass spectrometry-based techniques (metastable ion-, collisional activation-, collision-induced dissociative ionization-, neutralization-reionization-, charge stripping/charge separation-, and charge stripping/electron-capture-induced decomposition mass spectroscopy), by energy measurements and labeling experiments. Four distinct singly charged ions could be identified: **(1)**  $\text{H}_3\text{C}-\text{NH}-\text{NH}^+$ , **(2)**  $\text{H}_3\text{C}-\text{N}-\text{NH}_2^+$ , **(3)**  $\text{H}_2\text{C}-\text{NH}-\text{NH}_2^+$ , and **(4)**  $\text{H}_2\text{C}=\text{N}-\text{NH}_3^+$ . Ions (1), (2), and (3) are generated by direct bond cleavage reactions in 1,2-dimethylhydrazine, 1,1-dimethylhydrazine and 2-hydrazinoethanol molecular ions, respectively. Ion (4), it was proposed, was formed by isomerization of (3). There is a possibility that (3) and (4) collapse to the bridged structure:



Metastable  $\text{CH}_5\text{N}^{+2}$  ions fragment to  $\text{NH}_4^+ + \text{HCN}$  and to  $\text{HC}=\text{NH}^+ + \text{NH}_3$ . An atlas of mass spectra of organic compounds contains numerous mass spectra of organic hydrazine derivatives [457].

Unsymmetrical dimethylhydrazine, MMH, and hydrazine in air can be detected and identified by ion mobility spectrometry (IMS) at low concentrations, but with interference from ammonia [458]. The optimal spectrometer operating conditions, for the detection of hydrazine, MMH, and UDMH in the presence of ammonia were incorporated into a hand-held portable instrument capable of near real-time detection. Ammonia is still an interferent in the IMS detection of the parent hydrazine. The use of ketones as dopant chemicals has been shown to be effective in the ion mobility spectrometric determination of the hydrazines.

The unimolecular dissociation reactions of ionized MMH,  $\text{CH}_3\text{NHNH}_2^+$ , 1,1-dimethylhydrazine,  $(\text{CH}_3)_2\text{NNH}_2^+$ , and tetramethylhydrazine,  $(\text{CH}_3)_2\text{NN}(\text{CH}_3)_2^+$ , were investigated using tandem MS, threshold photoelectron photo-ion coincidence spectroscopy, and variational transition state theory [197]. The modeled thresholds for the ion dissociation yielded new thermochemistry for these  $\text{N}_2$ -containing ions. The low-energy dissociation pathways of the methyl-substituted hydrazine radical cations correspond to the losses of a hydrogen atom, a methyl radical, and/or a rearrangement process leading to the loss of methane.

#### 4.7.12 Proton Magnetic Resonance Analysis of Methylhydrazines

The Proton Magnetic Resonance (PMR) signals of protons contained in amino, methyl, or dimethyl groups differ sufficiently to allow a quantitative determination of hydrazine, MMH, and UDMH in binary or ternary mixtures. All four possible combinations can be handled by a single PMR scan [459]. Tetramethylsilane was used as internal standard. Water interferes because the rate of proton exchange between the hydrazines and water is fast enough to wash out the sharpness of the peaks. The actual measurement takes less than 10 s. To calculate the percentage of hydrazine, MMH, and UDMH in the mixture, the relative areas under the  $-\text{NH}_2$  and  $-\text{CH}_3$  peaks were measured, corrected statistically to area per proton, and inserted into simple data reduction equations. The method was tested on 27 different mixtures, and the average absolute deviation in molar fraction was less than 0.01.

#### 4.7.13 Trace Analysis of MMH Vapors in Air

Because the olfactory threshold for MMH vapor is above the concentration at which permanent damage can be caused by continued MMH inhalation, it is very important to monitor workplaces with sensitive analytical devices. One cannot rely on the human sense of smell alone to receive a warning when dangerous MMH concentrations are exceeded. This applies to hydrazine itself as well as many volatile hydrazine derivatives. The methylhydrazines have a more pronounced (“fishy”) odor and are more readily detected than hydrazine itself.

The olfactory threshold for hydrazines is discussed in Section 11.14. Analytical methods are now needed that are more sensitive than our noses and provide a more quantitative answer. The sensitivity requirements for MMH detection instrumentation are inevitably tied in with the TLVs and emergency exposure limits (EELs) established by various government agencies for the protection of workers inside and the general public outside of the factories and test sites. The two sets of numbers, the instrument sensitivity capability and the government maximum allowable limit, seem to “leapfrog” each other where the government regulators are reasonable enough not to establish limits so low that they cannot be verified, but nevertheless often set them so low that each lowering constitutes a new challenge to the instrument industry. The limits for hydrazines have been lowered twice by several orders of magnitude within

the past three decades. Therefore, the instrument industry was constantly struggling to come up with instruments that could reliably detect the new TLVs or even fractions of the new TLVs to provide some level of confidence or to be prepared for the next imminent lowering of the TLV. To the uninvolved bystander it sometimes looked as if the availability of more sensitive detection methods (more sensitive than the current TLV) spawned a new round of calls from the occupational hygiene/medical community for again lowering the TLVs and EELs.

Similar methods and instruments are used for both hydrazine and MMH and respond to both. Only a few instruments are capable of discerning between hydrazine and MMH. The following sections are subdivided by active and passive sampling methods. With *active* we understand that the system needs a pump to force air through the apparatus. *Passive* samplers or badges depend on diffusion of ambient air and air movements (often the draft of the working person moving through the working environment). Passive methods have the advantage that they do not require a portable power source, but they are probably not as accurate as active samplers. Other methods of subdividing a chapter on trace analyzers would be by *direct reading* and *not direct reading* instruments.

It is very difficult to maintain a current list of commercially available vapor detection instruments that are suitable for the detection and monitoring of hydrazine, MMH, and UDMH concentrations. Lists of instruments that had been assembled in previous books on hydrazines [460] quickly became obsolete because some manufacturers went out of business, others merged, and a few new ones entered the field. In addition to the need to monitor hydrazines, many test and launch sites had simultaneous requirements to detect and monitor nitrogen dioxide from leaking dinitrogen tetroxide or mixed oxides of nitrogen (MON). Instruments were sought that could detect and separately identify both hydrazine fuels and nitrogen oxide oxidizers. These instruments were generally described as *hypergolic vapor detectors*.

Progress in the area of toxic rocket propellant vapor detection has been significant during the past decades, necessitated by the realization that there is a wide range of potential adverse physiological effects caused by hydrazines. Most of the work performed on propellant vapor detectors in the US was aimed at the detection of the more volatile MMH, which was used in the Space Shuttle OMS/RCS and in the MINUTEMAN and PEACEKEEPER ICBM third stages deployed in missile silos. Only relatively little work has been conducted specifically for the less volatile hydrazine  $\text{N}_2\text{H}_4$ . Surveys of missile propellant vapor detectors have been published in the literature from time to time but quickly became obsolete. A table of summary publications dealing with hypergol vapor detectors that was published in a hydrazine book in 2001 now has only historical value. For a now outdated review of the history of hypergol vapor detection instrument and passive sampler development and testing, see [460]. All information on detectors and samplers is too complex and quickly outdated to be repeated here. The following is only a random sampling of some of the analytical methods used for the detection and quantitation of MMH and other hydrazines. Initially, one will have

to rely on manufacturer's literature to select a system that satisfies the requirements of a given rocket propellant installation, and then verify manufacturer's claims by on-site evaluation under real operating conditions.

Most of the active instruments and passive badges capable of detecting and quantifying MMH vapor in air work equally well for UDMH and hydrazine vapors. Therefore, the information contained here in the MMH chapter will not be repeated in the UDMH chapter.

#### **4.7.13.1 Sampling Methods for Methylhydrazines in Air** **Liquid-Filled Impingers and Wet Chemical Methods**

Two different instruments, Technicon Auto-Analyzer, in which an aerosol captures electrons in a radium source and causes a decrease in electron current, and the Mine Safety Appliances Billion-Aire, which absorbs MMH from a gaseous stream pumped from the exposure chamber into a liquid containing iodine in potassium iodide, which decreases in color after reaction with the MMH, were compared for the continuous analysis of exposure chamber atmospheres [461–463]. The transmittance of the solution was measured continuously in a flow colorimeter and could be related to the concentrations of the MMH. The reaction of iodine with MMH was adapted to the analysis of MMH vapor in air. By adjustment of pH and potassium iodide concentration, stoichiometric reduction of iodine in solution was accomplished. This method permitted the absolute measurement of MMH concentrations in standard bag samples, which were then utilized for calibration of the MSA Billion-Aire analyzer.

#### **Solid Sorbent Tubes**

Measurements at the NASA Kennedy Space Center (KSC) showed that occupational exposure of technicians to hydrazine and MMH vapors was well within tolerable limits even after the lowering of the TLV from 100 to 10 ppb in 1991 [464]. Sampling methods were sensitive enough to measure exposure levels at or below the proposed American Conference of Governmental Industrial Hygienists (ACGIH) TLV of 10 ppb/8 h. The operations monitored included propellant transfer operations, flight hardware processing, and launch vehicle fueling operations that occurred at KSC or the adjacent CCAFS. A similar set of 128 air samples taken and analyzed for hydrazine, MMH, and UDMH at NASA White Sands test facility in 1991 showed that hydrazine or MMH concentration in most work areas was below the proposed TLC of 10 ppb [465]. The air samples were taken by aspirating air through glass tubes filled with USSS No. 30–60 granular sulfuric acid impregnated fire brick at a rate of 1 L/min for 10 min. The sorbent was then leached with buffer solution in an ultrasonic agitator and the solution analyzed by HPLC with electrochemical detection. Several samples were reported as “None detected,” but the detection limit was unfortunately not stated (it is assumed to be below 2 ppb). Parallel tests showed the dubious value of conventional Interscan 4186 measurements, which did not correlate with the absorption tube readings at all.

Instead of air sampling with liquid absorbent dilute acids in impingers (“bubblers”), it is more practical to use solid absorbents, which consist of inert granular ceramic carriers impregnated with acid, held in sampling tubes through which air is drawn at a controlled rate and for a known duration of time. Some of these solid sorbent tubes and the subsequent spectrophotometric analysis capture MMH as well as UDMH [466]. With this particular method, the relative error of measurement was less than 17%, and the recovery rate was better than 80%.

### **Sample Dilution Methods**

Sometimes the concentrations of MMH or NTO to be measured may be higher than the upper range of instruments at hand and the air samples need to be diluted before admitting them to the instrument. An MMH vapor sample-diluter was constructed for 3 to 1 dilution. A 3 to 1 diluter would bring samples containing 500 ppm MMH into the range of the existing instrument [467, 468].

### **Calibration Methods for MMH Analyzers**

All field analyzers have to be brought back to the central laboratory from time to time to be re-calibrated. Calibration is done with vapor generators, which can provide an air stream with a known amount of MMH vapor in it. The reproducible vapor concentrations are usually generated with permeation tubes.

## **4.7.14 Active Analysis Methods for Methylhydrazines in Air**

### **4.7.14.1 Gas Detector Tubes**

The popular Draeger tube for MMH was tested again for accuracy with MMH vapors from a vapor generator that was calibrated with the *p*-dimethylaminobenzaldehyde (PDAB) method on air samples drawn through an impinger with acid [469]. These tubes change color from yellow to blue in the presence of MMH or other base-forming gases (hydrazine, amines, ammonia). At levels of 1 and 2 ppm MMH the results of the tubes averaged within the required  $\pm 20\%$  deviation.

### **4.7.14.2 Paper Tape Analyzers**

A portable detector for mixed-hydrazine propellant fuel (MHF-3) vapors at low concentrations for shipboard use was developed at the Naval Research Laboratory [470]. This active detector consisted of PDAB-impregnated paper and responded to hydrazine or MMH within the range 0.5–10 ppm. PDAB was also the reagent used in an E41 chemical warfare agent alarm modified to fit the needs of the Air Force in monitoring the air for MMH leaks in MINUTEMAN III silos [471]. The same E41 alarm system was also tested as a candidate for use as a shipboard detector on board Condor missile-carrying ships and found to perform reliably for MMH detection [472]. The principle of this test method was to impinge an air stream on a tape impregnated with PDAB. The presence

of hydrazine or MMH resulted in an orange spot. The change in color was observed by a system with a photoelectric cell.

The MDA Autospot Model 3060 and MDA 7100 analyzers, which used the discoloration of paper tape impregnated with phosphomolybdic acid, were evaluated for remote sampling of MMH using an auxiliary pump [473, 474]. One of the first paper tape instruments was the AutoStep hydrazine analyzer made by GMD Systems, Inc., a company that was later absorbed by Bacharach [475]. The GMD MK-2 is a microprocessor-controlled instrument with direct liquid crystal display meter readout and full data storage facilities. Some of the performance requirements established for the detector were: accuracy of plus or minus 1 ppb tested at 10 ppb; linear range of 0 to 400 ppb; zero and span drift of plus or minus 2 ppb in 4 h; response time of less than 4 min to 90% tested at 10 ppb; error due to temperature change from 273 to 313 K (0 to 40 °C) at 45% relative humidity (RH) within  $\pm 20\%$ ; and error due to humidity change from 10 to 80% within  $\pm 25\%$ . Evaluation tests, other than the RH test, were performed using hydrazine, MMH, and UDMH vapors ranging from 1 to 400 ppb at 298 K (25 °C) and 45% RH.

#### 4.7.14.3 Electrochemical Analyzers

The NASA KSC evaluated three different instruments in 1987, including the ESI-7000 (electrochemical), Interscan LD-18 (electrochemical), and the Miran 101 (IR absorption) [476]. At that time, the ESI-7000 was the preferred instrument for continuous area monitoring for MMH and NO<sub>2</sub>. NASA later started development of a second-generation Hypergolic Fuel Vapor Detection System, and a wider range of all known commercially available technologies was considered, including electrochemical, IR, photoionization, and optically scanned chemically treated paper tape [477, 478]. Fifteen instruments were procured, and a preliminary series of tests for basic performance was completed in 1990. Several of the sensors were susceptible to variations in RH, which is typical for the Florida climate.

The Olfactron 6110 analyzer once made by the Control Systems Division of Tele-dyne Inc had separate sensors for NO<sub>2</sub> and hydrazine-type fuels. The Olfactron was calibrated in the laboratory and then field tested for MMH and UDMH at a static rocket test site and its results were compared with cumulative measurements with bindone personal monitor badges [479]. The studies with the Olfactron Model 6110 showed this instrument to be deficient in several respects: **(1)** field calibration with UDMH for MMH detection could not be accomplished as designated by the manufacturer, and **(2)** the reproducibility of the estimation of repeated exposures was limited to short-term events and could not be accepted for operational situations.

#### 4.7.14.4 Infrared-Stimulated Acoustic Microphone Sensors

Methylhydrazine vapor in air can be detected by a high-throughput, all-fiber near-IR spectrometer based on an integrated acousto-optic tunable filter and an erbium-doped fiber amplifier [480]. This tunable filter was based on Bragg interactions

between a waveguide and surface acoustic waves. Advantages included all-fiber construction, smaller size, narrower spectral resolution (1.7 nm), higher diffraction efficiency (37%), and lower rf power requirement (150 mW). A relatively narrow spectral tuning range (about 80 nm) was the only drawback for this integrated tunable filter. However, this disadvantage was overcome by using the filter for measurements in which its tuning range was coincident with the light source and also with absorption bands of analytes. The all-fiber nature, compactness, high throughput and high sensitivity of this spectrophotometer made it particularly suitable for on-line and real-time detection of trace gases in hostile environments, including leak detection of MMH at a limit of detection of 191 ppm.

#### 4.7.14.5 Infrared Diode Lasers as a Radiation Source for Spectrophotometers

The design of a diode laser-based leak detection system operating in the range from 6350 to 6650  $\text{cm}^{-1}$  (1.49 to 1.58  $\mu\text{m}$ ) was based on peak absorption cross-section measurements of MMH, as determined from fixed wavelength absorption measurements recorded at various pressures [172, 173].

#### 4.7.14.6 Thin Film Chemiresistors

Thin film chemiresistors have been tested for the detection of MMH and hydrazine [481]. HypergoLeak [482] is a polymer nanowire-based chemoresistive sensor. The fabricated polymer nanowires have proven capable of detecting hypergolic fuels and oxidizers. The nanowires have been used to detect 10–300 ppm MMH and 10–100 ppm  $\text{NO}_2$ , with the capability to detect lower concentrations. The response of the nanowires correlated well with the analyte concentrations determined by other methods.

#### 4.7.14.7 Gas Chromatographic Methods

The detection of hydrazine type fuel vapors in air has been studied using GC and colorimetric methods that are adaptable to the Army's E41 Chemical Agent Alarm vapor detector. Gas chromatography with a flame ionization detector can detect 1.0 ppm mixed hydrazine fuel-5 (MHF-5) vapor (mostly MMH) and 0.5 ppm UDMH. In parallel, UDMH has been detected by a colorimetric method using phosphomolybdic acid. The E41 alarm using this principle can trigger an alarm to 0.5 ppm UDMH in about 30 s [483].

Methylhydrazine in air can be determined by capillary gas chromatography [484]. The results showed that good linearity can be obtained in range 0–54 mg/L, and the minimum detectable concentration was 0.6 mg/L.

#### 4.7.15 Passive Personal Dosimeter Badges (Direct Reading)

Colorimetric detectors depend on the reaction of MMH vapor with a reagent chemical to produce a colored compound. The reagent is usually deposited on a strip of filter paper or chromatogram sheet. The intensity of the color produced by reaction with



MMH is proportional to the MMH concentration in the contaminated atmosphere and the time of exposure. Similar badges have been developed for hydrazine and UDMH. Several of the badges in use also responded to ammonia and were not specific for one particular hydrazine or alkylhydrazine.

Simple, direct-read monitoring systems for hydrazines (hydrazine, MMH, and UDMH) consist of a badge-type monitor and a color comparator [485]. The badge operates on the principle of diffusion and it indicates the presence of hydrazine(s) by forming a color change. The color change occurs when the targeted vapor diffuses and reacts with a flat indicator layer. The intensity of the color developed is directly proportional to the exposure dose. For quantitative measurement of exposure doses of hydrazines, the intensities of the colors developed are compared with color standards in the color comparators. The minimum detectable limits for hydrazine, MMH, and UDMH are 4.5, 6, and 10 ppb  $\times$  h respectively. Cross interferences of several organic and inorganic substances known as normal satellites of hydrazines, including up to 25 ppm ammonia, were examined. None of the tested substances showed any effect on the performance of the hydrazines' systems. The hydrazine and MMH systems use the same sensor. This sensor is ten times more sensitive to hydrazine and MMH than to UDMH.

#### 4.7.16 Analysis of Trace Contaminants in MMH

Absorption of atmospheric carbon dioxide into hydrazine and formation of carbazic acid have been the cause of numerous corrosion incidents. Similarly, carbon dioxide absorption into MMH and resulting corrosion problems were also the reason for the development of the following gravimetric procedure for the analysis of carbon dioxide and methylcarbazic acid in MMH [351]. In this method a 10-mL sample of MMH in CO<sub>2</sub>-free water is reacted with 10 mL of a barium hydroxide solution prepared by dissolving 10 g of Ba(OH)<sub>2</sub> in 500 mL of CO<sub>2</sub>-free water. The precipitate is filtered through a tared fritted glass filter, washed, dried, and weighed. Because sulfate ion (if it was present as a contaminant) would cause a precipitate as well, the weighed precipitate is then washed with 0.1 N hydrochloric acid, water, dried, and weighed again. The barium carbonate would dissolve in HCl, but barium sulfate would remain in the crucible. It was verified gravimetrically that the precipitate is barium carbonate and not barium methyl carbazate. It was assumed that methylcarbazic acid and MMH methyl carbazate (the form in which dissolved CO<sub>2</sub> exists in MMH) hydrolyze to free carbonate ion under the conditions of this analysis. MMH absorbs carbon dioxide rapidly from the air. Therefore, all sample weighing must be done under CO<sub>2</sub>-free nitrogen. Typical propellant samples contained 25 to 224 ppm CO<sub>2</sub>.

In trying to answer the question if *N*-nitrosodimethylamine detected during disposal of MMH is caused by UDMH contamination in the MMH or is to be expected even from perfectly pure MMH, a very sensitive method was developed for analysis of trace contamination of UDMH in MMH, which involved forming the hydrazones

with adamantanone instead of acetone, followed by capillary GC separation and mass spectrometric identification [486]. The acetone hydrazones of MMH and UDMH were not sufficiently stable for this application, but the adamantanone hydrazone gave better results. The bulk of the adamantanone group prevents enolization and other side reactions, leading to instability of the derivative in the GC at a high temperature. The adamantanone derivatives also contained more carbon and were easier to detect than the acetone hydrazones in a GC with FID. The UDMH derivative, a trace contaminant, eluted prior to the MMH derivative, which was desirable because the larger peak of the MMH derivative may be trailing a bit and would cover (hide) the trace of UDMH. The adamantanone derivatives of UDMH and MMH were sufficiently thermally stable for GC analysis, but decomposed slowly on standing, even in the absence of air or light. The samples should therefore be analyzed within 0.5 and no more than 4 h after derivatization. The GC separation used 15-m capillary columns coated with crosslinked poly(ethylene glycol) or a polysiloxane, and 0.02 to 0.33% UDMH was detected in all propellant-grade MMH samples analyzed at NASA WSTF.

## 5 Properties of Methylhydrazinium(1+) Salts

Methylhydrazine forms salts with strong acids. In aqueous solution with nitric acid only the singly protonated salt, methylhydrazinium(1+) nitrate, MMHN,  $[\text{H}_3\text{CNH}_2\text{-NH}_2]^+[\text{NO}_3]^-$  is formed. If MMHN is dissolved in concentrated nitric acid, the diprotonated salt can be obtained.

### 5.1 Thermal Stability of Alkylhydrazinium Salts

The thermal stability of alkylhydrazinium salts varies over a wide range of temperatures at which onset of exothermic decomposition can be observed. Most alkylhydrazinium salts are potentially explosive and data on thermal stability must be known before these chemicals can be safely stored and transported as dry solids. Even salts that may not necessarily be considered for a particular application such as in a rocket propellant or an explosive are included here, although such applications are frequently the motivation for thermal stability studies. In addition to those salts with oxidizing anions where instability of the salt must be expected, many alkylhydrazinium salts with inert anions decompose exothermically as well. There is still no complete understanding of the effect of the anion on the stability of alkylhydrazinium salts. Methods and instruments for studying thermal stability of hydrazinium salts include DTA, TGA, DSC, ARC, on-line MS of gaseous products, and IR/FTIR spectrophotometry. The same methods are also used to study the thermal stability of alkylhydrazine liquids.

Thermal stability—or rather thermal instability—of alkylhydrazinium salts ranks all the way from a mild endothermic decomposition to a sometimes violently exothermic, in fact explosive or even detonative decomposition.

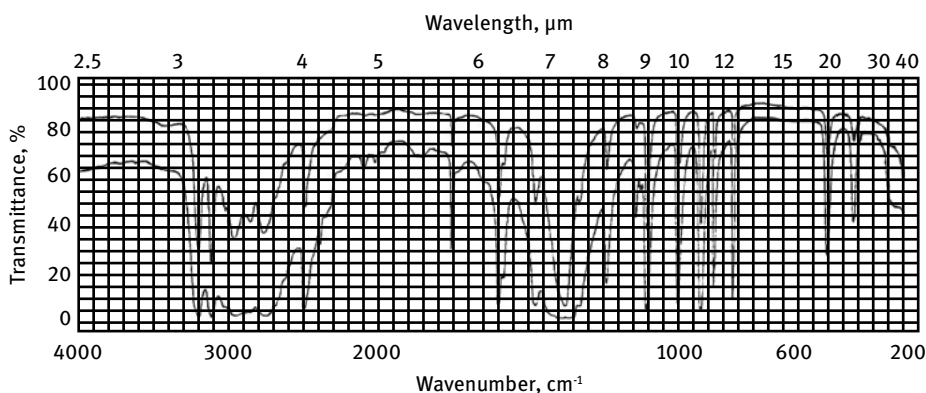
## 5.2 Properties of Methylhydrazinium(1+) Nitrate

The salt of major concern is methylhydrazinium(1+) nitrate, MMHN,  $\text{H}_3\text{CNHNH}_3\text{NO}_3$ ,  $\text{C}_1\text{H}_7\text{N}_3\text{O}_3$ , CAS RN [29111-69-1],  $M = 109.09 \text{ g/mol} = 9.1667 \text{ mol/kg}$ , which sometimes forms inadvertently from residual bipropellants in NTO/MMH thrusters from the dribble volume after the engine has shut down. Under adverse conditions, the salts formed from uncombusted propellants may accumulate in the engine and explode next time the engine is operated, resulting in severe pressure spikes. The ground test experience using low-thrust attitude control engines has shown a correlation between the pressure spike phenomena and the residue formation. Methylhydrazinium(1+) nitrate melts at 310.6–314.6 K (37.5–40.5 °C) and has a density of  $1.541 \text{ g/cm}^3$ .

### 5.2.1 Infrared Spectra of Methylhydrazinium Nitrate

The MMHN IR spectrum is similar to that of MMH, with the exception of the peak at  $1375 \text{ cm}^{-1}$ , which is due to the nitrate ion [487]. The absorptions between  $3200$  and  $3000 \text{ cm}^{-1}$  and the absence of the strong peaks at  $2800 \text{ cm}^{-1}$  indicate that the proton is attached to the nitrogen atom that already carries the methyl group.

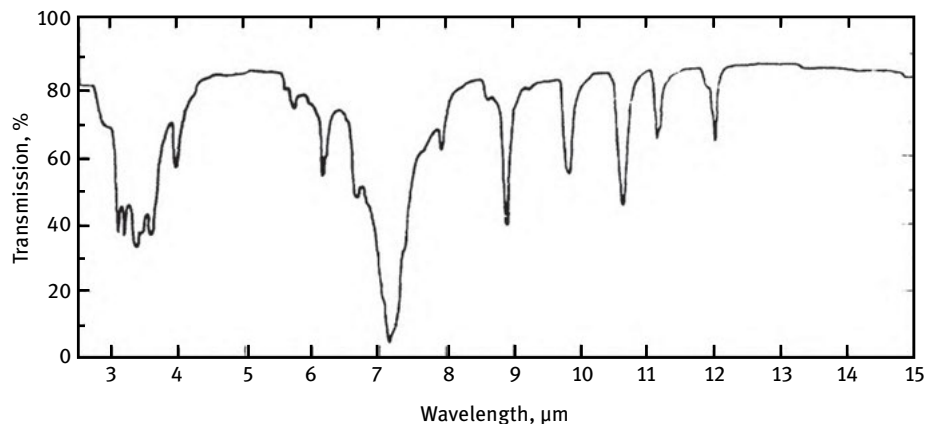
The physical, chemical, and safety properties of MMHN were thoroughly investigated as part of a research program to explain hard start phenomena in hypergolic rocket engines [325, 488, 489]. The work at USBM included the measurement of IR spectra of MMHN, such as the one shown in Figure 30 [490].



**Figure 30:** Infrared spectrum of methylhydrazinium nitrate. (Reproduced and modified from [490].)

Methylhydrazine and  $\text{NO}_2$  were reacted in laboratory vacuum chambers under non-ignition conditions and residues were collected and analyzed [326, 327]. The main constituent of the condensed reaction products was MMHN.

Combustion residues were collected from NTO/MMH engines firing into a vacuum chamber at either steady-state or pulse-mode and the IR spectra were compared with those of MMHN shown in Figure 31 [491].



**Figure 31:** Infrared spectrum of methylhydrazinium nitrate. (Reproduced and modified from [491].)

Exhaust from NTO/MMH thrusters is a potential source of plume contamination for cooled sensor optics on satellites. The effect of MMH nitrate on scatter at  $3.39\text{ }\mu\text{m}$  was investigated as a function of temperature within the range 200–350 K and as a function of thickness [492]. The space-simulated deposition of MMH nitrate took place under high vacuum onto a bare beryllium mirror.

### 5.2.2 Thermodynamic Properties of Methylhydrazinium Nitrate

The heats of combustion of MMHN,  $[(\text{CH}_3)_2\text{H}_2\text{NNH}_2][\text{NO}_3]$  were determined experimentally and calculated thermodynamically [493]. The agreement between the experimental and theoretical values (in parentheses) was satisfactory: 1136 (1090) kJ/mol = 10418 (9996) kJ/kg = 2490 (2389) kcal/kg.

### 5.2.3 Molecular Structure of Methylhydrazinium Nitrate

Methylhydrazinium nitrate forms monoclinic crystals, space group  $P2_1/c$  with the unit cell parameters of  $a = 3.7794(4)\text{ }\text{\AA}$ ,  $b = 11.342(1)\text{ }\text{\AA}$ ,  $c = 11.107(1)\text{ }\text{\AA}$ ,  $\beta = 99.09(1)^\circ$ ,  $V = 470.15(9)\text{ }\text{\AA}^3$ ,  $Z = 4$ , and  $\rho_{\text{XRD}} = 1.5411(3)\text{ g/cm}^3$  [494]. The methylhydrazinium ion has four hydrogen bonds connecting it to neighboring nitrate ions. The terminal  $\text{NH}_2$  nitrogen atom is connected via hydrogen bonding to two nitrate ions, the central

nitrogen atom to a nitrate ion and another methylhydrazinium ion (N—N distance = 2.938(2) Å). The arrangement of methylhydrazinium ions and nitrate ions in the crystal lattice has been illustrated in an ORTEP plot together with bond lengths.

### 5.2.4 Thermal Stability of Methylhydrazinium Nitrate

When heated, MMHN dissociated rapidly and the gaseous dissociation products recombined and deposited on available cold surfaces inside the test apparatus (quartz spring balance). Results of mass loss rate measurements at 298, 328, and 367 K (25, 55, and 94 °C), all at low pressures (30 μm Hg), were as follows: 0, 0.04, and 0.35 mg min<sup>-1</sup> cm<sup>-2</sup>.

When MMHN in the semisolid form of an engine residue was heated at 443 K (170 °C) and under atmospheric pressure conditions, it converted to methylammonium nitrate. In the DTA, a melting endotherm was observed at 314 K and the exotherm peaked at 481 K [487].

Methylhydrazinium and methylammonium nitrate are among the white deposits frequently observed in post-firing NTO–MMH rocket engines as a result of incomplete combustion. Because the nitrates are potentially detonable, additional safety investigations were carried out on their thermal decomposition [491, 495–497]. MMHN has a melting point of 310.6–314.6 K (37.5–40.5 °C) and begins to decompose at 400 K. The thermal decomposition of MMHN at temperatures between 353 and 473 K (80 and 200 °C) produced (in order of abundance): methylamine, water, dinitrogen, NO, NO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, CH<sub>3</sub>N<sub>3</sub>, N<sub>2</sub>O, and O<sub>2</sub>. Vacuum DTA with simultaneous on-line mass spectrometric analysis of the decomposition products revealed methylamine, water, nitrogen, nitric oxide, oxygen, and nitromethane among the products. Decomposition was complete at 500 K.

The decomposition of MMH acid salts MMH•HNO<sub>3</sub> and MMH•HCl was studied in their respective 4-M aqueous acid solutions at 345.9 K (72.8 °C) [236]. The chloride salt was perfectly stable over a period of 346 h. In that same period, on the other hand, the nitrate salt decomposed to the extent of 73%. The decomposition products included N<sub>2</sub>, CH<sub>3</sub>NH<sub>2</sub>, NH<sub>3</sub>, and C<sub>2</sub>H<sub>6</sub>. The presence of both N<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> suggests the presence of methyl radicals that could result from the formation of CH<sub>3</sub>N=NH.

Methylhydrazinium nitrate crystals are deliquescent and hygroscopic. Water coordinated to the molecules cannot be removed in vacuum, and heating under vacuum results in decomposition. Longer storage under atmospheric conditions leads to yellow or even brown liquids. The crystal structure of MMHN was determined, the thermal, shock, and friction sensitivity of this compound was investigated, and the products formed during the thermal decomposition were analyzed [494].

Pyrolysis of methylhydrazinium(1+) nitrate was investigated by a confined rapid pyrolysis setup with heating rates on the order of 2000 K/s, coupled to a rapid-scan FTIR spectrometer [498, 499]. Both MMH•HNO<sub>3</sub> and MMH•2HNO<sub>3</sub> started to decompose at about 393 K (120 °C). The nitrates first decompose to release abundant HNO<sub>3</sub>,

which then reacts with the MMH cation to form species such as  $\text{CH}_3\text{ONO}_2$ ,  $\text{CH}_3\text{N}_3$ ,  $\text{HN}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and small amounts of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ .

### 5.2.5 Strand Burning of Methylhydrazinium Nitrates

The strand burning rate of methylhydrazinium(2+) nitrate was studied by using a high-pressure strand burner with optical access, coupled with a high-speed camera for capturing and analyzing the combustion characteristics [498, 499]. It was also attempted to study the burn rate of methylhydrazinium(1+) nitrate. However, it was difficult to ignite the methylhydrazinium(1+) nitrate. This is probably for two reasons: **(1)**  $\text{MMH}\cdot\text{HNO}_3$  is a fuel-rich compound; and **(2)**  $\text{MMH}\cdot\text{HNO}_3$  is very hygroscopic. During the preparation process, the  $\text{MMH}\cdot\text{HNO}_3$  strand can absorb enough water from the ambient atmosphere to form a colloidal slurry. The absorbed water makes it difficult to ignite.  $\text{MMH}\cdot 2\text{HNO}_3$  is stoichiometric and its burn rate increased almost linearly from 0.56 mm/s at 0.1 MPa (1 atm) to 14 mm/s at a gauge pressure of 5.5 MPa (gauge) (800 psig). At 6.9 MPa (1000 psi), its burn rate was about 400 mm/s.

### 5.2.6 Detonability of Methylhydrazinium Nitrate

Neat MMHN molten at 318 K and contained in a 25-mm diameter schedule 40 steel pipe underwent a low-velocity detonation (LVD; 2 mm/ $\mu\text{s}$ ) when boosted with 50 g of tetryl and zero gap [500]. In a gap test, molten MMHN exhibited minimum film thicknesses of 1.5 and 1.8 mm for propagation at 2.2 to 2.3 mm/ $\mu\text{s}$ . Mixtures of MMHN and MMH may be found in the residues from leakage or incomplete combustion in rocket engines operating on NTO/MMH. Samples of 90% MMHN and 10% water or 90% MMHN and 10% MMH did not propagate detonation in a wedge test with a wedge taper from 6.2 mm to zero.

In similar tests, it was confirmed that even very concentrated solutions containing 90% MMHN did not sustain detonation in layers as thick as 1.25 cm. The pure molten methylammonium nitrate showed LVD behavior with a detonation velocity of 2200 m/s, and a critical film thickness of 0.03 cm [490].

Methylhydrazinium nitrate showed poor sensitivity toward shock or friction. No impact sensitivity detonation was observed in the drop hammer test (5 kg, 50 cm) [494]. Also, no detonation was observed when grinding the compounds in a mortar. MMHN was insensitive to an electric discharge of about 20 kV. Fast heating with a Bunsen burner resulted in melting and at higher temperatures in a vigorous decomposition under gas evolution. Slow heating gave a slow decomposition at temperatures higher than 333 K (60 °C).

### 5.2.7 Toxicity of Methylhydrazinium Nitrate

Technicians who are servicing post-flight NTO/MMH thrusters without protecting themselves with gloves may accidentally absorb MMHN through the skin. Dermal

exposure tests with rats and hamsters have shown that MMHN is readily absorbed through the skin and that the topical LD50 of MMHN is similar to that of MMH [501, 502]. In a study of the effects of MMHN on mitochondrial function of rat hepatocytes, MMHN and other hydrazinium nitrates decreased the mitochondrial function in a dose-dependent manner [503]. Toxicity data for MMHN are summarized in Table 47 [504].

### 5.3 Properties of Methylhydrazinium(1+) Azide

Methylhydrazinium(1+) azide crystals melt at 341 K (68 °C). In the DSC there was a melting endotherm peak at 342.4 K (69.3 °C) and another weak endotherm at 424.6 K (151.5 °C). Methylhydrazinium(1+) azide crystals are orthorhombic, space group *Pnma* with unit cell parameters of  $a = 9.962(1) \text{ \AA}$ ,  $b = 5.1316(5) \text{ \AA}$ ,  $c = 9.2280(9) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $V = 471.77(9) \text{ \AA}^3$ ,  $Z = 8$ , and  $\rho_{\text{XRD}} = 1.2545(2) \text{ g/cm}^3$ . The hydrogen-bonded methylhydrazinium and azide ions form layers. The methyl groups of the methylhydrazinium ions are above and below these layers, so that two methyl groups are between each layer [505, 506]. Similar tests were performed for dimethylhydrazinium azide [507].

Methylhydrazinium(1+) azide showed almost no sensitivity toward shock or friction. No detonation was observed after dropping a weight of 5 kg from 50 cm onto this compound, nor was any detonation observed when grinding the compound in a mortar.

### 5.4 Properties of Methylhydrazinium(1+) Nitroformate

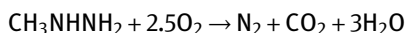
Methylhydrazinium nitroformate crystals were prepared and characterized by XRD, NMR, Raman, and IR spectroscopy along with five other nitroformate salts of aliphatic amines [508].

## 6 Combustion of MMH

Methylhydrazine is a monopropellant and a fuel. MMH monopropellant decomposition can be characterized by measuring strand burning rates of liquid MMH in a quartz capillary or in a consumable straw. There are numerous strand burning rate measurements on hydrazine, and similar ones, but not as many, strand burning rate measurements have been made on MMH and even on UDMH. In addition, burning rates of strands or droplets of MMH in oxidizing atmospheres needed to be measured.

## 6.1 MMH Flames in Oxidizing Atmospheres

In analogy with the study on self-heating and spontaneous heating of hydrazine [509], the self-heating and spontaneous ignition in the combustion of MMH in oxygen were examined [510]. The combustion according to:



is exothermic with  $-1340 \text{ kJ/mol}$  ( $-320 \text{ kcal/mol}$ ). The critical conditions of pressure, temperature, diluents, and oxidizer–fuel ratio were examined in this investigation. Uncommon among gas-phase reactions, the combustion of MMH is dominated by thermal effects, and no obvious symptoms of radical chain branching could be detected. The technique used by Gray consisted of premixing MMH and oxygen at ambient temperature and admitting it to a heated, evacuated vessel while simultaneously recording temperature and pressure until ignition occurred. A thermocouple in the center of the vessel would frequently read temperatures higher than the wall temperature before ignition occurred, indicating a self-heating mechanism preceding actual ignition. An activation energy for the  $\text{O}_2/\text{MMH}$  reaction was derived from the slope of a  $\ln(P_c/T_a^2)$  versus  $1/T_a$  curve, where  $P_c$  is the critical pressure at which ignition occurs and  $T_a$  is the initial temperature of the Pyrex vessel. The calculated activation energy was  $80 \text{ kJ/mol}$  ( $19.1 \text{ kcal/mol}$ ), which compared well with  $101 \text{ kJ/mol}$  for hydrazine itself and  $67.3 \text{ kJ/mol}$  for UDMH.

## 6.2 Droplet Burning of MMH in Oxidizing Atmospheres

The burning of MMH droplets in an  $\text{NO}_2$  atmosphere is the key mechanism for hypergolic rocket engines with NTO/MMH. The application of this rocket propellant combination and the ignition delay of impinging liquid NTO and liquid MMH will be discussed in future volumes on hypergolic bipropellant combinations.

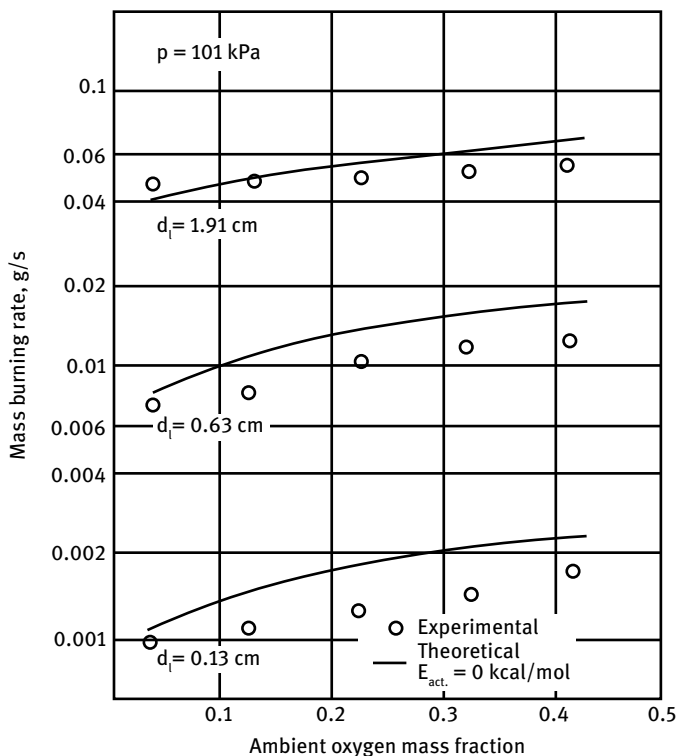
The burning of MMH and UDMH droplets in oxidizing atmospheres (other than  $\text{NO}_2$ ) was studied as a means of separating the monopropellant decomposition and oxidizer-supported flames of MMH or UDMH combustion, and also in comparison with hydrazine [511–513]. The flat-flame burner could be fed with lean fuel mixtures, generating oxygen-rich hot gases in which secondary combustion of the droplet vapor decomposition products would take place. The conditions included  $1660\text{--}2530 \text{ K}$  at ambient pressure. The tests used single droplets suspended from a quartz filament measuring  $100 \mu\text{m}$  in diameter as well as porous Alundum spheres. Droplet diameter could thus be varied from  $0.11$  to  $1.91 \text{ cm}$ . The fuel droplets were burned in the hot gaseous combustion products of a flat-flame burner to simulate rocket engine operating conditions. The flat-flame burner could be fed with lean fuel mixtures, generating oxygen-rich hot gases in which secondary combustion of the droplet vapor decom-



position products would take place. The conditions included 1660–2530 K at ambient pressure. Decomposition flames were not luminous at all, but oxidation flames of all three fuels showed two separate distinct zones of luminosity.

Whereas the results of the hybrid model and a bipropellant evaporation model were quite different for hydrazine, the distinction was not as pronounced for MMH or UDMH. In the hybrid mode, the monopropellant decomposition of the fuel prior to combustion was taken into consideration. The results indicated that fuels capable of hybrid combustion showed increasing burning rate with increasing ambient oxygen concentration (Figure 32), diameter, and ambient temperature. Similar graphs for hydrazine instead of MMH have already been shown in this publication, the *Encyclopedia of Liquid Fuels*, chapter “Hydrazine.”

Comparing the hydrazine and MMH decomposition rates, it is obvious that MMH monopropellant droplet burning proceeds more slowly than that of hydrazine in spite of the higher volatility of MMH and increased luminosity of MMH decomposition flames.



**Figure 32:** Methylhydrazine droplet mass burning rate at various oxygen concentrations. (Reproduced and modified from [22] as adapted from [511].)

Methylhydrazine droplet burning in  $N_2O_4$  atmospheres was studied over a wide range of pressures and Reynolds numbers to simulate processes near the injector plane inside a bipropellant rocket engine [514]. The oxidizer droplet adjacent to the fuel droplet substantially influenced the flame configuration and the vaporization rate of the fuel droplet. At low Reynolds numbers ( $N_{Re} < 20$ ) the fuel droplet vaporization rate increased due to either a leading or a trailing oxidizer droplet. At high  $N_{Re}$ , the fuel droplet evaporation rate was not much influenced by the proximity of an oxidizer droplet. Multiple flame configurations and vaporization rates characteristic of temperature-sensitive, high activation energy Arrhenius kinetics, which occurred under certain flow conditions for *n*-octane droplets burning in air, were not exhibited by the NTO/MMH hypergolic propellants, which were characterized by a low activation energy of reaction.

In a study of the evaporation of MMH droplets at high pressure, the MMH droplet radius and temperature at different environmental pressure was computed and compared with experimental results [95]. The rate of evaporation, the heat transfer coefficient, and the mass transfer coefficient were considered and computed and they agreed well with the test data. The effect of the Lewis number on the limit pressure of evaporation was evaluated and it showed that the evaporation model and the computational method were correct. This method may be used to evaluate the evaporation of other fuels.

### 6.3 MMH Flames in Oxidizing Atmospheres

The hypergolic ignition and combustion of MMH in rocket engines will be presented in a future *Encyclopedia of Hypergolic Bipropellant Combinations*.

#### 6.3.1 MMH Flames in Nitrogen Dioxide Atmospheres

If both oxidizer and fuel tanks of an NTO/MMH propulsion system leak and form separate puddles on the ground, ignition will occur at the boundary of the two puddles. Because  $N_2O_4$  evaporates faster than MMH, the atmosphere in the vicinity of this mishap will be  $NO_2$ -rich and hover over the liquid MMH pool. An experimental study of an NTO/MMH counterflow pool flame was conducted to obtain data that had to be matched to proposed detailed chemical reaction mechanisms [515]. The flames were observed and videotaped through high-speed imaging of chemiluminescence of broad-band light emission with Band Pass Filters centered at  $310 \pm 5$  nm and  $430 \pm 5$  nm. One-dimensional numerical simulations with detailed chemical kinetics were performed to help explain the flame structures observed in the experiment, considering, along with the proposed reaction mechanisms, the MMH puddle evaporation environment at the boundary conditions. The experimental results showed a multi-layered flame structure of an NTO/MMH non-premixed flame composed of two orange

flames and one weak blue/white flame. Results obtained in numerical simulations indicated that NTO/MMH forms the multi-layered flame structures of two orange flames owing to  $\text{NH}_3$  decomposition and  $\text{NO}_2$  recombination, and the blue/white flame was in the region between the two orange flames.

## 7 Handling of MMH

Because of the toxic and corrosive properties of hydrazines including MMH and UDMH, these compounds should not be handled in the literal sense of the word, that is, with bare hands or in intimate contact with the skin. The toxic and corrosive properties of hydrazines make it mandatory that precautions necessary for safe handling be sufficiently understood. Once the proper precautions for storage and transfer of hydrazines have been taken, hydrazines can be handled as safely as any other hazardous chemicals. Adequate operator training in propellant loading will prevent future accidents. It is the objective of this chapter to provide the MMH user with at least the most important information to get the job done safely and successfully.

The main application for MMH is in space propulsion. Space propulsion system hazards for hydrazines and other rocket propellants are summarized in the *Space Propulsion Hazards Manual* [516–518], a three-volume series useful for the planning of ground-service equipment and fueling operations. It was even intended to convert this paper manual to a CD-ROM with hypertext crosslinks.

Hypergolic propellants, NTO and MMH, can be handled safely if propellant loading personnel is properly trained. A 2-day training course for the safe handling of hypergols was developed and used for training purposes at NASA [519]. The design of hypergolic propellant ground service equipment for fueling launch vehicles and satellites at NASA KSC is outlined in [520].

### 7.1 Storage, Transportation, and Disposal of MMH

Storage facilities for MMH are needed at the point of production, as a method of government stockpiling of strategically important fuels, logistics at the point of consumption to assure against interruptions of supply, and finally, for the storage of waste propellant waiting to be reprocessed or destroyed.

#### 7.1.1 Storage Compatibility Requirements and Setback Requirements for Liquid Propellants

Quantity-distance regulations set forth in the US Army Safety Manual [521] first categorize all propellants into four hazard groups I through IV, then assign six storage com-

patibility groups A through F. Hydrazine, MMH, UDMH, Ae-50, and mixed amine fuels have been classified in Hazard Group III and Storage Compatibility Group C. A 200-kg (440-lb) drum of MMH in unprotected storage requires a setback of 180 m (600 ft) from inhabited buildings, public traffic routes, and other storage structures containing incompatible propellants. If the drum is in a protected bunker, the setback requirement is reduced to 39 m (130 ft). For ten drums of MMH, the unprotected setback is still the same, 180 m, but the protected setback is increased to 63 m (210 ft).

### 7.1.2 Reportable Quantities for Storage of MMH under SARA Title III

The presence of Extremely Hazardous Substances in quantities in excess of the Threshold Planning Quantity (TPQ) in the vicinity of inhabited areas requires certain emergency planning activities to be conducted. A consolidated list of chemicals subject to reporting requirements under Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA), also known as the Emergency Planning and Community Right-to-Know Act (EPCRA), and chemicals listed under section 112<sup>®</sup> of Title III of the Clean Air Act of 1990 was posted on an Environmental Protection Agency (EPA) web site for distribution and downloading in November 1998. This “Mother of all Lists” has been prepared to help firms handling chemicals to determine whether they need to submit reports under sections 302, 304, or 313 of SARA Title III (EPCRA) and, for a specific chemical, what reports may need to be submitted. Releases of Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) hazardous substances, in quantities equal to or greater than their reportable quantity (RQ), are subject to reporting to the National Response Center under CERCLA. Such releases are also subject to state and local reporting under section 304 of SARA Title III (EPCRA). The provisions of the Act are found at 40 CFR Parts 350 through 372. SARA Title III has two distinct goals: to encourage and support advance emergency planning for responding to chemical accidents, and to provide local governments and the public with information about possible chemical hazards in their communities. The TPQs for various hydrazines are summarized in Table 38 and 39.

**Table 38:** Threshold planning quantity of hydrazines.

| CAS RN   | Chemical name     | Reportable quantity (pounds) | Threshold planning quantity (pounds) |
|----------|-------------------|------------------------------|--------------------------------------|
| 302-01-2 | Hydrazine         | 1                            | 1000                                 |
| 60-34-4  | Methylhydrazine   | 10                           | 500                                  |
| 57-14-7  | Dimethylhydrazine | 10                           | 1000                                 |

CAS RN = Chemical Abstracts Service Registry Number

Data source: [522]

**Table 39:** Hydrazines in the consolidated list of chemicals subject to emergency planning.

| CAS RN   | Chemical name         | Quantity, lb       |        |           |               | RCRA CODE |
|----------|-----------------------|--------------------|--------|-----------|---------------|-----------|
|          |                       | Sec. 302 (EHS) TPQ | EHS RQ | CERCLA RQ | CAA 112(r) TQ |           |
| 57-14-7  | 1,1-Dimethylhydrazine | 1000               | 10     | 10        | 15000         | U098      |
| 60-34-4  | Methylhydrazine       | 500                | 10     | 10        | 15000         | P068      |
| 302-01-2 | Hydrazine             | 1000               | 1      | 1         | 15000         | U133      |

CAS RN = Chemical Abstracts Service Registry Number, EHS = extremely hazardous substance, RQ = reportable quantity, TPQ = threshold planning quantity, CAA = Clean Air Act, TQ = threshold quantity, RCRA = Resource Conservation and Recovery Act

Note: Hydrazines in the Consolidated List of Chemicals Subject to the Emergency Planning and Community Right-To-Know Act (EPCRA) and Section 112(R) of the CAA, as amended November 1998.

Data source: [523]

## 7.2 Transportation Regulations for MMH

This section is only an incomplete summary of regulations and recommendations affecting the storage and the transfer of hydrazines. Regulations change daily and the hazardous materials coordinator for a chemical company or rocket test site will need to follow updates on a day-to-day basis. This is a full-time job.

The transportation of hydrazines in interstate commerce must comply with the Code of Federal Regulations CFR 49, § 172.101. According to the 1987 revision of that document, MMH was then classified as a **Flammable Liquid** and **Poison**. Because regulations change frequently, it is advisable to check the most recent revision for the applicable requirements before shipping any hydrazines. For transportation, MMH is in Hazard Class 6.1 and has the UN number 1244. The RQ is 10 kg.

## 7.3 Off-Loading of MMH from Spacecraft

Occasionally, it becomes necessary to off-load (de-tank) propellants from a fueled satellite or space probe because the launch date has been postponed or because repair work on a damaged spacecraft cannot be conducted in proximity to loaded propellants.

Off-loading has become necessary for the European GALILEO (MMH and NTO), ARTEMIS (MMH) and ROSETTA (MMH). Note: ARTEMIS was ESA's first GEO data relay communication satellite. Not to be confused with the US planned crewed mission revisiting the Moon, also called Artemis. All spacecraft in this category used bipropellant systems and tanks with surface tension propellant management devices (PMDs). In most cases only the fuel was removed and the oxidizer was left in the tanks, because

its removal or depressurization might introduce gas bubbles into the capillary gallery or the bubble traps and cause loss of NO from MON. Also, evaporation of NTO or MON leaves behind a thin film of nitric acid that would make the corrosion environment even worse than in NTO. There are no generally accepted guidelines for off-loading of propellants from spacecraft, so the personnel in charge of the operations had to develop their own procedures. Some spacecraft do not even have a drain at the lowest point in the system that allows all liquid to be drained by gravity. Other line plumbing systems may have check valves that allow liquid to flow only in one direction, into the tank, and not out of the tank. Most plumbing schematics have dead-ended passages where propellants pool and cannot be removed by flushing.

In the case of ROSETTA, the cancellation of the ROSETTA launch to Comet Wirtanen in 2003 left the spacecraft fully fueled but with no target launch date [524]. While a new mission scenario was being devised it was necessary to make the spacecraft as safe as possible to carry out essential work on the payload and subsystems. It was required to offload all of the MMH fuel to minimize the explosive potential of the spacecraft. In addition, a reduction of the MMH vapors remaining in the spacecraft tanks to a maximum of 1200 ppm was required. Fortunately, MMH is more volatile than hydrazine and MMH is easier to remove than hydrazine. There was no need to unload the MON oxidizer, but a method was proposed to inert the oxidizer tank if the need should arise for an unforeseen reason.

## 7.4 Evaporation and Atmospheric Dispersion of MMH Spills

Chapter “Hydrazine” in *Encyclopedia of Liquid Fuels* contains a fairly detailed summary of studies and computer models for predicting the rate of evaporation and atmospheric dispersion of MMH spills, in addition to similar studies for hydrazine itself, UDMH, Ae-50, and NTO. Only a few of these models include degradation of MMH vapors by autoxidation, photolysis, or adsorption on aerosol particles in the air.

## 7.5 Spill Neutralization of MMH Spills

In spite of all care devoted to planning and conducting storage and transfer of hydrazines, occasional spills may occur. Transfer personnel should be well trained in the containment and neutralization of hydrazine spills. Disposal and spill cleanup of hydrazine(s) fuels has been practiced for many decades and there is a good database on available methods for safe handling of these propellants, for instance chapter 2 in [525].

The most frequently used spill neutralization agent for small spills of hydrazines is liquid chlorine bleach, which is available in most households. In the more storable solid form, hypochlorite is available as calcium hypochlorite (HTH<sup>®</sup>) as a swimming

pool disinfectant. In the experiments with MMH or UDMH and hypochlorite, GC-MS and GC-FTIR analysis of the reaction mixture revealed numerous reaction products that might also be poisonous [526–529]. Bioremediation of MMH spills in high concentrations may not be possible owing to the toxicity of MMH to bacteria in the water and in the soil (see Section 11.12).

Covering up a propellant spill with a layer of foam will not neutralize it, but it will prevent or retard vaporization for a limited time while plans for more permanent neutralization of the propellant spill are being made and equipment for remote manipulation of the spill is put in place. High expansion foams can both quench fires and form a temporary but sufficiently durable barrier to limit the concentrations of vapors from spilled combustible and/or toxic liquids to acceptable levels. Spills of MMH in cargo holds or other closed spaces on ships require special precautions during decontamination to prevent the formation of flammable vapors [530].

## 7.6 MMH Leaks and Leak Detection

Methylhydrazine leaks in propellant storage areas could be detected with the same color-changing indicator paint that has also been tested with UDMH and NTO. Indicating paints irreversibly change color at the point where the leakage occurred [531, 532]. They can be used for detection of NTO as well as UDMH, Aerozine-50, MMH, or hydrazine.

Methylhydrazine or other propellants leaking into vacuum are going to cool by evaporation down to the triple-point temperature and liquid droplets soon freeze and turn into MMH snow. This condition was simulated by spraying liquid MMH into a vacuum chamber with visual (video camera) observation [533].

An all-optical leak detector incorporates a self-referenced, fiber-optics-based sensor platform for detecting MMH at ambient temperatures from 227 to 344 K (–46 to +71°C) [534]. This leak detector can be calibrated to detect leaks in the parts-per-million to parts-per-billion range in air. An optical sensor system can be networked to monitor multiple locations and in real time. An organically modified silicate (Ormocil) matrix was used to develop an optical leak detector for MMH.

## 7.7 MMH Venting to Vacuum and Inerting of Upper Stages

Explosions and fragmentations of spent upper stages or decommissioned satellites in space have been blamed on residual propellants and have created clouds of orbital debris. International space policies now require that upper stages and satellites be emptied of all residual propellants and be passivated (=inerted) at end-of-life.

A numerical study has been performed to evaluate the ARIANE 5 third-stage inerting by the separate venting of MMH and NTO third-stage tanks to vacuum after the

deployment of payloads and prior to re-entry. Two-dimensional viscous flow calculations have been performed through the venting nozzles, and two-dimensional simulations were used from the nozzle exit conditions to determine the plume characteristics [535, 536]. The flow rate decay with decreasing feed pressure was analyzed, and correlations were proposed to describe the plume spatial and temporal distribution. The solid-liquid-vapor phase diagrams of MMH and NTO were required for the analysis, and equilibrium phase changes were examined. It was concluded that the gaseous species produced by the venting process will not condense on surfaces warmer than 250 K. The phase change assessment requires further non-equilibrium condensation analysis, with experimental validation.

## 7.8 Vapor Scrubbers for MMH Fumes

Venting a supply tank after transferring MMH by pressurized transfer from one tank to another releases pressurant gas saturated with MMH vapors that need to be neutralized before they can be released to the atmosphere in the proximity of operators. The fumes have to be passed through scrubbers with sprays or bubble caps of a liquid absorbent or through cartridges with expendable solid sorbents similar to a gas mask canister. Liquid sorbent scrubbers are for stationary large installations where the liquid is recirculated with pumps. Solid sorbents are for small, portable applications. Plain water would absorb some of the MMH, but adding a non-volatile acid to the water spray makes it more effective. Absorbents that have been proposed or proven for removal of hydrazine vapors (as described in *Encyclopedia of Liquid Fuels*, chapter “Hydrazine”) may work equally well with MMH.

### 7.8.1 Vapor Scrubbers for MMH Fumes Using Liquid Absorbents

If only water is used as the scrubber liquid for removal of MMH vapors from vented pressurant gas, the efficiency of the scrubber and the vapor–liquid equilibrium is governed by Henry’s law. The Henry’s law constants have to be known to design a scrubber and determine how many stages are required to achieve satisfactory absorption of hydrazine(s) vapors contained in the pressurant gas of propellant tanks [537]. During the early 1980s NASA KSC initially used bubble-cap scrubber towers 0.5 m wide and 6 m high with 18 plates to absorb propellant vapors from gases vented from MMH servicing equipment into water [538]. Each plate carried 16 bubble caps, typical for chemical industry absorption towers. The propellant vapor was washed with water and the MMH-laden water was subsequently treated with hypochlorite in a separate installation. The scrubber was tested with gases containing 100 ppm hydrazine, 150 ppm MMH, 45000 ppm MMH, or 110000 ppm UDMH, and the effectiveness of the scrubber was verified by sampling the off-gas with Dräger tubes. Numerous alternative reagents have been proposed for hydrazine or MMH



removal. The scrubber system was later converted to operate on citric acid solutions instead of plain water. The bubble-cap scrubber was later replaced by a portable, skid-mounted  $1.8 \times 1.8 \times 3$  m system containing four vertical columns packed with Raschig rings. The four columns drained by gravity into a common 2800-L scrubber liquor tank located beneath the towers. The gas flowed through each of the four towers in series. Development tests were performed with 50000 to 200000 ppm MMH in the inlet gas [539]. The outlet MMH concentrations ranged from 0.3 to 1 ppm MMH, which was considered acceptable at that time. At the KSC, NASA disposes of the MMH-contaminated scrubber liquor through incineration. As an alternative, MMH in the solution can be destroyed by chlorination, but some of the citric acid will be destroyed as well, producing undesirable chlorinated hydrocarbons.

Fourteen percent aqueous citric acid solutions have been used with good success for hypergol vapor scrubbers, but sometimes mold grows on the citric acid solutions in storage while they are not in use. A biocide may have to be added to keep mold from growing. For disposal, the MMH-saturated citric acid solution, which still has to be treated as hazardous waste, is usually incinerated in a flare stack.

Hypergolic fuel and oxidizer scrubbers were examined to determine pass-through emissions produced during actual hypergol transfers [540]. Scrubber liquor used in the fuel scrubber was 14% citric acid solution and the scrubber liquor in the oxidizer scrubber was 5% NaOH + 12% Na<sub>2</sub>SO<sub>3</sub> solution.

Methylhydrazine vapor can be removed with 99.9% efficiency using scrubbers containing acetylacetone solutions as scrubbing liquors [541]. The acetylacetone converts MMH to a non-toxic heterocyclic compound. This approach may reduce the cost of scrubbers that otherwise have to be constructed from corrosion-resistant stainless steel to resist corrosive oxidizing agents previously used in destroying the residual MMH, and in addition it makes the exhausted scrubbing solution easily disposable.

$\alpha$ -Ketoglutaric acid (= 2-ketoglutaric acid, AKGA, HOOCCH<sub>2</sub>CH<sub>2</sub>C(O)COOH), a water-soluble solid, has been proposed for hydrazine or MMH vapor absorption from air or for decontamination of hydrazine- or MMH-contaminated rocket propulsion systems [542, 543]. The reaction of  $\alpha$ -ketoglutaric acid with hydrazine or MMH forms a non-volatile, non-toxic heterocyclic pyrimidine compound. A critical review of the patent claims and preliminary laboratory tests with  $\alpha$ -ketoglutaric acid for hydrazine or MMH vapor absorption or decontamination of hydrazine- or MMH-contaminated rocket propulsion systems concluded that the uncertainties of the completeness of the reaction and lack of complete identification of all reaction products prevented the practical application of this chemical under real-life rocket launch site ground service equipment conditions [544]. When reacting 0.73-M  $\alpha$ -ketoglutaric acid (AKGA) solutions in bench-top lab tests, a solid formed with hydrazine but not with MMH. In more dilute 0.2-M AKGA solutions no precipitate formed with either hydrazine or MMH. Another keto compound tested in hydrazine or MMH scrubber liquids was ethyl acetoacetate H<sub>3</sub>C—C(O)—CH<sub>2</sub>—C(O)—O—CH<sub>2</sub>CH<sub>3</sub> but its reaction with hydrazine or MMH produced a gummy, sticky substance

(a carbinolamine intermediate converting to 3-methylpyrazol-5-one) which clung to the walls and was difficult to remove.

### 7.8.2 Comparison of MMH Scrubber and Disposal Methods

The various organizations using hydrazine and hydrazine fuels are searching for improved ways to minimize vapor hazards during transfer and drum/tank car cleanup by installing propellant vapor scrubbers. The KSC has installed hypergolic vapor scrubbers for some of the fuel-handling operations [537, 540]. Vapor flow rates of 0.28–11 m<sup>3</sup>/min. and equilibrium vapor pressures from fuels up to 310 K (100 °F) warm must be considered. KSC vent stacks are 15 cm in diameter and 11 m tall. An engineering study considered and compared incineration, carbon adsorption, and condensing and refrigeration as alternatives to the scrubber design that served as a baseline. An alternative to direct flame incineration is catalytic incineration. The higher initial investment for platinum or rhenium catalysts might be compensated for by fuel savings in the long run because catalytic incinerators operate at a much lower temperature. Energy requirements for refrigeration as a means of vapor emission control would be excessive, and refrigeration is not an effective method for vapor control.

A LN<sub>2</sub>-cooled cryogenic cold trap was evaluated for the removal of MMH vapor from pressurant gases vented from fuel tanks following static tests or fueling of space vehicles [545]. Scrubbers (either bubbling impingers or trickle bed or bubble-cap counter-current designs) sometimes lack the efficiency for the complete removal of MMH or N<sub>2</sub>O<sub>4</sub>.

Four scrubbers of the S70-1094 type were in operation at NASA KSC launch pads and the Hypergolic Maintenance Facility [546]. These units were designed and built by Martin Marietta Corp., Denver. Each unit measured 2 × 2.4 × 3.3 m (6.5 × 8 × 11 ft) and weighed 2724 kg (6000 lb) dry and 3360 kg (7400 lb) wet. A 15% citric acid solution was recirculated by 100-gal/min. pumps and sprayed into a packed bed trickle bed absorption tower of 0.76-m (30-in) diameter and 2.1 m (7 ft) tall. The contaminated gas flow (up to 3.14 L/s = 400 scfm) passed through two beds in series. The first bed (1.2 m = 4 ft high) absorbed 99.5% of the MMH entering the unit. The second stage improved that removal by another 0.1–0.2% (absolute).

The MMH content of near-exhausted scrubber liquid from citric acid-filled scrubbers can be monitored using coulometric analysis [411]. The same method was also used to analyze gas samples collected with 0.1-N sulfuric acid-filled impingers in the exhaust stack of gases leaving the scrubber in order to verify 100% removal efficiency of the scrubbers.

Hypergolic fuels and oxidizer pressurant gases are (were) vented during fueling and deservicing of the Space Shuttle and other spacecraft and cleansed of toxic propellant vapors before being allowed to vent to the environment. The scrubbers are not 100% efficient and traces of propellant vapors pass through the apparatus. Scrubber emissions are difficult to measure owing to the intermittent purge flow and to the

presence of suspended scrubber liquor droplets. An alternative method of emissions monitoring was introduced [547, 548]. It was suggested that emissions can be determined from field scrubbers without direct measurement of vent flow rates and escaped hypergol vapor concentrations. This alternative approach was based on the scrubber efficiency, which was previously measured during normal steady-state operations, and on the accumulated weight of hypergol captured in the scrubber liquor, which is part of the routine monitoring data of scrubber liquors. The emissions from scrubbers can be calculated by measuring the buildup of hypergol propellant in the liquor, and then using the appropriate efficiency to calculate the fugitive emissions. An estimate of the total emissions from 16 scrubbers at NASA KSC over a period of 3 years indicated that 0.3 kg/year of fuel (MMH and hydrazine) and 234 kg/year of nitrogen dioxide were emitted [549, 550].

### 7.8.3 Vapor Scrubbers for MMH Fumes Using Solid Absorbents

Vapor-absorbent canisters widely in use for servicing F-16 Emergency Power Units (EPUs) with H-70 fuel can potentially be used for MMH absorption as well. The canisters contain potassium permanganate deposited on a granular material. A window reveals a color change when the cartridge is exhausted. F-16 fighter maintenance is done at many air bases all over the world. Pressurant gas from spent F-16 EPUs containing H-70 blend is usually vented through a 7.5-L (2-gal) stainless steel bucket containing 3.8 L (1 gal) of ordinary chlorine bleach (5% NaOCl). As an alternative, a transparent cartridge containing a dry chemical (100 g of alumina granules impregnated with potassium permanganate  $\text{KMnO}_4$ ) has been tested [539]. The  $\text{KMnO}_4$  undergoes a highly visible color change from purple to brown as the result of hydrazine or MMH absorption. The cartridge requires secondary treatment before being disposed of safely.

A candidate scrubber medium, AKGA, a solid adsorbed onto a silica-based substrate was examined as a potential alternative to the hydrazine-family hypergolic fuel neutralization techniques utilized at NASA KSC [551]. Earlier patents indicated that AKGA will react with hydrazines to produce non-hazardous, possibly biodegradable products. The use of AKGA aqueous solutions was demonstrated as a replacement neutralizing agent for citric acid, which was used as a scrubbing agent in liquid scrubbers at NASA KSC. Specific properties of the adsorbent examined include reaction efficiency, the loading capacity of AKGA onto various silica substrates, and the comparison of AKGA media performance with that of the citric acid vapor scrubber systems at KSC and a commercial vapor scrubber medium. Preliminary investigations showed hydrophobic aerogel particles to be a suitable substrate for the deposition of AKGA. AKGA-Aerogel absorbent was more efficient and cost effective than commercially available fixed bed scrubber media, although much less cost effective than liquid-based citric acid stationary or semi-portable, skid-mounted scrubbers (although possibly safer and less labor intensive). A comparison of all three alternative scrubber technologies (liquid AKGA, solid-phase AKGA, and

commercially available sorbent materials) was made considering both hypergol vapor neutralization capabilities and relative costs, compared with the citric acid scrubbing technology in use at NASA-KSC. A critical review of the patent claims and preliminary laboratory tests with AKGA for hydrazine or MMH vapor absorption or decontamination of hydrazine- or MMH-contaminated rocket propulsion systems concluded that the uncertainties of the completeness of the reaction and lack of complete identification of all reaction products has so far prevented the practical application of this chemical under real-life rocket launch site ground service equipment conditions [544].

For propellant vapors vented from propellant tanks in space, the liquid scrubber approach is not feasible. Solid sorbents or cryo traps have to be used to neutralize and immobilize vapors from propellant transfer operations in orbit. Refueling of satellites in orbit with storable propellants involves venting part or all of the displaced gas from the tank being refilled during the filling operation. Pressurant gas from the source propellant tanks has to be vented on completion of the operation. This gas will be saturated with propellant vapor, and it may also have significant amounts of entrained fine droplets (mist) of propellant. Various possible ways of neutralizing vented MMH and NTO propellants were examined [552]. The mass of propellant vented in a typical refueling operation can be in the range of 0.2–5% of the tank capacity, depending on vapor pressure of the propellant, tank temperature, and ullage volume. Four potential neutralization schemes were examined, including chemical decomposition, chemical reaction, condensation, and adsorption. Chemical decomposition to essentially inert materials is thermodynamically feasible for both MMH and  $N_2O_4$  and would be the simplest and easiest neutralization method to implement. Chemical decomposition would require more complex control. Condensation would require a cryogenic refrigeration system and a very efficient cold trap/phase separator. Adsorption systems are much heavier, which is a severe penalty for every kilogram of mass that has to be lifted into orbit.

It has been proposed to add an absorption tower packed with granular activated alumina downstream of the scrubber outlet to securely remove all traces of propellant vapors from the contaminant-laden gases that are vented from a pressurized tank [553]. For MMH, the gases would first be bubbled through 10% sulfuric acid to remove the bulk of the MMH and then cleaned up in the alumina bed. It was not planned to reuse the alumina as regeneration may be more expensive than obtaining new material. The hazardous waste category of the spent alumina had not been established.

## 7.9 MMH Wastewater Decontamination

There are many wastewater treatment methods for hydrazine- and UDMH-containing wastewaters that can be applied equally well to MMH-containing wastewaters.

### 7.9.1 MMH Wastewater Decontamination by UV/Ozone Treatment

One of the more effective treatment methods is a combination of ozone and UV illumination. Ozonation products of wastewater containing hydrazine and hydrazine-related rocket fuels were characterized [554, 555]. Minor amounts of nitrate were produced from the ozonation (synonyms: ozonization, ozonolysis) of hydrazine, MMH, and UDMH. This was probably a result of ammonia or nitrosamine oxidation. MMH ozonation produced methanol and several other peaks, probably formaldehyde, formic acid, and formaldehyde monomethylhydrazone.

The rate of hydrazine destruction by UV ozonation is greatest at a pH of 9.1. The improvement attributable to UV illumination was small for hydrazine itself, but significant for the methylhydrazines. One of the oxidation products observed was methanol. The oxidation of MMH and UDMH by ozone alone is not complete but leads to organic by-products that may also be toxic [321]. Products of partial ozonization of MMH included methanol, formaldehyde, formic acid, and formaldehyde methylhydrazone. Products of partial ozonization of UDMH included acetone, formaldehyde methylhydrazone, formaldehyde dimethylhydrazone, NDMA, dimethylformamide, and tetramethyltetrazene. Aquatic bioassays with fish and *Daphnia* indicated that the toxicity of the propellant rinse waters was somewhat reduced as the result of ozonization. Again, it must be emphasized that ozonation alone is not completely effective in decontaminating MMH-contaminated wastewater. Mechanisms of various photolytic reactions of hydrazines and nitrosamines are summarized in Section 4.3.

The NASA WSTF acquired an ozone generator capable of producing 2.75% ozone in oxygen and installed it in a pilot-scale reactor [556–558]. It was important to feed the ozone generator with dry oxygen and maintain its temperature below 287 K to optimize the ozone yield. The UV ozonator reactor was a rectangular chamber with six spray nozzles capable of flowing 3.8 L/min and atomizing the liquid into a fine spray. The residence time of the droplets during each passage was ~14 s. Twenty-three low-pressure UV lamps rated at an average output of 6.6 W of UV light were mounted through the sides of the chamber. The power consumption of the UV lamps was 152 W. The liquid containing 300–700 ppm MMH to be treated was circulated by pumps and flowed back into a sump. The liquid (132 L/batch) was recirculated until the desired destruction level (non-detectable level of NDMA) was achieved. Experiments with hydrazine lasted 78 h, MMH 180 h, and UDMH 334 h. It was detected that one of the slowest, rate-determining steps is the oxidation of methanol to formaldehyde. Ozone dissolves in cold water better than in hot water. Dissolved ozone continues to react during extended storage of solutions in the sump in the dark and the MMH-derived chlorine-oxidizable contaminant level continued to drop slowly during inactive off-time, while the treated waste was stored in a pond.

The NASA WSTF then fabricated and tested a full-scale 85.2-m<sup>3</sup> (2,250-gal) hydrazine wastewater treatment system [559]. The system was based on an IITRI design featuring the use of ozone and UV to destroy the hydrazines and NDMA. A series of 21 tests evaluated the performance of the system using synthetic mixtures of hy-

drazine, MMH, and UDMH at concentration levels of 100 and 3900 ppm. In addition, one of these tests was performed on actual wastewater obtained from a Vandenberg Air Force Base launch site sump. The tests demonstrated that the UV ozonization system would satisfactorily reduce the hydrazine concentration to less than 5 ppb and the NDMA concentration to less than 100 ppt.

### 7.9.2 MMH Wastewater Decontamination by Reaction with Hypochlorite

The reaction of MMH with sodium hypochlorite does not go to completion and a large number of oxidation products form. Nearly 30% of the original nitrogen remains in solution in the form of different nitrogen compounds. During the treatment, the solution gradually turned yellow as more hypochlorite was added. The color persisted if the solution was allowed to stand after the gas evolution had ceased [526]. Addition of carbon dioxide to MMH solutions prior to neutralization with liquid bleach increased the number of organic products seen in the reaction mixture.

### 7.9.3 MMH Wastewater Decontamination by Reduction Treatment

Dilute aqueous solutions of hydrazine, MMH, or UDMH can be decomposed by catalytic reduction with nickel/aluminum (Ni-Al) alloy under basic conditions [560, 561]. The reaction is based upon dissolution of Al from the Ni-Al alloy in aqueous media to form aluminum ion and hydrogen gas. The resultant finely divided nickel catalyzes reduction of the hydrazine, nitrosoamine, and/or nitroamine by the hydrogen produced. Greater than 99% of propellants contained in dilute hydrazine or MMH aqueous solutions were decomposed when reacted with Ni-Al alloy in 0.5 M sodium hydroxide. The major reaction product of MMH was methylamine. Control experiments with plain Al powder rather than Ni-Al alloy showed no effect on hydrazine, MMH, or UDMH. Spill pillows containing Ni-Al alloy and solid sodium hydroxide were also tested and found to be effective in the absorption and decomposition of MMH in aqueous solutions. These results showed that reductive decomposition of hydrazine, MMH, or UDMH is a promising method for propellant hydrazine(s) waste water treatment and spill control.

### 7.9.4 MMH Wastewater Decontamination by Bioremediation

The disposal of wastewater containing hypergolic propellants (including MMH rinse waters) by keeping them in an open holding pond with bioregeneration through water hyacinths has been tested in Florida [525, 562]. The products of the scrubbing reaction of MMH and NaOCl are  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CH}_4$ . The waste MMH scrubber liquor consisted of aqueous solutions containing small amounts of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$  as well as large amounts of  $\text{CH}_3\text{OH}$ . This waste was scheduled to be disposed of in stabilization ponds along with nitrate and nitrite salt solutions obtained as waste liquors from the  $\text{N}_2\text{O}_4$  scrubbers.

Effluent from an MMH scrubber can be neutralized and kept in a holding pond for complete oxidation and interaction with aquatic plants [563]. Active contributions by sunlight-induced neutralization–oxidation reactions may accelerate the biological process.

## 7.10 Personnel Protection Equipment for MMH

Protective clothing to be worn by personnel in the vicinity of a pressurized MMH system depends on the type of operation to be performed [564]. A group of 28 glove materials, 9 suit materials, and 3 other materials were tested for permeability to MMH, hydrazine, or NTO following exposure to these propellants for 90 min. [565, 566]. Breakthrough times were calculated for predefined “breakthrough” concentrations of 16 ppb MMH and saturation concentrations of 1.6 ppm MMH. These breakthrough times were tabulated for several samples of each material used in the tests. Breakthrough times were determined and correlated with static permeation rates. Of the 28 glove materials, 9 had breakthrough times for hydrazine of less than 90 min. (2 of these shorter than 10 min.), 1 was marginal, 3 had barely detectable permeation, and 15 resisted permeation for at least 90 min.. The comparable times for MMH were much shorter, namely 19, 5, 1, 1, and 7 min. This indicated that it is more difficult to find good gloves for MMH protection than for hydrazine protection.

Several decontamination procedures for personal protective suit materials in use at NASA WSTF, including Chloropel (a chlorinated polyethylene) were tested after the material was subjected to NTO or MMH [567]. Each exposure sequence was followed by a simple room temperature water wash decontamination sequence. Two versions of heated decontamination sequences were used: **(1)** a simple purged heated sequence, and **(2)** a heated evacuation sequence. After the second water decontamination sequence these two versions of heated decontamination sequences were used to further reduce the concentration of residual fuel trapped in the material.

### 7.10.1 Gas Masks for Protection Against MMH Vapors

The MSA rocket propellant gas mask canister BMN-SSW has an indicator that changes color when the capacity of the gas mask is exhausted. Its absorbing capacity for MMH has been determined [568].

### 7.10.2 Full-Body Suits for Protection Against MMH

In hypergolic propellant spill tests at NASA WSTF, it was determined that the exterior of the protective equipment may be exposed to vapor concentrations as high as 800 ppm MMH. These results were then used for permeation testing of different protective clothing materials [569, 570].

The self-contained atmospheric protection ensemble (SCAPE) suits used at NASA launch sites are made from a chlorobutyl-coated Nomex fabric. The fabric and its coating is subjected to wear and tear and its integrity needs to be monitored daily [571].

Splash evaporation tests of propellants spilled on space suit materials at three different initial sample temperatures showed that most propellant spills freeze almost immediately in vacuum [572, 573]. Hydrazine supercooled to 355 K and then froze to ice, which was near the triple-point temperature. The force needed to scrape frozen hydrazine from the material sample by scraping and the time needed to sublime frozen hydrazine under one solar flux (simulated with a heat lamp) was measured. MMH did not freeze but evaporated before much ice could form. MMH was the only propellant that visually damaged the suit material. Aluminized Mylar layers were found to be dissolved in the area where the propellant had impinged on the fabric. Supercooled MMH dissolved the aluminized Mylar layers of the suit ensemble, and both hydrazine and MMH caused cracking in the polycarbonate helmet visor, but not in the helmet material alone.

Permeation resistance was determined by measuring the breakthrough time and time-averaged vapor transmission rate of MMH through the fabric of two types of personal protective equipment (PPE) suits [574]. The two types of PPE evaluated were the totally encapsulating ILC Dover Chemtursion, Model 1212 chemical protective suit and the FabOhio polyvinyl chloride (PVC) splash garment. Two exposure scenarios were simulated: **(1)** a saturated vapor exposure for 2 h, and **(2)** a brief MMH “splash” followed by a 2-h saturated vapor exposure. Time-averaged MMH concentrations inside the totally encapsulating suit were calculated by summation of the area-weighted contributions made by each suit component. Results showed that the totally encapsulating suit provides adequate protection at the new 10-ppb Threshold Limit Value Time-Weighted Average (TLV-TWA). The permeation resistance of the PVC splash garment to MMH was poorer than any of the totally encapsulating suit materials tested. Breakthrough occurred soon after initial vapor or “splash” exposure

Calculations showed that the maximum allowable permeation rates of hydrazine fuels through chlorinated polyethylene were of the order of  $0.05$  to  $0.08 \text{ ng cm}^{-2} \text{ min}^{-1}$  for encapsulating suits with low breathing air flow rates (of the order of 5 scfm or 140 L/min.) [575]. Above these permeation rates, the 10 parts-per-billion (ppb) TLV-TWA could be exceeded.

## 8 Materials of Construction for MMH

Quite often data for a particular material of construction may be available for one of the other three propellant hydrazines, but not for the hydrazine of interest. To a limited extent, it is possible to extrapolate metals compatibility data from one hydrazine to another. For metallic materials, the extrapolation is easier than for non-metals. Metals found to be compatible with hydrazine are most likely to be compatible with MMH and



UDMH too. Similarly, metals found to be compatible with MMH are most likely to also be compatible with UDMH. Polymeric organic materials are more likely to swell in UDMH than in MMH or hydrazine.

Materials compatibility data available from the literature often do not normally distinguish between static and dynamic compatibility, yet flowing propellants can be much more corrosive than what is observed in a static immersion test.

## 8.1 Materials Compatibility Test Methods

Experimental methods for determining the compatibility of hydrazine(s) fuels with materials of construction were already described in *Encyclopedia of Liquid Fuels*, chapter “Hydrazine.” Methods that have been successfully used for anhydrous hydrazine  $N_2H_4$  can equally well be used for MMH and UDMH and their mixtures.

### 8.1.1 Short-Term Exposure Tests

Before one endeavors to start long-term materials compatibility tests, a quick screening test is useful to eliminate materials that are obviously incompatible. Such open-air, visual observation tests in a Petri dish will also need to be performed on materials that are not necessarily wetted with hydrazine by design, but may be exposed to hydrazine in the case of an accidental propellant spill during fueling or a leak. A procedure for casual exposure of materials to hypergolic fluids has been developed [576]. A “casual” exposure is assumed to last less than 240 min. Fabric and splash shield and goggle materials intended to be used for PPE need to be subjected to more rigorous tests.

### 8.1.2 Medium-Term Exposure Tests

Before any material of construction in contact with MMH is allowed to fly on NASA missions, the reactivity of MMH with such materials of construction must be tested in accordance with NASA-STD-6001B Test 15 [577]. This test was previously published as part of NASA Handbook (NHB) 8060.1. In this apparatus, two identical test chambers made of Pyrex glass partially filled with MMH are connected to pressure transducers, but only one chamber contains the material sample under test immersed in MMH. The apparatus is immersed in a constant temperature bath at 344 K (71 °C = 160 °F) and the test is continued for 48 h. The pressure rise is not allowed to exceed the pressure rise measured when the same test is done with a reference material, CRES-304 for metals and Teflon for non-metals. In the case of the hydrazine fuels, the gas evolution rate is  $<7.0 \times 10^{-3}$  standard  $cm^3\ cm^{-2}\ h^{-1}$ . The post-test specimen is weighed and examined for changes in appearance, dimensions, and tensile strength. The off-loaded MMH liquid is analyzed for leached contaminants. Similar tests are done in the same apparatus for compatibility of materials with UDMH, anhydrous hydrazine, or dinitrogen tetroxide.

## 8.2 MMH Compatibility with Metals

Many summaries and survey papers on materials compatibility have been published, of which the following few may serve as starting points for further study. Most of these publications deal with more than one propellant, so the MMH data needs to be sorted out and separated from the rest of the data. A good summary of materials compatibility data for MMH is in the NASA WSTF MMH Manual [90].

A survey on MMH material compatibility (now obsolete) tried to assemble literature data on materials compatibility, but yielded only a few hard fact data [578]. The 6-year interim status report of the materials compatibility tests at JPL at 316 K (43°C) included data on CRES-303, CRES-304L, Ti-6Al-4V, and Al-6061-T6, which were considered acceptable and continued in tests with MMH, but samples of CRES-347 in MMH showed slight corrosion and it was rated as not acceptable for 10-year missions [239]. However, DOT allowed MMH to be shipped in CRES-347 containers. Initially, more than 700 test ampoules (including some with MMH or NTO) were placed in long-term storage testing at 316 K (110°F). Intermediate results after up to 5 years in storage at 316 K (110°F), based on the opening of 108 ampoules including 4 ampoules containing MMH were reported in [239]. At that time (1976), 578 specimen capsules remained in active test, and some were scheduled to remain in test for a full 10 years.

Additional tests with MMH at JPL included the materials Al-5052, Al-5083, Al-5086, Al-5154, Al-5254, Al-5454, Al-5652, Al-6061, and CRES-316, CRES-316L, and CRES-430 as single coupons and also in the welded form [579]. Storage tests were conducted using specification-grade MMH and a special grade (doped with water and carbon dioxide) for a period of 123 days at a temperature of 344.2 K (71.1°C = 160°F). Based upon the experimental test results, it was concluded that **(1)** aluminum alloy types 5052, 5086, 6061, and CRES types 316, 316L, 321, and 430 are compatible with both grades of MMH, and **(2)** that these materials and similar generic types would be suitable materials for use as shipping and storage containers for MMH propellant.

The 10-year compatibility results milestone report contained the results of the opening and examination of 36 ampoules containing hydrazine and 8 with MMH [228, 229]. After 10 years, 164 specimens plus 28 hydrazine controls remained in storage.

It is unfortunate that many materials compatibility studies did not specify the grade of MMH used, which may have contained various amounts of impurities that would have affected the metal compatibility. Some materials compatibility tests may have contained a trace of CFC-113 (Freon® TF), which was used as a cleaning fluid and not completely removed from the ampoules before inserting the samples. If hydrazine, MMH, or UDMH becomes accidentally contaminated with halocarbons, the corrosion of braze joints and the resulting rate of gas evolution is extremely bad [580, 581].

The selection of materials of construction has become very difficult for long-term space missions because frequently insufficient real-time, long-term storage data are available. The time available until the decision date/launch date is often too short to conduct a real-time evaluation. Many missions now exceed 15 years of design life. The

need for a test that allows metals compatibility testing to be accelerated was the driving force behind the development of an electrochemical test method [582]. Although this method was mostly used for anhydrous hydrazine, 2.1–3.1%  $\text{H}_2\text{O}$  as well as 10 and 30 ppm  $\text{Cl}^-$  were tested in MMH to demonstrate the usefulness of this accelerated compatibility test method for other propellants. Small amounts of  $\text{Cl}^-$  made  $\text{N}_2\text{H}_4$  or MMH incompatible with Al-6061-T6.

Metallic materials found to be acceptable for anhydrous hydrazine service are generally acceptable for MMH or UDMH service as well because hydrazine is a stronger electrolyte and more corrosive. For non-metallic polymeric materials, the organic hydrazines may cause more swelling and permeation than anhydrous hydrazine. In MMH, a very thin oxide coating was noted on two Al-6061-T6 specimens after 10-year storage at 316 K [228]. Although up to 100 ppm Al was found to be dissolved in the propellant, no catalytic effect was noted. Both CRES-304L and -347 exhibited minor corrosion and caused MMH discoloration. Analysis of off-loaded MMH showed 100 ppm Fe. Surprisingly, even Ti-6Al-4V showed some corrosion in MMH. Corrosion products were deposited in the vapor-exposed area and at the liquid–vapor interface. A small quantity of sediment was detected in a capsule that also contained chloride contamination. All three metals were rated acceptable for MMH service, but only a small number of off-loaded propellant samples were analyzed.

If MMH becomes accidentally contaminated with halocarbons (chlorofluorocarbon cleaning fluids or lubricants), the corrosion of braze joints is extremely bad [581, 583]. Sometimes halogenated solvents were used to clean only the pressurant gas system, which ordinarily would never be exposed to hydrazine(s), but pressurant gas carried residual solvent vapors into the propellant tank, where it reacted with MMH. In reproducing the problem in the laboratory, MMH was doped with 0.25 to 2.5% Freon-TF, and 96Sn/4Ag solder, Ti-6Al-4V, iridized aluminum 6061-T6, and stainless steel samples were immersed in the adulterated propellant for 63 days, becoming corroded. Corrosion in Freon-contaminated hydrazine or MMH was not caused by chloride. However, metal corrosion occurred when specimens were exposed to hydrazine and MMH that had been doped with hydrogen fluoride. A possible mechanism for formation of hydrogen fluoride includes dechlorination of Freon to form chlorotrifluoroethylene ( $\text{CFCl}=\text{CF}_2$ ), which then reacts with hydrazines to liberate fluoride.

Because a complete compilation of all materials compatibility data with hydrazine fuels would easily fill another book equal in volume to this, a compromise format had to be sought in presenting materials compatibility data here. Therefore, Table 40 serves mostly as a guideline without providing too much detail for locating additional information on materials compatibility.

Many of the reports referenced here deal with more than one propellant in addition to MMH. Sometimes the same report contains valuable additional information on dinitrogen tetroxide (NTO) or other rocket propellants, which were already discussed in *Encyclopedia of Oxidizers*.

**Table 40:** Literature references to compatibility of metals with methylhydrazine.

| Material                | Ullage pressure rise | Weight change of test coupons | Analysis of residual MMH | Tankage and tensile tests | Stress corrosion     |
|-------------------------|----------------------|-------------------------------|--------------------------|---------------------------|----------------------|
| <i>Aluminum</i>         |                      |                               |                          |                           |                      |
| Al-1100                 | [230]                | —                             | —                        | —                         | —                    |
| Al-2014-T6              | [230]                | —                             | —                        | —                         | —                    |
| Al-6061-T6              | [228–230]            | [228, 229]                    | [228, 229]               | —                         | [228, 229]           |
| <i>Stainless steels</i> |                      |                               |                          |                           |                      |
| CRES-303                | [228, 229]           | [228, 229]                    | [228, 229]               | —                         | [228, 229]           |
| CRES-304L               | [228, 229]           | [228, 229]                    | [228, 229]               | —                         | [228, 229]           |
| CRES-316                | [228, 229]           | [228, 229]                    | [228, 229]               | —                         | [228, 229]           |
| CRES-321                | [230]                | —                             | —                        | —                         | —                    |
| CRES-347                | [228, 229]           | [228, 229]                    | [228, 229]               | —                         | [228, 229]           |
| CRES-410                | —                    | —                             | —                        | —                         | [584]                |
| <i>Other steels</i>     |                      |                               |                          |                           |                      |
| AISI-4130               | —                    | —                             | —                        | —                         | [584]                |
| 17-7PH                  | [230]                | —                             | —                        | —                         | —                    |
| <i>Titanium alloys</i>  |                      |                               |                          |                           |                      |
| Ti-6Al-4V               | [228–230]            | [228, 229]                    | [228, 229]               |                           | [228, 229, 585, 586] |
| Ti-15V-3Cr-3Al-3Sn      | [587–589]            | —                             | —                        | [587–589]                 | —                    |
| <i>Other alloys</i>     |                      |                               |                          |                           |                      |
| Inconel-X-750           | [230]                | —                             | —                        | —                         | —                    |

Even after published data are located, there are often serious questions and some doubt about the reliability of these data and their applicability to the current materials selection task at hand. None of the publishers accepts any responsibility for the accuracy of these data. The conditions under which the compatibility was determined vary widely from laboratory to laboratory and there are only a few standardized test procedures.

### 8.3 MMH Compatibility with Aluminum Alloys

The aluminum alloys Al-1100-0, Al-2014-T6, and Al-2219-T87 were rated compatible with MMH for 300 h at 135 °C, with no corrosion or MMH decomposition [590, 591]. In looking for materials for advanced spacecraft valves, several hundred literature references on 21 different propellants that were in use as of 1967 or anticipated to be used within the next 10 years, including MMH, were assembled, but the report on pages 1-20 through 1-22 lists only material and temperature for compatibility, not duration of im-

mersion [592]. The report indicated that Al-3003, Al-5052, Al-5154, and Al-6061 alloys were compatible with MMH at 373 K (100 °C) or below for short-term use (2 weeks) [593].

Other propellant material compatibility tests at high temperatures showed an exothermic reaction of Al-2014-T6 and Al-6061-T6 alloys with MMH at temperatures in the 658–663 K (385–390 °C) range, which was lower than what was observed with CRES alloys [247]. No relationship with compatibility at lower temperatures could be inferred.

Heating MMH to 373 K (100 °C) for 7 days in contact with aluminum alloys Al-1100, Al-2014, Al-6061, corrosion-resistant steels types 321, 347, 17-7, and Inconel X-750 showed no increase in the decomposition of propellant and no noticeable corrosion of the metal surfaces [230].

In MMH, a very thin oxide coating was noted on two Al-6061-T6 specimens after 10 years at 316 K [228]. Although up to 100 ppm Al was found to be dissolved in the propellant, no catalytic effect was noted. Surprisingly, even Ti-6Al-4V showed some corrosion in MMH. Corrosion products were deposited in the vapor-exposed area and at the liquid–vapor interface.

#### **8.4 MMH Compatibility with CRES Alloys**

There was no significant corrosion or propellant decomposition with CRES-303 in contact with MMH for 1368 days at 316 K (43 °C) or with CRES-304L for 130 days at 316 K (43 °C) [239]. Corrosion was limited to faint tarnishing of the specimens. Approximately ten other test specimens (CRES-303, CRES-304L, CRES-316, CRES-347) were still undergoing testing, and after 6 years of exposure to MMH at 316 K (43 °C) no serious corrosion or propellant decomposition effects were noticeable.

The inlets to propellant valves are usually protected by filters to retain particles that might get lodged on the valve seat and cause the valve to leak when it is commanded shut. The screen material on the filters has to be compatible with the propellant, which in the case of hydrazines is not as difficult a task as with oxidizers. The corrosion product (carbazate, carbonate) film growing on the thin metal wires might cause a narrowing of the passages and increase the pressure drop or embrittle the wires. Similar wire mesh is used in surface tension propellant management devices in propellant tanks for zero-g operation. The long-term effects of propellant immersion on fine micronic stainless steel wire cloth were studied for hydrazine, MMH, and UDMH, and six other propellants [594, 595]. Immersion times reported in the literature ranged from 3 months to 7 years.

The stability and materials compatibility of MMH are greatly affected by the presence of impurities. Among the factors affecting the compatibility of MMH with stainless steel are the chemical composition of the oxide layer on the metal and the surface roughness. A number of techniques for modifying the Cr/Fe ratio at the 304L stainless steel surfaces were investigated [353]. It was concluded that thermal oxidation

gives the highest ratio (measured using X-ray Photoelectron Spectroscopy) followed by electropolishing, chemical treatments, and mechanical treatments.

## 8.5 Stress Corrosion Cracking in MMH

Most stress corrosion tests with various stressed (loaded) metal specimens are conducted in salt water environments. For many missiles or launch installations on coast lines, this may be an external rather than internal exposure condition. Magnesium chloride solutions are often used to produce worst case conditions simulating sea water. MMH is not a strong electrolyte, but contaminants, in particular chloride, in MMH can lead to crack growth and rupture of stressed metal, typically in pressurized tank walls.

Although AISI 4130 is generally not recommended for anhydrous hydrazine service because it rusts too easily, it is compatible with MMH and UDMH, based on static compatibility test results. With 4130 no crack extension occurred in UDMH up to at least 2000 h, whereas MMH caused growth after 500 h and hydrazine, after about 60 h. Stress corrosion susceptibility was evaluated for several alloys in hydrazine-type fuels [584]. The evaluation was on the basis of crack growth in wedge opening loaded fracture specimens. The alloys tested were classified in order of decreasing susceptibility as follows: CRES-4130, CRES-410, Inconel 718, Ti-6Al-4V, Al-6061-T6. The aluminum alloys showed no susceptibility. The order of decreasing stress corrosion cracking promotion for the fuels was hydrazine > MMH > UDMH. Crack growth susceptibility is related to contamination levels of water and carbon dioxide.

An investigation of the stress corrosion susceptibility of Ti-6Al-4V alloy in various fluids was initiated because of failures of this alloy in both dinitrogen tetroxide and absolute methanol. The study indicated that Ti-6Al-4V alloy is susceptible to stress corrosion cracking in absolute methanol in the annealed, solution-treated, and aged conditions. The threshold value for annealed material appeared to be near 50% of the yield strength or approximately 70000 psi, whereas the value of solution treated and aged material was somewhat less. Long-term exposure tests (2 years) indicated that the Ti-6Al-4V alloy is not susceptible to stress corrosion cracking in MMH, Aerozine-50, distilled water, absolute ethanol, Freon PCA, Freon MF, hydraulic oil (MIL-H-5606), acetone, absolute isopropanol, RP-1 fuel or trichloroethylene [585]. The titanium alloy Ti-15V-3Al-3Cr-3Sn (which allows the shear-spin forming of propellant tank hemispheres much more readily than Ti-6Al-4V) is not susceptible to stress corrosion in MMH for 1000 h at 322 K (120 °F). Sustained-load tests were performed at 322 K (39 °C) up to 1000 h with thin-gauge tensile specimens containing semi-elliptical surface flaws and stressed to 80% of the critical plane-strain stress-intensity factor.

## 8.6 MMH Compatibility with Non-Metallic Materials

Just as hydrazine and alkylhydrazines may attack metals, hydrazines may also alter chemical bonds and mechanical properties of organic polymers. Non-metallic materials are needed as gaskets, seals, containment bladders, diaphragms, and lubricants. In addition, it has been attempted to replace metals with lighter-weight engineering thermoplastics in support structures and tank walls where they would be in constant contact with the hydrazines. It has been very difficult to find totally compatible materials for each of these applications. Polymers found to be compatible with UDMH are most likely also compatible with MMH and hydrazine; similarly, polymers found to be compatible with MMH are most likely also compatible with hydrazine, but polymers known to be compatible with hydrazine may dissolve or swell in either MMH or UDMH.

Kalrez (“the material born to fly”) is often used for MMH gaskets in bipropellant systems, but is not suitable for hydrazine in monopropellant systems [242]. Kynar 460 may cause problems in MMH in contact with steel [596]. The exothermicity of MMH and Kynar was tested by DSC [597]. Teflon is the most inert polymer for gaskets and seals, yet at very high temperatures it can react with hydrazine or MMH and release fluoride ions [598].

Thermoplastic liquid crystal polymers including Vectra A 625 and Vectra C 950 were evaluated as components for MMH propellant turbopumps [599, 600]. The weight loss after only 7-day immersion in MMH was excessive, 11.6 to 22%, and these materials have no use in an MMH environment.

Composite overwrapped tanks with a thin metal shell allowed considerable mass savings in spacecraft design. If propellant is accidentally spilled on the outside or it leaks through a pinhole in the shell, the integrity of the composite overwrap may be jeopardized and the tank may burst [601].

An O-ring material used in storable propellant components on many NASA spacecraft designs was discontinued by the manufacturer and NASA’s stockpiles were expected to be depleted soon. NASA NESC initiated a materials compatibility characterization effort to evaluate multiple replacement material options. Material properties of multiple replacement candidates were tested, looking at weight change, swelling, hardness, compression set and tensile strength in representative environments to help identify suitable replacements [602]. See also [603].

### 8.6.1 Positive Expulsion Bladders and Diaphragms for MMH

Standard Teflon/aluminum laminate bladders employed as MMH zero-g propellant management devices on Mariner Mars 71 space probe failed because of cracks and tears near an aluminum seal ring that formed the mouth of the bladder [604]. These failures occurred during flight-acceptance tests with inert solvents (Freon TF and isopropanol) used as simulant fluids. It was found that one of the laminate polymers, FEP

120, was particularly solvent-sensitive and it was then eliminated from future laminates for expulsion bladders.

Seamless Teflon-positive expulsion bladders were used for MMH and Aerozine-50 propellants on Apollo Command Module, Service Module, Lunar Descent Module, and even on the S-IVB upper stage RCS [605]. A similar bladder was used for MMH on the unmanned Lunar Orbiter velocity control system.

Composite Teflon–aluminum foil bladders were evaluated for the Surveyor lunar lander vernier propulsion system in an effort to reduce helium permeation and propellant (MON-10 or MMH/H<sub>2</sub>O) saturation with pressurant gas [606, 607]. If the propellants were partially or fully saturated with helium, the large quantities of gas coming out of solution and the resulting two-phase flow decreased the dynamic response of the vernier engines. Propellant permeation into the ullage space was only a minor problem.

Bladders tested were initially made of multiple sprayed layers of tetrafluoroethylene (TFE) and fluoroethylene propylene (FEP). TFE was manufactured similar to a sintered powder metallurgical part by compressing the powder. FEP was similar in character to a true thermoplastic material. The major problem was bladder tearing during three-axis vibration, in particular at the lower temperature range [608, 609].

The ERIS projectile used two each of the NTO and MMH tanks in a cruciform structure in two opposing quadrants [610]. Both inner and outer rolling diaphragms were made of soft Al-1100-0. A thickness of 0.5 mm (0.020 in) was optimal with regard to rigidity under high-g loads and stiffness and resistance to feed pressure  $\Delta p$ . During expulsion, pressure acting on the piston surface peeled both the inner and the outer diaphragm away from their respective walls. The piston moved down the tank axis until it bottomed out. The Al-2219 composite-overwrapped pressure vessel (COPV) tanks were rated for an operating pressure of 2550 psia and 10 g axial, 4 g lateral acceleration. These tanks were instrumental in several successful flight tests. Other tanks were stored for 1 year and the contents fired through a set of thrusters in ground tests.

### 8.6.2 Lubricants for MMH Service

A perfluoro polyether grease made by DuPont, Krytox 240, appears to be compatible with hydrazine and MMH based on gas evolution measurements and corrosion of the metals [592]. Krytox greases contain a polymer of tetrafluoroethylene and perfluoroalkylpolyethers of the general formula  $F[CF(CF_3)CF_2O]_nCF_2CF_3$ . Krytox 240AC was widely used for servicing the Space Shuttle OMS/RCS bipropellant systems and did not interfere with the combustion process in a bipropellant engine.

### 8.6.3 Tubing for MMH Samplers

The selection of materials for the propellant vapor manifold for remote sampling of MMH vapors in rocket launch sites or during animal exposure tests required a special study. There was not so much concern about MMH inadvertently destroying



the tubing as concern about samples hanging up in the tubing on their way from the sampling location to a central analyzer. It was shown that with MMH, substantial MMH losses were incurred in metal tubing, and best results were obtained with tubing made from perfluorinated polymers [611]. The plastics tested for MMH and UDMH sampling included polyethylene-lined ethyl vinyl acetate, high-density polyethylene (HDPE), polypropylene, Teflon TFE (polytetrafluoroethylene), Teflon FEP (polytetrafluoroethylene–polyhexafluoropropylene), and Teflon PFA (polytetrafluoroethylene–perfluoropropyl vinyl ether) [612]. All tubing performed in an approximately equal manner with regard to sample retention, response time, and ease of cleanout with methanol. Although the polyethylene-lined ethyl vinyl acetate tubing appeared most suitable for MMH, Teflon FEP, and HDPE performed best for UDMH sampling.

Unrecognized vapor loss by permeation and oxidation in incompatible plastic tubing has thrown severe doubt on the validity of animal inhalation toxicity test results with hydrazine(s) vapors conducted in the 1980s. The animals were inadvertently exposed to concentrations of toxic vapors that were orders of magnitude higher than what the analysis instrument at the end of a long sampling line indicated.

## 8.7 Cleaning Agents for MMH Systems

The reactivities of several selected halogenated precision cleaning solvents with MMH have been determined by analysis of the rates of formation of halide ion decomposition products [613]. The solvents tested were Asahiklin AK 225, Asahiklin AK 225 AES, HFE 7100, HFE 7100 DE, Vertrel XF, Vertrel MCA, Vertrel MCA, Plus, 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113), and trans-1,2-dichloroethylene (DCE). All of the solvents except DCE exhibited significant reactivity with MMH, particularly HFE 7100 DE and CFC-113.

# 9 Propellant System Components for MMH

## 9.1 Propellant Flight Tanks for MMH

The second edition of the hydrazine book contained two tables with flight propellant tanks for hydrazine and MMH [22]. It has not been possible to keep those tables up-to-date and therefore they have been eliminated from the current book. New tank designs become available every year and it is difficult to keep this table up to date.

Many tank suppliers have changed names and/or ownership since they first started making propellant tanks. The name shown in earlier tables may not be the name under which the company currently operates. Many MMH tanks can also be used for NTO oxidizers with only minor modifications and changes of the part

number. Satellite designers prefer both tanks to be from the same supplier to facilitate integration and center of mass control. Although a table for hydrazine tanks would include both diaphragm (bladder) and surface tension PMD tanks, a table for MMH would show exclusively surface tension PMD or PMD-free tanks. This is because bipropellant satellites and bipropellant fuel tanks tend to be bigger than hydrazine monopropellant tanks and diaphragms and bladders can only be built up to a certain size. Only very few MMH diaphragm or bladder tanks were ever built.

Surface tension and contact angles of MMH must be known for the design of surface tension tanks for use in a zero-g environment in space. Surface tension tanks have fine-mesh screens in the forms of chimneys, vanes, and galleries to collect and hold propellants in position near the tank outlets even in a zero-g environment, such that only liquid and no pressurant gas can enter the engines [614–616].

## 9.2 Propellant In-Space Gauging

The difficulties in estimating remaining propellant in a propellant tank in a satellite in space and predicting the remaining useful life of the satellite apply to all liquid propellants, not only to MMH. A brief discussion of propellant gauging methods was already provided in *Encyclopedia of Liquid Fuels*, chapter “Hydrazine.”

Three Insat satellites using NTO/MMH bipropellant for both apogee firing and on-orbit station keeping and attitude control used careful propellant consumption book keeping in combination with telemetered residual tank pressure data to predict remaining propellants at the end of the mission [617, 618]. The system operated with regulated helium pressure during apogee firings and orbit insertion, then isolated the pressurant tank from the propellant tanks and continued to operate in a blowdown mode. Analytical models were developed to predict the bipropellant propulsion subsystem performance. The NTO/MMH unified bipropellant propulsion system flown on the OLYMPUS and ITALSAT satellites was very similar to the INSAT in that it also operated with regulated helium pressure during apogee firings and orbit insertion, then isolated the pressurant tank from the propellant tanks and continued to operate in a blowdown mode [619]. Propellant gauging depended on record keeping and telemetry of blowdown mode feed pressure decrease. After all other means of propellant gauging are exhausted, most spacecraft designers ruefully come back to the good old PVT methods, and computer simulations of flight systems help to understand telemetry data or data from drop tower zero-g simulation tests [620].

## 9.3 In-Space Propellant Shifts

Thermal pumping between connected tanks in satellites with multiple tanks has already been identified as the cause of unwanted center-of-gravity shifts. In addition,

even in satellites with individual, single tanks with surface tension PMDs, temperature differentials can cause unexpected migration of propellant from one screen compartment to another by evaporation and condensation [621]. This would apply to all propellants, not only to MMH. It is important that the compartment next to the outlet remains filled as long as possible or the propellant delivered to the thrusters will begin to ingest pressurant gas bubbles.

#### 9.4 Flow Control Valves for MMH

There are many, many enable valves, check valves, latching valves, and flow control valves available for MMH service both on the ground and in flight vehicles, and a supplier survey would have to be updated every few months.

Extrusion of a polytetrafluoroethylene (PTFE) pilot seal located in the Space Shuttle Orbiter Primary Reaction Control Subsystem (PRCS) thruster fuel valve has been implicated in 68 ground and on-orbit fuel valve failures. A rash of six extrusion-related in-flight anomalies over a six-mission span from December 2001 to October 2002 led to the formation of a multi-disciplinary team to solve the problem [622, 623]. Propellant exposure tests showed that some extrusion is produced by thermal cycling; however, a review of thruster service histories did not reveal a strong link between thermal cycling and extrusion. Failure analysis of failed hardware revealed the presence of fuel–oxidizer reaction product inside the fuel valve pilot seal cavity, and DSC showed that the residue (MMHN) was intimately associated with the pilot seal material problem. Residue of similar composition could be produced by adjacent oxidizer valve leakage even in the absence of thruster firing. See also [624].

### 10 Safety Properties of MMH

Handling safety properties include, besides toxicity (which is discussed in detail at the end of this chapter), predominantly flammability and detonability. This section deals with safety properties for MMH and MMH mixtures. This chapter is restricted to the conditions conducive to (inadvertent) vapor decomposition or combustion, whereas more academic studies of the decomposition or combustion mechanism and kinetics are discussed in Section 4.1. For detonability, only limits of detonability and required modes of initiation are discussed here.

Useful summaries of the hazard properties of MMH and other rocket propellants have been published by several organizations, including the Air Force Space Propulsion Hazards Manual *Space Propulsion Hazards Manual* [516–518], a three-volume series useful for the design of ground-service equipment and the planning of fueling operations. Another very useful three-volume series is the *Hazards of Chemical Rockets and Propellants* handbook published by the former CPIA. Volume 1 deals with safety,

health, and the environment [625]. Volume 2 is for solid propellants (not yet discussed here), and Volume 3 is for liquid propellants [626]. NASA WSTF has put together three very practical handbooks, one on *Ignition and Thermal Hazards of Selected Aerospace Fluids* (including hydrazine, MMH, UDMH, and Ae-50) [627], one on *Fire, Explosion, Compatibility, and Safety Hazards of Monomethylhydrazine* [90], and a similar handbook on *Fire, Explosion, Compatibility, and Safety Hazards of Hydrazine* [243]. These handbooks were originally published in loose-leaf format in a ring binder and could be updated periodically. Two of those were later also published by the American Institute of Aeronautics and Astronautics (AIAA) under the aerospace specification series [90, 628]. These handbooks and other survey papers such as the comparison study of explosion hazards of hydrazine and MMH in aerospace launch vehicle environments [241] cite numerous WSTF test reports as references, but most of these cited reports have unfortunately never been deposited with NTIS and are not available to the general public. When MMH first became available, hydrazine(s) manufacturers published summaries of the safety properties of MMH, but these are now out-of-date [1].

Uncertainties with regard to vapor pressure can make it difficult to accurately predict hazards from propellant vapors, and how long it would take to vent propellant vapor residues remaining in a test area after a leak or an accident [93].

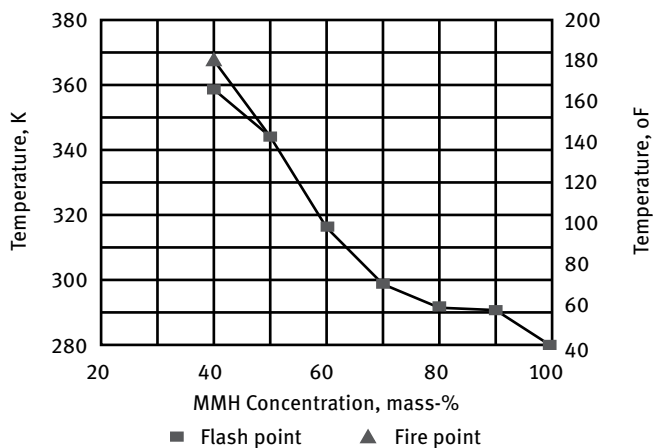
### 10.1 Flash Point of MMH in Air

The “ignitability” or, scientifically more accurately, the flash point, is determined by heating the liquid in an open cup and moving a pilot flame back and forth over the surface until the pool in the pan catches on fire. This test using brass cups is extensively used for characterization of petroleum products. The Cleveland open-cup method is described in ASTM Method D92-85 and the Tag closed-cup method is described in ASTM Method D56-82. Another Tag open-cup flash point test is described in ASTM Method D1310-86. Because hot MMH reacts with brass, a glass insert must be used for MMH tests. Occasional puffs of ignition are observed below the flash-point temperature when the pilot flame is moved across the surface, but sustained combustion may or may not occur. The temperature above which sustained combustion occurs is called the “fire point.”

The flash point of hydrazine itself is significantly higher than that of its methyl derivatives, MMH (294 K = 70 °F) or UDMH (274.2 K = 34 °F; all three data based on the Cleveland open cup method). Both MMH and UDMH are classified as flammable liquids.

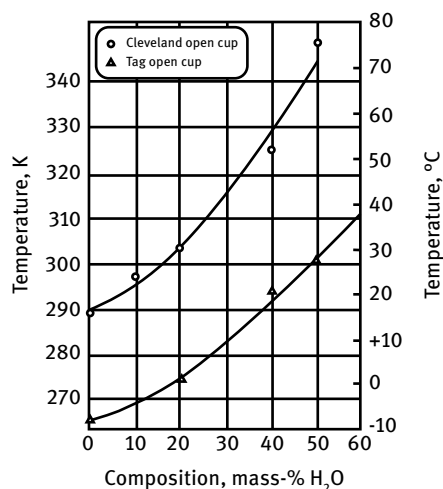
The Lonza-Arch web site lists an MMH Cleveland Open-Cup flash point of 294.2 K (21.1 °C = 70.0 °F). Differing flash points of MMH were reported earlier by Olin: a Tag Open-Cup flash point of MMH in 1962 (17 °C = 290 K), and a Cleveland Open-Cup flash point in 1986 (21.1 °C = 294.2 K). Either one of the two differs from later testing

performed by NASA in a Tag open-cup tester [629]. The NASA tests gave a Tag open-cup flash point of  $7^{\circ}\text{C} = 280\text{ K}$  (corrected for sea level conditions), 10 K lower than the Olin data point. At the high altitude above sea level of White Sands with an atmospheric pressure of only 0.85 bar (12.4 psia), the measured flash point of 99.5% MMH was  $-2^{\circ}\text{C} = 271\text{ K}$ . The pressure correction to report data for sea level pressure by adding 9 K was derived from earlier tests with other flammable fluids. The effect of water dilution on the Tag open cup flash point of MMH is shown in Figure 33.



**Figure 33:** Flash and fire points of methylhydrazine–water mixtures using the Tag open-cup method. (Graph created by Schmidt 2016, based on data from [629].)

Note: Data corrected for sea level conditions.



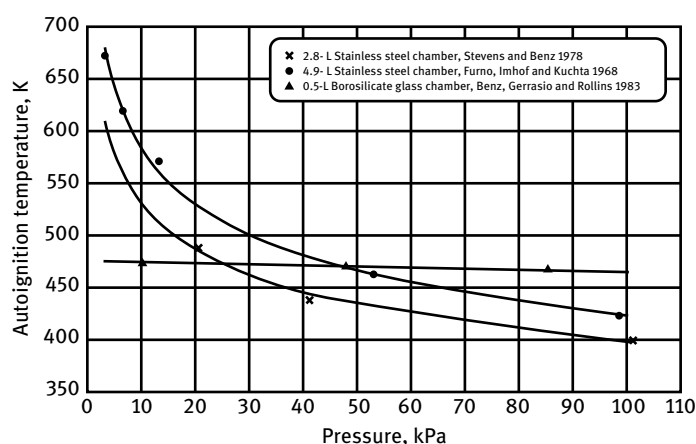
**Figure 34:** Effect of water dilution on the flash point of methylhydrazine. (Reproduced and modified from [630].)

Similar to the hydrazine flash point and fire point curve for anhydrous hydrazine, the flash and fire points coincide until the MMH concentration drops below 50% by weight and the two curves begin to diverge. Mixtures containing only 35 or 30% MMH were not ignitable at temperatures near the boiling point of water. The effect of water dilution on the flash point of MMH is shown in Figure 34. A similar chart exists for Ae-50.

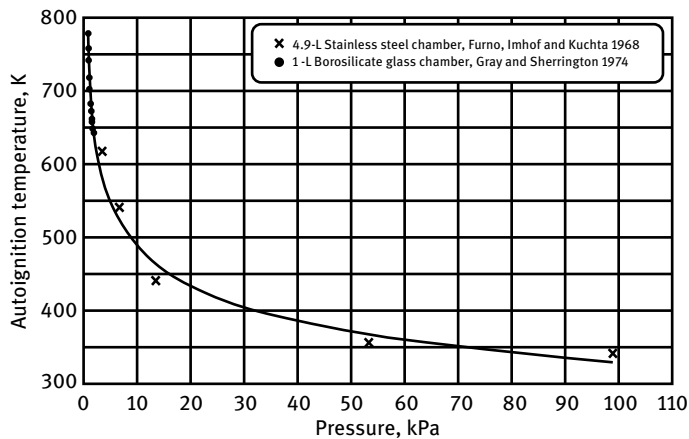
## 10.2 Auto-Ignition Temperature of MMH in Air

The auto-ignition temperature of a fluid is the minimum temperature at which a combustible fluid with or without an oxidizer (usually air) spontaneously ignites and produces a flame. Auto-ignition temperature depends on the composition and pressure of the combustible vapor and on the type of hot surface present. It also depends on the amount of confinement, if the vessel is vented or not. Upward propagation in a gravity field aids ignition (the source of ignition is at the bottom of the test vessel). One method used for determination of self-ignition temperatures of combustible fluids uses the Setchkin apparatus. The auto-ignition temperature of MMH vapors in oxygen is about 100 K lower than that in air (Figure 35 and 36).

The auto-ignition temperatures of MMH and Aerozine-50 in air were tested at three pressures in an altitude-simulated auto-ignition test system (a 500-mL round-bottom borosilicate glass flask), as summarized in Table 41. MMH auto-ignition occurred over a narrow range of temperatures and did not show the wide scatter of data as did hydrazine. The auto-ignition temperatures of hydrazine, MMH, and UDMH in air and oxygen at atmospheric pressure in glass and steel vessels are summarized in Table 42.



**Figure 35:** Auto-ignition temperature of methylhydrazine in air. (Reproduced and modified from [90].)



**Figure 36:** Auto-ignition temperature of methylhydrazine in oxygen. (Reproduced and modified from [90].)

**Table 41:** Auto-ignition of methylhydrazine/air and Aerozine-50/air mixtures.

| Pressure           |      | Temperature |     |
|--------------------|------|-------------|-----|
| kPa                | psia | K           | °F  |
| <i>MMH</i>         |      |             |     |
| 85.5               | 12.4 | 468         | 382 |
| 48.2               | 7.0  | 470         | 386 |
| 10.3               | 1.5  | 474         | 393 |
| <i>Aerozine-50</i> |      |             |     |
| 85.5               | 12.4 | 458         | 365 |
| 31.0               | 4.5  | 463         | 374 |
| 5.2                | 0.75 | 468         | 383 |

Data source: [631]

**Table 42:** Auto-ignition temperatures of hydrazines in air and oxygen at atmospheric pressure.

| Oxidizer  | Air         |             | Oxygen      |             |
|-----------|-------------|-------------|-------------|-------------|
|           | Glass 0.2 L | Steel 4.9 L | Glass 0.2 L | Steel 4.9 L |
| Fuel      |             |             |             |             |
| Hydrazine | 543         | 451         | 423         | 371         |
| MMH       | 457         | 423         | —           | 345         |
| UDMH      | 525         | 499         | 497         | 457         |

Note: All temperatures in K

Data source: [632]

**Table 43:** Auto-ignition temperatures of hydrazines in air and oxygen as a function of initial pressure.

| Fuel      | Oxidant | Vessel volume, L | Lowest observed auto-ignition temperature, K |     |     |     |     |
|-----------|---------|------------------|----------------------------------------------|-----|-----|-----|-----|
|           |         |                  | Pressure, mm Hg                              |     |     |     |     |
|           |         |                  | 740                                          | 400 | 100 | 50  | 25  |
| Hydrazine | Air     | 0.2              | 543                                          | 518 | —   | —   | —   |
| Hydrazine | Air     | 4.9              | 451                                          | 518 | 705 | 747 | —   |
| Hydrazine | Oxygen  | 0.2              | 423                                          | 489 | 575 | 623 | 723 |
| Hydrazine | Oxygen  | 4.9              | 371                                          | 383 | 603 | 663 | 697 |
| MMH       | Air     | 4.9              | 423                                          | 463 | 571 | 619 | 671 |
| MMH       | Oxygen  | 4.9              | 345                                          | 358 | 441 | 541 | 617 |
| UDMH      | Air     | 0.2              | 525                                          | 527 | —   | —   | —   |
| UDMH      | Air     | 4.9              | 499                                          | 518 | 537 | 573 | —   |
| UDMH      | Oxygen  | 0.2              | 497                                          | 503 | 531 | 573 | 627 |
| UDMH      | Oxygen  | 4.9              | 457                                          | 478 | 523 | 533 | 543 |

Note: All Temperatures in K; Data in *italics* are interpolated

Data source: [632]

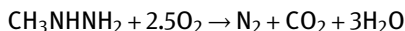
The same two vessels were used to measure the effect of initial pressure on the auto-ignition temperature of hydrazine, MMH, and UDMH. The results are summarized in Table 43.

A CRES-304 chamber measuring 15.7 cm in diameter and 14.7 cm high was used to study the pressure dependence of the auto-ignition temperature of MMH in air at 20–100 kPa [633]. The chamber pressure was adjusted to the desired pressure by evacuation. The chamber was heated prior to injection of the fuel sample. The fuel sample was temperature conditioned to 322 K prior to injection. Photocells, thermocouples, and pressure transducers were used to sense the reaction. The test sequence was such that MMH was injected into the test chamber, which had been preconditioned. If auto-ignition occurred, then the same quantity of fuel was injected for a subsequent test at a temperature that was 10 °F lower than before. The process was repeated until the lowest auto-ignition level for temperature, pressure, and amount of hydrazine injected was verified. In two test series with hydrazines in air at four different pressures, this required 336 individual tests for MMH [634]. For comparison, the ignition delay of hydrazine in air varied from 0.5 to 27 s. The ignition of MMH was more sluggish and the ignition delay varied from 1 to 82 s. The auto-ignition temperature of MMH was lower than that of hydrazine under all test conditions. For MMH, it decreased from 500 to 450 K when the pressure was increased from 20 to 100 kPa. For hydrazine it decreased from 488 to 400 K over the same pressure range. In both cases, measured overpressure agreed closely with that predicted for a deflagration and was far lower than what would have to be expected if a detonation had occurred. No ignitions were observed at pressures below 6.5 kPa. For MMH, the lowest pressure at which an auto-ignition was obtained was 20.6 kPa at a temperature of 488 K. An older publication listed the auto-ignition temperature of MMH in air as 469 K [1].



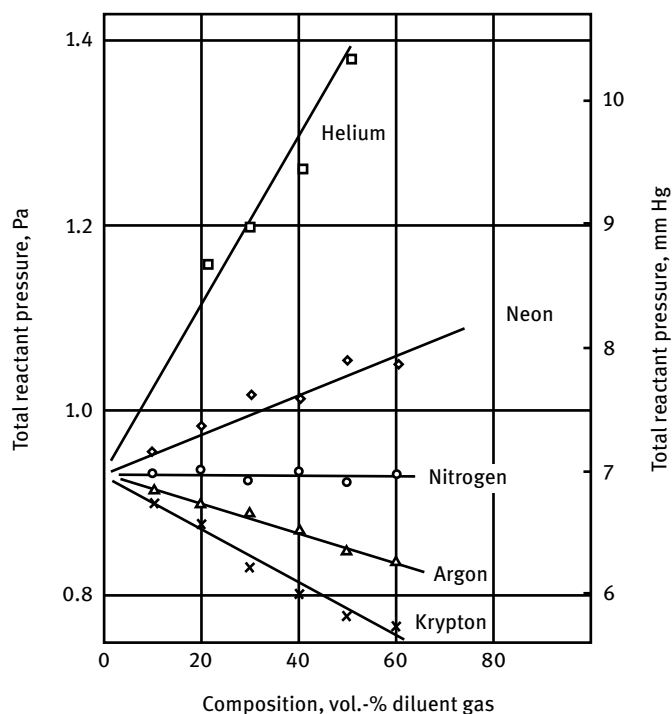
### 10.3 Auto-Ignition Temperature of MMH in Other Atmospheres

A study similar to an earlier study on self-heating and spontaneous heating of hydrazine investigated the self-heating and spontaneous ignition in the combustion and oxygen-free decomposition of MMH [510]. The combustion according to:



is exothermic with  $-1340 \text{ kJ/mol}$  ( $-320 \text{ kcal/mol}$ ). The critical conditions of pressure, temperature, diluents, and oxidizer–fuel ratio leading to ignition were examined in this investigation. Uncommon among gas-phase reactions, the combustion of MMH was dominated by thermal effects, and no obvious symptoms of radical chain branching kinetics could be detected. The technique used in this experiment consisted of pre-mixing MMH and oxygen at ambient temperature and admitting it to a heated, evacuated vessel while simultaneously recording temperature and pressure until ignition occurred. A thermocouple in the center of the vessel would frequently read temperatures higher than the wall temperature before ignition occurred, indicating a self-heating mechanism preceding actual ignition. An activation energy for the  $\text{O}_2$ –MMH reaction was derived from the slope of a  $\ln(P_c/T_a^2)$  versus  $1/T_a$  curve, where  $P_c$  was the critical pressure at which ignition occurred and  $T_a$  was the initial temperature of the Pyrex vessel. The calculated activation energy for MMH was  $80 \text{ kJ/mol}$  ( $19.1 \text{ kcal/mol}$ ), which compares with  $101 \text{ kJ/mol}$  for hydrazine itself and  $67.3 \text{ kJ/mol}$  for UDMH. In evaluating the effect of diluent gases on the pressure required for ignition, helium dilution required a higher pressure, nitrogen dilution had little effect and argon and krypton dilution lowered the pressure down to which ignition could be achieved (Figure 37).

The auto-ignition flammability characteristics of hydrazine fuels in  $\text{NO}_2$  atmospheres was investigated at the US Bureau of Mines [630, 632, 635]. Minimum auto-ignition temperatures were determined at various pressures from 3.3 to 98.6 kPa (25 to 740 mm Hg) for hydrazine, MMH and UDMH in air, oxygen, and nitrogen dioxide with either nitrogen or helium diluents. Lower auto-ignition temperatures were obtained in nitrogen dioxide (coming from dinitrogen tetroxide) than in oxygen. Generally, the AIT values for most of the combustibles increased slightly with decreased pressure and oxidant concentration to some critical value, and then they tended to increase noticeably. They also varied with the size of the reaction vessel. The spontaneous ignition temperatures (S.I.T.) of air/MMH vapor mixtures and air/UDMH vapor mixtures in contact with 100 percent  $\text{NO}_2$  were determined in the I-8 apparatus. These tests were conducted in the same manner as described previously. The results of these tests are shown in Figure 38. These results showed that for the same combustible concentrations the MMH had lower S.I.T.'s than did UDMH up to a concentration of 6.8 percent combustible; above this concentration the reverse was true. A similar phenomenon was observed for the S.I.T.'s of the liquids when they were injected into  $\text{NO}_2$ -air atmospheres. Further S.I.T. tests were conducted with these combustibles using mixtures of  $\text{NO}_2$  and air as the oxidizing atmosphere in place of the pure  $\text{NO}_2$ . The results of these

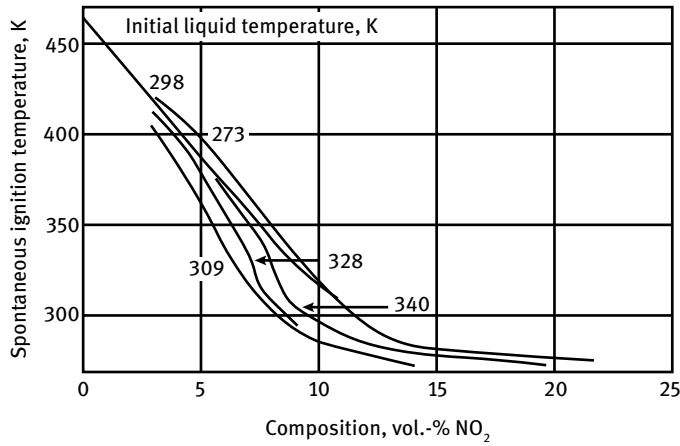


**Figure 37:** Effect of dilution on critical partial pressure  $p(\text{O}_2) + p(\text{MMH})$  in mixtures  $\text{MMH} + 2\text{O}_2 + \text{diluent X}$  at 703 K as a function of percentage diluent X added. (Republished and modified from [510], with permission of ©1974 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

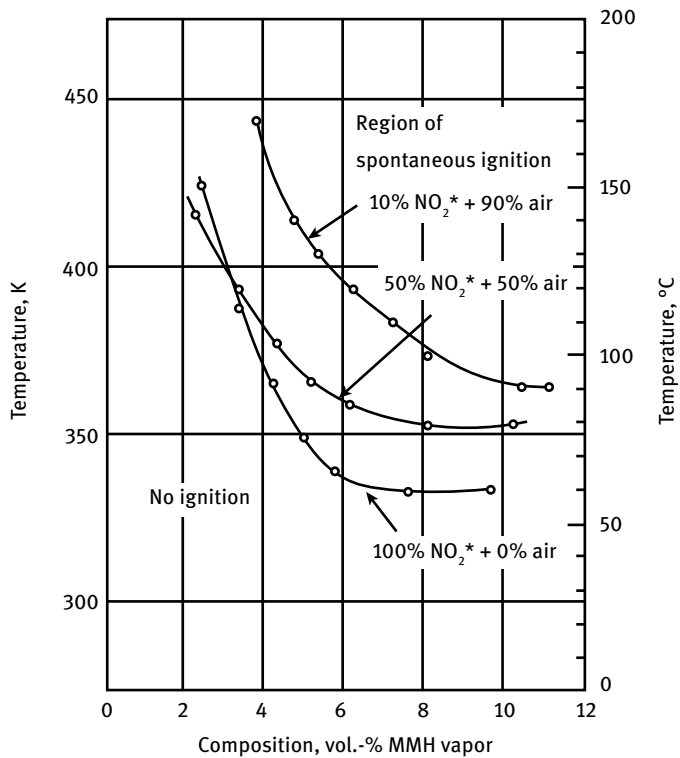
tests using two different  $\text{NO}_2$ -air mixtures (50 volume-percent  $\text{NO}_2$  and 10 percent  $\text{NO}_2$ ) are shown in Figure 38 for MMH and a similar image for UDMH in chapter “Dimethylhydrazines” of this volume, the *Encyclopedia of Liquid Fuels*.

Measuring the spontaneous ignition temperature of MMH as a function of  $\text{NO}_2$  concentration in air, and varying the temperature of the injected liquid, it appears that one specific MMH temperature (309 K) resulted in the most sensitive ignition situations. The technique used was to inject small amounts (70  $\mu\text{L}$ ) of fuel into a uniformly heated 250- $\text{cm}^3$  borosilicate glass Erlenmeyer flask containing air and  $\text{NO}_2$ . Under these conditions, hydrazine itself was more difficult to ignite than methylhydrazines. With increasing ambient temperature, ignition occurred at lower and lower  $\text{NO}_2$  concentrations, as shown in Figure 38 for MMH. Helium dilution narrowed the auto-ignition range, and pressure increase widened it.

The data (taken from different USBM reports) in Figure 38 (above) and Figure 39 (below) represent similar conditions leading to spontaneous ignition of MMH liquid in  $\text{NO}_2$ /air mixtures at 298 K. The asterisk on  $\text{NO}_2^*$  is supposed to indicate that this is an equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in the vapor state.

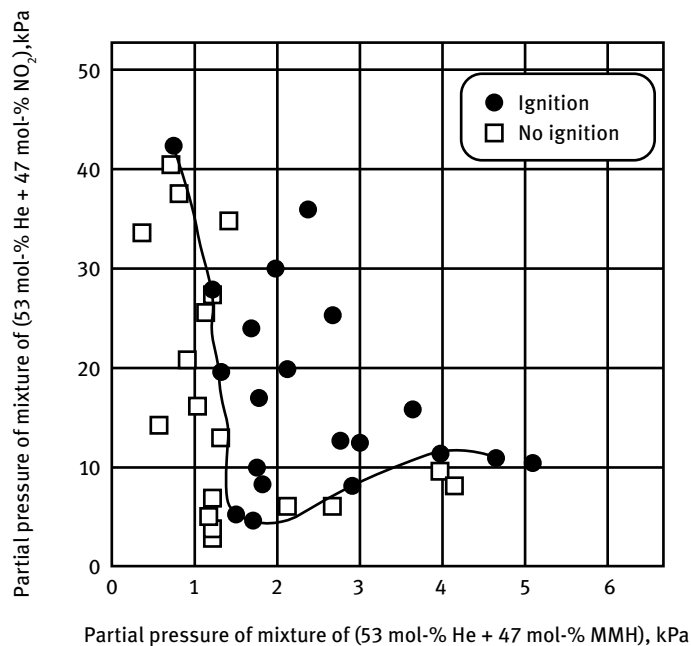


**Figure 38:** Minimum spontaneous ignition temperatures of liquid methylhydrazine at various initial temperatures in  $\text{NO}_2$ -air mixtures as a function of  $\text{NO}_2$  concentration. (Reproduced and modified from [90], as adapted from [635].)



**Figure 39:** Spontaneous ignition temperature of methylhydrazine in  $\text{NO}_2$ /air mixtures at 298 K as a function of MMH concentration. (Reproduced and modified from [630].)

Kinetic models derived for the  $\text{NO}_2/\text{N}_2\text{O}_4$  and MMH vapor reaction were confirmed by measuring the ignition boundaries of  $\text{NO}_2/\text{N}_2\text{O}_4$  and MMH vapor as a function of helium dilution, mixture ratio, and pressure at room temperature [329]. The ignition of  $\text{NO}_2$  and MMH vapors diluted in helium was measured for gas–vapor mixtures containing 20, 30, 40, or 47% propellant in helium. The results for the 47% mixtures are shown in Figure 40. Note that the limit is offset toward fuel-rich mixtures. This offset became more visible with higher dilutions.



**Figure 40:** Dinitrogen tetroxide/methylhydrazine vapor flammability diagram at room temperature (295 K). (Republished and modified from [329], with permission of ©2006 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

The minimum pressure for ignition as a function of mixture ratio showed a minimum at equivalence ratios of 1.0 for He mixtures with 20–30% propellants, 1.5 for 40%, and 2.0 for 47% propellants. This type of laboratory study with vapor-phase reactions is of interest for explaining ignition delays with liquid–liquid reactions in rocket engines.

#### 10.4 Flammable Range of MMH Vapors in Air

The limits of flammability of combustible vapors and gases depend on composition, temperature, pressure, mode of initiation, geometry of vapor space, and the direction of propagation [636, 637]. It is impossible to discuss here all these parameters in de-

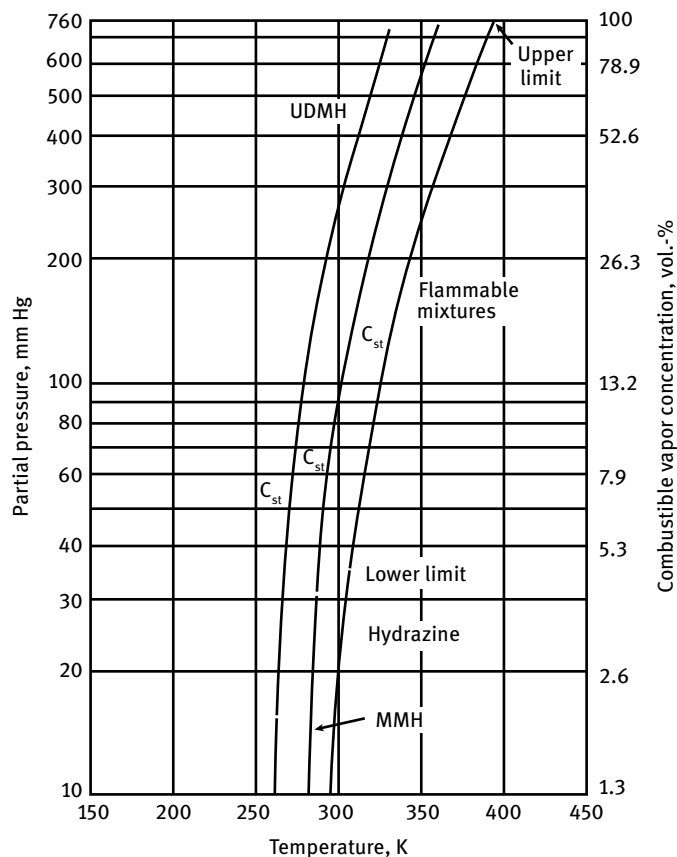
tail, mainly because they have not yet been determined in such detail for hydrazine and MMH. Most of the hydrazine(s) work was done for limits of flammability in air, but some information is also available for other oxidizing atmospheres (oxygen, nitric oxide, nitrogen dioxide) or in dilution with inerting compounds (nitrogen, heptane, water). Because the methylhydrazines are more volatile than hydrazine, there is more concern about forming flammable mixtures with these fuels than with hydrazine itself.

To evaluate the potential fire hazard of MMH and UDMH and compare it with that of better known flammable fluids already in use (e.g., gasoline), the following properties are examined here: limits of flammability, auto-ignition temperature, flash point, and minimum required ignition energy. A comparative hazard evaluation must be based on a consistent set of data, all obtained with the same method. The results of flammability or auto-ignition of one and the same compound will vary widely depending on the method and the apparatus used. It would be desirable for all investigators to use standardized flammability test methods. Unfortunately, only the flash-point procedure is covered by an ASTM standard (ASTM D98). For the other fire hazard properties, there exist no standard procedures applicable to MMH, and the results vary from investigator to investigator, depending on the method used, making a comparison very difficult. Most data on flammability characteristics of combustible gases, and vapors other than hydrazines were obtained by the US Bureau of Mines (USBM) using a setup that has become known as the USBM Flammability Tester [636]. Results obtained with this apparatus are considered reliable, but are typically obtained only for gases and vapors at room temperature. The flammable ranges of hydrazine and its methyl derivatives shown in Figure 41 are superimposed on vapor pressure curves, even though the actual flammability testing was conducted at higher temperatures.

The flammability limits of MMH in air are 2.5% by volume (lower limit) and  $97 \pm 2\%$  (upper limit), as reported by an MMH manufacturer, but the type of apparatus was not stated, and obviously 97% MMH in air can only be reached at elevated temperatures [1].

Reducing the pressure below sea-level pressure narrows the flammability range. As the pressure decreases, the two flammability limits approach each other until they merge at a point where no flame propagation is possible. This is the lower pressure limit of flammability, regardless of the composition of the flammable mix. The low pressure limit is still dependent on the ignition energy and the dimensions of the test apparatus.

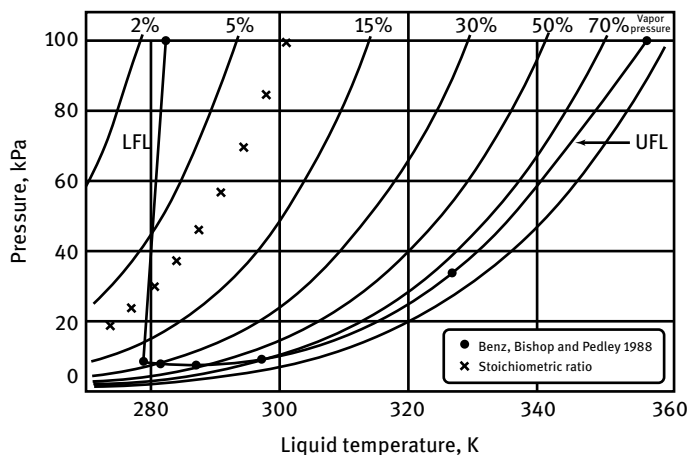
The ignition limits of hydrazine/air and MMH/air mixtures at reduced pressures were measured in a 2-L CRES-304 chamber measuring 15 cm in diameter without provisions for stirring the gas-vapor mix [631, 633, 638]. A 750-mJ spark jumping a 3.2-mm gap was used to initiate the mixtures. A capacitor bank delivered approximately 1J within 2ms. Overpressure data from the closed vessel indicated that all mixtures merely deflagrated rather than detonated. For anhydrous hydrazine, the flammable range narrowed as the pressure decreased, until below 4 kPa partial



**Figure 41:** Flammability range of hydrazine, methylhydrazine, and unsymmetrical dimethylhydrazine in air. (Reproduced and modified from [637].)

pressure no ignition occurs at any of the several mixture ratios tested. Similar tests were performed with MMH. In this apparatus, in the absence of air, a 1-J spark did not ignite pure MMH vapor at the boiling point of MMH (360.8 K). Temperature had little effect on the lower limit of flammability of unsaturated MMH vapor in air. For MMH in air, the lowest pressure for flammability was 3.1 kPa (0.45 psia) with a mixture containing 7.7% MMH. At 366 K, the lower limit is at 2.8 vol-% MMH and the upper limit is at 95.7% MMH as shown in Figure 42 [627].

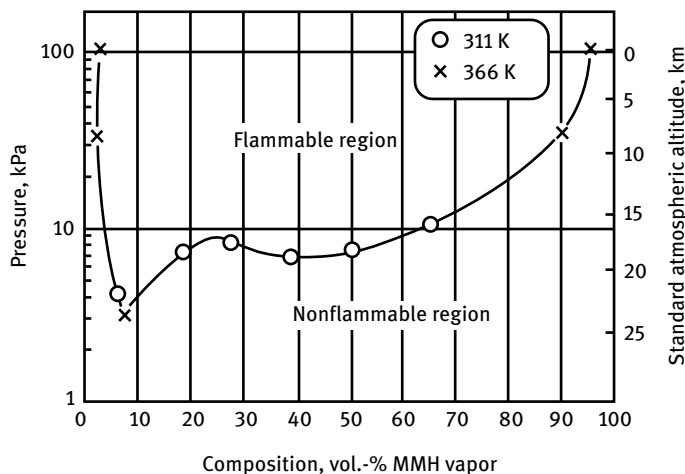
Similar tests with MMH gave positive ignitions within the entire range tested down to 7 kPa. The minimum ignition pressure of air/MMH was observed at 3.14 kPa with an MMH concentration of 7.7% by volume. No ignition was obtained in 100% MMH vapor anywhere below 100 kPa. The flammability curve (flammable range boundary plotted in a pressure versus % by volume MMH graph) showed an unusual double-lobed



**Figure 42:** Flammability limits above liquid methylhydrazine in air as a function of temperature and pressure. (Reproduced and modified from [90] based on [627].)

shape, which has not yet been explained. Graphing these data for just two temperatures with only the lower and upper limits shown gives a curve that has an unusual sinusoidal undulation in the range between 25 and 50% MMH (Figure 43).

Methylhydrazine is more flammable than hydrazine. Flammability in the vapor phase as tested in the NASA apparatus was effectively suppressed by adding 25% by volume water to MMH at 300 K.



**Figure 43:** Effect of pressure on the limits of flammability of methylhydrazine in air. (Reproduced and modified from [627])

## 10.5 Card Gap Sensitivity of MMH and MMH Mixtures

The card gap sensitivity of MMH/N<sub>2</sub>H<sub>4</sub>/HN mixtures is shown in Figure 50 in Section 13.3.5.2 on MMH fuel blends. As can be seen from this graph, MMH at the corner is safely distanced from the boundary of detonable mixtures in this ternary system. MMH is not detonable at zero cards.

## 10.6 Electrostatic Discharge Sensitivity of MMH

The minimum ignition energy of 2.9 vol.-% MMH vapor in air was 2.9–3.4 mJ, as determined in a flow-through system that was better suited to high boiling liquids than the static ASTM system [639]. Designers for propellant storage and transfer facilities should adhere to the recommendations provided in National Fire Protection Association 77 *Static Electricity* [640].

## 10.7 MMH Decomposition in Proximity to Pyrovalves

Mars Observer was lost shortly after sets of pyrovalves had been fired in preparation for the arrival at Mars. Although a different scenario involving oxidizer permeation through the Teflon seats of check valves was a more likely cause of the accident, safety testing of MMH reactions in pyrovalves with and without blowby was part of the Mars Observer investigation [641–644]. After two earth satellites were lost due to blowby from pyrovalves igniting hydrazine (not MMH), the sensitivity of MMH exposed to hot blowby products of an actuated pyrovalve was also experimentally evaluated using both a pyrovalve simulator and commercial pyrovalves in test configurations simulating a MMH-based propulsion system. Additional testing at NASA WSTF looked at the hazard potential of MMH decomposition initiated by pyrovalve blowby, in this case as part of the Space Station Interim Control Module (ICM) propulsion system safety evaluation. This involved propellant lines with substantial outer diameters of 19 mm (¾ in). The propulsion system developed by NRL was at one time planned to be used as an Interim Control Module on the International Space Station (ISS) in case the Russian Zvezda service module was not delivered on time. The influence of pyrovalve blowby was a serious concern during system development because of earlier incidents where two satellites were lost owing to pyrovalve interaction with anhydrous hydrazine. By comparison with results of previous pyrovalve simulator tests using water to establish water-hammer effects and tests using the more reactive hydrazine, MMH was found to be insensitive to blowby in all tests performed. Specifically, test results showed no evidence that the blowby caused a self-sustaining, exothermic decomposition event with MMH in three pyrovalve simulator tests, an ICM MMH tank outlet configuration test, or two ICM MMH tank inlet configuration tests. MMH did not undergo explosive decom-



position under test conditions in identical hardware, which had previously resulted in destructive reactions with anhydrous hydrazine  $\text{N}_2\text{H}_4$  as part of the LANDSAT-F and TELSTAR-402 failure investigations.

### 10.8 Detonability of MMH Vapors

MMH vapor diluted with argon was decomposed in a 38.4-mm i.d. shock tube behind a reflected shock wave at 1040–1370 K, 140–455 kPa, and in mixtures containing 97 to 99 mol-% argon, and the kinetic rate data obtained from experiments with argon-diluted MMH were used to predict the detonability of undiluted MMH vapor [645]. The computer model predicted that MMH vapors are much less susceptible to detonation than hydrazine vapors. The predicted detonation cell diameter was large in relation to the tube diameter used in this study.

The same equipment was also used for studying the detonation of  $\text{O}_2$ /MMH vapor/ $\text{N}_2$  mixtures initiated by an incident shock wave [292]. The detonation velocity of mixtures consisting of 52.4 mol-%  $\text{O}_2$ /47.6% MMH (equivalence ratio  $\phi = 2.27 = \text{fuelrich}$ ) at an initial pressure of 2 kPa was 2400 m/s. This value was below that predicted from C-J calculations for this mix.

The structure of shock waves and the conditions conducive to detonation of hydrazine, MMH and UDMH by themselves or in  $\text{Ar}/\text{O}_2$  mixtures were analyzed in order to determine criteria for the detonability limits [646]. Under these conditions, hydrazine and MMH were pyrolyzed and UDMH was oxidized behind a shock wave to determine the induction periods.

There is continued concern about the explosive decomposition of residual MMH in propellant tanks of expendable or reusable space transport vehicles returning from orbit and re-entering the atmosphere. The concern is that an explosion of the MMH tank might propel fragments into low orbits occupied by other satellites. Similar concerns had been expressed earlier about anhydrous hydrazine tanks left uncontrolled in orbit (such as those on the PEGASUS HPU upper stages) or re-entering at the end of a mission.

The European Automated Transfer Vehicle (ATV) was a supply cargo vehicle for the ISS. The European Automated Transfer Vehicle and the US DRAGON both use NTO/MMH for attitude control and orbit adjustment, reentering with partially filled MMH tanks. The ATV is expendable and designed to burn up during re-entry in unpopulated areas. In contrast to the ATV, the Space-X CARGO DRAGON and CREW DRAGON are reusable, but they re-enter without their service module. There is concern that explosions of the propellant tanks in the ATV or the service module will change the footprint of where parts may splash into the ocean if they do not completely burn up in the atmosphere [647–649]. Visual observations of the breakup of the ATV JULES VERNE during its re-entry into the atmosphere indicated that the breakup was actually different from what computations had predicted [650]. The

ATV carried MMH for its own consumption and UDMH as cargo for resupply for the ZVEZDA service module on the ISS. When the supply ship undocked from the ISS, and after the re-entry burn, there were 135 and 144 kg of MMH remaining in the two fuel tanks. There were also 260 and 277 kg of MON remaining in the two oxidizer tanks. Therefore, a total of 819 kg of available propellants were capable of igniting with each other or with hot air from the re-entry aerobraking. The tanks might rupture owing to simple overheating and vapor pressure buildup, or owing to MMH decomposition. The overheating seems to be more probable. The first explosion occurred at an altitude estimated at 75 km. This event caused the disintegration of the vehicle into several fragments. A second explosion occurred 35 s after the main explosion. This event happened in one of the main fragments produced by the initial vehicle disintegration. The spacecraft also had lithium ion batteries on board. The scenario with the first explosion initiated by MMH decomposition is the most probable as lithium emission lines in the spectrum from the explosion started showing up only with a delay of 5 s.

A computational analysis of the re-entry heating of the ATV examined the ignition and explosion potential of MMH/NTO, UDMH/NTO, and MMH with atomic oxygen from the re-entry plasma [651, 652]. The simulations examined the internal flow field, which is at chemical equilibrium with a low fraction of atomic oxygen. The temperature and oxygen partial pressure were not high in the middle of the vehicle: of the order of 1300 K and 50 Pa. Close to the walls, particularly on the top part of a fissure, the heat-flux and the pressure were very high: 500 kW/m<sup>2</sup> and 1950 Pa. The temperature rose up to 3000 K, a level high enough to start the dissociation of diatomic oxygen. Its partial pressure reached a level of 500 Pa. This part of the ATV is very close to the location of propellant tanks, which could be damaged by the local high levels of heat flux and temperature. However, the predictions showed a high level of diatomic oxygen in the whole vehicle and the explosion analysis established that this species is the best candidate to ignite a chemical reaction in the space surrounding the tanks. This is due to a partial pressure more than one order of magnitude higher than the minimum ignition pressure. These computational results predicted a high risk of explosion if the propellants enter in contact with the internal flow.

## 10.9 Adiabatic Compression Sensitivity of MMH

Most other monopropellants, in particular organic nitro compounds and nitrate esters, are known to be sensitive to adiabatic (i.e., isentropic) compression. With those compounds, the sudden temperature increase in a collapsing bubble is sufficient to initiate detonation and, at the same time, additional bubbles provide a mechanism for propagation of LVD. A monopropellant of that type that has not been thoroughly degassed or is even filled with bubbles from transportation vibrations/sloshing or transfer from one container to another propagates LVD once a source of initiation is present. In contrast, liquid bulk MMH could not be initiated to detonation by rapid or adia-

batic compression. An adiabatic compression sensitivity study conducted at Aerojet measured four fuels (hydrazine, MMH, MHF-5, and MHF-7) in contact with 11 metallic materials of construction [247]. The U-tube apparatus used for these experiments has subsequently been adapted for safety investigations by several other research groups. It consisted of a tube measuring 6.35 mm (0.25 in.) in O.D. bent to the shape of a U 152 mm (6 in.) high and closed on one end by a plug. The propellant sample (3 mL) filled only the lower one-tenth of the nitrogen-filled tube. The entire assembly could be lowered by remote control into a temperature-controlled bath prior to the test. The upstream end could be rapidly pressurized with nitrogen by using a fast-acting valve and a burst disk at a rate of 2064 MPa/s (300000 psi/s). Positive tests were indicated by burst or bulged tubes. Neither MMH nor MHF-7 was sensitive to adiabatic compression up to temperatures of 533 K (500 °F). Hydrazine vapor was the most sensitive compound tested; MMH vapor was able to desensitize hydrazine vapor. In the U-tube test series at Aerojet, none of the 35 tubes from 10 different metals tested at four different compression rates and temperatures up to 540 K (512 °F) with MMH exploded.

In trying to predict the temperature rise as the result of adiabatic, isentropic compression from theoretical calculations, previous work had validated the SRK EOS for computing isentropic compression temperatures for MMH vapor [94]. That work showed a significant difference between treating MMH as a real fluid and as an ideal gas. Isentropic compression or expansion of two-phase mixtures, e.g., liquid/vapor, of MMH. This analysis included re-evaluation of the published low-temperature vapor pressure correlation and recalculation of a pseudo-Mollier diagram,  $\ln(T)$  vs.  $S$ , for saturated liquid and saturated vapor using integration of the orthobaric heat capacity, demonstrating the usefulness of this pseudo-Mollier diagram.

#### **10.10 Water (Fluid) Hammer and Surge Flow Conditions Conducive to Rapid Compression Events in MMH**

Hydrazine has a lower compressibility than MMH or water and therefore is more likely to encounter pressure spikes where water hammer or surge flow conditions are encountered. Although there is less concern about MMH causing problems of the type observed with anhydrous hydrazine, fluid hammer and surge flow pressure spikes with MMH have been measured and predicted by fluid dynamic computer models. Most of the computer models described here are not unique to MMH and can be applied to flow properties of other propellants as well.

Several publications deal with the manifold filling (“priming”) and water hammer fluid dynamic aspects of bipropellant systems, many of those using MMH as the bipropellant fuel. Although there is less concern about MMH undergoing explosions caused by “adiabatic” rapid compression, these data should be summarized here nevertheless. In many cases, the analytical computational methods used to model the fluid dynamics of bipropellants can be applied to calculating the behavior of hydrazine

in monopropellant feed systems. Experimental techniques for determining the safety threshold of water hammer and surge flow in bipropellant systems can be equally well used for examining hydrazine monopropellant systems.

Startup hydraulic transients in a feed system dropping MMH from a reservoir at 10 MPa into an evacuated U-shaped tube section were calculated, including bending forces exerted on the U-tube while the liquid front is rushing at 50 m/s through the bend, suddenly changing direction [653]. It appears that forces exerted by the liquid flow were at one time sufficient to rupture weak weld sections when the lines were not properly tied down (this event is not described in detail). It was recommended to firmly clamp the tubing to make it immovable to eliminate stresses on the welded section. There is no chemical reaction involved in bending these tubes. It is a strictly mechanical phenomenon.

A simplified model was derived to describe the flow of MMH (and NTO) into evacuated and pressurized straight lines, which allows prediction of peak pressures [654]. The following simplifying assumptions were made in this model:

- Gas solubility in liquid propellant is negligible.
- Vapor formed by propellant evaporation is negligible in comparison with the amount of pressurant gas in the line.
- Owing to high shock speeds (helium) the gas is everywhere at the same pressure.
- Gas behaves adiabatically.
- Propellant lines are rigid.

Valve opening times had only a slight effect on the pressure history for pressurized lines. Calculated peak pressures were greatest for downstream line lengths of 30 to 60 cm. MMH, a less dense liquid than NTO, attains higher flow velocity in the evacuated line and higher impact pressures. If one attempts to equalize the peak pressures, the MMH line should be made a little longer than the NTO line. Longer upstream lines between the propellant tank and the isolation valve also reduce the pressure spikes.

Shuttle-launched payloads required three inhibits to prevent accidental propellant leakage into the payload bay. For a typical Shuttle-launched satellite there were a pyrovalve, a latching valve, and the thruster control valve. Testing of a satellite bipropellant propulsion subsystem manifold with water as the reference fluid was conducted to measure pressure spikes at the latch valve after opening the pyrovalve [655, 656]. There was concern that the impact of the surge flow on the closed latch valve might damage the valve seat or flip the valve open. Tests were conducted with gas-filled and evacuated straight tube sections and with branched flow passages. It was concluded that surge pressure spikes due to quick priming rates of pyrovalves (opening times ~3 ms) are not any worse than those caused by opening electromagnetic latch valves (opening times ~25 ms). Friction in the trunk feed line greatly reduces the potential for surge pressure spikes in the branch lines.

A more detailed model was used to describe feed system transients in the aft propulsion subsystem of the Space Shuttle, a bipropellant system housed in two pods

containing the Orbit Maneuvering System (OMS) and the Aft Reaction Control Subsystem (ARCS) [657]. The line diameters in this system range all the way from 38 to 6 mm. Water hammer pressure spikes resulting from engine shutdown and sudden valve closings were significant and needed to be limited to prevent damage to instrumentation and valves. A replica of the feed system was built for hot engine firings of the all-up propulsion subsystem on the ground. Different duty cycles were simulated, which required two or more valves to close simultaneously and the resulting pressure spikes were recorded. The actual system was more compliant than predicted. Tests were conducted with both helium-saturated and unsaturated propellants. The worst pressure spikes ( $10.9 \text{ MPa} = 1588 \text{ psi}$ ) were caused by firing three thrusters in-synch simultaneously for a 0.08 s on/0.08 s off duty cycle.

A similar method of characteristics model called Liquid Rocket Transient Code was applied to the main engines of the TITAN-4 launch vehicle [658]. Modeling of this system was complicated by the presence of accumulators, which serve to suppress pogo problems. All studies referenced above dealt with flow into or against closed, dead-ended cavities. A slightly different situation exists with injector manifolds in bipropellant thrusters filling with propellant at the start and draining propellant at the end of each pulse. Here, the start-up flow impinges on a narrow but open injector bore at the end of the line. The thrust build-up and decay portions of each thrust-time curve represent the major unknown and depend on the injector filling time and the injector draining time (emptying the dribble volume). Impulse bit reproducibility of bipropellant thrusters is important, but varies with altitude if bipropellant thrusters are used for RCS or roll control of launch vehicles as they leave or re-enter the atmosphere. Experiments with injector manifolds in a vacuum chamber were conducted with water and fluorocarbon F-12 as inert substitutes for hypergolic propellants [659]. Analytical equations were derived to predict manifold filling times for different operating conditions and injector geometries. This information is useful for the systems designer as well as the rocket engine designer.

The attitude control system of the planned European space plane HERMES was planned to be similar to that of the Space Shuttle. The pressure-fed NTO/MMH system would have been similar to that of satellites, but more complex as it also had to serve deorbit maneuvers and operate during atmospheric re-entry. A method-of-characteristics code named SIR-3S based on an existing code similar to Hytrap was used to model water hammer dynamics of the HERMES ACS system [660]. The propellant distribution system manifold was feeding propellant to 400-N and 10-N thrusters. Two of the high- and two of the low-thrust REAs may operate in pulse mode and close simultaneously, resulting in pressure waves propagating upstream in the system. The pressure fluctuations may cause mixture ratio shifts that reduce the thrust to 50% of nominal thrust. It was also attempted to determine the natural frequency of the plumbing system, dependent on the line length and tubing wall material.

Experimental test results of surge flow with water in simplified straight and 90° bent line geometries were compared with numerical simulations computed for MON,

MMH, or water using ANABEL software [661]. This computer program can perform computations of transient compressible/uncompressible monophasic or diphasic flows with separated phases in fluidic networks, allowing the prediction of water hammer and also pressure losses. With a push pressure of 40 bar, the predicted pressure spikes at the end of the line were 172 bar for MMH, 200 bar for MON and 183 bar for water.

A comparison was made between thermal demonstration test results and dynamic simulation of water hammer effects resulting from activation of fast-acting isolation valves in the flight-like system of the Japanese HTV propulsion system [662]. The objective was to reduce surge pressures associated with manifold activation of on-orbit vehicles utilizing rapid-response isolation valves.

Fluid hammer experiments were conducted with MMH, NTO, or water in the Propulsion Laboratory of Office National d'Etudes et de Recherches Aérospatiales (the French aerospace lab) [663]. The objective of that study was to generate a reliable experimental database on the fluid hammer phenomenon with real propellants (MMH and NTO) to validate the physical models implemented in the numerical codes. This database with real propellants extended the database obtained by the von Karman Institute on surrogate fluids (water, ethanol, and acetaldehyde). For each real propellant, experiments were performed for a vacuum pressure in the propellant line below and above the saturation pressure of the fluid to highlight the influence of the physical phenomena encountered (vaporization, cavitation) on the fluid hammer. With MMH, fluid hammer frequency and amplitude decreased for increased vacuum pressure. Only one experiment was performed with NTO for a vacuum pipe pressure below the saturation pressure. Compared with MMH and water experiments performed under the same operating conditions, the fluid hammer amplitude and frequency with NTO were smaller. Regarding the peak temperature in the gas pocket, very small variations were recorded for water and MMH whereas the temperature increase for NTO was more than 350 °C.

Rapid closing of a propellant valve shutting off a flow of MMH may cause pressure spikes by water hammer, and such pressure spikes may near-adiabatically compress bubbles of MMH vapor trapped in other parts of the system. MMH was not sensitive to water hammer pressure spikes [664].

## 11 Toxicity of MMH

In the following, the emphasis is on providing all necessary information on the safe handling and toxicity of MMH. In many cases, publications do not deal with just MMH by itself, but also look at the toxicity of MMH in comparison with other hydrazines. Consequently, this chapter contains some information on hydrazine  $N_2H_4$  and UDMH in addition to the info on MMH, and duplication with information provided in other chapters on hydrazine  $N_2H_4$  and UDMH is unavoidable.

When comparing molecular structures of hydrazine, MMH, and UDMH, MMH seems to take an intermediate position when it comes to counting the number of methyl substituent groups. However, this is not the case when comparing the toxicity of the three hydrazines. With most of the methods of administration of MMH in animal exposure tests, MMH is more toxic than either of the other two hydrazines [665, 666].

For discussion of possible adverse effects of MMH in an occupational environment, two types of inadvertent exposure have to be mainly considered: vapor inhalation or liquid splashes. The first type of exposure would cause predominantly respiratory and systemic effects, whereas in the latter case skin effects and eye effects must be considered in addition to respiratory and systemic effects. Accidental oral ingestion does happen, but is less likely and is readily diagnosed.

There are a few valuable review articles and summaries on hydrazine(s) toxicity such as Toth 1988 with 326 references [667], Moloney 1983 with 200 references [668], and Choudhary and Hansen 1998 with 131 references [669]. Many toxicity reviews have included SDMH (which is not used as a rocket propellant and is used in small quantities only for laboratory toxicity tests) but have omitted the practically more important MMH.

The US Air Force, as one of the main users of propellant hydrazines, has conducted a long series of toxicity studies and published the results in a series of reports which are summarized in a bibliography [670]. When comparing the inhalation hazard potential of MMH with that of the other hydrazines, not only the toxicity (often expressed as lethal concentration 50 [LC50], that is, the concentration at which 50% of a statistically significant number of test animals perished within a specified observation period) but also the vapor pressure factors in on the handling hazard. The quotient of vapor pressure divided by LC50 (in arbitrary units) is called the *Hazard Index*. Table 44 gives a comparison of the hazard indices of the three propellant hydrazines, also in comparison with the oxidizer NTO, which is usually also present in all installations where MMH is used as a fuel.

**Table 44:** Hazard indices of hydrazine and methylhydrazines.

| Compound                           | Formula                                          | Vapor pressure at 298 K<br>(25 °C = 77 °F), mm Hg | LC50, 4 h,<br>ppm | Hazard index,<br>mm Hg/ppm |
|------------------------------------|--------------------------------------------------|---------------------------------------------------|-------------------|----------------------------|
| Hydrazine                          | N <sub>2</sub> H <sub>4</sub>                    | 14.4                                              | 570               | 0.03                       |
| Methylhydrazine                    | CH <sub>3</sub> NHNH <sub>2</sub>                | 49.6                                              | 74                | 0.67                       |
| Unsymmetrical<br>dimethylhydrazine | (CH <sub>3</sub> ) <sub>2</sub> NNH <sub>2</sub> | 156.8                                             | 252               | 0.62                       |
| For comparison:                    |                                                  |                                                   |                   |                            |
| Dinitrogen tetroxide               | N <sub>2</sub> O <sub>4</sub>                    | 875                                               | 67                | 13                         |

Data source: [671]

The following individual subsections are subdivided by the part of the body affected. As with many other toxic substances, the response may be species-dependent or even strain-dependent; for instance, MMH may cause cancer in one species of test animal, but not in another.

Exposure to acute doses of MMH can cause a variety of symptoms and pathological changes depending on the concentration of MMH and the animal species. Symptoms include diarrhea, emesis, salivation, irritation of mucous membranes, dyspnea, and convulsions. At lethal doses, cause of death is usually respiratory depression. Findings at necropsy on dogs and monkeys exposed to lethal and near-lethal levels of MMH are variable but may include pulmonary congestion with hemorrhage, hepatic congestion, and kidney damage ranging in severity from mild swelling of the renal tubular epithelium to vacuolization and coagulative necrosis of these cells. The range between a lethal or near-lethal concentration of MMH, producing major or pathological changes and overt symptoms, and a concentration having minimal effect is very narrow; the dose–response curve is extremely steep.

One of the prime target organs of poisoning by hydrazine and hydrazine derivatives is the liver. Symptoms include fatty degeneration of liver tissue, centrilobular damage, changes in glycogen content, and loss of mitochondrial activity. In the blood, MMH causes hemolytic anemia, methemoglobinemia, hypoglycemia, and Heinz body formation. It affects the coagulation mechanism. Numerous enzymes are disturbed by the presence of hydrazines. The metabolic pathway of hydrazines can be traced by a number of experimental techniques that help to explain the observed symptoms. Symptoms in the kidney and urinary tract that were caused by hydrazine(s) included changes in creatinine clearance and rate of glucose resorption. Other symptoms caused by hydrazine, MMH, or UDMH included increased salivation, hyperventilation, vomiting, diarrhea, and increased neuromuscular activity (spasms). Because MMH is an amino compound, it interferes quite actively with amino acid chemistry in the body, in particular protein metabolism.

### 11.1 Inhalation Toxicity of MMH

This section contains a summary of acute toxicity studies with experimental animals. Most of these studies were done for inhalation toxicity of MMH, which was expected to be the most likely mode of accidental entry of poisons into the body for accidents with humans in places where MMH is manufactured and used.

The use of rodent whole-body exposure data to set TLVs for exposure of humans at the work place has been criticized, but there are no other generally accepted methods to determine safety data. It has been argued that the rodents often lick themselves and that they absorb more hydrazine by ingestion than inhalation. This would not be the case for humans.



Unfortunately, of all modes of administration in animal tests, controlled inhalation concentration levels are the ones most difficult to maintain in an animal experiment because hydrazines are so reactive and may autoxidize in the air of the exposure chamber or may be absorbed by the fur of the animals or the bedding materials in the cage. In some instances, 96–99% of hydrazine metered into the air stream was decomposed or adsorbed after a single pass through the exposure chamber with or without dead or living animals in it. There is typically more scatter and less confidence in inhalation data than those obtained with other modes of administration, such as injection.

The data are analyzed using statistical methods, typically a probit plot, in the dose–response relationship, from which then a lethal concentration 50 (LC50) or lethal dose 50 (LD50) can be derived. This number indicates the concentration or dose at which 50% of the animals in an exposed group survive after a stated observation period. Quite often, investigators report the duration of exposure, but fail to specify the post-exposure observation period within which fatalities are counted.

#### 11.1.1 Short-Term (Acute) Inhalation Toxicity of MMH

Table 45 is a summary of exposure conditions for MMH inhalation acute toxicity tests.

**Table 45:** Methylhydrazine inhalation animal acute toxicity tests for determination of LC50.

| LC50, ppm | Exposure frequency, h/day | Total duration  | Test animal |
|-----------|---------------------------|-----------------|-------------|
| 74        | 4                         | Single exposure | Rat         |
| 56        | 4                         | Single exposure | Mouse       |
| 143       | 4                         | Single exposure | Hamster     |

Data source: [672]

Examinations of organs from necropsied dogs, rats, and mice exposed to MMH or UDMH at acute toxic concentrations revealed no significant pathological changes [672]. However, in surviving dogs after MMH exposure, there was evidence of hemolysis of erythrocytes. In the group including hydrazine, MMH, UDMH, and SDMH, MMH was the most toxic of the vapors tested for acute toxicity, whereas hydrazine was the least toxic.

Rats, mice, beagle dogs, squirrel monkeys, and rhesus monkeys were exposed to various measured concentrations of MMH in air vapor for specified time periods [673, 674]. Rodents were exposed for 30-, 60-, 120-, and 240-min. periods; dogs and squirrel monkeys, for 15, 30, and 60 min., and rhesus monkeys for 60 min. only. The toxicity of MMH for the five animal species was defined by determinations of LC<sub>50</sub> values, pathology, observations of responses, measurements of body weight in rats and mice, and blood chemistry and hematology tests on dogs, and rhesus monkeys. Squirrel mon-

keys proved to be the most sensitive and rats the least sensitive to the lethal effects of MMH. MMH exposure produced definite but transient, hemolytic changes in dogs and, to a lesser extent, in rhesus monkeys. Male and female rhesus monkeys (three to five per group) and male squirrel monkeys (two to four per exposure group) were exposed to MMH vapor for 60 min (rhesus monkeys) and 15, 30, or 60 min (squirrel monkeys; Table 46).

**Table 46:** Lethality in non-human primates and dogs following inhalation exposure to methylhydrazine.

| Duration, min. | Species         | Exposure, ppm | Concentration × Time,<br>ppm × min | Mortality ratio |
|----------------|-----------------|---------------|------------------------------------|-----------------|
| 15             | Squirrel monkey | 300           | 4500                               | 1/4             |
| 15             |                 | 340           | 5100                               | 1/2             |
| 15             |                 | 376           | 5640                               | 3/3             |
| 15             | Beagle dog      | 380           | 5700                               | 0/2             |
| 15             |                 | 390           | 5850                               | 1/2             |
| 15             |                 | 400           | 6000                               | 3/5             |
| 30             | Squirrel monkey | 130           | 3900                               | 0/3             |
| 30             |                 | 150           | 4500                               | 2/3             |
| 30             |                 | 170           | 5100                               | 2/2             |
| 30             | Beagle dog      | 180           | 5400                               | 0/2             |
| 30             |                 | 190           | 5700                               | 1/3             |
| 30             |                 | 200           | 6000                               | 2/2             |
| 60             | Rhesus monkey   | 160           | 9600                               | 0/5             |
| 60             |                 | 170           | 10200                              | 2/3             |
| 60             | Squirrel monkey | 75            | 4500                               | 0/2             |
| 60             |                 | 85            | 5100                               | 2/4             |
| 60             |                 | 90            | 5400                               | 2/2             |
| 60             | Beagle dog      | 92            | 5520                               | 0/3             |
| 60             |                 | 104           | 6240                               | 3/3             |

Data source: [674]

For the rhesus monkeys there were no deaths following a 60-min. exposure to a mean concentration of 160 ppm. For the rhesus monkeys, no deaths occurred during the exposure period. A 60-min. LC<sub>50</sub> of 162 ppm was calculated for the rhesus monkeys. For the squirrel monkeys, deaths occurred as early as 2 h post-exposure, although most deaths occurred between 10 and 24 h post-exposure. The 15-, 30-, and 60-min. LC<sub>50</sub> values for the squirrel monkeys were 340, 145, and 82 ppm respectively. In the same publication, the acute lethal toxicity of rats, groups of 10 that were exposed to MMH at 30, 60, 120, or 240 ppm for 30, 60, 120, or 240 min. resulted in 30-, 60-, 120-, and 240-min. LC<sub>50</sub> values of 427, 244, 127, and 78 ppm respectively. Groups of 20 male

ICR mice were exposed to a range of MMH concentrations for 30, 60, 120, or 240 min. and the LC50 values for 30-, 60-, 120-, and 240-min. exposures were 272, 122, 92, and 65 ppm respectively.

Groups of 10 male Syrian golden hamsters were exposed to MMH at concentrations of 460, 620, 810, 910, 1110, or 1380 ppm for 1 h followed by a 14-day observation period [675]. Immediate irritation of the eyes and nose followed by labored breathing and gasping were observed in all exposure groups. The onset of these signs appeared to be concentration-dependent; signs appeared more rapidly as the concentration increased. Coordination was affected, although the hamsters did not become prostrate. Convulsions were observed during the last few minutes of exposure in hamsters of the highest exposure group. These convulsions continued as long as 1 h post-exposure. Hamsters that died did so within 24 h post-exposure, and all survivors exhibited notable body-weight loss. A 1-h LC50 of 991 ppm was calculated based upon these data. Gross examination revealed lung and liver congestion, and concentration-related alveolar irritation. Histopathological examination revealed concentration-related pulmonary edema and hemorrhage (observed only in hamsters exposed to the two highest concentrations).

In another inhalation test, dogs, monkeys, and rats were exposed to 1 ppm MMH for 24 h [676]. No adverse effects were observed during the exposure, in the clinical tests obtained biweekly during the post-exposure observation period, or in histopathological examination of animals sacrificed 30 day following exposure.

#### **11.1.2 Long-Term (Chronic) Inhalation Toxicity of MMH**

The animal pathology resulting from intermittent medium-term exposure to MMH vapors, using mice, rats, dogs, and monkeys, showed various types of organ damage [677]. The exposure pattern was 6 h/days, 5 days/week. Groups of 4 female monkeys, 8 female dogs, 10 male rats, and 10 male mice were exposed to 0 (control), 2, and 5 ppm for 6 weeks. The optical microscopic examination of microsections of tissues from monkeys and rats showed no experimentally induced lesions. Mice livers at the 5-ppm exposure level showed centrilobular cholestasis, bile duct proliferation, and centrilobular hemosiderosis. Kidneys and spleens also showed hemosiderosis. Bile duct proliferation could be seen in mice at 2 ppm, but one could notice the difference between animals exposed to 2 or 5 ppm. No such effect could be observed in dogs. In a second test series, the same number of fresh animals was exposed to 0 (control), 0.2 ppm continuously, and 1 ppm intermittently for 6 months, except that no monkeys were in the 1-ppm intermittent exposure test. No changes were seen in monkeys, dogs, or rats. Mice suffered hepatic splenic and renal tubular hemosiderosis, which was most pronounced in the group that was exposed continuously for 2 months.

Mice, rats, dogs, and monkeys exposed to 0.2-ppm MMH continuously for 6 months. showed toxic symptoms and hemolytic changes comparable with those observed in the intermittent exposure to 1 ppm MMH [676]. These two exposure

conditions were approximately equivalent in terms of total weekly dose ( $C \times T$  product). Rat growth rate was depressed during a 0.1-ppm/90-day inhalation test. Beagle dogs showed significant increases in serum phosphorus and alkaline phosphatase. Significant hemolytic effects of MMH were obvious from blood analysis of hematocrit, hemoglobin, RBCs, white blood cells, and reticulocytes in dogs and monkeys during and after the exposure and comparing with results before exposure or simultaneously kept controls. Some animals also showed gross pathological changes as livers with a nutmeg appearance. No adverse effects were seen in animals exposed to 0.04 ppm.

Dogs, monkeys, rats, and mice exposed to 2 and 5 ppm MMH intermittently for 6 months, all showed distinct hepatic damage [673, 674, 678]. Some of the mice died during the exposure, but only at the two highest concentrations.

Extending these tests (but not concurrent tests!) to lower concentrations, groups of 8 dogs, 4 rhesus monkeys, 50 Wistar rats, and 40 ICR mice were exposed for 6 months to 0.2, 1, 2, and 5 ppm MMH intermittently for 6 h/day, 5 days/week [679]. Another group was exposed to 0.2 ppm continuously for 6 months. The major chronic effects observed were caused by the affinity of MMH to RBCs. The effects were greatest in dogs, but also noticeable in monkeys. All exposed animals were sacrificed and necropsied immediately at the end of the 6-month exposure period. Results of these experiments have shown that MMH produced a dose-related hemolytic anemia with Heinz body formation for which there appears to be no threshold effect level. Anemia was reversible upon removal of animals from further exposure. Without a post-exposure observation period, it was possible that some latent effects of MMH exposure were overlooked. Dose-dependent changes in the myeloid/erythroid elements of bone marrow were also observed.

Four animal species were exposed for 1 year to selected vapor concentrations of MMH to determine its long-term toxic and oncogenic effects [680]. Year-long exposures of animals to MMH were conducted at a wide range of concentrations: 0.02, 0.2, 2.0, 5.0 ppm (rats); 0.02, 0.2, 2.0 ppm (mice); 0.2, 2.0, 5.0 ppm (hamsters); and 0.2, 2.0 ppm (dogs). Rats, mice, and hamsters were held for 1 year post-exposure whereas dogs were held for 5 years post-exposure. Exposed hamsters showed pathological changes characteristic of chronic irritation of the respiratory tract. Submucosal cysts, rhinitis, and epithelial hyperplasia increased in incidence in the exposed hamsters. Nasal tumors were present in hamsters exposed to the two higher concentrations. There were significant increases in irritation of the nasal cavity such as nasal inflammation, plasmacytosis, and hemorrhage in the mandibular lymph nodes of exposed mice. Adenomas and adenomatous polyps were seen in the nasal mucosa of a few mice exposed to 2.0 ppm MMH. There were significant increases in primary lung and liver tumors in the mice exposed to 2.0 ppm. No neoplastic changes were found in either the rats or the dogs.

## 11.2 Oral and Injection Toxicity of MMH

A large number of studies were performed where MMH was introduced into the body of test animals other than by inhalation or skin absorption. MMH was administered by intratracheal intubation, intravenous injection, intraperitoneal injection, subcutaneous injection, or orally with or without use of a stomach tube. The acute toxicity of MMH when introduced into the body through pathways other than inhalation is summarized in Table 47. In all cases listed in these tables hydrazine was more toxic than any of the methylhydrazines. This comparison is based on a weight basis (mg administered/kg body weight of animal). Under ordinary conditions of hydrazine usage, the

**Table 47:** Acute toxicity of methylhydrazine based on oral, topical, or injection administration methods.

| Dose, mg/kg                                                        | Mode of administration | Test animal | Symptoms observed                | Mortality ratio | References |
|--------------------------------------------------------------------|------------------------|-------------|----------------------------------|-----------------|------------|
| 28 ± 1.7                                                           | Intraperitoneal        | Mouse       | 50% convulsant dose              | —               | [681]      |
| 26                                                                 | Intraperitoneal        | Mouse       | Convulsions                      | LD50            | [682]      |
| 32                                                                 | Intraperitoneal        | Mouse       | Convulsions                      | —               |            |
| 29                                                                 | Intraperitoneal        | Mouse       | —                                | LD50            | [683]      |
| 44.5 ± 6.5                                                         | Intraperitoneal        | Hamster     | —                                | LD50            | [504]      |
| 28                                                                 | Intraperitoneal        | Rat         | Convulsigenic                    | LD50            | [684]      |
| 43.3 ± 2.3                                                         | Intraperitoneal        | Rat         | —                                | LD50            | [504]      |
| 15                                                                 | Intraperitoneal        | Cat         | Death                            | LD50            | [685]      |
| 33.2 ± 5.4                                                         | Intravenous            | Mouse       | —                                | LD50            | [681]      |
| 33 ± 4.5                                                           | Intravenous            | Rat         | —                                | LD50            |            |
| 38.2 ± 2.3                                                         | Intravenous            | Rat         | —                                | LD50            | [504]      |
| 12.3                                                               | Intravenous            | Rabbit      | Convulsion, respiratory distress | LD50            | [501]      |
| 12                                                                 | Intravenous            | Mongrel dog | —                                | LD50            | [681]      |
| 96                                                                 | Percutaneous           | Rabbit      | —                                | —               | [501]      |
| 49                                                                 | Percutaneous           | Guinea pig  | —                                | —               |            |
| 326 ± 39                                                           | Topical                | Hamster     | —                                | LD50            | [504]      |
| 285 ± 47                                                           | Topical                | Rat         | —                                | LD50            |            |
| 133 ± 7                                                            | Oral                   | Rat         | —                                | LD50            |            |
| 72 ± 9                                                             | Oral                   | Hamster     | —                                | LD50            |            |
| [H <sub>3</sub> CNHNH <sub>3</sub> NO <sub>3</sub> ] (MMH Nitrate) |                        |             |                                  |                 |            |
| 71 ± 15                                                            | Oral                   | Rat         | —                                | LD50            | [504]      |
| 17.3 ± 0.4                                                         | Intravenous            | Rat         | —                                | LD50            |            |
| 20.5 ± 1.6                                                         | Intraperitoneal        | Rat         | —                                | LD50            |            |
| 183 ± 16                                                           | Topical                | Rat         | —                                | LD50            |            |
| 22.1 ± 2.6                                                         | Oral                   | Hamster     | —                                | LD50            |            |
| 21.2 ± 3.6                                                         | Intraperitoneal        | Hamster     | —                                | LD50            |            |
| 239 ± 55                                                           | Topical                | Hamster     | —                                | LD50            |            |

Additional toxicity data sources: [686, 687]

prime concern should be respiratory toxicity, on which basis hydrazine is less hazardous because of its lower volatility. The experiments summarized in Table 47 may not all have administered free methylhydrazines in solution. In many instances, the free bases were neutralized to pH 7 and dissolved in isotonic saline, in particular for intraperitoneal or intravenous administration.

Technicians servicing post-flight NTO/MMH thrusters and not wearing protection might be exposed to MMHN, a solid and hygroscopic substance. This is why MMHN was included in Table 47.

Prior to 1963, little was known about the mechanism of toxic action of hydrazine(s). The possibility of interference with  $\gamma$ -aminobutyric acid formation and vitamin B<sub>6</sub>-dependent enzymes was just beginning to emerge. A better understanding of the mechanism has been gained only during the past 50 years. Descriptions of the symptoms of acute poisoning of rats by hydrazines suggested that hydrazine N<sub>2</sub>H<sub>4</sub> itself acts in a way that is different from MMH or UDMH.

Table 48 is a juxtaposition of acute toxicities of hydrazine in comparison with MMH and UDMH. Based on these data, MMH is the most poisonous with the lowest LC50 and LD50 of the three rocket fuels tested.

**Table 48:** Comparison of acute toxicity of hydrazine, methylhydrazine, and unsymmetrical dimethylhydrazine (sorted by mode of administration).

| Test animal                                             | Mode of administration | N <sub>2</sub> H <sub>4</sub> | MMH | UDMH | References |
|---------------------------------------------------------|------------------------|-------------------------------|-----|------|------------|
| <i>Inhalation LC50 in ppm/4 h</i>                       |                        |                               |     |      |            |
| Mouse                                                   | Inhalation             | 252                           | 56  | 172  | [672]      |
| Rat                                                     | Inhalation             | —                             | 74  | 252  | [672]      |
| Rat                                                     | Inhalation             | 570                           | —   | —    | [688]      |
| <i>LD50 in mg/kg within a 10-day observation period</i> |                        |                               |     |      |            |
| Mouse                                                   | Intraperitoneal        |                               | 32  | 290  | [688]      |
| Mouse                                                   | Intraperitoneal        | 163                           | —   | —    | [689]      |
| Rat                                                     | Intraperitoneal        | —                             | —   | —    | [688]      |
| Rat                                                     | Intraperitoneal        | 64                            | 28  | 102  | [684]      |
| Rat                                                     |                        | —                             | 33  | 119  | [688]      |
| Mouse                                                   | Intravenous            | 57                            | 33  | 250  | [688]      |
| Dog                                                     | Intravenous            | 25                            | 12  | 60   | [688]      |
| Mouse                                                   | Oral                   | 59                            | 33  | 265  | [688]      |
| Rat                                                     | Oral                   | 60                            | 32  | 122  | [688]      |

Three groups of hamsters and drinking solutions were used to investigate the carcinogenic effect of MMH in drinking water: **(1)** Control—drinking water adjusted to pH 3.5 with HCl; **(2)** buffered MMH solution—0.01% MMH in drinking water adjusted to pH 3.5 with HCl; **(3)** unbuffered MMH solution—0.01% MMH in drinking water not pH ad-

justed [690]. Each of the groups receiving MMH consisted of 30 hamsters. There were 17 controls. At the beginning of the study, the hamsters were approximately 5 months old. A 0.01% MMH/tap water solution stored in feeder bottles suffered a loss of approximately 60% of the MMH content over a 24-h period. If the tap water was chlorinated, that alone would destroy much of the MMH. The pH of the MMH/water solution had a great effect on rate of decomposition. To determine hemolytic effects of MMH, hematocrit and RBC measurements were made on blood samples taken by orbital puncture from 5 hamsters in each experimental group at 7, 11, and 15 months. Depressed hematology values, evidence from RBC destruction was clearly demonstrated for both groups of MMH-dosed animals. The overall tumor incidence for group I (MMH + tap water) was 16%, group II (MMH + pH 3.5 water) was 24%, and group III (control) was 31% (!). These findings are in contrast to the findings of Toth and Shimizu [691]. They reported a 54% incidence of Kupffer cell sarcomas, a 14% incidence of cecal tumors, and an overall tumor incidence of 101% in 50 male hamsters. Ninety-nine control animals had an overall tumor rate of 27% (!) with no Kupffer cell sarcomas and 1 cecal tumor reported. The dosage of MMH in the Toth and Shimizu study was 0.01% administered in drinking water for the lifetime of the animals. The small numbers of animals involved in both laboratory studies plus the absence of a high incidence of neoplasia in the MacEwen and Vernot experimental groups precludes valid conclusions on the oncogenicity of MMH administered at 0.01% in water *ad lib* for life to hamsters, and the results were in essence negative.

### 11.3 Blood Effects of MMH

In the reaction between MMH and blood, a concurrent effect of some physiological importance following exposure is the oxidation of hemoglobin to methemoglobin. There are species differences in the level of hemoglobin oxidation under the influence of MMH. The necessity for the presence of oxygen during the reaction was demonstrated, and during the course of the reaction some nitrogen and methane were liberated. Measurable methemoglobin occurred over a relatively narrow range of MMH concentration [692]. Denaturation of the globulin and precipitate formation occurred when MMH was in excess, possibly because of the reaction with sulfhydryl groups of the protein. As the aerobic MMH/hemoglobin reaction *in vitro* proceeded, the mixture turned from bright red to purple brown in appearance, during which an observable release of gas occurred.

The effects of MMH on human RBCs were studied *in vitro* [693, 694]. These effects are characteristic of oxidant damage and included methemoglobin formation, Heinz body production, and a decreased level of reduced glutathione. Cell morphology was examined by light microscopy and the cells showed a distorted appearance with a loss of the biconcave shape after 2-h exposure. There was no change in cell osmotic fragility. MMH did not exhibit any effect on various protective enzyme sys-

tems involved in maintaining the redox equilibrium in the cell. It appeared that the hemolytic effect of MMH observed *in vivo* was caused either by a direct action of this oxidant on cell membrane (which was not obvious on fixed morphological observation) or by the effect of Heinz bodies on cellular integrity leading to a decreased cellular 'deformability' and premature removal of the injured cells from the circulation by the spleen, or both.

The direct effect of MMH on the cytoplasm of red cells is manifested by Heinz body formation. *In vitro* MMH/blood reactions were examined to study the effects of MMH on human RBCs [695]. Glutathione (GSH) levels, methemoglobin, and Heinz body production were measured. Biological reduction in the red cell was maintained by GSH and various reductases, which required either NADH from the Embden–Meyerhof pathway or NADPH from the hexose monophosphate shunt (HMP) pathway. The activities of glutathione reductase (GSSG-R) and two enzymes in the HMP pathway, glucose-6-phosphate dehydrogenase and 6-phosphogluconic dehydrogenase, were determined as a decrease in HMP enzyme activity could partially explain the striking susceptibility of mammalian RBCs to MMH exposure and a decrease in GSSG-R could explain the decrease in GSH. Osmotic fragilities of red cells were examined as a measure of red cell membrane integrity. The development of Heinz bodies was followed by light microscopy and freeze-cleave electron microscopy, and an attempt was made to correlate morphological alterations in red cells exposed to MMH with biochemical and functional changes. Methylhydrazine concentration in the blood can be correlated with the received dose by using a nomogram [696, 697].

Hemolysis is the breaking up of red blood corpuscles (erythrocytes), rendering them ineffective for the transport of oxygen. Blood cell destruction and anemia are less frequently observed after inhalation or subcutaneous injection, but only in severe cases of chronic poisoning.

Methylhydrazine was injected into rats, rabbits, and guinea pigs, and subsequent levels of methemoglobin in the blood were measured [698]. Peak levels of methemoglobin occurred within an hour, but were less than 5% of blood hemoglobin, with doses of MMH up to 0.54 mmol/kg. In contrast, 5- to 8-fold higher levels have been previously observed in anesthetized dogs treated with comparable doses of MMH. *In vitro* incubations of MMH with blood from rats, rabbits, guinea pigs, dogs, and human subjects produced peak levels of methemoglobin within an hour. Peak levels were 4- to 8-fold higher when human or canine blood was incubated with MMH than when rat, rabbit, or guinea pig blood was similarly incubated. These results demonstrated that there is a marked difference among species in the levels of methemoglobin found either *in vivo* after MMH injection or *in vitro* during incubation of blood with MMH.

During an *in vitro* study of the MMH effect on blood, the aerobic MMH–hemoglobin reaction caused the appearance of the mixture to change from bright red to purple brown in appearance, during which an observable release of gas occurred [692]. With high MMH to heme ratios, more than 2:1 on a molar basis, rapid denaturation and precipitation followed. At lower ratios the rate of hemoglobin con-



version was directly proportional to the MMH level. Identification of the compound formed as methemoglobin was based on spectral analysis of the compound itself and comparison with published spectra. In unlimited aerobic reactions of MMH with dog blood, both the rate of methemoglobin formation and the total reached were directly proportional to the original concentration of MMH.

The hemolytic action among all the alkyl hydrazines is most pronounced with MMH [672]. Excessive MMH exposure can readily be recognized by methemoglobinemia [699]. Anemia caused by MMH is characterized by methemoglobinemia, a decreased level of reduced glutathione, and Heinz body formation. Human red cells were exposed *in vitro* to three levels of MMH for 2, 4, or 6 h. Glucose utilization, lactate production, and ATP levels were measured to determine effects on glucose metabolism. Osmotic fragilities, red cell potassium concentration, and malonyldialdehyde levels were measured to assess membrane effects [694]. This effect is species dependent [698]. However, when comparing the erythrocyte damage in freeze-etched specimens by MMH and phenylhydrazine, extremely high doses of MMH were required to produce the same effect as that caused by phenylhydrazine at low concentrations [700].

As opposed to MMH, hydrazine and UDMH cause hematological changes in rabbits or mice only at very high concentrations [701]. At high concentrations, hematological changes are frequently overshadowed by other symptoms of acute poisoning.

In the group of three hydrazines tested (hydrazine, MMH, and UDMH), MMH was the most effective agent at producing hemolytic anemia in test animals [702]. Effects of MMH, such as methemoglobinemia and Heinz body formation, were observed at MMH concentrations 8–10 times lower than the concentration at which the first effects were observed for hydrazine itself. In contrast, UDMH did not cause methemoglobinemia or Heinz body formation.

The amount of methemoglobin formed is a sensitive indicator that can be correlated with the MMH dose received, as shown not only in animal tests with anesthetized dogs, but also with human blood *in vitro*. Because the methemoglobin content of blood from an accident victim can be rapidly determined, it has been proposed to use the methemoglobin concentration as an index for the severity of exposure [703]. Of course, this index is reliable only if no other toxic agents that also cause methemoglobinemia (e.g., NO<sub>2</sub>) are involved.

Methylhydrazine may disturb the blood clotting mechanism. The *in vivo* effects of MMH on the coagulation mechanism, in particular the prothrombin activating mechanism and the fibrinolytic mechanism, was studied in rats anesthetized with ether [704]. The MMH concentration chosen was 60% of the LD<sub>50</sub> determined in separate experiments. No significant changes were found in the prothrombin time or partial thromboplastin time, but the thromboplastin generation time was increased, and total profibrinolysin was decreased significantly.

### 11.4 Central Nervous System Effects of MMH

Similar to the mechanism for hydrazine, a likely mechanism for MMH-induced seizures is the formation of the methylhydrazone of pyridoxal phosphate, a reaction that takes this coenzyme away from the synthesis of glutamic acid decarboxylase (GAD), an essential precursor of putative central neural inhibitory transmitter such as  $\gamma$ -aminobutyric acid.

Laser surface photobleaching, electron microscopy, and electrophysiological measurements on hydrazine- and MMH-treated vertebrate cell cultures demonstrated a marked effect of MMH on cell mitochondria and  $\text{Ca}^{2+}$  ion flux [705]. *In vitro* cells treated with  $\text{N}_2\text{H}_4$  or MMH showed changes in lateral surface mobility. Methylhydrazine and other hydrazines inhibit  $\gamma$ -aminobutyric acid (GABA) synthesis in the central nervous system (CNS), but others cause a several-fold increase of GABA levels in the brain [706].

Exposure to MMH can cause dose-related CNS disturbances ranging from tremors to tonic-clonic convulsions to death [707]. Diazepam (DZ) acts at the GABA receptor site, and it is also here that ivermectin (AVM) is pharmacologically active. Mice were injected with 30 mg/kg MMH. Groups of 12 mice each were then given varying doses of AVM (5, 10 or 15 mg/kg), or AVM + DZ combinations (5 mg/kg AVM with 5 mg/kg DZ, 10 mg/kg AVM with 5 mg/kg DZ). Times elapsed to first convulsion and time to death were recorded over the next 7 h and all groups were monitored over the next 7 days. Times to convulsion were not altered with AVM alone, but death was significantly prevented with AVM dosages. A combination treatment of 10 mg/kg AVM with 5 mg/kg DZ resulted in no seizures or deaths.

The latent effect of MMH on the tendency of cats to suffer seizures (stimulated by electrodes) lingers on for a long time after MMH administration [708, 709]. Using a statistical index of seizure susceptibility, it was shown that cats with prolonged seizure latencies also showed significantly higher post-discharge thresholds.

Lethal doses of 18 mg MMH/kg (intraperitoneally) and sublethal doses of 9 and 5 mg MMH/kg (intraperitoneally) were used to study lethal, convulsive and sub-convulsive symptoms in cats [710]. The onset latency of these symptoms was directly related to dose.

Cats were trained and tested in a special runway apparatus to provide a reliable indication of performance changes over a 6-h period following the administration of 1, 2 or 4 mg/kg MMH [685, 711]. These low doses significantly altered locomotor performance, both during drug session testing and saline control testing carried out 24 h later. Within 30 min after injection of all three doses of MMH, runway performance was depressed. At 2 and 4 mg/kg, this influence was profound and was associated with overt physiological symptoms of toxicity. A total disruption of performance occurred with 4-mg/kg doses when tested 2–5 h after administration. Performance was still depressed after 24 h following 4 mg/kg, but was actually facilitated at this same point following the lower 1- and 2-mg/kg doses. For these doses, a pre-convulsive syndrome

was described involving recurrent and sustained symptoms including vomiting, panting, salivation, hyperactivity, and subcortical seizure activity. The acute toxicity LD<sub>50</sub> value for MMH was established as 15 mg/kg, and the CD50 as 7 mg/kg. Doses of 18, 9, and 5 mg/kg were then studied systematically in an effort to classify lethal, convulsive, and sub-convulsive symptoms. Convulsions were specifically delayed or prevented in animals trained to suppress movement through the use of a special electroencephalogram (EEG) conditioning technique.

The effects of dorsal column lesions on electrocortical activity and susceptibility to MMH-induced seizures in cats were studied with 11 animals, prepared with indwelling cortical electrodes over hind-limb and fore-limb projection areas of somatosensory cortex, which received bilateral lesions of the dorsal columns at either high (C1–C3) or low (C5–T1) cervical levels [712]. After a 3-week postsurgical period, each animal was administered a convulsive dose of MMH. Seizure latency was measured from the time of MMH injection to the onset of tonic–clonic convulsions. Latency data were compared with those from intact animals ( $N=18$ ). Results indicated a progressive and significant increase in seizure latency with more encephalad dorsal column transection.

Methylhydrazine may have adverse effects on the CNS. In one of the first test series involving nine macaque monkeys, at the rate of one injection per day, two control injections of saline alternated with two MMH intraperitoneal injections (each containing 2.5 or 5 mg MMH/kg) [713, 714]. The two MMH injections were 48 h apart. No difference in performance could be observed as the result of any of the injections at either concentration level, but there was a greater incidence of clinical signs in the group receiving a higher dose. The few performance decrements observed would usually precede clinical signs of incipient poisoning. In a similar test, nine macaque monkeys were injected twice with either 2.5 or 5 mg MMH/kg [715]. Operant task performance was not affected by either dosage of MMH, but there was a greater incidence of clinical symptoms in those monkeys exposed to 5 mg/kg. In over half the cases, performance degraded prior to clinical symptoms becoming apparent, typically within 1–2 h after the first MMH poisoning. In 3/18 cases clinical symptoms did appear without a performance decrement, but in 4/18 cases a performance decrement occurred in the absence of clinical symptoms. When initial 2.5 or 5.0 mg/kg injections are given one might predict that performance decrements might occur between 1 and 2 h and clinical symptoms between 2 and 2.5 h in about half the subjects. A second exposure might be expected to produce performance decrements between 1 and 2 h and clinical symptoms between 2 and 3 h in the majority of subjects. If a subject is influenced by MMH, clinical symptoms will likely disappear between 3 and 9 h following injection, and performance should return to baseline level between 3 and 30 h.

Two other monkeys, whose behavior was maintained on an avoidance schedule that required continued discrimination of cues, were given 0.5–4 mg MMH/kg injections [716–719]. Exposure to these comparatively low doses resulted in significant behavioral stimulation. There seemed to be a cumulative effect of repeated exposure in intervals of 24 h.

### 11.5 Brain Effects of MMH

In advanced states of MMH poisoning, the victim suffers seizures and convulsions that seem to be triggered by blockage of essential brain centers. Significant effort has been devoted to studying this mechanism in test animals and finding possible preventive or curative agents.

The influence of hydrazine, MMH, and UDMH upon possible transmitter substances in rat brain was studied to determine the time elapsed between injection and onset of convulsions [720]. Mesencephalon-diencephalon, medulla, cortex, and cerebellum were separately examined. All the hydrazines increased 5-hydroxy-tryptamine, particularly in cortex, where a three-fold increase was found. All the hydrazines increased norepinephrine by small amounts (48% maximum), the effects being greatest in the cortex and least in the mesencephalon-diencephalon. MMH and UDMH lowered GABA by small amounts (17% maximum) in medulla, cortex, and the mesencephalon-diencephalon, but the effects on cerebellum were small or absent.

The toxic action of MMH or UDMH may be mediated by the inactivation of pyridoxal in the brain. One possibility considered was the formation of a hydrazone between the pyridoxals and the substituted hydrazine. Pyridoxal-dependent enzymes were investigated [721]. MMH inhibited both glutamic acid decarboxylase and DOPA decarboxylase. Transaminases that required AKGA as a substrate were not affected by the hydrazines tested. A mathematical model for hydrazines-induced convulsions was developed that can predict the time lapse after administration of the convulsigen and the onset of seizure if only three data points are given.

The brain effects and behavioral changes as the result of MMH intoxication were studied by electroencephalography in cats [710, 722]. The acute lethal toxicity value (LD50) for MMH was established at 15 mg/kg, and the convulsive toxicity value (CD50) at 7 m/kg. Doses of 18, 9, and 5 mg/kg were then studied systematically in an effort to classify lethal, convulsive, and sub-convulsive symptoms.

The cerebral neuroelectric evoked response in the unanesthetized cat showed that convulsive doses of MMH consistently produced a large increase in the primary negative response of the somatic sensory cortex, which progressively changed with time and approached peak levels starting approximately 1 h before seizure onset [723]. The response changes may be a useful index of impending seizure in a variety of toxic and clinical conditions.

It was shown that MMH disturbs the blood cerebrospinal fluid glucose flux, but catastrophic failure of the performance of brain and nerve cells embedded in that fluid is not caused by elevation of glucose levels observed following MMH administration in monkeys [724, 725]. The convulsions following intravenous administration of MMH to mice or rats are caused by direct action on the brain because they are abolished caudal to a cord transection or by treatment with *d*-tubocurarine [681]. Convulsions are also elicited in the anesthetized dog when MMH is injected into the cisterna magna.

Whereas doses of 1–9 mg/kg administered cisternally produced convulsions, doses in excess of this caused death within a few minutes. When data from mice convulsion,  $\log(\text{time to onset of convulsions})$  were plotted against  $\log(\text{dose})$ , a straight-line relationship was obtained. In mice, MMH-induced seizures can be prevented completely with secobarbital (50 mg/kg), phenobarbital (100 mg/kg), or Mesantoin (200 mg/kg). A survival rate of 90–100% has been achieved in mice by repeated administration of anti-convulsants for a period of 30 h following administration of an otherwise 100% fatal dose of 60 mg MMH/kg. So far, repeated attempts to extend the same treatment to dogs have failed. In an attempt to localize the site of convulsant action in dogs, the neuraxis was transected at various levels to find the lowest portion of the CNS that might initiate hydrazine-induced convulsions. Decorticated, decerebrated, and cervical cord-dissected animals responded differently. The results indicate that a small area in the midbrain is essential for the occurrence of convulsions in dogs poisoned by MMH or UDMH.

The influence of sub-convulsive exposure to MMH on sleep-waking patterns and upon thalamocortical conduction was measured by polygraphic recordings classifying states of sleep and wakefulness over a 10-h period following either saline or MMH (5 mg/kg, intraperitoneal) injections [726]. MMH at this dose caused no overt behavioral disruption on transient observation; however, analysis of polygraphic data disclosed a significant depression of sleep and disruption of normal diurnal rhythms. Sleep suppression lasted approximately 6 h and was followed by a profound sleep rebound. The influence upon sleep could have equally serious and different consequences in performance.

A lumped parameter mathematical model including extracellular fluid, intracellular fluid, and cerebrospinal fluid compartments has been applied to describe MMH distribution kinetics in the blood and cerebrospinal fluid of Rhesus monkeys [727, 728]. Ten monkeys with an average weight of 5.5 kg, were given intravenous infusions of MMH whereas blood and cerebrospinal fluid samples were periodically collected and analyzed for MMH. The mathematical model was used to simulate the infusions and the simulations were compared with experimental data to validate the model and to evaluate the mass transfer parameters required by the model.

Toxic and convulsive responses to MMH were compared in two groups of rhesus monkeys [729]. One group received 12 weeks of feedback training with reinforcement provided for the production of rhythmic central cortical 12–14 Hz EEG activity (the sensorimotor rhythm or SMR) in the absence of movement and concurrent 8–11 Hz EEG activity. A second group was also studied but without feedback training. Three of the four trained animals demonstrated reliable acquisition of the rewarded response. Following training, a convulsive dose of MMH was administered to both groups. Trained animals showed a significantly prolonged latency to generalized seizures, fewer overall seizures, and a greater incidence of sustained quiescent behavior. Toxic responses of the two groups, including emesis and episodes of agitated behavior, were comparable. These findings indicate that the threshold for MMH-induced seizures can be

modified in primates through EEG feedback training, as shown previously in the cat. A specific change in central motor control mechanisms was proposed as an explanation for this effect.

### 11.6 Cardiac Effects of MMH

The cardiovascular effects of hydrazines may be related to changes in norepinephrine and histamine levels in the heart muscle. Studies of the effect of hydrazine, MMH, and UDMH injections on blood pressure and heart rate in the conscious or anesthetized dog showed that the effects caused by the four hydrazines were quite different [682]. The cardiac slowing induced by MMH or hydrazine has been ascribed to medullary (vagal) stimulation because changes in rate were not observed after nerve blocking with hexamethonium injections.

Methylhydrazine (0.31 mmol/kg) or hydrazine (0.31 mmol/kg) produced significant elevations of norepinephrine in the heart of rats [730]. The increase caused by MMH can be explained by the fact that it is also a potent monoamine oxidase (MAO) inhibitor, but the effect of hydrazine is more difficult to explain. MMH also acts as a diamine oxidase inhibitor. In a group of several hydrazine derivatives tested, MMH was the only one that also increased histamine levels in the heart.

### 11.7 Dermal (Cutaneous) Toxicity of MMH

Most hydrazines, including MMH, are water soluble and can permeate the skin barrier. They also often form chemical bonds to carbonyl and acid groups in the skin material. In one series of tests, when applied directly to the skin of rabbits, hydrazine caused corrosive skin disintegration, whereas MMH caused a mild edema, which disappeared after 24 h, leaving a bleached appearance at the site of application [501].

In skin absorption tests with MMH on dogs with doses up to 270 mg/kg, no permanent effects were observed as the result of a single application [731, 732]. Water washing and tannic acid solution soaking were evaluated as first aid treatments to arrest MMH absorption through the skin [733]. The blood plasma MMH concentration and the progressed state of methemoglobinemia as it is commonly observed during the first 2 h after application of MMH to the chests of dogs can be expressed as a function of body weight and dose [696, 697]. Calculations are made easy by use of a nomogram, which may allow one to extrapolate to other body weights and (with some precautions) other species. In the absence of dose–response data from humans, these graphs are for the time being the best source for prediction of the effects of accidental MMH spills on the skin of propellant-handling personnel.

Methylhydrazinium nitrate is never produced in bulk as an industrial commodity (unlike methylammonium nitrate). It may form inadvertently during the shutdown of

bipropellant thrusters from the dribble volume of oxidizer and MMH slowly reacting after combustion has ceased. Technicians or astronauts who are servicing post-flight NTO/MMH thrusters without protecting themselves with gloves may accidentally absorb MMHN through the skin. Tests with rats and hamsters have shown that MMHN is readily absorbed through the skin and that the topical LD50 of MMHN is similar to that of MMH (when compared on a molar basis) [501, 502] (see Table 47).

A study of the toxicokinetics of MMH percutaneous absorption in rabbits was based on two kinetic models and compared with test results where MMH 10 mg/kg was administered intravenously in rabbits in one test and MMH 25 or 6 mg/kg was administered percutaneously [734]. The toxicokinetic characteristics of MMH in rabbits showed that MMH can be absorbed rapidly and the rate of diffusion crossing skin would be very fast. The speed of distribution through the body was much faster. MMH was distributed throughout the body and accumulated in peripheral compartments. The elimination of MMH was quite rapid.

### 11.8 Eye Effects (Ocular Toxicity) of MMH

Ocular toxicity studies of hydrazine and methylhydrazines showed that hydrazine caused permanent corneal damage, whereas methylhydrazines showed transient effects for only 2–7 days [504]. A study of the effect of MMH on frog cornea showed that even though MMH is a weaker base than hydrazine, the transparency of the cornea suffered more rapidly [735].

Animal test results showed that MMH easily passes through the blood/aqueous humor barrier to enter the aqueous humor bathing the endothelial layer of the cornea. Dog corneas became edematous within 5–6 h after MMH has entered the anterior chamber. The MMH concentration in the aqueous humor was ~75% of that in the blood. In clamped cornea tested *in vitro*, marked swelling occurred within 15–20 min after exposure to MMH at concentrations of  $10^{-2}$  to  $10^{-4}$  M. Lower MMH concentrations ( $10^{-5}$  to  $10^{-7}$  M) caused the same amount of swelling, only after a longer lag time. The rate of swelling was reduced soon after the MMH was removed.

Methylhydrazine caused hydration of the endothelium, with subsequent swelling of the cornea. Pharmacological doses of arginine inhibited the swelling effect of MMH [736].

### 11.9 Therapy and Prophylaxis of MMH Poisoning: Treatment of Accidental Poisonings with MMH

Propellant handling personnel should undergo routine periodical health examinations and their medical records need to be reviewed for slow changes in body functions. Considerable information that is useful in evaluating the adequacy of

control measures can be obtained by compiling and analyzing clinical laboratory results, physical findings and subjective complaints.

Although there are recommendations on the treatment of accidental poisonings with hydrazine  $N_2H_4$  or UDMH, no such specific recommendations could be found for cases of MMH poisoning. Eighteen different compounds were tested for their therapeutic effect against hydrazine, MMH, or UDMH poisoning (intraperitoneal, mice) [682]. Of those found to be effective, arginine and ornithine provided clear-cut protection from death and convulsion caused by otherwise fatal hydrazine doses, but the two amino acids were ineffective against MMH or UDMH. Amino-oxyacetic acid or pyridoxine provided effective protection against MMH or UDMH poisoning but were ineffective against hydrazine.

Although a significant number of experimental studies were performed in the late 1950s through the mid-1960s, conflicting information exists concerning the most appropriate treatment for accidental exposures of humans to hydrazines. A cross-sectional study evaluating the most commonly suggested therapies against poisonings by the most common rocket fuels such as hydrazine, UDMH, MMH, and Aerozine-50, therapies such as pyridoxine, traditional anti-seizure therapies, or arginine is needed to clarify the treatment implications for human exposure [737]. Treatments that have been useful for hyperammonemic states, such as those for urea cycle defects, have significant potential for the improvement of treatment for hydrazine(s) accidental exposure.

Anyone reading about the results of various experimental animal studies dealing with prophylaxis and therapy of hydrazine poisoning using pyridoxine = vitamin  $B_6$  may still have some doubts as to whether this chemical would help in human accident situations. The protective efficiency of pyridoxine and other forms of vitamin  $B_6$  has been disputed and questioned. There are summaries of hydrazine or UDMH accidents and several accounts of the successful application of pyridoxine therapy to victims of hydrazine or UDMH poisonings, but it is not known if the same therapy would help in cases of poisonings by MMH.

Dogs treated with single intraperitoneal injections of up to 30 mg MMH/kg as part of a renal toxicity study were successfully protected from the acute convulsigenic effects by co-administration of 100–200 mg pyridoxine/kg. In a group of 11 dogs treated with 10 mg MMH/kg, 7 were protected with 100–200 mg pyridoxine/kg. Most of the unprotected dogs died within a few hours, whereas protected animals lived to the scheduled necropsy after 1 day. In a group of 12 dogs exposed to 15 mg MMH/kg, all animals could be protected by 200 mg pyridoxine/kg. Similar results were obtained at 20 and 30 mg/kg.

Large doses of pyridoxine reduced the convulsant effect of MMH in cats [708, 709]. The convulsive, toxic, and lethal effects of a single subcutaneous injection of MMH given to Swiss mice were successfully prevented by administering pyridoxine hydrochloride before and/or after injection [738]. Exposure to MMH can produce convulsions and death, probably because of the inhibitory effect of MMH on GABA synthesis.



A widely recommended prophylactic and therapeutic agent is pyridoxine, but because of the large amounts required, and the low solubility of pyridoxine, the injection volumes required for effective treatment can result in severe tissue irritation and trauma. The therapeutic effects of muscimol, DZ, and pyridoxine, and certain combinations of these compounds, against MMH-induced convulsions and lethality were tested by injecting mice with convulsive and lethal doses of MMH, and with varying doses of the three antidotes or combinations of them, and recording the incidence of convulsions and death, and the times needed to achieve an effect [739]. All drugs had a protective effect, but combinations containing DZ and either pyridoxine or muscimol were the most effective antagonists to MMH convulsions and death. The dose–response curves were shifted to the right, and the times to convulsion and to death were significantly prolonged. One group of mice (10 male and 10 female) were given 40 mg MMH/kg, and a mortality rate of 80–100% was observed. The same dose together with two injections of 200 mg pyridoxine hydrochloride/kg each at 1-h intervals did not cause any fatalities in either of another two groups of 10 mice. Combinations of DZ and pyridoxine were the most effective antagonists against MMH-induced convulsions and death. These types of tests were later extended to rhesus monkeys, also with monitoring of brain function in EEGs [729, 740, 741]. Three groups of monkeys were exposed to either MMH alone or MMH with simultaneous pyridoxine administration. Animals receiving MMH alone displayed emesis, preictal responses, and generalized seizures within the first 75 min after MMH injection. MMH/pyridoxine-treated animals showed some emesis but no preictal or ictal behavior during this period. MMH/pyridoxine-treated animals that were also restrained in a primate restraint chair did not show these symptoms. Immobilization reduced the susceptibility to hydrazine-induced seizures. Pyridoxine does not appear to be as effective against MMH poisoning as it appeared to be against UDMH poisoning. Based on tests in male ICR mice, combinations of pyridoxine and DZ or muscimol were more effective than pyridoxine alone [742].

The behavior-changing effect of MMH on the learned behavior of monkeys can be mitigated if pyridoxine is administered intramuscularly simultaneously with MMH intraperitoneally [718]. Ten macaque monkeys were trained on a complex behavioral program containing both aversively avoided and appetitively rewarded tasks. One group was given MMH only, and the other group was given MMH with the prophylactic antidote of pyridoxine. The second group was able to continue to perform tasks in which the first group failed.

The pyridoxal hydrazones of the various hydrazines form as intermediates during metabolism of hydrazines, surprisingly with an exceptionally high toxicity of their own [743]. A comparative study was made of the toxicity and convulsion activity of MMH, UDMH, and their pyridoxal and pyridoxal-5-phosphate hydrazones. The hydrazones of UDMH were more toxic than UDMH itself. In the case of MMH, the convulsion times of hydrazones and free MMH were about equal; but death appeared earlier with the hydrazones. This work implies that pyridoxal exacerbates rather than alleviates the convulsant activity of UDMH and MMH, and thus should not be considered an

antidote. It was discovered that the pyridoxal hydrazone of UDMH is more toxic than UDMH, which is truly remarkable. With MMH and its hydrazone, the convulsion times are equal, but death occurred earlier with the hydrazone.

In rhesus monkeys that were restrained in a chair, the convulsant effect of 15 mg MMH/kg could be avoided by anti-convulsant drugs, pyridoxine, and DZ [740, 741]. Valproic acid or carbamazepine were not effective.

The influence of arm restraint and pyridoxine respectively on preventing seizures in MMH-poisoned monkeys was investigated [744]. Control animals with no protective prophylactic treatment displayed emesis, pre-ictal responses and generalized seizures within the first 75 min. post-MMH-injection. Pyridoxine-treated animals showed emesis but no pre-ictal or ictal behavior during this period, whereas arm-restrained animals showed no emesis, pre-ictal or ictal behavior. Control animals exhibited at least three generalized seizures, after which chemotherapy was administered within the first 100 min. post-MMH-injection. Neither pyridoxine-treated nor arm-restraint animals showed any generalized seizures during a standard 240-min. observation period, although both groups eventually displayed emesis and pre-ictal responses. The protective effects of pyridoxine were interpreted within the context of established neurochemical influences of the hydrazines on the synthesis of the inhibitory neurotransmitter GABA.

## 11.10 Effects of MMH on Metabolism

The effects of MMH on metabolism, the immune system, enzymes in the brain, liver, and the blood were already summarized in a chapter of the hydrazine book [745].

### 11.10.1 Metabolic Fate of MMH

Besides observing adverse effects of MMH on various parts of the body, it is also of interest to determine which pathways MMH follows through the body and what fraction is excreted unchanged or as an intermediate additive with other metabolites or totally metabolized to nitrogen and water [746]. MMH resembles ammonia in being more rapidly excreted in acidic urine. Metabolic changes (not just digestion) suffered by hydrazines as they pass through the body are called “biotransformation.” In addition, toxicokinetic studies look at the rate at which the poison is distributed throughout the body and at what rate it disappears through either metabolism or clearance in the unadulterated state. Many of the early studies of metabolic pathways were done by identifying agents that could block a vital step of a metabolic cycle, then observing which metabolic substrates accumulate when the blocking agents are administered to living animals. Additional information is available in the hydrazine book [745].

### 11.10.2 Kidney Function (Nephrotoxic) Effects of MMH

In kidney function studies with dogs, the effects of hydrazine, MMH, or UDMH on *p*-aminohippurate (PAH) clearance were studied experimentally [747]. Dogs received 0.63 mMol hydrazine/kg, 0.63 mMol MMH/kg, or 0.5 mMol UDMH/kg intravenously. The animals were anesthetized during the experiment, and PAH and inulin were administered along with an intravenous infusion of dextrose. Dogs exposed to hydrazine had significantly decreased PAH and inulin clearance rates and decreased renal plasma flow (RPF) rates during the first 4 h after hydrazine injection. The decreased glomerular filtration rate (GFR) was attributed to decreased RPF. The decreased PAH clearance was most likely caused by decreased GFR and impedance in active transport by the proximal tubular epithelium. Animals also developed hemoglobinemia and hemoglobinuria. Dogs exposed to MMH had decreased PAH and inulin clearance rates. Within minutes after MMH administration, methemoglobin began to appear in the blood, and it appeared in the urine within 1 h. Intraperitoneal injections of 25–60 mg/kg MMH caused proximal tubule damage in kidneys of rats [748].

A new effect (not previously observed) as the result of chronic exposure of dogs to MMH was the severe renal damage. Histopathological examination of the kidneys revealed proteinaceous precipitates in the proximal tubules [749]. Monkeys exposed to MMH showed no change in renal function [676, 750]. Four groups of monkeys were given different MMH doses intraperitoneally as follows: (1) 7.5 mg/kg single injection; (2) 2.5 mg/kg daily for 14 day; (3) 5 mg/kg every other day for 14 day; and (4) 5 mg/kg daily for 5–10 days. A fifth group was kept as a control group and received saline injections only. The GFR was determined by endogenous creatinine clearance. RPF was determined by infusion of sodium PAH. Kidney tissue samples were taken by needle biopsy. There was no statistically significant change in renal function in any of the animals. However, examination of kidney biopsy samples under SEM revealed major changes in the subcellular morphology in all groups of monkeys as a result of MMH exposure. Changes were observed in both proximal and distal tubule cells. Changes were most pronounced in the animals from group 2 (as defined earlier in this paragraph). The nephrotoxic effects of exposure to MMH are much more severe in dogs than in monkeys. The animals exposed to 0.2 ppm MMH continuously for 6 months showed toxic alterations and hemolytic changes comparable with those observed in the animals with intermittent exposure to 1.0 ppm MMH. These two exposure conditions were approximately equivalent in terms of total weekly dose in parts per million  $\times$  hours.

In cases of acute MMH poisoning of dogs, most of the MMH was excreted through the kidneys and could be detected in the urine, although part of it may have been temporarily tied up with carbonyl compounds (sugars) from which it was released on hydrolysis [749, 751]. Unlike other hydrazines, MMH given to dogs produced RBC damage, leading to hemoglobinemia, hemoglobinuria, and severe hemoglobinuric nephropathy. This expressed itself by the appearance of hemoglobin in the tubules and the development of absorption droplets in the lining epithelial cells. If a large

dose of MMH was given, the epithelium later took on a different appearance, with the formation of giant cells or syncytial masses around the hemoglobin aggregates. The renal lesion was reversible if complications were avoided, and the only late effect was marked hemosiderosis of the kidneys, liver, spleen, and lymph nodes. Detailed histopathology was conducted on kidneys removed from dogs exposed to single intraperitoneal doses of 5–30 mg MMH/kg, and sacrificed after 8 h, 12 h, 2 days, or 8 days [752–754]. The animals receiving more than 10 mg/kg were protected against convulsions by administration of 100 to 200 mg/kg of pyridoxine hydrochloride. MMH excretion was similar to that of hydrazine, its parent base, except that MMH possessed a lower reabsorption rate.

### 11.10.3 Liver Toxicity (Hepatotoxic) Effects of MMH

Isolated hepatocytes and liver microsomes incubated with MMH, UDMH, or SDMH produced free radical intermediates that were detected by ESR spectroscopy by using 4-pyridyl-1-oxide-*t*-butyl nitron (4-POBN) as a spin trapping agent [755]. The spectral features of the spin adducts derived from all three hydrazine derivatives corresponded to the values reported for the methyl free radical adduct of 4-POBN. In the microsomal preparations, inhibitors of the mixed function oxidase system and the destruction of cytochrome P450 by pretreating the rats with  $\text{CoCl}_2$  decreased the free radical formation. Methimazole, an inhibitor of the flavin adenine dinucleotide-containing mono-oxygenase system, similarly decreased the activation of UDMH, but not that of MMH or SDMH. The addition to liver microsomes of physiological concentrations of GSH lowered by approx. 80% the intensities of the ESR signals. Consistently, incubation of isolated hepatocytes with methylhydrazines decreased the intracellular GSH content, suggesting that GSH can effectively scavenge the methyl free radicals. The results suggested that methyl free radicals could be the alkylating species responsible for the toxic and/or carcinogenic effect of methylhydrazines. It was theorized that CoQ10 scavenges free radicals generated from MMH or its metabolites. Other enzymes involved include cytochrome oxidase and MAO inhibitors and cytochrome P450 as an activator [756]. Cytochrome P450 is a heme-containing protein that takes part in many reactions of xenobiotics during biotransformation processes [757]. Of particular interest are reactions involving free radicals during oxidative metabolism of hydrazine derivatives, as some of these may lead to cancer. The metabolism of alkylhydrazines via oxidation by cytochrome P450 systems may involve carbon-centered free radicals.

Single toxic doses of MMH caused little morphological change in the liver [758]. No effects on hepatic protein synthesis by SDMH or MMH were observed. Liver mitochondria exhibited distinct changes as a result of fatty liver degeneration caused by hydrazine poisoning. Similar effects may be caused by MMH [705, 759]. Even naturally occurring MMH-containing glycosides such as gyromitrin can cause adverse effects on the lipids of rat liver [77, 78].

### 11.11 Carcinogenic Effects (Carcinogenicity) of MMH

A book on *Hydrazines and Cancer* was published in 2000 by Toth [760]. It is a very thorough review of carcinogenicity and includes test data with both natural and man-made chemicals, including MMH and UDMH. The same topic was discussed from a slightly different point of view, but in much more detail in Sections 4.4.3.8 and 4.4.3.9 of our 2001 book on hydrazines [745], including chapters on carcinogenicity, teratogenicity, and mutagenicity.

Several hydrazines have been shown to be carcinogenic in animal tests. As part of the overall effort to understand the conditions leading to development of cancer, and in order to find a cure of this highly complex disease, carcinogenic actions of hydrazines have been thoroughly studied. The carcinogenic action is most pronounced with SDMH and UDMH, not MMH.

### 11.12 Bacteriostatic Activity of MMH

Any toxic chemical spilled into the sewer system that finds its way into the sewage treatment plant bioreactors may do serious harm to the live bacteria that are performing the dirty job of cleaning up the sewage water so that it can be released into surface waters. As it turns out, depending on the concentration of the alkylhydrazine, some bacteria not only are not harmed, but actually thrive on it, in particular after part of the population has undergone mutations to become more hydrazine resistant.

The toxicities of hydrazine, MMH, and UDMH were determined for mixed and uni-cultures of nitrifying bacteria, denitrifying bacteria, and anaerobic methanogenic bacteria [761–763]. MMH was more toxic than hydrazine, which was more toxic than dimethyl hydrazine. The toxicity level numbers were small enough to preclude biological waste treatment of these compounds. Hydrazine was co-metabolized to nitrogen gas by *Nitrosomonas*.

During a series of experiments on the death rate kinetics of hydrazine-exposed cultures, it was noted that bacteria continued to grow in nutrient-free media, which suggested metabolites derived from lysed cells might have been metabolized. This observation in conjunction with reports on the effects of hydrazine intoxication on carbohydrate metabolism prompted an investigation of the effects of MMH, UDMH, or  $N_2H_4$  on the utilization of arbitrarily selected saccharides and compounds involved in intermediary metabolism as a means of elucidating mechanism of action. An *Enterobacter cloacae* strain called D-31 showed the ability to develop (mutate into) hydrazine-resistant strains that survived hydrazine, MMH, or UDMH exposure much better than did the average population from which they were derived [764–767].

When testing the toxic effects of hydrazines on the growth dynamics and early death rates of soil microorganisms, the order of toxicity was  $N_2H_4 > MMH > UDMH$  [766–768]. The bacterial response, measured turbidimetrically in a mineral salt

medium, was a delay in the onset of logarithmic growth, with  $\geq 0.05$  ppm  $\text{N}_2\text{H}_4$  exerting an inhibitory effect. Responses were dose dependent and suggested a two-phase mechanism, possibly involving a bactericidal and a bacteriostatic effect. An *Enterobacter cloacae* strain called D-31 exposed to 10 ppm hydrazine, 20 ppm MMH, or 50 ppm UDMH showed the ability to develop hydrazine-resistant strains that survived hydrazine, MMH, or UDMH exposure much better than did the average population from which they were derived [769, 770]. The increase in final growth yield when D-31 adapted to 20 ppm MMH or 50 ppm UDMH is not yet completely understood. It appears to be selective only, rather than both selective and inductive. As hydrazine is actually produced as an intermediate in some nitrogen-fixing bacteria, the breeding of hydrazine-resistant bacteria or bacteria that thrive on hydrazine should be no surprise. The following explanations were suggested: **(1)** a bactericidal effect that significantly reduced the inoculum concentration; **(2)** as the culture ultimately resumed a normal growth pattern, the degradation of the fuels to non-toxic substances, or to an ineffective concentration; and **(3)** an adaptive mechanism that enabled the organism to overcome the inhibitory effects.

The metabolism of soil bacteria exposed to MMH was further elucidated by isotope labeling [771]. In studies with  $^{14}\text{CH}_3\text{NHNH}_2$ , the majority of the  $^{14}\text{C}$  trapped in the metabolic products in the off-gassing from soil bacteria cultures was in the form of  $^{14}\text{CO}_2$ . At concentrations from 10 to 100  $\mu\text{g/g}$ , MMH did not have any toxic effects on soil respiration or on soil bacterial or fungal populations. Strains of *Achromobacter* sp. that had a high capacity for hydrazine digestion also had a good appetite for MMH. Soil respiration (total  $\text{CO}_2$  evolution) in hydrazine-treated soils was initially inhibited, and the extent of inhibition was proportional to the initial hydrazine concentration (0, 250, and 500  $\mu\text{g/g}$  tested) [772]. Bacterial populations were also reduced initially, but fungal populations were not affected. MMH at concentrations ranging from 10 to 500  $\mu\text{g/g}$  did not inhibit soil respiration. Biological degradation of MMH is slow in comparison with abiotic autoxidation.

### 11.13 MMH Leakage and Spill Incident History

Thermal blankets are made from Mylar with vapor-deposited gold coatings to maximize reflection, and keep the heat in the spacecraft to prevent the propellants from freezing while in orbit. Accidental MMH spills on thermal blankets caused severe damage and ignition in air [773, 774], a small quantity (“a cup full”) of MMH accidentally leaked on a thermal blanket made of gold-coated Mylar film in the STS right OMS pod (RV01) of Columbia (OV-102) and auto-ignited in air. Technicians had unknowingly opened a line that contained a small amount of liquid MMH. Apparently, instructions had been given to the technicians to remove the blankets and install spill protection, but this was not completed and it was not incorporated into the procedure. The gold foil of the MLI blanket acted as a catalyst while the blanket batting absorbed and con-

centrated the released MMH. The cause of the fire was a result of the ventilated surface area creating the correct conditions for combustion of MMH. The batting acted as an insulator effectively containing the heat of the reaction, transferring the heat back to the MMH, and allowing the temperature to increase to the boiling temperature of MMH ( $360.6\text{ K} = 87.5^\circ\text{C} = 189.5^\circ\text{F}$ ). Ignition of the blanket followed once the vapor fumes reached the auto-ignition temperature of MMH ( $194^\circ\text{C} = 382^\circ\text{F}$ ). A technician used nearby flame-retardant coveralls to extinguish the flames. It was later determined that MMH and gold are not compatible. MMH dissolved the polymer film and caused damage to the thermal blanket. In a laboratory experiment after the accident, the temperature rise when MMH was spilled onto a thermal blanket in atmospheres of different oxygen content was proportional to the oxygen concentration. No warming was observed under nitrogen. The cause of ignition appeared to be the oxidation of MMH catalyzed by finely divided gold. Thermal blankets are made from Mylar or Kapton with vapor-deposited gold coatings to maximize reflection, and to retain the heat in the spacecraft to prevent the propellant from freezing.

When examining the safety of lifting the MINUTEMAN-III upper stage out of missile silos during decommissioning, there was some concern about auto-ignition of MMH vapors from liquid MMH accidentally spilled into missile silos [775].

In a different environment, part of MMH leaked into the vacuum of outer space freezes and may cluster around the leak site. The frozen MMH will slowly melt and sublime [776].

#### 11.14 Olfactory Threshold of MMH

There is a wide discrepancy in reported olfactory threshold values for MMH and the other hydrazines. Several sources agree that one should not rely on the odor of hydrazines as a warning for imminent acute or subacute exposure because it may cause olfactory fatigue. Also, the olfactory threshold is far above the established safe levels. Table 49 summarizes the reported olfactory threshold of hydrazines in comparison with former and current ACGIH TLVs. Methylhydrazines have a more distinct fishy odor, although it would be difficult to differentiate them from methylamine or dimethylamine, common constituents of fish degradation products [777].

The odor threshold levels for UDMH and  $\text{NO}_2$  have been generally quoted at 6 to 14 parts per million (ppm by volume) for UDMH and 5 ppm for  $\text{NO}_2$ . Seven years of field experience by propellant loading personnel have indicated that the actual odor thresholds are considerably below these literature values [779]. As odor threshold levels are used by safety and operating personnel at Cape Kennedy as an indication of exposure, it was considered appropriate to evaluate this field experience. On the basis of these data and the results of some controlled studies, it was concluded that the actual odor thresholds are 0.5 ppm or less for  $\text{NO}_2$  and less than 0.3 ppm for UDMH.

**Table 49:** Olfactory threshold and exposure limits of methylhydrazine in comparison with other hydrazines.

| Type of data        | Hydrazine         | References     | MMH               | References      | UDMH              | References     |
|---------------------|-------------------|----------------|-------------------|-----------------|-------------------|----------------|
| Olfactory threshold | 69–83<br>3–4      | [778]<br>[672] | 1–3<br>—          | [672, 778]<br>— | <0.3<br>6–14      | [779]<br>[672] |
| ACGIH-TLV (1998)    | 0.01 (skin)<br>A3 | —              | 0.01 (skin)<br>A3 | —               | 0.01<br>(skin) A3 | —              |

ACGIH = American Conference of Governmental Industrial Hygienists, TLV = threshold limit value

In a human volunteer test with six recruits being exposed to 30, 50 or 90 ppm MMH in air, the 30-ppm exposure was described by most individuals as “easily noticeable moderate intensity” and “strong highly penetrating” [780]. 50 or 90 ppm produced only faint to moderate irritation.

### 11.15 Epidemiology of Workers Potentially Exposed to MMH

All three hydrazines: hydrazine itself, MMH, and UDMH were implicated in an epidemiological, retrospective study of causes of death among former workers at a large aerospace company in California [781, 782]. The purpose of the study was to estimate the effects of occupational exposures to selected chemicals on cancer mortality among nuclear and aerospace workers who were employed at Rocketdyne/Atomics International between 1950 and 1993. The results of this retrospective cohort study suggested that exposure to hydrazine or other chemicals associated with the same jobs at rocket-engine test stands increased the risk of dying from lung cancer and possibly other cancers [783, 784]. However, the hydrazine chemicals were just a few of several other chemicals and adverse conditions that these workers might have been exposed to while working in various jobs in the defense and aerospace industry. Any one of these other chemicals could have caused the observed effects and hydrazine(s) cannot be singled out as the sole cause. There were no records of actual working place concentrations of hazardous vapors in the air that could be correlated with the effects observed in victims several decades later.

A similar retrospective cohort mortality study of 8372 Rocketdyne workers employed 1948 to 1999 at the Santa Susana Field Laboratory came to a different conclusion [785]. Non-significant associations were seen between lung cancer and hydrazines, and stomach cancer and years worked as a test stand mechanic. No trends over exposure categories were statistically significant. It was concluded that work at the rocket engine test facility or as a test stand mechanic was not associated with a significant increase in cancer mortality overall or for any specific cancer.



## 11.16 Maximum Allowable Exposure Limits for MMH Vapors

### 11.16.1 Long-Term Exposure Limits for MMH

Permissible Exposure Limits (PELs) for MMH vapors in places of employment are established by the US Occupational Safety and Health Administration as published in 29 Code of Federal Regulations Part 1910.1000. Table Z1A of that standard lists several hundred controlled chemicals, including MMH. The very first list published by OSHA in response to the Occupational Safety and Health Act of 1970 simply adopted the existing ACGIH TLVs from the 1968 booklet. The TLV for hydrazine in those days was 1 ppm, and there were no ill effects reported in the working population during the decades while this limit was in effect. The PEL is an enforceable government-imposed limit, but the ACGIH TLV is a guideline recommended by a professional organization. Table Z1A includes 613 chemicals. Table Z2 includes 21 chemicals, but none of the hydrazines. For each chemical, it lists a transitional PEL, a TWA, STEL, and a ceiling limit C that may not be exceeded even if the exposure is compensated for by exposure to zero contamination for the rest of the work shift. In addition, several chemicals, including all hydrazines, have a “skin” notation. The TWA is the employee’s average airborne exposure in any 8-h work shift of a 40-h work week, which shall not be exceeded. A TWA is a calculation that combines exposure times and concentrations measured throughout the work shift into a single concentration, which is often compared with the TLV to see if the facility is in compliance or not. The short-term exposure limit (STEL) is the employee’s 15-min TWA exposure, which shall not be exceeded at any time during a work day unless another time limit is specified in a parenthetical notation below the limit. PELs from the most recent version of Table Z1A are summarized in Table 50. The most recent version of Table Z1 is available on the OSHA web site [786].

National Academy of Sciences/National Research Council (NAS/NRC) Subcommittee on Certain Interim Acute Exposure Guideline Level (AEGl) values were published in the Federal Register of 30 October 1997 (62 FR 58840-58851). These chemicals included: aniline, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, fluorine, hydrazine, and methylhydrazine.

**Table 50:** Time-weighted average and short-term exposure limits.

|           | Transitional 8-h PEL <sup>a</sup> |                   |      | TWA |                   |
|-----------|-----------------------------------|-------------------|------|-----|-------------------|
|           | ppm                               | mg/m <sup>3</sup> | Skin | ppm | mg/m <sup>3</sup> |
| Hydrazine | 1                                 | 1.3               | X    | 0.1 | 0.1               |
| MMH       | C 0.2                             | C 0.35            | X    | —   | —                 |
| UDMH      | 0.5                               | 1                 | X    | 0.5 | 1                 |

PEL = public emergency limit, TWA = time-weighted average

<sup>a</sup> Per 29CFR 1910.1000 Table Z1A Data, January 2017 Revision

The most widely accepted TLVs are those established by the ACGIH. The definition for TLV reads: “Threshold limit values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed to day after day 8 h/day, 40 h/week without adverse effect.” Three series of ACGIH publications are particularly useful in establishing and maintaining safe working conditions at places of employment (regardless if the workplace contains hydrazines or not): The annually updated pocket-sized TLV booklet, for instance, the 2017 issue [787], the little more detailed *Guide to Occupational Exposure Values* [788], and the most detailed loose-leaf issue of *Documentation of the Threshold Limit Values and Biological Exposure Indices*, now in five ring binders that as of 2017 was in its seventh edition, a five-volume set, are the standard reference sources in this field, updated periodically with supplements [789, 790]. The 7<sup>th</sup> Edition Documentation summarizes and evaluates the scientific data from which its TLV<sup>®</sup> or BEI<sup>®</sup> values are derived. Individual sections from this collection are downloadable for MMH [791] and UDMH [792].

The NIOSH REL for MMH is 0.04 ppm (0.08 mg/m<sup>3</sup>) for a 2-h maximum excursion and a skin, ceiling, and suspect carcinogen notation. The OSHA PEL is 0.2 ppm (0.35 mg/m<sup>3</sup>) with a skin notation. See also the MAK-Collection for Occupational Health and Safety [793].

### 11.16.2 Emergency Exposure Limits

Emergency exposure limits for hydrazines were established by the Committee on Toxicology, National Research Council, National Academy of Sciences (NAS) and defined as follows: “The Emergency Exposure Limit for short-term exposure to an airborne contaminant is a concentration which, when inhaled for a specified single brief period, rare in the lifetime of an individual, is believed not to result in a period of disability or interfere with the performance of his assigned task.”

The EEL was established for healthy young males under close medical supervision. Emergency exposure limit data are available only for a fraction of all those chemicals for which TLVs were established. Limited data are available for methylhydrazines. Emergency Exposure Limits for hydrazines as recommended by the NAS-NRC are listed in Table 51 along with the TLVs [794, 795]. As can be seen from this table, the ratio between EEL (10 min.) and TLV valid at that time varies from 200 to 30, depending on the fast-acting nature of the compound.

It is obvious that exposure limits undergo periodic updates and revisions, depending on additional toxicity data becoming available, and depending on the risk that is considered acceptable for military service personnel, government employees, industry workers, or the general public. This table will need to be updated periodically.

For a decade after MMH was first introduced into the inventory, EEL values for MMH had been based on minimal information consisting primarily of acute effects, but the acute effects of MMH are seen only at lethal or supralethal dose levels. In or-

**Table 51:** Olfactory threshold and exposure limits for methylhydrazine.

| Type of data        | MMH concentration, ppm by volume | References                   |
|---------------------|----------------------------------|------------------------------|
| Olfactory threshold | 1–3                              | [672, 778]                   |
| ACGIH-TLV (1981)    | C 0.2 (skin)                     | ACGIH                        |
| ACGIH-STEL (1981)   | —                                |                              |
| ACGIH-TLV (1998)    | 0.01 (skin) A3                   |                              |
| NRC-EEL, 10 min     | 90                               | [796]                        |
| EEL, 10 min         | 10                               | [797]                        |
| NRC-EEL, 30 min     | 30                               | [796]                        |
| EEL, 30 min         | 7                                | [797]                        |
| NRC-EEL, 60 min     | 15                               | [796]                        |
| EEL, 60 min         | 3                                | [797]                        |
| NRC-STPL, 10 min    | 9                                | Committee on Toxicology 1974 |
| NRC-STPL, 30 min    | 3                                |                              |
| NRC-STPL, 60 min    | 1.5                              |                              |
| NRC-PEL, 10 min     | 90                               |                              |
| NRC-PEL, 20 min     | 30                               |                              |
| NRC-PEL, 30 min     | 15                               |                              |

ACGIH = American Conference of Governmental Industrial Hygienists; TLV = threshold limit value, STEL = short-term exposure limit, EEL = emergency exposure limits, NRC = National Research Council, STPL = short-term public limit, PEL = public emergency limit.

der to fill this data gap, a series of experiments were conducted to define an atmospheric concentration of MMH that would produce no irreversible injury and no clinical evidence for CNS injury [798, 799]. Dogs, monkeys, rats, and mice were exposed to MMH vapors for periods of 15, 30, and 60 min. to concentration  $\times$  time (CT) doses of 900 ppm-min. The 900-ppm-minute CT dose of MMH, which was 25% of the LC concentration for the most susceptible animal species tested, included a safety margin below the lowest dose reported to produce marginal decrement of performance in trained cats and monkeys. In view of the negative finding in all species exposed to the 900 ppm-minute CT dose level of MMH, an upward revision of previous EEL values was recommended.

Human volunteer tests in exposure chambers in which only the heads of the human subjects were exposed to 90 ppm MMH for 10 min. under close medical supervision indicated that the 10-min. EEL set at this limit was properly selected [780]. Ninety ppm MMH was more irritating than ammonia at the 30-ppm level, but less irritating than ammonia at the 50-ppm level. Pre- and post-exposure clinical tests showed that the individuals did not suffer any permanent adverse effects as the result of this test.

### 11.16.3 Immediately Dangerous to Life and Health Limits

In addition to establishing an EEL, some agencies have begun to collect information and publish information on the Immediately Dangerous to Life and Health (IDLH) con-

**Table 52:** Immediately dangerous to life and health limits for hydrazines.

| Compound        | Original IDLH (SCP), ppm | Revised IDLH, ppm |
|-----------------|--------------------------|-------------------|
| Hydrazine       | 80                       | 50                |
| MMH             | 50                       | 20                |
| UDMH            | 50                       | 15                |
| For comparison: |                          |                   |
| Ethanol         | 15000                    | 3300              |
| Ammonia         | 500                      | —                 |

IDLH = Immediately Dangerous to Life and Health, SCP = standard completion program

Data source: [800, 801]

centrations of fast-acting acute poisons. The NIOSH/CDC home page has IDLH information posted for hydrazine and MMH. The recommended limits are summarized in Table 52 in comparison with several other commonly used hazardous chemicals

The National Advisory Committee for Acute Exposure Guideline Levels (NAC/AEGL Committee) for Hazardous Substances of the NRC used various criteria to develop AEGL limits for the general population (Table 53). AEGL-3 is the airborne concentration of a substance at or above which it is predicted that the general population, including “susceptible” but excluding “hypersusceptible” individuals, could experience life-threatening effects or death. This estimate of a threshold for

**Table 53:** Proposed Acute Exposure Guideline Level (AEGL) values for alkylhydrazines.

| Compound | Classification limit | 30-min.                            | 1-h                               | 4-h                                 | 8-h                                 | Endpoint                                                                            |
|----------|----------------------|------------------------------------|-----------------------------------|-------------------------------------|-------------------------------------|-------------------------------------------------------------------------------------|
| MMH      | AEGL-1               | N/A                                | N/A                               | N/A                                 | N/A                                 | N/A                                                                                 |
|          | AEGL-2               | 2 ppm<br>(3.8 mg/m <sup>3</sup> )  | 1 ppm<br>(1.9 mg/m <sup>3</sup> ) | 0.2 ppm<br>(0.4 mg/m <sup>3</sup> ) | 0.1 ppm<br>(0.2 mg/m <sup>3</sup> ) |                                                                                     |
|          | AEGL-3               | 6 ppm<br>(11.3 mg/m <sup>3</sup> ) | 3 ppm<br>(5.6 mg/m <sup>3</sup> ) | 0.7 ppm<br>(1.1 mg/m <sup>3</sup> ) | 0.3 ppm<br>(0.6 mg/m <sup>3</sup> ) | 1-h LC <sub>50</sub> of 82 ppm reduced 3-fold to estimate a lethality threshold     |
| UDMH     | AEGL-1               | N/A                                | N/A                               | N/A                                 | N/A                                 | N/A                                                                                 |
|          | AEGL-2               | 6 ppm<br>(14.7 mg/m <sup>3</sup> ) | 3 ppm<br>(7.4 mg/m <sup>3</sup> ) | 0.8 ppm<br>(2 mg/m <sup>3</sup> )   | 0.4 ppm<br>(1 mg/m <sup>3</sup> )   | Behavioral changes and muscle fasciculations in dogs exposed to 360 ppm for 15 min. |
|          | AEGL-3               | 22 ppm<br>(54 mg/m <sup>3</sup> )  | 11 ppm<br>(27 mg/m <sup>3</sup> ) | 3 ppm<br>(7.4 mg/m <sup>3</sup> )   | 1.5 ppm<br>(3.7 mg/m <sup>3</sup> ) | Lethality threshold of 327 ppm for 1 h estimated from 1-h LC <sub>50</sub> in dogs  |

Data source: National Research Council, National Advisory Committee, [804–806]

irreversible effects was justified because of the absence of exposure–response data related to irreversible or other serious, long-lasting effects and the dose–response relationship indicated by the insufficient data that were available on MMH or UDMH. For AEGL-3 of MMH, lethality data (1-h LC50 of 82 ppm) for squirrel monkeys [673, 674] was adjusted using a modifying factor of 3 to estimate a lethality threshold (27 ppm). The AEGL-3 for UDMH was derived from the 1-h LC50 (981 ppm) for UDMH in dogs [802, 803].

In a 2001 re-evaluation of AEGL data for MMH, the 10-min. AEGL-3 was set at 16 ppm and the 10-min. AEGL-2 value was derived from a 3-fold downward adjustment of the 10-min. AEGL-3 value and was set at 5.3 ppm [807]. In a 2001 re-evaluation of AEGL data for UDMH, the 10-min. AEGL-2 was set at 18 ppm and the 10-min. AEGL-3 level was set at 65 ppm [808]. For a historical perspective of rationales for establishing EELs, see also Smyth [797].

### 11.17 Long-Term Exposure in Closed Environments

The 8-h/day, 40-h/week exposure cycles for the working population are quite different from those of astronauts working and living in space stations or navy personnel in submarines. A different set of criteria has to be generated for these conditions. Spacecraft Maximum Acceptable Concentrations (SMACs) were established by NASA for potential contaminants in closed environments [809]. A draft table of derived SMACs was to be submitted to the National Research Council Committee on Toxicology for review before implementing the new limits on all future space flights [810]. For MMH, SMAC limits of 0.002 ppm were proposed for all exposure durations, because a different metabolic mechanism/target organ is involved than with hydrazine  $N_2H_4$ . Although one would intuitively expect the toxicities of hydrazine and MMH to be similar, NASA toxicologists arrived at quite disparate SMAC values.

## 12 Environmental Effects of MMH

In view of the growing concern of the public about the environmental effects of hazardous chemicals and in view of increasing legislative action on the control of chemical hazards, this book would be incomplete without a section on the environmental effects of MMH. This information can generally be derived from other paragraphs on toxicity and autoxidation, but it is worthwhile considering MMH chemistry from the standpoint of an environmentalist.

Fortunately, and in contradistinction to polychlorinated biphenyl, dioxin, or dichlorodiphenyltrichloroethane (DDT), there is little to be said about the endurance of hydrazine and hydrazine derivatives because they degrade so rapidly under the influence of air (oxygen), light, and soil bacteria. This is one of the most distinct

advantages of hydrazine-derived chemicals in numerous agricultural and industrial applications such as pesticides, boiler feedwater treatments, or anticorrosion additives. The biodegradability of hydrazine derivatives is one of the reasons why some hydrazine-based pesticides have been chosen to replace more persistent, chlorinated organics (DDT) that may accumulate in the food chain and/or are suspected endocrine disruptors.

### 12.1 Sources of Information on Environmental Toxicity of MMH

Under the sponsorship of the US Air Force Civil and Environmental Engineering Development Office (CEEDO, later AFESC-ESL) at Tyndall AFB, FL, a series of conferences on the environmental chemistry of hydrazine fuels were held in 1977, 1979, and 1987. The proceedings from these three meetings [811–813] constitute a valuable resource for studying the environmental effects of hydrazine fuels.

During the period 1970 through 1985, the US Air Force Medical Research Laboratory hosted a series of *Annual Conferences on Environmental Toxicology*. Some of these conferences contained several individual papers on hydrazines, although several conferences did not deal with hydrazines at all.

The US EPA has issued several *Health and Environmental Effects Profiles* for hydrazine and UDMH, but not for MMH. Howard's *Handbook of Environmental Degradation Rates* [814] gives data for a large number of chemicals, including MMH, UDMH, SDMH, hydrazine, and NDMA. The environmental chemistry of hydrazines continues to receive interest, as indicated by summary and review publications [815].

### 12.2 Aquatic Toxicity of MMH

The toxicity of hydrazine, MMH, and UDMH was measured in static LC<sub>50</sub> estimations using two freshwater fish, golden shiners, and channel catfish, and two invertebrates, amphipods and isopods. The data did not clearly indicate that the invertebrates were more sensitive than the fish to the chemicals and that the relative toxicities of the hydrazines were different. The aquatic toxicity LC<sub>50</sub> values of several hydrazines to several species are compiled in Table 54. The results in the first four rows of the table are the result of tests run in five different concentrations, ranging from 0.5 to 100 ppm. The catfish were most sensitive to hydrazine itself, less to MMH, and much less to UDMH.

#### 12.2.1 Aquatic Toxicity of MMH to Algae

In evaluating the toxicity of hydrazines to several species of unicellular green algae (*Selenastrum capricornutum* [S.], *Dunaliella tertiolecta* [D.], *Chlorella stigmatophora* [C.]), and trying to establish a dose–response relationship, hydrazine was

**Table 54:** Aquatic toxicity of hydrazines toward fish and invertebrates.

| Species                       | N <sub>2</sub> H <sub>4</sub> | MMH  | UDMH    | References |
|-------------------------------|-------------------------------|------|---------|------------|
| <i>LC50 (ppm)</i>             |                               |      |         |            |
| Amphipods                     | 0.04                          | 1.2  | 4.7     | [816]      |
| Isopods                       | 1.3                           | 0.8  | 12.4    | [816]      |
| Channel catfish               | 1.0                           | 3.5  | 11.3    | [816]      |
| Golden shiner                 | 1.1                           | 2.3  | 34      | [816]      |
| <i>LC50 (mg/L)</i>            |                               |      |         |            |
| Fathead minnows 96-h bioassay | 4.5                           | 1.22 | 0.35    | [318]      |
| Daphnia 48 h                  | 0.1 to 1.0                    | <5   | 5 to 10 | [318]      |

found to be the most toxic, MMH less, and UDMH least toxic. The objective of the studies was to determine the no-effect safe concentration (SC) and a median effect concentration EC<sub>50</sub> concentration, which causes a 50% reduction of growth of the algae. Three types of freshwater were tested: oligotrophic (10% Standard Algal Assay Medium = SAAM nutrients), intermediate (33% SAAM), and eutrophic (100% SAAM). Slightly higher concentrations were tolerated under eutrophic as opposed to under oligotrophic conditions. MMH was less toxic, with an SC of 0.2 µL/L tolerated under spill conditions; UDMH was even less toxic, with an SC between 1 and 3 µL/L. Hydrazine was approximately 200 times more toxic to algae than MMH or UDMH. The toxicity of the compounds studied was directly correlated with compound stability during the static (no replenishment) bioassays. Hydrazine, the most stable in the various algal growth media, was the most toxic, whereas UDMH, the least stable, was also the least toxic (Table 55). Aerozine-50 aquatic toxicity was identical to that of hydrazine, its most toxic constituent [817].

**Table 55:** Toxicity of hydrazines to algae in freshwater and seawater.

| Water type              | Test organism           | Initial concentration of compound, µL/L<br>(Based on sixth day EC <sub>50</sub> counts) |                  |     |                  |      |                  |
|-------------------------|-------------------------|-----------------------------------------------------------------------------------------|------------------|-----|------------------|------|------------------|
|                         |                         | Hydrazine                                                                               |                  | MMH |                  | UDMH |                  |
|                         |                         | SC                                                                                      | EC <sub>50</sub> | SC  | EC <sub>50</sub> | SC   | EC <sub>50</sub> |
| Oligotrophic freshwater | <i>S. capricornutum</i> | 0.001                                                                                   | 0.03             | 0.2 | 0.5              | 2.0  | 5.0              |
| Oligotrophic seawater   | <i>D. tertiolecta</i>   | 0.0005                                                                                  | 0.0008           | 0.8 | 1.1              | 0.1  | 2.3              |

EC = effect concentration, SC = safe concentration

Data source: [818]

Algae toxicity testing with hydrazine, MMH, and UDMH was conducted in seawater with salinities of 16, 24, and 35 ppt [819]. There was little difference between the SC and EC50 values obtained at various brackish and seawater salinity levels. For *aufwuchs* benthic biomass, MMH was much more toxic than hydrazine, because the no-effect level was between 0.01 and 0.15 mg MMH/L. With UDMH, there was a significant reduction in the photosynthesis index for *aufwuchs* in the tanks containing initial UDMH concentrations of 10 and 93 mg/L.

### 12.2.2 Aquatic Toxicity of MMH to Bacteria in Water

This section is closely related to the toxicity of MMH toward bacteria in soil, which is discussed in more detail in Section 12.5. Much of the work on the toxicity of MMH toward water-borne bacteria stems from the concern for the continued health and performance of active sludge waste treatment systems in the event that a MMH spill should be washed into the sewer.

The toxicity of hydrazine, MMH, and UDMH to four enriched bacterial cultures: *Nitrobacter*, *Nitrosomonas Nitrobacter*, anaerobic bacteria, and denitrifying bacteria was measured in incubators [761–763, 820]. In addition, the metabolic digestion of hydrazine by *Nitrosomonas Nitrobacter* was examined. The toxicity studies utilized batch bioassay methods with response measured in terms of substrate metabolism rates as measured by gas evolution. Batch tests were run for 6 days with hydrazine, 10 days with MMH, and 14 days with UDMH. The results showed that hydrazine produced a 50% reduction in metabolism rate for *Nitrobacter*, *Nitrosomonas Nitrobacter*, anaerobic bacteria, and denitrifying bacteria at concentrations of about 15, 165, 100, and 100 mg/L respectively; MMH at 15, <1, 75, and 10 mg/L respectively; and UDMH at 1800, 35, 2300, and 12500 mg/L respectively. With anaerobic bacteria, recovery was observed for the three lowest hydrazine doses at 2.7, 13.3, and 133 mg/L. When recovery occurred between days 2 and 5, the accumulated feed was rapidly digested and the daily gas production would temporarily exceed that of the controls. Very high doses of UDMH were required to produce significant toxicity for denitrifying bacteria. Hydrazine was the least toxic of the three fuels to *Nitrosomonas*. *Nitrosomonas* was largely unaffected by hydrazine doses that proved toxic to other bacteria. The metabolism study used <sup>15</sup>N-labeled hydrazine sulfate followed by mass spectrographic analysis of the captured gas. *Nitrosomonas* were found to metabolize some hydrazine to nitrogen gas on a short-term basis, but could not metabolize MMH or UDMH. It was concluded that spills of any of these three fuels could be expected to seriously disrupt the natural bacterial balance in the aquatic environment. Use of biological waste water treatment for detoxification of these three fuels was not recommended.



### 12.2.3 Aquatic Toxicity of MMH to Invertebrates, Amphibians, and Crustaceans

Some data on toxicity of MMH to invertebrates, amphibians, and crustaceans were already included in Table 54. A bioassay using two freshwater invertebrates, isopods (*Asilidae*) as well as amphipods (*Hyaella azteca*), and two species of fish (*Ictalurus punctatus* Rafinesque, channel catfish, and *Notemigonus crysoleucas*, golden shiner) and exposing them to hydrazine, MMH, or UDMH showed that hydrazine was the most toxic of the three compounds tested [816]. Hydrazine was more toxic than MMH or UDMH to amphipods, and there was no difference between MMH or UDMH. A study was conducted to determine the LC50 of hydrazine to bay mussels (*Mytilus edulis*) and the mud flat crab (*Hemigrapsus oregonensis*) [819]. For crabs and mussels, it was not possible to calculate an LC50 for MMH, because there was 100% mortality at 0.15 mg/L and no mortality at 0.012 mg/L [821]. Aquatic bioassay studies with fresh or partially ozonized MMH or UDMH with *Daphnia* showed an EC50 of 0.1 to <10 mg/L [320, 321].

### 12.2.4 Aquatic Toxicity of MMH to Fish

The acute toxicity of hydrazine, MMH, UDMH, and Ae-50 to the common guppy (*Lebistes reticulatus*) was tested in three to four static, unaerated bioassays, each using hard and soft water [822, 823]. The LC50 after 96 h of exposure differed significantly depending on the hardness of the water used. For example, the hard-water/soft-water LC50 ratio data were as follows: MMH, 3.26/2.58; UDMH, 10.1/26.5; and Ae-50, 2.25/1.17 mg/L. Hydrazine was the most toxic compound and UDMH the least toxic to common guppies. Hydrazine was significantly more toxic in soft water than in hard water, whereas UDMH was the opposite. The results of bioassays in which survival times of fish pre-exposed to these compounds were compared with those previously unexposed, along with other observations, indicate that the toxic effects of the hydrazines are cumulative.

The 336-h LC50 of MMH for stickleback was 0.01 mg MMH/L, as opposed to 1.1 mg hydrazine/L for hydrazine N<sub>2</sub>H<sub>4</sub> [821, 824]. Because MMH concentrations decreased to 65% within 6 h, in one series the MMH concentration was maintained by renewing the solutions daily. No fish survived the first day of exposure in a jar containing an initial MMH concentration of 3.2 mg/L [819]. In another jar containing an initial MMH level of 1 mg/L, there were no survivors after 49 h. The MMH LC50 for duplicate samples were 1.4 and 1.9 mg/L at 24 h, 0.6 and 0.46 mg/L at 48 h, and 0.32 and 0.4 mg/L at 96 h. In one test, all fish died within 96 h in tanks that contained initial UDMH concentrations of 10 and 19.3 mg/L. There was no detectable excess of free UDMH in the tank within 7 h of its introduction. It was also noted that in a static system, simulating a spill into a lake or pond, UDMH stratified on the surface owing to its lower density. In a real spill, the organisms staying near the surface would be more seriously affected than bottom dwellers.

Aquatic bioassay studies with fathead minnows showed LC50 values of 4.5, 1.2, and 0.35 mg/L for hydrazine, MMH, and UDMH respectively [321, 554]. As hydrazine and alkylhydrazines react with dissolved oxygen, LC50 or EC50 could be lower in practice.

### 12.3 Environmental Fate of MMH in Air

The rate of evaporation of MMH and the other two propellant hydrazines was measured in Petri dishes in the laboratory under carefully controlled climatic conditions [825, 826]. Table 56 summarizes some of the evaporation rate and half-life data of the three most commonly used hydrazines. As one can see, there is a gradual increase in the rate of evaporation as well as half-life time from hydrazine to MMH and from MMH to UDMH. The investigators did not realize that hydrazine mass loss by evaporation in ambient air is partially counteracted by carbon dioxide absorption, which causes a mass gain.

**Table 56:** Rate of evaporation and environmental decay of hydrazine fuels.

| Compound  | Evaporation rate <sup>a</sup> ,<br>mg cm <sup>-2</sup> min <sup>-1</sup> | Half-life time |             |
|-----------|--------------------------------------------------------------------------|----------------|-------------|
|           |                                                                          | Air, h         | Water, days |
| Hydrazine | 0.49                                                                     | 1.10           | 7           |
| MMH       | 1.7                                                                      | 2.7            | 10          |
| UDMH      | 13                                                                       | 100            | 10          |

<sup>a</sup> In stagnant air at 291–294 K, based on data from a 177-cm<sup>2</sup> dish

Data source: [825, 826]

Reactions of MMH with selected species of interest that are found in the environment, mostly in the high atmosphere, have been investigated [827]. Included were aqueous phase reactions that can occur in atmospheric aerosols, rain drops, groundwater, or soils in contact with groundwater, as well as selected gas phase reactions. Reactants included oxygen and hydrogen peroxide (both reactants in the presence and absence of catalysts), ozone, nitrous acid, sulfur dioxide, and acetone (as a model for environmental ketones and aldehydes). Rate constants for the reactions have been determined, or upper limits set. By far the fastest reactions measured were those involving the hydrazines and ozone with (second-order) rate constants up to  $2.4 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ .

#### 12.3.1 MMH Atmospheric Decay Studies in Plastic Foil Lined Chambers

A study was designed to experimentally evaluate the atmospheric fate of UDMH, MMH, and unsubstituted hydrazine N<sub>2</sub>H<sub>4</sub> in laboratory chambers under controlled

conditions [828]. Because of the need for detailed information on the gas-phase chemistry of propellant hydrazines, the following specific supporting studies were undertaken: flash photolysis-resonance fluorescence measurements of the absolute rate constants for the reaction of hydrazines with hydroxyl (OH) radicals; a study of the rates and products of the dark reactions of ozone with hydrazine, MMH, and UDMH; and an investigation of the  $\text{NO}_x$ -photooxidation of these same hydrazines under simulated atmospheric conditions. The latter two studies were conducted using a 30000-L outdoor irradiation chamber equipped with a 10-m base path optical system coupled to an FTIR spectrometer. The results of the studies showed that, upon release into the atmosphere, all three of the hydrazines investigated could be rapidly consumed by reaction either with ozone or with OH radicals present in the atmosphere, depending on the nature of the atmosphere into which the emissions occur. With respect to reaction with OH, the tropospheric half-life for hydrazine is expected to range from 1 h in polluted urban atmospheres to up to 3 to 6 h in unpolluted atmospheres, with substituted hydrazines being consumed at about the same rate. With respect to reaction with ozone, the half-life for unsubstituted hydrazine would range from less than 10 min. during ozone pollution episodes to less than 2 h in the natural troposphere, with the half-lives for MMH and UDMH being at least a factor of 10 shorter. Therefore, under most conditions, reaction with ozone will be the most efficient mode of degradation of hydrazines released into the high atmosphere. A major release of MMH in an area of high ozone pollution could subject nearby downwind regions to possibly significant levels of methyl hydroperoxide, methyldiazene, or diazomethane. A similar scenario for UDMH would form nitrosamines, which in turn react in sunlight to form the relatively more stable nitramines.

Methylhydrazine and atmospheric ozone formed  $\text{CH}_3\text{OOH}$ ,  $\text{H}_3\text{CN}=\text{NH}$ , formaldehyde,  $\text{H}_2\text{CN}_2$ , and  $\text{H}_2\text{O}_2$  with lower yields of  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$ .  $\text{H}_3\text{CN}=\text{NH}$  already present in a reacted mixture rapidly disappeared after more ozone was added. Formaldehyde was observed only in mixtures with an excess of ozone, not in mixtures with an excess of MMH [829].

A 4-year research program at NASA WSTF resulted in a very detailed and very thorough report of reaction rates of hydrazines in air under various conditions [830]. The objective of the study was to provide further insight into the mechanisms by which propellant hydrazines decompose in the atmosphere. It was difficult to eliminate interference owing to wall permeation from the plastic foil-lined test chambers. Four different methods were used: a static environmental chamber [302], a packed microreactor, an atmospheric pressure laminar flow reactor [304], and FTIR adsorption spectra of surface-adsorbed species. In one series of tests, using a 6515-L Teflon film-lined chamber made of 0.013-cm (5-mil) FEP foil with a surface : volume ratio of  $3.39 \text{ m}^{-1}$ , stirred with a PTFE-coated fan, the measurements were troubled by permeation. The chamber was surrounded by another polyethylene film-walled chamber at a distance of 5 cm, which could be purged with nitrogen to prevent diffusion of ambient air into the test cham-

ber. Permeation was the main mechanism for hydrazine(s) disappearance, as the rate of disappearance in nitrogen was the same as that in air. The half-life times of hydrazine, MMH, and UDMH in the Teflon chamber were 40, 19, and 60 h respectively. The presence of water (14600 ppm) or carbon dioxide (300 or 1000 ppm) accelerated the disappearance, but the two effects were not cumulative. Panels of various materials under study were inserted into the chamber to study surface-catalyzed effects. Very rapid oxidation of hydrazine occurred on corroded aluminum panels. MMH was less reactive on the corroded aluminum surfaces. The rate of MMH disappearance increased with the square of the surface area of added aluminum panels. The  $\text{Al}/\text{Al}_2\text{O}_3$  catalyzed oxidation of MMH yielded methyldiazene ( $\text{HN}=\text{NCH}_3$ ) as an intermediate and traces of methanol. The relative reactivities of hydrazine, MMH, and UDMH were 130:7.3:1 respectively.

In a packed tubular microreactor at a slightly elevated temperature in air, hydrazine was oxidized too rapidly to be measured on all metal powders and building material samples (sand, concrete, cinder blocks) [303]. The rate of MMH oxidation was slow enough to be measured, and the activity of the materials relative to CRES-304 = 1.0 could be ranked as follows: Fe 210 >  $\text{Al}_2\text{O}_3$  120 > Zn 41 > CRES-316 23 > Ti 10 > Cr 7 > Al 2 > CRES-304 1 > Ni ~ 1. Products of MMH oxidation were methanol, methyldiazene, methane, and some ammonia. UDMH proved to be much less reactive than either hydrazine or MMH. Only trace amounts of reaction products were noted, which were not identified. Trimethylhydrazine or tetramethylhydrazine were essentially unreactive under these conditions.

The laminar flow reactor consisted of a rectangular chamber made from polymethylmethacrylate plastic with four 40 × 60-mm KCl windows for multiple passage of diagnostic IR beams at different locations downstream from the injection and mixing zone [304]. Hydrazine or MMH vapor was mixed with air or ozonated air, flowed through the test section, and exhausted into a fume hood. This dynamic flow setup allowed chemical kinetic measurements at atmospheric pressure free from wall effects. The following IR bands (with absorption coefficients given in parentheses) were used to analyze for hydrazine:  $958\text{ cm}^{-1}$  ( $5.87\text{ atm}^{-1}\text{ cm}^{-1}$ ), MMH:  $888\text{ cm}^{-1}$  ( $4.69\text{ atm}^{-1}\text{ cm}^{-1}$ ), and ozone:  $1058\text{ cm}^{-1}$  ( $7.31\text{ atm}^{-1}\text{ cm}^{-1}$ ). Diffuse FTIR of hydrazines adsorbed on deuterated silica powder showed that the surface adsorption is primarily physical and that adsorbed hydrazines do not undergo molecular changes when adsorbed. In conclusion, although oxygen is the major reactive constituent of air, its homogeneous rate of reaction with hydrazines is so slow that air contaminants such as ozone or  $\text{NO}_x$  and airborne particulates have an overwhelming effect on the overall rate of hydrazine(s) disappearance. Using the rate constants derived from the laminar flow reactor, it was predicted that the half-life time of hydrazine or MMH in a moderately contaminated day-time atmosphere is less than 2 h owing to reaction with ozone and hydroxyl radicals. The presence of hydrazine may actually increase the  $\cdot\text{OH}$  and  $\cdot\text{OOH}$  free radical concentration in air.

### 12.3.2 Studies in Lined Steel Chambers

A special Teflon-lined steel chamber was built by the AFESC-ESL laboratory at Tyndall AFB in Florida and used for detailed studies of hydrazine(s) decay kinetics in air. The steel enclosure prevented ambient atmospheric oxygen from diffusing through the plastic foil into the chamber. Atmospheric decay studies in the laboratory have shown that hydrazine oxidation in air is highly dependent on the available surface area and the composition of the surface material. Because the decay rate is greatly influenced by heterogeneous reactions, one has to be careful when extrapolating from laboratory data to real ambient conditions with unconfined air spaces.

After variable results with polymer foil as a chamber wall material, a Teflon-coated, stainless steel sphere measuring 1 m in diameter was constructed at ESL as a tool for conducting studies of the atmospheric chemistry of hydrazines [831–833]. A spherical chamber shape was chosen because it had the most favorable surface:volume ratio and would help to minimize unwanted surface effects. The spherical chamber has a 15% advantage over cylindrical designs and a 24% advantage over traditional cubical smog chambers. Three cylindrical adapters measuring 25 cm in diameter were welded to the chamber, two for optics and one for sample handling. Smaller ports served for optical alignment, vacuum connections, stirring fan mount, and drain. The temperature could be controlled from 278 to 323 K (5 to 50 °C = 41 to 122 °F). The chamber could be evacuated to 0.0007 Pa (0.000005 Torr). Gas samples were introduced from an external manifold. Solid samples of various kinds could be placed into the interior of the chamber through a 30-cm (12-in) sampling port to determine their effects on gases under study. The chamber was equipped with an *in situ*, multi-pass optical system that allowed variable IR path lengths of up to 106 m (348 ft) for identification of reactants, intermediates, and products of the reactions. Adding a light source to measure hydrazine photochemical decay reactions typical for daytime releases into the atmosphere was considered. Addition of a residual gas analyzer would be useful to quantify oxygen and nitrogen concentrations as reactants and reaction products and verify low leakage rates at near-vacuum chamber pressures. Similar tests were conducted with hydrazine and UDMH vapors.

### 12.4 Environmental Fate of MMH in Water

In the absence of bacteria, in sterile water, but exposed to air and sunlight, MMH still degrades quickly. The rate of MMH degradation is dependent on water pH, temperature, hardness, other dissolved mineral content, and sunlight. Hard and soft water samples with and without the addition of MMH were examined over a 96-h period for changes in alkalinity (with two different pH indicators), pH, specific conductance, EDTA hardness, and dissolved oxygen [834]. The dissolved oxygen content changed more rapidly in hard water than in soft water.

## 12.5 Environmental Fate of MMH in Soil

Similar to problems with experiments on persistence and biological effects of spilled hydrazines in surface waters, it is very difficult to conduct soil toxicity and degradation experiments under carefully controlled conditions, because so many variables are involved [835]. Hydrazines may reversibly adsorb on soil inorganic or organic matter, become irreversibly oxidized by soil minerals, or simply decompose catalytically to nitrogen and ammonia. *A Handbook of Environmental Degradation Rates* [814] gives the following estimates summarized in Table 57 for half-life times of hydrazines in non-sterile soils. These numbers are “best estimates, based on scientific judgment, based upon estimated unacclimated aqueous aerobic biodegradation half-life” [814].

**Table 57:** Estimated half-life time of hydrazines in soil.

| Compound name | High estimate, days | Low estimate, days |
|---------------|---------------------|--------------------|
| Hydrazine     | 7                   | 1                  |
| MMH           | 24                  | 13                 |
| UDMH          | 22                  | 8                  |
| SDMH          | 28                  | 7                  |
| NDMA          | 180                 | 21                 |

Data source: [814]

It is difficult to determine adsorption isotherms of MMH and other hydrazines in soils because most of the hydrazines decompose before a complete adsorption/desorption cycle can be completed. The interaction of soils and hydrazines is very complex and depends on the type of soil (sand, clay, humus) and the oxidants present. Oxidants would be air, adsorbed air pollutants (e.g., ozone, peroxides), highly oxidized minerals, or active oxidizers produced as metabolic products by bacteria (e.g., nitrogen dioxide). The current section deals only with the abiotic degradation of hydrazines in soil. The degradation process is potentially greatly accelerated by certain types of soil bacteria. Soil percolation/adsorption tests were conducted with MMH and UDMH (0.1% solutions) through/on four different types of soils (sand, clay, organic, and one typical for Vandenberg AFB, VAFB) [311, 312]. The soil samples were mostly sandy soils with little cation exchange capacity. All soils were dried at 353 K for 24 h, which should have killed most of the soil bacteria. In soil percolation tests, fuel solutions were applied to a 200-g soil sample in a column and leached with 500 mL of water. Yellow autoxidation products interfered with subsequent colorimetric determinations. GC-MS was a more reliable method, even in the presence of autoxidation products. Table 58 summarizes the adsorption/extraction results obtained after soaking 3-g soil samples for 20 min with 30 mL of 0.002 vol.-% solutions.

**Table 58:** Adsorption/extraction results of hydrazine fuels in soil.

| Propellant | Soil    | Adsorbed, % | Extracted w. 0.1 N HCl, % | Non-recovered, % |
|------------|---------|-------------|---------------------------|------------------|
| Hydrazine  | Sand    | 1 ± 1       | 2 ± ?                     | —                |
| Hydrazine  | VAFB    | 58          | 44                        | 14               |
| Hydrazine  | Organic | 53          | 25                        | 28               |
| Hydrazine  | Clay    | 77          | 59                        | 18               |
| MMH        | Sand    | 0 ± ?       | 3 ± ?                     | —                |
| MMH        | VAFB    | 51          | 46                        | 5                |
| MMH        | Organic | 46          | 26                        | 20               |
| MMH        | Clay    | 73          | 64                        | 8                |
| UDMH       | Sand    | 0 ± ?       | 5 ± ?                     | —                |
| UDMH       | VAFB    | 31          | 20                        | 11               |
| UDMH       | Organic | 26          | 15                        | 11               |
| UDMH       | Clay    | 80          | 30                        | 50               |

Data source: [312]

No fuel interaction was observed with clean sand (as in the percolation studies), but strong effects were observed in all natural soil samples. The strongest interaction was with clay-type soils. Hydrazine and MMH were more reactive than UDMH in all soils.

Hydrazines can be adsorbed and desorbed by soil colloids in essentially unchanged form or can be irreversibly chemisorbed [836–838]. The interactions of MMH with soil constituents and with soils were examined using (1) batch/slurry techniques, (2) continuous-flow stirred reactor techniques, and (3) column extraction techniques. In addition, IR, XRD, and microcalorimetry were used to study hydrazine–soil interactions. Four different types of clays were used: montmorillonite, kaolinite, illite, and bentonite. Humic acid and fulvic acid were extracted and isolated from humus-rich soils. In the presence of clay suspensions, part of the original MMH added to the suspension was absorbed by the homoionically exchanged montmorillonite and another part was oxidized.

The environmental fate and distribution of MMH spills in the soil may depend on adsorption/desorption equilibria between MMH adsorbed in clay and MMH vapor [839]. Isotherms were obtained at 298, 308, and 318 K for the sorption and desorption of MMH by sodium-exchanged montmorillonite and kaolinite clays, and by an iron(III)-exchanged kaolinite preparation. Isotherm data were analyzed in conjunction with data from XRD diffraction and IR spectroscopy in order to investigate the sorbate–sorber interaction mechanisms. Similar isotherm analyses were carried out for the sorption of water vapor, which could be expected to compete with MMH for sorption sites. Sorption by Na<sup>+</sup>–kaolinite was essentially reversible but some hysteresis was evident in desorption from the iron clay.

Methylhydrazine and hydrazine autoxidation were studied in the presence of colloidal hematite, a common soil mineral [840]. The reaction was followed colorimetri-

cally and analyzed using sorption isotherms. Although one should think that hematite should be a good catalyst, instead it was found that autoxidation in the presence of the hematite was attenuated when compared with autoxidation in water only. This indicated that the interaction between the hydrazines and the hematite in some way protects the hydrazines by complexation, hydrogen bonding between the hydrazines and the oxygens, or the first hydration spheres, on the hematite. Environmental implications of this finding include enhanced transport of the compounds through the groundwater with the colloidal hematite as a vector, and increased residence times in the environment. The specific interaction between the hydrazines and hematite was investigated using FTIR-ATR (attenuated total reflection), enabling direct spectral analysis of the interaction and its changes with time and dependence on pH. These analyses indicated that the interaction is probably due to electrostatic interactions, including hydrogen bonding between the hydrazines and the oxygens, or the first hydration spheres, on hematite. It was found that the interaction changed with time, and that the interaction was stable to heating, and appeared to have a long lifetime, indicating a strong final interaction. Similar results were found when the FTIR-ATR was used to analyze the interaction of the hydrazines with common clay minerals. The toxicity of hydrazines on soil microflora indicated that in the absence of hematite or clay minerals, the autoxidation of the hydrazines is rapid enough that the microbes were only exposed to harmless end products. No evidence for the stimulation of microbial growth in the presence of the hydrazines was found.

## 12.6 Biodegradation of MMH

Bioremediation of MMH spills in soil may be possible only after sufficient dilution with water and only in the presence of the right type of soil bacteria and nutrients for their propagation. The same applies to spills of hydrazine or hydrazine hydrate (H-70).

Adaptive mechanisms allow some bacteria to thrive on hydrazines instead of being killed by them. Three possible adaptive mechanisms by which soil bacteria may survive inhibitory or exterminating environments are:

- (1) environmental selection of pre-existing resistant variants in a population;
- (2) mutation to resistant variants; and
- (3) induction of specific enzyme systems that counteract the effects of the toxic ingredient.

To determine if an inductive, selective, or mutation mechanism is involved in the resistance of bacteria to hydrazine fuel toxicity, the effects of  $N_2H_4$ , MMH, and UDMH on the growth kinetics of *Enterobacter cloacae* cultures that had been previously exposed to low levels of each of the fuels were studied *in vitro* [769, 770]. One concentration was selected for each fuel that was shown to increase the lag time significantly but would eventually permit the culture to grow to maximum yield. The concentrations selected



were 10 ppm for  $N_2H_4$ , 20 ppm for MMH, and 50 ppm for UDMH (ppm measured by volume, not by mass).

The toxicity of hydrazine, MMH, and UDMH were determined for mixed and uni-cultures of nitrifying bacteria, denitrifying bacteria, and anaerobic methanogenic bacteria [761–763]. MMH was more toxic than hydrazine, which was more toxic than UDMH. The toxicity level numbers were low enough to preclude biological waste treatment of these compounds.

Despite the fact that axenic bacterial cultures are inhibited by all three propellant hydrazines, it was reported that soil respiration, and total bacterial and fungal populations in soil, were not inhibited by hydrazine at concentrations of 100  $\mu\text{g/g}$  and lower. Even at 500  $\mu\text{g/g}$ , only total bacterial populations in soil were inhibited by the presence of hydrazine. Hydrazine rapidly disappeared in soil, so next to investigate was the effect of MMH on soil microbial activity and on degradation of MMH in soil [841]. Two hundred grams of soil were placed in 500-mL wide-mouth glass bottles with screw caps, and 16 mL of deionized water were added. MMH was applied to the soil samples to give concentrations of 0, 10, 50, 100, 200, and 500  $\mu\text{g/g}$ . After mixing, glass beakers containing 20 mL of 0.2–0.5-N KOH were placed in the bottles for trapping  $CO_2$  evolved from metabolic activity of the bacteria. Further study was initiated to test the capacity of two hydrazine-degrading bacteria, *Achromobacter* sp. and *Pseudomonas* sp., to degrade MMH in the soil [842]. A strain of *Achromobacter* sp. and a strain of *Pseudomonas* sp. that had the capacity to degrade hydrazine in the presence of a second nitrogen source such as ammonium nitrate were used for this study. The bacteria were maintained in a basal mineral medium containing 10  $\mu\text{g/g}$  of MMH or 100  $\mu\text{g/g}$  of hydrazine in culture fluids and cell suspensions. MMH in soil samples was extracted with cold and deoxygenated 0.1M HCl and then determined using a colorimetric method. In addition,  $^{14}\text{C}$  radioisotope-labeled MMH was used for determination of the disappearance of MMH and the formation of metabolites and radioactivity in culture fluids and metabolites was determined by scintillation counting.

A lab study of the batch culture degradation of rocket test site wastewater containing mixtures of MMH, citric acid, and their reaction product showed that the organic contaminants were degraded by *Achromobacter* sp., *Rhodococcus* B30 and *Rhodococcus* J10 [843, 844]. Although the *Achromobacter* sp. showed a preference for the degradation of the citric acid, the *Rhodococcus* sp. were most effective in digesting MMH and MMH citrate. The aerobic biodegradation of wastewater that contained mixtures of highly concentrated MMH/hydrazine/citric acid and their reaction product was studied on a laboratory-scale fixed film trickle-bed reactor [845]. The degrading organisms, *Achromobacter* sp., *Rhodococcus* B30, and *Rhodococcus* J10, were immobilized on coarse sand grains used as support media in the columns. Under continuous recirculating flow conditions, *Rhodococcus* sp. degraded the MMH content of the wastewater from a concentration of 10 to 2.5 mg/mL within 12 days and the hydrazine from ~0.8 to 0.1 mg/mL in 7 days. The *Achromobacter* sp. was equally efficient in degrading the organics present in the wastewater, reducing the concentration of MMH from 10 to

~5 mg/mL within 12 days and that of hydrazine from ~0.8 to 0.2 mg/mL in 7 days. The pseudo first-order rate constants of 0.137 and 0.232 day<sup>-1</sup> were obtained for the removal of MMH and hydrazine respectively in wastewater in the reactor column. In the batch cultures, rate constants for the degradation were 0.046 and 0.079 day<sup>-1</sup> for MMH and hydrazine, respectively. These results demonstrated that the continuous flow bioreactor achieved greater degradation efficiencies than those obtained when the wastewater was incubated with the microbes in growth-limited batch experiments. It was noted that wastewater containing hydrazine was more amenable to microbial degradation than wastewater predominantly containing MMH, in spite of the longer initial lag period observed for hydrazine-containing wastewater. The results of the laboratory scale study were intended to be used in the design and operation of an industrial-size immobilized biofilm reactor for the treatment of MMH- and hydrazine-contaminated wastewater from rocket test sites.

### 13 Fuel Mixtures with MMH

Methylhydrazine has been mixed with other fuels to achieve desirable physical properties (low freezing points), better performance, or improved hypergolic ignition as a fuel. In addition to fuel mixtures that were intended to be used with a hypergolic oxidizer (NTO, inhibited red fuming nitric acid [IRFNA], ClF<sub>3</sub> or ClF<sub>5</sub>), MMH has been the main constituent of monopropellant mixtures such as MHF-5 and MHF-1, where improvement was achieved by adding an MMH-soluble oxidizer such as HN. The compositions of various MMH fuel mixtures are listed in Table 59.

**Table 59:** Composition of mixed hydrazine fuel (MHF) blends containing methylhydrazine.

| Designation         | Composition, mass-%                                                                         |                               |      |                  |
|---------------------|---------------------------------------------------------------------------------------------|-------------------------------|------|------------------|
|                     | MMH                                                                                         | N <sub>2</sub> H <sub>4</sub> | HN   | H <sub>2</sub> O |
| MHF-1               | 45.3                                                                                        | 23.3                          | 31.4 | —                |
| MHF-2               | see chapter “Dimethylhydrazines” on UDMH fuel blends in <i>Encyclopedia of Liquid Fuels</i> |                               |      |                  |
| MHF-3               | 86                                                                                          | 14                            | —    | —                |
| MHF-4               | 50.5                                                                                        | 32.5                          | 17.0 | —                |
| MHF-5               | 55                                                                                          | 26                            | 19   | ≤2               |
| MHF-5A              | 68                                                                                          | 13                            | 19   | —                |
| MHF-5B              | 58.3                                                                                        | 21.6                          | 19.0 | 1.1              |
| MHF-5B <sup>a</sup> | 58.0                                                                                        | 23.0                          | 19.0 | —                |
| MHF-6               | 73.0                                                                                        | 16.5                          | —    | 10.5             |
| BAF-1014            | 24.0                                                                                        | 66.7                          | —    | 9.3              |
| BAF-1185            | 50.5                                                                                        | 29.8                          | —    | 19.7             |

<sup>a</sup> From [79]

### 13.1 Mixtures of MMH with Hydrazine

There are numerous binary and ternary fuel mixtures of MMH with hydrazine. Not all of these are worth referencing here in detail, and some are only of historical interest, so the following sections are only a sampling of some of the information that is available. No claim is made here as to the completeness of the chapter on MMH fuel mixtures. Additional data on MMH fuel blends can be found in USAF Propellant Handbook, Hydrazine Fuels [79]. Some of the data listed there were marked only as “provisional data,” which apparently would need confirmation from another source before they can be published. None of those data is repeated here. Physical properties of MMH–hydrazine mixtures were already described in Sections 2.4.1.2 and 2.7.2.

Aerozine-76, Ae-76, was a blend of 76% MMH and 24% hydrazine at one time formulated by Aerojet to contain the same amount of carbon as Aerozine-50 and intended as a replacement for Ae-50. It freezes at  $\sim 237\text{K}$  ( $-33^\circ\text{F}$ ). No additional data could be found.

### 13.2 Mixed Hydrazine Fuel 3

The most thoroughly investigated fuel mixture with MMH is MHF-3, also called M-86, which has been considered as a fuel in combination with many different hypergolic oxidizers. The main advantage of such combinations was their storability at room temperature and hypergolic ignition (to be discussed in a future *Encyclopedia of Hypergolic Bipropellant Combinations*, chapter “Hypergolic Combinations with Nitrogen Oxides”). In addition to its use as a fuel, MHF-3 has also been used as a monopropellant and actually has flown as a gas generant for emergency power supplies on early versions of the French/British Supersonic Transport SST CONCORDE.

#### 13.2.1 Physical Properties of MHF-3

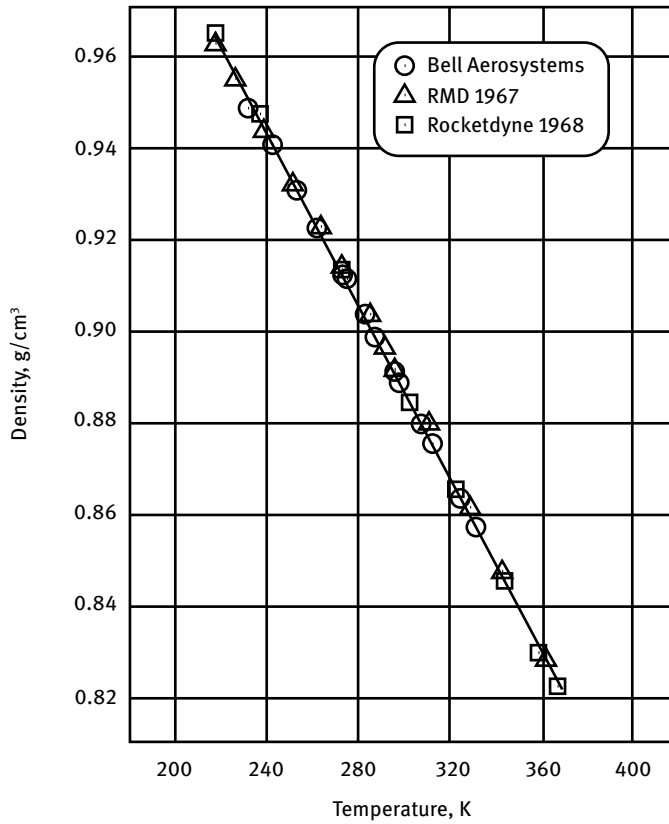
The USAF Propellant Handbooks, Hydrazine Fuels, Vol. 1. contains a unit (Unit 2.7) with physical properties of MHF-3 from which the following were copied [846]. It also contains numerous graphs depicting the physical properties of MHF-3 as a function of temperature, both in SI and American engineering units.

##### 13.2.1.1 Density of MHF-3

The density of MHF-3 from 219 to 367 K ( $-54$  to  $+94^\circ\text{C}$ ) can be expressed as a linear function of temperature

$$\rho = 1.1716 - 9.4836 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin. The density of MHF-3 is illustrated in Figure 44.



**Figure 44:** Density of MHF-3. (Reproduced and modified from [79].)

### 13.2.1.2 Velocity of Sound and Compressibility of MHF-3

The velocity of sound in MHF-3 as a function of temperature can be represented by the linear equation:

$$c = 2808.5 - 4.0427T$$

where  $c$  is the velocity of sound in m/s and  $T$  is the temperature in kelvin. The adiabatic compressibility of MHF-3 can be derived from the sonic velocity and density and is represented by the following polynomial equation:

$$\beta_a = 1.6201 \times 10^{-4} + 1.9278 \times 10^{-6}T - 6.8281 \times 10^{-9}T^2 + 8.9935 \times 10^{-12}T^3$$

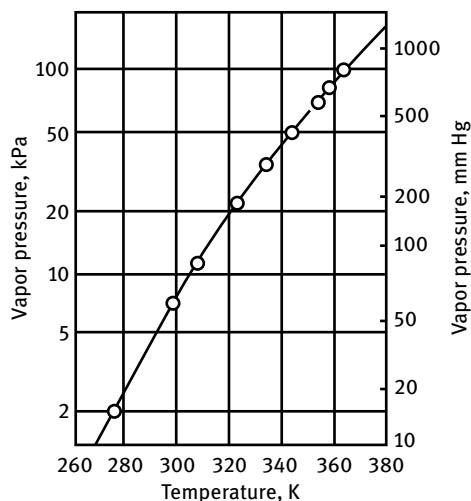
where  $\beta_a$  is the adiabatic compressibility in  $\text{atm}^{-1}$  and  $T$  is the temperature in kelvin.

### 13.2.1.3 Vapor Pressure of MHF-3

The vapor pressure of MHF-3 is dominated by the vapor pressure of its more volatile, more prevalent component, MMH. The vapor pressure of MHF-3 within the range from 273 to 363 K (0 to 90 °C) can be calculated from the equation:

$$\log P = 8.2748 - (1956.91/T)$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. The vapor pressure of MHF-3 is illustrated in Figure 45.



**Figure 45:** Vapor pressure of MHF-3.  
(Reproduced and modified from [79].)

### 13.2.1.4 Viscosity of MHF-3

The absolute viscosity of liquid MHF-3 can be calculated from the equation:

$$\log \mu = -11.179 + \frac{9291.8}{T} - \frac{2.7687 \times 10^6}{T^2} + \frac{2.9336 \times 10^8}{T^3}$$

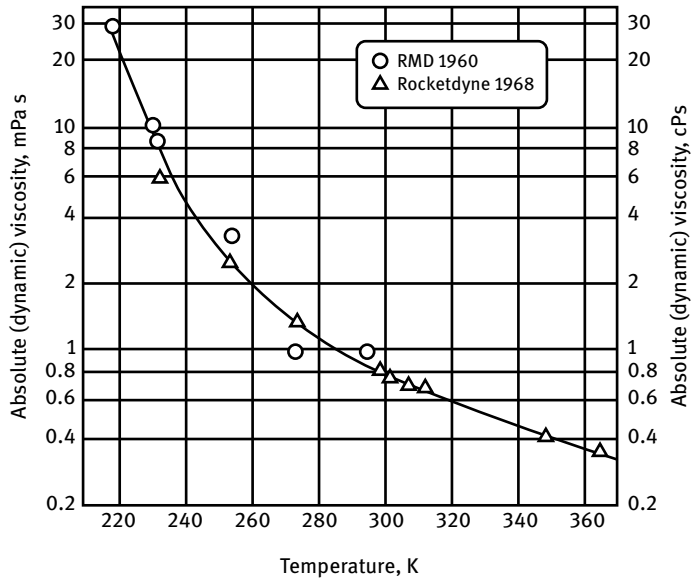
where  $\mu$  is the absolute viscosity in cPs and  $T$  is the temperature in kelvin. The absolute viscosity of MHF-3 is illustrated in Figure 46.

### 13.2.1.5 Surface Tension of MHF-3

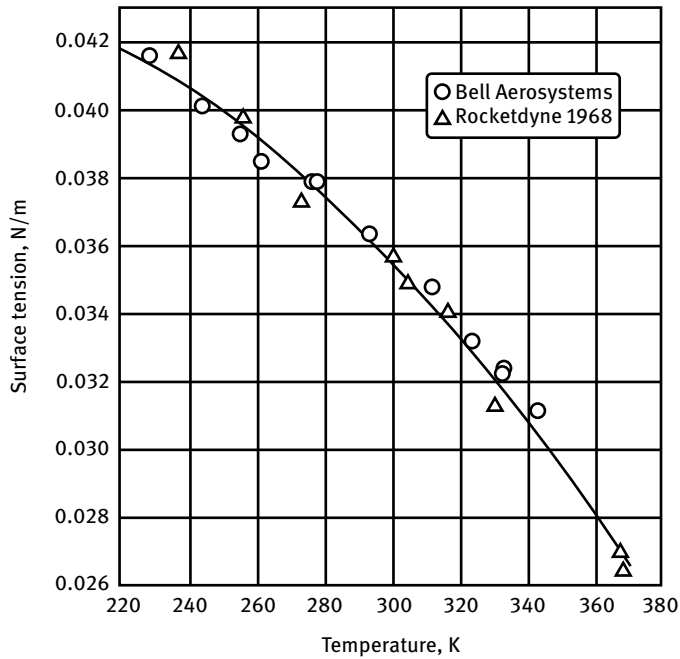
The surface tension of MHF-3 within the range from 229 to 367 K (−44 to 94 °C) can be calculated from the equation:

$$\sigma = 37.4305 + 0.09252 T - 3.2915 \times 10^{-4} T^2$$

where  $\sigma$  is the surface tension in dyn/cm and  $T$  is the temperature in kelvin. To convert from dyn/cm to N/cm, divide by  $10^5$ . The surface tension of MHF-3 is illustrated in Figure 47.



**Figure 46:** Absolute viscosity of liquid MHF-3. (Reproduced and modified from [79])



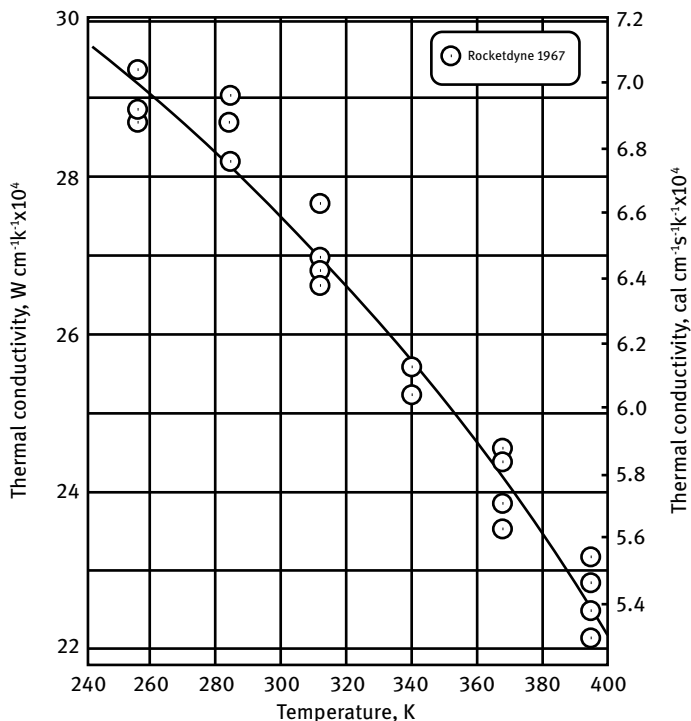
**Figure 47:** Surface tension of MHF-3. (Reproduced and modified from [79])

### 13.2.1.6 Thermal Conductivity of MHF-3

The thermal conductivity of MHF-3 within the range from 255 to 395 K (–18 to 122°C) can be calculated from the equation:

$$\lambda = 7.3524 \times 10^{-4} + 5.0303 \times 10^{-7} T - 2.5343 \times 10^{-9} T^2$$

where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin. To convert from  $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$  to  $\text{W m}^{-1} \text{K}^{-1}$ , multiply by 418.4. The thermal conductivity of liquid MHF-3 is illustrated in Figure 48.



**Figure 48:** Thermal conductivity of liquid MHF-3. (Reproduced and modified from [79].)

### 13.2.2 Chemical Properties of MHF-3

The chemical composition of MHF-3 is defined by Military Specification MIL-P-81342(WP) – Propellant, Mixed Hydrazine Fuel, MHF-3 [847] as listed in Table 60.

#### 13.2.2.1 Analysis of MHF-3

Analytical methods to be used for quality control and acceptance tests of MHF-3 are specified in MIL-P-81342(WP).

**Table 60:** Specification requirements for MHF-3 as per MIL-P-81342(WP).

| Constituents                                | Composition, mass-%                                          | Specification requirements               |
|---------------------------------------------|--------------------------------------------------------------|------------------------------------------|
| Methylhydrazine                             | $86.0 \pm 2.0$                                               | MIL-P-27404                              |
| Hydrazine                                   | $14.0 \pm 2.0$                                               | MIL-P-26536                              |
| Water, plus soluble impurities <sup>a</sup> | 2.0 maximum                                                  | —                                        |
| Particulate                                 | 10 mg/L                                                      | —                                        |
| Density                                     | $0.892\text{--}0.896\text{ g/cm}^3$ at 298 K (25 °C = 77 °F) | Method 402.2 of FED-STD-791 (ASTM-D941). |
| Freezing point                              | $<219.26\text{ K} = -54.4\text{ °C} = -65\text{ °F}$         | ASTM-D1177                               |

<sup>a</sup> Water content shall be 1 mass-% maximum if fuel is to be used for metallized slurry fuels

### 13.2.2.2 Gas Chromatographic Methods for Analysis of MMH Mixtures

The MMH/N<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>O assay per MIL-P-81342(WP) can be done by GC at 373 K (100 °C). The recommended column filling was 30% Quadrol (*N,N,N',N'*-tetrakis-3-hydroxypropyl ethylenediamine) on 30–50 mesh firebrick in a column measuring ¼ in. diameter × 5 ft, a kind of antique method. Modern gas chromatographs using Chromosorb or capillary columns easily separate the three ingredients. Amine impurities may include methylamine, which elutes first.

Improved separation of all three hydrazines and water was achieved by using a stationary phase that is chemically similar to hydrazine [848]. In this case, 2-hydrazinopyridine, a polar liquid of low volatility, was used as the stationary phase in 10% concentration on Fluoropak 80. A synthetic blend consisting of 27.9% N<sub>2</sub>H<sub>4</sub>, 27.9% MMH, 22.2% UDMH, and 21.9% H<sub>2</sub>O was analyzed in replicate ten times, and mean errors (uncorrected for response factors) ranged from –0.4 (UDMH) and –0.3 (MMH) to +0.8% (N<sub>2</sub>H<sub>4</sub>) absolute. The constituents elute in the sequence UDMH, H<sub>2</sub>O, MMH, and N<sub>2</sub>H<sub>4</sub>.

The GC method recommended by Olin for the analysis of hydrazine/MMH mixtures such as MHF-3 used a ¼-in. × 6-ft stainless-steel column packed with 30–60 mesh with 15% triethanolamine on Chromosorb W. Recommended column temperature is 378 K. A response factor of 0.978 is used for hydrazine and 1.152 for MMH when calculating the results. The water response factor must be determined from case to case by analyzing a mixture with a known content of water. Gas chromatographic separation of hydrazine and MMH in combination with a wet chemistry method for total hydrazines eliminated the need to change columns when water must be expected in N<sub>2</sub>H<sub>4</sub>/MMH mixtures [849]. A ¼ × 12-in. copper (!) column packed with 23% Carbowax 1500 on Johns-Manville C-22 firebrick, isothermal at 363 K, was used for N<sub>2</sub>H<sub>4</sub>/MMH separation. Copper as tubing material for the column is *not* a good choice when working with hydrazines. Total hydrazines were then titrated with 0.1 M KIO<sub>3</sub>. The difference was assumed to be water.



Another GC method for the analysis of MMH fuel blends used a column packed with 10% Dowfax 9N9 on Teflon 6 [360]. The peaks appeared in the order of water, MMH, and hydrazine. The composition analyses were duplicated within  $\pm 0.5\%$  of the amount of the individual components present in a synthetic mixture. Nowadays, nobody still uses packed columns and much better separation can be achieved with capillary columns.

Hydrazine/MMH and hydrazine/UDMH mixtures can be analyzed by reactive column GC [383]. Linearity of methane production with sample size could be demonstrated if decomposition occurred on a copper oxide catalyst heated to 573 K. The hydrazine/MMH mixtures gave linear methane peak area response at between 20 and 80% MMH, but the practically more important 86% MMH mixture was not run, leaving some questions as to the suitability of this method for MHF-3 analysis. In repetitive analysis of 50:50  $\text{N}_2\text{H}_4$ /MMH mixtures, a coefficient of variation of 1.7% (for MMH) was obtained, corresponding to a standard deviation of  $\pm 0.9\%$  relative.

In another reactive GC method, nitrogen content of hydrazine mixtures was determined in an apparatus coupled with the GC using chromic acid or bromide–bromate solution as an oxidant [850]. Gaseous products were collected in a bulb, which was part of the by-pass injector. At the end of the reaction the products were determined chromatographically.

#### 13.2.2.3 Titrimetric Methods for Analysis of MMH Mixtures

Mixtures of hydrazine and MMH were determined by an oxidation-aldehyde method based on the selective reaction of  $\text{N}_2\text{H}_4$  with salicylaldehyde and subsequent titration of MMH with potassium iodate. Two aliquots were used, (a) for determining total hydrazines, (b) for determining MMH, by titration with potassium iodate. The  $\text{N}_2\text{H}_4$ , precipitated as salicylidine azine, was determined by difference. It was attempted to extend Malone's method using salicylaldehyde in the presence of excess perchloric acid to determine admixtures of  $\text{N}_2\text{H}_4$  and MMH [401]. The excess perchloric acid was back-titrated with sodium acetate. This non-aqueous acid–base method was simple and effective but required the use of two standard titrants.

#### 13.2.3 Materials Compatibility for MHF-3 Equipment

Mixed hydrazine fuels contain mostly MMH in a mixture with either hydrazine–HN or hydrazine by itself (MHF-3). Maraging steels are preferred for pressure tanks, but the rate of pressure buildup with MHF-3 was prohibitive. It has been attempted to retard the decomposition of MHF-3 by electroplating or electroless plating steel tanks internally with nickel [851–855]. Some coatings other than nickel, for instance, cadmium, would also reduce the rate of gas evolution. The ability of cadmium to reduce the catalytic activity of maraging steels makes it a preferred coating, but cadmium is gradually corroded by MHF-3, making it a sacrificial coating. Electroless

nickel from a hypophosphite bath was more durable and easier to apply to the interior of tanks. Unprotected maraging steels, AM-355 and Inco-718, were not compatible with MHF-3. Although the EPU on the CONCORDE SST was flown only for a short period, a description of transportation regulations for fueled EPUs continues to exist in 49CFR § 173.172. It describes tanks having either a welded aluminum bladder or an elastomeric bladder with a maximum internal volume of 46 L (12 gal). The outer vessel must have a minimum design gauge pressure of 1275 kPa (185 psi) and a minimum burst gauge pressure of 2755 kPa (400 psi). The nesting bellows tank used to hold 28.6 kg (63 lb) of M-86 propellant on board the CONCORDE SST EPU was manufactured by Metal Bellows Corporation. It had an expulsion efficiency of 83% and had demonstrated 140 full expulsion cycles, more than was ever needed for ordinary EPU applications.

An all-glass apparatus with an attached all-glass Bourdon tube called a “Staco” cell was used to measure gas evolution of MHF-3 in contact with a number of metals at 347 K [856]. A mirror was mounted on the tip of the Bourdon tube, and the tube deflection could be read with a beam of light reflected from the mirror. Each tube had to be individually calibrated while dry, as no two thin-walled glass Bourdon tubes were alike. The compatibility of various pure metals with MHF-3 was determined at 347 K (74 °C = 165 °F). Metals investigated included titanium, copper, iron, aluminum, and nickel under the annealed and cold-worked conditions, and chemically deposited chromium. Tests were conducted in an all-Pyrex, torch-sealed pressure vessel. Pressure changes were recorded over a 94-day period. The worst pressure rise, 0.6 and 0.2 psi/day, was with annealed and cold-worked iron or copper. Post-exposure evaluations of the metals were made by electron microscopic examination, microprobe analysis, and tensile tests. Each specimen was weighed before and after the 94-day immersion in MHF-3. All specimens underwent a small loss in weight. The weight losses of the various metals did not correlate with the degree of propellant decomposition. For instance, titanium caused no pressure increase in the cell, yet its weight change, compared with other metals, was relatively high. The greatest variation in physical tensile strength properties due to MHF-3 exposure was found in the cold-worked aluminum. All the other metals tested showed no property changes greater than the expected variation of testing. Cold-worked Al and Ti samples gradually annealed themselves during the 347 K exposure. Table 61 gives a summary of hydrazine blends materials compatibility tests.

Compatibility of MHF-3 in comparison with hydrazine, MHF-5, MGGP-1, MGGP-3, and BAF-1185 was tested in pressure vessels made from Al-1100-0, Al-2014-T6, Al-6061-T6, CRES-347 steel or Inconel 718 for 1 year at 347 K (165 °F) [857]. The lowest pressure rise was in the aluminum alloys and the highest pressure rise was in CRES-347, accompanied by propellant discoloration to dark amber and reddish brown.

**Table 61:** Literature references to mixed hydrazine fuel (MHF) materials compatibility tests.

| Blend designation | Materials tested                              | Type of tests                                                                               | References |
|-------------------|-----------------------------------------------|---------------------------------------------------------------------------------------------|------------|
| MHF-3             | Al-1100-00, Al-2014-T6, CRES-347, Inconel-718 | Tank storage, pressure rise, fuel analysis, weld samples                                    | [857]      |
| MHF-3             | Ti, Cu, Fe, Al, Ni, Cr                        | Glass ampoules for 94 days at 347 K                                                         | [856]      |
| MHF-3             | Ni coating on maraging steel SS301            | Tank test for 1 year at 344 K                                                               | [851]      |
| MHF-5             | Al-1100, Al-2219, CRES-321, Ti-6Al-4V         | Tank storage, pressure rise, 2050 days                                                      | [134]      |
| MHF-5             | Al-2014-T6, CRES-347                          | Tank storage, pressure rise, fuel analysis                                                  | [857]      |
| MHF-5             | Al-2219-T86                                   | 11 tanks in storage, both rolling metal diaphragm and surface tension screen, pressure rise | [858, 859] |
| MHF-7             | Al-1100, Al-2219, CRES-321, Ti-6Al-4V         | Tank storage, pressure rise, 2050 days                                                      | [134]      |
| BAF-1185          | Al-1100-00, CRES-347, Inconel-718             | Tank storage, pressure rise                                                                 | [857]      |

#### 13.2.4 Toxicity of MHF-3

The toxicity of MHF-3 is determined by its most volatile and most prevalent constituent, MMH.

#### 13.2.5 Safety Properties of MHF-3: Flash Point of MHF-3 in Air

Mixed hydrazine fuel MHF-3 has a flash point of 297 K (24 °C) in air. The spontaneous ignition hazards of MHF-3 (M86) were measured in air and at low pressures [860]. The hazard is very similar to that of MMH itself. Spill decontamination methods were developed for MMH-based propellant mixtures such as MHF-3 or MHF-5 [861].

### 13.3 Mixed Hydrazine Fuel 5

Another thoroughly investigated monopropellant mixture with MMH is MHF-5. MHF-5 is a ternary mixture of MMH, hydrazine, and HN. Hydrazinium nitrate was added to the MMH/hydrazine mixture to avoid formation of soot and to increase its performance as a monopropellant. There are also two variants of this propellant mixture, designated as MHF-5A and MHF-5B. MHF-5 was originally intended for the CONDOR ship-borne missile program and the freezing point was thought to be 202 K (–71 °F), but that was due to supercooling and later investigations showed that the freezing point was actu-

ally 230 K (−43 °F). An interim candidate was MHF-5A, which was formulated to meet a 208 K (−65 °F) freezing point requirement, but it was superseded by MHF-5B after the freezing point requirements were relaxed and a freezing point of 230.4 K (−45 °F) was considered acceptable. All three versions of MHF-5 contain the same amount of HN, 19% HN by mass. The main difference in the three formulations is the amount of MMH. MHF-5B was used for development tests of the CONDOR missile, but the missile was never put into service on any US Navy ship or jet airplane. A solid-propellant air-to-ground missile developed for the Navy in a parallel program, AGM-53, also under the same name CONDOR, did not advance to deployment either.

The gross formula of MHF-5B would be  $C_{0.5784}H_{5.2486}N_{2.0918}O_{0.2755}$ , or, normalized to  $C=1$  where the factor is  $1/0.5784=1.7289$ , the gross formula would be  $C_1H_{9.074}N_{3.616}O_{0.476}$ , indicating that this formula is still under-oxidized for the complete conversion of all carbon to CO.

### 13.3.1 Physical Properties of MHF-5

The USAF Propellant Handbooks, Hydrazine Fuels, Vol. 1, contains two similar units (Unit 2.17 and Unit 2.18) with physical properties of MHF-5 and MHF-5B from which the following properties were copied [862]. It also contains numerous graphs depicting the physical properties of MHF-5 and MHF-5B as a function of temperature, both in SI and American engineering units. MHF-3 has flown whereas MHF-5 has not. Therefore, unlike the format of the MHF-3 section, none of the many graphs from that collection was reproduced here in order to conserve space. Instead, several mathematical equations were given, which allow the user to calculate properties as a function of temperature.

Physical properties of MHF-5 are summarized in Table 62. The physical properties of MHF-5 and MHF-5B are very similar. The following section contains a mix of MHF-5 and MHF-5B properties.

#### 13.3.1.1 Density of MHF-5B

The density of MHF-5B within the range 215 to 344 K (−58 to +71 °C) can be calculated from:

$$\rho = 1.2492 - 8.2274 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin. There is also an equation that allows us to calculate the density of MMH/ $\text{N}_2\text{H}_4$ /HN mixtures as a function of chemical composition and temperature:

$$\rho = 1.2490 - 7.948 \times 10^{-4} - 5.199 \times 10^{-8} T^2 - 1.512 \times 10^{-3} M + 4.42 \times 10^{-3} N$$

where  $\rho$  is the density in  $\text{g/cm}^3$ ,  $T$  is the temperature in kelvin,  $M$  is the mass-% MMH, and  $N$  is the mass-% HN.

**Table 62:** Physical properties of MHF-5, MHF-5A, and MHF-5B.

| Property                              | SI units                             | Other units                                                                    |                                                              |
|---------------------------------------|--------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------|
| Freezing point                        | 231 K                                | ~-42 °C                                                                        | ~-43 °F                                                      |
|                                       | 212 K                                | -60 °C                                                                         | -77 °F <sup>a</sup>                                          |
|                                       | 229 K                                | -44 °C                                                                         | -48 °F                                                       |
| Vapor pressure                        | 26.2 kPa at 328 K                    | 196 mm Hg at 55 °C                                                             | 3.8 psia at 130 °F                                           |
| Density at 298 K (77 °F)              | 0.996 g/cm <sup>3</sup> <sup>a</sup> | —                                                                              | 62.2 lb/ft <sup>3</sup> <sup>a</sup>                         |
| Density at 328 K (130 °F)             | 0.968 g/cm <sup>3</sup> <sup>a</sup> | —                                                                              | 60.4 lb/ft <sup>3</sup> <sup>a</sup>                         |
| Density at 298 K (77 °F)              | 1.002 g/cm <sup>3</sup> <sup>a</sup> | —                                                                              | —                                                            |
| Density at 328 K (130 °F)             | 0.974 g/cm <sup>3</sup> <sup>a</sup> | —                                                                              | —                                                            |
| Viscosity at 233 K                    | —                                    | 38 cPs <sup>a</sup>                                                            | —                                                            |
| Viscosity at 298 K                    | —                                    | 1.98 cPs <sup>a</sup>                                                          | —                                                            |
| Viscosity at 328 K                    | —                                    | 1.1 cPs <sup>a</sup>                                                           | —                                                            |
| Heat capacity at 298 K (77 °F)        | —                                    | —                                                                              | 0.677 BTU lb <sup>-1</sup> °F <sup>-1</sup>                  |
| Thermal conductivity at 298 K (77 °F) | —                                    | 7.5<br>× 10 <sup>-4</sup> cal cm <sup>-1</sup> s <sup>-1</sup> K <sup>-1</sup> | 0.1819 BTU h <sup>-1</sup> ft <sup>-1</sup> °F <sup>-1</sup> |

<sup>a</sup> Data for MHF-5B

Data source: [110]

**13.3.1.2 Vapor Pressure of MHF-5**

The vapor pressure of MHF-5 within the range 273 to 368 K (0 to 95 °C) can be calculated from

$$\log P = -61.243 + 5725.80/T + 0.20818 T - 2.0727 \times 10^{-4} T^2$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.

**13.3.1.3 Viscosity of MHF-5B**

The absolute viscosity of MHF-5B within the range 233 to 366 K (-40 to 93.3 °C) can be calculated from the equation:

$$\log \mu = -3.9625 + \frac{3087.4}{T} - \frac{9.7161 \times 10^5}{T^2} + \frac{1.2820 \times 10^8}{T^3}$$

where  $\mu$  is the absolute viscosity in cPs and  $T$  is the temperature in kelvin.

**13.3.1.4 Thermal Conductivity of MHF-5**

The thermal conductivity of liquid MHF-5 consisting of 55% MMH, 26% N<sub>2</sub>H<sub>4</sub>, and 19% HN, was reported (at 298 K) as  $7.5 \times 10^{-4}$  cal cm<sup>-1</sup> s<sup>-1</sup> K<sup>-1</sup> (0.1819 BTU h<sup>-1</sup> ft<sup>-1</sup> °F<sup>-1</sup>) [110]. The thermal conductivity of MHF-5 can be calculated from:

$$\lambda = 9.4074 \times 10^{-4} - 6.3264 \times 10^{-7} T$$

where  $\lambda$  is the thermal conductivity in cal cm<sup>-1</sup> s<sup>-1</sup> °C<sup>-1</sup> and  $T$  is the temperature in kelvin. To convert from cal cm<sup>-1</sup> s<sup>-1</sup> °C<sup>-1</sup> to W m<sup>-1</sup> K<sup>-1</sup>, multiply by 418.4.

### 13.3.2 Chemical Properties of MHF-5

The chemical composition of MHF-5 is defined by Military Specification MIL-P-81507 – Propellant, Mixed Hydrazine Fuel, MHF-5, as listed in Table 63. MHF-5 formulations lack thermal stability [863].

**Table 63:** Specification requirements for MHF-5 as per MIL-P-81507.

| Constituents                   | Composition, mass-%                 | Specification requirements               |
|--------------------------------|-------------------------------------|------------------------------------------|
| Methylhydrazine                | $55.0 \pm 2.0$                      | MIL-P-27404                              |
| Hydrazine                      | $26.0 \pm 2.0$                      | MIL-P-26536                              |
| Hydrazinium nitrate            | $19.0 \pm 2.0$                      | —                                        |
| Water, plus soluble impurities | $\leq 2.0$                          | —                                        |
| Particulate                    | 10.0 mg/L                           | —                                        |
| Density at 298 K               | 1.00 to 1.02 g/cm <sup>3</sup>      | Method 402.2 of FED-STD-791 (ASTM-D941). |
| Freezing point                 | $202.1 \pm 2.8$ K ( $-71 \pm 5$ °F) | ASTM-D1177                               |

### 13.3.3 Materials Compatibility of MHF-5 and MHF-5B

Pressure rise was measured during long-term storage tests with MHF-5 in CRES-321 tanks with 2% ullage, and the pressure rise was very fast, 1.27 MPa (185 psi) in 8 months. In Al-2219, the pressure rise was only 34 kPa (5 psi) when stored at ambient temperature and 860 kPa (125 psi) when stored at 328 K [110].

### 13.3.4 Equipment for Handling of MHF-5 and MHF-5B

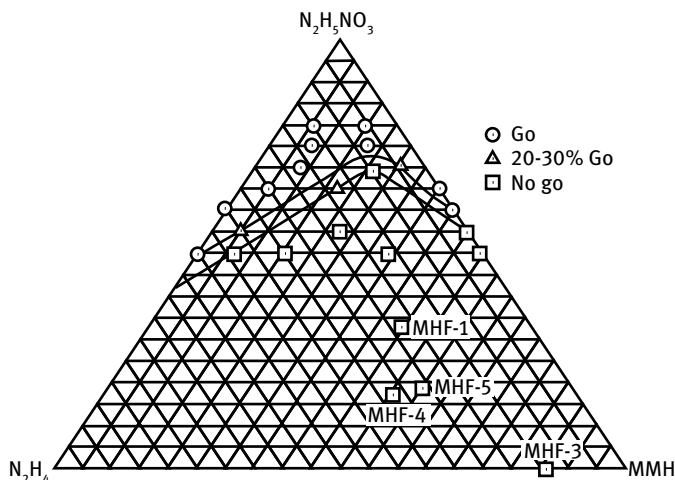
As part of the long-term storage program at AFRPL, General Dynamics supplied 23 tanks filled with MHF-5, NTO, or ClF<sub>5</sub> [864]. The tanks contained either surface tension screen PMDs or rolling metal diaphragm positive expulsion devices and were connected to three different types of expulsion pressurization devices: solid propellant gas generators, liquid propellant gas generators, or compressed gas bottles. These assemblies were stored for up to 10 years.

Propellant tanks for MHF-5 long-term storage tests need to be carefully cleaned and passivated before filling them with MHF-5 [865]. For comparison, storage of MHF-5 in metal tanks is much more difficult than that of MHF-3 because it is more corrosive [595, 858, 859].

### 13.3.5 Safety Properties of MHF-5 and MHF-5B

#### 13.3.5.1 Drop Weight Sensitivity of MHF-5 and MHF-5B

If MHF-5, MHF-5B, or MHF-1 freeze slowly, HN precipitates and accumulates at the bottom, constituting an increased safety hazard. Even after the mixture thaws and it is not stirred soon after to re-mix it, its bottom layer may be more sensitive to shock.



**Figure 49:** Drop weight impact sensitivity of methylhydrazine/ $\text{N}_2\text{H}_4$ /hydrazinium nitrate mixtures. (Reproduced and modified from [79].)

Mixtures would then be in the apex area of the triangular chart in Figure 49, an area one would always try to avoid. Mixtures containing >35% HN are shock sensitive. The mass of the impactor and the drop height were not specified in the source of this graph. It is assumed that the impactor mass was 2 kg.

#### 13.3.5.2 Card Gap Sensitivity of MHF-5 and MHF-5B

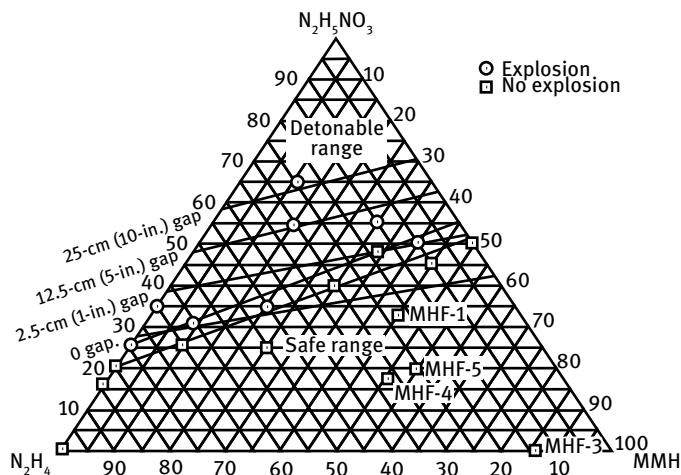
A graph showing the card gap sensitivities of ternary MMH/ $\text{N}_2\text{H}_4$ /HN mixtures including MHF-5 and MHF-5B is shown in Figure 50. As can be seen in this graph, mixtures with 30–40% HN are detonable even with a 25-cm (10 in) gap. MHF-1 is very close to the boundary of detonability, but still on the safe side.

### 13.4 Mixed Hydrazine Fuel 1

Another thoroughly investigated monopropellant mixture with MMH is MHF-1, which has been considered as a monopropellant and hypergolic fuel with RFNA, NTO, or  $\text{ClF}_3$ . Data points for MHF-1 properties were already shown in several of the MMH/ $\text{N}_2\text{H}_4$ /HN ternary mixture property charts, in comparison with the properties of MHF-5.

#### 13.4.1 Physical Properties of MHF-1

The USAF Propellant Handbooks, Hydrazine Fuels, Vol. 1, contains a unit (Unit 14) with physical properties of MHF-1 from which the following properties were copied



**Figure 50:** Card gap sensitivity of methylhydrazine/ $\text{N}_2\text{H}_4$ /hydrazinium nitrate mixtures. (Reproduced and modified from [79].)

[866]. It also contains numerous graphs depicting the physical properties of MHF-1 as a function of temperature, both in SI and American engineering units, but we could not reproduce all of those here owing to a lack of space. It is unlikely that MHF-1 will be used again, so the data are only of historical interest.

Mixed hydrazine fuel-1 was dropped from consideration because of its high rate of pressure buildup during hermetic storage tests and also because of its high viscosity and its tendency to explode in open-cup burning tests where the volatile fuels burn first and the HN-enriched residue explodes.

#### 13.4.2 Chemical Properties of MHF-1

The chemical composition of MHF-1 is 45.3% MMH, 31.4%  $\text{N}_2\text{H}_5\text{NO}_3$ , and 23.3%  $\text{N}_2\text{H}_4$ . With such a high HN content, this formulation is borderline to detonability and shock sensitivity limits shown in some of the previous triangular charts. The gross formula of MHF-1 is  $\text{C}_{0.48183}\text{H}_{5.12553}\text{N}_{2.16187}\text{O}_{0.48562}$ , or, normalized to  $\text{C} = 1$ , the gross formula would be  $\text{C}_1\text{H}_{10.637}\text{N}_{4.4868}\text{O}_{1.008}$ , which shows that this mixture contains more than sufficient oxygen to burn all carbon to CO and thus it should have a very clean, soot-free exhaust when it is used as a monopropellant.

#### 13.4.3 Toxicity of MHF-1

The acute toxicity of MHF-1, a mixture of 45.3% MMH, 23.3%  $\text{N}_2\text{H}_4$ , and 31.4% HN, is essentially identical to that of MMH [867].



### 13.5 Ternary Fuel Mixtures of MMH with Hydrazine and Water

Adding water to MMH/hydrazine fuel mixtures would decrease the performance as a fuel, but would also lower the freezing point. There are three fuel blends with these three constituents that have been characterized, but no flight applications are known. The compositions of these three mixtures have already been shown in Table 59.

#### 13.5.1 Mixed Hydrazine Fuel 6

Another thoroughly investigated monopropellant mixture with MMH is MHF-6, which has been considered a low-freezing point fuel, although adding water would lower the performance compared with MHF-3. MHF-6 consists of 73.0% MMH, 18.5%  $\text{N}_2\text{H}_4$ , and 10.5%  $\text{H}_2\text{O}$ . This composition can also be written as 73% MMH and 27% hydrazine hydrate  $\text{N}_2\text{H}_5\text{OH}$ . It is roughly midway between MHF-3 and BAF-1185 in composition and many of its properties are similar to those of the latter two fuels.

The advantage of MHF-6 over MHF-3 or MHF-1 is that it can be prepared from hydrazine hydrate, hydrazine, and MMH instead of anhydrous hydrazine and MMH. MHF-6 would be a better regenerative coolant, result in lower flame temperatures, at the expense of lower specific impulse. The empirical formula for MHF-6 is  $\text{C}_{1.58437}\text{H}_{12.73128}\text{N}_{4.19845}\text{O}_{0.582815}$ .

#### 13.5.2 Physical Properties of MHF-6

The USAF Propellant Handbooks, Hydrazine Fuels, Vol. 1, contains a unit (Unit 2.19) with physical properties of MHF-6 from which the following properties were copied [868]. It also contains numerous graphs depicting the physical properties of MHF-6 as a function of temperature, both in SI and American engineering units. The freezing point of MHF-6 was marked on Figure 25 as 219.3 K ( $-53.9^\circ\text{C}$ ).

##### 13.5.2.1 Density of MHF-6

The density of MHF-6 over the temperature range from 219 to 347 K ( $-54$  to  $+74^\circ\text{C}$ ) can be calculated from the equation:

$$\rho = 1.1951 - 9.1500 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin.

##### 13.5.2.2 Vapor Pressure of MHF-6

The vapor pressure of MHF-6 over the range 318 to 366 K ( $45$  to  $93^\circ\text{C}$ ) can be calculated from the equation:

$$\log P = 8.1579 - (1937.63/T)$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.

### 13.5.3 Chemical Properties of MHF-6

The chemical composition of MHF-6 is defined by Military Specification MIL-P-81726 – Propellant, Mixed Hydrazine Fuel, MHF-6 [869], as listed in Table 64. Apparently, the armed forces must have had an application for MHF-6 in mind because it is one of the few MMH-based fuels that has advanced to the stage of having a MIL-SPEC issued for it.

**Table 64:** Specification requirements for MHF-6 per MIL-P-81726.

| Constituents       | Composition, mass-%                                                                     | Specification requirements               |
|--------------------|-----------------------------------------------------------------------------------------|------------------------------------------|
| Methylhydrazine    | $72.5 \pm 0.5$                                                                          | MIL-P-27404                              |
| Hydrazine          | $17.0 \pm 1.0$                                                                          | MIL-P-26536                              |
| Water, de-ionized  | $10.5 \pm 0.5$                                                                          | —                                        |
| Soluble impurities | 0.5 max.                                                                                | —                                        |
| Particulate        | 10 mg/L maximum                                                                         | —                                        |
| Density            | $0.922 \text{ g/cm}^3$ at $298 \text{ K} = 25^\circ\text{C}$                            | Method 402.2 of FED-STD-791 (ASTM-D941). |
| Freezing point     | $216.5 \pm 1.7 \text{ K} = -56.7^\circ\text{C} = -70^\circ\text{F} \pm 3^\circ\text{F}$ | ASTM-D1177                               |

## 13.6 BAF-1014

BAF-1014 or BA-1014 is a ternary mixture of MMH, hydrazine, and water, similar to MHF-6 and BAF-1185. BAF-1014 consists of 24.0% MMH, 66.7%  $\text{N}_2\text{H}_4$ , and 9.3%  $\text{H}_2\text{O}$ . Properties of BAF-1014 are described in the USAF Propellant Handbook, Hydrazine Fuels. Vol. 1, Unit 2.20 [870]. BAF-1014 and BAF-1185 as fuels with some oxygen in the form of water in their composition were formulated to be used as fuels in combination with fluorine or interhalogens ( $\text{ClF}_3$  or  $\text{ClF}_5$ ) as oxidizers. The oxygen in the fuel was there to combine preferentially with carbon, forming carbon monoxide instead of soot in the exhaust. It is believed that the first two letters in the BAF designation were derived from the name of the company where the fuels were developed, Bell Aerospace.

### 13.6.1 Physical Properties of BAF-1014

The freezing point of BAF-1014 was marked on Figure 25 as  $254 \text{ K}$  ( $-19.2^\circ\text{C}$ ).

### 13.6.2 Density of BAF-1014

The density of BAF-1014 as a function of temperature over the range  $258$  to  $298 \text{ K}$  ( $-15$  to  $+25^\circ\text{C}$ ) can be calculated from the linear equation:

$$\rho = 1.2422 - 8.673 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g/cm}^3$  and  $T$  is the temperature in kelvin.

### 13.6.3 Vapor Pressure of BAF-1014

The vapor pressure of BAF-1014 over the range 268 to 365 K (−5 to +92°C) can be calculated from the equation:

$$\log P = 7.7766 - (1862.50/T)$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.

### 13.7 BAF-1185

BAF-1185 or BA-1185 is a ternary mixture of MMH, hydrazine, and water, similar to MHF-6 and BAF-1014. BAF-1185 consists of 50.5% MMH, 29.8%  $\text{N}_2\text{H}_4$ , and 19.7%  $\text{H}_2\text{O}$ . Properties of BAF-1185 are described in the USAF Propellant Handbook, Hydrazine Fuels. Vol. 1, Unit 2.21 [871]. The freezing point of BAF-1185 was marked on Figure 25 as 219.2 K (−53.9°C). The density of BAF-1185 as a function of temperature over the range 225 to 345 K (−48 to +72.4 °C) can be calculated from the linear equation:

$$\rho = 1.2066 - 8.4742 \times 10^{-4} T$$

where  $\rho$  is the density in  $\text{g}/\text{cm}^3$  and  $T$  is the temperature in kelvin.

### 13.8 Mixtures of MMH with UDMH

The properties of mixtures of MMH with UDMH could be discussed under the heading MMH or UDMH. It was decided to place this section here under MMH.

**Table 65:** Densities and viscosities of the eutectic solution of methylhydrazine–unsymmetrical dimethylhydrazine.

| Temperature |       | Density                | Absolute viscosity | Kinematic viscosity |
|-------------|-------|------------------------|--------------------|---------------------|
| K           | °C    | $\text{g}/\text{cm}^3$ | cPs                | cSt                 |
| 298         | 25.0  | 0.8211                 | 0.617              | 0.751               |
| 283         | 10.0  | 0.8358                 | 0.809              | 0.968               |
| 273         | 0.0   | 0.8454                 | 1.004              | 1.188               |
| 263         | −10.0 | 0.8552                 | 1.299              | 1.519               |
| 253         | −20.0 | 0.8650                 | 1.743              | 2.015               |
| 243         | −30.0 | 0.8747                 | 2.489              | 2.846               |
| 233         | −40.0 | 0.8844                 | 3.866              | 4.371               |
| 223         | −50.0 | 0.8940                 | 6.607              | 7.390               |
| 213         | −60.0 | 0.9033                 | 13.68              | 15.14               |
| 203         | −70.0 | 0.9118                 | 36.06              | 39.55               |
| 200.6       | −72.5 | 0.9160                 | 49.97              | 54.55               |

Data source: [60]

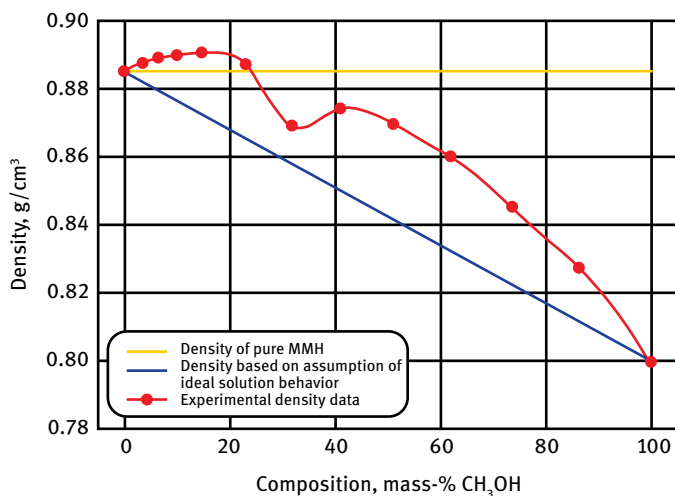
The phase relations of the system MMH/UDMH showed a eutectic freezing at 193 K ( $-80^{\circ}\text{C} = -112^{\circ}\text{F}$ ) at the composition: 39.8 mass-% MMH and 60.2% UDMH. Eutectic mixtures of MMH and UDMH have densities of  $0.9033\text{ g/cm}^3$  at 213 K ( $-60^{\circ}\text{C}$ ) and  $0.9118\text{ g/cm}^3$  at 203 K ( $-70^{\circ}\text{C}$ ). The viscosities of these mixtures are 13.68 cPs at 213 K ( $-60^{\circ}\text{C}$ ) and 36.06 cPs at 203 K ( $-70^{\circ}\text{C}$ ) [60]. See the data in Table 65. There are no known flight uses of MMH/UDMH fuel blends.

### 13.9 Other Fuel Mixtures with MMH

In search of a freezing point suppressant for MMH in bipropellant systems, five different organic additives and water were tested to measure the effects on freezing points, densities, vapor pressures, and to calculate the potential effect on bipropellant performance with NTO as the oxidizer [226]. The additives tested in quantities between 5 and 40% were: urea, acetamide, 1-methyl-1-phenylhydrazine, *N,N*-dimethylformamide, and formamide. Other than water, which would have lowered performance and caused corrosion, *N,N*-dimethylformamide was the best candidate additive for lowering the freezing point without excessive losses of performance. Addition of 5% *N,N*-dimethylformamide lowered the freezing point to below 203 K ( $-70^{\circ}\text{C}$ ), increased the density at 299 K ( $26.5^{\circ}\text{C}$ ) to  $0.875\text{ g/cm}^3$ , and increased the boiling point to 362 K ( $91^{\circ}\text{C}$ ).

Fuel mixtures of MMH with methanol were tested as fuels with RFNA. It was proposed that MMH needs or can use more oxygen during combustion with RFNA. This suggested that MMH could benefit from the addition of an oxygenating agent. Therefore, MMH was “oxygenated” with methanol up to 45 mol-% and reacted with RFNA [872]. The results in Figure 51 show that the density of the mixtures does not follow ideal solution behavior. For methanol concentrations below 23 mass-% the density of the mixture was actually greater than that of pure MMH, as noted by the horizontal line added to Figure 51. The data point in Figure 51 at 32 mass-% methanol does not appear to follow the trend of the other data points in the figure. This inflection point could suggest that two different phenomena are taking place within this system that begin at approximately 23 mass-% methanol and extend to 41 mass-% methanol. It is known that water additions to hydrazine produce hydrates, and similar phenomena may occur in MMH/MeOH.

Mixing MMH and methanol was slightly exothermic. Generally, the mixing of hydrazines with other polar compounds is exothermic. When measuring the heat of mixing for different mixture ratios, a maximum heat of mixing for the MMH/methanol mixtures occurred between 40 and 50 mass-% methanol. Three distinct zones were apparent when graphing the  $\Delta H_{\text{mix}}$  as a function of  $X_{\text{MeOH}}$ . The first was a zone extending to ~20 mass-% methanol (~24 mol-% methanol), this was followed by an inflection point that occurred at the identical concentration to that seen in the volume change on mixing results, and a third zone with near linear  $\Delta H_{\text{mix}}$  data. The maximum with  $-474\text{ J/g} = -0.045\text{ BTU/g}$  was at ~43 mass-% MeOH.



**Figure 51:** Density of methylhydrazine/methanol mixtures. (Republished and modified from [872], with permission of ©2005 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

### 13.10 Gelled MMH Fuels

Substantial effort has been devoted over the past decades to gelled MMH fuels, both metallized and without metal additions, but they have yet to find a flight application. Several decades of continued government funding of gelled propellant research have not resulted in a propellant formulation that meets storability requirements of the real world in a battlefield situation.

The promise of gelled fuels was that they would be less susceptible to leakage, even if one or both tanks were hit by shrapnel in a battlefield situation. The shrapnel would still render the one missile unusable, but at least the punctured tank would not start a fire and affect other, still operational missiles in the launch canisters or in the magazine by fratricide.

Gelled propellants are non-Newtonian fluids and therefore exhibit a non-linear relationship between the stress and deformation rate. Depending on the gelling agent used, gelled propellants may also have a finite yield stress. Stresses applied to the fluid below the yield stress do not cause the fluid to flow, but they deform like a solid. Numerous rheological models for non-Newtonian fluid mechanics exist and the choice of rheological model for a particular fluid depends on how well they match experimental data.

A difficulty in preparing gels is the tendency of gelling agents to form lumps as soon as they contact any liquid. The lumps would only slowly disperse and it would take a long time to obtain a uniform gel. Another problem is trapping gas bubbles.

Preparing gels under vacuum with a high-shear mixer may avoid these problems. To avoid the formation of lumps, the hydroxypropyl cellulose (HPC) powder is added slowly in steps of 1%, followed by an intensive period of stirring.

One aspect of the long-term storability of gelled propellants that has often been overlooked is syneresis. Syneresis is the segregation of the gelled propellant into a gelled phase and a liquid phase. Typically, this happens if the tank has an ullage space and the MMH can vaporize from the surface of the gel if temperature differentials exist between the liquid and the ullage. The other mechanism for gel segregation is just the aging of the gel structure, similar to the hardening of polymers with age.

There are only a few open literature papers describing the rheological properties of gelled MMH. Most of those also discuss the gelling of oxidizers to be paired with the gelled MMH in hypergolic bipropellant propulsion systems, usually for tactical missiles.

The rheological properties depend on how fast or how slow a viscosity measurement is performed (shear rate) and the shear history of the fluid. Thixotropy is a time-dependent fluid property where the fluid viscosity decreases with time when shear is applied. Time-dependent fluids retain information of their shear history in the gel microstructure.

A review of the status of gelled MMH and IRFNA system technologies described three types of IRFNA/MMH gels that had been developed for tactical missile applications [873]. The three types are: high performance aluminum-loaded gels, medium performance carbon-loaded gels, and lower performance unloaded gels. Each gel suits a particular application best as the smoke plume visibility increases with increasing performance. For a battlefield situation, a low signature, no-smoke exhaust would be preferred.

Measurements of viscosity hydroxypropyl cellulose shear rate curves for various gel propellants including 2 to 4 mass-% hydroxypropyl cellulose/MMH and 3 to 5 mass-% silica/IRFNA gels were plotted over a range of viscosity measurements on a common plot, although no distinctions were made between different gellant concentrations and the viscosity variation for a single gellant concentration [874]. Thixotropy and yield stress measurements were performed to further classify the behavior of the gel propellants. Hydrazine-based fuels, gelled with polysaccharides, were characterized as shear-thinning pseudoplastic fluids with low shear yield stress. Creep tests were conducted on two rheological types of gels with different gellant content and the results were fitted by a viscoelastic constitutive model. The effect of temperature on the rheological properties of gel propellant simulants was also investigated. A general rheological classification of gel propellants and simulants was proposed.

It is assumed that the same gelling agents that were proven to work for MMH would also work for gelling UDMH, but there has been less interest in gelled UDMH

than gelled MMH. See also [875, 876]. Hydroxypropyl cellulose or fumed silica or a combination of the two can be used for gelling MMH [877, 878].

### 13.10.1 Selection of Gelling Agents

A wide range of organic gelling agents has been tested with MMH, similar to efforts with gelled hydrazine or kerosene [879]. KLUCEL<sup>®</sup> HPC, is a non-ionic water-soluble cellulose ether, which has been used as a gelling agent for MMH. In non-rocket applications, HPC is mainly used as a thickener for adhesives, paint removers, and food, as well as a binder in the chemical and pharmaceutical industries. Cellulose-based derivatives such as HPC, hydroxyethyl cellulose (HEC) and hydroxyalkyl cellulose have been used successfully to gel MMH. Gels with KLUCEL<sup>®</sup> showed little or no thixotropic behavior in comparison with highly thixotropic gels featuring an inorganic gelling agent such as SiO<sub>2</sub> [880]. The viscosity was reduced when shear was applied to the gel; however, the viscosity returned to the original value when the shear stress was removed. Rheological measurements of gelled MMH were performed using a rotational rheometer, applying shear rates up to 1000 s<sup>-1</sup>. The MMH/HPC gel showed a Newtonian plateau for low shear rates where the applied shear rate had no considerable influence on the gel viscosity. For higher shear rates a reduction in viscosity could be observed. The viscosity reduction with increasing shear was less in comparison with silica gels. For shear rates higher than approximately 0.1 s<sup>-1</sup> the MMH gel had a higher viscosity than kerosene gels with the same amount of gelling agent.

In continuation of earlier studies [880], HPC, a polysaccharide, was evaluated as a gelling agent for MMH and the viscosity of the unloaded gels was measured under different shear conditions [877]. In solutions, the polysaccharide chains expand and uncoil, resulting in the formation of an entangled network and an increase in the solution viscosity. Gelled MMH samples were prepared that contained both HPC and fumed silica. The viscosity–shear rate relationship of the MMH and RFNA gels was investigated over a shear rate range from 0.001 to 1000 s<sup>-1</sup>. HPC-based MMH gels were not thixotropic. There were no changes in viscosity after 1-month storage, but such a short storage time is meaningless in view of military storability requirements. The time-independent nature of HPC-based gels made it possible to measure a single sample multiple times without altering the rheology. However, this measurement was not possible because the MMH gels changed (owing to oxidation and CO<sub>2</sub> absorption) in open air, altering the rheology within 10 min of the start of the air exposure. Another gelling agent for alkylhydrazines is polyacrylamide [881].

Methylhydrazine gels with gelling agents consisting of hydroxypropyl methyl cellulose containing 19 to 24 mass-% methoxy groups and 4 to 12 mass-% propoxy groups, dihydroxyethyl cellulose or HPC containing about 4.6 propoxy groups per glucose unit have been patented [882].

Hydroxyethyl cellulose has been frequently used to gel hydrazine and/or alkylhydrazines [883]. MHF-3 and hydrazine were gelled with a combination of 5% cellulose acetate and 1% HEC [884]. MHF-3 and hydrazine were gelled with a combination of 1.5% HEC and 6% colloidal silica [885].

Quaternary alkylammonium salts of polyacrylic acid (Carbopol-940) are effective gelling agents for hydrazine and hydrazine/alkylhydrazine mixtures [886]. See also [887, 888].

### 13.10.2 Metallized Gelled MMH Fuels

A metallized gelled MMH fuel can be made of MMH, 1–3% HPC, metallic fuel particles, and 0.05–0.3% dimethylurea [889, 890]. The metallic fuel particles can be aluminum, magnesium, boron, beryllium, zirconium, aluminum hydride, magnesium hydride, beryllium hydride, or zirconium hydride.

The most thoroughly examined metallized gelled MMH fuel was MICOM Gel, which consisted of 60% aluminum, 38% MMH, and 2% gellant/stabilizer [891]. MICOM Gel had a density of  $1.49 \text{ g/cm}^3$  at 298 K, suffered no settling after 30 min at 500 g acceleration in a centrifuge and in the DSC it may exotherm at 466 K (380 °F).

During the 1960s and 1970s, considerable effort was devoted to developing storable, gelled, hydrazine-based fuels containing various concentrations of aluminum powder. As general interest in these fuels subsided, the one factor that remained to be demonstrated was the storability of gelled fuels for periods of time exceeding 10 years.

Using nano-aluminum made by an exploding wire arc in vacuum (like ALEX) instead of micron-size aluminum powder was expected to produce better metallized gels in MMH or UDMH [892]. The gelling agent was still the same one claimed in earlier patents, HPC with dimethylurea. Numerous static test firings have been conducted with metallized MMH fuels and hypergolic oxidizers, but none of these combinations has found any flight application.

One of the potential benefits of gelled liquid fuels is that gelled liquid fuel propulsion systems in missiles meet Insensitive Munitions (IM-LOVA) safety criteria, whereas many of the solid propellant missiles currently in service do not. For example, an AQM-37A target drone rocket propulsion systems loaded with gelled bipropellants successfully passed the bullet impact, fast cookoff, and slow cookoff IM test requirements of MIL-STD 2105A. Extensive safety testing, in particular cookoff behavior, has been done with gelled propellant propulsion systems. There are many gelled propellant hazard evaluation reports, but in spite of all the widely publicized and favorable test data, gelled systems have not yet been deployed in the field.



### 13.10.3 Carbon-Loaded Gelled MMH Fuels

The disadvantage of metal-loaded MMH gels is the formation of metal oxides in the exhaust that leave a highly visible contrail wherever a missile propelled by such fuels is traveling. In a battlefield situation, that gives away the location of the launch site. A potential additive and gelling agent to MMH is finely divided carbon. Carbon suspensions would increase the density, density-specific impulse, and viscosity of loaded MMH gels, without leaving a tell-tale trace in the exhaust, because CO<sub>2</sub> and CO remain invisible.

Despite the availability of viscosity data, knowledge of the viscosity of a gel such as carbon-gelled MMH is not sufficient to predict the pressure drop across an injector in a rocket engine. The discharge coefficient is assumed and hardware must be fabricated and tested to verify the validity of the assumed discharge coefficient. The propellant formulator does not know the impact on the injector design when the viscosity profiles of gel fuels and oxidizers are altered. Without information about the impact of viscosity on the injector design, one cannot distinguish between hardware design problems and propellant formulation problems.

### 13.10.4 Gelled MHF-3 Fuels

MHF-3 can be gelled with the same gelling agents that also have been shown to work with MMH. Gelling agents proposed for MHF-3 include ethyl cellulose or colloidal silica [885], or fumed SiO<sub>2</sub> and HEC. Another metallized gelled MMH fuel was NOTSGEL-A. NOTSGEL-A consisted of MHF-3, aluminum, and gelling agents. A series of stable suspensions called NOTSGELS have been prepared by suspending metal additives in hydrazine fuel blends, such as MHF-3, and preparation, rheological properties, density, mechanical stability, thermal stability, storage stabilities, and shipboard storage tests were discussed. Other metallized MHF-3 gels contained boron powder instead of aluminum and their expulsion properties were tested as well [893].

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# Nitramines

## Nitramines

Nitramines are discussed here in the volume on liquid fuels because they are derived from amines that are also contained in this volume and because the addition of one or more nitramine groups to the hydrocarbon skeleton is not sufficient to bring the molecule to stoichiometric or positive oxygen balances. The oxygen balances of all nitramines in this chapter are negative.

This chapter starts with a description of the open-chain, acyclic, linear alkyl-nitramines. The solid cyclic nitramines of more practical importance, such as RDX, HMX, and higher molecular mass nitramines are discussed in Sections 13 and 15.1 and their applications will be discussed in a future volume on solid propellant energetic materials. The current section of this chapter in the initial sections deals only with aliphatic, linear, acyclic nitramines, and is only an incomplete overview over some of the properties of these compounds. Some of these compounds were only prepared for kinetic or molecular structural studies, not as rocket propellants. These nitramines are of less practical importance as rocket propellants than the RDX and HMX and HNIW-type heterocyclic nitramines. Although they have the word “amine” in them, they don’t behave like the amines that we have come to know as hypergolic fuels in other chapters of this volume. They are more acidic than alkaline (caustic).

## 1 Alkylnitramines (Alkylnitroamines)

Substitution of one or more hydrogens from the nitrogen in the amino group of primary amines by nitro groups converts alkyl amines from bases into acids due to the electron drain by the nitro group away from the amino nitrogen; thus, the remaining hydrogen is released more easily. If only one nitrogen-bound hydrogen atom is replaced in an alkylamine, one obtains alkylnitramines (alkylnitroamines), and the remaining nitrogen-bound hydrogen N—H is quite acidic and forms stable salts with alkali metals and alkaline earth metals and some organic bases. The simple ( $C_{\leq 3}$ ) nitramines are liquids and are not typically used as explosives or propellant ingredients. They are prepared mostly for kinetic studies of the nitramine decomposition mechanism or as building blocks for other energetic compounds. Higher molecular weight liquid nitramines with low vapor pressures are used as energetic plasticizers in solid propellants.

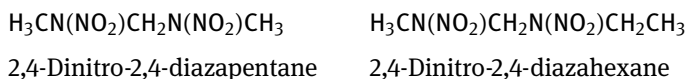


### 1.1 Nomenclature of Alkylnitramines

Both terms nitramine and nitroamine are in use in the propulsion community. Neither one is fully IUPAC nomenclature compliant. The shorter term nitramine is preferred here, but if one conducts a literature search, it helps to use both spellings, without and with the extra letter “o.”

The location of nitro groups on the nitrogens that are part of an aliphatic amine can be identified by numbers or by placing apostrophe signs on the nitrogens as in *N,N'*-dinitroalkylenediamines if the compound contains two C—N—C nitrogen atoms or *N,N',N''*-trinitroalkylenetriamines if the compound contains three C—N—C nitrogen atoms and each of them carries an —NO<sub>2</sub> group.

When numbers are used, which is the more systematic way of nomenclature, the numbers indicate the location of the nitrogen atoms in the hydrocarbon chain with the term “aza” such as in 2,4-diazapentane for methylene-di(aminomethyl)-amine and numbers indicate the location of the nitro groups as in 2,4-dinitro-2,4-diazapentane or 2,4-dinitro-2,4-diazaheptane.



If there are other substituents (azido, chloro, hydroxy, nitro, nitroxy) on the alkyl groups that are linked to the —N(NO<sub>2</sub>)— nitramine, they should be listed in accordance with IUPAC regulations in the sequence of priority or in alphabetical order.

The words nitro and aza are sometimes combined to form the term nitraza. To add to the confusion about proper nomenclature for nitramines, compounds like di-*n*-propylnitramine  $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{N}(\text{NO}_2)-\text{CH}_2-\text{CH}_2-\text{CH}_3$  were once supposed to be named di-*n*-propylnitramide for indexing purposes. This compound could also be called 4-nitrazaheptane. Nitramide (nitramine),  $\text{H}_2\text{NNO}_2$ , is the parent compound of all alkyl and aryl nitramines but it is unstable, as is its dinitro analog, dinitramide (dinitramine),  $\text{HN}(\text{NO}_2)_2$  [1].

### 1.2 Literature about Alkylnitramines

A historical summary on nitramines, a sometimes forgotten, but very useful resource collecting dust on some book shelves, included information on ethylenedinitramine, propylenedinitramine, pentaerythrityl tetranitramine, 1,2,3-trinitrazapropane, *N*-(β-nitroxyethyl)nitramine (NENA), *N*-(β-trinitroxyethyl)methylnitramine (MeNENA), *N*-(β-trinitroxyethyl)ethylnitramine (EtNENA), *N,N*-bis(β-nitroxyethyl)nitramine (DINA), and several similar compounds, including physical and sensitivity properties and methods of preparation [2]. Although very old, it still contains some useful information.

Aliphatic nitramino alcohols, 2-nitro-2-aza-alkan-1-ols,  $\text{RN}(\text{NO}_2)\text{CH}_2\text{OH}$ , as well as their ethers and esters, are useful intermediates in the synthesis of other nitramines. The general method for synthesis of nitramino alcohols is the reaction of primary nitramines with formaldehyde, with an *N*-alkyl-*N*-hydroxymethyl-nitramine as an intermediate [3].

Methods of making primary aliphatic nitramines were reviewed in a summary with 207 references covering literature up to the end of 1967 [4]. In that summary, in addition to the well-known traditional methods for the preparation of nitramines, little known methods for making them were examined and prospects for their further development were discussed.

Primary aliphatic nitramines can be prepared by a four-step procedure [5]: (1) acylation of the parent alkyl amine to form a urethane, (2) nitration of the urethane, (3) ammonolysis of the *N*-nitrourethane, and (4) acidification to release the free nitramine from its ammonium salt.

Synthetic routes to *N*-nitro compounds are summarized in an excellent book by Agrawal and Hodgson [6]. For instance, chapter 5, *Synthetic Routes to N-Nitro Functionality* (pp. 191–261, with 221 references) describes many synthetic routes to nitramines. Chapter 6 of the same book lists *Energetic Compounds 2: Nitramines and Their Derivatives* (pp. 263–291, with 92 references). It was found that only weakly basic amines can be nitrated under highly acidic conditions. Strong amine bases are largely protonated under such conditions with the positive charge on nitrogen repelling electrophilic nitrating species, whereas weaker bases have a higher proportion of free amine base present under the same conditions. Thus, very weakly basic amines or those with a poor affinity for protons are nitrated (“nitraminated”) more readily than stronger bases. See also [7].

### 1.3 Physical Properties of Alkylnitramines

As an introduction, here we summarize literature references that deal with physical properties of nitramines as a group instead of individual chemical compounds. This is an opportunity to study the effect of the location of the nitramine group in the molecule on the properties of the nitramine and compare the properties. Properties of some of the more important individual nitramine compounds will be summarized in subsequent sections.

#### 1.3.1 Melting Points of Alkylnitramines

It is important to know the exact melting points of nitramines because the melting points often coincide with incipient decomposition. Nitramines are used as explosives, energetic additives to propellants, and as energetic plasticizers. Most nitramines melt at very high temperatures that prevent their use as castable explosives. Most

nitramine explosive charges have to be pressed or plasticized to formulate a PBX which is easier to form to the desired shape of an explosive charge, such as in a shaped charge. Other nitramines are used as plasticizers and in this instance it would be desirable to have a low melting point to make the compounds processable at room temperature.

Melting points of nitramines can be predicted roughly by an empirical method based on molecular mass and molecular structure [8]. The average deviation of predicted temperature from measured temperatures was 5.4% (see also [9]). These methods are based on the elemental composition of energetic compounds and the contributions of some specific polar groups/structural moieties as additive and nonadditive functions, respectively.

### 1.3.2 Densities of AlkylNitramines

For some applications of alkylnitramines, such as in explosives, the density is an important performance parameter. Densities of alkylnitramines can be determined experimentally and several measured data for individual compounds are listed further down, or can be predicted theoretically. One of the first predictive methods was based on the group additivity method [10], comparing predictions for 173 energetic compounds with experimental results.

Correlations to predict density based on two different models were introduced for 82 different energetic compounds including 5 acyclic and cyclic nitramines, 9 nitrate esters, and 13 nitroaliphatic compounds whose molecules contained functional groups common to CHNO explosives [11–13]. Additional work expanded the list of energetic materials to 172 compounds [14]. Root mean square (rms) deviations for acyclic and cyclic nitramines were worse than for nitrate esters and nitroaliphatic explosives. This method is a simple procedure for calculating density of energetic compounds and gave good results as compared to group additivity methods for estimating the density of organic explosives.

Another efficient and convenient method for predicting the crystalline densities of energetic nitramines was established based on quantum chemical computations [15]. Density functional theory with four different basis sets and various semiempirical molecular orbital methods have been employed to predict the molecular volumes and densities of a series of energetic nitramines including acyclic, monocyclic, and polycyclic/cage molecules. The densities predicted by the semiempirical MO methods were all higher than the experimental data.

### 1.3.3 Thermodynamic Properties of Nitramines

#### 1.3.3.1 Enthalpies of Formation of AlkylNitramines

The enthalpies of formation of several acyclic alkylnitramines are listed in Table 1.

Enthalpies of formation of condensed phase nitramines, nitrate esters, nitroaliphatics, and related energetic compounds which contain at least one of the

**Table 1:** Enthalpy of formation of alkylnitramines.

| Compound name                                       | Gross formula                                                | Molecular mass |         | Enthalpy of formation |         |          |        |
|-----------------------------------------------------|--------------------------------------------------------------|----------------|---------|-----------------------|---------|----------|--------|
|                                                     |                                                              | g/mol          | mol/kg  | kcal/100 g            | kcal/kg | kcal/mol | kJ/mol |
| Ethyl nitramine                                     | C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 90.08          | 11.1012 | -22.85                | -228.5  | -20.58   | -86.1  |
| Propyl nitramine                                    | C <sub>3</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>  | 104.11         | 9.6052  | -25.79                | -257.9  | -26.85   | -112.3 |
| Diethyl nitramine                                   | C <sub>4</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 118.14         | 8.4645  | -21.57                | -215.7  | -25.48   | -106.6 |
| <i>N,N</i> -Dinitro-<br><i>n</i> -butylamine (DNBA) | C <sub>4</sub> H <sub>9</sub> N <sub>3</sub> O <sub>4</sub>  | 163.13         | 6.1301  | -1.3                  | -13     | -79.69   | -333   |
| Tetranitroethylene-<br>diamine                      | C <sub>2</sub> H <sub>4</sub> N <sub>6</sub> O <sub>8</sub>  | 240.09         | 4.1651  | +19.8                 | +198    | +824.7   | +3451  |

Data sources: [16,17]

functional groups including N—NO<sub>2</sub>, C—ONO<sub>2</sub> or nonaromatic C—NO<sub>2</sub> can be interpolated from a collection of measured heats of combustion of different energetic materials based on elemental composition and various structural and functional group parameters of CHNO energetic compounds [18]. Enthalpies of formation for 78 energetic compounds including nitramines, nitrate esters, or nitroaliphatics were calculated by an empirical formula and compared with experimental data. The root mean square (rms) deviations for 19 well-known energetic compounds were also compared with results from complex quantum mechanical computations which showed very similar rms deviations of 23.8 and 21.3 kJ/mol for empirical and quantum mechanical calculation methods, respectively. Predicted condensed-phase heats of formation for other 59 energetic molecules with complex molecular structures had significantly more scatter with an rms deviation of 42.3 kJ/mol from experimentally measured heats of formation. This method can provide reliable predictions for energetic compounds compared to the calculated outputs of the best empirical and complex quantum mechanical methods [19].

The enthalpies of formation in the standard (liquid or solid) state and in the gas phase of a series of secondary nitramines, including dimethyl-EDNA, were calculated on the basis of the experimental energies (enthalpies) of combustion and vaporization measurements [20]. The enthalpies of combustion of nitramines were calculated from the energies of combustion measured with a calorimeter and the enthalpies of vaporization were experimentally measured for 13 substances with a microcalorimeter. An analysis of the main thermochemical values (the enthalpies of formation in the gas phase and the enthalpies of evaporation) showed that the energy properties of the nitramine group are independent of the structure of the molecules studied and of the number of functional groups in them. Table 2 presents data for the heat of combustion, enthalpies of formation in the solid and vapor state and the heat of evaporation (sublimation) of dialkylnitramines. The enthalpies of formation of the alkylnitramine radicals made it possible to calculate the bond dissociation energies in the nitramines and their radicals of different structures. It was shown that all alkyl dinitramines stud-

Table 2: Standard enthalpies of formation of condensed phase and gaseous dialkylnitramines.

| Compound name                                                                    | $\Delta H_{\text{comb}}$ |              | $\Delta H_f^\circ$ |          | $\Delta H_{\text{evap}}^\circ$ |            | $\Delta H_f^\circ(\text{G}), \text{Experiment}$ |             | $\Delta H_f^\circ(\text{G}), \text{Calculation}$ |          |
|----------------------------------------------------------------------------------|--------------------------|--------------|--------------------|----------|--------------------------------|------------|-------------------------------------------------|-------------|--------------------------------------------------|----------|
|                                                                                  | kJ/mol                   | kcal/mol     | kJ/mol             | kcal/mol | kJ/mol                         | kcal/mol   | kJ/mol                                          | kcal/mol    | kJ/mol                                           | kcal/mol |
| $\text{Me}_2\text{NNO}_2(\text{C})^a$                                            | 1569 ± 1                 | 375.1 ± 0.3  | -75                | -17.9    | 67 ± 1                         | 16.1 ± 0.3 | -8 ± 2                                          | -1.8 ± 0.5  | -9                                               | -2.1     |
| $\text{Et}_2\text{NNO}_2(\text{L})^a$                                            | 2896 ± 2                 | 692.1 ± 0.5  | -107               | -25.6    | 47 ± 1                         | 11.3 ± 0.2 | -60 ± 3                                         | -14.3 ± 0.6 | -63                                              | -15      |
| $n\text{-Pr}_2\text{NNO}_2(\text{L})$                                            | 4199 ± 3                 | 1003.5 ± 0.6 | -163               | -39      | 57 ± 1                         | 13.7 ± 0.2 | -106 ± 3                                        | -25.3 ± 0.6 | -104                                             | -24.8    |
| $\text{MeN}(\text{NO}_2)\text{CH}_2\text{N}(\text{NO}_2)\text{Me}(\text{C})$     | 2272 ± 0.4               | 543.1 ± 0.1  | -51                | -12.3    | 103 ± 0.4                      | 24.5 ± 0.1 | 51 ± 1                                          | 12.2 ± 0.2  | 56                                               | 13.3     |
| $\text{MeN}(\text{NO}_2)(\text{CH}_2)_2\text{N}(\text{NO}_2)\text{Me}(\text{C})$ | 2909 ± 2                 | 695.3 ± 0.4  | -94                | -22.5    | 111 ± 1                        | 26.5 ± 0.3 | 17 ± 2                                          | 4 ± 0.5     | 13                                               | 3.1      |
| $\text{MeN}(\text{NO}_2)(\text{CH}_2)_6\text{N}(\text{NO}_2)\text{Me}(\text{C})$ | 5521 ± 3                 | 1319.5 ± 0.7 | -200               | -47.7    | 126 ± 2                        | 30 ± 0.4   | -74 ± 3                                         | -17.7 ± 0.8 | -69                                              | -16.6    |
| <i>N</i> -nitropiperidine(L)                                                     | 3304 ± 2                 | 789.6 ± 0.4  | -93                | -22.2    | 53 ± 1                         | 12.6 ± 0.2 | -40 ± 2                                         | -9.6 ± 0.5  | -40                                              | -9.5     |
| <i>N,N'</i> -dinitropiperazine(C)                                                | 2664 ± 2                 | 636.8 ± 0.4  | -53                | -12.7    | 103 ± 1                        | 24.6 ± 0.3 | 50 ± 2                                          | 11.9 ± 0.5  | 44                                               | 10.5     |

<sup>a</sup> (C) crystalline, (L) liquid  
Data source: [20]

ied decomposed via the radical mechanism with the elimination of the  $\text{NO}_2$  group at the first stage (Section 17.3). Therefore, if data on the enthalpies of formation in the gas phase are available, the enthalpies of formation of radicals of the  $\text{RN}\bullet\text{NO}_2$  type and the bond dissociation energies of the nearest environment of the  $\text{N}-\text{NO}_2$  group can be calculated.

### 1.3.3.2 Heats of Combustion of Nitramines

A similar method was described for estimating the gross and net (upper and lower) heats of combustion of energetic compounds, including acyclic and cyclic nitramines [21]. Elemental compositions as well as the presence of some specific polar groups and molecular fragments are important parameters in that model. A comparison of the predicted results with measured data showed that this method gave reliable predictions of heats of combustion with respect to group additivity method and computed values based on atom-type electrotopological state indices for several energetic compounds where the model can be applied.

### 1.3.3.3 Heats of Fusion of Alkylnitramines

A similar interpolation method was used for the prediction of the heats of fusion of nitramines [22]. Heats of fusion of some nitramines, averages formed from measured values gathered from several different sources in the literature, are summarized in Table 3.

**Table 3:** Heat of fusion of nitramines.

| Compound name                                                     | Heat of fusion |          |
|-------------------------------------------------------------------|----------------|----------|
|                                                                   | kJ/mol         | kcal/mol |
| 1,3-Dinitro-1,3-diazacyclobutane (TETROGEN)                       | 26.32          | 6.29     |
| 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)                      | 33.01          | 7.89     |
| 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX)              | 32.10          | 7.67     |
| 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW) | 42.70          | 10.21    |
| 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX)      | 36.11          | 8.63     |
| 2,4,6-Trinitro-2,4,6-triazaheptane (TNAHP)                        | 34.01          | 8.13     |
| 1,4-Dinitro-1,4-diazabutane (EDNA)                                | 23.24          | 5.56     |

Data source: [22] and from literature data

Similar methods for predicting the heat of sublimation of nitramines are based on empirical comparison and identification of the contributions by functional groups [23].

### 1.3.4 Molecular Structure of Nitramines

The high polarity of the nitro group in nitramines contributes to the relatively high melting points of nitramines and their tendency to form adducts among themselves

or with other compounds. Many studies have been conducted to better understand the relationship between molecular structure of nitramines and their melting points and thermal stability. Most nitramines start decomposing as soon as they melt.

The CNDO/2 electronic structure of nitramines was used to explain their tendency toward self-association and complexation with phenol via hydrogen bonding [24]. The charge distributions within 19 nitramines indicated that complexation involved the O atoms of the NO<sub>2</sub> group. The heat of self-association of secondary nitramines exceeded that of primary ones.

### 1.3.5 Bond Energies of N—N Bonds in Nitramines

An *ab initio* SCF computational study of six nitramines R<sub>1</sub>R<sub>2</sub>NNO<sub>2</sub> has been carried out with the objective of gaining a better understanding of how the properties (bond orders, dipole moment, and electrostatic potential) of the >N—NO<sub>2</sub> group are affected by the natures of R<sub>1</sub> and R<sub>2</sub> [25]. In most instances, the >N—NO<sub>2</sub> portions of the molecules are planar, due to the strong electron-withdrawing effect of the nitro group. One consequence is that the N—NO<sub>2</sub> bonds possess some degrees of double bond character. Their bond orders range from 1.36 to 1.63, with the weaker bonds corresponding to the more electron-withdrawing R<sub>1</sub> and R<sub>2</sub> group. The strong negative electrostatic potentials normally associated with the lone pairs of amino-type nitrogens are greatly weakened or eliminated in most of these molecules and several of them show evidence of significant hyperconjugation, resulting in enhanced acidity.

The structure, electron density distribution, energetic, and electrostatic properties of simple nitramine-based energetic molecules were determined using density functional theory [26]. In the NO<sub>2</sub> group substituted molecules, the N—N bond distance increased with the increase of NO<sub>2</sub> groups, whereas in C—N bonds, this effect is smaller, and the distances are almost equal. The topological analysis of electron density reveals that the electron density of C—N and N—N bonds are significantly decreasing with the increase of NO<sub>2</sub> groups in the nitramine molecules. The charge concentration decreases with the increase of NO<sub>2</sub> groups, which leads to weakening of the N—N bonds in the molecules. Computational chemistry may aid in the molecular design of more energetic and/or more stable nitramines [27].

### 1.3.6 Optical Properties of Nitramines

The UV absorption bands associated with nitramino groups have been investigated in a variety of compounds of known structure [28]. The groups may be characterized by the UV spectrum, and the number of each type of group present in a given compound may be estimated from an analysis of the shape and intensity of the absorption spectrum. These correlations have been applied to the elucidation of the structure of new compounds isolated in the course of an investigation of the chemistry of RDX.

A number of nitramines, including methylenedinitramine, ethylenedinitramine, nitrourea, nitrourethane, nitroguanidine, and RDX were prepared, purified and their UV and IR spectra examined for future analysis applications [29]

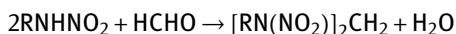
It was shown that the use of *ab initio* harmonic force fields, IR and Raman intensities, and depolarizations made possible a rigorous interpretation of the experimental spectra of the simplest aliphatic nitramines  $\text{H}_2\text{NNO}_2$ ,  $\text{CH}_3\text{NHNO}_2$ ,  $(\text{CH}_3)_2\text{NNO}_2$ , and their isotopomers [30, 31]. Some common patterns of the geometrical parameters, vibrational spectra and force fields of the simplest nitramines can be seen. The scale factors, which were introduced to correct for systematic errors by fitting the parameters to the observed frequencies, were mutually adjusted during the solution of the inverse vibrational problem and can be used to analyze spectra of larger molecules.

Vibrational spectra of several nitramines in the long-wave region ( $50\text{--}450\text{ cm}^{-1}$ ) show the self-association of nitramines [32]. The frequencies of intra- and intermolecular vibrations need to be separated to achieve a tentative assignment of the frequencies of self-associative complexes.

## 1.4 Chemical Properties of Nitramines

### 1.4.1 Reactions of Nitramines

The pre-eminent reaction of primary nitramines is that of salt formation with bases. There are hundreds of salts of nitramines described in the literature and many qualify as energetic materials. There are studies on the  $\text{pK}$  of nitramines as a functions of molecular structure, but those are mostly of academic interest and not reviewed here. Condensations of primary aliphatic nitramines with formaldehyde, aided by 90% sulfuric acid, lead to methylenebis(nitramines) [33]:



### 1.4.2 Decomposition of Nitramines

A review of the thermal decomposition of *N*-nitro-compounds based on a list of 108 literature references indicated that a nonchain radical mechanism with cleavage of the  $\text{N--NO}_2$  bond in the rate-determining step is the most probable mechanism [34]. A systematic summary of kinetic parameters of the thermal decomposition of *N*-nitro-compounds supported this conclusion.

A manometric method combined with GC and GC/MS was used for detailed analysis of kinetics and products of thermal decomposition for the homological series of primary nitramines in the melted state with general formula  $\text{R--NHNO}_2$ , where  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $n\text{-Pr}$ ,  $n\text{-Bu}$ ,  $i\text{-Bu}$ ,  $\text{tert-Bu}$ ,  $\text{O}_2\text{NHN}(\text{CH}_2)_3$ ,  $\text{NC}(\text{CH}_2)_2$ ,  $\text{O}_2\text{NHNCH}_2$ ,  $\text{O}_2\text{NHNCH}_2\text{N}(\text{NO}_2)\text{CH}_2$ , with the objective to determine how the nitramine structure influences decomposition rate [35]. Arrhenius equation parameters of the decomposition reactions were in the range  $E_a = 106.3\text{--}129.9\text{ kJ/mol}$  and  $\log A = 9.55\text{--}12.72$ . A linear correlation was found between the decomposition rate constant logarithm and nitramines  $\text{pK}_a$  and indicated that the primary step in nitramine thermal decomposition is ionization. The proposed mechanism of thermal decomposition was based on ionization and the following decomposition of a nitramine molecule, protonated by amino nitrogen.



Kinetics and activation parameters of the solution thermolysis of the three nitramines: dimethylnitramine, diisopropylnitramine, and *N*-nitropiperidine were determined over the temperature range 473–573 K (200–300 °C) in different solvents and compared to some isotope-labeled nitramines [36]. Each formed the corresponding nitrosamine as the only, or major, condensed phase product. For dimethylnitramine the products were completely characterized. The rate-determining step was homolysis, the N–NO<sub>2</sub> bond being the most obvious point for first attack.

The thermal decomposition of various types of nitramines (acyclic, cyclic, and multifunctional) was examined experimentally by analyzing 13 different nitramines in solution and in the melt [37, 38]. The nitramines included acyclic mononitramines [dimethylnitramine (DMN), diethylnitramine (DEN), dipropylnitramine (DPN), and diisopropylnitramine (DIPN)], cyclic mononitramines [*N*-nitro-piperidine (NPIP) and *N*-nitropyrrolidine (NPyr)], cyclic dinitramines [*N*-dinitropiperazine (pDNP), 1,3-dinitro-1,3-diazacyclopentane (DNI), and 1,3-dinitro-1,3-diazacyclohexane (mDNP)], and 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), hexanitro-hexaazaisowurtzitane (HNIW), and 1,3,3-trinitroazetidine (TNAZ). For the acyclic and cyclic mono- and di-nitramines, the corresponding nitrosamines were the only or major condensed-phase product. By comparing the results and the molecular structures of the nitramines, certain trends which increased the rate of decomposition were observed, such as (1) increasing carbon chain length, (2) increasing the number of nitramine functionalities, (3) situating the dinitramine groups in meta position to each other, and (4) decreasing the ring size (increasing the ring tension). Since all the nitramines exhibited first-order decomposition and activation energies in the range 188–230 kJ/mol (45–55 kcal/mol), it was postulated that the triggering mechanism remains N–NO<sub>2</sub> homolysis even in complex nitramines. The internal hydrogen transfer mechanism postulated for dimethylnitramine also appears to be operative in the more complex species.

The decomposition of most nitramines is dependent on pressure. The decrease of reaction rate with increasing pressure was presumed to indicate that homolysis of the N–NO<sub>2</sub> bond is the rate-determining step of the process [39].

DSC thermograms of eight linear and seven cyclic nitramines predominantly with methylenenitramine groupings were measured, and a linear relationship was found between the onset of endotherm or peak temperatures of melting of these compounds and the melting points of their aliphatic structural analogues (i.e., hydrocarbon homomorphs with no heteroatoms) [40]. A similar relationship between the corresponding heats of fusion was discovered. On the basis of these facts, the melting points and heat of fusion were predicted for a series of cyclic nitramines.

The mechanism of decomposition of nitramines has been studied theoretically using quantum chemical methods to calculate the heats of formation and free energies of the nitramines H<sub>2</sub>NNO<sub>2</sub> and CH<sub>3</sub>NHNO<sub>2</sub> as well as of some molecular radical species which might arise from the decomposition process [41]. The thermochemical properties of transition state activated complexes, the bond energies, and dissociation en-

ergies obtained from these calculations were used to determine decomposition pathways of more important propellant nitramines such as HMX and RDX. The results indicated that at high temperatures, bond fission of the nitro group (with a bond energy of  $\sim 200$  kJ/mol) should play an important role as the initial decomposition step. At lower temperatures, the five-centered HONO elimination with a dissociation energy of  $\sim 170$  kJ/mol is possible but has a small pre-exponential factor compared to experimental decomposition rates. Another decomposition mechanism, involving attack by autocatalytic generated H atoms, which provides a lower energy pathway ( $\sim 128$  kJ/mol) with nitrosamines as intermediates can lead to  $N_2O$  formation. The H atom attack can also lead to HCN and  $NO_2$  formation through pathways analogous to the initial N— $NO_2$  bond breaking process.

The thermal decomposition of 1,4-dinitropiperazine and 1,4,4-trinitropiperidine was compared to that of other nitro compounds and difluoroamino compounds [42]. Geminal bis(difluoroamino) compounds appeared to be somewhat more stable than the corresponding *gem*-dinitro compounds, although they released more heat during decomposition. The decomposition of *gem*-bis(difluoroamino) and *gem*-dinitro compounds exhibited similarities. Both experienced loss of one geminal  $NX_2$  group followed by the rearrangement of the remaining  $-NX_2$ . Where a nitramine functionality was present, the nitroso analogue was observed as a major decomposition product.

A critical review of the published data on the mechanism of decomposition of secondary nitramines concluded that the first step of decomposition always includes cleavage of the N— $NO_2$  bond, which is followed by various secondary reactions and sometimes by chain reaction processes [43].

A method to predict activation energies of thermal decomposition of nitramines by interpolation showed that the activation energies of acyclic nitramines can be expressed as a function of optimized elemental CHNO composition [44]. The method was applied to cyclic nitramines that contain more than five members. The root mean square (rms) and the average deviations were 5.67 and 3.98 kJ/mol, respectively, for 14 known nitramines with different molecular structures. The method was also tested with moderate success for 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW) and 4,10-dinitro-2,4,6-tetroxa-4,10-diaazaisowurtzitane (TEX).

### 1.4.3 Analysis of Nitramines

Analytical methods for nitramines are important for quality control of nitramine energetic materials and for the detection of traces of nitramines in places where they do not belong, e.g., the baggage of airline travelers. Nitramines can be analyzed by thin layer chromatography and the separated spot can be made visible by spraying with diphenylamine and illuminating with UV for 30 min. [45].

A review paper summarized the available analytical methods in the open literature for the determination of some aliphatic and cyclic nitramines [46]. Since the nitramines are found in complex matrices and/or in very low concentrations, an ex-

traction step is often necessary before their determination. Liquid–liquid extraction using dichloromethane and solid phase extraction with an activated carbon-based adsorbent have been the two most common extraction/trapping methods.

### 1.5 Explosive Sensitivity of Nitramines

A relationship was found between the 50% initiation probability drop weight impact sensitivity of 16 nitramines, on the one hand, and heats of fusion,  $^{15}\text{N}$  NMR chemical shifts of aza atoms in reaction centers, parameters of low-temperature thermolysis, and oxygen balances of nitramines studied, on the other hand [47]. Several drop weight impact sensitivity values were predicted for other nitramines. The impact sensitivity of nitramine molecules depends on the electronic configuration within their reaction centers and on their conformational stability and intensity of their intermolecular interactions. The reaction centers are the same as in the case of initiation of the nitramines by explosive shock.

For groups of nitramines and nitroaliphatics, taken separately, it was shown that shock sensitivity is related to the strengths of all  $\text{N}-\text{NO}_2$  and/or  $\text{C}-\text{NO}_2$  bonds in the molecules, taken in conjunction with their overall sizes [48]. The reciprocals of the bond lengths were used as measures of bond strengths, while molecular mass was taken as the indicator of molecular size. Linear correlation coefficients of 0.94 and 0.98 were obtained, respectively, for nitramines and nitroaliphatics of a variety of structural types. These results are indicative of the importance of the  $\text{N}-\text{NO}_2$  and  $\text{C}-\text{NO}_2$  bonds in the shock-induced decomposition of nitramines and nitroaliphatics.

The electrostatic discharge sensitivity of nitramines may be related to their detonation pressure [49] or their molecular structure [50]. Spark sensitivity of explosives is an important area of investigation. Numerous accidental explosions have been triggered by an electrostatic discharge. Therefore, correlations were sought between the spark sensitivity and certain molecular orbital characteristics of some nitramine type explosives, such that the spark sensitivity of yet untested energetic materials could be predicted from the known properties or similar, related chemical compounds [51]. As a start of that project, semi-empirical and DFT calculations were carried out and investigations revealed that the nitramines undergo decomposition in the electric field mainly via their anionic states.

A simple model for prediction of the relationship between friction sensitivity and activation energy of thermolysis of cyclic and acyclic nitramines on the basis of their molecular structures assumed that friction sensitivity of an energetic  $\text{CHNO}$  compound can be expressed as a function of activation energy of thermolysis and the contribution of specific molecular structural parameters [52]. For a group of 21 nitramines with different molecular structures, the root mean square and the average standard deviations were 14.2 and 17.8 N, respectively, as compared to experimental values.

## 2 Mononitramines

This section deals mostly with specific aliphatic nitramines that contain only one nitro group on the amino group. The name dinitramine can be ambiguous, as the two nitro groups can be either attached both to the same nitrogen that was once an amine, or they can be attached to two separate nitrogen atoms, usually at the end of an alkane chain. There are only few aromatic nitramines of significance. Tetryl is one of them. Isocyclic, alicyclic, and heterocyclic nitramines are discussed in Sections 11 through 16.

This first section is on open-chain (acyclic, linear) alkylnitramines (also called alkylnitroamines), such as diethylnitramine  $\text{C}_2\text{H}_5\text{N}(\text{NO}_2)\text{C}_2\text{H}_5$ . These nitramines can be used as model substances for the study of decomposition of other, more complex nitramines. The higher molecular mass open-chain alkylnitramines can be used as plasticizers for double-base solid propellants.

### 2.1 Methylnitramine and Dimethylnitramine

#### 2.1.1 Methylnitramine

Methylnitramine, also known as  $\text{H}_3\text{CNHNO}_2$ ,  $\text{C}_1\text{H}_4\text{N}_2\text{O}_2$ , *N*-methylnitramine, methyl-nitroamine, monomethylnitramine; methanamine, *N*-nitro-; CAS RN [598-57-2], is unstable and shock sensitive. Methylnitramine forms clear, needle-shaped crystals, melting at 311 K (38 °C), which start to decompose about 433 K (160 °C). Other sources give the melting point as 308 K (35 °C) and the decomposition temperature as 359 K (86 °C). It is an especially effective sensitizer for explosives because it has an explosive group ( $-\text{NHNO}_2$ ) which is resistant to hydrolysis in solution. It is very soluble in water and it is underoxidized with an oxygen balance of  $-42\%$ .

Methylnitramine can be prepared by nitrating dimethylurea with a mixture of sulfuric acid and nitric acid with subsequent separation of 1,3-dimethyl-1,3-dinitrourea by the use of a solvent with recovery of a dimethyldinitrourea in organic solvent, with hydrolysis of the dimethyldinitrourea with hot water to yield methylnitramine [53]. Methylnitramine decomposes explosively when in contact with concentrated sulfuric acid. Another method for preparation of alkylnitramines starts with nitration of alkyl amides like *N*-monosubstituted formamide [54]. This method is also suitable for synthesis of methylenedinitramine from a bis-amide. Another method for the preparation of methylnitramine is the addition of *N,N*-dimethyl-*N,N*-dinitrooxamide to a solution of ammonia at 273 K (0 °C).

Methylnitramine,  $\text{CH}_3\text{NHNO}_2$ , or *aci*-methylnitramide has been suspected to be an intermediate in the thermal decomposition of methylammonium nitrate [55]. If methylnitramine is an intermediate, the weakest bond ( $\text{N}-\text{NO}_2$ ) should break first.

Methylnitramine has been investigated mostly as a model substance for other (more stable) nitramines and as an intermediate in the decomposition of RDX or HMX.

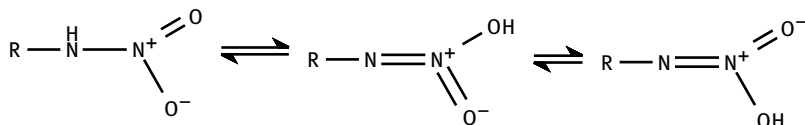
It was studied mostly in the vapor phase and due to its hazardous nature it is rarely prepared in the liquid state. Some of the studies were strictly theoretical in nature and avoided handling the material. The principal reactions of the primary event of *N*-methylnitramine unimolecular decomposition have been investigated, and the results indicated various reaction mechanisms [56].

Calculations of the complex potential energy surface and reaction mechanisms for the unimolecular isomerization and decomposition of methylnitramine indicated that there are four low-lying energy routes: (1) the N–N bond fission pathway; (2) a sequence of isomerization reactions via  $\text{CH}_3\text{NN}(\text{OH})\text{O}$ ; (3) the HONO elimination pathway; (4) the isomerization and the dissociation reactions via  $\text{CH}_3\text{NHONO}$  [57]. The rate constants of each initial step (rate-determining step) for these channels and the Arrhenius expressions of the channels over the temperature range 298–2000 K were calculated. The calculated overall rate constants was  $6.9 \times 10^4$  at 543 K, which was in good agreement with experimental data. Based on the analysis of the rate constants, the dominant pathway should be the isomerization reaction to form  $\text{CH}_3\text{NN}(\text{OH})\text{O}$  at low temperatures, while the N–N bond fission and the isomerization reaction to produce  $\text{CH}_3\text{NHONO}$  are expected to be competitive with the isomerization reaction to form  $\text{CH}_3\text{NN}(\text{OH})\text{O}$  at high temperatures.

The dissociation energies of N–NO<sub>2</sub> bonds of primary and secondary *N*-nitramines have been investigated using nonempirical methods and DFT methods [58]. The basic tendencies in the changes of the geometrical and electronic structures, formation enthalpies, and dissociation energies were then analyzed in a homologous series of nitramines differing only by  $-\text{CH}_2-$ . Various alternative mechanisms of the gas-phase monomolecular thermal decomposition have been studied based on the example of *N*-methylnitramine decomposition. Decomposition by way of the aci-form formation and its further multistage destruction is the most probable way of decomposition of the primary *N*-nitramines.

Stable salts are formed between monomethylnitramine (methylnitroamine) and alkali or alkaline earth metals. The IR and Raman frequencies of the  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Me}_4\text{N}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Mg}^{2+}$  salts of  $\text{MeNHNO}_2$  were not appreciably affected by the cation or by transition from the crystalline state to solution [59].

*N*-methylnitramine forms needle-shaped orthorhombic crystals. The crystal structure of methylnitramine is space group *Pbca* with the cell parameters of  $a = 8.865(4) \text{ \AA}$ ,  $b = 6.673(3) \text{ \AA}$ ,  $c = 11.324(6) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 669.9(6) \text{ \AA}^3$ ,  $Z = 8$ , and  $\rho_{\text{calcd.}} = 1.508 \text{ g/cm}^3$ . *N*-Methylnitramine is a weak acid with  $\text{p}K_{\text{a}} = 6.0$ . Three tautomeric forms are responsible for the acidity of *N*-methylnitramine.



*N*-methylnitramine forms alkali metal, earth-alkaline metal, and transition-metal salts, and also forms stable salts with ammonia, hydrazine, hydroxylamine, guanidine, and aminoguanidine [60, 61]. The Mannich reaction of *N*-methylnitramine with formaldehyde yields 2-nitro-2-azapropanol, which can be used for the synthesis of other energetic compounds.

### 2.1.2 Dimethylnitramine

Dimethylnitramine, also known as *N*-nitrodimethylamine, 2-nitro-2-azapropane, *N,N*-dimethylnitramine,  $\text{H}_3\text{C-N}(\text{NO}_2)\text{-CH}_3$ , DMN, DMNA, CAS RN [4164-28-7] is one of the simplest alkylnitramines with a melting point of 322–326 K (49–53 °C) and a density of 1.109 g/cm<sup>3</sup>.

Dimethylnitramine can be prepared by adding a highly concentrated (90%) dimethylammonium nitrate/water solution to acetic anhydride containing 1% hydrochloric acid as a catalyst at a temperature of 313 K (40 °C). Excess acetic anhydride must be converted to acetic acid and removed by distillation. The yield of DMN is 70% as based on dimethylammonium nitrate. Dimethylnitramine can also be prepared by reaction of nitryl chloride with lithium dimethylamide.

Dimethylnitramine is closely related to dimethylnitrosamine, a potent carcinogen that can form during pyrolytic decomposition of cured meat and some vegetables. Both are the most troublesome products of partial combustion and environmental deterioration of unsymmetrical dimethylhydrazine (UDMH). UDMH was once made by reduction of dimethylnitrosamine and could also be made by reduction of dimethylnitramine. It was stated that dimethylnitramine as the intermediate for UDMH production is less toxic than dimethylnitrosamine.

The heat of combustion of DMN is  $376.1 \pm 1.0$  kcal/mol determined calorimetrically, which corresponds to a standard enthalpy of formation of  $-71.1 \pm 4.2$  kJ/mol ( $-17.0 \pm 1.0$  kcal/mol) [62]. From the same source, the heat of combustion of diethylnitramine is  $-692.4 \pm 2.0$  kcal/mol determined calorimetrically, which corresponds to a standard enthalpy of formation of  $-105.8 \pm 8.4$  kJ/mol ( $-25.3 \pm 2.0$  kcal/mol).

Dimethylnitramine melts at 329–330 K (56–57 °C). In the DSC, DMN begins to melt at 328.3 K with a peak at 330.9 K and the heat of fusion is 17.24 kJ/mol [40]. The density of DMN is 1.090 g/cm<sup>3</sup> and its enthalpy of formation is  $-72.4$  kJ/mol ( $-17.3$  kcal/mol =  $-192$  cal/g).

Because DMN is one of the simplest nitramines, it often has been studied as a model compound to elucidate the decomposition mechanisms of other more complex and economically more important nitramines. The kinetics and mechanism of the thermal decomposition of DMN and dimethylnitrosamine have been studied at high temperatures in a shock tube with IR, laser, and UV diagnostics and at lower temperatures in a static system [63]. The understanding of the chemistry of these model compounds is an important step toward a better understanding of the complex

mechanism of decomposition and burning characteristics of larger nitramines such as RDX and HMX.

The kinetics and mechanism of the thermal decomposition of DMN have been investigated at low temperatures (466–524 K) in a static system and at high temperatures (800–1200 K) in a shock tube with IR laser and UV diagnostics [64]. Detailed kinetic modeling has shown that the key initiation step is the dissociation of DMN into  $\text{NO}_2$  and the dimethylamino radical. The more energetic steps leading to CO were found to be a series of chain reactions starting from methyl radicals. One can extrapolate from this to a reaction scheme for the vapor phase thermal decomposition of RDX.

Dimethylnitramine has been extensively studied as a simple analog expected to exhibit some of the reactions important in cyclic nitramine decomposition. Much of the work on decomposition of nitramines centered around the scission of the N– $\text{NO}_2$  bond. The initial breakage of the N– $\text{NO}_2$  bond can be initiated thermally or, more selectively, by UV photolysis using monochromatic radiation. As a prototype for more complex nitramines, the gas-phase decomposition of DMN was studied in three laser-pyrolysis systems [65]. Results in two of these systems, unlike those reported in the literature, indicated that a nitro–nitrite rearrangement pathway is competitive with the expected (and previously invoked) N– $\text{NO}_2$  bond scission. This rearrangement pathway has been obscure because it can lead to some of the same products that are yielded by the bond scission route. The principal evidence for nitro–nitrite rearrangement includes the following: Arrhenius parameters for decomposition that are two orders of magnitude too low; molecular-beam, mass-spectrometrically sampled laser pyrolysis studies; and *ab initio* calculations that found a rearrangement pathway at slightly lower energy than that of simple bond scission. These results suggested that such rearrangement pathways may be a common feature of nitramine decomposition.

Tunable laser-induced fluorescence was used to probe the formation of ground state  $\cdot\text{OH}$ , NO and  $\text{NO}_2$  photoproducts [66]. These results provided new insight into the physical and chemical processes that occur in the decomposition of DMN.

For a comparison of thermally and photolytically initiated decomposition of DMN, the UV absorption of gas phase, room temperature dimethylnitramine was measured from 185 to 325 nm [67]. The spectrum had two distinct features whose maxima occurred at 193 nm (6.4 eV) and 230 nm (5.4 eV). Absorption cross-section at selected wavelengths between 185 and 325 nm were derived in accordance with Lambert–Beer law.

The photolysis of DMN was studied as a simple analog expected to exhibit some of the same processes important in cyclic nitramine decomposition [68]. The source of UV monochromatic radiation at 248 nm was an excimer laser.

A comprehensive scheme of the thermolysis mechanisms of methylnitramine and dimethylnitramine was derived using *ab initio* calculations, and the thermochemical preference of these or other possible decomposition reaction pathways were predicted and most energy-favored routes have been proposed [69, 70].

## 2.2 Ethylnitramine and Diethylnitramine

Dialkylnitramines can be prepared by reaction of a dialkylcarbonyl halides  $R_2NC(O)X$  with nitric acid in trifluoroacetic acid anhydride [71] or by reaction of dialkylcarbonyl halides with silver nitrate (only 28% yield). Diethylnitramine,  $(CH_3CH_2)_2NNO_2$ , crystals melt at 376–378 K (103–105 °C), have a refractive index of  $n_D^{25} = 1.4528$ , a density of 1.057 g/cm<sup>3</sup>, and can be purified by sublimation at 318 K at 80 Pa (45 °C at 0.6 mm Hg) or 388–391 K at 6.6 kPa (115–118 °C at 50 mm Hg). The heat of combustion of ethylnitramine, *N*-nitroethylamine,  $C_2H_5NHNO_2$ , is 1559 kJ/mol (372.5 kcal/mol) [72].

Diethylnitramine is the parent compound of a more energetic nitramine, diethylnitramine dinitrate (dinitroxyethyl nitramine, DINa) which is described in Section 4.8. Diethylnitramine  $(CH_3CH_2)_2NNO_2$  was chosen as a reference compound for density functional theory calculations to predict the heats of formation (HOFs) for various heterocyclic nitramine and  $R-NF_2$  compounds via designed isodesmic reactions [73].

## 3 Dinitramines

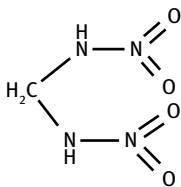
The name dinitramine is ambiguous because it does not identify whether the two nitro groups are attached to the same nitrogen (as in dinitramidic acid) or separate nitrogen atoms as discussed here. We should change the heading of this section to read “*N,N'*-Dinitramines” to make it clear that the compounds described in this category contain two nitrogens and each of those carries only one nitro group with an  $N-NO_2$  linkage.

For some applications of nitramines, such as plasticizers in double-base propellants, a lower melting point would be desirable. Lower melting points can be achieved by mixing several nitramines. Binary phase diagrams were measured by DSC for mixtures of methylnitramine with 2,4-dinitro-2,4-diazapentane and showed a eutectic temperature of 285.1 K at a eutectic composition with a methylnitramine mol fraction of 0.565, and a eutectic temperature of 280.3 K for a mixture of methylnitramine with 2,4-dinitro-2,4-diazahexane and a methylnitramine mol fraction of 0.653 [74]. For both systems simple eutectic behavior was observed.

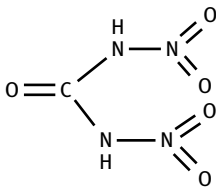
### 3.1 Methylenedinitramine

Methylenedinitramine; also known as methanediamine, *N,N'*-dinitro-; *N,N'*-dinitromethylenediamine, 1,3-dinitro-1,3-diazapropane, *N*-(nitramidomethyl)nitramide, MEDINA,  $(NO_2)NHCH_2NH(NO_2)$ ,  $CH_2N_6O_4$ , CAS RN [14168-44-6],  $M = 136.067$  g/mol, is not thermally stable enough to be used as propellant or explosive ingredient [75]. It melts at 375 K (102 °C) with considerable decomposition [76]. The structure is similar to that of dinitrourea, CAS RN [176501-96-5], except the center of the molecule is formed by a methylene  $>CH_2$  group instead of a carbonyl  $>C=O$  group.



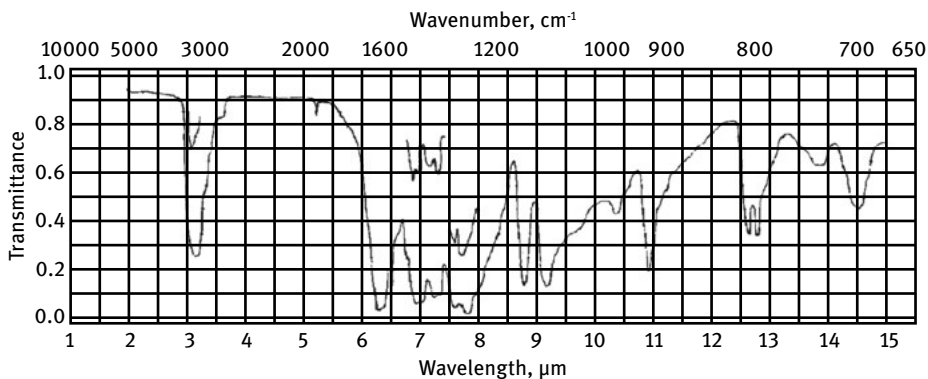


Methylenedinitramine

*N,N'*-Dinitrourea

Methylenedinitramine forms orthorhombic crystals with the unit cell parameters  $a = 9.06 \text{ \AA}$ ,  $b = 11.33 \text{ \AA}$ ,  $c = 5.09 \text{ \AA}$ ,  $Z = 4$ , and a measured density of  $1.735 \text{ g/cm}^3$ , compared to the calculated XRD density of  $1.72 \text{ g/cm}^3$  [77]. Nitration of a suspension of methylenediformamide in acetic anhydride with WFNA produced methylenedinitroformamide which on hydrolysis gave methylenedinitramine [78]. Methylenedinitramine can be stabilized by addition of picric acid or styphnic acid [79]. Methylenedinitramine is a useful intermediate in the synthesis of other nitramines, including cyclic nitramines [80].

Methylenedinitramine is an intermediate product of biodegradation of RDX. It forms stab-sensitive salts with heavy metal cations. The related compound *N*-methyldinitramine  $\text{H}_3\text{CN}(\text{NO}_2)_2$ , is discussed in Section 17. An IR spectrum of methylenedinitramine is shown in Figure 1

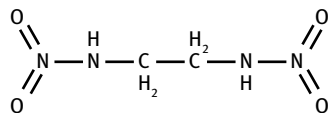


**Figure 1:** Infrared spectrum of methylenedinitramine. (Reproduced and modified from [81].)

### 3.2 Ethylenedinitramine

Ethylenedinitramine, also known as ethylenedinitroamine, *N,N'*-dinitroethylene diamine, tetranitroethylenediamine, *N*-(2-nitramidoethyl)nitramide, dinitroethylenediamine, EDNA, Halite, Haleite, 1,4-dinitro-1,4-diazabutane,  $(\text{CH}_2-\text{NH}-\text{NO}_2)_2$ ,

$\text{C}_2\text{H}_6\text{N}_4\text{O}_4$ , CAS RN [505-71-5],  $M = 150.0934 \text{ g/mol}$ , is a dibasic acid and forms salts with alkali metals and many organic nitrogen bases.



Ethylenedinitramine

Its applications as an energetic and nitrogen-rich additive in rocket propellant formulations will be summarized in a future set on solid propellants. As a military explosive, it possesses an advantage of combining high brisance with a comparatively low sensitivity. It was used together with TNT during World War II but is no longer used today. Another characteristic of EDNA is its relatively low explosion temperature.

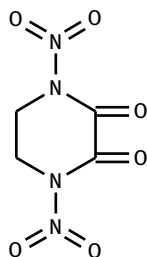
Ethylenedinitramine is a relatively economic explosive. With an oxygen balance of  $-32\%$  for complete combustion to  $\text{CO}_2$ , it would require additional oxidizer to make full use of its fuel value in a rocket propellant.

### 3.2.1 Preparation of Ethylenedinitramine

Ethylenedinitramine can be prepared by nitration of ethyleneurea with mixed acid, to yield dinitroethyleneurea which then liberates carbon dioxide and forms ethylenedinitramine. The starting reactant ethyleneurea is prepared by reacting ethylene diamine with ethyl carbonate under elevated pressure.

Various methods were investigated for preparation of EDNA from ethylenediamine. EDNA has been prepared previously by hydrolysis of 1,3-dinitro-2-imidazolidone, which can be made by nitration of 2-imidazolidone. 2-Imidazolidone can be prepared by heating a mixture of anhydrous ethylenediamine and diethyl carbonate in a sealed tube, but the yield may be low and the product may be difficult to purify. Moreover, the preparation of anhydrous ethylenediamine is a tedious process. Instead, 2-imidazolidone can be obtained in 63% yield (based on the diethyl carbonate) from commercial aqueous 60–65% ethylenediamine without the use of a sealed-tube reaction [82]. A mixture of excess aqueous ethylenediamine and diethyl carbonate was heated, the excess reagents and water were removed by distillation, and the residue, presumably the ethylenemmonourethane  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCOOC}_2\text{H}_5$ , was cyclized by the action of heat. In another method ethylenebisurethane, prepared from aqueous ethylenediamine and ethyl chlorocarbonate, was nitrated with 98% nitric acid, and the dinitroethylenebisurethane  $[\text{CH}_2\text{N}(\text{NO}_2)\text{COOC}_2\text{H}_5]_2$  was converted into EDNA in an overall yield of 87% by alkaline hydrolysis or by ammonolysis. The rapid rate of the reaction with aqueous ammonia at room temperature is noteworthy: in a few minutes the carbethoxy groups were removed and the water-soluble ammonium salt of EDNA was formed. The nitration of cyclic ethyleneoxamide with 98%  $\text{HNO}_3$  in acetic anhydride at 273–278 K ( $0\text{--}5^\circ\text{C}$ ) gave the cyclic dinitro

derivative *N,N'*-dinitropiperazine-2,3-dione, 1,4-dinitro-2,3-piperazinedione, CAS RN [165896-98-0], in good yield in the form of glistening prisms with m.p. 470–471 K (197–198 °C).



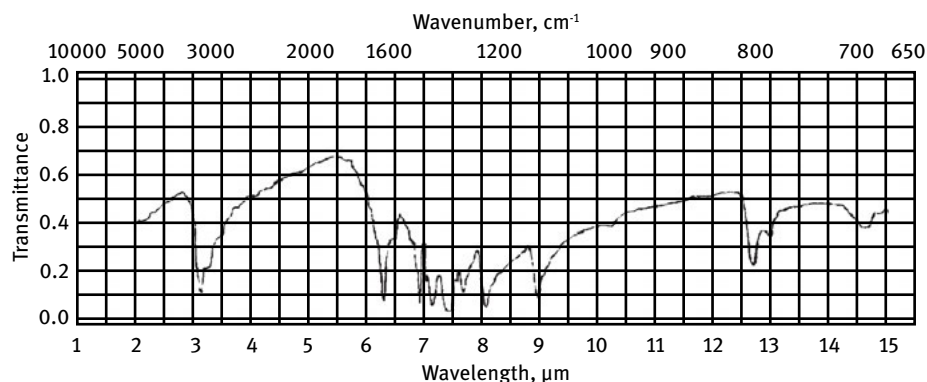
*N,N*-Dinitropiperazinedione

### 3.2.2 Physical Properties of Ethylenedinitramine

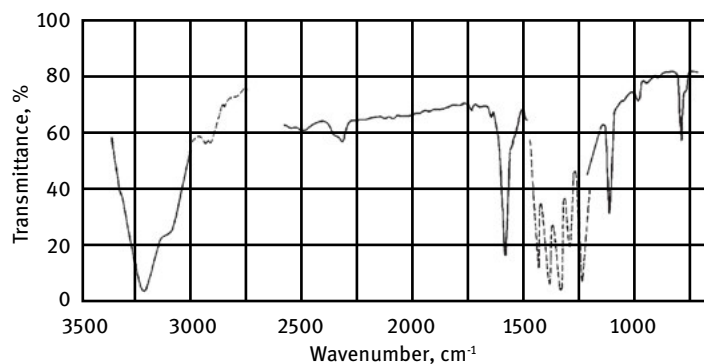
The physical properties of ethylenedinitramine are summarized in Table 4. An exhaustively detailed summary of properties of EDNA is provided in *Fedoroff Encyclopedia of Explosives*, volume 6 [83]. It also has information regarding properties of EDNA salts on page E243–E244. These salts can also be used as explosives or propellant ingredients. The US Army Material Command's *Engineering Design Handbook* contains a complete set of data on EDNA performance as an explosive [84].

**Table 4:** Physical properties of ethylenedinitramine.

| Property                     | SI units                | Other units                |                     | References |
|------------------------------|-------------------------|----------------------------|---------------------|------------|
| Molecular mass               | 150.0934 g/mol          | 6.662 mol/kg               | —                   | [85]       |
| Melting point                | 449.3 K                 | 176.2 °C (dec.)            | 349.2 °F (dec.)     | [86]       |
|                              | 447.6–448.1 K           | 174.5–176 °C               | —                   | —          |
|                              | 449.3 K                 | 176.2 °C                   | —                   | [87]       |
| Density at 25 °C             | 1.71 g/cm <sup>3</sup>  | 1.71 g/cm <sup>3</sup>     | —                   | [86]       |
| Density                      | 1.749 g/cm <sup>3</sup> | 0.0632 lb/in. <sup>3</sup> | —                   | [17]       |
| Enthalpy of formation        | –103.8 kJ/mol           | –165.3 cal/g               | –24.81 kcal/mol     | [86]       |
|                              | = –691.6 kJ/kg          |                            |                     |            |
|                              | –99.22 kJ/mol           | –158 cal/g                 | –23.71 kcal/mol     | [17]       |
|                              | –104.6 ± 1.7 kJ/mol     | –166.5 ± 2.7 cal/g         | –25 ± 0.40 kcal/mol | [87]       |
| Isochoric heat of combustion | 1552 kJ/mol             | 370.9 kcal/mol             | —                   | [72]       |
|                              | 1506 ± 1.7 kJ/mol       | 360 ± 0.40 kcal/mol        | 2.4 kcal/g          | [87]       |
|                              | 1549 kJ/mol             | 370.3 kcal/mol             | —                   | [88]       |



**Figure 2:** Infrared spectrum of ethylenedinitramine. (Reproduced and modified from [81].)



**Figure 3:** Infrared spectrum of ethylenedinitramine. (Reproduced and modified from [29].)

Two very similar IR spectra for EDNA from two different sources are shown in Figures 2 and 3.

Ethylenedinitramine and tetramethylenedinitramine are homologues and their IR spectra are very similar. The IR spectra of crystalline ethylenedinitramine, tetramethylenedinitramine, and their perdeuterated derivatives were measured and assignments of the frequencies for the NH valence and deformation vibrations were made based on the isotope effect [89]. The bands in the IR spectra of these two compounds that experience the maximum shift as a result of deuteration must belong to the N—H bond. The bands at 1600 cm<sup>-1</sup> were once assigned to asymmetric valence vibrations of the nitro group which is incorrect.

Vibrational spectra of *N,N'*-dinitroalkylenediamines of the O<sub>2</sub>NNH(CH<sub>2</sub>)<sub>n</sub>NHNO<sub>2</sub> type for *n* = 1, 2, and 3 were measured for the natural nitrogen distribution and <sup>15</sup>N isotope-labeled compounds in the nitro group and deuterium-substituted amino

groups [90]. The isotope shifts in the absorption vibrational spectra allowed a more reliable assignment of most of the absorption bands.

The vibrational spectra of EDNA salts of the  $M^+ [^-N(NO_2)CH_2CH_2N(NO_2)^-]M^+$  ( $M = Li, Na, K, NH_4$ ) and  $[^-N(NO_2)CH_2CH_2N(NO_2)^-]M^{++}$  ( $M = Mg, Ni$ ) type were examined in aqueous solutions and in the solid state [91]. The frequencies of the nitramine moiety did not depend on the cation it was paired with, except for the  $Ni^{2+}$  salt, which may be coordinated differently. The differences in the IR spectra of the solid samples and the Raman spectra of solutions of the nickel salt and other salts of *N,N'*-dinitroethylene-diamine can be explained by the difference in the coordination of the cations.

The molar heat capacity of EDNA in the range from 200–448 K (–73 to +175 °C) can be described by the following linear equation

$$C_p = (3 \pm 0.8) + (0.13 \pm 0.003) \times T$$

where  $C_p$  is the molar heat capacity in  $\text{cal mol}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin [87]. The molar heat capacity of EDNA at 298 K is  $175.3 \text{ J mol}^{-1} \text{K}^{-1}$  ( $41.9 \text{ cal mol}^{-1} \text{°C}^{-1}$ ).

### 3.2.3 Chemical Properties of Ethylenedinitramine

EDNA is a dibasic acid and forms salts with alkali metals and many organic nitrogen bases. It is insoluble in ether, sparingly soluble in water and alcohol, and soluble in dioxane and nitrobenzene. EDNA is not hygroscopic. EDNA melts at 448 K (175–176 °C) and in the DTA thermogram, the maximum of the exotherm peak is at 475 K (202 °C) [92].

Methylene dinitramine,  $CH_2(NHNO_2)_2$ , MEDINA, and its homologue ethylene dinitramine,  $O_2NNHCH_2CH_2NHNO_2$ , EDNA are weak acids. The  $pK_a$  of MEDINA and EDNA in water are –4.8 and –5.9, respectively. They form salts with sodium hydroxide, potassium hydroxide, or hydrazine hydrate.

#### 3.2.3.1 Properties of Nitramine Salts

The enthalpies of combustion of the nitramines and their salts were measured in a bomb calorimeter and the enthalpies of formation calculated therefrom [93]. The results are summarized in Table 5. This table also contains the heats of solution of the compounds in water and the heats of dilution.

The diammonium salt of *N,N'*-dinitro-1,2-ethanediamine,  $[CH_2NNO_2(NH_4)]_2$ ,  $C_2H_{12}N_6O_4$ ,  $M = 184.15 \text{ g/mol}$ , melted at 452–453 K (179–180 °C), and in the DTA thermogram the maximum of the exotherm peak was at 464 K (191 °C) accompanied by a violent decomposition [94]. The enthalpy of formation of the diammonium salt of *N,N'*-dinitro-1,2-ethanediamine is  $-335 \text{ kJ/mol}$  ( $-80.10 \text{ kcal/mol} = -435 \text{ cal/g}$ ) [95].

The enthalpy of formation of the dihydrazinium salt of *N,N'*-dinitro-1,2-ethanediamine  $[CH_2NNO_2(N_2H_5)]_2$ ,  $C_2H_{14}N_8O_4$ ,  $M = 214.184 \text{ g/mol}$ ,  $\Delta H_f^{298} = -180.2 \text{ kJ/mol}$  ( $-43.07 \text{ kcal/mol} = -201 \text{ cal/g}$ ) [96].

**Table 5:** Enthalpies of formation, dissolution, and dilution of primary nitramines and their salts at 298 K.

| Compound formula                                                          | $\Delta H_f$       | $\Delta H_{sol}$ | $\Phi_L$ | $\Delta H_f$ (recommended) |
|---------------------------------------------------------------------------|--------------------|------------------|----------|----------------------------|
|                                                                           | kJ/mol             | kJ/mol           |          | kJ/mol                     |
| $\text{CH}_3\text{NHNO}_2(\text{C})$                                      | $-73.39 \pm 0.25$  | $16.36 \pm 0.13$ | -1.38    | $-73.24 \pm 0.28$          |
| $\text{CH}_3\text{NNO}_2 \bullet \text{N}_2\text{H}_5(\text{C})$          | $-74.43 \pm 0.42$  | $21.63 \pm 0.42$ | 1.38     | $-77.2 \pm 1.2$            |
| $\text{CH}_2(\text{NHNO}_2)_2(\text{C})$                                  | $-62.22 \pm 0.42$  | $23.68 \pm 0.08$ | -7.91    | $-62.07 \pm 0.44$          |
| $\text{CH}_2(\text{NNO}_2)_2 \bullet 2\text{N}_2\text{H}_5(\text{C})$     | $-51.80 \pm 1.25$  | $59.62 \pm 0.08$ | 38.36    | $-54.7 \pm 1.6$            |
| $\text{CH}_2(\text{NNO}_2)_2\text{Na}_2(\text{C})$                        | —                  | $9.83 \pm 0.04$  | —        | $-520.91 \pm 0.44$         |
| $\text{CH}_2(\text{NNO}_2)_2\text{K}_2(\text{C})$                         | —                  | $8.91 \pm 0.04$  | —        | $-543.67 \pm 0.44$         |
| $(\text{CH}_2)_2(\text{NHNO}_2)_2(\text{C})$                              | $-103.76 \pm 0.42$ | $40.38 \pm 0.08$ | -3.64    | $-103.68 \pm 0.43$         |
| $(\text{CH}_2)_2(\text{NNO}_2)_2 \bullet 2\text{N}_2\text{H}_5(\text{C})$ | $-94.14 \pm 0.85$  | $49.92 \pm 0.13$ | 15.48    | $-95.3 \pm 1.6$            |
| $(\text{CH}_2)_2(\text{NNO}_2)_2\text{Na}_2(\text{C})$                    | —                  | $7.15 \pm 0.04$  | —        | $-547.41 \pm 0.43$         |
| $(\text{CH}_2)_2(\text{NNO}_2)_2\text{K}_2(\text{C})$                     | —                  | $8.95 \pm 0.08$  | —        | $-572.89 \pm 0.43$         |
| $(\text{CH}_2)_6(\text{NHNO}_2)_2(\text{C})$                              | $-211.8 \pm 1.1$   | $51.4 \pm 1.2$   | -0.92    | $-211.9 \pm 2.2$           |
| $(\text{CH}_2)_6(\text{NNO}_2)_2 \bullet 2\text{N}_2\text{H}_5(\text{C})$ | $-207.74 \pm 0.75$ | $61.50 \pm 0.85$ | 16.31    | $-207.7 \pm 2.6$           |

Data Source: [93]

### 3.2.4 Safety Properties of Ethylenedinitramine

On the hot plate, EDNA explodes above the deflagration point temperature of 453 K = 180 °C = 356 °F. The impact sensitivity of EDNA in the Bundesanstalt für Materialforschung und -prüfung (BAM) impact sensitivity tester is 8 N m.

### 3.2.5 Toxicity of Ethylenedinitramine

The LD50 of EDNA in mice by oral administration was 540 mg/kg.

### 3.2.6 Explosive Performance of Ethylenedinitramine

In the lead block test a 10-g sample of EDNA exploding will create a cavity volume of 410 cm<sup>3</sup>. The detonation velocity of EDNA confined in a steel tube and compressed to a density of 1.65 g/cm<sup>3</sup> is 7570 m/s.

## 3.3 Alkyl-substituted Ethylenedinitramine Derivatives

Ethylenedinitramine is already a relatively stable nitramine, yet its stability can be improved by substituting one or two of the reactive hydrogens on the NH groups with methyl groups. The two methylEDNA compounds have been thoroughly characterized, but have not found practical applications.

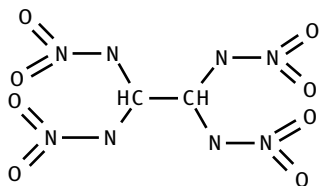
Alkylation of EDNA with methyl iodide leads to *N*-methyl-ethylene-dinitramine (m.p. 394–395 K = 121–122 °C) and *N,N'*-dimethyl-ethylenedinitramine (m.p. 410 K = 137 °C). The drop weight sensitivity (50% point) of *N,N'*-dimethyl-ethylenedinitramine was 51 cm, less sensitive in comparison to that of RDX (50% = 35 cm). *N,N'*-Dinitro-*N*-methyl-1,2-diaminoethane,  $\text{O}_2\text{NN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NHNO}_2$ ,  $\text{C}_3\text{H}_8\text{N}_4\text{O}_4$ , melts at 393–394 K (120–121 °C) and in the DTA the maximum of the exotherm peak is at 483 K (210 °C). *N,N'*-Dinitro-*N,N'*-dimethyl-1,2-diaminoethane,  $\text{O}_2\text{NN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{NO}_2$ ,  $\text{C}_4\text{H}_{10}\text{N}_4\text{O}_4$ , melts at 409–410 K (136–137 °C) and in the DTA the maximum of the exotherm peak is at 558 K (285 °C), which is higher than that of EDNA or the monomethylEDNA [94]. The reaction of EDNA with ethylene dibromide produced *N,N'*-dinitropiperazine, a cyclic nitramine.

### 3.4 Linear Dinitramines with $\text{C}_{n \geq 2}$ Chains

*N*-Methyl-*N,N'*-dinitroethylenediamine, also known as 2,5-dinitrazapentane, *N*<sup>1</sup>-methyl-*N*<sup>1</sup>,*N*<sup>2</sup>-dinitro-1,2-ethanediamine, *N*-methyl-*N,N'*-dinitro-1,2-ethanediamine, MeEDNA,  $\text{H}_3\text{CN}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{NHNO}_2$ ,  $\text{C}_3\text{H}_8\text{N}_4\text{O}_4$ , CAS RN [10308-90-4], is a methyl derivative of EDNA. The molecular weight of MeEDNA is 164.12 g/mol. The measured melting point is 393.6–394.9 K (120.5–121.8 °C). The predicted density is  $1.371 \pm 0.06 \text{ g/cm}^3$  at 293 K (20 °C). Like EDNA, MeEDNA is a relatively strong acid with a predicted  $\text{p}K_a$  of  $6.11 \pm 0.10$  at 298 K (25 °C).

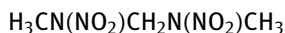
2,4-Dinitro-2,4-diazapentane, also known as 2,4-dinitrazapentane, DNDA5,  $\text{H}_3\text{CN}(\text{NO}_2)\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_3$ ,  $\text{C}_3\text{H}_8\text{N}_4\text{O}_4$ , CAS RN [13232-00-3], is an isomer of MeEDNA. 2,4-Dinitro-2,4-diazapentane melts at 328–330 K and the heat of fusion is 16.48 kJ/mol and its homologue 2,5-dinitro-2,5-diazahexane, dimethylethylenedinitramine, DMeEDNA,  $\text{H}_3\text{CN}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_3$ , melts at 408–410 K and the heat of fusion is 29.37 kJ/mol [40]. It can be synthesized from methylnitramine and dihalogenomethanes [97].

*N,N',N'',N'''*-tetranitro-1,1,2,2-ethanetetramine, *N*-(1,2,2-trinitramidoethyl)nitramide,  $\text{C}_2\text{H}_6\text{N}_8\text{O}_8$ , CAS RN [117080-06-5],  $M = 270.118 \text{ g/mol}$ , can form energetic salts with many organic bases [98].

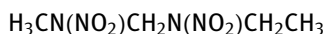


*N*-(1,2,2-trinitramidoethyl)nitramide

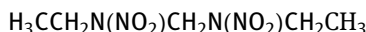
The following DNDA compounds (dinitro-diaza-alkanes) have been evaluated as energetic plasticizers, not as pure compounds but as mixtures containing varying proportions of two or three of these compounds:



DNDA-5 *N,N'*-dimethylbis-nitramine, 2,4-dinitro-2,4-diazapentane



DNDA-6 *N*-methyl-*N'*-ethyl-bisnitramine, 2,4-dinitro-2,4-diazaheptane



DNDA-7 *N,N'*-diethylbisnitramine, 3,5-dinitro-3,5-diazaheptane

DNDAs can be prepared by nitration of *N,N'*-dimethylurea and *N,N'* diethylurea, hydrolysis of the dinitrodimethylurea and dinitrodiethylurea and condensation of the methyl- and ethylnitramine [99–101].

In another method for the synthesis of dinitro-diaza-alkanes from alkylamines and esters, a dialkyl ester of a dicarboxylic acid is reacted with a primary alkylamine to form the dialkyldiamide of the dicarboxylic acid. The dialkyldiamide is nitrated to form the dialkyldinitroamide of the dicarboxylic acid and the resulting dialkyldinitroamide is reacted with methylamine and/or ethylamine in an aqueous medium to yield a alkylnitroamine and the dimethyldiamide and/or diethyldiamide of the dicarboxylic acid, and the alkylnitramine needs to be isolated from that mixture [102].

The physical property data for several DNDA compounds are listed in Table 14. 3,5-Dinitrazaheptane,  $\text{H}_3\text{CCH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_3$ , DNDA-7, CAS RN [134273-34-0], a symmetrical molecule, is a constituent of DNDA-57.

Dinitrodiazaalkanes (DNDA-57) are mixtures of linear nitramine plasticizers and find use in low-temperature sensitivity coefficient propellants. DNDA-57 is a mixture of 2,4-dinitro-2,4-diazapentane (DNDA-5), 2,4-dinitro-2,4-diazaheptane (DNDA-6), and 3,5-dinitro-3,5-diazaheptane (DNDA-7) with varying percentage composition of  $40 \pm 5\%$ ,  $44 \pm 5\%$ , and  $11 \pm 2\%$ , respectively. A synthesis process of DNDA-57 was improved by slight modification of the reaction parameters to obtain good yield and the process was scaled up [103]. The mixture was thoroughly characterized by spectroscopic and thermal methods as well as GC/MS to determine the fragmentation pattern. It was found that the decomposition of DNDA-5, DNDA-6, and DNDA-7 follow identical patterns. DNDA-57 is relatively insensitive to friction and impact.

2,4-Dinitrazaheptane,  $\text{H}_3\text{CN}(\text{NO}_2)\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_3$ , CAS RN [168983-72-0], DNDA-6, an asymmetric molecule, is an ingredient in a mixture of several nitramines called DNDA-57. The crystallization behavior of several dinitramines with plasticizing abilities in a nitrocellulose-(NC-)based gel was examined because the ability of these compounds to interact with NC is an important parameter for the development of double-base propellants [104, 105]. It was shown that, on the basis of their crystallization behavior, the nine studied dinitramines can be categorized into three



different groups. Whereas the first group (large symmetrical molecules) exhibited a strong crystallization tendency, the second group (asymmetric compounds) had low crystalline contents and showed a good interaction capacity with nitrocellulose. DNDA-6 (2,4-dinitro-2,4-diazahehexane) had the most pronounced interaction with nitrocellulose, due to its lowest content of crystalline plasticizer.

The energetic plasticizer mixture DNDA-57 as well as pure DNDA-6 resulted in promising propellant formulations having better ballistic properties as well as better cold elasticity [106]. The thermoanalytical properties of DNDA-5, DNDA-6, and DNDA-7 as well as of binary and ternary mixtures of these compounds were measured by TGA of the single components and cyclic DSC measurements of the pure components as well as of binary and ternary mixtures. Pure DNDA-6 had the lowest glass transition temperature of about 213 K ( $-60^{\circ}\text{C}$ ) (Onset  $T_g$ ) and the smallest melting enthalpy. Based on low  $T_g$  values, the use of DNDA-6 as a plasticizer should yield the best cold brittleness of new NC-propellant formulations. The onset-of-melting temperature of DNDA-6 ( $309\text{ K} = 36^{\circ}\text{C}$ ) was much above the lowest onset-of-melting temperature of the binary and ternary DNDA mixtures (about  $273\text{ K} = 0^{\circ}\text{C}$  for suitable mixtures of DNDA 5 DNDA-6 and for suitable ternary mixtures about  $269\text{ K} = -4^{\circ}\text{C}$ ).

## 4 Alkylnitramines with Explosophoric Substituents in the Alkyl Group

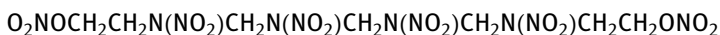
The energy content of dialkylnitramines can be increased by replacing terminal hydrogens in the hydrocarbon skeleton by energetic groups, such as nitroxy, nitro, nitramino, azido or difluoroamino groups. Of special interest are dialkylnitramines with two geminal nitro groups in the 2-position of the alkyl chains. Some of these nitroalkylnitramines are liquids and can be used as energetic plasticizers in double-base or composite propellants. Although in other sections of this book the nitroalkyl compounds are discussed ahead of the nitroxyalkyl compounds, the order has been reversed here because there is more to write about the nitroxyalkylnitramines than about the nitroalkylnitramines.

### 4.1 Nitroxyalkylnitramines (Nitratoalkylnitramines)

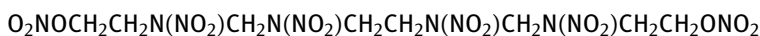
Nitroxyalkylnitramines can have one, two or more methylene groups between the nitroxy group and the nitramine group. The most common ones are those containing **two** methylene groups between the nitroxy group and the nitramine group, which are called nitroxyethylnitramines (NENAs). The nitroxy**ethyl**nitramines with different alkyl groups on the nitramine nitrogen will be discussed in a separate section in this chapter.

The effect of varying the number of methylene groups between the nitroxy group and the nitramine group on the thermal stability of nitroxyalkylnitramines was studied in the hope of obtaining plasticizers that are thermally more stable than *n*-butyl-*N*-(2-nitroxyethyl)nitramine (BuNENA).

Amino alcohol compounds such as propylamino propanol and ethylamino butanol are needed as precursors for production of energetic plasticizers similar to BuNENA. Straight chain aliphatic alkoxyalkylnitramines with three and four  $-\text{CH}_2-$  units between the nitrate ester and nitramine were synthesized in an effort to obtain plasticizers that are more stable than BuNENA which has two  $-\text{CH}_2-$  units [107]. However, unlike in BuNENA synthesis, various unwanted side reactions occurred in the nitration of amino alcohols. Fortunately, it was possible to considerably suppress the formation of side products in the nitration of propylamino propanol by using a solvent and an appropriate concentration of nitric acid. Other low-volatility nitroxyalkylnitramine compounds included 1,11-dinitrato-3,5,7,9-tetranitrazoundecane,



$\text{C}_7\text{H}_{14}\text{N}_{10}\text{O}_{14}$ , and 1,12-dinitrato-3,5,8,10-tetranitrazadodecane

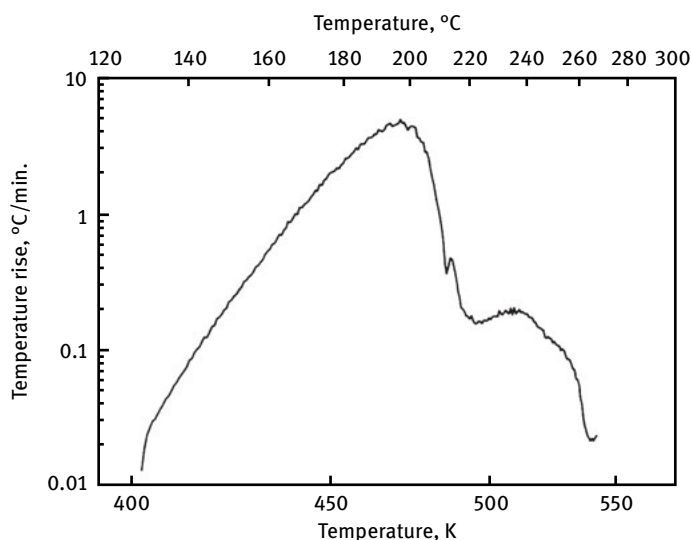


$\text{C}_8\text{H}_{16}\text{N}_{10}\text{O}_{14}$  [108]. These high explosives were called TENA 1 and TENA 2, being **T**etranitramines as well as **N**ENA derivatives. Their synthesis from the alkyl chlorides with silver nitrate is rather expensive.

The heats of explosion  $Q_{\text{ex}}$  of six linear dinitramines (DNDA5, DNDA6, DNDA7, EDNA, M-EDNA, and DM-EDNA), three dinitramines with azido groups (DN3, AZD6, and BAED), and six nitrateethylnitramines (DINA, MeNENA, EtNENA, BuNENA, BNE-MEDINA, and BNE-EDNA) were determined by combustion in a calorimeter bomb, sometimes in mixtures with nitrocellulose (NC) [109]. It was noted that for some substances the determination did not result in constant  $Q_{\text{ex}}$  values, which questioned the general applicability of the method. In order to explain this nonlinear behavior, a detailed investigation was started. Constant  $Q_{\text{ex}}$  values lying over 4000 J/g with a small deviation were obtained for compounds with an oxygen balance above  $-60\%$ , whereas in the range of  $-60$  to  $-70\%$  the  $Q_{\text{ex}}$  values between 3400 and 3700 J/g presented pronounced deviations. For compounds with an oxygen balance below  $-70\%$ , the calculated  $Q_{\text{ex}}$  value increased strongly with rising percentages of the compounds in mixtures with NC. Neither the type of explosophoric groups such as  $-\text{NNO}_2$ ,  $-\text{ONO}_2$ , or  $-\text{N}_3$  nor the nitrogen content or the type of energetic additive (RDX or NC) in the analyzed mixtures had any decisive effect on the  $Q_{\text{ex}}$  deviations. 1-Nitroxy-3-nitrazapentane or 1-nitroxy-3-nitrazabutane in mixtures with 2-azidoethanol or 1,3-diazidopropanol can be used as monopropellants [110].

#### 4.1.1 Thermal Stability of Nitroxyalkylnitramines

The thermal decomposition behavior of several energetic plasticizers including 58.8/41.2 mass-% *N*-methyl-*N*-ethyl-NENA (NENA = 2-nitratoethylnitramine) and DANPE (1,5-diazido-3-nitrazapentane) and uncured binders was investigated in 10 mass-% solutions in toluene by adiabatic self heating in an accelerating rate calorimeter (ARC) [111]. The closed ARC system prevented the solutions from evaporating and maintained adiabatic conditions. The cells with a diameter of 1 in. were made from titanium. All undiluted energetic substances would deflagrate destructively after a short period of controllable self heating. The advantage of the investigation of solutions was that the decomposition of the energetic substances could be followed in a fully controlled way. With the self-heat rate curves, one can characterize the plasticizers and binders with respect to the decomposition temperature range, the heat quantity, and the heat generation rate. The Arrhenius parameters and the released heats of reaction were then determined from the self heat rate curves, which were typically reactions of first order. A secondary reaction was found in the case of the ARC trace of a 10% solution of Me/Et-NENA in toluene (Figure 4). Presumably, the second reaction is the decomposition of the nitramine group in connection with the residual part of the already decomposed nitric acid ester group. The onset temperature of decomposition was 403 K (130 °C) for Me/Et-NENA. The activation energy was  $165.1 \pm 0.4 \text{ kJ/mol}$  and the pre-exponential factor was  $1.449 \times 10^{16} \text{ s}^{-1}$ . Me/Et-NENA had the lowest onset temperature of several energetic plasticizers and binders tested. At an extrapolated temperature of 358 K (85 °C) the

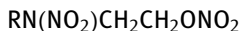


**Figure 4:** Decomposition ARC thermogram of 10% *N*-methylNENA/ 90% *N*-ethylNENA mixture. (Republished and modified from [111], with permission of ©1999 Elsevier Science & Technology Journals; permission conveyed through RightsLink.)

measurable heat generation rate in the ARC would be  $25\mu\text{W/g}$ . DANPE also had a relatively low extrapolated  $25\mu\text{W/g}$  temperature of  $379.2\text{K}$  ( $106.1^\circ\text{C}$ ) while glycidyl azide polymer (GAP) started at about  $387\text{K}$  ( $114^\circ\text{C}$ ).

## 4.2 Nitroxyethylnitramines

The nitroxyethylnitramine (nitratoethylnitramine) family compounds (NENAs) are effective plasticizers in energetic formulations, particularly in nitrocellulosic systems. NENAs contain both nitrate ester and nitramine functionalities, and have the following structure:



where R can be a methyl, ethyl, propyl, isopropyl, butyl, or pentyl group. The structurally related 1,5-diazido-3-nitrazapentane, or DANPE, is discussed here following the alkyl-NENAs. The NENAs have been known since the 1940s, when DINA (dinitroxyethyl nitramine) was scaled-up for use in Navy flashless gun propellants. It was not until the late 1970s that researchers at Eglin AFB began to use NENAs in gun propellants that required low flame temperatures and low molecular weight [112].

NENAs are readily manufactured by nitration of commercially available alkyl ethanolamines, in good yields (80%):



Sometimes mixtures of nitroxylalkylnitramines give better results in double-base propellants than the pure compounds by themselves. Mixtures of nitroxylalkylnitramines are liquids at room temperature, while the pure compounds may be solids. Instead of mixing separately prepared DINA and alkylNENA, mixtures of the hydroxyalkylamine precursors can be co-nitrated [113, 114].

The use of NENAs as plasticizers in gun and rocket propellants allows the production of propellants with excellent properties such as high burning rates, reductions in flame temperature and product gas molecular weight, and higher specific impulse (based on moderate loadings of 60–70% RDX in a nitrocellulose/NENA binder, also containing nitroguanidine) [115–117].

Heats of combustion of NENA plasticizers and associated azido derivatives can be calculated by a simple yet reliable and accurate method [112]. Heats of formation (Table 6) can then be derived from the heats of combustion and used to calculate a wide range of gun propellant performance.

Not only do NENA compounds promise low combustion gas molecular weight products, but this characteristic (in combination with conventional ingredients) makes higher energy levels possible. Derivatives of NENAs carrying azido groups in place of nitrato groups promise even greater potential due to their positive heats of formation.

**Table 6:** Properties of condensed phase alkylNENAs.

|                                    |          | MeNENA | EtNENA | PrNENA | BuNENA | PentyINENA |
|------------------------------------|----------|--------|--------|--------|--------|------------|
| Molecular mass                     | g/mol    | 165.1  | 179.1  | 193.2  | 207.2  | 221.1      |
| Enthalpy of formation $\Delta H_f$ | kJ/mol   | -149.8 | -164.0 | -174.1 | -200.8 | -206.7     |
|                                    | kcal/mol | -35.8  | -39.2  | -41.6  | -48.0  | -49.4      |

Data source: [112]

The application of NENAs as energetic plasticizers in specific solid propellant formulations will be described in a future volume on solid propellants. Here we discuss only the preparation, physical, chemical, and safety properties of the pure compounds. NENAs possess good thermal stability, they readily plasticize nitrocellulose, and other polymers, generate low molecular weight combustion gases, and have low impact sensitivity [118]. Additional important properties are listed in Table 7, but the enthalpy of formation numbers shown here exactly as copied from the source are obviously wrong because these numbers for the liquid compounds should all be negative, which also applies to the numbers reported by other investigators. Apparently these data were derived from heats of combustion and either the upper or the lower heat of combustion was used.

**Table 7:** Properties of condensed phase alkylNENAs.

|                            | MeNENA  | EtNENA  | PrNENA | BuNENA     | PentyINENA |
|----------------------------|---------|---------|--------|------------|------------|
| Molecular mass             | 165.1   | 179.1   | 193.2  | 207.2      | 221.1      |
| $\rho$ , g/cm <sup>3</sup> | 1.53    | 1.32    | 1.264  | 1.211      | 1.178      |
| Melting point, K           | 311–313 | 274–278 | 271    | 246–245    | 265–268    |
| Melting point, °C          | 38–40   | 1–5     | -2     | -27 to -28 | -8 to -5   |
| Oxygen balance, %          | -43.6   | -67.0   | -87.0  | -104.0     | -119.1     |
| DSC onset exotherm, K      | 491     | 483     | 483    | 483        | —          |
| DSC onset exotherm, °C     | 218     | 210     | 210    | 210        | —          |
| $\Delta H_f$ , kJ/mol      | 1113    | 784     | 503    | 259        | 47         |
| $\Delta H_f$ , kcal/mol    | 266     | 197.3   | 120.2  | 61.9       | 11.23      |

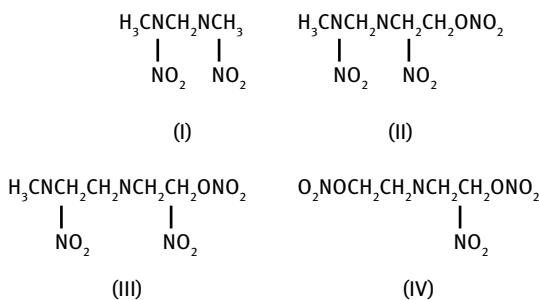
Data source: [119] as quoted from Simmons [118]

The molecular structures of nitroethylnitramine (NENA), its tautomers, and its charged forms were calculated quantum chemically, using various basis sets at the levels of *ab initio*, and density functional theories (DFT) [120]. NENA may be sensitive to negative charge development, resulting in rupture of the —O—NO<sub>2</sub> bond. Conformational and molecular dynamics studies gave predicted geometrical parameters,

energies, and IR spectra. Calculations indicated that the *s-cis* conformation of NENA should be slightly more stable than the *s-trans* conformation. The tautomers have very comparable total energy values to NENA. On the other hand, on the basis of homolytic bond dissociation energies (BDE) for  $\text{—O—NO}_2$  bonds in the structures, it was proposed that the presence of the tautomers in the bulk of NENA should somewhat decrease its sensitivity.

The volatility of three 2-nitroxyethylnitramine (NENA) compounds in an NC-based double-base propellant was compared to those of diethylene glycol dinitrate (DEGDN), and nitroglycerin (NG) using TGA at constant temperature at three different temperatures [121]. Initial concentration of plasticizer and degree of nitration of NC were also varied. The NENA plasticizers had lower vaporization rates than DEGDN or NG.

Alkylsulfamates react with ethylene oxide to form *N*-ethanolsulfamates, and *N*-di(ethanol)sulfamates which can be nitrated to form energetic nitroxyalkyl-nitramines. As a result of nitration, a quaternary nitramine mixture (QNM) was obtained in 60–70% yield [122]. The QNM consisted of 2,4-dinitro-2,4-diazapentane (I), 1-nitroxy-3,5-dinitro-3,5-diazaheptane (II), 1,7-dinitroxy-3,5-dinitro-3,5-diazaheptane (III), and 1,5-dinitroxy-3-nitro-3-azapentane (IV).



The QNM is a low-melting substance with a melting point from 291 to 323 K, depending on ratio of the components, and an enthalpy of formation of  $\Delta H_f = -813 \text{ kJ/kg}$ . The ratio of components I, II and III in the QNM was determined from the ratio of the  $^1\text{H}$  NMR signals of the methylene protons between the nitramine groups  $\text{—N(NO}_2\text{)CH}_2\text{N(NO}_2\text{)}$  and of the methylene group adjacent to the nitramine group of the ethyl nitrate moiety  $\text{—N(NO}_2\text{)CH}_2\text{ONO}_2$ . Azidation of the QNM in a DMF yielded a quaternary azide mixture (QAM) consisting of 2,4-dinitro-2,4-diazapentane (I), 1-azido-3,5-dinitro-3,5-diazaheptane, 1,7-diazido-3,5-dinitro-3,5-diazaheptane, and 1,5-diazido-3-nitro-3-azapentane.

The ideal gas phase thermochemical properties of ethyl-2-mitrato-1-nitramine (NENA) and its family of alkyl substituted compounds methyl-, ethyl-, propyl-, butyl-, and pentyl-NENA were calculated and presented in NASA-type polynomial format that can be used for rocket performance calculations [123]. See also [124].

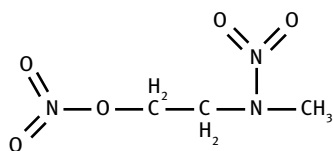
### 4.3 2-Nitroxyethylnitramine, NENA

The simplest nitramine in this group is 2-nitroxyethylnitramine, NENA,  $\text{O}_2\text{NOCH}_2\text{CH}_2\text{NHNO}_2$ . This compound and its alkylated homologues can be synthesized by first forming the nitrate salts of hydroxyalkylamines, followed by nitration in acetic anhydride [2, 125].

NENA is a liquid at room temperature but freezes at 288 K (15 °C). The oxygen balance of NENA is  $-15.9\%$ . It is thermally stable up to 573 K (300 °C) and volatile at that temperature. The impact sensitivity (50% point) of NENA reported from two different sources is 191 or 107 cm. The hydrogen on the nitrogen adjacent to the *N*-nitro group is acidic and this compound forms ammonium and silver salts. The pH of a NENA solution in water is 2.7. In the lead block test, the power of NENA was 134% that of TNT.

### 4.4 Methyl-2-nitroxyethylnitramine, MethylNENA

The first NENA homologue is 2-nitroxyethyl methyl nitramine, also known as 2-(methylnitroamino)ethyl nitrate, 2-[methyl(nitro)amino]ethyl nitrate, methyl-NENA, methylNENA, MeNENA,  $\text{C}_3\text{H}_7\text{N}_3\text{O}_5$ , CAS RN [17096-47-8],  $M = 165.105 \text{ g/mol}$ .



MethylNENA

MeNENA is the simplest of the alkylated NENA compounds, with other notable members in this family being Et- and *n*-BuNENA. MethylNENA is a solid at room temperature and melts at 311–313 K (38–40 °C). It is thermally stable up to 573 K (300 °C). The impact sensitivity is more than 90 cm (RDX for comparison: 48–50 cm). The density of the liquid is  $1.40 \text{ g/cm}^3$  and the density of the solid at 298 K = 25 °C is  $1.53 \text{ g/cm}^3$ . The properties of methylNENA are summarized in Table 8.

It was attempted to lower the melting point of MeNENA by mixing it with other nitramines [2]. It is soluble in acetic acid and can be recrystallized from solutions in acetic acid.

The energetic plasticizer *N*-methyl-*N*-(2-nitroxyethyl)nitramine and its precursor *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate were synthesized by nitration of 2-(methylamino)ethanol and characterized by XRD, multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ), vibrational spectroscopy (IR and Raman), mass spectrometry, and DTA [127]. For the synthesis of *N*-methyl-*N*-(2-nitroxyethyl)nitramine, a colorless

**Table 8:** Properties of methylNENA.

| Property                          | SI units               | Other units    | References         |
|-----------------------------------|------------------------|----------------|--------------------|
| Oxygen balance to CO <sub>2</sub> | -43.6%                 | —              | —                  |
| Melting point                     | 311–313 K              | 38–40 °C       | —                  |
|                                   | 312–313.5 K            | 39–40.5 °C     | CAS                |
| Density, solid at 298 K           | 1.53 g/cm <sup>3</sup> | —              | CAS                |
| Heat of combustion                | 2031.2 kJ/mol          | 485.5 kcal/mol | [112]              |
|                                   | 1994.8 kJ/mol          | 476.8 kcal/mol | [126] <sup>a</sup> |
| Enthalpy of formation             | -149.81 kJ/mol         | -35.8 kcal/mol | [112]              |
|                                   | -186.1 kJ/mol          | -44.5 kcal/mol | [126] <sup>a</sup> |
|                                   | -149.8 kJ/mol          | -35.8 kcal/mol |                    |

<sup>a</sup> As referenced in NIST Chem WebBook [85]

crystalline solid, the commercially available 2-(methylamino)ethanol can be nitrated in a mixture of pure nitric acid and acetic anhydride in the presence of zinc chloride as catalyst. The intermediate *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate can be isolated as a colorless, fine crystalline solid upon mixing of the reaction mixture with diethyl ether. The crystal structure parameters of *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate and *N*-methyl-*N*-(2-nitroxyethyl)nitramine at 173 K are summarized in Table 9.

MeNENA showed three signals in its <sup>1</sup>H NMR spectrum. The methyl group C3 exhibited a singlet signal at 3.47 ppm, whereas the two methylene groups showed multiplet signals at 4.27 (C2) and 4.87 ppm (C1). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum also showed three signals, with C3 having a shift of 39.9 ppm, C2 being at 50.7 ppm, and C1 having a downfield shift of 70.8 ppm. The <sup>14</sup>N NMR spectrum exhibited two signals: one for the nitroxy group at -38 ppm and one for the nitro group at -23 ppm. The DTA thermogram (Figure 5) showed a *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate melting point with an onset at 346 K (73 °C) and a decomposition starting at 407 K (134 °C). For comparison, the parent acid, MeNENA began to melt at 304 K (31 °C) and began to decompose at 453 K (180 °C).

The theoretical detonation velocity of MeNENA was predicted to be 8050 m/s in comparison to that of RDX which was predicted to be 8748 m/s.

#### 4.5 Ethyl-2-nitroxyethylnitramine, EthylNENA

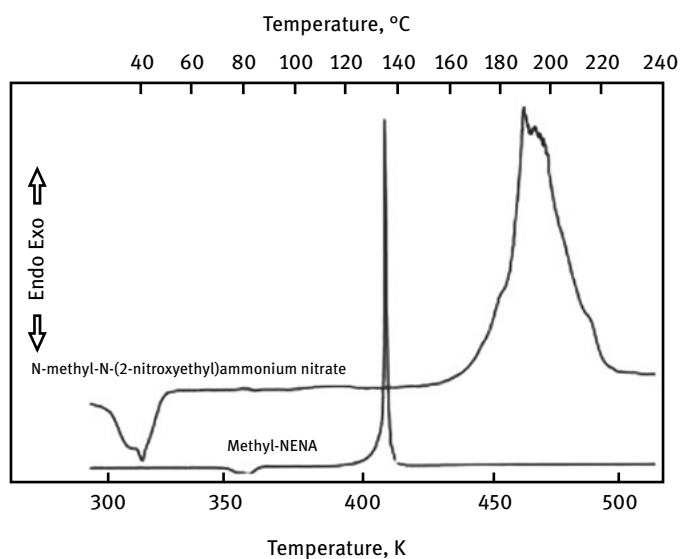
The next homologous member of the group of nitramines is 2-nitroxyethyl ethyl nitramine, also known as 2-(ethylnitroamino)ethyl nitrate, 2-(ethylnitroamino)-ethanol 1-nitrate, O<sub>2</sub>NO—CH<sub>2</sub>—CH<sub>2</sub>—N(NO<sub>2</sub>)—CH<sub>2</sub>—CH<sub>3</sub>, C<sub>4</sub>H<sub>9</sub>N<sub>3</sub>O<sub>5</sub>, ethyl-NENA,



**Table 9:** Crystallographic data of *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate and *N*-methyl-*N*-(2-nitroxyethyl)nitramine.

| Property               | <i>N</i> -methyl- <i>N</i> -(2-nitroxyethyl)-<br>ammonium nitrate | <i>N</i> -methyl- <i>N</i> -(2-nitroxyethyl)-<br>nitramine  |
|------------------------|-------------------------------------------------------------------|-------------------------------------------------------------|
| Empirical formula      | C <sub>3</sub> H <sub>9</sub> N <sub>3</sub> O <sub>6</sub>       | C <sub>3</sub> H <sub>7</sub> N <sub>3</sub> O <sub>5</sub> |
| Molecular mass         | 183.13 g/mol                                                      | 165.12 g/mol                                                |
| Crystal system         | orthorhombic                                                      | monoclinic                                                  |
| Space group            | <i>Pca</i> 2 <sub>1</sub> (No. 29)                                | <i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)                 |
| <i>a</i>               | 12.5637(8) Å                                                      | 9.7280(10) Å                                                |
| <i>b</i>               | 5.5612(5) Å                                                       | 7.3794(7) Å                                                 |
| <i>c</i>               | 11.2936(7) Å                                                      | 11.7814(15) Å                                               |
| $\alpha$               | 90°                                                               | 90°                                                         |
| $\beta$                | 90°                                                               | 125.816(11)°                                                |
| $\gamma$               | 90°                                                               | 90°                                                         |
| <i>V</i>               | 789.08(10) Å <sup>3</sup>                                         | 685.82(16) Å <sup>3</sup>                                   |
| <i>Z</i>               | 4                                                                 | 4                                                           |
| $\rho_{\text{calcd.}}$ | 1.542 g/cm <sup>3</sup>                                           | 1.599 g/cm <sup>3</sup>                                     |

Data source: [127]

**Figure 5:** DTA thermograms for *N*-methyl-*N*-(2-nitroxyethyl)ammonium nitrate and MeNENA with a heating rate of 5 °C/min. (Republished and modified from [127], with permission from ©2011 John Wiley & Sons; permission conveyed through RightsLink.)

**Table 10:** Physical properties of liquid ethylNENA.

| Property                                         | SI units                                          | Other units                      | References |
|--------------------------------------------------|---------------------------------------------------|----------------------------------|------------|
| Molecular mass                                   | 179.13 g/mol                                      | 5.5825 mol/kg                    | —          |
| Freezing point                                   | 277–278.5 K<br>278 K                              | 4–5.5 °C<br>—                    | CAS<br>—   |
| Boiling point                                    | 473 K (dec.)                                      | 200 °C (dec.)                    | —          |
| Density                                          | 1.32 g/cm <sup>3</sup><br>1.339 g/cm <sup>3</sup> | —<br>—                           | CAS<br>—   |
| Refractive index $n_D^{25}$                      | 1.479                                             | —                                | —          |
| Heat of combustion                               | 2696.3 kJ/mol                                     | 644 kcal/mol                     | [112]      |
| Enthalpy of formation                            | –164.03 kJ/mol<br>–164 kJ/mol                     | –39.2 kcal/mol<br>–39.2 kcal/mol | [112]<br>— |
| Oxygen balance for combustion to CO <sub>2</sub> | –67%                                              | —                                | —          |

ethylNENA, EtNENA, CAS RN [85068-73-1], which is a yellow oil at room temperature and freezes at 277–278.5 K (4–5.5 °C). The properties of ethylNENA are summarized in Table 10. MEN-42 is a eutectic mixture of methyl- and ethyl-NENA.

#### 4.6 *n*-Propyl-2-nitroxyethylnitramine, ProNENA

*n*-Propyl-2-nitratoethylnitramine, also known as *n*-propyl-2-nitroxyethylnitramine, 2-nitropropylaminoethanol nitrate ester, ProNENA, O<sub>2</sub>NO—CH<sub>2</sub>—CH<sub>2</sub>—N(NO<sub>2</sub>)—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>, C<sub>5</sub>H<sub>11</sub>N<sub>3</sub>O<sub>5</sub>, CAS RN [82486-83-7] is less well characterized than the other three NENAs. It can be used as a plasticizer in double-base propellants. The physical properties of *n*-ProNENA are summarized in Table 11.

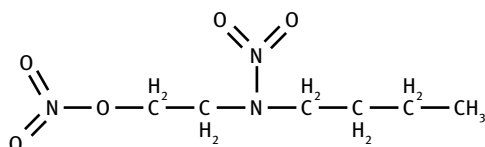
#### 4.7 *n*-Butyl-2-nitroxyethylnitramine, BuNENA

Another member of the group of nitramines is 2-nitroxyethyl *n*-butyl nitramine, also known as *n*-butyl-*N*-(2-nitroxyethyl)nitramine, *n*-butyl-nitratoethyl-nitramine, *N*-*n*-butyl-*N*-(2-nitroxyethyl)nitramine, 2-(butylnitroamino)ethanol nitrate, 2-[butyl(nitro-amino)ethyl nitrate, O<sub>2</sub>NO—CH<sub>2</sub>—CH<sub>2</sub>—N(NO<sub>2</sub>)—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH<sub>3</sub>, C<sub>6</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>, butyl-NENA, butylNENA, BuNENA, CAS RN [82486-82-6], *M* = 207.184 g/mol, which is a yellow oil that freezes at 263.2 K (–9.9 °C). *n*-Butyl-2-nitroxyethylnitramine is

**Table 11:** Physical properties of *n*-propylNENA.

| Property                                         | SI units                       | Other units                    | References |
|--------------------------------------------------|--------------------------------|--------------------------------|------------|
| Molecular mass                                   | 193.16 g/mol                   | 5.1770 mol/kg                  |            |
| Oxygen balance for combustion to CO <sub>2</sub> | −87%                           | —                              | [128]      |
| Freezing point                                   | 271 K                          | −2 °C                          | —          |
| Density                                          | 1.260 g/cm <sup>3</sup>        | 0.0455 lb/in. <sup>3</sup>     | —          |
| Enthalpy of formation                            | −178.2 kJ/mol<br>−154.9 kJ/mol | −42.6 kcal/mol<br>−37 kcal/mol | —<br>[128] |

a combination of a nitrate ester and a nitramine, carrying two types of explosophoric groups in the molecule:



ButylNENA

BuNENA can be used as an energetic plasticizer in double-base propellants. In the pure state, BuNENA is a colorless oily liquid with a density of 1.21 g/cm<sup>3</sup> and a freezing point of 264 K = −9 °C. Practical grades may have the appearance of a yellow oily liquid.

#### 4.7.1 Preparation of *n*-ButylNENA

*n*-Butyl-2-nitroxyethylnitramine can be prepared from *n*-butylethanolamine and nitric acid with acetic anhydride and a chloride source for catalysis. *n*-BuNENA is an energetic plasticizer for solid propellant formulations. The laboratory synthesis of *n*-BuNENA was scaled up to the 1 kg batch size and the compound was fully characterized by spectral data and elemental analysis [129]. *n*-BuNENA was formulated with composite modified double-base (CMDB) and extruded double-base (EDB) propellant compositions. The results showed an improvement in mechanical properties and burning rate over a wide range of pressure along with acceptable limits of hazard and thermal stability as compared to diethyl phthalate-plasticized propellant systems.

It was attempted to gain some insight into the BuNENA synthesis pathway. Step 1 involved *N*-butyl-ethanolamine addition to 98% HNO<sub>3</sub> to form a salt mixture; step 2 was addition of acetic anhydride/acetyl chloride catalyst to the salt mixture. A number of potential intermediates, by-products, and decomposition products from this pro-

cess were identified/synthesized for use as analytical standards [130]. Potential intermediates and by-products formed during BuNENABuNENA synthesis were identified. These included nitrate salts, acetate ester, nitramine alcohol, and a free nitrate ester. The rate of consumption of acetyl nitrate was measured in order to limit its accumulation in the reaction vessel, which would be an operational hazard.

*N*-Methyl-*N*-(2-nitroxyethyl)nitramine (MeNENA), *N*-ethyl-*N*-(2-nitroxyethyl)nitramine (EtNENA), and *n*-butyl-*N*-(2-nitroxyethyl)nitramine (BuNENA) were prepared by the reactions of methylethanolamine, ethylethanolamine, or butylethanolamine and nitric acid with acetic anhydride, respectively [131]. The structures of the NENAs were identified by  $^1\text{H}$  NMR, IR, and elemental analysis. The parameters affecting the yield and purity of EtNENA, such as temperature, reaction time, nitric acid, and acetic anhydride were optimized. The optimum conditions were given: mol ratio of (ethyl ethanolamine):(nitric acid):(acetic anhydride) = 1:2.6:2.4, the reaction temperature of the first stage 278–283 K (5–10 °C), the reaction temperature of the second stage 313–318 K (40–45 °C), reaction time 15 min. Under these conditions, the yield of EtNENA was over 84% and the purity of the refined product was greater than 98%. The physical, chemical, and safety properties and thermal decomposition of alkyl-NENAs were also measured.

#### 4.7.2 Physical Properties of *n*-ButylNENA

Some physical properties of BuNENA were already included in Table 7. The physical properties of *n*-BuNENA are summarized in Table 12.

It is unclear why someone would want to dissolve BuNENA in DMSO, but apparently there must be an application for this. The densities and viscosities of binary liquid mixtures of BuNENA with DMSO were measured at 298, 313, 323, and 343 K (25, 40, 50, and 70 °C) by using a pycnometer and an Ubbelohde-type capillary viscometer [134]. The experimental data of viscosities, temperature, and composition were fitted to theoretical relations. The average relative error of calculated data was between 0.17 and 1.53%.

#### 4.7.3 Chemical Properties of *n*-Butyl-NENA

BuNENA is a weak acid. Its predicted  $\text{p}K_{\text{a}}$  is  $-8.52 \pm 0.70$ .

##### 4.7.3.1 Reactions of *n*-Butyl-NENA

One disadvantage of NENA plasticizers is a potential incompatibility with AP. Such AP and nitrate esters compatibility issues have often been resolved by the inclusion of free radical scavengers (2-nitrodiphenylamine or alkaline additives such as sodium bicarbonate). Neither have proved effective for NENAs. Alkylureas were considered as stabilizers for NENAs when used in combination with AP [135].

**Table 12:** Physical properties of *n*-butylNENA.

| Property                                         | SI units                       | Other units    | References |
|--------------------------------------------------|--------------------------------|----------------|------------|
| Molecular mass                                   | 207.1845 g/mol                 | 4.8266         | [85]       |
| Oxygen balance for combustion to CO <sub>2</sub> | −104.25%                       | —              | —          |
| Onset temperature of decomposition               | 483 K                          | 210 °C         | [132]      |
| Freezing point                                   | 264 K                          | −9 °C          | [133]      |
| Melting point                                    | 246 K                          | −27 °C         | [132]      |
| Boiling point                                    | 620 K (dec.)                   | 347 °C (dec.)  |            |
| Density                                          | 1.22 g/cm <sup>3</sup>         | —              | [133]      |
|                                                  | 1.21 g/cm <sup>3</sup>         | —              | [132]      |
|                                                  | 1.211 g/cm <sup>3</sup>        | —              | —          |
| Density, predicted                               | 1.242 ± 0.06 g/cm <sup>3</sup> | —              | CAS        |
| Refractive index $n_D^{25}$                      | 1.4750                         | —              | —          |
| Enthalpy of formation, liquid                    | −192.5 kJ/mol                  | −928.94 kJ/kg  | [133]      |
|                                                  | −192.47 kJ/mol                 | −46.0 kcal/mol | [112]      |
|                                                  | −192.9 kJ/mol                  | −46.1 kcal/mol |            |
| Heat of combustion, liquid                       | 4026.6 kJ/mol                  | 962.4 kcal/mol | [112]      |
| Heat of explosion                                | 1083 J/g                       | —              | —          |

A semiempirical molecular orbital theory method was used to study the interaction of BuNENA with polyethylene glycol (PEG), HTPB, GAP, poly(3-azidomethyl)-3-methyl-oxetane or poly(3,3-bis(azidomethyl)-oxetane) binders in solid propellants [136]. Binding energies were only approximately obtained. Except in the case of BuNENA with PEG, the strength of the intermolecular interaction of complex systems decreased with decreasing degree of polymerization.

#### 4.7.3.2 Decomposition of *n*-Butyl-NENA

Thermal stability and compatibility in terms of DSC compatibilities and vacuum stabilities for pure methyl-, ethyl-, and butyl-NENAs and DINa, as well as mixtures of these and testing results with mixtures of these with several propellant ingredients including RDX, AN, and polyNIMMO were compared to those of standard nitrate ester plasticizers [115]. Specific comparisons were made to BDNPA/F, butanetriol trinitrate (BTTN), and methyltrimethylolmethane trinitrate (TMETN). As with vacuum stability results, it was shown that performance parameters are very favorable with regard to other ingredients.

Thermal stability studies of combinations of NENA/AP mixtures and various stabilizing ingredients using DSC in both isothermal and scanning modes, vacuum stability as well as stability at atmospheric pressure have led to a better understanding

of the reactions between AP and NENAs as well as the discovery of novel stabilizing materials that could be used with these mixtures. Surprisingly, nitroguanidine was established as an especially good stabilizer [116, 137]. Comparisons were made between nitroguanidine (NQ) and commonly used stabilizing ingredients such as 2-nitrodiphenylamine (2-NDPA) and ethylcentralite.

BuNENA, having nitramine and nitrate ester moieties in the molecule, is prone to autocatalytic decomposition. A stability analysis has indicated that it is a moderately stable compound and does not require additional stabilizer [138]. The stability and sensitivity of *n*-BuNENA as compared with GTN is much higher, but like all nitrate esters, it suffers from inherent instability due to the low O–NO<sub>2</sub> bond energy. The decomposition is accompanied by moderate heat generation and gas production. It is also accelerated by the presence of moisture. The decomposition reaction is a hydrolysis which leads to the formation of *n*-butyl-ethanolnitramine (Bu-ENA) and nitric acid. Stability of BuNENA can be measured by the Bu-ENA formation rate and by microcalorimetry. The stability of high quality material is good enough that a stabilizer is not necessarily needed. As the main reaction is initiated by hydrolysis, it is recommended that BuNENA is stored in dry conditions. Surprisingly, DSC did not differentiate very well between stable and unstable samples. The main difference is found in the peak areas, not in the onset or peak maximum temperatures. The interim decomposition product Bu-ENA is still an energetic material with an exothermic decomposition behavior.

#### 4.7.3.3 Analysis of *n*-Butyl-NENA

The purity requirements for BuNENA are documented in the European specification STANAG 4583.

#### 4.7.3.4 Applications of *n*-Butyl-NENA

Applications of BuNENA as a plasticizer for CMDB and composite propellants will be discussed in detail in future sets on solid propellants. In this section, references to some publications on BuNENA and similar nitramine plasticizers and their potential applications are provided.

The development history and contemporary status of nitroxyethylnitramines (NENAs) and properties of propellants and explosives containing NENAs as plasticizers and their possible applications have been reviewed [139].

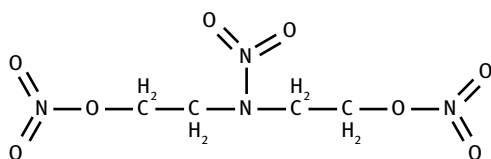
Gun propellant compositions containing BuNENA as an energetic plasticizer with varying percentage of RDX have been studied theoretically and experimentally [140]. Experimental data indicated that BuNENA based propellants are superior to dioctyl phthalate plasticized propellants with respect to ballistic performance.

BuNENA is an energetic plasticizer with excellent performance. In gun propellants, BuNENA has the advantages of high plasticizing ability, good process performance, low sensitivity, high energy, and it can improve the mechanical properties of

the formulations [141]. For instance, in HTPE-bonded (hydroxyl-terminated ethylene oxide-tetrahydrofuran block co-polyether) rocket propellant, BuNENA increased energy, decreased sensitivity, and improved mechanical properties of the propellant.

#### 4.8 Di(nitroxyethyl)nitramine, DINA

If both terminal C-atoms in diethylnitramine carry a hydroxyl group and both hydroxyl groups are esterized with nitric acid, one obtains a very energetic nitramine, 1,5-dinitroxy-3-nitrazapentane, also known as 1,5-dinitrato-3-nitrazapentane,  $\beta,\beta$ -dinitroxydiethylnitramine, DINA, di(nitroxyethyl)nitramine, diethanoldinitrate nitroamine, dioxyethylnitramine dinitrate, dihydroxyethylnitramine dinitrate, di-2-hydroxyethylnitramine dinitrate, 1,5-dinitrato-3-nitrazapentane, diethanolnitramine dinitrate; ethanol 2,2'-nitroiminodinitrate; ethanol, 2,2'-(nitroimino)di-, dinitrate (ester); 2,2'-dinitroxydiethylnitramine, dinitrate ester of di(2-hydroxyethyl)nitramine, dihydroxyethylnitramine dinitrate, 2-[nitro(2-nitrooxyethyl)amino]ethyl nitrate, (nitroimino)di-2,1-ethanediyl dinitrate,  $\text{O}_2\text{NO}-\text{CH}_2-\text{CH}_2-\text{N}(\text{NO}_2)-\text{CH}_2-\text{CH}_2-\text{ONO}_2$ ,  $\text{C}_4\text{H}_8\text{N}_4\text{O}_8$ , CAS RN [4185-47-1],  $M = 240.128$  g/mol. The molecule is slightly underoxidized with an oxygen balance of -26.6%. DINA is a combination of a nitrate ester and a nitramine, carrying two types of explosives groups in the same molecule:



Di(nitroxyethyl)nitramine

##### 4.8.1 Preparation of DINA

DINA can be prepared from diethanolamine and nitric acid with acetic anhydride as a dehydrating agent and in the presence of hydrochloric acid as a catalyst [142]. The nitration product is stabilized by boiling in water to remove partially nitrated intermediates (nitrosamine), followed by dissolution in acetone and reprecipitation with water. The product is recrystallized from acetone by precipitating it with water. DINA forms colorless crystals and is insoluble in water.

##### 4.8.2 Physical Properties of DINA

Nobody would want to heat DINA to the boiling point, but if it is done (by remote control), the boiling point is 475 K (202°C = 396°F). Several other properties of DINA

**Table 13:** Properties of 1,5-dinitroxy-3-nitrazapentane (DINA).

| Property                       | SI units                       | Other units                 | References |
|--------------------------------|--------------------------------|-----------------------------|------------|
| Molecular mass                 | 240.1283 g/mol                 | 4.1644 mol/kg               | [85]       |
| Melting point                  | 324.4 K                        | 51.3 °C = 124.3 °F          | [86]       |
|                                | 326 K                          | 52.8 °C = 127 °F            | —          |
|                                | 322.6 K                        | 49.5–50.5 °C                | CAS        |
| Boiling point                  | 475 K                          | 202 °C = 396 °F             | —          |
| Density                        | 1.488 g/cm <sup>3</sup>        | —                           | [86]       |
|                                | 1.620 g/cm <sup>3</sup>        | —                           | —          |
| Density, calculated, predicted | 1.570 ± 0.06 g/cm <sup>3</sup> | —                           | CAS        |
| Nitrogen content, mass-%       | 23.34                          | —                           | [86]       |
| Oxygen balance, %              | –26.6                          | —                           | [86]       |
| Enthalpy of formation, solid   | –316 kJ/mol                    | –75.5 kcal/mol              | [86]       |
|                                | –301 kJ/mol                    | –71.9 kcal/mol = –299 cal/g | —          |
|                                | –311 kJ/mol                    | –74.3 kcal/mol              | [126]      |
|                                | (corrected for pressure)       |                             |            |
|                                | –306.8 ± 1.5<br>(re-analyzed)  | –73.3 kcal/mol              | [143]      |
| Enthalpy of formation, liquid  | –257.42 kJ/mol                 | –61.5 kcal/mol              | [112]      |
| Heat of combustion, liquid     | 2459.9 kJ/mol                  | 587.9 kcal/mol              | [112]      |
| Heat of combustion, solid      | 2410.6 ± 1.5 kJ/mol            | 576.1 kcal/mol              | [143]      |
| Detonation velocity, confined  | 7580 m/s                       | 25000 ft/s                  | [86]       |
| Impact sensitivity             | 6 N m                          | —                           | [86]       |

are summarized in Table 13. Double-base propellants plasticized with DINA instead of nitroglycerin are named “Albanite.”

### 4.8.3 Chemical Properties of DINA

DINA is a weak acid. The acid constant  $pK_a$  was predicted to be  $-10.40 \pm 0.70$  at 298 K.

#### 4.8.3.1 Thermal Stability of DINA

The thermal decomposition of DINA was examined to determine whether the N–NO<sub>2</sub> linkage or the C–O–NO<sub>2</sub> linkage is the first to break. When examining the critical conditions of thermal explosions of DINA, there was good agreement of the experimental values of temperatures and heat evolution with calculated values from Semenov’s theory [34, 144].



The kinetics of the thermal decomposition of diethylnitramine dinitrate were studied by three different methods: by gas liberation, by the change in weight, and by heat evolution [145]. The reaction is first order and the rate constant, activation energy, and pre-exponent were calculated.

#### 4.8.4 Strand Burning of DINA

The combustion stability of DINA [2,2'-(nitroimino)diethanol dinitrate] was determined in a manometric bomb calorimeter and the effect of initial temperature on the combustion stability was also determined [146]. The presence of a molten layer on the surface of the explosive had no effect on the combustion stability. However, whether normal or accelerating combustion, or even explosion, occurred depended upon the charge density. Combustion stability decreased as the density decreased. The initial temperature had no effect on the combustion stability of DINA. Its combustion stability depended mainly upon the charge density.

The strand burning of DINA cast into 0.9-cm diameter  $\times$  3 cm height beakers was measured in a constant pressure bomb [147]. At an initial temperature of 293 K (20 °C) and 1–100 bar pressure, the burning velocity of sym-dinitroxydiethylnitramine can be described by the equation

$$v = (0.03 + 0.008P)$$

where  $v$  is the burning rate in cm/s and  $P$  is the pressure in bar. At elevated starting temperatures, at the initial conditions of 328 K (55 °C) and 5–25 bar pressure, the burning rate of the molten, liquid compound can be described in accordance with the equation

$$v = (0.045 + 0.0125P)$$

where  $v$  is the burning rate in cm/s and  $P$  is the pressure in bar. The temperature coefficient was virtually independent of pressure. At the initial conditions of 293 K (20 °C) and 8 bar and higher, formation of a bright white flame was noticed at a certain distance from the surface of the liquid top layer of the sample. With increasing pressure, this distance decreased and at  $p = 25$  bar the bright flame touched the surface of the sample. The dependence of the distance between the lower edge of the flame and the surface of the condensed phase of the compound was described by the equation:

$$L = \frac{700}{P^{2.5}}$$

where  $L$  is the distance in cm and  $P$  is the pressure in bar.

The effects of  $K_2CrO_4$ ,  $K_2Cr_2O_7$ ,  $(NH_4)_2Cr_2O_7$ , graphite, and mixtures of graphite with lead and copper salts on the burning rate of DINA were examined by visual observation in a combustion bomb [148]. Surface effects were predominant with graphite additives, especially with ternary mixtures of graphite with lead and copper salts. The

active component of the chromium compounds appeared to be an amorphous oxide of Cr formed at 593–603 K (320–330 °C). The most effective of the additives studied was  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , possibly due to the high temperature and infrared radiation of the incandescent particles resulting in a burning velocity of 0.5 mm/s.

The strand burning rate of DINA was measured in 6- to 32-mm glass tubes with 1-mm walls at atmospheric pressure [149]. Combustion rates in relation to the diameter of the DINA specimens were studied. Steady-state flame propagation was possible only in tubes which were >13 mm in diameter. Between 15 and 32 mm, the burning rate was independent of tube diameter and remained at 0.135 mm/s.

The burning rate of DINA at atmospheric pressure was shown to be determined by the rate of heat evolution in the reaction zone of the condensed phase as well as by the heat flux radiated from the gas phase [150]. The effects of two groups of additives on the strand burning rate of DINA were examined, including ammonium persulfate, hydrazinium sulfate, and hydroxylammonium sulfate, which increased the burning rate through the intensification of heat evolution in the condensed phase, and also soot and compounds of hexavalent chromium, lead, and copper, which accelerated burning as a result of additional heat flux from incandescent condensed particles formed on the burning surface.

The effect of adding 2.6–4%  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ , or  $\text{K}_2\text{CrO}_4$  on the burning mechanism of DINA and DINA containing 2% glycerol trinitrate (GTN) was investigated in a combustion bomb [151].

The strand burning rate of DINA with and without catalysts was measured in 18-mm glass tubes at atmospheric pressure or 7-mm quartz tubes for experiments at elevated pressures [152]. The strand burning rate of uncatalyzed DINA at atmospheric pressure was 0.08 mm/s. The catalysts, PbO,  $(\text{CH}_3\text{COO})_2\text{Cu}$ , and carbon black had a significant effect on the burning rate. A mixture of 5.5%  $(\text{CH}_3\text{COO})_2\text{Cu}$  and 1.5% PbO increased the burning rate to 0.15 mm/s and a mixture of 3%  $(\text{CH}_3\text{COO})_2\text{Cu}$ , 1.5% PbO and 1% carbon black increased the burning rate to 0.45 mm/s.

The effects of the addition of 5%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ , or  $\text{NH}_2\text{OH} \cdot 0.5\text{H}_2\text{SO}_4$  on the combustion velocity of DINA in the condensed phase were also investigated [153]. The additives lowered the temperature of the beginning of exothermic decomposition of DINA to 453–463 K (180–190 °C) and increased the summary heat effect of its thermal decomposition to almost twice as much as without additives  $\leq 879$ – $962$  J/g ( $\leq 210$ – $230$  cal/g). The additives increased the burning velocity of DINA and changed its burning properties in the condensed phase.

The combustion of DINA was studied at atmospheric pressure with and without catalytic additives [154]. The strand burning rate is determined by the rate of heat evolution in the reaction zone of the condensed phase as well as by the heat flux from the flame in the gas phase. Two groups of additives were examined: (1) compounds such as  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , hydrazinium(2+) sulfate, and hydroxylammonium sulfate, which increase the burning rate by way of an intensification of heat evolution in the condensed phase, and (2) compounds of hexavalent chromium and composite additives,

including carbon soot, and lead and copper salts which accelerate burning as a result of additional heat flux from incandescent condensed particles formed on the burning surface and heated to 1273–1473 K (1000–1200 °C) by the heat from heterogeneous catalytic reactions. In the case of the chromium compounds, the active ingredient responsible for the catalytic effect is  $\text{Cr}_2\text{O}_3$  formed in a combustion front.

#### 4.8.5 Safety Properties of DINA

In a U-tube adiabatic compression sensitivity test apparatus with variable, preselected push pressure and constant bubble size, DINA and BuNENA were less sensitive than GTN, DEGDN, or EGDN [155].

#### 4.8.6 Explosive Performance of DINA

The volume of explosion gases of DINA is 924 L/kg and the heat of explosion is 5458 kJ/kg = 1304 kcal/kg for combustion to liquid water and 5025 kJ/kg = 1201 kcal/kg for combustion to steam. The detonation velocity of a confined charge is 7580 m/s = 25000 ft/s at  $\rho = 1.47 \text{ g/cm}^3$ . The impact sensitivity is 0.6 kpm = 6 Nm in the BAM tester.

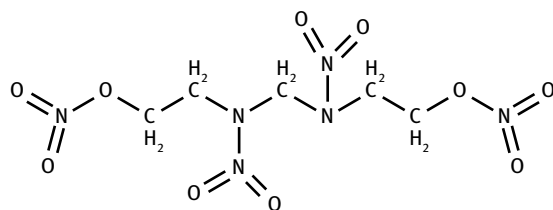
#### 4.8.7 Applications of DINA

DINA is an energetic plasticizer for double-base propellants. DINA has been used as a gelatinizer for nitrocellulose and is a powerful explosive in its own right, comparable to RDX and PETN. Double-base propellants based on DINA instead of glycerol trinitrate were named “Albanite” because of the white color of the mixture.

An energetic plasticizer mixture based on 1,5-dinitrato-3-nitrazapentane (DINA) and 1,5-diazido-3-nitrazapentane had a eutectic freezing point below 248 K (–25 °C). When this eutectic mixture was combined in a propellant composition along with HMX, GAP, and AP, it resulted in propellants equivalent to GTN-based systems but with improved storability.

## 5 Linear Nitratoalkyl Nitramines with Two or More Nitramine Groups

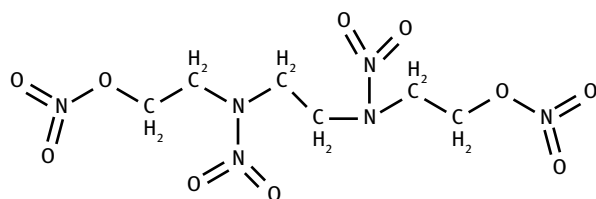
1,7-Dinitroxy-3,5-dinitrazaheptane, 2,2'-bis-[methylenebis(nitroimino)]ethanol 1,1'-dinitrate, 2-[nitro-[nitro(2-nitrooxyethyl)amino]methyl]amino]ethyl nitrate,  $\text{C}_5\text{H}_{10}\text{N}_6\text{O}_{10}$ ,  $\text{O}_3\text{NCH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{NO}_3$ , CAS RN [71545-64-7], is a symmetrical molecule and a nitramine with a higher molecular weight and lower vapor pressure than some of the other NENAs which are also used as plasticizers.



1,7-Dinitroxy-3,5-dinitrazaheptane

1,7-Dinitroxy-3,5-dinitrazaheptane has a molecular mass of 314.17 g/mol, melts at 365–366 K (92–93 °C), and has a predicted density of  $1.658 \pm 0.06 \text{ g/cm}^3$  at 293 K (20 °C).

Its homologue, 1,8-dinitroxy-3,6-dinitrazaoctane, 1,8-dinitrato-3,6-dinitrazaoctane, 1,8-dinitrato-*N,N'*-dinitro-3,6-diazaoctane, 2-[nitro-[2-[nitro(2-nitrooxyethyl)-amino]ethyl]amino]ethyl nitrate,  $\text{O}_3\text{NCH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{NO}_3$ ,  $\text{C}_6\text{H}_{12}\text{N}_6\text{O}_{10}$ , DNDO, CAS RN [82744-29-4], is a symmetrical molecule and a nitramine with a higher molecular weight and lower vapor pressure than some of the other NENAs which are also used as plasticizers.



1,8-Dinitroxy-3,6-dinitrazaoctane

It has a molecular mass of 328.19 g/mol, a melting point (measured) of 333–335 K (60–62 °C), and a predicted density of  $1.593 \pm 0.06 \text{ g/cm}^3$  at 293 K (20 °C).

A more energetic derivative of GTN would be a GTN where one or more of the nitrate ester groups on the propane skeleton have been replaced by nitramino groups. 1-Nitramino-2,3-dinitroxypropane and 1,2,3-trinitraminopropane were prepared by multistep reactions from the corresponding amines and characterized by means of multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ), vibrational spectroscopy, elemental analysis, mass spectrometry, DSC, and TGA [156]. Heats of combustion were measured by oxygen bomb calorimetry and validated by quantum theoretical methods. Both compounds are superior in their performance data to GTN and PETN. In comparison to GTN the sensitivities towards mechanical stimuli was greatly reduced. 1-Nitramino-2,3-dinitroxypropane crystallized in the monoclinic space group *P*21 with an XRD density of  $1.799 \text{ g/cm}^3$ , while 1,2,3-trinitraminopropane crystallized in the orthorhombic space group *Pnma* with an XRD density of  $1.783 \text{ g/cm}^3$ . 1-Nitramino-2,3-dinitroxypropane

melts at 338 K (65°C) and started to decompose at 443 K (170°C). 1,2,3-Trinitraminopropane melts at 406 K (133°C), starts to decompose at 456 K (183°C) and has an enthalpy of formation of +1.450 kJ/g (for comparison: PETN -1.590 kJ/g, GTN -1.548 kJ/g).

## 6 Nitroalkylnitramines

Nitroalkylnitramines are useful plasticizers, similar to nitroalkylnitramines (nitroxyalkylnitramines).

The simplest nitroalkylnitramine would be nitromethylnitramine,  $\text{O}_2\text{NCH}_2\text{NHNO}_2$ , but this compound is not stable. One will typically want to have at least two carbon atoms between the nitro group and the nitramine group to obtain better stability. The next homologues would be 2-nitroethylnitramine  $\text{O}_2\text{NCH}_2\text{CH}_2\text{NHNO}_2$ , and its isomer, nitromethylmethylnitramine  $\text{O}_2\text{NCH}_2\text{N}(\text{NO}_2)\text{CH}_3$ , but they still lack the desired thermal stability.

The next step to more energetic nitroalkylnitramines are those that contain nitro groups on both alkyl groups flanking the nitramino group, such as bis(2-nitroethyl)nitramine  $\text{O}_2\text{N}-\text{CH}_2\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{NO}_2$ , 1,5-dinitro-3-nitrazapentane. Each of the terminal carbon atoms in the  $\beta$ -position of the ethyl groups can carry not only one, but also two or even three nitro groups to make an even more energetic molecule.

Seven linear dinitramines including 5-methyl-2,4-dinitro-2,4-diazaheptane (MDNH), 2,6-dimethyl-3,5-dinitro-3,5-diazaheptane (DMDNH), 2,4-dinitro-2,4-diazaheptane (DNH), and 5,7-dinitro-5,7-diazaundecane (DNU) were synthesized by condensation reactions of nitramines with formaldehyde in an acidic medium, recrystallized for purification, and crystal structures, melting points, melting enthalpies, glass transition temperatures, and densities were measured [157]. Some of the results are summarized in Table 14. When plotting the melting points versus molecular mass, a sine-wave shaped curve developed, with melting points depending on the level of symmetry in the molecule.

### 6.1 *gem*-Dinitroethylnitramines

Most of the work described so far has dealt with nitramines that carried only one nitro group in the alkyl chain of carbon atoms with a  $\text{C}-\text{NO}_2$  group. The oxygen balance of such compounds can be improved by inserting two or more nitro groups into the alkyl side chain of carbon atoms. But will those dinitroalkylnitramines be thermally stable? The thermal decomposition of C,N-disubstituted *gem*-dinitroethylnitramines in dilute solutions in inert solvents is a first-order reaction and it is unaffected by the polarity of the solvent [158]. The rate constant is largely controlled by the steric effect of the substituent at the carbon atom bearing the *gem*-nitro groups. A correlation was found

**Table 14:** Thermal and density data of dinitramines.

| Compound abbreviation | Melting point |      | Melting enthalpy<br>J/g | Glass transition point |       | Density, pycn.<br>g/cm <sup>3</sup> |
|-----------------------|---------------|------|-------------------------|------------------------|-------|-------------------------------------|
|                       | K             | °C   |                         | K                      | °C    |                                     |
| DNDA5                 | 327.5         | 54.4 | 102.3                   | 228.7                  | −44.4 | 1.498                               |
| DNDA6                 | 304.7         | 31.6 | 108.2                   | 214.8                  | −58.3 | 1.419                               |
| DNDA7                 | 348           | 75   | 163.9                   | 263                    | −10.1 | 1.384                               |
| MDNH                  | 334.6         | 61.5 | 106.3                   | —                      | —     | 1.396                               |
| DMDNH                 | 358.2         | 85.1 | 127                     | —                      | —     | 1.323                               |
| DNH                   | 309           | 36   | 110                     | 215.5                  | −57.6 | —                                   |
| DNU                   | 345           | 72   | 125                     | —                      | —     | —                                   |

Data source: [157]

between the rate constant and the steric constant *E* of the substituent. This correlation permitted prediction not only of thermal stability of yet unexplored compounds, but also of an eventual change of the decomposition mechanism.

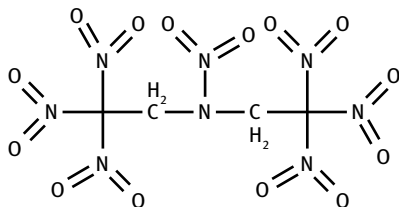
Bis(2,2-dinitroethyl)nitroamine can be synthesized by oxidative nitration of the condensation products from nitromethane and formaldehyde with sodium nitrite and silver nitrate, a subsequent reaction with KOH leading to potassium 2,2-dinitroethanol, followed with a Mannich condensation with ammonia, and finally nitration with fuming nitric acid and concentrated sulfuric acid [159].

Bis(2,2-dinitroethyl)nitramine-based salts (BDNENA salts) can be formed by replacing the trinitro group with a *gem*-dinitro group. A C-deprotonated anion could be obtained by deprotonation of BDNENA to form salts paired with nitrogen–hydrogen-rich cations. Energetic bis(2,2-dinitroethyl-*N*-nitro)ethylenediamine-based salts exhibiting favorable physical properties, good detonation properties, and relatively low impact sensitivities were synthesized in high yield by direct reactions of bis(2,2-dinitroethyl-*N*-nitro)ethylenediamine with organic bases such as aqueous ammonia, ethylenediamine, hydrazine hydrate, guanidine, aminoguanidine, diaminoguanidine, triaminoguanidine, 3,4,5-triamino-1,2,4-triazole, and *N*-carbamoylguanidine [160, 161]. The resulting salts were characterized by multinuclear <sup>1</sup>H and <sup>13</sup>C NMR, IR, DSC, and elemental analysis. Thermal decomposition kinetics and several thermodynamic parameters of some salts were obtained under nonisothermal conditions by DSC. The densities of the energetic salts paired with organic cations were in the range 1.60–2.02 g/cm<sup>3</sup> as measured with a gas pycnometer. Based on the measured densities and calculated heats of formation, predicted detonation pressures and velocities were calculated and found to be 23.6–44.8 GPa and 7790–9583 m/s, which makes them potentially useful as energetic materials. The most dense and thermally most stable salts was the guanidinium salt with a density of 2.02 g/cm<sup>3</sup>, an onset of decomposition at 414 K (141 °C) and an enthalpy of formation of +59.40 kJ/mol.

Addition reactions of polynitro alcohols with 2-nitro-2-azapropyl isocyanate yield symmetrically and asymmetrically substituted nitramino carbamate derivatives [61].

## 6.2 *gem*-Trinitroethylnitramines

Bis-(2,2,2-trinitroethyl)nitramine, di(2,2,2-trinitroethyl)nitramine,  $C_4H_4N_8O_{14}$ , BTNENA, is one of the few explosives with a positive oxygen balance: +14.4%.

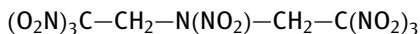


BTNENA

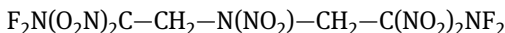
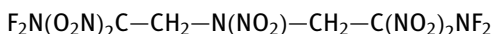
It has a molecular weight of 389.1 g/mol and a nitrogen content of 28.80%. The enthalpy of formation data reported in the literature range from  $-27.6 \text{ kJ/mol} = -71.2 \text{ kJ/kg} = -17.0 \text{ kcal/kg}$  ([86, 133]) to  $+13 \text{ cal/g} = +5.06 \text{ kcal/mol} = +21.2 \text{ kJ/mol}$  [17].

Bis(2,2,2-trinitroethyl)nitramine (BTNENA) with a detonation velocity of 8661 m/s and a density of  $1.97 \text{ g/cm}^3$  was used as the main ingredient in some composite explosives in China, but this type of energetic material is no longer used because of its high sensitivity and chemical instability.

The theoretical enthalpies of gaseous bis(2,2,2-trinitroethyl)nitramine and derivatives in which one or several  $-\text{NO}_2$  groups were substituted by  $-\text{NF}_2$  and/or  $-\text{ONO}_2$  groups were calculated by a density functional theory method using different basis sets [162].

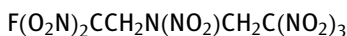


Depending on which method was used, the enthalpy of formation of the compound above was predicted to be between +104 and +159 kJ/mol, which does not match any of the measured values. One of the substituted compounds was 1,1,3,5,5-pentanitro-1,5-bis(difluoroamino)-3-azapentane



Depending on which method was used, the enthalpy of formation of the compound above was predicted to be between +35 and +74 kJ/mol. The heats of formation decreased with progressive  $-\text{NF}_2$  and  $-\text{ONO}_2$  substitution for  $-\text{NO}_2$ , but the heat of explosion increased as  $-\text{ONO}_2$  and  $-\text{NO}_2$  groups were replaced by  $-\text{NF}_2$  groups.

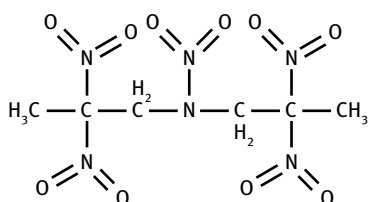
The similar energetic compound (2-fluoro-2,2-dinitroethyl)-2,2,2-trinitroethyl-nitramine



was synthesized and characterized by XRD, IR, Raman, NMR, elemental analysis, MS, and DSC [163]. The heats of formation were calculated by quantum mechanical methods. Predicted detonation pressure, detonation velocity, energy release, and adiabatic temperature were computed. The sensitivity towards impact, friction, and ESD was determined using the BAM standardized test methods.

### 6.3 Bis-2,2-dinitropropylnitramine

The thermal decomposition of *N*-nitro-*N*-bis-(2,2-dinitropropyl)amine, also known as *N,N*-bis(2,2-dinitropropyl)nitramide,  $C_6H_{10}N_6O_{10}$ , BDNPN



BDNPN

proceeds with autoacceleration [164]. The molecule is composed of two *gem*-dinitropropyl groups bonded to a central nitramine group. The first step of the process is monomolecular. The nature of the substituents in nitroamines did not influence the energy of dissociation of the  $N-NO_2$  bond. The increased reactivity of the compounds studied in comparison with *N*-nitrodialkylamines is due to the positive contribution to the entropy of activation, associated with steric hindrances to rotation around the  $N-NO_2$  bond.

Bis(2,2-dinitropropyl)-nitramine has a density of  $1.78 \text{ g/cm}^3$ . It crystallizes with two formula weights in the C-centered monoclinic space group  $C2$  (no. 5) with unit cell parameters  $a = 10.726(4) \text{ \AA}$ ,  $b = 5.992(3) \text{ \AA}$ ,  $c = 10.400(4) \text{ \AA}$ , and  $\beta = 110.01(3)^\circ$  [165]. A comparison of the thermochemical data of BDNPN, RDX, and TNAZ revealed that BDNPN has the highest impetus and lowest flame temperature within this group of molecules. See also [166].

If the 1,3,3-trinitro derivative of azacyclobutane, TNAZ, was an open-chain nitroalkylnitramine, it would be discussed here. However, because the nitro groups are attached to a closed ring, azetidine, the properties of TNAZ are discussed in the chapter "Heterocyclic Amines" in this set, based on the structure of the ring molecule to which the nitro groups have been attached.



## 7 Azidoalkylnitramines

Three nitramines containing 2-azido-1,1-dinitroethyl groups have been synthesized. One of these compounds, 1,7-diazido-2,2,4,6,6-pentanitro-4-azaheptane, possesses a high density of  $1.835 \text{ g/cm}^3$ , and some of the physical and safety properties are also reported [167].

Based on the modification of molecular structure of nitroform nitramines, one azidomethyl group was introduced into the molecule to replace one nitro group of nitroform nitramines, and three high energy density *gem*-dinitroazidoalkylnitramines were synthesized, identified, and characterized [168]. The *gem*-dinitroazidoalkylnitramines have high density ( $1.7\text{--}1.8 \text{ g/cm}^3$ ), high nitrogen content (ca. 40%), satisfactory oxygen balance ( $-23$  to  $-35\%$ ), high positive enthalpy of formation (ca.  $+500 \text{ kJ/mol}$ ), and acceptable thermal stability (thermal decomposition onset temperature ca.  $473 \text{ K} = 200^\circ\text{C}$ ).

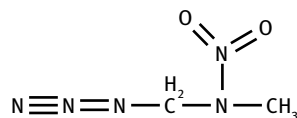
A group of azidoalkylnitramines have been evaluated as plasticizers for gun propellants, including 1,6-diazido-2,5-dinitrazahexane (DADNH), 1,5-diazido-2,4-dinitrazapentane (DADZP), 1,3-diazido-2-nitrazapropane (DANP) 1,5-diazido-3-nitrazapentane (DANPE also known as DIANP), and 1,7-diazido-2,4,6-trinitrazaheptane (DATH) [169]. It is projected that impetus values  $>1400 \text{ J/g}$  will be possible at flame temperatures of approximately  $\sim 3500 \text{ K}$ . If flame temperature was not a constraint, impetus values above  $1500 \text{ J/g}$  would be possible.

Diazido nitramines offer significantly more impetus than RDX and have impetus values as neat ingredients ranging from  $1500$  to  $1750 \text{ J/g}$ . Unfortunately, these nitramines have very high isochoric flame temperatures  $T > 4000 \text{ K}$ , and hence, are of limited usefulness due to high barrel wear. New compounds are required which have the proper stoichiometry to generate lower molecular weight gases, and a suitable  $\Delta H_f$  to provide a reasonable flame temperatures [170].

When examining the kinetic laws and mechanisms of the thermal decomposition of azidonitramines in the gaseous phase, in molten state, and in solutions, it was found that homolysis is a first order reaction, and the rate limiting stage has Arrhenius's parameters  $E_a = 144.8\text{--}166.5 \text{ kJ/mol}$ ,  $\log A = 13.53\text{--}14.97$ , what is not typical for monofunctional alkylazides and alkylnitramines [171]. The thermolysis of the azido group initiates decomposition. Nitramino groups in  $\beta$ - or  $\alpha$ -position to azido groups increase the decomposition rate by 1–2 orders of magnitude, as compared with nitramino groups in the  $\delta$ -position.

### 7.1 1-Azido-2-nitro-2-azapropane and 1-Azido-3-nitro-3-azapentane

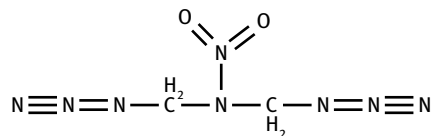
1-Azido-2-nitro-2-azapropane, also known as 1-azido-2-nitrazapropane, *N*-(azido-methyl)-*N*-methyl-nitramide, 1-azido-*N*-methyl-*N*-nitromethanamine,  $\text{C}_2\text{H}_5\text{N}_5\text{O}_2$ , ANAP, CAS RN [55680-29-0],  $M = 131.093$  g/mol,



1-Azido-2-nitro-2-azapropane

was synthesized from 1-chloro-2-nitro-2-azapropane and sodium azide [172]. The highly energetic compound was characterized using vibrational (IR and Raman) and multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ), elemental analysis, and low-temperature single crystal XRD. 1-Azido-2-nitro-2-azapropane represents a covalently bound liquid energetic material which contains both a nitramine unit and an azide group in the same molecule. It was hydrolytically stable at ambient conditions and was very sensitive to friction and impact stimuli. See also [173].

An even more energetic nitramine molecule can be synthesized when both methyl groups carry an azido group:

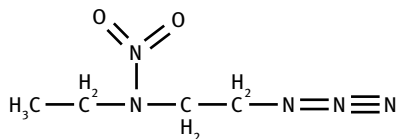


1,3-Diazo-2-nitrazapropane

This energetic compound is called 1,3-diazo-2-nitrazapropane or *N,N*-bis(azido-methyl)nitramide, DANP, 1-azido-*N*-(azidomethyl)-*N*-nitromethanamine,  $\text{C}_2\text{H}_4\text{N}_8\text{O}_2$ , CAS RN [67362-62-3], molecular mass 172.106 g/mol. 1,3-Diazo-2-nitrazapropane is a colorless liquid with an oxygen balance of  $-37.2\%$ , a nitrogen content of  $65\%$ , a melting point of  $265\text{ K } (-8^\circ\text{C})$ , a density of  $1.430\text{ g/cm}^3$ , and an enthalpy of formation of  $+583\text{ kJ/mol } (+139.3\text{ kcal/mol}, +809\text{ cal/g})$ . The reduced-pressure boiling point at  $0.45\text{ mm Hg}$  is  $370\text{ K}$  at  $60\text{ Pa}$  ( $97^\circ\text{C}$  at  $0.45\text{ mm Hg}$ ).

Another azidoalkyl nitramine is ethyl 2-azidoethylnitramine, 1-azido-3-nitro-3-azapentane, *N*-(2-azidoethyl)-*N*-ethyl-nitramide, 2-azido-*N*-ethyl-*N*-nitroethanamine or 2-azido-*N*-ethyl-*N*-nitroethylamine, ethylAENA,  $\text{C}_4\text{H}_9\text{N}_5\text{O}_2$ , CAS RN [89130-64-3],

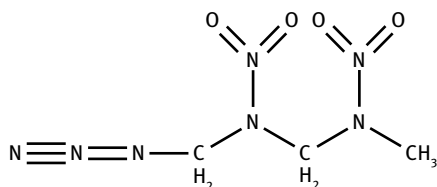
molecular mass 159.15 g/mol, which carries only one terminal azido group on one of the two ethyl groups



Ethyl 2-azidoethylnitramine  
 $\text{H}_3\text{CCH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{N}_3$

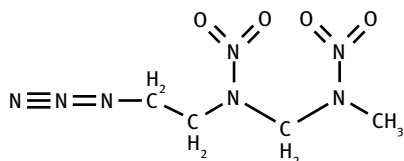
Ethyl 2-azidoethylnitramine is a colorless liquid with a melting point below 258 K ( $-15^\circ\text{C}$ ), a density of  $1.200\text{ g/cm}^3$ , and an enthalpy of formation of  $+205.6\text{ kJ/mol}$  ( $+48.9\text{ kcal/mol}$ ,  $+307\text{ cal/g}$ ).

A similar azidoalkylnitramine is *N*-(azidomethyl)-*N'*-methyl-*N,N'*-dinitro-methanediamine, 1-azido-2,4-dinitrazapentane,  $\text{C}_3\text{H}_7\text{N}_7\text{O}_4$ , CAS RN [1414934-28-3], but very little is known about it:



1-Azido-2,4-dinitrazapentane

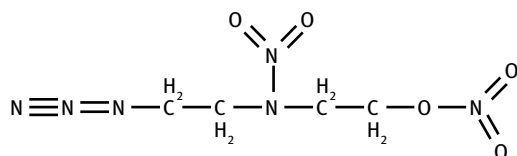
One of its homologues is 1-azido-3,5-dinitro-3,5-diazahehexane, 1-azido-3,5-dinitrazahexane, also known as *N*-(2-azidoethyl)-*N'*-methyl-*N,N'*-dinitro-methanediamine,  $\text{C}_4\text{H}_9\text{N}_7\text{O}_4$ , CAS RN [201596-35-2] which has a melting point of  $307.6\text{--}398.6\text{ K}$  ( $34.5\text{--}35.5^\circ\text{C}$ )



1-Azido-3,5-dinitrazahexane

An energetic plasticizer containing nitramino, azido, and nitroxyl groups in a linear molecular structure, pentanol-3-nitrazo-5-azido nitrate, 2-[2-azidoethyl(nitro)-amino]ethyl nitrate, PNAN, was synthesized via reaction in dimethyl sulfoxide

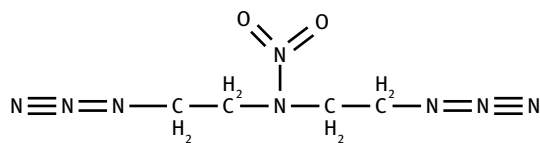
solution, using 1,5-dinitrato-3-nitrazapentane (DINA) and sodium azide as starting materials [174]. The structure of PNAN was characterized by IR,  $^1\text{H}$  NMR, and elemental analyses. The density was  $1.46\text{ g/cm}^3$ , decomposition temperature  $445\text{ K}$  ( $172^\circ\text{C}$ ), glass transition temperature  $232\text{ K}$  ( $-41^\circ\text{C}$ ), viscosity  $19.5\text{ mPas}$ , friction sensitivity  $12\%$ , and impact sensitivity  $56\%$ .



Pentanol-3-nitrazapentane (PNAN)

## 7.2 1,5-Diazido-3-nitrazapentane

1,5-Diazido-3-nitrazapentane, also known as 1,5-diazido-3-nitro-3-azapentane, *N,N*-bis(2-azidoethyl)nitramide,  $\text{C}_4\text{H}_8\text{N}_8\text{O}_2$ , DIANP, DANPE, CAS RN [89130-65-4], carries one terminal azido group on each of the two ethyl groups of a nitramine



1,5-Diazido-3-nitrazapentane

The oxygen balance of DANPE is  $-79.93\%$  and the nitrogen content is  $55.98\% \text{ N}$ .

### 7.2.1 Preparation of DANPE

1,5-Diazido-3-nitrazapentane (DANPE) was synthesized from *N*-nitrodihydroxyethylamine dinitrate  $\text{O}_2\text{NO}-\text{CH}_2-\text{CH}_2-\text{N}(\text{NO}_2)-\text{CH}_2-\text{CH}_2-\text{ONO}_2$  (DINA) and sodium azide, via azidation, extraction, washing, filtration, and vacuum distillation [175]. Its structure was characterized by IR, NMR, and elemental analyses. A parametric study of the optimum reaction conditions for synthesizing DANPE (=DIANP) identified the following optimum operating conditions: mass ratio of DINA to sodium azide about  $1 : 0.59$ ; solvent DMSO; reaction temperature  $353\text{--}358\text{ K}$  ( $80\text{--}85^\circ\text{C}$ ), and reaction time  $7\text{--}8\text{ h}$ . The yield of DANPE (=DIANP) was about  $80\%$  and purity was  $98\%$ . In a similar effort, the optimum conditions for a  $73\%$  yield and  $99.6\%$  purity were as follows: reaction temperature  $373\text{ K} = 100^\circ\text{C}$ , reaction time  $6\text{ h}$ , standing for

3–5 days [176]. The organic impurity was separated and characterized as 1-hydroxy-5-azido-3-nitrazapentane.

1,5-Diazido-3-nitrazapentane can also be synthesized using diethylnitramine dinitrate and sodium azide as starting materials [177]. The kinetic equation describing this synthesis reaction was established and the effect of temperature on the reaction rate was studied. The results indicated that the reaction is of second order under these experimental conditions. The rate constants of the reaction at temperatures of 363, 366, 368, and 371 K (90, 93, 95, and 98 °C) were  $2.11 \times 10^3$ ,  $4.72 \times 10^3$ ,  $6.55 \times 10^3$ , and  $1.20 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$ , respectively. The apparent activation energy  $E_a$  and pre-exponential factor  $A$  of this reaction were 28.87 kJ/mol and  $7.67 \times 10^3 \text{ L/min}$ .

1,5-Diazido-3-nitrazapentane has been made by reacting diethanolamine and nitric acid to form 1,5-dinitrato-3-nitrazapentane (DINA) and then reacting the DINA with metal azide to form the 1,5-diazido-3-nitrazapentane [178, 179].

A two-step process for producing 1,5-diazido-3-nitrazapentane (DANPE = DIANP) involves the steps of nitrating diethanolamine with nitric acid in a halogenated solvent such as methylene chloride to form 1,5-dinitrato-3-nitrazapentane (DINA) as an intermediate, solvent transferring DINA from the halogenated solvent to DMSO, adding sodium azide to the resulting solution to form DANPE as the product, and solvent-transferring DANPE from the DMSO to another halogenated solvent, e.g., methylene chloride [180–182]. Thus, both DINA intermediate and DANPE product can be prepared in solution, and both can also be purified in solution, eliminating the necessity for isolating the neat, hazardous compounds.

An improved preparation of 3-nitro-1,5-diazido-3-azapentane was described and some properties of four azido compounds were determined [183]. The heat of combustion of 1,5-diazido-3-nitrazapentane is 3265.3 kJ/mol (16.313 kJ/g). The standard enthalpy of formation of 1,5-diazido-3-nitrazapentane is +539.74 kJ/mol (+2696.5 J/g).

### 7.2.2 Properties of DANPE

DANPE is a yellow liquid with a melting point of 276 K (2.7 °C = 37 °F) and a boiling point (with incipient decomposition) of 500 K (227 °C = 441 °F). The density of DANPE is  $1.330 \text{ g/cm}^3$ . The enthalpy of formation of DANPE is +594 kJ/mol (+141.9 kcal/mol = +709 cal/g). Other sources [112] gave a heat of combustion of 3899 cal/g and an enthalpy of formation of +540 kJ/mol (+129.0 kcal/mol). In the DSC, the first signs of exotherms are observed at 519 K = 246 °C. 1,5-Diazido-3-nitrazapentane lowers the flame temperature in gun and rocket propellants without visual lessening of burning rates. In addition, the azido nitramine produces low molecular weight combustion products. Applications of DANPE as a plasticizer in solid propellants are discussed in Section 7.2.9. See also [184].

In order to be active as a plasticizer, 1,5-diazido-3-nitrazapentane, DANPE, has to be soluble in nitrocellulose and miscible with other plasticizers. The solubility parameters of DANPE were estimated by a group contribution method and determined

experimentally by turbidity titration [185]. The solubility of DANPE in different solvents was studied and the results showed that the estimated values were in accordance with the determined ones. The solubility parameter of DANPE was determined as  $22.29 \text{ (J/mL)}^{1/2}$ .

### 7.2.3 Mixtures Containing DANPE

Pure 1,5-dinitrato-3-nitrazapentane (DINA) and 1,5-diazido-3-nitrazapentane (DANPE) are solids at room temperature, but a eutectic mixture of the two is a liquid at room temperature and has a freezing point below  $\sim 248 \text{ K}$  ( $\sim -25^\circ\text{C}$ ) [186, 187]

### 7.2.4 Analysis of DANPE

Trace impurities in purity standard 1,5-diazido-3-nitroazapentane DANPE can be analyzed by GC [188]. The sample was dissolved by THF, and separated by a capillary column ( $30 \text{ m} \times 0.32 \text{ mm}$ ,  $5 \mu\text{m}$ ) with temperature programming. The external standard method was employed for quantitative analysis. The relative standard deviations of determination results were 2.16–2.67% ( $n = 6$ ).

The assay of 1,5-diazido-3-nitrazapentane can also be determined by potentiometric titration in DMSO as solvent, first adding sodium hydroxide solution to hydrolyze the azide, then adding an excess of  $\text{AgNO}_3$  to precipitate the azide as  $\text{AgN}_3$  and back titrating with 1-N bromide solution [189]. The purity of standard DANPE was 99.85% and the relative standard derivation was 0.13%. There was no significant variation between the results obtained by electrochemical titration and HPLC.

### 7.2.5 Thermal Decomposition of DANPE

A numerical method of computing the kinetic parameters (the activation energy  $E_a$ , the pre-exponential constant  $A$  and the reaction order  $n$ ) of exothermic decomposition of energetic materials via an exothermic rate equation was applied to six energetic materials [190]. The values of  $E_a$ ,  $A$ , and  $n$  were measured for the exothermic decomposition of six typical energetic materials including 1,6-diazido-2,5-dinitrazahexane (I), 1,5-diazido-3-nitrazapentane (II), 2,2,4,7,9-hexanitro-5-methyl-4,7-dinitrazadecane (III), 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate (IV), 1,4-dinitro-2,3-dioxo-1,4-dinitrazacyclohexane (V), and others.

The thermal decomposition behavior of several energetic plasticizers including DANPE (1,5-diazido-3-nitrazapentane) was investigated in 10 mass-% solutions in toluene by adiabatic self heating in an accelerating rate calorimeter (ARC) and the effect of solvent and sample cell was eliminated by extrapolation [111]. At the lowest detectable heat flow of  $25 \mu\text{W/g}$ , DANPE had a relatively low extrapolated onset of thermal decomposition temperature of  $379.2 \text{ K}$  ( $106.1^\circ\text{C}$ ), while GAP was predicted to start to decompose at about  $387 \text{ K}$  ( $114^\circ\text{C}$ ). The activation energy of the decomposition of DANPE was  $167.3 \pm 0.2 \text{ kJ/mol}$  and the pre-exponential factor was  $9.903 \times 10^{14} \text{ s}^{-1}$ .

### 7.2.6 Molecular Structure of DANPE

A set of linear aliphatic azido nitramines was designed on paper (on screen) and studied by density functional theory methods to find new promising azido nitramines applicable to propellants as plasticizers and to investigate the effect of the methylene nitramino group  $(-\text{CH}_2\text{NNO}_2-)_n$  on performance [191]. The reliability of the predictions of the theoretical method was tested by comparing the theoretical densities with experimental data. The thermodynamic properties (heat capacity, enthalpy and entropy of formation), density  $\rho$ , detonation pressure  $P$ , detonation velocity  $D$ , specific impulse  $I_{\text{sp}}$ , and stability were predicted. With an increase in the number  $n$  of  $(-\text{CH}_2\text{NNO}_2-)_n$  groups, the thermodynamic properties,  $\rho$ ,  $P$ , and  $D$  increased, while the stability decreased slightly. There were linear relationships between thermodynamic properties and  $n$ . Each  $-\text{CH}_2\text{NNO}_2-$  group improved the enthalpy of formation by 67.59 kJ/mol on average. It reached a maximum when  $n = 4$  and changed little when  $n \geq 5$ . Similar  $(-\text{CH}_2\text{NNO}_2-)_n$  studies were performed for cyclic nitramines instead of linear nitramines. It is worth noting that the  $I_{\text{sp}}$  values of all linear compounds were higher than that of HMX.

### 7.2.7 Safety Properties of DANPE

The sensitivity safety properties of 1,5-diazo-3-nitrazapentane and its responses to heat or mechanical stimuli were measured under different levels of severity of the stimuli [192]. At the same time, TNT equivalence of DANPE was tested at different shock wave overpressures to identify the hazard level of DANPE manufacturing plants. The experimental results showed that DANPE cannot be ignited by igniters or flames, and the self-initiation temperature of DANPE was 499 K (226 °C). The TNT equivalence of DANPE in the shock wave overpressure range of 0.02 to 0.3 MPa was 0.4–0.6.

### 7.2.8 Toxicity of DANPE

DANPE is fairly toxic by dermal absorption and by ingestion. The compound has no potential for causing sensitization. The DANPE exhibited increases in chromosomal aberrations and a positive mutagenic response in cell cultures [193, 194]. It was recommended to use extreme caution to prevent DANPE from coming into contact with the skin since studies indicate this material is an effective skin penetrant. In the event of skin contamination, one must flush immediately with large volumes of water. Abrasive soap may increase absorption through the skin. Protective clothing should be worn by workers when there is the potential for accidental contact and splash guards should prevent splashing onto people or onto equipment that people handle. Work clothing should be changed if it becomes contaminated with DANPE.

A 90-day application of DANPE has the potential to cause testicular hypospermatogenesis in male rabbits and an apparent inhibition of mature ovarian follicles formation in female rabbits [195]. A no-observed-adverse-effect level was not achieved in the male rabbits but was achieved in female rabbits at the 27.3 mg/kg dose level.

A 2- and 6-week feeding of DANPE caused testicular hypospermatogenesis in male rats and pneumonitis in female rats [196]. A no-observed-adverse-effect level (NOAEL) was not achieved in male rats but was achieved in female rats at the  $56 \text{ mg kg}^{-1} \text{ day}^{-1}$  level. An oral approximate lethal dose (ALD) value for DANPE in male rats was  $1498 \text{ mg/kg}$  and in female rats it was  $617 \text{ mg/kg}$ . DANPE had a dermal toxicity ALD of  $2129 \text{ mg/kg}$  for male rabbits and  $3192 \text{ mg/kg}$  for female rabbits. DANPE has a primary eye irritant classification of “c” producing mild injury to the cornea. In addition, some injury to the conjunctiva was found. It has a skin irritant classification of “I” producing no primary irritation of the intact skin or no greater than mild primary irritation of the skin surrounding an abrasion. DANPE produced no sensitization reaction in guinea pigs.

### 7.2.9 Applications of DANPE

In view of the proposed application of DANPE as an energetic plasticizer for single-base and double-base propellants, the interaction of DANPE with NC has been studied by experiments and by computational models.

The processing characteristics, microstructures, and mechanical properties of an azidoalkylnitramine-plasticized gun propellant and a double-base gun propellant which were both prepared by a method avoiding volatile solvents were studied by means of a two roller calender, scanning electron microscopy (SEM), and a tensile strength tester [197]. The results indicated that the rolling and plasticizing temperature, plasticizing times, and molding pressure of the azidoalkylnitramine-plasticized gun propellant for the high nitrogen contents (12.6% N or 13.0% N) of NC were lower than those of a conventional NC/GTN double-base gun propellant. DANPE can efficiently plasticize the high nitrogen content of NC. The mechanical properties of the gun propellant with DANPE were improved within a wide range of temperatures. The plasticizing action of DANPE on the high nitrogen content of NC was better than that of GTN.

The mechanical properties, binding energies, and radial distribution functions of pure substances (NC, GTN, DIANP) and NC/DIANP and NC/GTN blends were calculated by molecular dynamics simulations [198]. Results showed that DANPE weakens the rigidity of NC networks and improves its plasticity. This action of DANPE on NC is better than that of GTN. The mechanical properties (modulus) of NC/DANPE blends are related to binding energies. A greater binding energy corresponds to higher mechanical modulus, which is thought to be due to a stronger interactive force between NC and GTN compared to that of NC with DANPE.

The plasticizing effect of DANPE on NC, four NC with different nitration degrees (7.2, 9.5, 10.4, and 12.0% N) as well as binary DANPE/NC mixtures with mass ratios of 1:3 were designed in a computer and investigated by molecular dynamic simulations with the COMPASS force field [199]. For comparison, GTN and GTN/NC mixtures with the mass ratio of 1:3 were also simulated. The miscibility of the mixtures was predicted using solubility parameters. The solubility parameters obtained from the MD



simulations were in reasonable agreement with few experimental data. The mechanical properties, e.g., elastic coefficients, modulus, Cauchy pressure, Poisson's ratio, were predicted and the results showed that both GTN and DANPE can effectively improve the mechanical properties of NC. Mechanical properties are better at higher temperatures. For the NC with higher N%, DANPE has better plasticizing effects than the conventional plasticizer GTN, while the situation is reversed for the NC with lower N%.

Similar molecular dynamics and dissipative particle dynamics simulations were performed to investigate the compatibility and mechanical properties of DANPE with GAP for different simulated chain length ( $n$ ) of GAP with  $n = 5, 10, 20, 30$ , and  $40$  [200]. Results showed that GAP and DANPE have good miscibility with each other. Compared with the mechanical properties of the pure GAP, it was found that addition of DANPE can enhance the plastic properties of GAP for improved tenacity and ductility.

A series of computations of substituted diazidoalkylene compounds based on  $N_3(CH_2)_nN_3$  for  $n = 5, 7, 9$ , such as azidoalkylnitramines, azidoalkyl nitrates, and azidoalkyl nitro compounds, predicted that azidoalkylnitramines would possess the best energetic properties, similar to azidoalkyl nitrates which were predicted to have the best thermodynamic properties [201]. These substituents slightly decreased the thermal stability and the azido nitrate esters had the worst thermal stability. Systematical inspection of the substituent effect can direct experimental researchers to synthesize modified azido compounds purposefully and selectively. Results showed that  $-NNO_2$ ,  $-NO_2$ , and  $-ONO_2$  all can improve the thermodynamic and energetic properties and the performance increases with the increasing number of substituent groups. The improvement contribution to the thermodynamic properties in decreasing order was  $-ONO_2 > -NO_2 > -NNO_2$ , and that to the energetic properties was  $-NNO_2 > -ONO_2 > -NO_2$ .

### 7.3 1,3-Diazido-2-nitrazapropane

1,3-Diazido-2-nitrazapropane, also known as 1,3-diazido-2-nitro-2-azapropane, 1-azido-*N*-(azidomethyl)-*N*-nitromethanamine,  $N_3CH_2N(NO_2)CH_2N_3$ ,  $C_2H_4N_8O_2$ , DANP, is a sufficiently stable compound and one of the most powerful liquid explosives with a high enthalpy of formation and a low freezing point.

1,3-Dihydroxy-2-nitrazapropane is a by-product of RDX production by nitration of urotropine (hexamethylenetetramine). Due to the extreme susceptibility of this compound towards hydrolysis, it can be transformed into a more stable diacetate ester through the reaction with sodium acetate in acetic acid. Azidation then leads to DANP. Other synthetic routes to 1,3-dihydroxy-2-nitrazapropane are described in the literature starting from nitramide, nitrourethane, or urea.

DANP can be made by reacting 1,3-dichloro-2-nitrazapropane with an aqueous solution of sodium azide, extracting the solution with methylene chloride, and separat-

ing the 1,3-diazido-2-nitrazapropane from the extracted solution by distillation [202]. The 1,3-dichloro-2-nitrazapropane was made from 1,3-diacetoxy-2-nitrazapropane.

An alternative method to prepare 1,3-diazido-2-nitrazapropane (DANP) involves the following five stages: (1) nitration of urea to make *N,N'*-dinitrourea [203], (2) condensation of the nitration product with formaldehyde to make 1,3-dihydroxy-2-nitrazapropane, (3) acylation (chlorination) of 1,3-dihydroxy-2-nitrazapropane, (4) chlorination of 1,3-diacetoxy-2-nitrazapropane with HCl, and (5) azidation of the dichloro derivative to make DANP [204]. This synthesis method is selective and enables isolation of pure 1,3-diazido-2-nitrazapropane free from impurities. Physical properties of DANP are summarized in Table 15.

**Table 15:** Physical properties of DANP.

| Property                  | SI units                 | Other units   |
|---------------------------|--------------------------|---------------|
| Molecular mass            | 172.11 g/mol             | 5.8102 mol/kg |
| Melting point             | 265 K                    | −8 °C         |
| Freezing point            | 216 K                    | −57 °C        |
| Density                   | 1.4320 g/cm <sup>3</sup> | —             |
| Decomposition temperature | > 423 K                  | > 150 °C      |
| Refractive index at 23 °C | 1.5265                   | —             |
| Enthalpy of formation     | +4330 kJ/kg              | +745 kJ/mol   |
| Detonation velocity       | 7108 m/s                 | —             |

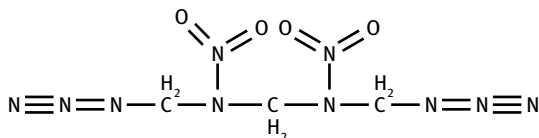
Data source: [204]

A detailed theoretical investigation of 1,5-diazido-3-nitrazapentane (DANP) and 1,7-diazido-2,4,6-trinitrazaheptane (DATNH) was carried out using density functional theory and molecular mechanics computational methods [205]. The crystal structures, spectra, thermodynamic properties, heats of formation, detonation velocity, detonation pressure, specific impulse, and thermal stability were estimated. Possible initiation steps of pyrolysis were the breaking of N—NO<sub>2</sub>, C—N<sub>3</sub>, and N—N<sub>2</sub> bonds for both compounds and the cyclization of the adjacent nitro and azido groups for DATNH. Results showed that the rupture of N—NO<sub>2</sub> and N—N<sub>2</sub> (via hydrogen transfer) may happen simultaneously as the initial step of pyrolysis. DANP has higher stability than DATNH, while DATNH has better detonation performance than DANP. DANP has a lower specific impulse than RDX, while DATNH has a higher specific impulse than RDX.

#### 7.4 1,5-Diazido-2,4-dinitrazapentane and 1,6-Diazido-2,5-dinitrazaheptane

1,5-Diazido-2,4-dinitrazapentane, also known as *N,N'*-bis(azidomethyl)-*N,N'*-dinitromethanedi-amine, *N*-(azidomethyl)-*N*-[[azidomethyl(nitro)amino]methyl]nitramide, C<sub>3</sub>H<sub>6</sub>N<sub>10</sub>O<sub>4</sub>, CAS RN 55680-28-9, DADZP, with an oxygen balance of −32.5%, is

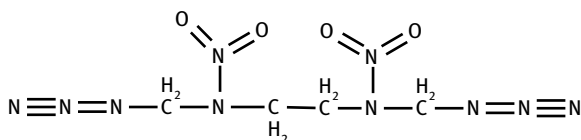
a colorless solid with a melting point of 353 K ( $80^{\circ}\text{C} = 176^{\circ}\text{F}$ ) and a density of  $1.700\text{ g/cm}^3$ .



1,5-Diazido-2,4-dinitrazapentane

The enthalpy of formation of DADZP is  $+751\text{ kJ/mol}$  ( $+179.6\text{ kcal/mol} = +730\text{ cal/g}$ ).

The only difference between the previous compound and the following symmetrical dinitramine compound is the additional methylene group in the center of the molecule. 1,6-Diazido-2,5-dinitrazahexane, *N,N'*-bis(azidomethyl)-*N,N'*-dinitro-1,2-ethanediamine, also known as *N*-(azidomethyl)-*N*-[2-[azidomethyl(nitro)-amino]ethyl]nitramide

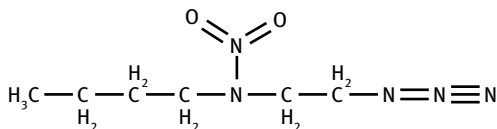


1,6-Diazido-2,5-dinitrazahexane

CAS RN [40627-93-8], DADNH, EDANN,  $\text{C}_4\text{H}_8\text{N}_{10}\text{O}_4$ , is a colorless solid with a molecular mass of  $260.18\text{ g/mol}$ , a melting point of  $349\text{ K}$  ( $76^{\circ}\text{C}$ ), a density of  $1.610\text{ g/cm}^3$ , and an enthalpy of formation of  $+590\text{ kJ/mol}$  ( $+141.0\text{ kcal/mol} = +542\text{ cal/g}$ ). The onset temperature of exothermic decomposition as determined by an ATK Thiokol simulated bulk autoignition test was  $386\text{ K}$  ( $113^{\circ}\text{C} = 235^{\circ}\text{F}$ ). Another azidonitramine in this category is *n*-butyl azidoethylnitramine (BuAENA).

### 7.5 *n*-Butyl Azidoethylnitramine

The heat of reaction of the synthesis process of *n*-butyl azidoethylnitramine, also known as *N*-(2-azidoethyl)-*N*-*n*-butyl-nitramide, BuAENA,



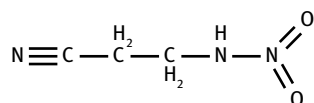
*n*-Butyl azidoethylnitramine

was measured using a calorimeter [206]. The apparent kinetic parameters of the process were obtained by Levenberg-Marquardt's algorithm for least-squares estimation of nonlinear parameters. The results showed that in the process, the enthalpy of reaction ( $\Delta H$ ) was  $-18.1 \text{ kJ/mol}$ . The adiabatic temperature rise  $\Delta T$  was  $11.1 \text{ K}$ , the reaction order was  $0.97$  for BuNENA and  $0.05$  for  $\text{NaN}_3$ , respectively. The activation energy of the reaction was  $15.31 \text{ kJ/mol}$ , and the pre-exponential constant was  $0.27 \text{ mol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}$ .

*n*-Butyl(2-azidoethyl)nitramine has a refractive index of  $n_D^{24} = 1.4870$ , a freezing point below  $195 \text{ K}$  ( $-78^\circ\text{C}$ ), and a very low impact sensitivity beyond the range of the instrument ( $>150 \text{ in. lb}$ ) [207].

## 8 Cyanoalkylnitramines

Cyanoalkylnitramines (nitiloalkylnitramines) carry a cyano group in the alkyl rest which would increase their heat of combustion. Examples are 2-cyanoethylnitramine, *N*-nitro-2-cyanoethylamine, *N*-(2-cyanoethyl)nitramide, 3-(nitroamino)propanenitrile,  $\text{C}_3\text{H}_5\text{N}_3\text{O}_2$ , CAS RN [62984-38-7],  $M = 115.091 \text{ g/mol}$ :



2-Cyanoethylnitramine

The hydrogen on the NH group is quite acidic and forms metal salts. Thermal decomposition kinetics of sodium, potassium, rubidium, and copper salts of *N*-nitro-2-cyanoethylamine were studied in melt by a manometric method combined with IR spectroscopy [208]. The rate constant was practically independent of the metal cation nature. The limiting stage in the decomposition reaction may be the homolysis of the C–N bond to form cyanoethyl and metal nitramide radicals, based on parameters of the Arrhenius equation and activation entropy for the limiting stage.

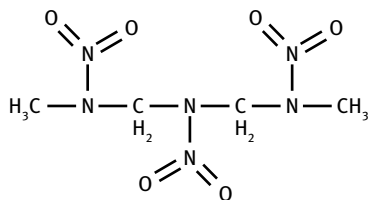
## 9 Linear Trinitramines

Every NH group adjacent to an  $\text{NO}_2$  group is acidic and a variety of salts have been formed from nitramines, including nitramines that contain more than one  $-\text{NH}-\text{NO}_2$  group.

### 9.1 2,4,6-Trinitro-2,4,6-triazaheptane

The simplest trinitramine is 2,4,6-trinitro-2,4,6-triazaheptane, also known as *N,N*-bis-[[methyl(nitro)amino]methyl]nitramide, *N*-methyl-*N'*-[[methyl(nitro)amino]methyl]-

*N,N'*-dinitromethanediamine, TNAHP,  $C_4H_{10}N_6O_6$ , CAS RN [13126-25-5],  $M = 238.159$  g/mol,

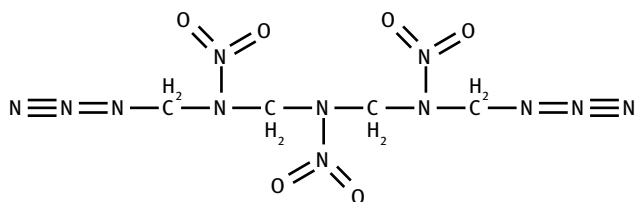


TNAHP

with a melting point of 440–442 K and a heat of fusion of 34.0 kJ/mol.

## 9.2 1,7-Diazido-2,4,6-trinitro-2,4,6-triazaheptane

Trinitramines with terminal azido groups have lower vapor pressure than many other compounds with comparable energy content. One example is 1,7-diazido-2,4,6-trinitrazaheptane, also known as *N,N*-bis[[azidomethyl(nitro)amino]methyl]nitramide, *N*-(azidomethyl)-*N'*-[[[(azidomethyl)(nitro)amino]methyl]-*N,N'*-dinitromethanediamine, DATH,  $C_4H_8N_{12}O_6$ , CAS RN [62209-57-8],  $M = 320.183$  g/mol:



1,7-Diazido-2,4,6-trinitrazaheptane

which is a solid with a molecular mass of 320.19 g/mol, an oxygen balance of –30%, a melting point of 277 K (4 °C), and an enthalpy of formation of +613 kJ/mol (+146.5 kcal/mol = +458 cal/g). Other sources listed a melting point of 379 K (136 °C).

1,7-Diazido-2,4,6-trinitro-2,4,6-triazaheptane (DATH) was synthesized in 75.3% yield starting with urotropine as precursor by nitration, chlorination, and azido substitution steps [209]. The density of DATH was 1.71 g/cm<sup>3</sup>, melting point 408–410 K (135–137 °C), detonation velocity 8300 m/s ( $\rho = 1.64$  g/cm<sup>3</sup>), heat of combustion 10800 kJ/kg, temperature of onset of decomposition 465 K (192 °C), friction sensitivity 25 kg<sub>f</sub>/cm<sup>2</sup>, impact sensitivity 25 cm with a 2-kg weight.

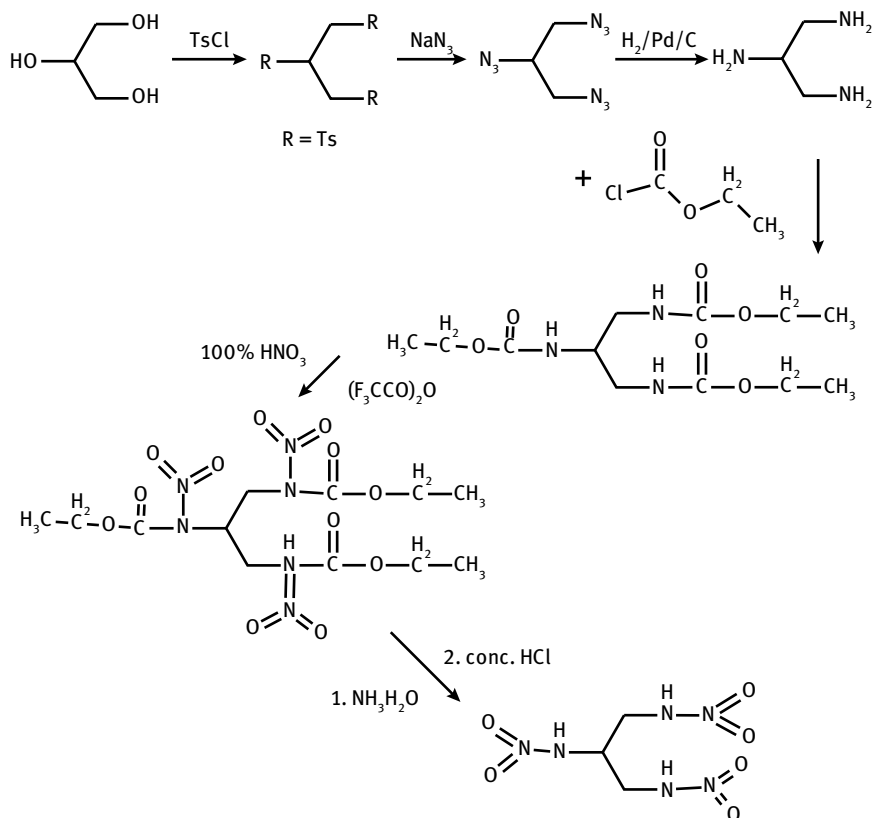
Adding azide-containing ingredients such as 1,7-diazido-2,4,6-trinitrazaheptane (DATH) and/or 1,6-diazido-2,5-dinitrazaheptane (DADNH) as oxidizers and 1,3-diazido-2-nitrazapropane (DANP) as a plasticizer results in improved solid propellants [210]. It was found that compatible propellants with acceptable physical properties could be formulated from these ingredients. Furthermore, the high energy potential of these systems was verified by ballistic testing.

The thermal decomposition characteristics of 1,7-diazido-2,4,6-trinitrazaheptane (DATH) and multicomponent systems containing DATH were studied by using DSC, TGA, and differential thermogravimetric analysis (DTG) techniques [211]. Based on mass loss measurements, three  $\text{—NO}_2$  groups in the DATH molecule break away first from the main chain when DATH is heated up to 473 K (200 °C). Following this process, the azido groups and the residual molecule decomposed rapidly to release a great amount of heat within a short time. In the multicomponent systems, DATH underwent a strong interaction with the binder of the double-base propellant and a weak interaction with RDX. The burning rates of two typical NC-based propellants were determined by using a Crawford bomb. The results showed that the burning rate rose by about 19–66% when 23.5% DATH was substituted for RDX in a minimum smoke propellant.

The thermal decomposition behavior of a low-signature propellant containing 1,7-diazido-2,4,6-trinitrazaheptane (DATH) was investigated by DSC, TGA, and differential thermogravimetric analysis (DTG) [212]. Several analysis methods were used to study the physicochemical structure of surface before and after combustion and the burning flame structure of this kind of propellant. Because DATH decomposes to produce a great quantity of  $\text{N}_2$  gas, the structure of burning surface of the propellant is obviously different from that of RDX-CMDB propellants. The evolution of  $\text{N}_2$  gives rise to the formation of many bubbles and pores on the burning surface. These pores can increase the burning rate because of extending the burning surface and increasing thermal-transfer intensity. In comparison with decomposition and combustion processes of RDX-CMDB propellants, the propellant containing DATH creates different decomposition products from the condensed phase to the fizz zone.

### 9.3 1,2,3-Trinitraminopropane

1,5-Dinitro-3-nitramino-1,5-diazapentane, 1,2,3-trinitraminopropane, 1,2,3-tris-nitraminopropane, *N*-(2,3-dinitramidopropyl)nitramide, TRINP,  $\text{C}_3\text{H}_7\text{N}_6\text{O}_6$ ,  $\text{O}_2\text{NNHCH}_2\text{CH}(\text{NHNO}_2)\text{CH}_2\text{NHNO}_2$ , can be made from glycerol via a six-step synthetic method [213, 214]. Glycerol was converted to the 1,2,3-triaminopropane and nitrated to form 1,2,3-trinitraminopropane with an onset of thermal decomposition at 456 K (183 °C). Trinitraminopropane is an analog to trinitoxypropene, glycerol trinitrate, where all nitrate groups have been replaced by nitramino groups.



1,2,3-Trinitraminopropane melts at 406 K (133 °C), has an XRD density of 1.753 g/cm<sup>3</sup>, and has a predicted enthalpy of formation of +1450 kJ/kg (for comparison: PETN: −1590 kJ/kg). The calculated detonation pressures were 35.62 GPa (for comparison: PETN: 31.39 GPa). The calculated detonation velocities were 8933 m/s (for comparison: PETN: 8564 m/s). Other properties of TRINP are listed in Table 16 along with those of PETNA. Table 17 contains a list of properties of TRINP and its ammonium, hydrazinium, and hydroxylammonium salts.

## 10 Linear and Branched Tetranitramines

### 10.1 Pentaerythritol-Based Nitramines

Pentaerythritol is well known as a backbone for pentaerythritol tetranitrate (PETN), a powerful explosive and next to RDX and HMX one of the most widely used explosives.

Replacing the nitrate ester groups in PETN with nitramine groups results in an even more powerful explosive, pentaerythritol tetranitramine, *N*-[3-nitramido-

Table 16: Properties of pentaerythritol tetranitramine and 1,2,3-trinitraminopropane.

| Compound name                           | Gross formula     | Molecular mass | Onset of thermal decomposition |            | Density <sup>a</sup> | Enthalpy of formation |        | Predicted detonation pressure | Predicted detonation velocity | Impact sensitivity |
|-----------------------------------------|-------------------|----------------|--------------------------------|------------|----------------------|-----------------------|--------|-------------------------------|-------------------------------|--------------------|
|                                         |                   |                | K                              | °C         |                      | kJ/g                  | kJ/mol |                               |                               |                    |
| Pentaerythritol tetra-nitramine (PETNA) | $C_5H_{12}N_8O_8$ | 312.2          | 456                            | 183        | 1.778                | -0.193                | -60.25 | 31.6                          | 8657                          | 6                  |
|                                         |                   | 223.13         | 456                            | 183 (m.p.) | 1.753                | +1.450                | +323.5 | 35.6                          | 8933                          | 20                 |
| 1,2,3-Trinitramino-propane (TRINP)      |                   |                |                                |            |                      |                       |        |                               |                               |                    |
| For comparison:                         |                   |                |                                |            |                      |                       |        |                               |                               |                    |
| PETN                                    | $C_5H_8N_4O_{12}$ | 316.14         | 433                            | 160        | 1.778                | -1.548                | -489.4 | 31.4                          | 8564                          | 2.9                |
| RDX                                     | $C_3H_6N_6O_6$    | 222.12         | 503                            | 230        | 1.816                | +0.42                 | +93.3  | 35.2                          | 8977                          | 7.4                |

Data source: [214]

<sup>a</sup> Gas pycnometer



**Table 17:** Properties of pentaerythritol tetranitramine (PETNA), 1,2,3-trinitraminopropane (TRINP), and their nitrogen base salts.

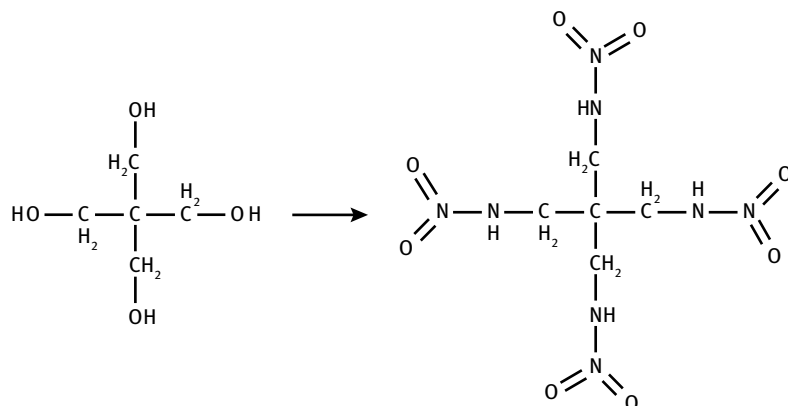
| Compound abbreviation                               | $T_{\text{dec}}$ |     | $\rho$            | $\Delta H_f^{298}$ | $P_{\text{det}}$ | $v_{\text{det}}$ |
|-----------------------------------------------------|------------------|-----|-------------------|--------------------|------------------|------------------|
|                                                     | K                | °C  | g/cm <sup>3</sup> | kJ/mol             | GPa              | m/s              |
| Pentaerythritol tetranitramine PETNA                | 456              | 183 | 1.78              | −60.3              | 31.59            | 8657             |
| PETNA (NH <sub>4</sub> ) <sub>4</sub>               | 451              | 178 | 1.55              | —                  | 24.66            | 7707             |
| PETNA (N <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> | 445              | 172 | 1.57              | —                  | 26.88            | 8002             |
| PETNA (NH <sub>3</sub> OH) <sub>4</sub>             | 452              | 179 | 1.50              | —                  | 22.07            | 7374             |
| 1,2,3-Trinitraaminopropane TRINP                    | 456              | 183 | 1.75              | +324.9             | 35.63            | 8933             |
| TRINP (NH <sub>4</sub> ) <sub>3</sub>               | 433              | 160 | 1.52              | —                  | 23.83            | 7622             |
| TRINP (N <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> | 458              | 185 | 1.56              | —                  | 26.80            | 8012             |
| TRINP (NH <sub>3</sub> OH) <sub>3</sub>             | 442              | 169 | 1.48              | —                  | 23.68            | 7656             |
| For comparison:                                     |                  |     |                   |                    |                  |                  |
| PETN                                                | 433              | 160 | 1.77              | −520.8             | 31.39            | 8564             |
| TNT                                                 | 568              | 295 | 1.65              | −67.2              | 19.53            | 6881             |
| RDX                                                 | 503              | 230 | 1.81              | +92.6              | 35.17            | 8977             |

Data source: [215]

2,2-bis(nitramidomethyl)propyl]nitramide, PETNA, that exists as colorless crystals at ambient temperature, melts at 439.9–440.5 K (166.8–167.4 °C) (with incipient decomposition) and thermally decomposes at 456 K (183 °C). A similar compound can be formed starting with 1,2,3-propanetriol [213, 214]. The properties of pentaerythritol tetranitramine and 1,2,3-trinitraminopropane are summarized in Table 16 in comparison to those of PETN and RDX.

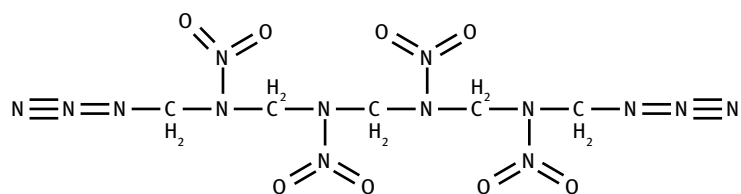
Polynitramines, pentaerythritol tetranitramine (PETNA) and 1,2,3-trinitraminopropane (TRINP), were treated with aqueous ammonia, hydrazine hydrate, or hydroxylamine in methanol at room temperature to obtain their corresponding salts in excellent isolated yields [215]. All new compounds were characterized by IR, NMR, DSC, and elemental analysis. Their energetic properties, such as impact sensitivity, detonation velocity, and detonation pressure, were also determined and compared with existing energetic compounds, such as PETN, RDX, and TNT. The properties of these compounds are listed in Table 17.

Impact sensitivities of all the compounds and salts were measured by using a BAM fall hammer apparatus with a 10 kg drop-weight and found to be no lower than 15 J. All the salts were less sensitive than the molecular precursors PETNA or TRINP as well as PETN (2.9 J) or RDX (7.4 J). The densities of salts were found to be slightly less than those of the parent acids.



## 10.2 Linear Azidoalkyltetranitramines

### 1,9-Diazido-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane



1,9-Diazido-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane

can be made by reacting 1,9-dichloro-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane or 1,9-dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane with sodium azide in dimethylformamide [216].

## 11 Open-chain Heterocyclic Nitramines

The name “heterocyclic nitramines” can apply to heterocyclic compounds like RDX where the nitramino group is part of the ring structure, or it can apply to heterocyclic compounds which carry a nitramino group as a ligand outside the ring structure. Both types are suitable as high energy density materials (HEDMs).

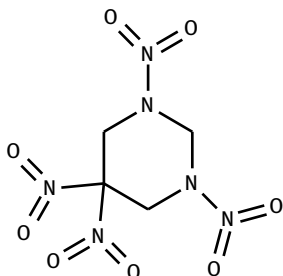
Trying to find the correct location to place the information on RDX in the book at hand depended on making a decision whether to list it here under nitramines (subsequent to open-chain linear nitramines) or list it in a chapter under heterocyclic compounds with triazines. This would mean that HMX also had to be moved as well to the

end of the chapter on 6- (and 8-) membered ring heterocyclic compounds. The decision was made to list RDX and HMX not under heterocyclic compounds but here in the same chapter as linear nitramines. Up to this point, the chapter was reserved for open-chain and linear nitramines. Now we start looking at nitramines that contain rings. This section contains information on  $RN(NO_2)R$  compounds where one or both R groups are heterocyclic rings. Examples of such nitramines are listed on pages 6 and 7 of a patent [217]. Example 5 of that patent describes a 1,1'-(2-nitrazo-1,3-propanediyl)-3,5-dinitro-1,2,4-triazole, which is truly a very energetic compound, a white crystalline powder, which melts at 468 K (195 °C) and explodes at 473 K (200 °C).

## 12 Six-Membered Ring Heterocyclic Nitramines

### 12.1 Six-Membered Ring Heterocyclic Nitramines with Two Nitrogens in the Ring

1,3,5,5-Tetranitrohexahydropyrimidine, DNNC,  $C_4H_6N_6O_8$ , CAS RN [81360-42-1],  $M = 266.126$  g/mol, has been considered as a replacement for RDX and even as a replacement for AP in solid propellants. The total oxygen content is 48.1% and the oxygen balance is -18%, which is better than that of RDX (-21.6%).



1,3,5,5-Tetranitrohexahydropyrimidine

DNNC was synthesized in small samples in a three-step procedure with 25-g batches, and the density was  $\rho = 1.82$  g/cm<sup>3</sup>, the enthalpy of formation was  $\Delta H_f = +46$  kJ/mol = +11 kcal/mol, and the melting point was 424–427 K (151–154 °C) [218]. The onset of exotherm in the DSC was 492 K (219 °C).

### 12.2 Six-Membered Ring Heterocyclic Nitramines with Three Nitrogens in the Ring

Cyclo-1,3,5-trimethylene-2,4,6-trinitramine, RDX, is unique in terms of thermal stability and energy content. In the search for even better cyclic nitramines, the effects of the structure of cyclic *N*-nitramines on the rate and mechanism of their thermolysis

were examined [219]. Manometry together with IR spectroscopy, mass spectrometry, and vapor gas chromatography were used to study the thermolysis of six-membered cyclic *N*-nitramines containing one, two, or three nitramine building blocks, as well as attached oxo, *gem*-dinitro, azide, nitroimino, amino, and tetrazolyl functional groups. This showed an effect of the conformation and functional groups on the rate, mechanism, and activation parameters of the rate limiting stage of thermolysis.

### 12.2.1 1,3,5-Trinitro-1,3,5-triazacyclohexane, Hexogen, Cyclonite, RDX

Cyclo-1,3,5-trimethylene-2,4,6-trinitramine, also known as 1,3,5-trinitro-1,3,5-triazacyclohexane, cyclotrimethylenetrinitramine, trimethylenetrinitramine, hexahydro-1,3,5-trinitro-1,3,5-triazine, 1,3,5-trinitroperhydro-1,3,5-triazine, 1,3,5-trinitrohexahydro-*s*-triazine, 1,3,5-trinitro-1,3,5-triazinane, hexogen, cyclonite, RDX,  $C_3H_6N_6O_6$ , CAS-RN [121-82-4],  $M = 222.12 \text{ g/mol}$ , oxygen balance  $-21.6\%$ , is a widely used energetic additive for solid propellants and an important explosive. Preparation and properties of RDX and HMX and similar heterocyclic nitramines are summarized here in the chapter “Nitramines” compounds instead of the chapter “Heterocyclic Amines,” which deals with all other heterocyclic ring compounds. Cyclic nitramines, which are heterocyclic compounds, are presented here. Applications of RDX in solid rocket propellant formulations (nitramine propellants) will be discussed in future sets on solid propellants. There is so much published information on RDX that a complete compilation would cover an entire book in its own right. This section, embedded in the chapter on heterocyclic nitramine compounds, is only an incomplete survey of some of the information on RDX that might be of interest to rocket propellant formulators. The references cited here are only a random collection of references from the vast literature, an incomplete list, but they give our readers a useful starting point for further research. Most of the publications cited in this section were motivated by the use of RDX and HMX as explosives and not their use as rocket propellant ingredients. Nevertheless, the propellant users benefit from the vast amount of information that was initially intended for the use of RDX and HMX as explosives. Next to AP and NC, RDX may be one of the most frequently used solid ingredients for solid rocket propellants. We do not discuss its application as an explosive here because that would fill another book, which can also be said for HMX. Most books on rocket propellants and explosives contain fairly detailed sections with information on RDX, so the reader who does not find the needed information in the section at hand will have no difficulty finding the necessary information in other sources.

#### 12.2.1.1 History of RDX

Cyclotrimethylenetrinitramine (RDX) was first patented in 1899 by Henning for medicinal use [220]. Its value as an explosive was not recognized until 1920 by Herz. Herz succeeded in preparing RDX by direct nitration of hexamine, but the yields

were low and the process was expensive and unattractive for large-scale production. After publication of von Herz's patents in 1920 [221, 222], the Armament Research Department at Woolwich, UK, began its investigation of RDX (British code name for **R**esearch **D**epartment **E**xplosive or **R**oyal **D**emolition **E**xplosive became the commonly used name for this compound). As a result of this research, the batch process was changed to a continuous flow process. RDX was not used as such as the main filling in British shells and bombs during World War II, but was added to TNT to increase the power of the explosive compositions. During the World War II, hexogen was manufactured in large quantities on both sides, using several different methods.

The oxygen balance of RDX is  $-21.6\%$  and it is thus substantially underoxidized. It is not correct to rank RDX as an oxidizer among the nitramine propellant ingredients.

#### 12.2.1.2 Preparation, Production, and Availability of RDX

The "classical" method of RDX production (Henning 1898) was the direct nitration of hexamethylene tetramine to hexogen using concentrated nitric acid. The concentrated reaction mixture was poured into iced water, and the product precipitated out. Hexamethylene tetramine has six methylene groups but RDX needs only three; thus, three methylene groups must be destroyed or split off by oxidation.

Most RDX is produced in crystalline form by one of two different manufacturing processes. The Woolwich or "nitric acid" process used by Société Nationale des Poudres et des Explosifs (SNPE) in France produces almost pure RDX with few impurities. The Bachmann [223] or "aceto-nitric" process produces mixed products of approximately 79% RDX, 6% HMX, and 15% intermediates. RDX produced by the Bachmann process may contain 4–17% HMX as a contaminant. This process is also called "KA process" (inventors: Knöffler and Apel; in USA: "Bachmann process"), where hexamethylenetetramine dinitrate is reacted with ammonium nitrate and a small amount of nitric acid in an acetic anhydride medium, forming hexamethylenetetramine dinitrate as an intermediate. By using hexamine dinitrate in lieu of formaldehyde only half the amount of water was produced, thus, requiring one half the usual amount of acetic anhydride. The waste acetic acid thus formed can be concentrated, subjected to the so-called ketene process, recycled, and the regenerated acetic anhydride can be re-used.

A continuous nitration of hexamethylenetetramine ("S-H process" after the inventors Schnurr and Henning) using highly concentrated nitric acid, accompanied by a decomposition reaction under liberation of nitrous gases, without destruction of the hexogen formed is patented [224]. The reaction mixture is then filtered to separate the product from the waste acid, followed by stabilization of the product by boiling under pressure and, if required, recrystallization.

In the K process (after the inventor Knöffler), an increased yield can be obtained by the addition of ammonium nitrate to the nitration mixture of hexamethylene tetramine and nitric acid, followed by warming. The formaldehyde that is split off as a by-product formed more hexamethylenetetramine with the added ammonium nitrate and was converted by the nitric acid into hexogen.

There are hundreds of publications dealing with the nitration (nitrolysis) of hexamethylene tetramine leading to a multitude of products; for instance, some papers have been published as a series of papers [225–231].

Another series of publications reported studies on the nitrolysis of hexamethylenetetramine by NMR spectrometry which is a good method to monitor the progress of the reaction and identify some of the intermediates *in situ* as they form and then are quickly consumed in the transformation into other products [232]. In another process, paraformaldehyde and ammonium nitrate are reacted in an acetic anhydride medium with formation of hexogen.

There is considerable variation between RDX batches from the various manufacturers as measured by card gap, critical diameter, and fragment impact tests. The explanation for these differences appears to lie in the crystal morphology rather than in any differences in chemical composition, but a major problem is that accurate information on the manufacturing processes and subsequent treatment of the commercial samples is usually not known.

Intermediates of the RDX/HMX synthesis process are not intended to be used as explosives by themselves, but they are useful tools in explaining the synthesis reactions and optimizing the yield and selectivity of the process. Instead of interrupting the synthesis and capturing the intermediates such as 1-acetylhexahydro-3,5-dinitro-1,3,5-triazine (TAX) and 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX) before they are consumed and end up as RDX or HMX, there are other methods to prepare the intermediates and use them to study the multistep synthesis process of RDX and HMX [233].

### 12.2.1.3 Crystallization of RDX

RDX that is to be incorporated in composite-modified double-base propellants must have a carefully controlled particle size and particle shape. The desired particle shapes can be obtained by crystallizing RDX from different solvents. At the same time, recrystallization removes impurities [234]. The effect of different solvents on the crystallization of RDX has been thoroughly investigated. Very useful information on the crystallization of chemicals with special reference to RDX and HMX has already been published [235], including nicely illustrated information on the best crystallization methods for RDX and HMX using different solvents and cooling rates.

Nano-RDX can be prepared by evaporation assisted solvent–antisolvent interaction [236]. Nanoparticles of RDX can be prepared by a simple re-precipitation method using acetone as solvent and water as the antisolvent. The effects of changing experimental parameters such as ratio of solvent to antisolvent, temperature of antisolvent during injection, and concentration of solution on particle size and morphology of RDX were systematically studied. The size of the particles was characterized using dynamic light scattering and field emission scanning electron microscopy. The mean particle size of the RDX nanoparticles according to SEM analysis ranged from 40 to 230 nm under different conditions of preparation. The UV/Vis absorption max-

imum of nano-RDX was found to be blue-shifted when compared to the absorption maximum for bulk RDX. Powder XRD results showed that RDX nanoparticles precipitated in a stable  $\alpha$ -RDX crystalline polymorph form. Fourier transform infrared (FTIR) spectroscopy was used to characterize the chemical nature of the nano-RDX. Thermal characterization of the RDX-nanoparticles was performed using simultaneous thermogravimetric analysis coupled with differential scanning calorimetry (TGA-DSC).

A significant research and development effort was made and is still ongoing on crystallization processes in order to master crystal quality, particle shapes, and/or size distributions of RDX and RDX replacements such as NTO. In the case of RDX or I-RDX, the objective is to reach the highest limit of shock insensitiveness thanks to a process developed and patented by the French–German Institute of Saint Louis (ISL) [237]. With the help of ISL scientists, EURENCO was able to produce at pilot scale several batches of VI-RDX (VI stands for very insensitive), which were proven to equal shock sensitivities of VI-RDX produced by ISL at laboratory scale and is now producing IRDX<sup>®</sup>. Chemring Nobel is also producing crystalline RDX [132].

### 12.2.2 Physical Properties of RDX

The physical properties of RDX are summarized in Table 18. Additional data for a wider range of temperatures are provided in the subsequent sections of this chapter.

**Table 18:** Physical properties of hexogen (RDX).

| Property                                 | SI units                |               | Other units    |           | References |
|------------------------------------------|-------------------------|---------------|----------------|-----------|------------|
| Molecular mass                           | 222.1163 g/mol          | 4.5021 mol/kg | —              | —         | [85]       |
| Melting point                            | 477 K                   | —             | 204 °C         | 399 °F    | [133]      |
| Density at 293 K                         | 1.82 g/cm <sup>3</sup>  | —             | —              | —         | [133]      |
| Density at 298 K                         | 1.806 g/cm <sup>3</sup> | —             | —              | —         | [238]      |
| Enthalpy of formation $\Delta H_f^{298}$ | +66.9 kJ/mol            | +301.4 kJ/kg  | +16.0 kcal/mol | +72 cal/g | [133]      |

Data source: [133]

Additional information on properties of RDX is available in the well-known common information sources [239–243].

RDX and four other high explosives were analyzed thoroughly in a round robin analysis exercise, comparing the results obtained in several international (NATO) laboratories on identical samples [244]. Although this report also contains information on the thermal stability, sensitivity, and physical properties of five high explosives (RDX, HMX, TNT, PETN, and tetryl), it is referenced mostly here in the RDX section because of the five explosives described, RDX is the only one that is actually used in substantial quantities in nitramine propellants. The report contains very clean IR and NMR spectra of the five explosives.

### 12.2.2.1 Melting Point of RDX

The melting point of RDX is  $477\text{ K} = 204\text{ °C} = 399\text{ °F}$ . In a DTA, RDX containing 0.2% HMX started to melt at  $465\text{ K}$  ( $192\text{ °C}$ ) and the maximum melting endotherm was at  $473\text{ K}$  ( $200\text{ °C}$ ). The same report [244] lists the melting point of RDX as  $474.9\text{--}475.5\text{ K}$  ( $201.9\text{--}202.5\text{ °C}$ ). NIST Chemistry WebBook [85] referenced a paper by Hall [245], which gave m.p. =  $478.5\text{ K} = 205.4\text{ °C}$ . The RDX used by Krien, Licht, and Zierath [87] melted at  $475.8\text{ K}$  ( $202.7\text{ °C}$ ).

The melting and thermodynamic properties of RDX were examined using a diamond anvil cell apparatus capable of pressures exceeding 10 kbar (1000 MPa) and  $523\text{ K}$  ( $250\text{ °C}$ ) [246]. The slope of the melting temperature versus applied pressure curve for RDX, as determined in a diamond cell, was found to be  $4.09 \pm 0.6\text{ °C/kbar}$  ( $0.0409 \pm 0.006\text{ °C/MPa}$ ). The density of liquid RDX at its melting point was calculated from this slope to be approximately  $1.63\text{ g/cm}^3$ . A phase diagram of binary RDX/HMX mixtures is shown in Figure 23 in Section 15.2.1.

### 12.2.2.2 Vapor Pressure of RDX

Knowledge of the vapor pressure of explosives like RDX is important for the ability to detect explosives in clandestine illegal operations. The vapor pressure of strand-burning RDX determines how much RDX evaporates before it decomposes in the flame front. RDX in nitramine propellants would sublime and leave vacant hollow spaces if it was too volatile when the propellant is exposed to high temperatures in tropical climates. The difficulty with measuring vapor pressure of RDX at higher temperatures beyond its melting point is that the samples begins to decompose and gas evolution disturbs the pressure measurements.

The vapor pressure of RDX and several other high melting explosives was computed using the Langmuir equation which utilized the mass loss measurements taken in a heated vacuum apparatus [247, 248]. The following equation was applicable to the temperature range of  $329\text{--}371\text{ K}$ :

$$\log_{10} P = 14.18 - 31110/(4.576 \times T)$$

where  $P$  is the pressure in mm Hg and  $T$  is the temperature in kelvin. The vapor pressure of RDX at  $321\text{ K}$  ( $48\text{ °C}$ ) is  $10^{-7}\text{ mm Hg}$ .

The vapor pressure of RDX was measured using a DSC method that placed RDX in a sealed cell of known volume with a small hole of known diameter at the top [249]. The data were curve-fitted and gave the vapor pressure equation

$$\log_{10} P = 7.678 - 4415.908/T$$

where  $P$  is the pressure in atm and  $T$  is the temperature in kelvin.

The vapor pressure of RDX was measured through isotope dilution analysis and a nonfragmenting field ionization mass spectrometer, and it was noted that their data were not consistent with those obtained by effusion methods and varied significantly



at some temperatures [250]. Data collected at temperatures of 347.15, 357.15, and 369.15 K was fitted to the Clausius–Clapeyron equation:

$$\log P = \frac{\Delta H}{2.303RT_0} - \frac{\Delta H}{2.303RT}$$

where  $P$  is the vapor pressure in mm Hg,  $T$  is the temperature in kelvin,  $T_0 = 840$  K,  $\Delta H = 13.6$  kcal/mol, and  $R$  is the gas constant  $R = 0.00198588$  kcal mol<sup>-1</sup> K<sup>-1</sup>. In comparison, the data by John et al. [250] follows a different slope when the  $\log P$  vs.  $T^{-1}$  is graphed and compared. The RDX concentration in air at 298 K (25 °C) is 0.8 ppb v/v.

Dionne et al. measured the vapor pressure of RDX directly in the range of 298–413 K using a vapor pressure generator coupled with a cold trap using a military-grade RDX sample obtained from the Federal Bureau of Investigation (FBI) and no further purification or purity analysis was carried out [251]. The measured data were combined with literature data and for temperature range 309–411 K fitted to an equation of the type:

$$\log_{10} P = +22.50 - \left( \frac{6473}{T} \right)$$

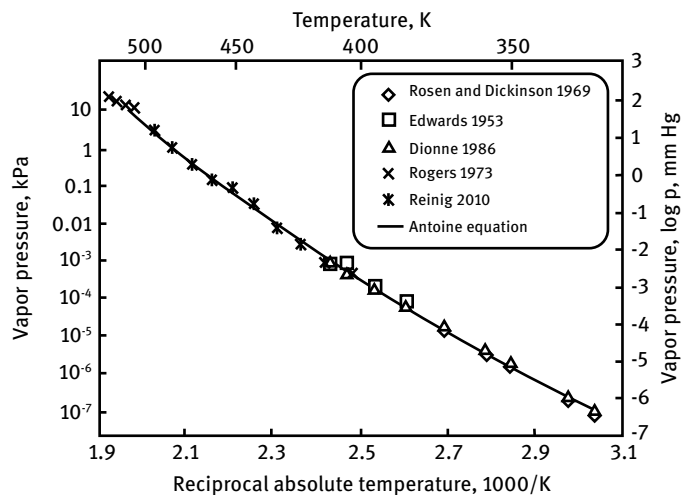
where  $P$  is the pressure in ppt and  $T$  is the temperature in kelvin.

In addition to vapor pressures measured by static and dynamic methods, vapor pressures of self-burning energetic materials can be derived from the surface temperature of burning solid specimens [252]. The vapor pressure of RDX was measured by a comparative GC method [253]. For two homologous compounds, the  $\log P$  versus the retention time exhibits a linear relationship. Increasing the temperature in a GC column will decrease the retention time of the analyte. The data from the Reinig GC measurements [253] were curve-fitted to give the parameters for an Antoine vapor pressure equation

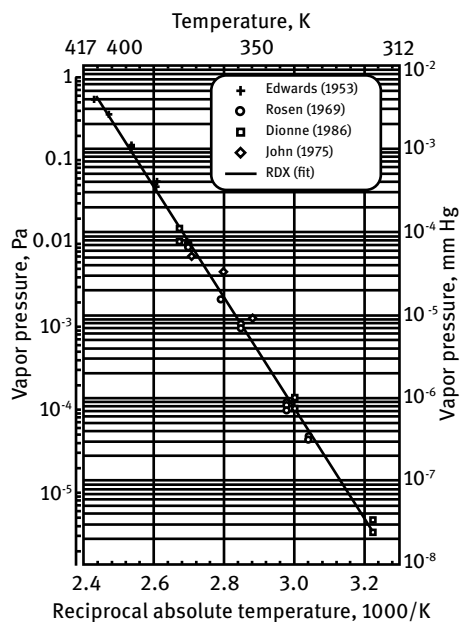
$$\log_{10} P = A - B/(C + T)$$

where  $P$  is the vapor pressure in mm Hg,  $T$  is the temperature in kelvin and  $A = 31.995$ ,  $B = 24883.728$ , and  $C = 313.210$  [253]. Figure 6 is a comparison of vapor pressure from the Antoine equation (solid line) with data from different authors

A critical review by Oestmark et al. looked at data from five papers that had been published on the vapor pressure of RDX and other explosives, trying to resolve discrepancies and establishing a baseline for comparison [254]. The combined data from four of those papers is illustrated in Figure 7, although three data sources are the same as the ones used for Figure 6. The figure also shows a Clausius–Clapeyron fit to this data, except the data from John [250] was excluded due to inconsistencies between values in the text and in the figure in his paper. It is possible to extrapolate the data in Figure 7 to room temperature using the Clausius–Clapeyron equation, but in order to obtain more reliable room temperature data, more exact measurements or possibly



**Figure 6:** Vapor pressure of RDX. (Reproduced and modified from [253], with permission from Dr. Michael Reinig 7 March 2021.)



**Figure 7:** Vapor pressure of RDX. (Republished and modified from [254], with permission from ©2012 John Wiley & Sons – Journals; permission conveyed through Copyright Clearance Center, Inc.)

modeling would be advisable. The Clausius–Clapeyron fit of the data for RDX led to the equation

$$\log P = A - \frac{B}{T} = 13.79 - \left( \frac{6637}{T} \right)$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin for the temperature range 310–411 K (37–138 °C). The vapor pressure for RDX at 298 K was extrapolated to be  $3.30 \times 10^{-9}$  mm Hg. The heat of sublimation is 127.1 kJ/mol (30.38 kcal/mol).

Additional vapor pressure data for RDX (and PETN and HMX) are available in the older literature [255, 256]. Thermodynamic data on evaporation and sublimation of RDX are listed in Table 19.

**Table 19:** Thermodynamic data on evaporation and sublimation of RDX.

| State of matter | Temperature interval (K) | Temperature dependence of pressure above condensed phase (pressure in atm) | Heat of evaporation (or sublimation) (kJ/mol) | References |
|-----------------|--------------------------|----------------------------------------------------------------------------|-----------------------------------------------|------------|
| Solid           | 343–447                  | $\ln P = 28.216 - 16143.4/T$                                               | (134.3)                                       | [256]      |
| Liquid          | 590–795                  | $\ln P = 19.925 - 12179.2/T$                                               | 101.3                                         | [252]      |

### 12.2.2.3 Density of RDX

The density distributions of six samples of Class 1 RDX were measured using the density gradient technique [238]. This technique was used in an attempt to distinguish between RDX crystallized by a French manufacturer (designated insensitive or IRDX) from RDX manufactured at Holston Army Ammunition Plant (HAAP), the current source of RDX for Department of Defense (DoD). Two samples from different lots of French IRDX had an average density of  $1.7958 \pm 0.0008$  g/cm<sup>3</sup>. The theoretical density of a perfect RDX crystal is 1.806 g/cm<sup>3</sup>. This yields 99.43% of the theoretical maximum density (TMD). For two HAAP RDX lots, the average density was  $1.786 \pm 0.002$  g/cm<sup>3</sup>, only 98.89% TMD. High performance liquid chromatography showed quantities of HMX in HAAP RDX. French IRDX also showed a 1.1 °C higher melting point compared to HAAP RDX in the DSC, consistent with no melting point depression due to the HMX contaminant. A second part of the program involved characterization of Holston RDX recrystallized using the French process. After reprocessing the average density of the Holston RDX was increased to 1.7907 g/cm<sup>3</sup>. The French IRDX contained no HMX, which is assumed to account for its higher density and narrower density distribution. Reprocessing of RDX from Holston improved the average density compared to the original Holston RDX, but the resulting HIRDX was not as dense as the original French IRDX. When the HRDX was reprocessed by SNPE to convert it to IRDX, the density distribution increased and the mean density increased to 1.791 g/cm<sup>3</sup> (99.04% TMD). Clearly, the French process for preparing IRDX was only partially successful in transforming the RDX from HAAP into IRDX of the same density as the original SNPE IRDX. Recrystallized Holston IRDX crystals were much larger (3–500 μm or more) than either the original Class 1 HAAP RDX or French IRDX.

The Peng–Robinson equation of state was applied to RDX, TNT, and RDX/TNT mixtures [257]. The pure RDX and TNT in both their liquid and solid phases, as well

liquid and solid mixtures of the two compounds were modeled for temperatures and pressures as high as 500 K and 2500 bar. The Peng–Robinson equation of state provided a good representation of experimental volumetric (e.g., density and bulk modulus), thermal (heat capacity), and phase behavior (melting temperature and solubility) data.

RDX crystals were grown during high acceleration (high g) in an ultracentrifuge [258]. These crystals were found to have a density  $\sim 0.6\%$  greater than crystals obtained at 1g and to have a greatly reduced defect content. The high-g crystals should therefore have significantly reduced shock sensitivity compared to commercial grade RDX. Crystal defects including voids and solution inclusions caused by temperature variation or evaporation at 1g are minimized and the RDX crystal density increases. A nitrogen pycnometer was used to measure the density of the RDX crystals grown at 1g and at 200000g. The density of the RDX crystals grown at 200000 g ( $1.7980 \pm 0.0003 \text{ g/cm}^3$ ) was found to be greater than the density of RDX crystals grown at 1g ( $1.7881 \pm 0.0003 \text{ g/cm}^3$ ) by  $0.0099 \text{ g/cm}^3$ . The density of the high-g crystal was 99.6% of the theoretical maximum density of RDX.

#### 12.2.2.4 Phase Transitions of RDX

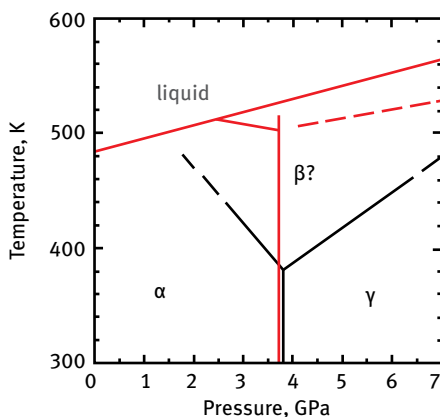
RDX exists in several polymorphic modifications. The two simplest polymorphic forms of RDX are designated  $\alpha$ - and  $\beta$ -RDX. The structure of  $\alpha$ -RDX has been determined by single crystal neutron diffraction [259]. The structure of  $\beta$ -RDX has not been determined because of the difficulty of obtaining and preserving well-formed crystals, even for short periods, owing to its extreme instability under ambient conditions. Many of the physical properties and the sensitivity to stimuli leading to explosion depend on the modification the crystals are currently in. The transition temperatures and pressures of phase transitions in RDX are listed in Table 20.

**Table 20:** Transition temperatures and pressures of polymorphic phase transitions in RDX.

| Phase transition            | Temperature |        | Pressure |       |
|-----------------------------|-------------|--------|----------|-------|
|                             | K           | °C     |          |       |
| $\alpha \rightarrow \gamma$ | 295–460     | 22–187 | 3.7 GPa  |       |
| $\alpha \rightarrow \beta$  | 477         | 204    | 101 kPa  | 1 atm |

Raman spectroscopy and optical imaging were used to determine the phase boundaries between various RDX polymorphs on single crystals at pressures up to 8.0 GPa and temperatures ranging from room temperature to 550 K [260]. Several distinct pressure regions were found in the RDX response at elevated temperatures: (1) melting of  $\alpha$ -RDX followed by decomposition, below 2.0 GPa, (2) decomposition of  $\alpha$ -RDX between 2.0 and 2.8 GPa, (3) irreversible transformation of  $\alpha$ - and  $\gamma$ -RDX to  $\epsilon$ -RDX between 2.8 and 6.0 GPa, and (4) decomposition of  $\gamma$ -RDX above 6.0 GPa. A triple point between

the  $\alpha$ -,  $\gamma$ -, and  $\epsilon$ -RDX was found at 3.7 GPa and 466 K. The  $\alpha \rightarrow \gamma$  phase transition was confirmed to occur at the same pressure,  $\sim 3.7$  GPa, regardless of temperature, in the range of 295–460 K. Furthermore, it was determined that  $\epsilon$ -RDX (1) has limited chemical stability under the pressure and temperature conditions where it is produced and (2) decomposes according to the autocatalytic rate law. The high pressure-high temperature polymorph was inferred to be the not very well defined  $\beta$ -RDX phase in these studies (Figure 8).



**Figure 8:** RDX phase diagram. (Reprinted and adapted from [260], with permission from ©2010 American Chemical Society; permission conveyed through RightsLink.) Legend: Dark black lines are from (Baer, Oxley, and Nicol [261]) (dashed lines, extrapolation of experimental data). Red lines are from (Nicol, Oxley, and Baer [262]) (dashed line, approximate phase boundary between  $\gamma$ - and HP-HT-polymorphs).

Raman spectroscopy has been used to determine the phase diagram and phase behavior of RDX at pressures up to 16 GPa and at temperatures from 150 to over 450 K [261]. Two new stable solid polymorphs have been identified: a high pressure/low temperature form that converts reversibly to  $\alpha$ -RDX (the form stable at ambient conditions) at 3.8 GPa, independent of temperature from 150 to 375 K. There were indications of a high pressure/high temperature form of RDX that was highly metastable, showed a very large hysteresis, and probably was identical with the polymorph known as  $\beta$ -RDX.

In order to study the effect of isotope substitution on phase changes, the phase diagrams of RDX-h6 and RDX-d6 have been examined by Raman spectroscopy up to pressures of more than 13 GPa at 295 K and 7.5 GPa between 150 and 450 K [262]. Two stable high pressure phases have been found:  $\gamma$ -RDX or RDX-III formed from  $\alpha$ -RDX above 3.8 GPa below 380 K.  $\beta$ -RDX formed when  $\alpha$ - or  $\gamma$ -RDX were heated.  $\beta$ -RDX can be retained metastably at low temperatures and may be related to a very unstable form occasionally recovered at ambient pressure. Deuterium isotopic substitution increased the temperature where  $\beta$ -RDX began to form on heating.

Phase changes between three solid ( $\alpha$ ,  $\gamma$ ,  $\epsilon$ ), one liquid, and decomposed phases of RDX were examined in experiments on single crystals at pressures up to 12.0 GPa and temperatures to 600 K in a diamond anvil cell [263]. Several distinct pressure regions were found in the RDX response at elevated temperatures. The boundaries between the  $\alpha$ ,  $\gamma$ , and  $\epsilon$  phases were determined with a triple point at 3.7 GPa and  $\sim 466$  K. The  $\alpha \rightarrow \gamma$

phase transition was confirmed to be reversible and to occur at the same pressure 3.7 GPa, regardless of temperature. The  $\epsilon$ -phase was found to exist only in a narrow range of pressures, from 2.8 to 6.0 GPa. Below and above these pressures,  $\alpha$ - or  $\gamma$ -RDX crystals decomposed or melted instead of transforming to  $\epsilon$ -RDX. Both the  $\alpha \rightarrow \epsilon$  and  $\gamma \rightarrow \epsilon$  transitions were irreversible at the phase boundaries.

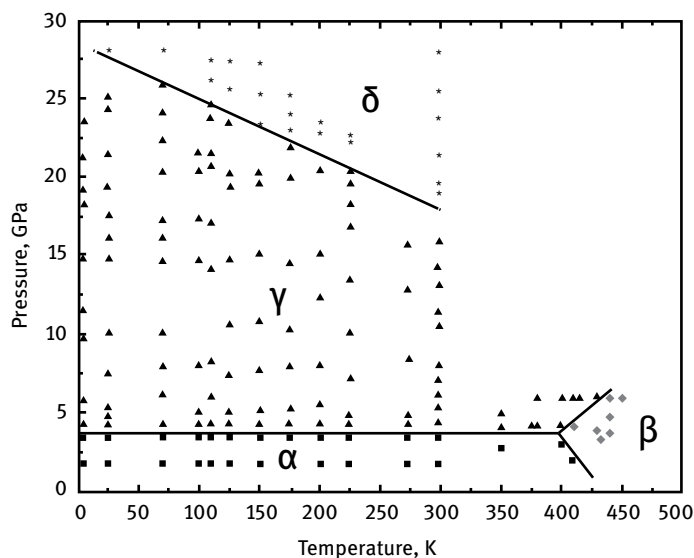
Three distinct solid phases were observed when high pressure and temperature structural changes for RDX were investigated at pressures up to 7.0 GPa and temperatures around 570 K in a diamond anvil cell apparatus using FTIR absorption, optical microscopy, and EDAX techniques [264]. The effects of pressure on the thermal decomposition kinetics as a function of RDX pressure were investigated using an IR absorption technique. Solid phase I ( $\alpha$ -RDX) was found to have a pressure enhanced reaction rate with an energy and volume of activation of 213 kJ/mol (51 kcal/mol) and  $-5.6 \text{ cm}^3/\text{mol}$ , respectively. Solid II was not observed to react and the observed reaction rate of solid III decreased with increasing pressure.

The  $\alpha$  and  $\beta$  phases of RDX were found to thermally decompose, while the  $\gamma$  phase transformed to either  $\alpha$  or  $\beta$  before reaching decomposition temperatures [265]. The decomposition rate of  $\alpha$  phase was found to increase with increasing pressure, suggesting a bimolecular-type mechanism.

A diamond anvil cell was used in conjunction with optical polarizing light microscopy (OPLM), FTIR, energy dispersive X-ray diffraction (EDAX), and micro FT-Raman spectroscopy to determine pressure/temperature/reaction phase diagrams for several nitramine compounds, including RDX and HNIW [266].

High-pressure phase transitions of RDX and HMX were studied in a diamond anvil cell with XRD and Raman spectroscopy [267]. The existence of a high-pressure phase, termed  $\delta$ -RDX, had not been confirmed until 2008, although it was suggested already nearly 20 years earlier. Very limited characterization of  $\delta$ -RDX existed and one of the primary goals of later studies was to investigate the temperature/pressure stability of this phase. The phase diagram of RDX was studied as a function of temperature and pressure by Raman spectroscopy at pressures up to 29 GPa and temperatures ranging from 4 to 298 K [268]. Three stable phases ( $\alpha$ ,  $\gamma$ , and  $\delta$ ) have been found and their phase stabilities have been investigated. Phase boundaries were studied as a function of pressure and temperature, permitting a delineation of the various polymorph stability fields. A pressure–temperature phase diagram is shown in Figure 9. The Raman spectra observed for the  $\delta$ -RDX phase as a function of temperature showed a larger number of vibrational modes in the Raman spectra than was noted in both the  $\alpha$ -RDX and  $\gamma$ -RDX spectra. This is probably due to an increase in the molecular symmetry as is found with  $\beta$ -RDX. New vibrational features near 235 and 430  $\text{cm}^{-1}$  were comparable to those previously reported for the  $\beta$ -RDX phase.

The linear coefficient of thermal expansion of RDX at 293 K is  $6.36 \times 10^{-5} \text{ K}^{-1}$  and the cubical coefficient of thermal expansion at 293 to 373 K is  $2.5 \times 10^{-4} \text{ K}^{-1}$ .



**Figure 9:** Temperature–pressure phase diagram of RDX. (Republished and modified from [268], with permission of ©2008 John Wiley & Sons – Books; permission conveyed through Copyright Clearance Center Inc.)

#### 12.2.2.5 Compressibility and Velocity of Sound of RDX

The compressibility of RDX crystals is anisotropic and depends on the crystal plane to which the load is applied. It also depends on the polymorph modification the crystal is currently in. The modification undergoes changes as pressure is applied. The compressibility of RDX has been studied both experimentally and theoretically–computationally. Compressibility is closely related to the speed of sound and the speed of sound is closely related to the detonation velocity of explosives like RDX. There are fewer experimental studies than computational studies.

#### Experimental Studies of RDX Compressibility

The propagation of detonation fronts and shock waves through RDX and other explosives depends on the compressibility of the material. The real-time, molecular-level response of oriented single crystals of RDX to shock compression was examined using Raman spectroscopy [269]. Single crystals of [111], [210], or [100] orientation were shocked under stepwise loading to peak stresses from 3.0 to 5.5 GPa. Two types of measurements were performed: (1) high-resolution Raman spectroscopy to probe the material at peak stress and (2) time-resolved Raman spectroscopy to monitor the evolution of molecular changes as the shock wave reverberated through the material. The frequency shift of the C–H stretching modes under shock loading appeared to be similar for all three crystal orientations below 3.5 GPa. Significant spectral changes were

observed in crystals shocked above 4.5 GPa. These changes were similar to those observed in static pressure measurements, indicating the rapid occurrence of the  $\alpha \rightarrow \gamma$  phase transition in shocked RDX crystals. The phase transition had an incubation time of  $\sim 100$  ns when RDX was shocked to 5.5 GPa peak stress. The  $\alpha \rightarrow \gamma$  phase transition under shock wave loading is connected to the onset of chemical decomposition in shocked RDX.

### Computational Studies of RDX Compressibility

Density functional theory and many other quantum chemical molecular modeling computational methods have been used by hundreds of investigators to predict the response of RDX and similar nitramines to sudden compression in a shock wave. Only a random sample of some of these studies is included here. Equations of state have been derived from measured compressibilities, from other measured molecular structure parameters, and from strictly theoretical considerations. The structural, electronic, and absorption properties of crystalline RDX under hydrostatic pressure of 0–50 GPa were studied using density functional theory [270]. As the pressure increased, the lattice constants and the unit cell volume gradually decreased. The compressibility of RDX crystal is anisotropic. The different changing trends of bond lengths and bond angles under pressures showed that both the ring opening and the N–NO<sub>2</sub> cleavage are possible to trigger the RDX decomposition. The interactions between electrons, especially for the valence electrons, are strengthened under the influence of pressure. The absorption spectra of RDX display more and stronger bands in the fundamental absorption region at high pressure.

Equations of state for the  $\alpha$  and  $\gamma$  polymorphs of RDX have been derived from their Helmholtz free energies [271]. The ion motion contribution to the Helmholtz free energy was represented by Debye models with density-dependent Debye temperatures that were parameterized to vibrational densities of states computed from dispersion-corrected density functional theory. By separating the vibrational density of states into low frequency modes of mainly lattice phonon character and high frequency modes of intramolecular character, it was possible to significantly improve the description of the heat capacity at low temperatures and the thermal contribution to the pressure. The static lattice energies for both polymorphs were constructed to reproduce published isothermal compression data. The equations of state have been applied to the prediction of the path of the principal Hugoniot in the equilibrium phase diagram.

#### 12.2.2.6 Solubility of RDX

RDX is practically insoluble in water. Its solubility in other solvents such as supercritical carbon dioxide is similar to that of HMX [272]. It is important to know the solubility of RDX if it has to be removed and possibly recycled from munitions during demilitarization with a suitable solvent. Solubilities of RDX in different solvents are listed in Table 21.



**Table 21:** Solubility of RDX in different solvents.

| Solvent                      | Solubility, g/100 mL solution at 303 K (30 °C), except <sup>a</sup> |
|------------------------------|---------------------------------------------------------------------|
| <i>N</i> -Methyl pyrrolidone | 73.7 <sup>a</sup>                                                   |
| Dimethyl sulfoxide           | 46 <sup>a</sup> (at 298 K = 25 °C)                                  |
| Dimethylformamide            | 34 <sup>a</sup>                                                     |
| $\gamma$ -Butyrolactone      | 16 <sup>a</sup>                                                     |
| Cyclopentanone               | 8.5 (at 298 K = 25 °C)                                              |
| Acetonitrile                 | 7.0                                                                 |
| Acetone                      | 6.9                                                                 |
| Nitromethane                 | 5.0                                                                 |
| Acetic anhydride             | 4.8                                                                 |
| Nitroethane                  | 3.0                                                                 |
| 1-Nitropropane               | 2.0                                                                 |
| 2-Nitropropane               | 2.0                                                                 |
| Propyl acetate               | 1.8                                                                 |
| Ethyl acetate                | 1.6                                                                 |
| Dioxane                      | 0.9                                                                 |
| Butyl acetate                | 0.8                                                                 |

<sup>a</sup> Grams/100 mL solvent

Data source: [273]

The objective of a program at Penn State University was to synthesize nano-sized energetic ingredients by rapid expansion of supercritical solution (RESS) process for future development of Insensitive Munitions (IM) systems using RDX as the model substance [274]. RDX was dissolved in supercritical CO<sub>2</sub> at 35.5 MPa (~5150 psig) and 329 K (56 °C) and sprayed through a 152  $\mu$ m (0.006 in.) nozzle into a low-pressure chamber. The solubility of RDX in supercritical CO<sub>2</sub> was very poor, so that higher pressure and temperature conditions and use of a co-solvent were considered to improve the output.

A technique of rapid expansion of supercritical solutions to produce nanocrystalline energetic materials was developed and characterized to produce nano-scale crystals of RDX. Nanocrystals of RDX were formed by expansion of supercritical solutions of RDX in carbon dioxide through a 100  $\mu$ m sapphire nozzle at initial pressures of 150–295 bar and temperatures of 323–363 K [275, 276]. Produced particles were characterized by field emission SEM, XRD, HPLC, and melting point analysis. The process produced particles with a mean size in the range of 110–300 nm with a narrow size distribution. The product was crystalline, as determined by XRD. This material would burn faster than macrocrystalline RDX.

The solubility of RDX in carbon dioxide was measured over a temperature and pressure range of 303 to 353 K and 6.9 to 48.3 MPa, respectively, and RDX was found to be relatively insoluble in CO<sub>2</sub>, with a maximum solubility of about 0.25 mg RDX/g CO<sub>2</sub> at the highest temperatures and pressures studied [272, 277–279].

### 12.2.2.7 Thermal Conductivity of RDX

Considerable discrepancies exist in the literature for values of the thermal conductivity of RDX. Thermal diffusivities and thermal conductivities of RDX and HMX were measured from room temperature into the decomposition region using a laser flash method [280, 281]. Thermal conductivities were calculated from the thermal diffusivity, specific heat, and density of each material.

The heat capacity, thermal conductivity, and thermal diffusivity of a range of other oxidizers, binders, and rocket propellants were determined and compared to literature data [282]. The thermal diffusivity  $\alpha$  of RDX for the range from 293 to 423 K (20 to 150 °C) can be described by the linear equation

$$\alpha = 1.52 \times 10^{-3} - 3.70 \times 10^{-6} t$$

where  $\alpha$  is the thermal diffusivity in  $\text{cm}^2/\text{s}$  and  $t$  is the temperature in °C. The thermal conductivity  $\lambda$  of RDX in the range from 293 to 423 K (20 to 150 °C) does not vary much with temperature and is close to

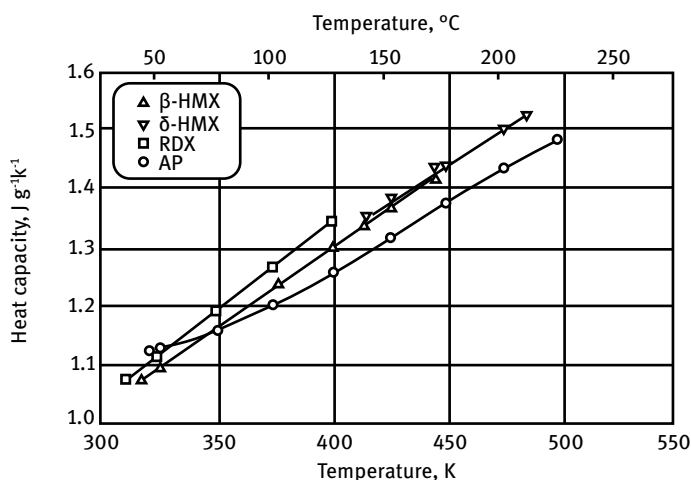
$$\lambda = 6.6 \times 10^{-4} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ } ^\circ\text{C}^{-1}$$

See also [283, 284].

### 12.2.2.8 Thermodynamic Properties and Thermal Properties of RDX

#### Heat Capacity of RDX

The specific heats of RDX and HMX were measured from room temperature into the decomposition region using a laser flash method [280, 281]. The specific heats of RDX and HMX are shown in Figure 10.



**Figure 10:** Heat capacities of RDX, HMX, and AP. (Reprinted and modified [280], with permission from ©1985 Old City Publishing granted by Dr. Ian Mellanby 10-May-2021)

The molar heat capacity of RDX in the range from 200–475 K (–73 to +202 °C) can be described by the following linear equation

$$C_p = 15 + 0.15 T$$

where  $C_p$  is the molar heat capacity in  $\text{cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin [87]. The molar heat capacity at 298 K is  $59.5 \text{ cal mol}^{-1} \text{ } ^\circ\text{C}^{-1}$ .

The heat capacity of RDX in the range from 293–423 K (20–150 °C) can be described by the following linear equation [282]:

$$c_p = 0.235 + 8.43 \times 10^{-4} t$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $t$  is the temperature in °C.

Heat capacity of RDX with a density of  $1.804 \text{ g/cm}^3$  in the range 310–440 K (37–167 °C) is

$$c_p = 0.232 + 0.00072 t$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$  and  $t$  is the temperature in °C. The mid-range standard deviation was  $0.004 \text{ cal g}^{-1} \text{ } ^\circ\text{C}^{-1}$ .

### Enthalpy of Formation and Heat of Combustion of RDX

The calculated standard enthalpy of formation for RDX as ideal gas in the gas phase is  $191.6 \pm 15 \text{ kJ/mol}$  and the calculated entropy is  $484.5 \pm 15 \text{ J mol}^{-1} \text{ K}^{-1}$  [285].

Table 22 provides a summary of published thermodynamic data for RDX. It is surprising that for a widely used energetic material like RDX the data for enthalpy of formation in the literature differ widely. Even a well-established, experienced agency like NIST on their Chemistry WebBook web site [85] gives just a juxtaposition of various data without the ability to rank their reliability and eliminate the less reliable ones. Along the same line, we can give only a collection of data with no verification. Most of these data were derived from heat of combustion measurements. It seems that

**Table 22:** Standard enthalpy of formation of RDX.

| Phase       | SI units  |        | Other units |        | References |
|-------------|-----------|--------|-------------|--------|------------|
|             | kJ/mol    | kJ/kg  | kcal/mol    | cal/g  |            |
| Solid       | +66.9     | +301.4 | +16.0       | +72    | [133]      |
|             | +61.55    | +277.1 | +14.71      | +66    | [241]      |
|             | +61.3     | +276.1 | +14.66      | +66    | [235]      |
|             | +79.1 ± 5 | +356   | +17 ± 1.2   | +76.5  | [87]       |
|             | +61.5     | +276.9 | +14.7       | +66.17 | [286, 287] |
|             | +61.5     | +276.9 | +14.69      | +66.1  | [288, 289] |
| Vapor (gas) | +192      | +864.4 | +45.9       | +206.6 | [290]      |

$$M = 222.1163 \text{ g/mol} = 4.5021 \text{ mol/kg}$$

the amounts of condensate and nitric acid in the condensate are two of the variables responsible for the scatter of data.

### Heat of Combustion of RDX

The heat of combustion of RDX is difficult to determine calorimetrically because the pure compound might explode instead of just burning in an oxygen-filled combustion bomb in a calorimeter. Even if complete combustion is achieved by taming the reaction by addition of diluents with known heats of combustion, collecting the condensate and correcting for the amount of nitric acid in the condensate introduces additional sources of error. Literature data for the upper heat of combustion of RDX (going to liquid water) are summarized in Table 23.

**Table 23:** Isochoric upper heat of combustion of RDX.

| SI units     |           | Other units |       | References |
|--------------|-----------|-------------|-------|------------|
| kJ/mol       | kJ/kg     | kcal/mol    | cal/g |            |
| 2124         | 9562      | 507.5       | 2285  | [291]      |
| 2100         | 9454      | 501.8       | 2260  | [239]      |
| 2120 ± 5.0   | 9544 ± 22 | 506 ± 1.2   | 2281  | [87]       |
| 2099         | 9454      | 501.8       | 2260  | [286]      |
| 2092.0 ± 2.1 | 9418 ± 9  | 500 ± 0.5   | 2251  | [72]       |
| 2122         | 9556      | 507.3       | 2285  | [292]      |

$$M = 222.116 \text{ g/mol} = 4.5021 \text{ mol/kg}$$

### Heat of Fusion and Solid-State Phase Transitions of RDX

RDX decomposes at the melting point, so it would be difficult to determine the heat of fusion calorimetrically. Domalski and Hearing [293] reported the enthalpy of fusion of RDX as 37.66 kJ/mol (9.00 kcal/mol). The heat of melting can be taken as 33.1 kJ/mol (7.9 kcal/mol or 35.6 cal/g) from Zeman [40]. The heat of fusion of a samples of RDX prepared by the Woolwich process melted at 478.4 K (205.3 °C) and the heat of fusion was  $30.77 \pm 2.69 \text{ kJ/mol}$  ( $7.356 \pm 0.642 \text{ kcal/mol}$ ) [294]. Other sources gave the heat of fusion as  $161 \text{ kJ/kg} = 35.76 \text{ kJ/mol} = 8.547 \text{ kcal/mol}$ .

A publication by Hall [245] gave the heat of fusion of RDX at the m.p. = 478.5 K = 205.4 °C as  $35.65 \pm 0.29 \text{ kJ/mol}$  ( $8.52 \pm 0.07 \text{ kcal/mol}$ ). Processes of solid phase transition, fusion, and decomposition in several nitramines have been investigated using DSC. The values for the temperatures and enthalpy changes  $\Delta H$  are reported in Table 24.

Calculating first-order rate constants for decomposition in the region of the solid → liquid transition of nitramines indicated a “premonitory” effect at temperatures below the melting point. With the exception of RDX (apparent  $E_a = 189 \pm 1.7 \text{ kJ/mol} = 45.2 \pm 0.4 \text{ kcal/mol}$ ), the apparent activation energies for decompo-

Table 24: Heat of solid phase transition, fusion, and decomposition of nitramines.

| Compound name                                   | Acronym | $T_t$                                 | $\Delta H_t$ | $T_{fus}$   | $\Delta H_{fus}$ | $T_{dec}$   | $-\Delta H_{dec}$ |
|-------------------------------------------------|---------|---------------------------------------|--------------|-------------|------------------|-------------|-------------------|
|                                                 |         | K                                     | kJ/mol       | K           | kJ/mol           | K           | kJ/mol            |
| 1,3,5-trinitro-1,3,5-triazacyclohexane          | RDX     |                                       |              | 478.5       | 35.6 ± 0.3       | 8.52 ± 0.07 | 569 ± 8           |
| 1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclooctane | HMX     | $\beta \rightarrow \delta$<br>ca. 460 | 9.83 ± 0.84  | 2.35 ± 0.20 |                  | ca. 540     | 694 ± 38          |
| 1,3-dinitro-1,3-diazacyclopentane               | DDCP    |                                       |              | 403         | ≈ 25.1           | ≈ 6.0       |                   |
| 1,3-dinitro-1,3-diazacyclohexane                | DDCHX   | 343                                   | 15.5 ± 1.2   | 3.7 ± 0.3   | 2.93 ± 0.08      | 0.70 ± 0.02 |                   |
| 1,3-dinitro-1,3-diazacycloheptane               | DDCHP   | 370                                   | ≈ 23.4       | ≈ 5.6       | ≈ 3.97           | ≈ 0.95      |                   |

Data source: [245]; Subscript legend: t = transition, fus = fusion, dec = decomposition

sition of the nitramines tended to be unrealistically high. This type of behavior with RDX may be related to molecular rotation in the solid state.

When searching for a relationship between bond dissociation energies of the weakest bond in the molecule and the heat of fusion, no unambiguous relationships could be found between the heat of fusion and bond dissociation energies of cyclic nitramines like RDX and HMX [295].

### Heat of Sublimation of RDX

Table 25 is a comparison between published literature enthalpy of vaporization values. The data vary considerably, depending on the method how the vapor pressure data were obtained, depending on the purity of the sample, and depending on the temperature range where the vapor pressure was measured. See also [296].

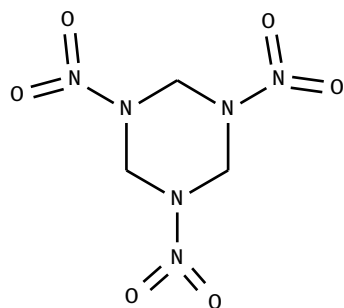
**Table 25:** Comparison between published literature enthalpy of sublimation values for RDX.

| $\Delta H_{\text{vap}}$ |     | References |
|-------------------------|-----|------------|
| J/mol                   | J/g |            |
| 24725                   | 111 | [250]      |
| 36716                   | 165 | [239]      |
| 47870                   | 216 | [255]      |
| 53820                   | 242 | [251]      |
| 56308                   | 254 | [247, 248] |
| 58293                   | 262 | [256]      |
| 63106                   | 284 | [253]      |
| 71245                   | 321 | [253]      |

$$M = 222.116 \text{ g/mol} = 4.5021 \text{ mol/kg}$$

#### 12.2.2.9 Molecular Structure of RDX

The chair conformation of  $C_{3v}$  symmetry with the  $\text{NO}_2$  groups in the axial positions was accepted for RDX. The molecular structure of RDX is



The good thermal stability of the compound is partially due to its symmetry.

A study using several different methods, such as IR, Raman, and NMR spectroscopy, dipole moment, and depolarized Rayleigh scattering measurements, and INDO calculations, suggested that the RDX molecule has approximate  $C_{3v}$  symmetry in solution, with some distortion associated with the  $\text{NO}_2$  groups [297]. The ring undergoes rapid interconversion in which the cyclic nitrogens oscillate about the planar ( $sp^2$ ) position. There are numerous computational chemistry studies of the molecular structure of RDX, most of them using density functional theory (DFT) methods. There is not enough space in this book to reference them all. Some of those studies also try to model changes in the molecular structure of RDX crystals as they are compressed in a shock wave and transition to a detonation. For theoretical prediction and interpolation of the density of solid nitramines, see also [11].

### Crystal Structure of RDX

XRD or neutron diffraction is the preferred tool for the investigation of the crystal structure of energetic materials, at atmospheric pressure as well as elevated pressure.

The crystal structure of RDX has been refined from single crystal neutron diffraction data. The compound crystallizes in the orthorhombic space group  $Pbca$ , with  $a = 13.182 \text{ \AA}$ ,  $b = 11.574(2) \text{ \AA}$ ,  $c = 10.709(2) \text{ \AA}$ ,  $Z = 8$ . The molecule consists of alternate  $\text{CH}_2$  and  $>\text{N}-\text{NO}_2$  groups in a puckered ring. The environment of the atoms is essentially tetrahedral, and the  $>\text{N}-\text{NO}_2$  groups are planar. The molecule possesses a plane of approximate mirror symmetry perpendicular to the plane defined by the three carbon atoms.

The unit cell dimensions of  $\alpha$ -RDX at atmospheric pressure are  $a = 1.318 \text{ nm}$ ,  $b = 1.157 \text{ nm}$ , and  $c = 1.071 \text{ nm}$ . The pressure–temperature phase diagram for RDX has been determined up to 573 K and 7.0 GPa using powder XRD, IR spectroscopy, and optical polarizing microscopy, and it was demonstrated that an orthorhombic  $\gamma$ -form is produced above 3.8 GPa at ambient temperature [265]. Several theoretical studies have reproduced the effects of hydrostatic compression on the crystallographic lattice parameters of the  $\gamma$ -form, but in the absence of experimental structural data, these predictions could not be verified.

The crystal structure of the high-pressure phase of  $\gamma$ -RDX, which is stable above 4 GPa at room temperature, was investigated by using IR spectroscopy and powder XRD measurements using a diamond anvil cell [298]. Although  $\gamma$  and  $\alpha$  phases were found to belong to the same space group  $Pbca$ , they exhibited a different crystal packing. The molecular structure of the  $\gamma$  phase exhibited the same conformation as that of the  $\alpha$  phase; however, the torsion angles of  $\text{N}-\text{NO}_2$  changed marginally.

Using a combination of X-ray single crystal and neutron powder diffraction, the crystal structure of the high-pressure  $\gamma$ -form of RDX has been determined at 5.2 GPa and showed that the RDX molecules adopt different conformations compared to the conformation found in the ambient-pressure  $\alpha$ -form [267, 299]. At pressures up to 3.85 GPa, all of the patterns could be refined using the orthorhombic ( $Pbca$ ) structure of the  $\alpha$  modification. High-pressure, single crystal XRD data were processed as

follows:  $\gamma$ -phase  $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$ ,  $M = 222.12$ , orthorhombic, space group  $Pca2_1$ , unit cell parameters  $a = 12.565009 \text{ \AA}$ ,  $b = 9.4769(6) \text{ \AA}$ ,  $c = 10.9297(9) \text{ \AA}$ ,  $V = 1301 \text{ \AA}^3$ ,  $P = 5.20(5) \text{ GPa}$ ,  $Z = 8$ ,  $\rho_c = 2.267 \text{ g/cm}^3$ . Across the  $\alpha \rightarrow \gamma$  transition, a 3% decrease in unit cell volume was observed. This is slightly larger than previously reported, but presumably reflects the higher precision of the lattice parameters obtained in the more recent study.

Whereas positions and intensities of diffraction peaks yield information on the crystal structure, peak profiles (e.g., width at half-height) are related to the real structure determined by crystallite sizes, shapes, and microstrains. The size/strain broadening of RDX XRD peaks was measured and interpreted based on crystal geometry [300].

A study of the crystal structure of the highly metastable  $\beta$ -form of RDX showed that the molecules adopt different conformations compared to the  $\alpha$ -form and that, contrary to previous reports, the  $\beta$ -form obtained at ambient pressure is not the same form as that obtained at elevated temperatures and pressures [301–303].

The other modification of RDX,  $\epsilon$ -RDX, a high-pressure, high-temperature form of RDX, has been structurally characterized using a combination of diffraction techniques, and a sample of this form has been successfully recovered at down to ambient pressure [304]. Table 26 is a compilation of the unit cell parameters of the four known polymorphs of RDX.

**Table 26:** Crystal structure and unit cell parameters of the four known polymorphs of RDX.

| Polymorph<br>Space group | $\alpha$ -RDX<br><i>Pbca</i> | $\beta$ -RDX<br><i>Pca2<sub>1</sub></i> | $\gamma$ -RDX<br><i>Pca2<sub>1</sub></i> | $\epsilon$ -RDX<br><i>Pca2<sub>1</sub></i> |
|--------------------------|------------------------------|-----------------------------------------|------------------------------------------|--------------------------------------------|
| $a$ , $\text{\AA}$       | 13.1661(40)                  | 15.0972(7)                              | 12.5650(19)                              | 7.5191(41)                                 |
| $b$ , $\text{\AA}$       | 11.5393(38)                  | 7.4563(6)                               | 9.4769(6)                                | 11.6430(49)                                |
| $c$ , $\text{\AA}$       | 10.6668(28)                  | 14.3719(11)                             | 10.9297(9)                               | 9.1765(39)                                 |
| $V$ , $\text{\AA}^3$     | 1620.6(5)                    | 1621.0(2)                               | 1301.5(2)                                | 804.4(4)                                   |
| $Z$                      | 8                            | 8                                       | 8                                        | 4                                          |
| $T$ , K                  | 220                          | 150                                     | 293                                      | 220                                        |

Note: Data for the  $\alpha$ - and  $\epsilon$ -forms refer to RDX-d6, and data for the  $\beta$ - and  $\gamma$ -forms refer to RDX-h6. Data were collected at 5.2 GPa for the  $\gamma$ -form.

Data source: [304]

### Computational Chemistry Calculations of RDX Properties

There are numerous computational chemistry calculations to predict properties and performance of RDX and similar molecules as explosives. The following is only a short summary of this literature. Calculations were performed to predict density of nitramine crystals [15], gas phase enthalpies of formation [305], and other properties.



Volume dependence of the total energy and vibrational properties of crystalline RDX were calculated using the density functional theory (DFT) [306]. For this molecular crystal, properties calculated with a generalized gradient approximation to the exchange-correlation energy differed drastically from experimental values. It was assumed that this discrepancy arose from the inadequacy in treating weak van der Waals interactions between molecules in the crystal, and an empirical van der Waals correction to DFT was shown to accurately account for the dispersion effects for the RDX crystal, while incurring little additional computational effort. The nonempirical van der Waals density functional method also provided an accurate description of the van der Waals corrections but with orders-of-magnitude more computation steps.

#### 12.2.2.10 Dipole Moment and Dielectric Constant of RDX

The dielectric constant of RDX at 298 K and 5 MHz is 3.14.

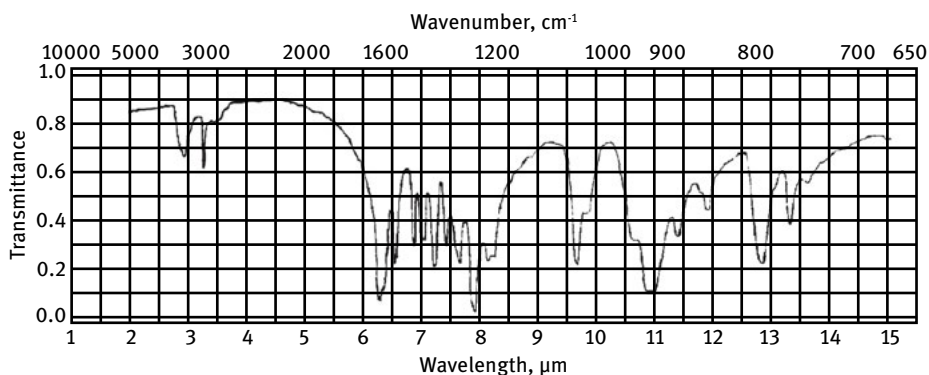
#### 12.2.2.11 Optical Properties of RDX

##### IR Spectra of RDX

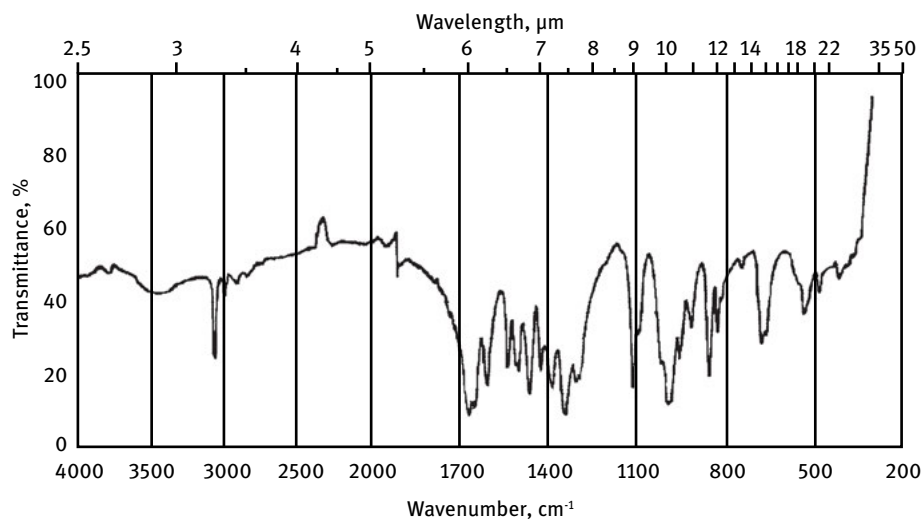
Two IR spectra of RDX, unfortunately some of only poor quality of reproduction, are shown in Figure 11 and 12.

The transmission IR and the laser excited Raman spectra of polycrystalline RDX have been measured in the range of 40 to 4000  $\text{cm}^{-1}$  [307]. To aid assignments in the spectral region of 400 to 4000  $\text{cm}^{-1}$ , the spectra of two types of  $^{15}\text{N}$ -labeled samples and the solution spectra in different solvents were also recorded (Figure 13). From these data, it was possible to assign many of the observed bands to intramolecular modes of the RDX molecule. The Raman active lattice modes also were resolved and found to be comparable to the lattice mode frequencies in solid cyclohexane.

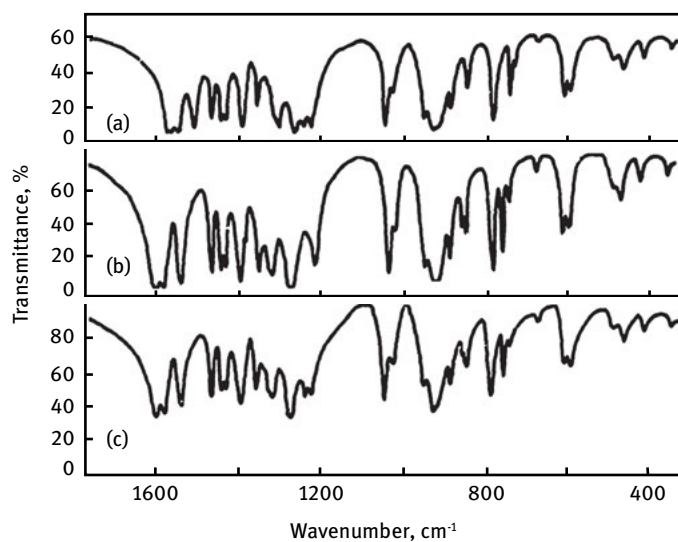
In a similar project, it was possible to make unambiguous vibrational band assignments in vibrational spectra of  $\alpha$ -RDX with the use of  $^{13}\text{C}$  and  $^{15}\text{N}$  (on ring) enriched RDX isotopologues [308]. Vibrational spectra were collected using Raman and



**Figure 11:** Infrared spectrum of RDX. (Reproduced and modified from [81])



**Figure 12:** Infrared spectrum of RDX. (Reproduced and modified from [244].)



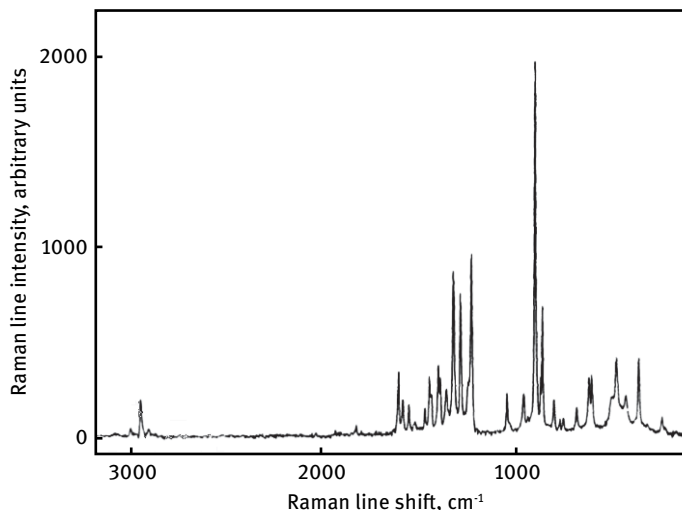
**Figure 13:** Transmission vs. frequency traces of the KBr pellet IR spectra of RDX between 400 and 1700  $\text{cm}^{-1}$  of (a) Nitro group labeled RDX (b) Ring labeled RDX (c) Unlabeled RDX. (Reproduced and modified from [307].)

IR spectroscopy in the solid state and compared to the results of *ab initio* normal mode calculations which were performed using density functional theory (DFT). The calculated isotopic frequency shifts, induced by  $^{13}\text{C}$  and  $^{15}\text{N}$  labeling, were in very good accordance with measured ones. The changes in vibrational modes associated with the isotopic substitutions were well modeled by the calculation and previous assignments of the vibrational spectra have been revised, especially where the exact nature of the vibrational modes had been either vague or contradictory.

The optical constants of RDX and HMX were determined using KBr pellet-FTIR transmission spectrometry in conjunction with dispersion theory, which accounts for radiation scattered by the KBr pellets [309]. Advantages of the FTIR/KBr pellet method are that optical constants can be obtained even in strongly absorbing regions with sufficient dilution and fine enough particles and they can be obtained over a broad spectral range. Optical properties of RDX and HMX were obtained from 2.5 to 18  $\mu\text{m}$  using scattering-corrected KBr pellet-FTIR transmission spectrometry. Absorption index ( $k$ ) was measured directly and refractive index ( $n$ ) was deduced using dispersion theory. At 10.6  $\mu\text{m}$  ( $\text{CO}_2$  laser wavelength) the absorption coefficients were  $2800\text{ cm}^{-1}$  for RDX and  $5670\text{ cm}^{-1}$  for HMX. The refractive indices in the visible range were 1.594 for RDX and 1.597 for HMX.

#### 12.2.2.12 Raman Spectra of RDX

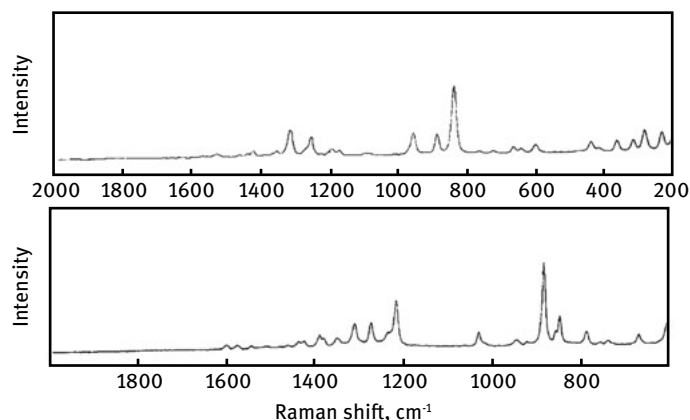
Fourier transform Raman (FTR) spectroscopy employing near-IR laser radiation at 1.06  $\mu\text{m}$  as the scattering source has been used to obtain Raman spectra of RDX and propellant formulations containing RDX, as shown in Figure 14, [310, 311].



**Figure 14:** Raman spectrum of RDX. (Reproduced and modified from [310].)

Raman spectra of RDX, HMX, and 30 other explosive materials to be used for the design of an explosive detection device were recorded. The samples were excited with the 1064 nm line from a diode-pumped Nd:YAG laser [312].

A comparison of the very similar Raman spectra of RDX and HMX is shown in Figure 15. Note that the two spectra have different scale expansions [312, 313].



**Figure 15:** Raman spectra of RDX (*bottom*) and HMX (*top*). (Republished and modified from [312], with permission of ©1995 Elsevier; permission conveyed through RightsLink.)

Raman spectroscopy has been used to investigate the  $\alpha \rightarrow \beta$  solid–solid phase transition of RDX in real time [314]. The thermal conversion of  $\alpha \rightarrow \beta$  at atmospheric pressure occurred at 477 K. Temperature-induced spectroscopic changes in the Raman spectrum of  $\alpha$ -RDX, such as peak shifting and broadening and disappearance of spectral bands confirmed the phase transition. For the interpretation of the experimental results, the structural and spectral characteristics of  $\alpha$ - and  $\beta$ -RDX have been studied by performing density functional theory (DFT) calculations for energies, geometries, vibrational frequencies, and NMR shielding constants. The theoretical data, using DFT approximation, and experimental results were consistent with each other. The results from these experiments showed that once  $\beta$ -RDX is formed by heating at slow rates, crystal transformation occurs near the melting point and no reversible change in the symmetry can be observed. The differences in the Raman spectra of both solid phases are evident and persistent. In addition, the results of calculated and experimental NMR chemical shifts ( $^{13}\text{C}$  and  $^{15}\text{N}$ ) confirmed the agreement between the  $\alpha$  conformer and the  $\beta$ -RDX structure.

### Refractive Index of RDX

The refractive index  $n_D^{20}$  of  $\alpha$ -RDX is 1.578, that of  $\beta$ -RDX is 1.597 and that of  $\gamma$ -RDX is 1.602. The molar refraction is 41.4.

### 12.2.3 Chemistry of RDX

The oxygen balance of RDX is  $-21.6\%$  for combustion to  $\text{CO}_2$  and thus it should not be designated as an “oxidizer” when added to CMDB propellants because it is thus substantially underoxidized. The nitrogen content is  $37.84 \text{ mass-\% N}$ . RDX is underoxidized, but a powerful explosive and a very useful ingredient for CMDB solid propellants. RDX would be stoichiometrically balanced if one assumed that combustion proceeds only to CO and not all the way to  $\text{CO}_2$ :



#### 12.2.3.1 Analysis of RDX

Analytical methods for RDX are summarized in [315]. Commercial grades of RDX were found to contain  $0.2\%$  HMX.

#### 12.2.3.2 Thermal Decomposition of RDX

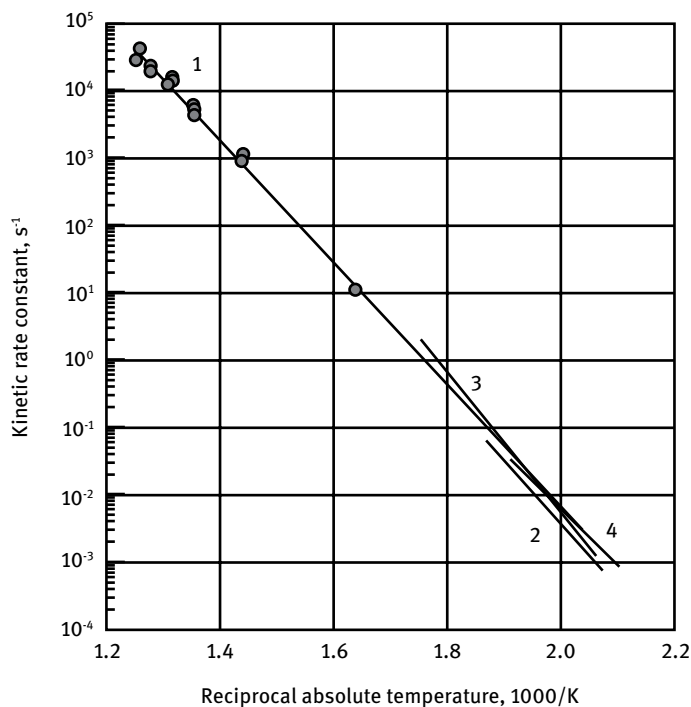
RDX is unique among the heterocyclic nitramines in that it has good thermal stability. The kinetics of RDX decomposition have been investigated exhaustively, be it either to explain limits to its thermal stability or in search of related compounds with even better thermal stability and higher performance. The study of thermal decomposition was done either experimentally or by calculations of its molecular structure, trying to identify the weak link in the molecule where the molecule starts breaking apart when heated. Several of the studies have been done looking at both RDX and HMX and comparing properties of the two. Because these publications can be cited either here, at HMX, or at both locations, there is some overlap and redundancy between these two sections in this book.

### Experimental Studies of RDX Decomposition

There are many thermal analysis techniques as well as specialized thermal techniques that are used to characterize explosives, including pressure measurement techniques, gaseous product analysis, DTA, DSC, TGA, combined TGA-DTA, and all have been applied to the study of the thermal stability of RDX and similar energetic materials [316].

The thermal decomposition of energetic materials is closely related to their strand burning rates. For an evaluation of kinetic data of RDX decomposition in combustion waves in a strand burner, the following data for RDX were taken from the literature: heat capacity  $c_p = 1.59 \text{ kJ kg}^{-1} \text{ K}^{-1}$  ( $0.38 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$ ), thermal conductivity  $\lambda = 2.3 \times 10^{-2} \text{ kJ s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$  ( $5.6 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1}$ ), and density  $\rho = 1.75 \text{ g/cm}^3$ , respectively. Thermal conductivity data for RDX and other solid rocket propellant oxidizers and binder materials are available from [282]. According to DSC studies, heat of reaction of RDX decomposition in the melt is equal to  $1080 \text{ kJ/kg}$  ( $258 \text{ cal/g}$ ) [317].

A comparison of RDX decomposition kinetics for the molten substance, shown in Figure 16, is based on kinetic parameters of RDX decomposition derived from



**Figure 16:** Comparison of kinetic parameters of the leading reaction on RDX combustion and decomposition in the melt. RDX combustion (1) Sinditskii et al. [252], (2) Rogers and Daub [249], (3) Robertson [318], and (4) Oxley et al. [38]. (Republished and modified from [252], with permission of ©2009 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

a combustion model for the temperature range 610–800K, which is above the temperature range accessible by DSC, and on the rate equation

$$k = 10^{15.92} \cdot \exp(-20890/T)$$

where  $k$  is the rate constant in  $\text{s}^{-1}$  and  $T$  is the temperature in kelvin. This rate equation is in good agreement with the experimental rate constants of RDX decomposition in the melt obtained at lower temperatures.

During a study of isothermal rates of RDX and other explosives by DSC, it was observed that several compounds gave two first-order curves with two different slopes at each temperature. The second curve was normally smaller than the first, and the rate constant obtained from the second curve was larger. The relative sizes of the two parts of the rate curve could be varied by changing the volume of the sample cell. The working hypothesis that seemed best to explain the observations was that the “tail” of the DSC rate curve was the result of decomposition in the vapor phase [249].

The decomposition of liquid RDX and HMX follows a unimolecular rate equation. The decomposition of RDX in dicyclohexyl phthalate or trinitrotoluene as solvent/diluent had a frequency factor approaching the normal value. A more concentrated solution of RDX decomposed faster than the dilute solutions. This fact and the anomalous frequency factor for the pure liquid were explained in terms of a chain reaction of short length with a temperature-dependent chain length [318]. The results on the decomposition of RDX showed that in solutions of dicyclohexyl phthalate or trinitrotoluene (TNT) the decomposition exhibited a unimolecular behavior, whereas neat RDX and HMX show an effect of neighboring molecules. Post-test analysis of the gases evolved in these experiments showed the presence of NO, N<sub>2</sub>O, N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>2</sub>O, and H<sub>2</sub>O. This early work provided the initial evidence that the decomposition of RDX and HMX occurs by transfer of an oxygen atom from the NO<sub>2</sub> group to the CH<sub>2</sub> group.

High-pressure elevated-temperature studies of HMX and RDX indicated that during chemical decomposition (and perhaps melting) the electrical resistance rapidly decreased about three orders of magnitude, attained a minimum, and thereafter generally increased with increasing temperature [319]. Pressure studies of these materials from about 10 to 40 kbar did not show a monotonic trend regarding the pressure dependence of the temperatures of most of the electrical anomalies, due to complex kinetic behavior.

The mechanisms that are used to explain the decomposition of RDX and HMX are based on results from simultaneous TGA modulated beam mass spectrometry (STMBMS) and time-of-flight (TOF) velocity-spectra measurements [320]. These methods are used to identify the decomposition products and to determine their formation rates as a function of time during the decomposition of the samples. Both nitramines form H<sub>2</sub>O, N<sub>2</sub>O, CH<sub>2</sub>O, NO, and CH<sub>3</sub>NHCHO during decomposition. RDX forms NO<sub>2</sub> and hydroxy-*s*-triazine, products associated with N—N bond breaking, whereas HMX forms C<sub>2</sub>H<sub>6</sub>N<sub>2</sub>O, CO, and a nonvolatile residue.

The effects of very high pressure on the thermal decomposition kinetics, chemical reactivity, and phase behavior of RDX, HMX, and nitromethane have been studied by a combination of measurement techniques in conjunction with a high pressure diamond anvil cell [321]. These techniques included (1) FTIR spectroscopy, (2) EDAX, (3) optical polarizing microscopy, and (4) Raman scattering. Studies were generally limited to the region where decomposition rates could be measured within reasonable laboratory time, i.e., below 10 GPa and 573 K. The pressure-temperature phase diagram for RDX was determined to 373 K and 7.0 GPa, delineating the stability fields of three solid phases,  $\alpha$ ,  $\beta$ , and  $\gamma$ , and the liquidus. The  $\alpha$  and  $\beta$  phases of RDX were found to thermally decompose, while the  $\gamma$  phase transformed to either  $\alpha$  or  $\beta$  before reaching decomposition temperatures. The decomposition rate of  $\alpha$  phase was found to increase with increasing pressure suggesting a bimolecular-type mechanism. Conversely,  $\beta$  HMX decomposition rates decreased with increasing pressure suggesting a unimolecular-type reaction mechanism.

### Slow Thermal Decomposition of RDX

As part of a multiyear, Multidisciplinary University Research Initiative (MURI) aimed at a better understanding of combustion instability in solid propellant rocket motors, the rates of decomposition and the burning rates of RDX and many other propellant ingredients have been investigated, and models to interpret the experimental results were established. Several of the publications referenced in that report give a good introduction into the mechanisms for RDX decomposition and are repeated here.

Numerous authors have investigated the rates and mechanisms of decomposition of RDX and HMX under slow heating conditions. The thermal decomposition of RDX was investigated in a static system below its melting point at 468 K (195 °C) [322]. The initial decomposition of RDX takes place in the vapor phase. Hydroxymethyl formamide and polymeric materials formed from hydroxymethyl formamide have been shown to be major products. These comparatively low molecular weight materials are highly hydrogen bonded liquids of low volatility which subsequently act as a solvent for decomposing RDX. Nitrogen, due to its effect on the rate of diffusion of RDX vapor away from the crystal surface, was shown to have a rate retarding effect. Other decomposition reaction products, such as formaldehyde, hydroxymethyl formamide, methylene diformamide, and 1,3,5-trinitrobenzene were all shown to enhance the reaction rate [323]. Different initial steps in the mechanisms were indicated for the gas phase and solution phase decompositions.

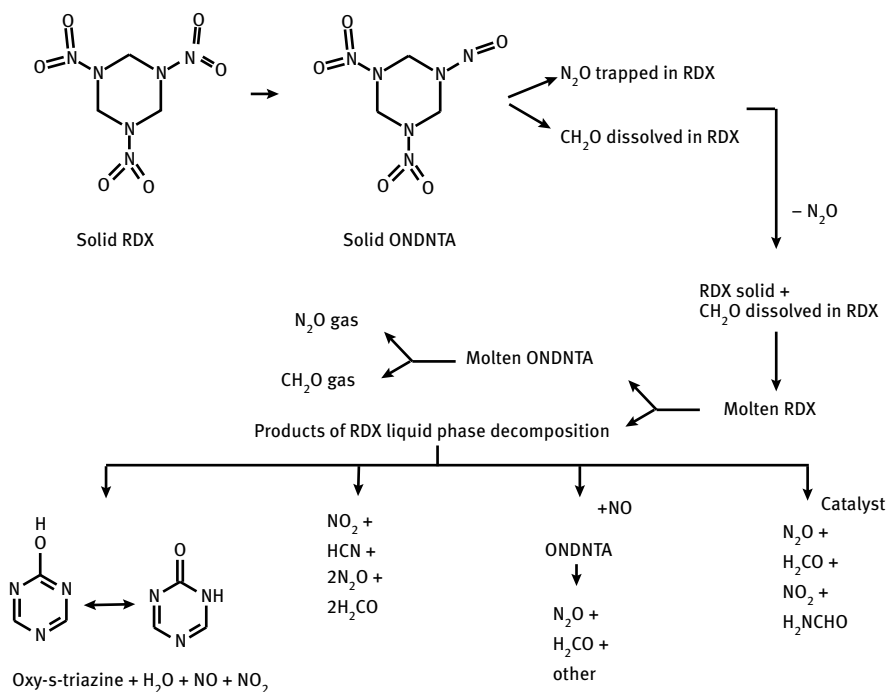
A review of the ignition and combustion chemistry of HMX and RDX came to the conclusion that direct diagnostic techniques have not yet been invented for subsurface (condensed-phase) or heterogeneous (gas–solid) processes during deflagration or energetic materials and sophisticated flame diagnostic techniques have not yet provided species concentration profiles in fast reactions [324]. Consequently, current knowledge of the combustion (and ignition) chemistry of these propellants comes from indirect sources, such as thermal decomposition experiments or isothermal gas-phase kinetic measurements. A new hypothesis was presented which tried to account for the phase-dependent decomposition rate constants of propellant molecules.

A very useful tool for identifying decomposition reactions of propellant ingredients is the simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) technique. This instrument allows the rate of selected gas phase product formation to be measured as a function of time and temperature and was applied to the study of the decomposition of RDX and other energetic materials [320, 325]. The results of the STMBMS analysis showed that RDX and HMX have similar decomposition mechanisms as well as similar degradation products [326].

Through the use of STMBMS measurements, TOF mass spectrometry velocity-spectra analysis, and  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{18}\text{O}$  labeled analogues of RDX, the thermal decomposition products of RDX have been identified as  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{CO}$ ,  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{H}_2\text{NCHO}$ ,  $\text{NO}_2$ ,  $\text{HONO}$ , oxy-*s*-triazine (OST), and 1-nitroso-3,5-dinitrohexahydro-*s*-triazine (ONDNTA), and all of their gas formation rates have been measured as a function of time [327]. From these results, the primary reaction pathways that



control the decomposition of RDX in both the solid and liquid phases have been identified. Four primary reaction pathways control the decomposition of RDX in the liquid phase between 473 and 488 K (200 and 215°C). Two pathways are solely first-order reactions in RDX. One produces predominantly OST and NO, and accounts for approximately 30% of the decomposed RDX; the other produces predominantly  $\text{N}_2\text{O}$  and  $\text{H}_2\text{CO}$  with smaller amounts of  $\text{NO}_2$ , CO, and  $\text{H}_2\text{NCHO}$  and accounts for 10% of the decomposed RDX. The third leads to formation of ONDNTA by reaction between NO and RDX, followed by the decomposition of ONDNTA to predominantly  $\text{H}_2\text{CO}$  and  $\text{N}_2\text{O}$ . The fourth reaction pathway consists of decomposition of RDX through reaction with a catalyst that is formed from the products of previously decomposed RDX. The third and fourth reaction channels each account for approximately 30% of the decomposed RDX. In addition to the two forms of OST shown in the schematic below, there may also be an  $\text{N} \rightarrow \text{O}$  oxide structure.



Experiments with solid-phase RDX have shown that its decomposition rate is much slower than that of liquid-phase RDX. ONDNTA is the only product that appears to be formed during the early stages of the decomposition of RDX in the solid phase. As the solid-phase decomposition progressed,  $\text{N}_2\text{O}$  and lesser amounts of  $\text{H}_2\text{CO}$  started to evolve and their rates of evolution increased until products associated with the liquid-phase RDX decomposition appeared and the rate of gas formation of all products rapidly increased. This behavior strongly suggested that the decomposition of

solid RDX occurs through formation of ONDNTA within the lattice. The subsequent decomposition of ONDNTA within the lattice formed  $\text{N}_2\text{O}$  and  $\text{H}_2\text{CO}$ , followed by the dispersion of  $\text{H}_2\text{CO}$  in the RDX, leading to its eventual liquefaction and the onset of the liquid-phase decomposition reactions.

The inter- vs. intramolecular origin of the products formed in the thermal decomposition of RDX was traced by using mixtures of differently labeled isotopologues of RDX [328]. The isotopic analogues of RDX used in the experiments included  $^{13}\text{C}$ ,  $^{15}\text{N}$ , and  $^{18}\text{O}$  labeled analogues of RDX. The fraction of isotopic scrambling and the extent of the deuterium kinetic isotope effect (DKIE) observed for the different thermal decomposition products indicated that isotopic scrambling does not occur for the bond in  $\text{N}_2\text{O}$  and only in small amounts (7%) in the C—H bonds in  $\text{H}_2\text{CO}$ , consistent with an assumed mechanism of their formation through methylene nitramine precursors. An intermediate product, oxy-*s*-triazine (OST) did not undergo isotopic scrambling and its rate of formation exhibited a DKIE of 1.5. These results were consistent with the formation of OST via unimolecular decomposition of RDX. Another product, ONDNTA, was found to be formed with complete scrambling of the N—NO bond, suggesting N—N bond cleavage and a radical recombination process in its formation.

It was observed that the standard DSC thermograms of RDX prepared by the Bachmann process at Holston and the other prepared by the Woolwich process by SNPE in France were noticeably different [294]. The SNPE RDX thermogram exhibited a sharp endothermic event attributed to the RDX melting process at 478.4 K (205.3 °C), which was immediately followed by thermal decomposition. The Holston RDX, on the other hand, exhibited a broad, generally twin-peaked endothermic event that occurred over the temperature range 461–478 K (188–205 °C), which was followed by thermal decomposition. An earlier study [329] of the thermal behavior of mixtures of RDX and HMX at high concentrations (70–100% by weight) of the latter found two endothermic events associated with the mixtures. One was observed at a consistent temperature of 460–461 K (187–188 °C) and the other over the temperature range 472–478 K (199–205 °C) with the temperature increasing as the RDX concentration was increased to a maximum of 30 mass-%. The former event was attributed to RDX melting and the latter to a polymorph transition. A complete temperature/composition melting point diagram is presented in Section 15.2.1.

If RDX is heated beyond its melting point, it is bound to decompose, ignite, and burn. The study of decomposition of liquid RDX would mostly benefit burning rate studies and studies of temperature profiles across the burning surface. However, for assessment of damage suffered by nitramine propellants at temperatures below the melting point of RDX, it is important to look at RDX decomposition in the solid state.

Through the use of simultaneous thermogravimetry modulated beam mass spectrometry, optical microscopy, hot-stage time-lapsed microscopy, and SEM measurements, the physical and chemical processes that control the thermal decomposition of RDX below its melting point in the range 433–462 K (160–189 °C) have been examined and identified [330]. Two gas-phase reactions of RDX were predominant during

the early stages: One involved the loss of HONO and HNO and led to the formation of  $\text{H}_2\text{O}$ , NO,  $\text{NO}_2$ , and oxy-*s*-triazine (OST) or *s*-triazine. The other involved the reaction of NO with RDX to form  $\text{NO}_2$  and 1-nitroso-3,5-dinitrohexahydro-*s*-triazine (ONDNTA), which subsequently decomposed to form a set of products of which  $\text{H}_2\text{CO}$  and  $\text{N}_2\text{O}$  were the most abundant. Products from the gas-phase RDX decomposition reactions, such as ONDNTA, deposited themselves on the surface of the cooler RDX particles and led to the development of a new set of reaction pathways that occurred on the surface of the RDX particles. An orange-colored nonvolatile residue (NVR) film was seen on the surface of the RDX particles. The NVR film was a nonstoichiometric and dynamic material, which reacted directly with RDX and ONDNTA. The competition between reaction of the dynamic NVR with RDX and its own thermal decomposition manifested itself in a rapid increase in the rate of evolution of the NVR decomposition products as the amount of RDX remaining in the sample neared depletion. The reactions between the NVR film and RDX on the surface of the RDX particles led to a localized environment that created a layer of molten RDX on the surface of the particles where reactions associated with the liquid-phase decomposition of RDX occurred. The combination of these reaction processes led to an acceleration of the reaction rate in the later stage of the decomposition process and created an apparent reaction rate behavior that has been referred to as autocatalytic in many previous studies of RDX decomposition.

The common degradation products for both RDX and HMX observed via STMBMS were  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{CO}$ , NO,  $\text{H}_2\text{O}$ , and  $\text{CH}_3\text{NHCHO}$ . Experiments were also carried out on isotopically labeled materials in order to gain additional mechanistic information about which reaction products arise from labeled functional groups in the starting material. Evidence suggested that the first observable product is  $\text{N}_2\text{O}$ . Detecting the degradation products during decomposition is vital because it allows one to determine the specific bonds that are breaking first as well as the order in which the breakage occurs. From this data, one can make kinetic assignments to specific bonds, which aids in determining the overall degradation mechanism. Since  $\text{N}_2\text{O}$  is the first observable product, this suggested that the N—N bond is the weakest in the molecule and that approximately 199 kJ/mol (47.5 kcal/mol) is needed to begin decomposition at this site. See also [320, 331].

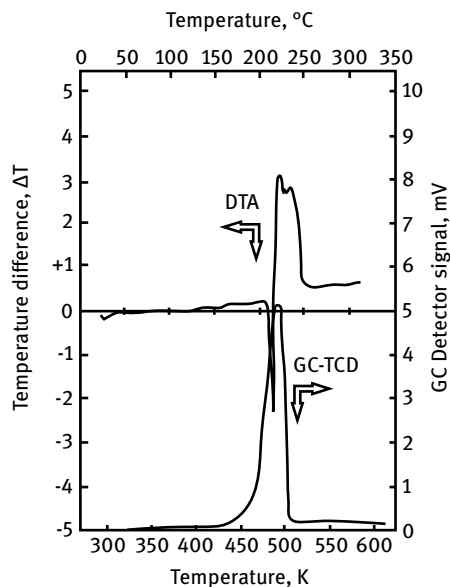
Although the activation energies for the liquid state decomposition of RDX have been reported in a number of studies, none of them addressed the dependence of the activation energy on the extent of conversion, either under an assumption of first-order kinetics or by using Kissinger's method. Activation energies reported up to the year 2000 ranged from 125 to 282 kJ/mol, depending on the instrumental method and the data reduction method used.

The thermal decomposition of RDX has been studied by TGA and DSC, and activation energies as a function of the extent of conversion,  $\alpha$ , have been determined by model-free isoconversional analysis of these data [332]. In open pans, evaporation is a prevalent process with an activation energy of  $\sim 100$  kJ/mol. TGA and DSC curves were measured for RDX in open pans or pierced lid pans and DSC curves were mea-

sured in closed pans at heating rates ranging from 7.5 to 20 °C/min. In the TGA, the pierced lid method gave more reproducible curve shapes. The major TGA mass loss occurred between 443 and 533 K (170 and 260 °C). A superposition of three DSC curves obtained in open, pierced, or closed pans clearly showed the contribution of evaporation to the endothermic part of the curves. Literature reports and the TGA and DSC data suggested that the liquid state thermal decomposition of RDX involves three major steps: vaporization, liquid phase decomposition, and gas phase decomposition. Confining the system in either a pierced pan or a closed pan promoted liquid state decomposition of RDX that occurred with an activation energy of ~200 kJ/mol, which suggests scission of an N—N bond as the primary decomposition step [333]. In such a confined environment, gas phase decomposition is a competing channel with an activation energy estimated to be ~140 kJ/mol. In a closed pan, RDX generated a heat release of ~500 kJ/mol that was independent of both the heating rate,  $\beta$ , and the mass.

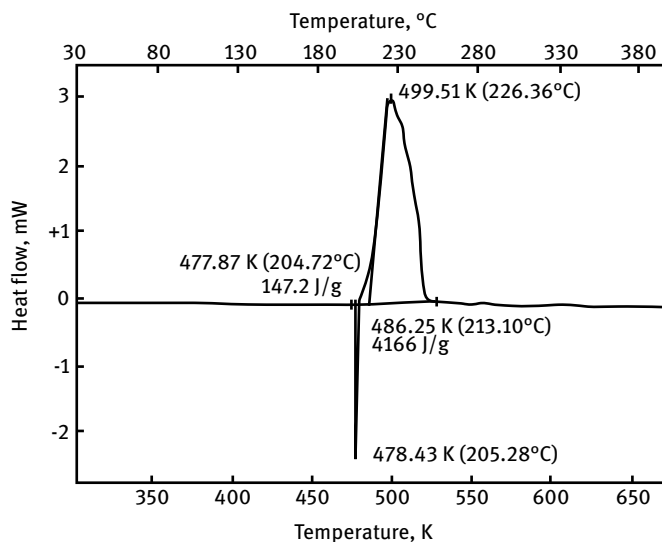
1-Nitroso-3,5-dinitro-*s*-triazine (ONDNTA) is an intermediate in the decomposition of RDX. In order to resolve the multistep process of RDX decomposition into individual reactions, the thermal decomposition of ONDNTA was investigated using the same methods previously used for RDX [334].

The slow thermal decomposition of RDX in a DTA starts with the onset of exotherm at 488 K and culminates at 508 K. The off-gassing of RDX decomposition products measured with a thermoconductivity GC detector (dashed line) was superimposed on the DTA trace (solid line) of RDX as shown in Figure 17. The melting endotherm is immediately followed by a decomposition exotherm. Gas evolution detected by the thermoconductivity bridge below the melting point is primarily sublimation and not decomposition.



**Figure 17:** Differential thermal analysis of RDX decomposition. (Reproduced and modified from [241].)

A sample of RDX prepared by the Woolwich process had a melting point of 478.43 K (205.28 °C) and immediately following the melting endotherm, it had a strong maximum exotherm at 499.51 K (226.36 °C) (Figure 18).



**Figure 18:** DSC Thermogram of RDX made by the Woolwich process. (Republished and modified from [294], with permission from ©2003 Taylor & Francis Ltd., <http://www.tandfonline.com>.)

Decomposition of  $\gamma$ -RDX under high pressure-high temperature conditions was examined to elucidate the reactive behavior of RDX crystals [335]. Vibrational spectroscopy measurements were obtained for single crystals in a diamond anvil cell at pressures from 6 to 12 GPa and temperatures up to 600 K. Global decomposition rates, activation energies and activation volumes at several pressures and temperatures below the pressure-temperature point for the  $\gamma$ -RDX decomposition were obtained. Similar to  $\epsilon$ -RDX, but in contrast to  $\alpha$ -RDX, it was found that pressure decelerated the decomposition of  $\gamma$ -RDX. The decomposition deceleration with pressure in the  $\gamma$ -phase can be attributed to pressure-inhibited bond homolysis step(s). The main decomposition species were identified as  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , in accordance with the species reported for the  $\alpha$ -phase decomposition at high pressures. The  $\gamma$ -phase plays a key role in RDX decomposition at pressure-temperature conditions relevant to shock wave initiation.

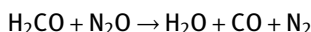
### Rapid Thermal Decomposition of RDX

As part of a multiyear, Multidisciplinary University Research Initiative (MURI) aimed at a better understanding of combustion instability in solid propellant rocket motors, the rates of rapid decomposition and the burning rates of RDX and many other propellant ingredients have been investigated, and models to interpret the experimental

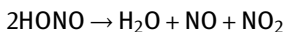
results were developed [336]. Several of the publications referenced in that report give a good introduction into the mechanisms for RDX decomposition and are included in the discussion here.

The combustion-like pyrolysis chemistry of energetic materials liberates products which then diffuse into the flame zone. High rate pyrolysis studies, which emphasize the condensed phase, can be grouped according to the method of heating: infrared laser and hot surface. A number of variations of these two methods have been developed. CO<sub>2</sub> lasers can be used in the pulsed or continuous wave mode to decompose the surface layer at heating rates on the order of 10<sup>7</sup> K/s. Two advantages of this method are that very fast heating can be achieved and chemical diagnostic techniques can be used in conjunction to determine the products that are formed. A disadvantage is that independent pre-test selection of the heating rate and final temperature is not possible so that kinetic determinations are difficult.

The flame structure of RDX under laser-assisted combustion conditions was studied to better understand related chemical and physical processes in the gas phase [337]. Experiments were conducted under pressures from 10 to 303 kPa (0.1 to 3 atm) with heat fluxes of 50 to 600 W/cm<sup>2</sup>. Gaseous products were extracted through the use of quartz microprobes and analyzed by a triple quadrupole mass spectrometer (TQMS). Temperature profiles were measured using microthermocouple techniques to investigate reaction zones in RDX flames. Flame behavior was observed using a high-magnification video system. Major species in RDX flames were identified as H<sub>2</sub>, H<sub>2</sub>O, HCN, H<sub>2</sub>CO, NO, HNC, N<sub>2</sub>O, and NO<sub>2</sub> at low masses ( $m/z \leq 47$ ). In addition to these species, H<sub>2</sub>C=NH with  $m/z = 29$  was found to exist in the near-surface reaction zone as an important minor species. Higher molecular weight species were found at  $m/z$  values of 47, 54, 56, 70, 81, and 97 and were identified as HONO, C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>O, C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>, and C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O, respectively. Increasing heat flux and decreasing pressure stretched out the reaction zones and were useful for investigating reactions near the deflagrating surface. The decomposition of RDX at the surface showed evidence of the two competing branch reactions into H<sub>2</sub>CO + N<sub>2</sub>O and HCN + HONO, as well as two subsequent reactions:



and



With the consideration of the four reactions, the branching ratio for the two decomposition pathways of RDX was estimated to be about 2 : 1.

When examining the impact of laser radiation on propellant surfaces, three distinct categories of laser-induced behavior were observed: laser-induced pyrolysis (LIP) characterized by decomposition without stable surface regression; laser-induced regression (LIR); and laser-assisted combustion (LAC) [338]. The latter two categories were characterized by stable regression of the surface, but with a luminous flame only

observed for LAC. Under LIP conditions, RDX exhibited a thick melt layer with considerable bubbling. Gas species within a bubble were measured, with the most abundant species being  $\text{CH}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$ . Species profiles for RDX at 0.5 and 1.0 atmospheres under LAC conditions were measured. Reaction of  $\text{CH}_2\text{O}$  and  $\text{NO}_2$  occurred directly above the surface followed by a final luminous flame due to reaction of HCN, NO, and  $\text{N}_2\text{O}$ . The kinetic model for RDX decomposition was in excellent agreement between model and experimental species profiles.

A gas phase molecular beam laser pyrolysis experiment provided convincing evidence that a major decomposition route of RDX is the concerted depolymerization of gas phase RDX to form three molecules of methylenenitramine,  $\text{H}_2\text{C}=\text{NNO}_2$ . Infrared multiphoton dissociation (IRMPD) of RDX in a molecular beam was used to investigate the mechanism of RDX thermal decomposition [339]. A beam of molecules was crossed by a pulsed TEA  $\text{CO}_2$  laser and velocity distributions of the various products were measured by the time-of-flight (TOF) technique as a function of the laboratory angle using a mass spectrometric detector. In contrast to the conventional view of simple bond rupture through loss of  $\text{NO}_2$  as the dominant primary channel in RDX decomposition, it was found that the dominant primary channel is concerted symmetric triple fission to produce three  $\text{H}_2\text{C}=\text{NNO}_2$  fragments which subsequently undergo secondary concerted dissociation to produce HCN,  $\text{H}_2\text{CO}$ , HONO (or  $\text{HNO}_2$ ), and  $\text{N}_2\text{O}$ . A total of two primary and four secondary dissociation channels were observed. Concerted reactions predominate over simple bond rupture not only in the number of channels (four vs. two), but also in the amount of products. A fair amount of translational energy release through concerted reaction channels was observed, which was significant for an explanation of the energies of RDX decomposition. Theoretical studies of the reactions leading to the autoignition of RDX vapor may be able to predict the point of runaway reaction in a cook-off situation [41, 340, 341].

Instead of aiming the laser at a solid block of RDX, it may be useful to incrementally pyrolyze only thin film layers. One can use a single laser pulse to heat a film of RDX sandwiched between two transparent windows at 77 K [342, 343]. The film can be heated to 1000 K in 35  $\mu\text{s}$  and by the use of FTIR spectroscopy, it was demonstrated that cleavage of the N— $\text{NO}_2$  bond is the initial step in fast decomposition of RDX.

Thin film laser pyrolysis a new experimental technique for detecting initial reaction products of thermal decomposition under conditions that simulate rapid combustion [344]. The apparatus consisted of a vacuum chamber with an  $\text{LN}_2$ -cooled cold finger, a quartz window, two CsI windows for IR transmission, a modified Knudsen oven containing approximately 10 mg of propellant. When the oven is heated to approximately 120 °C, the propellant is vaporized and condensed as a thin film (10  $\mu\text{m}$  or less) on the cold optical window. The laser is fired through the quartz window so that the thin film is irradiated with the pulsed output of a line-tunable ( $944\text{ cm}^{-1}$ )  $\text{CO}_2$  laser to heat them from 77 K to approximately 1000 K in 35  $\mu\text{s}$ . The films are then cooled back to 77 K in a few milliseconds by heat conduction into the film support. Then the IR ab-

sorption of the pyrolyzed residue can be measured by an IR spectrophotometer. This cycle of laser pyrolysis and infrared spectroscopy can be repeated on the same sample at successively higher laser fluence (to about  $4.7 \text{ J/cm}^2$ ). At higher fluence, additional reaction products were formed due to subsequent steps in the thermal decomposition mechanism. These products included NO,  $\text{N}_2\text{O}$ , HCN, and  $\text{CO}_2$ . Results of numerous experiments on RDX films showed that the initial step in the thermal decomposition mechanism under these conditions is unimolecular scission of a single N—N bond in the condensed phase. This reaction formed nitrogen dioxide, which was detected in its condensed dimerized form, dinitrogen tetroxide.

Experimental results from a CW  $\text{CO}_2$  laser pyrolysis/MS apparatus were compared to predictions from a one-dimensional model of such an apparatus [345]. In the experiments, a microprobe/triple quadrupole mass spectrometer system was used to measure quantitative gas-phase species profiles and a high-magnification video system was used to observe surface behavior and flame structure. Gas-phase species evolved from the surface and also inside a bubble were measured. The species identified at the surface were HCN,  $\text{NO}_2$ ,  $\text{H}_2\text{O}$ , NO, CO,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{H}_2$ , but no  $\text{CO}_2$  was found at the surface. Formaldehyde may have been present, but it could not be unambiguously identified. Species mol fractions measured at 1.0 atm and a heat flux of  $4 \text{ MW/cm}^2$  were used as input to a one-dimensional model along with a temperature profile obtained from the literature for similar experimental conditions. In order to obtain reasonable agreement between the model and the experiments for stable species, undecomposed RDX vapor had to be added to the initial species for the model calculations. However, even with this addition, the profiles for OH and NH did not match data available in the literature. The data were particularly helpful for comparing the products of pyrolysis to those from laser-assisted combustion. Hot surface or filament heating methods offer the advantage of fast pyrolysis with independent control over the heating rate and final temperature. The disadvantage is that the heating rates are lower than are possible with the  $\text{CO}_2$  laser. The most widely applied method of this type is T-jump/FTIR spectroscopy where the sample is a thin coating on a rapidly heated platinum wire or ribbon [346].

The decomposition of RDX was modeled as part of a more complex model of the platinum filament, energetic substance sample and surroundings as a system. The model showed that heating rates up to  $600 \text{ K/s}$  should be achievable while stopping and holding at a known and adjustable target temperature [347]. The predicted time elapsed to the point of rapid energy release by decomposing RDX agreed with measurements. The control voltage of the filament can be recorded simultaneously with rapid-scan FTIR spectra of the evolved products to obtain thermochemical information, product sequencing, and formation rates. Catalytic effects of the platinum filament have been shown to be negligible.

An alternate method used RDX samples confined in a rapidly heated cavity in place of the open filament. This approach improved the heat transfer to the sample but



sacrificed the opportunity to detect the earliest quenched products [348, 349]. T-Jump/FTIR spectroscopy has provided valuable mechanistic information, for example, on RDX and HMX [350].

*In situ*, rapid-scan FTIR spectroscopy in conjunction with the IR absorption intensities was used to construct concentration-time profiles for the gaseous products from thermolysis of RDX and HMX [351]. The pyrolysis cell was capable of attaining rapid heating rates (8–200 K/s) at various gas pressures (0.33 kPa–6.8 MPa = 0.048–1000 psi) and was an attempt to simulate, insofar as possible, combustor conditions. NO<sub>2</sub> was the predominant initial gas product from RDX and, along with HCN, from HMX. NO<sub>2</sub> rapidly diminished with time owing to its participation in secondary reactions. NO was a minor initial product, if it was present at all, but rapidly became a major product owing to secondary reactions. *Cis*- and *trans*-HONO were clearly present initially. Other species observed were N<sub>2</sub>O, H<sub>2</sub>CO, CO, CO<sub>2</sub>, H<sub>2</sub>O, and HNCO. Substantial sublimation of RDX occurred at low pressure resulting in the dominance of gas-phase decomposition (products derived from N–N bond rupture). Above atmospheric pressure, a crossover occurs from largely gas-phase to largely heterogeneous condensed phase decomposition reactions (products derived from C–N bond rupture). Therefore, condensed phase reactions must be involved along with gas-phase reactions when discussing nitramine decomposition under rocket motor conditions.

The decomposition characteristics of liquid-phase RDX were studied using FTIR spectroscopy of evolved gas-phase species from rapid thermolysis and of the condensate and residue formed from the decomposition, as well as time-of-flight mass spectrometry of the evolved gas-phase species [352, 353]. The sub-milligram sample was heated at rates of about 2000 K/s to a set temperature where decomposition occurred under isothermal conditions. Since RDX melts at around 478 K (205 °C), decomposition studies were conducted at temperatures ranging from 538 to 578 K (265 to 305 °C). Species detected by FTIR spectroscopy included CO, CO<sub>2</sub>, NO, N<sub>2</sub>O, NO<sub>2</sub>, *cis*-HONO, *trans*-HONO, HNCO, H<sub>2</sub>CO, HCOOH, HCN, 1,3,4-oxadiazole (*m/z* = 70), oxy-*s*-triazine (*m/z* = 97), and RDX. A decomposition mechanism dealing with the early liquid-phase decomposition and reactions of RDX was postulated based on the acquired experimental data and thermochemical analysis.

### Intermediates in the Thermal Decomposition of RDX

Electron paramagnetic resonance (EPR) provides direct observation of the concentrations of free radicals formed in the initial stages of decomposition processes, and the characteristic EPR spectra may provide identification of the observed species. The combined EPR information can then be compared with proposed mechanisms. Radical species identified by these studies included NO<sub>2</sub>, CH<sub>2</sub>N, and (NO<sub>2</sub>)<sub>2</sub>. Thermal decomposition of RDX below its melting point was observed by means of EPR in experiments performed on neat RDX and on RDX in solution with TNT [354]. Kinetic information for the production and depletion of an RDX intermediate radical species and for

the production of  $\text{NO}_2$  was obtained for RDX/TNT mixtures over a temperature range from 398 to 458 K (125 to 185 °C). The activation energy for the production of the RDX intermediate radical was 233 kJ/mol (55.6 kcal/mol), while apparent activation energies for the decay of this species and for the production of  $\text{NO}_2$  were 200 and 125 kJ/mol (47.7 and 29.8 kcal/mol), respectively. The RDX intermediate radical was also observed in neat RDX from 448 to 478 K (175 to 205 °C).

Another intermediate in the decomposition of RDX is the nitronylnitroxyl free radical [355], but a critical review of these data suggested that these radicals are not primary decomposition products, but are formed by the reaction of the radical products of thermal decomposition with molecular oxygen [356].

$\text{CH}_2\text{N}$  and  $\text{CH}_2\text{NO}$  are two key free radicals which play a pivotal role in the combustion of RDX and HMX near the burning surface. The H atom and OH radical produced by their decomposition are the most important chain-carriers in the combustion of these cyclic nitramine systems. Both  $\text{CH}_2\text{N}$  and  $\text{CH}_2\text{NO}$  radicals can be formed directly from the fragmentation of methylene nitramine,  $[\text{CH}_2\text{NNO}_2]$ , the building block of RDX and HMX [357].

RDX is thought to decompose largely by homolytic N—N bond cleavage, among other possible initiation reactions. Density functional theory (DFT) calculations indicated that the resulting secondary aminyl ( $\text{R}_2\text{N}^\bullet$ ) radical can abstract an oxygen atom from  $\text{NO}_2$  or from a neighboring nitramine molecule, producing an aminoxyl ( $\text{R}_2\text{NO}^\bullet$ ) radical [358]. Persistent aminoxyl radicals have been detected in electron-spin resonance (ESR) experiments and are consistent with autocatalytic “red oils” reported in the experimental literature. When the O-atom donor is a nitramine, a nitrosamine is formed along with the aminoxyl radical. Reactions of aminoxyl radicals can lead readily to the “oxy-*s*-triazine” product (such as the *s*-triazine *N*-oxide) observed mass spectrometrically by Behrens and co-workers [325]. In addition to forming aminoxyl radicals, the initial aminyl radical can catalyze loss of HONO from RDX.

### Experimental Studies of RDX Decomposition Kinetics

When now looking at a literature summary of the state of the knowledge of RDX and HMX decomposition mechanisms and products compiled in 1985, it is surprising how little was then known about the mechanism and intermediates of RDX and HMX decomposition [359]. There was mostly speculation about the mechanisms, typically assuming breakage of the N— $\text{NO}_2$  bond as the initial reaction. A list of identified reaction products was given, but it was not known where they came from or how they were formed. It was suggested to use isotope labeling, but (with a few exceptions using  $^{15}\text{N}$ ) it had not yet been extensively done at that time.

The thermal decomposition of 1,3,5-trinitro-2-oxo-1,3,5-triazacyclohexane (keto-RDX) was investigated by 70 eV electron impact and chemical ionization mass spectra [360]. The mass spectra were similar to those of RDX. The laser-induced mass-spectra implied that the first step of keto-RDX decomposition is the elimination of  $\text{NO}_2$  or HONO and subsequent cleavage of the triazacyclohexane ring. The activation en-

ergy was determined by two methods: (1) by measuring the rate of NO evolution by chemiluminescence and (2) by DSC per ASTM E 698–79. No significant differences in bond-breaking energies for RDX and keto-RDX were found. See also [361, 362].

### Computational Studies of RDX Decomposition Kinetics

Pathways involving initial cleavage of an N–N bond account for only about one third of the gas phase product yield. A theoretical classical orbital dynamics study supported the viability of this depolymerization pathway [363]. A model potential energy surface was constructed to approximately reproduce known features of the RDX molecule. Dissociation was assumed to take place either by simple N–N bond rupture or concerted triple bond fission, both are principal primary dissociation channels previously identified by molecular infrared multiphoton dissociation by Zhao, Hints, and Lee [339]. Dissociation rate branching ratios and rotational, vibrational, and translational energy distributions of the products were then determined as a function of ensemble energy for a potential energy surface having barriers of 160 and 200 kJ/mol (38.3 and 47.8 kcal/mol) to symmetric ring dissociation and to N–N bond fission, respectively. Calculated branching ratios and product-energy distributions were found to be in reasonable agreement with experimental values. See also [364].

A description of gas-phase reaction mechanisms of nitramine propellants was based on three chemical submodels and validated by comparison of model predictions with experimental measurements using reaction flux and sensitivity analyses to guide the process [365]. The submodels, validated over the entire range of experimentally studied conditions, were assembled to represent the gas-phase nitramine combustion mechanism. As an example of this iterative procedure, numerical results were presented for the ignition behavior of RDX.

In the gas phase, RDX is a relatively stable molecule which releases a large amount of energy upon decomposition. Although gas-phase unimolecular decomposition experiments suggest at least two major pathways, there is no mechanistic understanding of the reactions involving RDX or other energetic molecules (such as HMX and TATB) used in rocket propellants [366]. For the unimolecular decomposition of RDX, three pathways were proposed: (1) concerted decomposition of the ring to form three  $\text{CH}_2\text{NNO}_2$  ( $M = 74$ ) molecules, and (2) homolytic cleavage of an N–N bond to form  $\text{NO}_2$  ( $M = 46$ ) plus a free radical of RDX that is missing one  $\text{NO}_2$  group ( $M = 176$ ), which subsequently decomposes to form various products. Experimental studies suggest that the concerted pathway is dominant while theoretical calculations have suggested that the homolytic pathway might require significantly less energy. A third pathway was proposed: (3) successive HONO elimination to form 3HONO ( $M = 47$ ) plus stable 1,3,5-triazine (TAZ) ( $M = 81$ ) with subsequent decomposition of HONO to HO ( $M = 17$ ) and NO ( $M = 30$ ) and at higher energies of TAZ into three HCN ( $M = 27$ ). All three pathways were examined using first principles quantum mechanics density functional theory, including the barriers for all low-lying products. It was found that a threshold exists

at  $\sim 167$  kJ/mol ( $\sim 40$  kcal/mol) for which HONO elimination leads to TAZ plus 3 HONO, while N—N homolytic cleavage leads to RDR plus  $\text{NO}_2$ , and the concerted pathway is not allowed. Above  $\sim 218$  kJ/mol ( $\sim 52$  kcal/mol) the TAZ of the HONO elimination pathway can decompose into 3 HCN, while the HONO can decompose into  $\text{HO} + \text{NO}$ . Above  $\sim 251$  kJ/mol ( $\sim 60$  kcal/mol), the concerted pathway opens to form  $\text{CH}_2\text{NNO}_2$ . At a threshold of  $\sim 272$  kJ/mol ( $\sim 65$  kcal/mol), the RDR of the N—N homolytic pathway can decompose into other products. These predictions are roughly consistent with previous experimental results and should be testable with new experiments. This should aid the development of a kinetic scheme to understand combustion and decomposition of solid-phase RDX and related energetic compounds (e.g., HMX). The decomposition scheme for RDX is similar to that for HMX presented later.

For a mathematical expression describing the chemical structure and reactant/product profiles of RDX flames, key reactions and species were selected by numerical solution of a system of equations describing one-dimensional flows of a viscous, heat-conducting, reacting gas at pressures of 0.5–90 atm [367]. The structure of various flame zones and the role of individual steps and species in the chemical process were investigated. The chosen kinetic mechanism consisted of 263 elementary steps and 43 species, mostly based on literature data of rate constants of elementary steps. A typical flame structure was calculated for RDX combustion under irradiation as in laser-assisted combustion. Various reaction paths in the RDX vapor decomposition zone had to be considered, including the effects of the mass flow rate and two-dimensional nature of the gas flow on the flame structure. Calculation results were then compared to experimental data and agreed moderately well with each other.

A traditional solid-state chemistry approach, applied to the essentially molecular problem of the energetic barrier for decomposition, gave qualitatively new results to the thermal decomposition of solid RDX, and new perspectives in the detonation initiation theory development in general [368]. Quantum-chemical simulations of the thermal decomposition of solid RDX by means of the Hartree–Fock method combined with the cluster and periodic models indicated that the dissociation of the RDX molecule in the bulk crystal is characterized by the different energetic barriers for cleavage of N— $\text{NO}_2$  bonds, unlike the gas-phase molecule, where all three of the energies are equal. It was also shown that a rupture of the N— $\text{NO}_2$  chemical bond requires less energy for an isolated molecule than for a molecule placed in the bulk of the solid. The situation changes if the molecule is close to the free surface of the crystal. In this case, less energy is required to break the bond than for a bulk molecule. Similar observations were made for HMX decomposition [43].

### Catalysts for Thermal Decomposition of RDX

The general theory is that catalysts that can accelerate the decomposition of nitramines will also accelerate their burning rate. RDX is often added to composite modified double-base propellants or composite AP-based propellants to boost their performance and reduce their signature. In those applications, the propellant may

contain burning rate catalysts that will affect not only the burning of NC or AP, but will also affect the burn rate of RDX. Other burning rate increasing catalysts have been evaluated specifically for RDX-based nitramine propellants.

Effective burning rate catalysts for nitramine propellants had not yet been found as of 1984 [324]. One of the catalysts evaluated for nitramine decomposition is potassium decaborate  $K_2B_{10}H_{10}$  or potassium dodecaborate  $K_2B_{12}H_{12}$  [359]. The thermal decomposition of HMX, RDX, and propellants, with and without catalysis by  $K_2B_{12}H_{12}$  or  $K_2B_{10}H_{10}$ , was examined by GC-MS, including the less-volatile decomposition products [369]. Pyrolysis-GC-MS on HMX-GAP and HMX-PEG compositions with and without  $K_2B_{10}H_{10}$  showed that one of the products identified was probably 1,3,5-triazine. This was believed to be formed from HMX via 1,3,5,7-tetraazacyclooctatetraene; this is consistent with the known thermal decomposition behavior of cyclooctatetraene and its aza derivatives. 1,3,5-triazine formation by trimerization of HCN is believed to be relatively unimportant. There was also an unknown component whose highest mass peak was at  $m/e$  70, but formation of the  $m/e$  70 unknown decreased with increasing temperature. The decomposition and combustion of HMX and RDX, and of propellants derived from them, by salts containing boranate anions with alkali metal anions leads to propellants with higher burning rates. The pure salts appeared to be stable under vacuum or inert gas to about 973–1073 K (700–800 °C), but there was a report of  $H_2$  evolution at lower temperatures (ca. 573–873 K = 300–600 °C, depending on the nature of the salt) [370]. When the salts were heated together with RDX, considerable enhancement of the decomposition rate of RDX was observed. This began at the melting temperature of pure RDX and became intense, leading to a lower, much sharper decomposition exotherm. These observations seem consistent with a catalysis mechanism involving attack of the B–H hydrogens of the catalyst on the nitramine.

Perovskite-type  $LaMnO_3$  and  $La_{0.8}Sr_{0.2}MnO_3$  oxides with high specific surface areas have already been tested as catalysts for other applications, such as the catalytic decomposition of HAN- or HTP-based monopropellants. Now they have also been evaluated as catalysts for RDX thermal decomposition and characterized by XRD, FT-IR, SEM, and XPS [371]. The catalytic activities of perovskites on thermal decomposition of RDX were investigated by TGA-DSC techniques. The catalytic activity of  $La_{0.8}Sr_{0.2}MnO_3$  was higher than that of  $LaMnO_3$  for thermal decomposition of liquid RDX.

The addition of some coated aluminum nanopowders lowered the onset temperatures of RDX, TNT, and glycidyl azide polymer decomposition by ~20 °C [372]. Outgassing results obtained for various RDX/aluminum mixtures at 373 K (100 °C) showed that uncoated 120-nm Al enhanced the low-temperature solid-phase decomposition of RDX.

### 12.2.3.3 Radiolysis of RDX

Irradiation of RDX and HMX at the  $1.2 \times 10^6$  roentgen dose level caused no measurable nitramine decomposition [373].

#### 12.2.4 Strand Burning of RDX

RDX is never used as a rocket propellant by itself, only as an ingredient in composite-modified double-base propellants and in nitramine propellants. Thus studies of strand burning of RDX by itself, as summarized in this section, would be strictly of academic interest. In addition to linear strand burning studies of RDX pellets in constant pressure bombs, sometimes also the mass burning rates were derived from pressure curves in constant volume bombs ("ballistic bombs").

There are hundreds of publications on burning rates of solid propellants containing RDX, but a few less on burning rates of RDX by itself. As with any explosive, there is always the hazard that a well-behaved combustion of RDX may unexpectedly transition to a detonation.

The deceleration of chemical reactions in the deflagration of energetic materials by addition of inert ingredients was studied in a constant pressure bomb over the pressure range from 1 to 1000 atm [374]. It was shown that addition to RDX of deoxidants (10%) such as derivatives of urea, diphenylamine, or *o*-aminophenol decreased mass burning rates ( $R_m$ ) by a factor of two to three. Efficiency of the additives was greatest at low pressures and decreased with increasing pressure. One of the most effective additives, urethane, decelerated also the  $R_m$  of TNT, PETN, picric acid, nitroglycol, and DINA.

The deuterium isotope effect which identifies rate-controlling reaction steps in high energy processes was measured in combustion experiments with HMX/HMX-d8 and RDX/RDX-d6 [375]. The deuterium isotope effect directly identified the covalent chemical bond rupture which controls the energy release rate in the condensed phase reactions associated with decomposition and combustion processes. Although a complex myriad of chemical reactions occur during these events, the deuterium isotope effect operates throughout the actual process itself and is specific to the rate-determining bond rupture which controls the energy release rate of pure liquid and solid energetic compounds. HMX/HMX-d8 decomposition studies revealed that the thermochemical rate-controlling step is dependent upon physical state. Solid-state HMX decomposition is controlled by C—H bond rupture; its mixed-melt phase is regulated by the strength of attractive thermophysical crystal lattice interactions, and the liquid state is again chemically controlled, but in this case, by ring C—N bond cleavage. The deuterium isotope effect technique has been extended into the combustion regime using HMX and HMX-d8 and it was found that its global burn rate is kinetically controlled by condensed phase covalent C—H bond rupture.

Assuming a consistent mechanism between decomposition and combustion, the observed isotope effects suggested that a carbon–hydrogen bond rupture in HMX and RDX is the rate-controlling process in the combustion of nitramine propellants [376].

The condensed-phase kinetic deuterium isotope effect (KDIE) approach that determines the rate-controlling steps in a slow decomposition process can be extended into the progressively more drastic high energy regimes encountered with rapid pyrolytic decomposition/deflagration, plus the higher temperature/

higher pressure combustion, thermal explosion, and detonation events [377]. The KDIE can determine mechanistic relationships between the slow thermochemical decomposition process and more energetic events.

High pressure (3.55 and 6.89 MPa = 500 and 1000 psig) burn rate comparisons from the combustion of solid RDX and perdeuterium-labeled RDX-d6 cylindrical pressed pellets revealed a large kinetic deuterium isotope effect (KDIE) [378]. This experimental KDIE confirmed that chemical reaction kinetics are a significant mechanistic factor in controlling the inherent RDX burn rate and further showed the heterocyclic six-membered ring RDX rate-controlling mechanistic step during combustion is the same as that previously reported for its larger eight-membered ring HMX homologue.

A laser-stimulated recoil force technique can be used to perturb the steady combustion of an energetic material and the dynamic burning rate can be obtained from the recoil measured by a sensitive piezoelectric load cell. By tuning the frequency of the modulated laser radiation, the response of the burning surface can be measured and an eventual resonance frequency determined that indicates the propensity of this propellant to suffer failures from combustion instabilities. A “whistling Pete” may be acceptable for entertainment fireworks, but it is not a desirable property of a rocket propellant. Laser-stimulated recoil force measurements have been applied to burning RDX or HMX and many propellant ingredients and formulated propellants [379–382].

A CW CO<sub>2</sub> laser at heat fluxes of 100 and 300 W/cm<sup>2</sup> was used to assist the decomposition and combustion of RDX and HMX, while using a triple quadrupole mass spectrometer and a thermocouple to perform species and temperature profiles measurements in the gas phase [383]. The major species at the surface were H<sub>2</sub>O, H<sub>2</sub>CO, HCN, NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>, CO, and NO at atmospheric pressure with both heat fluxes. There was no CO<sub>2</sub> existing at the surface. The mol fraction of triazine was found to be approximately 2.5% at the surface, which had not been reported by previous investigators during combustion of RDX. These data were particularly helpful for comparing the products of pyrolysis to those from laser-assisted combustion. The temperature profiles in the gas phase and species concentrations obtained at the surface with heat fluxes of 100 and 300 W/cm<sup>2</sup> were used as inputs to a one-dimensional gas-phase flame model, but disagreement between the model and experiments for stable species was substantial. Hot surface or filament heating methods offer the advantage of fast pyrolysis with independent control over the heating rate and final temperature. The disadvantage of hot surface or hot filament heating is that the heating rates are lower than those that are possible with the CO<sub>2</sub> laser.

HMX burning laser and pressure-driven response experiments were conducted at 1, 2, and 3 atm in argon [384]. Under these conditions a mean laser flux was necessary to sustain combustion. In addition, microthermocouple measurements were performed to obtain information required to interpret the results and to estimate condensed phase heat release. Modeling of the gas-phase region was used to estimate the heat feedback from the flame to the surface. Due to the presence of the laser heat flux, the flame was significantly “stretched” resulting in heat feedback to the surface that

was substantially less than that without the laser flux. As a result of the lower heat feedback to the sample surface, the steady and unsteady laser fluxes dominated over the steady and unsteady heat feedback in the laser-driven testing, so the laser flux was not simply a perturbation on the steady heat feedback. Laser-driven response experiments on HNIW showed that the response amplitude decreased with an increase in pressure. The unsteady component of the laser flux induced an unsteady component of the gas-phase heat feedback that was out of phase with the laser flux. The laser-driven experiments measured the response of the propellant to this net unsteady flux that was incident on the propellant surface. The increase in pressure increased the unsteady gas phase heat feedback and hence decreased the net unsteady flux on the propellant surface and resulted in the lower response amplitudes.

Small perturbations of burning nitramines near the stability limit give rise to undamped oscillations of the burning rate. Measurements of strand burning rates of RDX and HMX in the range of 1–4 atm, with and without modulated laser augmenting irradiation, showed that at atmospheric pressure in addition to the usually recorded flame combustion regime, RDX has a regime of flameless gasification under irradiation [385]. Both of the regimes were followed by high-frequency oscillations exceeding 600 Hz. The source of these oscillations was assumed to be the boiling and rupture of bubbles at the surface.

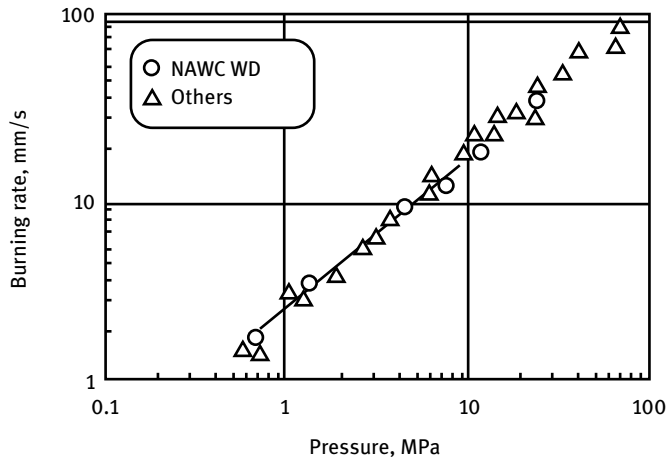
The strand burning rates of RDX were compared to those of ADN, HNF, HMX, CL20, and AP [386]. RDX powder was pressed into rectangular pellets using 20  $\mu$ L of acetone per 0.5 g pellet as a processing aid. The pellets were pressed at 621 MPa and held at that pressure for 5 min. The density of the resulting pellets was 95.5–99.1% of the theoretical maximum density. Figure 19 is a comparison of NAWCWD data with literature data. The data points match very closely.

Figure 20 is a graphical representation of the pressure and temperature sensitivity of burning rates of pressed pellets of RDX. The short section for 423 K initial temperature is the result of only two pressure data points available at 0.69 and 1.38 MPa.

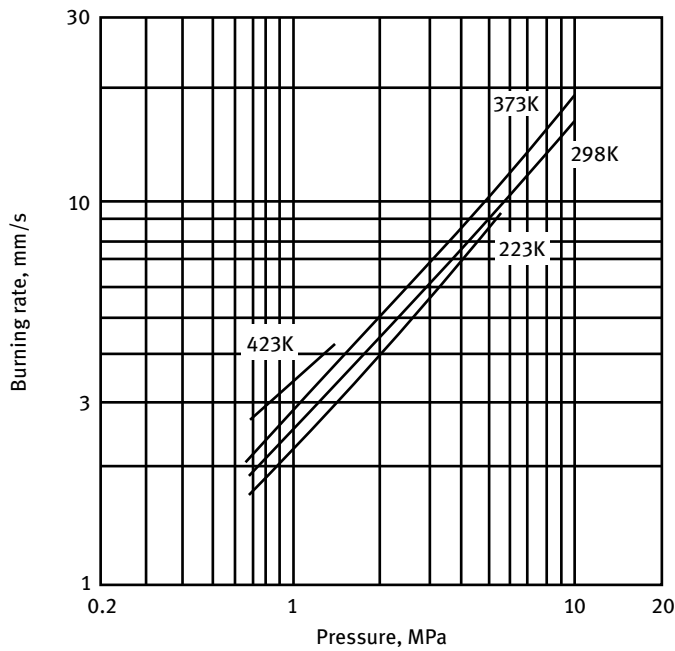
In extending conventional burning rate and pressure exponent measurements, additional data were used to determine the temperature sensitivity coefficient  $\sigma_p$  of the burning rate of RDX, HMX, HNIW, and three oxidizers [387]. The simplest means of determining a value of  $\sigma_p$  is to measure the burning rate of a particular material as a function of initial temperature, take the natural logarithm of the burning rate values, and determine the burning rate temperature sensitivity as the slope of the line through a plot of the natural logarithm of the burning rate vs. the initial temperature. The main requirement is to obtain a consistent and reliable set of burning rate data at various initial temperatures and pressures. Figure 21 gives a comparison of the temperature sensitivity coefficients of three nitramines. In the case of RDX, the temperature sensitivity goes through a minimum over a wide pressure range. The temperature sensitivities of the burning rates of HMX and HNIW are much higher than that of RDX.

Absorption spectroscopy has been applied to low-pressure, self-deflagrating RDX flames in an attempt to develop detailed chemistry combustion models [388, 389].

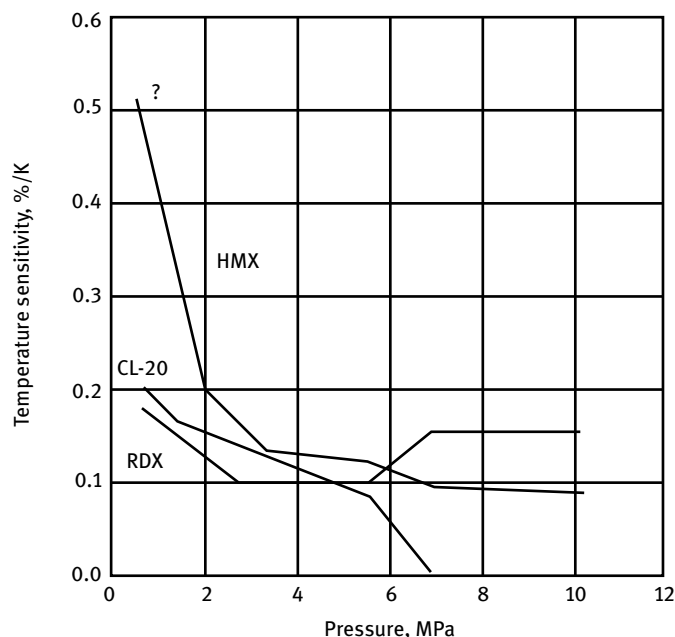




**Figure 19:** Strand burning rates of RDX pellets. Comparison of NAWCWD data with literature data. (Republished and modified from [386], with permission of ©1999 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)



**Figure 20:** Strand burning rates of RDX pellets at different temperatures. (Republished and modified from [386], with permission of ©1999 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)



**Figure 21:** Comparison of temperature sensitivity coefficients of burning rates of nitramines. (Republished and modified from [387], with permission of ©1999 American Institute of Aeronautics and Astronautics; permission conveyed through Copyright Clearance Center Inc.)

Semi-empirically determined production rates of reactants from the solid propellant surface together with a detailed gas-phase elementary reaction set were used to develop a kinetic model. The spatial profiles of two low-concentration, highly reactive, short-lived diatomic species, CN and NH, were obtained at pressures varying from 1 to 2 atm in air. Two major species, NO and OH, were also profiled using this technique. As the pressure was increased, the CN and NH concentrations peaked closer to the combusting surface over a smaller spatial extent. Measurements of the concentration of NO species showed a peak concentration of 25 mol-% occurring at a position of 0.12 mm above the surface of the propellant. In the final flame region, measured OH concentrations of 1.7 mol-% agreed well with adiabatic reaction calculations performed with the NASA Lewis thermochemical equilibrium code. The model peak positions and relative concentrations of NO, OH, CN, and NH were in good agreement with experiments. During the course of these spectroscopic measurements, burning rates for RDX over a pressure range of 1 to 2 atm were determined. These values ranged from 0.23 mm/s at atmospheric pressure to 0.50 mm/s for 2 atm and were noticeably lower than some of the other published measurements. Calculations based on the proposed model predicted a burning rate of 0.29 and 0.54 mm/s for the same pressure levels.

#### 12.2.4.1 Modeling of Strand Burning of RDX

The importance of a molten foam layer on the surface of a burning RDX propellant has been acknowledged, but models capable of predicting the concentration and temperature profiles across the flame zone were difficult to develop because of the complexity involved. A theoretical model which described the detailed reaction-zone structure of RDX pellets burning under constant ambient pressure was developed which considered a time-dependent, deflagrating RDX propellant which consisted of three different zones: (1) solid-phase conductive heating zone, (2) liquid/gas bubble two-phase reaction foam zone, and (3) gaseous chemically reacting flame zone [390]. The model included 38 chemical species and 158 chemical reactions. Major parameters that could be printed out with the output of this model included burning rate, foam layer temperature and species profiles, bubble dynamics (e.g., bubble growth and bubble velocity), and void fraction of the foam zone.

A similar model for self-sustained combustion of RDX pellets takes into account detailed chemical kinetics and transport phenomena in the gas phase, and thermal decomposition and subsequent reactions in the condensed phase [391]. The formation of gas bubbles in the subsurface layer due to molecular degradation and evaporation was also included to provide a complete realistic simulation. Various important aspects of RDX burning characteristics were systematically examined over a broad range of pressure, with special attention given to the effect of the subsurface two-phase flow on propellant deflagration. Good agreement between calculated and measured burning rates as well as their pressure and temperature sensitivities was achieved. Profiles of species concentrations revealed a multistage reaction mechanism in the gas phase. The temperature profile, however, exhibited a monotonic increase from the surface to the final flame zone. No evidence could be obtained for the existence of a temperature plateau in the dark zone, consistent with some earlier experimental observations of such a plateau.

Laboratory experiments as well as theoretical computations have contributed to a better understanding of the thermal decomposition and linear burning rates of nitramines; however, because of the lack of thorough experimental and theoretical data on the chemical structure of a combustion wave, the kinetics of the process in the narrow zone adjacent to the burning surface had not been adequately studied. A systematic review of literature data on the thermal decomposition was trying to summarize what was known and point in the direction where additional work was needed [367, 392–394].

A one-dimensional, steady-state numerical model of the combustion of homogeneous solid propellants like RDX or HMX was modeled in three regions: solid, two-phase (liquid and gas) and gas [395]. Conservation of energy and mass equations were solved in the two-phase and gas regions and the eigenvalue of the system (the mass burning rate) was converged by matching the heat flux at the interface of these two regions. The chemical reactions of the system were modeled using a global kinetic mechanism in the two-phase region and an elementary kinetic mechanism in the gas

region. There was reasonable agreement between experimental data for RDX, HMX, and GAP and model predictions for burning rate, temperature sensitivity, surface temperature, adiabatic flame temperature, species concentration profiles, and melt-layer thickness. The combustion characteristics of RDX and HMX are similar because of their similar chemistry. Differences in combustion characteristics arose due to differences in melting temperature, vapor pressure, and initial decomposition steps.

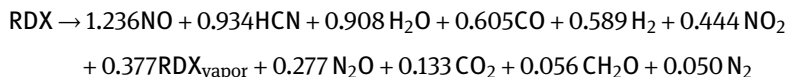
To develop a comprehensive model of nitramine propellant ignition and combustion, a numerical analysis was developed to solve both transient and steady-state combustion, including detailed finite rate chemical kinetics, thermodynamic phase transition, and subsurface reactions [396]. The model was then expanded to predict ignition phenomena. Modeling work was complemented by conducting fast thermolysis experiments with RDX, CAB, NC, and mixtures of RDX and binders. Intrusive mass spectroscopic techniques were utilized to acquire gas phase species profiles under conditions of laser-assisted burning of monopropellants and composite propellants. Nonintrusive diagnostic techniques were developed and used to determine temperature and species profiles within propellant flames at elevated pressures, which were needed for model validation.

RDX and HMX have similar structures and strand burning rates. However, the burning-rate temperature sensitivity  $\sigma_p$  is significantly different between RDX and HMX at low pressure. Efforts to mathematically model the steady-state burning of RDX and HMX with detailed chemical kinetics in the gas and decomposition in the condensed phase have succeeded in modeling burning rates at a specific initial temperature. However, all have underpredicted the  $\sigma_p$  trends of HMX at low pressure and have not differentiated between the  $\sigma_p$  values of RDX and HMX. RDX and HMX both burn with a thin multiphase surface of bubbles in the liquid melt layer. A liquid–bubble model was developed to improve  $\sigma_p$  predictions [397]. In order to predict the experimentally observed  $\sigma_p$  values with the model, first, evaporation in the subsurface was limited to near the gas–liquid interface. Second, the difference in surface temperature at different initial temperatures was adjusted to follow trends in experimental data. Third, the effect was added to the calculation of the bubble velocities. For RDX, there was little change in the calculated  $\sigma_p$  value with the addition of the liquid–bubble submodel.

#### 12.2.4.2 Flame Structure and Temperature Profiles of RDX Flames

The chemical flame structure of RDX or HMX burning in an air or argon atmosphere was investigated at a pressure of 0.1 MPa using molecular beam mass spectrometry [398, 399]. Eleven species ( $H_2$ ,  $H_2O$ , HCN,  $CO_2$ , CO,  $N_2$ ,  $N_2O$ ,  $CH_2O$ , NO,  $NO_2$ , and nitramine vapor [HMX or RDX]) were found in flames of RDX and HMX during self-sustained combustion. It was found that nitramine flames at a pressure of 0.1 MPa have a two-zone structure: In the first flame zone, the consumption of nitramine vapor (HMX or RDX),  $NO_2$ ,  $CH_2O$ , and partial consumption of  $N_2O$  with formation of  $H_2$ ,  $H_2O$ , CO,  $N_2$ ,  $CO_2$ , HCN, and NO occurs. In the first, narrow, zone

0.15 mm wide adjacent to the burning surface, decomposition of RDX vapor and the reaction of  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_2\text{O}$  with the formation of HCN and NO occur. In the second zone, 0.85 mm wide, HCN is oxidized by NO to form the final combustion products. Using experimental data, gross-reactions for the gasification of nitramines at atmospheric pressure were determined:



The same method was also applied to formulated propellants of RDX or HMX with GAP as the binder [400].

Experimental investigations of the burning wave structures of HMX and RDX were carried out by microthermocouple measurements at 1–70 atm [401]. Data on burning-surface temperature, heat release in solid, heat feedback from gas to solid, and heat-release rate in gas near the surface were obtained by this method. The data showed that in the condensed phase of combustion waves of nitramines, evaporation and thermal decomposition occur simultaneously, with heat release in the solid being negative at  $P < 5 - 10$  atm and positive at  $P > 5 - 10$  atm. Activation energies of HMX and RDX decomposition in combustion waves were derived from the burning rate dependence on initial sample temperature.

Temperature profiles of self-deflagrating RDX in a nitrogen environment at pressures up to 0.79 MPa were determined using UV/Visible absorption spectroscopy and fine-wire thermocouples [402]. The burning surface of RDX was covered by a very dynamic two-phase foam zone, and the thickness of the foam zone decreased very rapidly with an increase of pressure. The temperatures within the foam zone were readily identified in the thermocouple traces, especially at low pressures. Depending on the pressure, the temperature was found to be around 500–520 K at the bottom surface of the foam zone, and around 590–690 K at the top surface of the foam zone. These temperatures were higher than the RDX melting temperature (477 K at 1 atm). A relationship between RDX burning surface temperature and pressure was developed for pressures between 1 and 90 atm using data from this study and Zenin's data [401]. The final flame temperature of RDX increases with an increase of pressure: 2950 K at 0.17 MPa, 3002 K at 0.45 MPa, and 3204 K at 0.79 MPa, which agreed well with chemical equilibrium calculations. See also [365].

#### 12.2.4.3 Unsteady, Oscillatory Burning of RDX Flames

Combustion of RDX under self-deflagrating and  $\text{CO}_2$  laser-assisted conditions at atmospheric pressure in air was studied measuring near-surface temperature (embedded microthermocouple), melt layer thickness, and sensitivity of burning rate to initial temperature and radiant flux [403]. Unsteady burning measurements of oscillatory burning behavior were obtained using the laser-recoil technique. Thermocouple data showed a relatively thick (several hundred  $\mu\text{m}$ ) melt layer, which increased in thick-

ness with increasing laser flux, but remained at a relatively constant temperature of about 650 K. The fluctuating, spatially isothermal (time-averaged) nature of the melt layer suggested that a bubbling/mixing mechanism plays an important transport role in this zone. The temperature- and radiant flux-burning rate sensitivity data showed that the equivalence principle is reasonably accurate for RDX under these conditions.

One means to achieve the increased rocket propellant performance needs of the future is to increase solid rocket motor operating pressures. Increased operating pressures can be achieved with the improved rocket motor case technology that is currently available. While attractive, this mode of performance increase is not without its own practical limitations. Solid rocket propellants often experience an increase in burning rate pressure exponent at elevated pressures. A burning rate pressure exponent near unity may result in a motor explosion. Combustion instability is also an additional problem at elevated pressures. High pressure oscillations were observed in some of the closed bomb firings made with RDX and appear to be related to a delayed ignition. Burning rate measurements were measured for nitramines over the pressure range of 0.69 to 138 MPa [404]. A combination of high pressure window bomb and closed bomb combustion tests was used to obtain the combustion data.

### 12.2.5 Toxicity of RDX

The TLV TWA for RDX vapor inhalation in air is  $1.5 \text{ mg/m}^3$  (NIOSH). An IDLH value has not been established.

In a study of mammalian toxicity of RDX, acute oral LD<sub>50</sub> values were  $119.0 \pm 4.6$ ,  $118.7 \pm 4.5$ , and  $118.1 \pm 2.8 \text{ mg/kg}$  in male, female, and combined sexes of rats [405]. The corresponding mouse LD<sub>50</sub>s were  $97.2 \pm 8.7$ ,  $58.9 \pm 26.8$ , and  $80.3 \pm 9.6 \text{ mg/kg}$ , respectively. There were no statistically significant sex difference in either species. Toxic signs, including gasping, labored breathing and convulsions, indicated neurotoxicity. In the 90-day rat subchronic toxicity study,  $40 \text{ mg kg}^{-1} \text{ day}^{-1}$  was toxic, while the next lower dose ( $28 \text{ mg kg}^{-1} \text{ day}^{-1}$ ) was not. The only consistent toxic effect observed was decreased weight gain. Mice were less affected in the 90-day subchronic study, since a dose of  $320 \text{ mg kg}^{-1} \text{ day}^{-1}$  was required to produce definite toxicity. Effects seen included hyperactivity, unscheduled deaths, increased liver and kidney weight accompanied by hepatocellular vacuolization or microgranulomas and tubular nephrosis. RDX was not mutagenic in the Ames Salmonella/microsome test at doses up to  $1 \text{ mg/plate}$  and in the rat dominant lethal mutation test at doses up to  $50 \text{ mg kg}^{-1} \text{ day}^{-1}$ . RDX was not teratogenic to rats or to rabbits at doses up to  $20 \text{ mg kg}^{-1} \text{ day}^{-1}$  but that dose produced severe nonteratogenic toxicity. The two-generation reproduction study produced severe toxicity (particularly neurotoxic effects and unscheduled deaths) but no specifically reproductive toxicity at diets giving a nominal  $50 \text{ mg kg}^{-1} \text{ day}^{-1}$ .

#### 12.2.5.1 Environmental Effects of RDX

Contamination from unexploded munitions and explosive residues from partial explosions may persist in the environment for a long time. RDX or HMX from unex-

ploded ammunitions may soak into soil, where some of it is consumed by biodegradation [406]. The main concern from an environmental point of view is the waste water from RDX/HMX manufacturing plants which may still contain unreacted intermediates and spent acid. The solubility of RDX in water is relatively low, so that only little RDX product is in the filtrate after the product has crystallized. In comparison to those concerns, problems arising from the use of RDX or HMX in CMDB/nitramine rocket propellants are only minor. Because only limited resources were available when preparing this book, complete coverage of the environmental effects of RDX and/or HMX could not be included in this chapter of the book.

### **12.2.6 Handling of RDX**

One method to destroy RDX in contaminated waste water is by reduction in alkaline solution (dispersion) with aluminum powder, accelerated by ultrasound sonication [407]. Another method for treatment of RDX-contaminated waste water includes bioremediation in open ponds.

### **12.2.7 Explosive and Fire Hazards of RDX**

#### **12.2.7.1 Drop Weight Impact Sensitivity of RDX**

The drop weight impact sensitivity of RDX in the BAM test apparatus is 7.5 N m. Impact sensitivity of a 20-mg sample in the Bureau of Mines apparatus is 0.3 m with a 2-kg weight. Impact sensitivity of an 18-mg sample in the Picatinny apparatus is 0.2 m with a 2-kg weight.

Strain-gauge measurements on RDX and other explosives showed that the pressures attained during drop-weight impact are typically 0.5–1 GPa (5–10 kbar) and the duration of impact 300–500  $\mu$ s [408].

A dislocation pile-up avalanche model was used in an effort to explain the crystal size dependence for hot spot-controlled initiation of chemical decomposition in RDX crystals subjected to drop-weight impact testing [409]. Deformation-induced temperature rises, hot spot sizes and lifetimes are related to previously reported values for direct thermal decomposition and a chemical reaction heat generation rate was estimated from available kinetic data.

Looking into what creates hot spots and makes RDX crystals ignite during crushing impact, elastic, plastic, and cracking indentation measurements obtained in nano- to micro- to macroindentation hardness tests of RDX crystals were described on a hardness stress-strain basis and assessed in terms of a dislocation pileup avalanche mechanism for hot-spot generation associated with sudden crack formation [410, 411]. The model attempted to interpret particle size influence on the drop-weight height for 50% probability of onset of reaction and was extended to include results for  $\epsilon$ -HNIW crystals.

An interlaboratory comparison of seven lots of commercially available RDX was conducted to determine what properties of the nitramine particles can be used to as-

sess whether the RDX has relatively high or relatively low sensitivity [412]. The materials chosen for the study were selected to give a range of HMX content, manufacturing process and reported shock sensitivity. Impact sensitivity is not a good predictor of shock sensitivity for these types of RDX. Although most RDX has low HMX content, that characteristic alone is not sufficient to guarantee low sensitivity. A range of additional analytical chemistry tests (HPLC and DSC) were conducted on the material to see how they relate to sensitivity.

Reduced sensitivity RDX (RS-RDX) depends on both crystal structure and chemical composition (contaminant content). There are publications on work done to determine which property or properties may explain the less sensitive behavior of formulations with RS-RDX. There is no dedicated specification to apply to RS-RDX. Standard RDX produced by the Bachmann process (when re-crystallized under I-RDX conditions in order to obtain RS-RDX) does not retain its low sensitivity after aging. It has been shown that the higher sensitivity of RDX produced by the Bachmann process, or the evolution of sensitivity after aging of RS-RDX produced from Bachmann RDX, may be linked to the presence of HMX during crystallization. There are indications that removal of HMX from Bachmann RDX may lead to RS-RDX, which retains its RS character even after aging [413].

There is a relationship between the weakest N—N bonds in a cyclic nitramine molecule and its impact sensitivity [414]. The relationships found between the bond dissociation energy values and logarithms of impact sensitivity of these nitramines, expressed as drop energy, were not unambiguous.

The surface and thermal properties of seven different varieties of crystalline RDX from five different manufacturers were studied using DSC and atomic force microscopy (AFM) [415]. The specific varieties of the RDX studied were chosen because intensive characterization of the materials already existed including shock sensitivity and HMX impurity levels. AFM scans revealed a variety of surface defects. To quantify the surface defects on the crystalline surface of the RDX particles, surface roughness measurements were performed to correlate the observed surface, HMX impurity levels and DSC thermal curve properties with the known shock sensitivities of the material. It was found that a statistically significant relationship existed between surface roughness and the shock sensitivity of the material, while no relationship was observed between the DSC thermal properties and either surface roughness or shock sensitivity. The HMX content greatly affected the thermal properties of RDX but was not correlated with the shock sensitivity.

The shock sensitivity of RDX is dependent upon many factors including crystal size, morphology, internal defects, surface defects, and HMX content. With the arrival of reduced sensitivity RDX (RS-RDX) and the drive towards insensitive munitions, understanding what influences sensitivity has become a significant topic within energetic materials research. The parameters which influence sensitivity were investigated in a round robin analysis exercise. However, large discrepancies were seen between different laboratories involved in a round robin, so the results were inconclusive. It be-



came necessary to clarify how crystal properties and the manufacturing process affect RDX sensitivity [416]. Optical microscopy showed that internal defect content varied widely and was affected by the manufacturing process. A good correlation between sensitivity and defect quantity was seen for RDX lots produced by the same method. Microscopic examination showed a wide range of morphology variations, which was influenced by the method of production. Scanning electron microscopy also showed that surface defects were approximately correlated to shock sensitivity. However, general surface roughness agreed better with sensitivity than the number of specific defects such as cracks and holes. The mechanical properties of the RDX samples were investigated using nanoindentation. This showed a good correlation between the quantity of internal defects and modulus of elasticity, hardness, and creep. There was also a good agreement between these parameters and sensitivity. DSC results indicated that crystal size influenced the decomposition rate. The melting endotherm onset temperature and energy was correlated with HMX content.

Trapped gas bubbles may contribute to impact sensitivity of explosives. In order to eliminate contributions by adiabatically compressed gas bubbles as hot spots, some drop weight impact sensitivity tests have been conducted in a vacuum.

#### **12.2.7.2 Friction Sensitivity of RDX**

The friction sensitivity in the BAM friction test apparatus is 120 N pistil load.

#### **12.2.7.3 Explosive Shock Sensitivity of RDX**

The published literature on shock sensitivity of granular explosives like RDX or HMX presents a somewhat confusing picture. A particular problem is that the results of different studies often cannot be directly compared due to the different experimental methods and purity of the samples used to determine sensitivity. Some experimenters do not state which crystal polymorph modification of HMX was being tested.

In order to identify the most important crystal features that cause hot spots to develop in a granular explosive, various batches of gently consolidated, tapped granular RDX having a wide range of crystal shapes, void contents, and surface qualities were tested for their shock sensitivity. The range of possible factors included internal void content, particle size, HMX content, and the number and size of internal defects.

#### **12.2.7.4 Explosive Performance of RDX Detonation Velocity of RDX**

The detonation velocity of confined RDX is 8750 m/s at  $\rho = 1.76 \text{ g/cm}^3$ . When searching for a relationship between bond dissociation energies of the weakest bond in the molecule and the detonation velocity, no unambiguous relationships could be found between the logarithms of detonation velocities and bond dissociation energies of cyclic nitramines [417]. The reason of this lack of correlation mainly lies in real conformations of these molecules and intermolecular force effects in real crystals.

### Critical Diameter of RDX Detonations

A theoretical analysis of the effect of RDX particle size on critical diameter showed that the size of RDX particles has an effect on critical diameter: the smaller the particle size, the smaller the critical diameter of the charge [418, 419].

### Lead Block Indentation of RDX

The lead block bulging of the cavity caused by RDX detonation is  $415 \text{ cm}^3/10 \text{ g}$ . Other sources give the lead block indentation of RDX as  $480 \text{ cm}^3/10 \text{ g}$ . The Trauzl lead block indentation of RDX is 157% of that of TNT.

### Ballistic Mortar Performance of RDX

The ballistic mortar performance of RDX was calculated by a simplified method and compared to experimental measurements. The ballistic mortar performance of RDX was predicted to be 152% of that of TNT and measured as 150% of that of TNT [88].

#### 12.2.8 Intermediates in the RDX and HMX Synthesis

The cyclic nitramine 3,7-dinitro-1,3,5,7-tetraaza-bicyclo[3,3,1]nonane,  $\text{C}_5\text{H}_{10}\text{N}_6\text{O}_4$ , also called dinitropentamethylenetetramine (DPT), is an intermediate in the synthesis of HMX and RDX, and has an impact sensitivity lower than that of HMX or RDX. The DPT molecule has both the eight-membered C—N ring of HMX and the six-membered C—N ring of the RDX molecule. The crystal structure of DPT was determined by XRD for comparison with those of both HMX and RDX [420]. The crystals are monoclinic, space group  $P2_1/c$ , with  $a = 9.345(5) \text{ \AA}$ ,  $b = 8.284(5) \text{ \AA}$ ,  $c = 11.566(5) \text{ \AA}$ ,  $\beta = 103.6^\circ$ , and  $Z = 4$ . The XRD density of DPT is  $1.682 \text{ g/cm}^3$ .

### 12.3 RDX Derivatives

Substituting some or all of the hydrogens in the hexahydrotriazine ring which forms the skeleton of RDX with more energetic groups will result in energetic materials that have improved properties. Another variation is the replacement of one or more nitramine groups in RDX with other energetic linkages.

One of the derivatives where three of the hydrogens have been replaced with trifluoromethyl groups, is 1,3,5-trinitro-2,4,6-tris(trifluoromethyl)-hexahydrotriazine (TTFMRDX). Even more energetic compounds can be obtained if the hydrogens are replaced by difluoroamino groups instead of trifluoromethyl groups, which can be synthesized by way of 1,3-diazacyclohexane precursors [421].

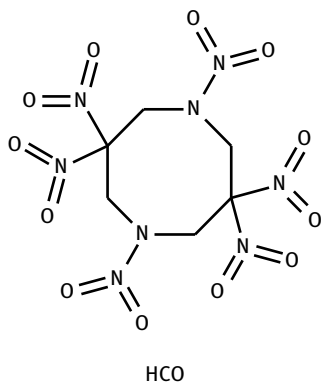
### 13 Seven-Membered Ring Heterocyclic Nitramines

1,3,5-Trinitro-1,3,5-triazacycloheptane; 1*H*-1,3,5-triazepine, hexahydro-1,3,5-trinitro-; hexahydro-1,3,5-trinitro-1*H*-1,3,5-triazepine,  $M = 236.14$  g/mol,  $C_4H_8N_6O_6$ , TNCHP, HOMO, CAS RN [5790-78-3], with a m.p. of 438 K (165 °C) (decomposition), a homologue of RDX, was obtained in 38% yield by the nitrolysis with 99%  $HNO_3$  at 275–277 K (2–4 °C) of finely powdered methylenebis(3,6-dinitro-1,3,6-triazacycloheptane), m.p. 478 K (205 °C) (decomposition) which was obtained in 94% yield by heating  $(CH_2NHNO_2)_2$  in 37% formalin to 333 K (60 °C), cooling the product to 293 K (20 °C), and adding 28%  $NH_3$  [228]. See also [422]. According to other information, 1,3,5-trinitro-1,3,5-triazacycloheptane melts at 440–441 K (167–168 °C) and in the DTA the temperature at the maximum of the exotherm peak is 554 K (281 °C) [94]. 1,3,5-Trinitro-1,3,5-triazacycloheptane has no practical importance, it is mostly used in comparative studies with RDX to see what effect the widening of the ring structure might have on thermal stability of this molecule. It will also be examined in comparison to HMX to see what effect the tightening of the ring has on the stability of this molecule. Working in the other direction, studies have been extended beyond HMX to nitramine rings with five or even six  $-CH_2-N(NO_2)-$  linkages.

*N*-Nitroazacycloheptane has only one nitramine group instead of three in the molecule. *N*-Nitroazacycloheptane boils at 358–360 K (85–87 °C) at 267 Pa (2.0 mm Hg) and its index of refraction is  $n_D^{26} = 1.5045$ .

### 14 Eight-Membered Ring Heterocyclic Nitramines

1,3,3,5,7,7-Hexanitro-1,5-diazacyclooctane (HCO) has been evaluated as an alternate to HMX. The gross formula for HCO is  $C_6H_8N_8O_{12}$  with a molecular mass of 384.2 g/mol and a total oxygen content of 50% and an oxygen balance of –16.7% which is better than that of HMX or RDX (–21.6%).

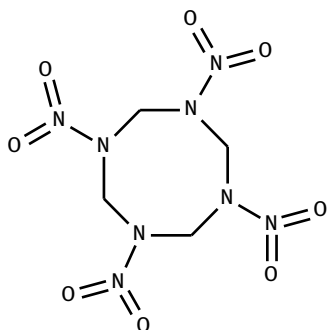


HCO was synthesized in small samples, and the density was  $\rho = 1.875 \text{ g/cm}^3$ , the enthalpy of formation was  $\Delta H_f = -27.3 \text{ kJ/mol} = -6.52 \text{ kcal/mol}$  and the melting point was 523 K (250 °C) with decomposition [218]. The intermediates in the six-step synthesis procedure of HCO were too sensitive to make a scale-up of its production feasible.

## 15 Eight-Membered Ring Heterocyclic Nitramines with Four Nitrogen Atoms in the Ring

### 15.1 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane, Octogen (HMX)

Cyclotetramethylenetetranitramine, also known as  $\text{C}_4\text{H}_8\text{N}_8\text{O}_8$ , octogen, HMX, 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, 1,3,5,7-tetranitro-1,3,5,7-tetrazocane, CAS RN [2691-41-0],  $M = 296.155 \text{ g/mol}$ , is one of the most powerful and thermally very stable explosives. It is used as a rocket propellant ingredient in nitramine propellants, sometimes in combination with RDX, but not as widely as RDX because it is more expensive to manufacture. Since its preparation is significantly more difficult than that of RDX, it is not as widely used as its lower nitramine homologue.



1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX)

The name HMX comes from **H**igh **M**elting **eX**plosive and not from “Her Majesty’s Explosive,” as some people have suggested.

#### 15.1.1 Preparation, Production, and Availability of HMX

HMX is often formed as a by-product during the manufacture of RDX by the Bachmann process (prepared from hexamethylenetetramine, ammonium nitrate, nitric acid, and acetic anhydride). It is obtained as the sole product when 1,5-methylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane is treated with acetic anhydride, ammonium nitrate, and nitric acid. This intermediate precursor can be made by reaction of acetic anhydride

with hexamethylenetetramine dinitrate. HMX produced by the Bachmann process may contain some RDX as a contaminant.

## 15.2 Physical Properties of HMX

The physical properties of HMX are summarized in Table 27. In the literature, physical properties are reported for  $\beta$ -HMX, unless otherwise specified.

**Table 27:** Physical properties of HMX

|                             | SI units               | Other units                  | References |
|-----------------------------|------------------------|------------------------------|------------|
| Molecular mass              | 296.1551 g/mol         | 3.3766 mol/kg                | [85]       |
| Density at room temperature | 1.96 g/cm <sup>3</sup> | —                            | [133]      |
| Melting point               | 471–478 K              | 198–205 °C                   | —          |
|                             | 548 K                  | 275 °C                       | [133]      |
|                             | 549–551 K              | 276–278 °C                   | [94]       |
|                             | 544.9 K                | 271.8 °C                     | [87]       |
| Vapor pressure at 298 K     | —                      | $3.01 \times 10^{-15}$ mm Hg | —          |

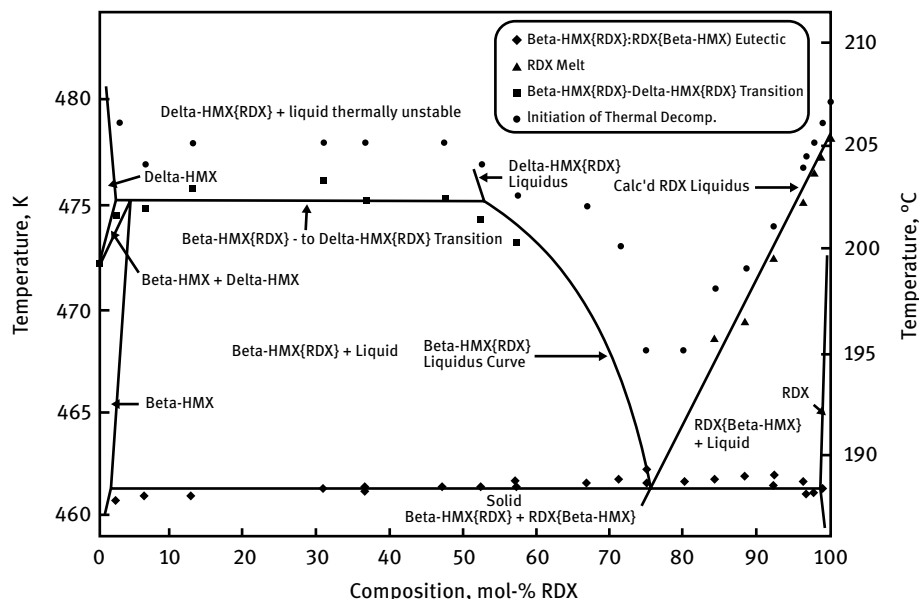
Data source: [133]

Additional information on properties of HMX is available in other well-known common information sources [239, 241, 243, 423].

### 15.2.1 Melting Point of HMX

The melting point of HMX is 540 K (267 °C), melting higher than its relative, RDX. HMX is frequently contaminated by RDX and vice versa. At other times, HMX is deliberately mixed with RDX to obtain desirable properties of such mixtures. In either case, knowledge of the phase diagram of the binary mixture is important information to have.

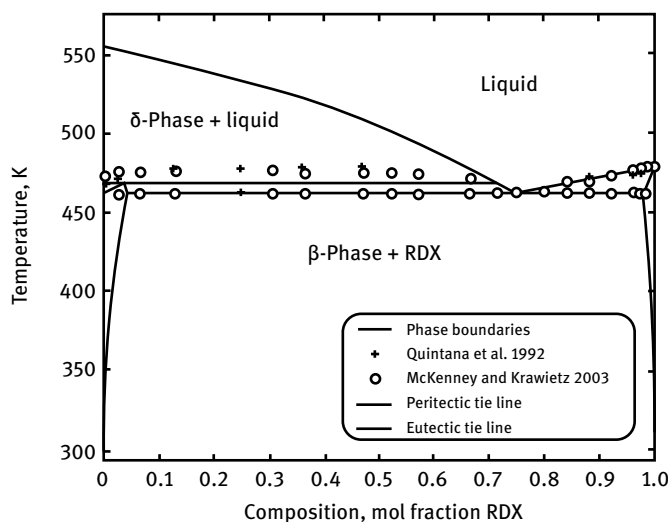
Two binary phase diagrams for the RDX/HMX system have been determined experimentally both with first melting mixtures and repeatedly remelting mixtures [294]. Liquidus curves have been predicted computationally for RDX and  $\beta$ -HMX. Mixtures exhibit the thermal characteristics associated with simple binary eutectic systems affected by observable HMX polymorphism. The HMX/RDX system is characterized by two binary eutectics, ideal behavior by the S-RDX component and thermal instability that is associated with liquid RDX and with excess solid  $\delta$ -HMX in the presence of liquid RDX (Figure 22). The melting temperatures associated with the two eutectics are governed by HMX polymorphism with the one melting at the lower temperature (461.6 K = 188.5 °C) involving  $\beta$ -HMX and S-RDX and the one melting at the higher tem-



**Figure 22:** HMX/RDX temperature/composition diagram from initial melting operations. (Republished and modified from [294], with permission from ©2003 Taylor & Francis Ltd., <http://www.tandfonline.com>.)

perature (464.5 K = 191.4 °C) involving  $\delta$ -HMX and S-RDX. The presence of both the  $\beta$ - and  $\delta$ -polymorphs of HMX were confirmed by XRD. The RDX melting temperatures were consistent with calculated liquidus temperatures.

Figure 23 presents a temperature-composition phase diagram of the HMX/RDX binary system at atmospheric pressure [424]. The solid curves represent the phase boundaries from a theoretical model. Figure 23 is an overall, coarse view, but the paper also contains three additional, detailed views where one has zoomed in on locations near the melting temperature of pure RDX, the eutectic point, and the peritectic point. Four single-phase regions are present:  $\beta$ -HMX-rich solid (labeled as  $\beta$ ),  $\delta$ -HMX-rich solid ( $\delta$ ), RDX-rich solid (RDX), and liquid. These four phases combine to form five distinct two-phase regions, each of which is represented by addition of the two constituent phases (e.g., the two-phase region between  $\beta$ -HMX-rich solid and RDX-rich solid is denoted as ( $\beta$  + RDX)). Three-phase equilibria are represented by points which denote the composition of the three phases that are in equilibrium. As a visual aid, the points were connected together with imaginary tie lines. The eutectic tie line connects the eutectic point, which represents the liquid, with points for the  $\beta$ -HMX-rich and RDX-rich solid phases. The peritectic tie line connects the peritectic point, which represents the  $\beta$ -HMX-rich solid, with points for the  $\delta$ -HMX-rich solid phase and



**Figure 23:** Temperature-composition phase diagram of the HMX/RDX binary system at atmospheric pressure. (Reprinted and adapted from [424], with permission from ©2017 American Chemical Society; permission conveyed through RightsLink.)

the liquid phase. Similar phase diagrams for the HMX/RDX system were presented for higher pressures, 500, 1000, 1500, and 2500 bar. The transition temperature increased with pressure more than the melting temperatures do. Consequently, the area of the  $\beta$  + liquid region increased with pressure, but the area of the  $\delta$  + liquid region decreased with pressure. Above 1653 bar, the melting point of  $\beta$ -HMX is lower than the transition temperature so that  $\delta$ -HMX no longer appears in the pure HMX phase diagram. The HMX/RDX system at these higher pressures becomes a simple, binary eutectic system where  $\beta$ -HMX is the only polymorph present. The peritectic temperature that signifies the transition of  $\beta$ -HMX-rich solid to  $\delta$ -HMX-rich solid (and liquid) is absent above 1653 bar.

### 15.2.2 Phase Transitions of HMX

HMX undergoes a series of phase transitions. A distinct feature of HMX is the strongly metastable nature of its polymorphs. Many of its properties change during those transitions. When listing properties of HMX, it is important to specify which of the modifications the properties were obtained for. In most cases the properties will be for  $\beta$ -HMX, unless otherwise specified. The transitions do not happen very quickly; thus, it is possible to obtain properties for  $\beta$ -HMX outside its normal stability range. The HMX phase of primary interest to the military is  $\beta$ -HMX because it has the highest density. There is much ambiguity in the literature regarding the thermodynamic stability of

$\alpha$ -HMX (if it exists at all). The  $\gamma$ -phase is not a true polymorph but rather is a hydrate with a stoichiometric ratio of four HMX molecules per water molecule.

A transition from the  $\beta$ -form of HMX to the  $\delta$ -form was observed at 431 K on heating at atmospheric pressure. This  $\beta \rightarrow \delta$  transition is typically associated with and precedes the thermal decomposition of HMX. The stability to pressure of each polymorph of HMX has been studied using Raman and infrared spectroscopy [425]. The observed behavior of the polymorphic forms is as follows:  $\beta$ -HMX is stable up to 5.4 GPa, and the  $\alpha$ -form is stable up to 4.2 GPa.  $\gamma$ -HMX converts to  $\beta$ -HMX at 0.55 GPa.  $\delta$ -HMX converts to a mixture of  $\alpha$ - and  $\beta$ -forms at pressures below 0.05 GPa. Further studies have shown that the  $\beta$ -form is stable up to 10.0 GPa [426]. Before melting HMX undergoes  $\beta \rightarrow \delta$  modification transition with the heat of transition of 9.83 kJ/mol (2.35 kcal/mol) [245]. See also [427, 428]. The heats of transformation of the four known polymorphic forms of octogen (HMX) were measured calorimetrically as listed in Table 28.

**Table 28:** Heats of transformation of polymorphic forms of HMX.

| Phase transition            | Temperature |         | Heat of transformation |                 |
|-----------------------------|-------------|---------|------------------------|-----------------|
|                             | K           | °C      | kJ/mol                 | kcal/mol        |
| $\alpha \rightarrow \delta$ | 466–474     | 193–201 | $7.41 \pm 0.21$        | $1.77 \pm 0.05$ |
| $\beta \rightarrow \delta$  | 440–456     | 167–183 | $9.79 \pm 0.13$        | $2.34 \pm 0.03$ |
| $\gamma \rightarrow \delta$ | 440–455     | 167–182 | $2.80 \pm 0.08$        | $0.67 \pm 0.02$ |

Data source: [87]

Literature values for the  $\beta \rightarrow \delta$  solid–state transition temperatures of HMX vary over a wide range, for instance, 440–456 K (167–183 °C), 456.9 and 441.9 K (183.8 and 168.8 °C), 422–424 K (149–151 °C), and 459.9 K (186.8 °C), and the literature heat of transition is 9.83 kJ/mol (2.350 kcal/mol).

When examining the thermal behavior of HMX/RDX mixtures by DTA and TGA, it was found that the temperature of polymorphic transformation of HMX showed an increase due to the presence of RDX [429]. The enthalpies of the endothermic transformations depended on the composition of the mixture, and there was a linear relationship up to 30 mass-% RDX. The existence of an eutectic with a composition of 30 mass-% HMX/70 mass-% RDX was postulated to explain the melting processes.

The four phases of HMX and its transitions were investigated using XRD [430, 431]. The phases were heated stepwise in a temperature range from 170 to 510 K, measuring a diffraction pattern after each step. The thermal expansion of the different phases and the volume changes during the phase transitions were obtained. Anomalies and strongly anisotropic expansions were observed with  $\beta$ - and  $\gamma$ -HMX. The highest thermal expansion was found with  $\gamma$ -HMX, followed by  $\delta$ ,  $\beta$ , and  $\alpha$ -HMX. The highest volume change was observed with the  $\beta \rightarrow \delta$  transition, followed by the  $\alpha \rightarrow \delta$  and the  $\gamma \rightarrow \delta$  transition.



The  $\beta \rightarrow \delta$  solid-state phase transition in HMX is thermodynamically first order with a measured latent heat, occurred via nucleation and growth, and exhibited a thermally activated rate of transformation. A two-state kinetic model of the system was constructed consisting of equilibrium terms first order in the  $\beta$  or  $\delta$  mol fraction simulating nucleation, and second order in  $\beta$  and  $\delta$  simulating growth [432, 433]. The model had four rate constants, the temperature dependence of which was described by eight parameters. The model was applied to both the  $\beta \rightarrow \delta$  and  $\delta \rightarrow \beta$  transformations over a temperature range from 300 to 700 K in order to assess the theoretical validity of the model and it reproduced the half-time of the transition over this entire range, spanning conversion times from  $10^6$  to  $10^{-4}$  s.

Complementing a parallel paper on thermodynamics, the transformation kinetics of the  $\beta \rightarrow \delta$  solid-state phase transition in HMX were measured with second harmonic generation of a monochromatic laser beam which provided a very high sensitivity, zero background probe of the  $\delta$  phase concentration [434]. This signal was used as a quantitative measure of the  $\delta$  phase mol fraction in HMX crystals. The spatial characteristics of the transformation were shown to be consistent with nucleation from a low density of initial sites, followed by rapid growth. In a series of isothermal experiments, the kinetic rates of both  $\beta \rightarrow \delta$  conversion and  $\delta \rightarrow \beta$  reversion were examined.

Differential scanning calorimetry (DSC) was used to measure the kinetics of the  $\beta \rightarrow \delta$  solid–solid phase transition of HMX [435]. Integration of the DSC signal gave a direct measurement of the degree of conversion. Data was analyzed by first-order kinetics, the Ozawa method and isoconversional analysis. The range of activation energies found in this work, centering around 500 kJ/mol, was much higher than previously reported values by Brill et al. [393] (204 kJ/mol), and Henson et al. [432] (200 kJ/mol).

The structural, vibrational, and thermodynamic properties of  $\beta$ -HMX crystals were studied using isothermal-isobaric molecular dynamics (NPT-MD) simulations [436]. When examining the variations of cell volume, lattice constants, and molecular geometry of solid  $\beta$ -HMX at different pressure and temperature, it was found that the N–N bond was significantly lengthened with increasing temperature, which suggested that it is relevant to the initial decomposition. An abrupt change was observed at 27 GPa for the volume and internal geometrical parameters. This was in good accordance with the experimental observation that there is a phase transition at 27 GPa, which was clearly due to a conformational change, and not a chemical reaction. The vibrational frequencies at ambient conditions agreed well with experimental results. Frequency discontinuities were observed at the same pressure where the phase transition occurred.

The transformation of a  $\gamma$  polymorph of HMX to a  $\beta$  polymorph is not easy to achieve. In order to obtain  $\beta$ -HMX from  $\gamma$ -HMX, a novel and economical method was developed using hot water [437]. The  $\beta$ -HMX thus obtained was characterized using TGA and DTA, HPLC, FTIR spectroscopy, Raman spectroscopy, and impact sensitivity.

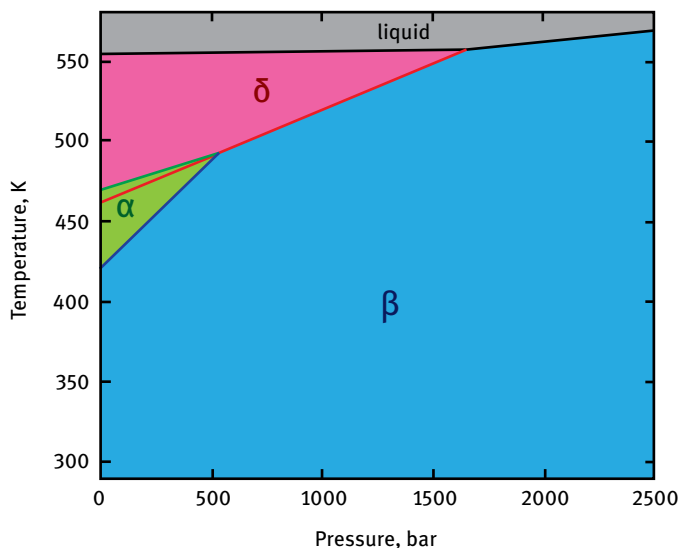
A physical model was developed to describe the phonon density of states for HMX and it was used to calculate a set of thermodynamic properties, such as the thermal expansion coefficient, bulk modulus, specific heat, and the Hugoniot curve [438]. The results were in good agreement with available experiments at low pressure and provided reasonable prediction capability at high pressures where data were not available due to the lack of experiments. Two types of phase transitions were compared: static phase transition and shock-induced phase transition. It was determined that the phase transition curves of the two mechanisms are quite different. The pressure required to induce a phase transition for HMX by shock loading is larger than that under static conditions.

Thermodynamic models were developed for the five most commonly studied phases of HMX: liquid HMX and four solid polymorphs ( $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -HMX) [424]. Graphs derived from these models showed results for the density, heat capacity, bulk modulus and sound speed, as well as a phase diagram that illustrates the temperature and pressure regions over which the various HMX phases are most thermodynamically stable. The models were based on the same equation of state previously used for RDX. This paper has a list of 23 different literature sources for the transformation temperature  $\beta \rightarrow \delta$  of HMX. The temperatures ranged from 430 to 460 K. Both HMX and RDX models were combined together so that the equation of state can also be applied to liquid and solid mixtures of HMX/RDX. This allowed one to generate an HMX/RDX phase diagram and calculate the enthalpy change associated with a few different kinds of phase transitions that these mixtures may undergo. A single equation of state was derived that was capable of modeling both pure HMX and HMX/RDX mixtures. By examining possible arrangements for the relative order of the six different solid–solid transition ( $\alpha - \beta$ ,  $\alpha - \gamma$ ,  $\alpha - \delta$ ,  $\beta - \gamma$ ,  $\beta - \delta$ , and  $\gamma - \delta$ ) temperatures, it was concluded that  $\alpha$ -HMX must be thermodynamically stable so that the HMX phase diagram should have an  $\alpha$  phase region, see Figure 24, which illustrates the phase diagram for HMX at very high pressures..

Equilibrium phase diagram of HMX in Figure 24 was generated by finding the phase with the lowest Gibbs free energy (chemical potential) for a given temperature and pressure. The dashed line shows the extrapolation of the  $\beta - \delta$  curve into the  $\alpha$  phase region. Because of strong nucleation and growth barriers exhibited by the HMX polymorphs, the phase diagram that is observed in practice may look more like one where the  $\beta$  phase region has been extended up to the curve so that the only observable solid–solid transition is  $\beta - \delta$ . See also [267, 439, 440].

### 15.2.3 Vapor Pressure of HMX

HMX exists in four polymorphic forms. Only two of the three published papers on vapor pressure of HMX clearly state the polymorphic form of the HMX used. The vapor pressure measurements by Rosen and Dickinson [248] stated that they have used  $\beta$ -HMX but  $\beta$ -HMX is only stable up to 115°C and most of their measurements were done



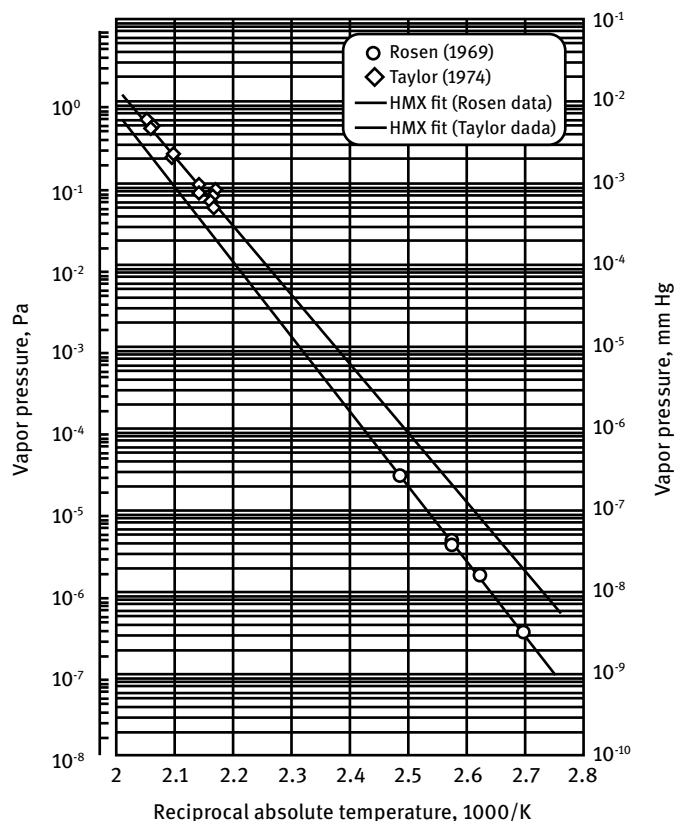
**Figure 24:** Equilibrium phase diagram of HMX at high pressures. (Reprinted and adapted from [424], with permission from ©2017 American Chemical Society; permission conveyed through RightsLink.)

above this temperature. This introduces some uncertainty in their data. Taylor [441] made measurements on  $\delta$ -HMX and at a much higher temperature. The critical review by Oestmark et al. looked at data from five papers that had been published on the vapor pressure of HMX and other explosives, trying to resolve discrepancies and trying to establish a baseline for further comparison [254]. The data from these papers are compared in Figure 25 together with fits to the Clausius–Clapeyron equation. The Clausius–Clapeyron fit of the data for HMX led to the equation

$$\log P = A - \frac{B}{T} = 16.1 - \frac{9125}{T}$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin for the temperature range 370–403 K (97–130 °C). The vapor pressure of HMX at 298 K was extrapolated to be  $3.01 \times 10^{-15}$  mm Hg. The heat of sublimation is 174.7 kJ/mol (41.75 kcal/mol).

The Clausius–Clapeyron equations should intersect at the phase transition temperature, but this is not the case. This further indicates that not all data used for this curve fit were reliable. However, the data presented by Rosen and Dickinson is considered the most accurate for calculating HMX vapor pressures at room temperature (Figure 26) [247, 248]. The vapor pressure of  $\beta$ -HMX at 395 K (121.9 °C) is  $10^{-7}$  mm Hg. The slope of the vapor pressure curve in Figure 26 corresponds to a heat of sublimation of 175.3 kJ/mol (41.9 kcal/mol).



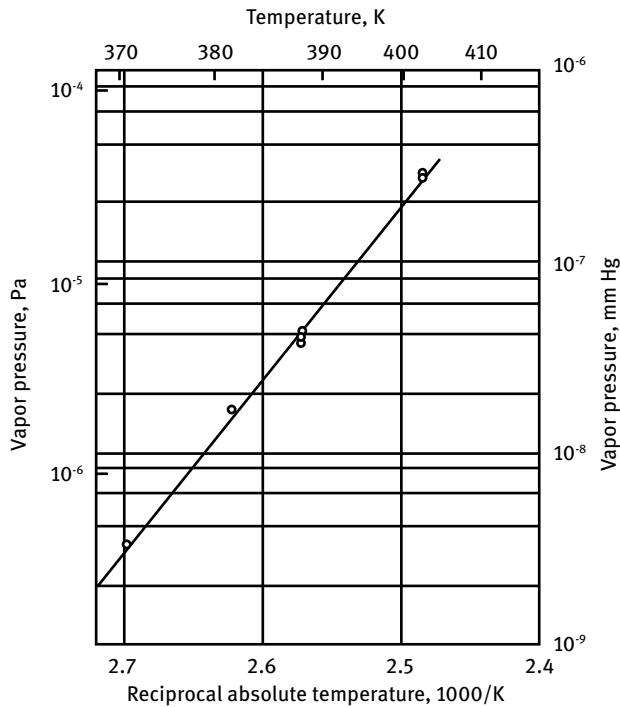
**Figure 25:** Vapor pressure of HMX. (Republished and modified from [254], with permission from ©2012 John Wiley & Sons – Journals; permission conveyed through Copyright Clearance Center, Inc.)

The vapor pressure of HMX in the temperature range 461 to 486 K (188 to 213 °C) has been measured by the Knudsen effusion method, and the enthalpy of sublimation over this range was calculated to be 161.9 kJ/mol (38.7 kcal/mol) [441]. Other measurements led to the heat of sublimation of 161.1–161.9 kJ/mol (38.5–38.7 kcal/mol) [256].

Based on the heat of HMX melting, the heat of phase change, and the heat of sublimation, a value 117.1 kJ/mol (28 kcal/mol) was adopted as the heat of HMX evaporation [252]. Starting from this figure and numerous converging data on the surface temperature at atmospheric pressure, a pressure dependence of liquid HMX surface temperature in the range 600–835 K was constructed based on the equation

$$\ln P = 21.717 - 14091.6/T$$

where  $P$  is the pressure in atm and  $T$  is the temperature in kelvin, as shown in Figure 27 [442].



**Figure 26:** Vapor pressure of  $\beta$ -HMX. (Reproduced and modified from [247].)

As part of developing a Peng–Robinson equation of state for HMX, the vapor pressure data from several sources were plotted to derive the coefficients  $a$  and  $b$  for this equation of state [424].

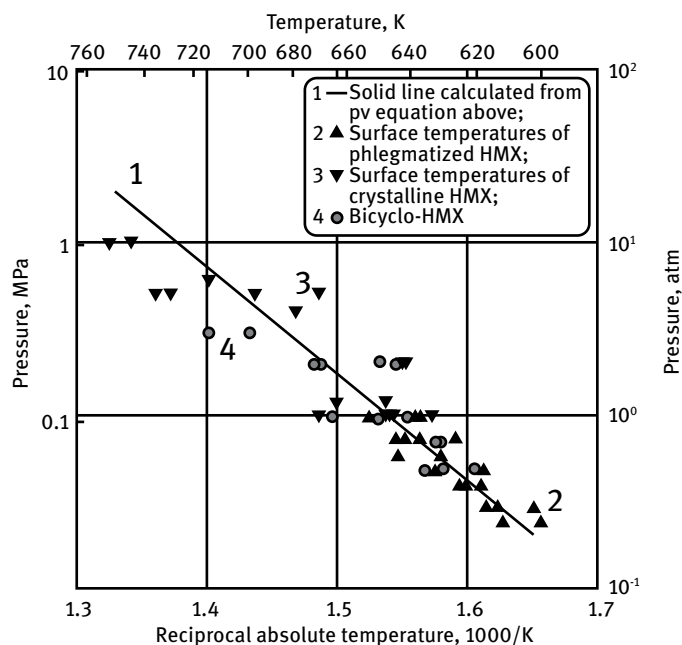
### 15.2.4 Density of HMX

HMX occurs in four crystal structure modifications at atmospheric pressure which all differ in their density. The densities of the four polymorphs are summarized in Table 29.

**Table 29:** Densities of HMX polymorphs

| Modification           | Density, g/cm <sup>3</sup> |
|------------------------|----------------------------|
| $\alpha$ -modification | 1.87                       |
| $\beta$ -modification  | 1.96                       |
| $\gamma$ -modification | 1.82                       |
| $\delta$ -modification | 1.78                       |

Data source: [133]



**Figure 27:** Vapor pressure above liquid HMX as a function of reciprocal temperature. (Republished and modified from [252], with permission of ©2009 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

Dimensional changes related to temperature cycling of the  $\beta$ - and  $\delta$ -polymorphs of HMX are important for a variety of applications. Debonding of crystals from the binder in a propellant, forming voids, might change the burning rate of a propellant. The coefficients of thermal expansion of  $\beta$ - and  $\delta$ -phases were measured over a temperature range of 253 to 488 K (–20 to +215 °C) by thermomechanical analysis (TMA) [443]. Dimensional changes associated with the phase transition were also measured, and the time–temperature dependence of the dimensional change was consistent with phase transition kinetics measured earlier by DSC. One HMX sample measured by TMA during its initial heating and again three days later during a second heating showed the  $\beta$ -to- $\delta$  phase transition a second time, thereby indicating back conversion from  $\delta$ - to  $\beta$ -phase HMX during those three days of storage. DSC was used to measure kinetics of the  $\delta$ - to  $\beta$  back conversion. The most successful approach was to first heat the material to create the  $\delta$  phase, then after a given period at room temperature, measure the heat absorbed during a second pass through the  $\beta$ - to  $\delta$ -phase transition. Back conversion at room temperature followed nucleation–growth kinetics, similar to the forward conversion. The linear coefficient of thermal expansion of HMX in the range 219–347 K is  $5.04 \times 10^{-5} \text{ K}^{-1}$ . The cubical coefficient of thermal expansion of HMX in the range 243–343 K is  $1.625 \times 10^{-4} \text{ K}^{-1}$ .

Isothermal pressure–volume equations of state of  $\beta$ -HMX at temperatures of 303, 373, and 413 K (30, 100, and 140 °C) under both hydrostatic and nonhydrostatic compressions were obtained using synchrotron angle-dispersive XRD [444]. The samples were heated to the isotherm temperature and compressed to up to 5.8 GPa. At all temperatures, HMX remained in the  $\beta$ -phase up to 5.8 GPa. However, at 413 K (140 °C) upon decompression from nonhydrostatic pressures above 4 GPa to ambient pressure, HMX underwent a phase transition to the  $\delta$ -phase. The same transition was seen upon decompression from hydrostatic compression to ambient pressure; however, parts of the sample remained in the  $\beta$ -phase, resulting in a mixed-phase sample. The XRD data were analyzed to yield unit-cell dimensions at each pressure, and further analyzed to yield coefficient of thermal expansion, bulk modulus, and the pressure derivative of the bulk modulus.

The phase behavior of HMX at ambient pressure was investigated by XRD [445]. The XRD patterns at elevated temperature showed that there was a co-existing temperature range of  $\beta$ - and  $\delta$ -phase during the phase transition process. In addition, mechanical forces can catalyze the conversion from  $\delta$ - back to  $\beta$ -phase. Based on the XRD diffraction patterns of  $\beta$ - and  $\delta$ -phase at different temperatures, the coefficients of thermal expansion was calculated by Rietveld refinement. For  $\beta$ -HMX, the linear coefficients of thermal expansion of a-axis and b-axis were about  $1.37 \times 10^{-5}$  and  $1.25 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ . A slight decrease in c-axis with temperature was also observed, and the value is about  $-0.63 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ . The volume coefficient of thermal expansion was about  $1.60 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ , with a 2.2% change from 303 to 443 K (30 to 170 °C). For  $\delta$ -HMX, the linear coefficients of thermal expansion of a-axis and c-axis are found to be  $5.39 \times 10^{-5}$  and  $2.38 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ , respectively. The volume coefficient of thermal expansion of  $\delta$ -HMX was about  $1.33 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ , with a 2.6% change from 303 to 503 K (30 to 230 °C). The results indicated that  $\beta$ -HMX has a similar volume coefficient of thermal expansion compared with  $\delta$ -HMX, and there is about 10.5% expansion from  $\beta$ -HMX at 303 K (30 °C) to  $\delta$ -HMX at 503 K (230 °C), of which about 7% may be attributed to the reconstructive transition.

The thermal expansion of the  $\beta$ -phase of HMX was studied in the temperature range of 123 to 303 K (−150 to +30 °C) [446].  $\beta$ -HMX is monoclinic with the unit cell parameters of  $a = 6.5255(10) \text{ \AA}$ ,  $b = 11.0369(18) \text{ \AA}$ ,  $c = 7.3640(12) \text{ \AA}$ , and  $\beta = 102.67(1)^\circ$ , space group  $P2_1/n$ . On cooling from room temperature to 123 K (−150 °C) the crystals underwent an anisotropic contraction with the a-axis virtually unchanged, while the b and c axes contract by approximately 1.8 and 0.6%, respectively. The disproportionate change in the a and c axes resulted in approximately a 0.4% change in the  $\beta$  angle. Despite the large differences in expansion along the different axes, no phase change was observed. HMX is more compressible in hydrostatic conditions ( $B_0 = 12.4 \text{ GPa}$  and  $B' = 10.4$ ) than in nonhydrostatic conditions ( $B_0 = 14.4 \text{ GPa}$ ,  $B' = 13.3$ ) [447].

### 15.2.5 Solubility of HMX

HMX is practically insoluble in water. Its solubility in other solvents such as supercritical carbon dioxide is similar to that of RDX, which is very low [272]. It is important to know solubility of HMX if it has to be removed from munitions during demilitarization with a suitable solvent. Solubilities of HMX in different solvents are listed in Table 30.

**Table 30:** Solubility of HMX in organic solvents

| Solvent                                 | Temperature, K |     |                  |                  |     |
|-----------------------------------------|----------------|-----|------------------|------------------|-----|
|                                         | 298            | 303 | 333              | 353              | 371 |
| <b>Solubility, g/100 g of solvent</b>   |                |     |                  |                  |     |
| Dimethylsulfoxide                       | 57             | —   | 68               | —                | 89  |
| Acetone                                 | 2.8            | —   | 4.2 <sup>a</sup> | —                | —   |
| Acetonitrile                            | 2.0            | —   | —                | 7.3 <sup>a</sup> | —   |
| $\gamma$ -Butyrolactone                 | 12             | —   | 20               | —                | 35  |
| <b>Solubility, g/100 mL of solution</b> |                |     |                  |                  |     |
| Dimethylsulfoxide                       | 23.6           | —   | —                | —                | —   |
| $\gamma$ -Butyrolactone                 | —              | 21  | —                | —                | —   |
| Cyclohexanone                           | —              | 5.2 | —                | —                | —   |
| Acetone                                 | —              | 2.2 | —                | —                | —   |
| Acetonitrile                            | —              | 2.0 | —                | —                | —   |
| Nitromethane                            | —              | 1.1 | —                | —                | —   |

<sup>a</sup> At the boiling point of the solvent

Data source: [273]

In a systematic study of the solubilities of representative explosives in various single and binary solvents, dimethylformamide (DMF) was judged to be a good overall solvent for explosives when factors such as the solubility values, physical properties, cost, availability, convenience, and toxicity of the solvent are considered. However, DMF forms a crystalline solvate with HMX and is not useful as a solvent for HMX [273, 448]. A butyrolactone–dimethylsulfoxide mixture was recommended as a solvent for HMX.

### 15.2.6 Thermal Conductivity of HMX

Thermal diffusivities and thermal conductivities of RDX and HMX were measured from room temperature into the decomposition region by use of a laser flash method [280, 281]. Thermal conductivities were calculated from the thermal diffusivity, specific heat, and density of each material.

The heat capacity, thermal conductivity, and thermal diffusivity of a range of other oxidizers, binders, and rocket propellants were determined and compared to literature



data. The thermal diffusivity  $\alpha$  of HMX for the range from 293 to 443 K (20 to 170 °C) can be described by the linear equation

$$\alpha = 2.62 \times 10^{-3} - 6.74 \times 10^{-6}t$$

where  $\alpha$  is the thermal diffusivity in  $\text{cm}^2/\text{s}$  and  $t$  is the temperature in °C. Likewise, the thermal conductivity  $\lambda$  of HMX for the range from 293 to 443 K (20 to 170 °C) can be described by the linear equation

$$\lambda = 1.19 \times 10^{-3} - 11.5 \times 10^{-7}t$$

where  $\lambda$  is the thermal conductivity in  $\text{cal cm}^{-1} \text{s}^{-1} \text{°C}^{-1}$  and  $t$  is the temperature in °C. Similar data are contained in the same publication for a wide range of oxidizers, binders, and solid propellants. See also [449].

## 15.2.7 Thermodynamic Properties of HMX

### 15.2.7.1 Heat Capacity of HMX

The heat capacity of HMX changes with each change of the crystal structure at one of the phase change transition points. The specific heats of HMX and RDX were measured from room temperature into the decomposition region by use of a laser flash method [280, 281]. At this rapid heating rate, no phase changes are taking place because they are slower. The specific heats of RDX and HMX are graphed for comparison in Figure 10 which was already shown in *Encyclopedia of Oxidizers* chapter “Perchlorate Oxidizers” and earlier in this volume in the section on “RDX.”

Heat capacity of HMX with a density of  $1.900 \text{ g/cm}^3$  in the range 310–440 K (37–167 °C) was

$$c_p = 0.231 + 0.00055t$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{°C}^{-1}$  and  $t$  is the temperature in °C [283]. The mid-range standard deviation was  $0.004 \text{ cal g}^{-1} \text{°C}^{-1}$ .

The molar heat capacity of  $\beta$ -HMX in the range from 200–452 K (–73 to +179 °C) can be described by the following linear equation

$$C_p = (28 \pm 3) + (0.15 \pm 0.009) \times T$$

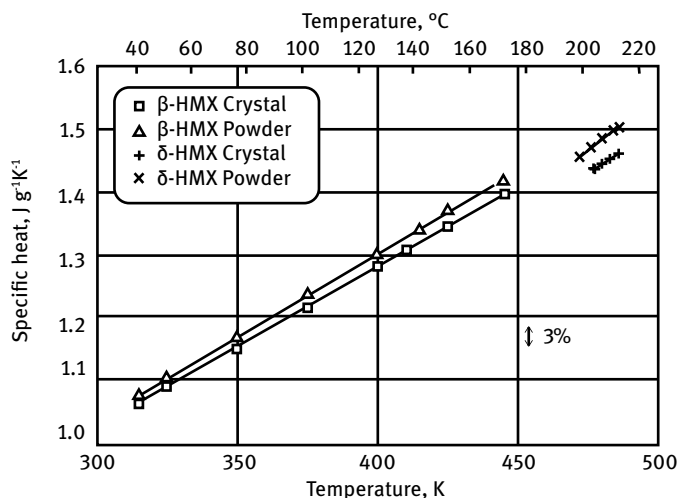
where  $C_p$  is the molar heat capacity in  $\text{cal mol}^{-1} \text{°C}^{-1}$  and  $T$  is the temperature in kelvin. The molar heat capacity of  $\beta$ -HMX at 298 K is  $307.9 \text{ J mol}^{-1} \text{K}^{-1}$  ( $73.6 \text{ cal mol}^{-1} \text{°C}^{-1}$ ). Similar data are available for  $\alpha$ -HMX,  $\gamma$ -HMX, and  $\delta$ -HMX.

The heat capacity of HMX for rapid heating in the range from 293–443 K (20–170 °C) can be described by the following linear equation [282]:

$$c_p = 0.230 + 6.60 \times 10^{-4}t$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{°C}^{-1}$  and  $t$  is the temperature in °C.

The specific heat of  $\beta$ -HMX and  $\delta$ -HMX in the temperature range 588 to 718 K (315–445 °C) was determined by DSC [450, 451]. The heat capacities for the two phases of HMX were nearly identical to within 1% (Figure 28). Heat capacities of single crystals were smaller than those of powdered samples. The start of the transformation occurred at 453 and 460 K for the single crystal and for the powdered sample, respectively. Unlike the specific heats, the transformation temperatures were dependent on the heating rate.



**Figure 28:** Specific heat of single crystal and powdered  $\beta$ -HMX and  $\delta$ -HMX. (Reproduced and modified from [450].)

#### 15.2.7.2 Enthalpy of Formation and Heat of Combustion of HMX

The calculated standard enthalpy of formation for HMX as ideal gas in the gas phase is  $275 \pm 30$  kJ/mol and the calculated entropy is  $608.7 \pm 15$  J mol<sup>-1</sup> K<sup>-1</sup> [285]. Based on sublimation measurements, an enthalpy of formation for gaseous HMX was predicted as 248.9 kJ/mol [452]. Table 31 provides a summary of published thermodynamic data for HMX. The enthalpy of formation is different for each of the four modifications of HMX. The transition enthalpies are listed in Table 33.

In addition to experimental calorimetric methods, the gas phase enthalpies of formation and thermodynamic functions of HMX and similar compounds can be calculated using quantum mechanical computational methods [305].

Isochoric upper heats of combustion of HMX are listed in Table 32.

#### 15.2.7.3 Heat of Fusion and Solid-State Phase Transitions of HMX

Because of rapid decomposition at the melting point, direct measurements of heat of melting are difficult to conduct. Using indirect measurements, a value 69.9 kJ/mol

**Table 31:** Standard enthalpy of formation of HMX.

| Phase     | SI units    |              | Other units |       | References |
|-----------|-------------|--------------|-------------|-------|------------|
|           | kJ/mol      | kJ/kg        | kcal/mol    | cal/g |            |
| Solid     | +75         | +253.3       | +17.9       | +60.5 | [133]      |
| Solid     | +75         | +253         | +17.93      | +60.5 | [241]      |
| Solid     | +75.6       | +255         | +18.06      | +61   | [235]      |
| Solid     | +75.02      | +253         | +17.93      | +60.5 | [239]      |
| β-HMX     | +87.9 ± 2.8 | +296.8 ± 9.4 | +21 ± 0.66  | +70.9 | [87]       |
| Ideal gas | 275 ± 30    | —            | —           | —     | [285]      |
| Gas       | 248.9       | —            | —           | —     | [293]      |

Molecular mass: 296.1551 g/mol = 3.3766 mol/kg

**Table 32:** Isochoric upper heat of combustion of HMX.

| Phase | SI units   |          | Other units |            | References |
|-------|------------|----------|-------------|------------|------------|
|       | kJ/mol     | kJ/kg    | kcal/mol    | cal/g      |            |
| Solid | 2792       | 9429     | 667.4       | 2253       | [423]      |
| β-HMX | 2820 ± 2.8 | 9523 ± 9 | 674 ± 0.66  | 2276 ± 2.2 | [87]       |

Molecular mass: 296.1551 g/mol = 3.3766 mol/kg

(16.7 kcal/mol) was obtained from the HMX-RDX melting-point diagram [296], while a considerably lower value was measured as the heat of dissolution of HMX in an inert solvent. The heats of dissolution in acetone, butyl acetate, or aniline were very similar and equal to ~26.4 kJ/mol (6.3 kcal/mol).

#### 15.2.7.4 Heat of Sublimation of HMX

The heat of sublimation of HMX is  $\Delta H_{\text{sub}}$  161.9 kJ/mol at 461–487 K [441]. Other sources gave an enthalpy of vaporization of 158.6 kJ/mol at 507 K (234 °C) [453]. See also [296].

#### 15.2.8 Molecular Properties of HMX

HMX occurs in four modifications, of which only the β-modification possesses a particularly high density and hence also a very fast velocity of detonation. The transition temperatures and stability ranges are summarized in Table 33 along with the transition enthalpies.

The crystal structure of α-HMX has been determined by single crystal XRD [454]. α-HMX crystallized in orthorhombic crystals, space group *Fdd2* (= *C*<sub>2v</sub>) with unit cell parameters of *a* = 15.14 Å, *b* = 23.89 Å, *c* = 6.013 Å and eight molecules in the unit cell. The molecules have a bucket-like shape with twofold symmetry. Bond lengths and angle all have normal values, but there are two rather short intermolecular C—O distances of 3.04 and 3.20 Å.

**Table 33:** Transition temperatures and transition enthalpies of HMX.

| Transition                  | Transition temperature |         |         | Transition enthalpy |       |       |
|-----------------------------|------------------------|---------|---------|---------------------|-------|-------|
|                             | K                      | °C      | °F      | kJ/mol              | kJ/kg | cal/g |
| $\alpha \rightarrow \delta$ | 466–474                | 193–201 | 379–394 | 7.40                | 25.0  | 5.98  |
| $\beta \rightarrow \delta$  | 440–456                | 167–183 | 333–361 | 9.8                 | 33.1  | 7.90  |
| $\gamma \rightarrow \delta$ | 440–455                | 167–182 | 333–359 | 2.80                | 9.46  | 2.26  |
| $\alpha \rightarrow \beta$  | 389                    | 116     | 241     | 2.38                | 8.04  | 1.92  |
| $\beta \rightarrow \gamma$  | 427                    | 154     | 309     | 7.0                 | 23.6  | 5.64  |
| $\alpha \rightarrow \gamma$ | —                      | —       | —       | 4.6                 | 15.5  | 3.71  |

Based on neutron diffraction measurements of the positions of hydrogen atoms, all hydrogen atoms in  $\beta$ -HMX are located close to nearby oxygen atoms, a few of which form intramolecular or intermolecular hydrogen bonds of the type C—H $\cdots$ O [455]. Several short intramolecular and intermolecular distances between oxygen and other atoms could be measured by this method. The heavy-atom locations obtained agreed with those from XRD determinations except for slight position shifts of a few atoms.

The crystal structure of  $\delta$ -HMX has been determined by direct XRD methods from counter intensities [456]. The crystals were hexagonal, space group  $P6_1(P6_5)$  with unit cell parameters of  $a = 7.711(2)$  Å,  $c = 32.553(6)$  Å, and  $Z = 6$ . The four C atoms of the eight-membered ring are planar and the molecule has approximate twofold symmetry about an axis perpendicular to this plane through the center of the ring. The shape of the  $\delta$ -HMX molecule is similar to that of the  $\alpha$ -polymorph which has crystallographic twofold symmetry.

The crystal structure of  $\gamma$ -HMX is monoclinic, space group  $Pn$ , with unit cell parameters of  $a = 13.27$  Å,  $b = 7.90(1)$  Å,  $c = 10.95(1)$  Å,  $\beta = 106.8^\circ$ ,  $Z = 2$ ,  $\rho_{\text{XRD}} = 1.82$  g/cm<sup>3</sup>,  $\rho_{\text{m}} = 1.78$  g/cm<sup>3</sup> at 293 K [457].  $\gamma$ -HMX is a hydrate. The two independent molecules in the unit of structure are similar to those in the  $\alpha$ - and  $\beta$ -polymorphs of HMX. Bond distances and angles and intermolecular contacts are similar to those in the  $\alpha$ - and  $\delta$ -polymorphs of HMX. HMX crystal structure data from older sources are summarized in Table 34.

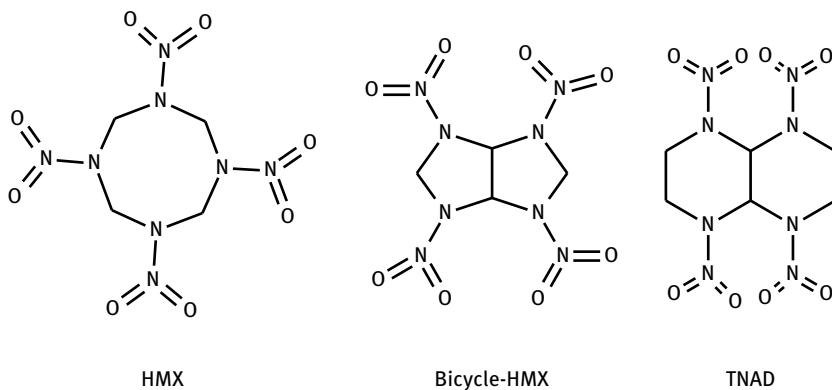
There has been a lot of work done on the molecular structure of heterocyclic nitramines, both experimentally as well as theoretically, to explain the thermal stability and energetic decomposition of materials like RDX, HMX, and CL-20, also in the search for even more stable or even more powerful nitramines than RDX, HMX, or CL-20. For instance, density functional theory calculations were performed to find relationships between the structures and performance of a series of highly energetic cyclic nitramines [458]. An isodesmic reaction method was employed to estimate the enthalpy of formation. The predicted detonation properties were calculated by using the Kamlet–Jacobs equation based on the theoretical densities and heat of formation. Results indicated the N—NO<sub>2</sub> group and aza N atom are effective substituents for enhancing the detonation performance. From the group of

**Table 34:** Crystal structure parameters of HMX polymorphs.

| Polymorph     | Crystal structure | Unit cell dimensions, nm                  | Space group          | Refractive index $n_D$                                                        |
|---------------|-------------------|-------------------------------------------|----------------------|-------------------------------------------------------------------------------|
| $\alpha$ -HMX | Orthorhombic      | $a = 1.514$<br>$b = 2.389$<br>$c = 0.591$ | $Fdd2$               | $\alpha = 1.561 - 1.565$<br>$\beta = 1.562 - 1.566$<br>$\gamma = 1.72 - 1.74$ |
| $\beta$ -HMX  | Monoclinic        | $a = 0.654$<br>$b = 1.105$<br>$c = 0.870$ | $P2_1/c$             | $\alpha = 1.589$<br>$\beta = 1.594$<br>$\gamma = 1.73$                        |
| $\gamma$ -HMX | Monoclinic        | $a = 1.095$<br>$b = 0.793$<br>$c = 1.461$ | $Pc_1P2/c$<br>$P2/n$ | $\alpha = 1.537$<br>$\beta = 1.585$<br>$\gamma = 1.666$                       |
| $\delta$ -HMX | Hexagonal         | $a = 0.766$<br>$c = 3.249$                | $P6_122$<br>$P6_522$ |                                                                               |

Data source: [241]

cyclic nitramines compounds examined, all except two exhibited better predicted detonation performance than HMX. The decomposition mechanism and thermal stability of these cyclic nitramines were analyzed via the bond dissociation energies. For most of these nitramines, the homolysis of  $N-NO_2$  is the initial step in the thermolysis, and species with bridged  $N-N$  bonds are more sensitive than others. Based on predicted detonation performance and thermal stability, twelve compounds were identified as promising candidates for high energy density materials (HEDMs).



Molecular dynamics calculations have been carried out to study and simulate initial decomposition processes in nitramines, in particular HMX polymorphs and related nitramines, in the crystalline state [459]. Three types of simulations with different conditions were performed to investigate the effect of the crystalline state on the decomposition processes of the molecule. When the simulation was performed with the gas phase value of the equilibrium  $N-N$  bond length but started from the crystallographic

structure as an initial conformation, large amplitude oscillations of the N—N bond lengths were observed in the trajectories. Another simulation, which took the crystal effects into account by adjusting the equilibrium N—N bond length, also showed the large amplitude oscillations of the N—N bond. In this case, it was also observed that excess vibrational energy of N—NO<sub>2</sub> is transferred to another N—NO<sub>2</sub> moiety. These results indicated the importance of compressed N—N bonds in the crystal for triggering the initial decomposition process of nitramines.

*Ab initio* crystal structure calculations based on statistical data on the organic crystal structural classes can predict crystal density of organic nitramines. Numerical calculations were carried out on the known crystal structures of three polymorphs of HMX [460]. The force-field parameters for the nitramine fragment have been improved to obtain the best correspondence between the predicted and observed molecular geometries. The predicted packings were found to be in reasonably good agreement with XRD structural data, while the computed lattice energies were not accurate enough to predict the observed heats of sublimation and the trend of polymorph stabilities. The method was also used to predict the possible crystal structures of eight isomeric azanitroadamantanes and wurtzitanes.

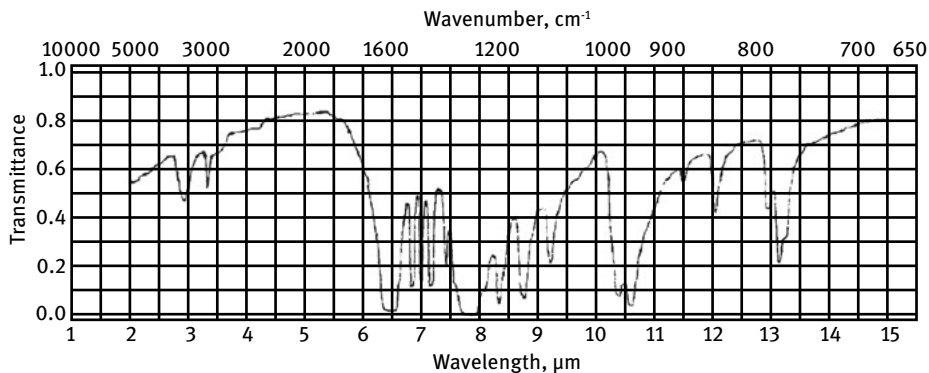
Chemical kinetic simulations of the reactions of HMX require knowledge of its enthalpy, entropy, and heat capacity in the gas phase and condensed phases. While some experimental measurements are available, most available thermochemical information has been obtained by analogy with the smaller species, RDX, and its reaction products. Using the Hartree–Fock method, structures, vibrational frequencies, and bond strengths for the isolated HMX molecule and its two major reaction products were calculated [461]. This, with some available experimental data, allows one to calculate the relevant thermochemical parameters for these species. With this information and some published experimental measurements of sublimation pressure, phase change enthalpies, and heat capacities, some thermochemical data for three condensed phases of HMX ( $\beta$ -HMX,  $\delta$ -HMX, and liquid HMX) were calculated and presented in both the JANAF and CHEMKIN format.

Density functional theory calculations were performed to predict the heats of formation for three eight-membered ring compounds and four six-membered ring compounds via designed isodesmic reactions [73]. In the isodesmic reactions designed for the computation of enthalpies of formation, diethylnitramine (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>NNO<sub>2</sub> and piperidine were chosen as reference compounds. The heats of formation for —NO<sub>2</sub> substituted derivatives are larger than those of —NF<sub>2</sub> substituent groups. Thermal stabilities were evaluated via bond dissociation energies. As a whole, the homolysis of C—NF<sub>2</sub> or C—NO<sub>2</sub> bonds is the main step for bond dissociation of C—NX compounds. Detonation properties of seven compounds were evaluated by using the Kamlet–Jacobs equation based on the calculated densities and heats of formation. It was found that 3,3,7,7-tetrakis(difluoroamino)octahydro-1,5-dinitro-1,5-diazocine (HNFX) and 3,3,5,5-tetrakis (difluoroamino)-1-nitro piperidine (N-nitro TDFAPP), with predicted density of ca. 2.0 g/cm<sup>3</sup>, detonation velocity of about 9.9 km/s, and detonation pressure of 47 GPa, are more energetic than HMX.

## 15.2.9 Optical Properties of HMX

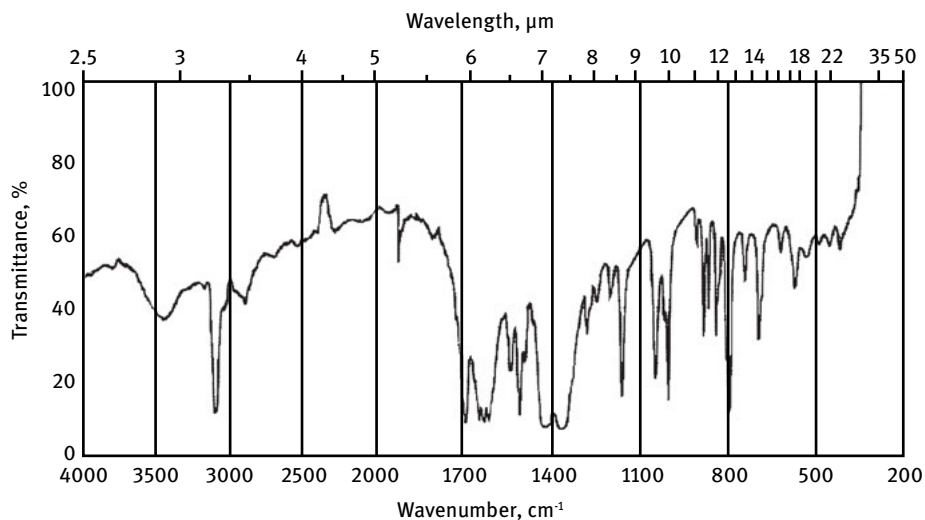
### 15.2.9.1 Infrared Spectra of HMX

The infrared spectra of  $\alpha$ -,  $\gamma$ -, and  $\delta$ -HMX are similar to each other but are substantially different from that of  $\beta$ -HMX in the longer wavelength regions. The IR spectra of HMX published in [462] or [81] were unfortunately not available in a quality that was reproducible (Figure 29). The images were very pale and required substantial re-work by a graphics illustrator.



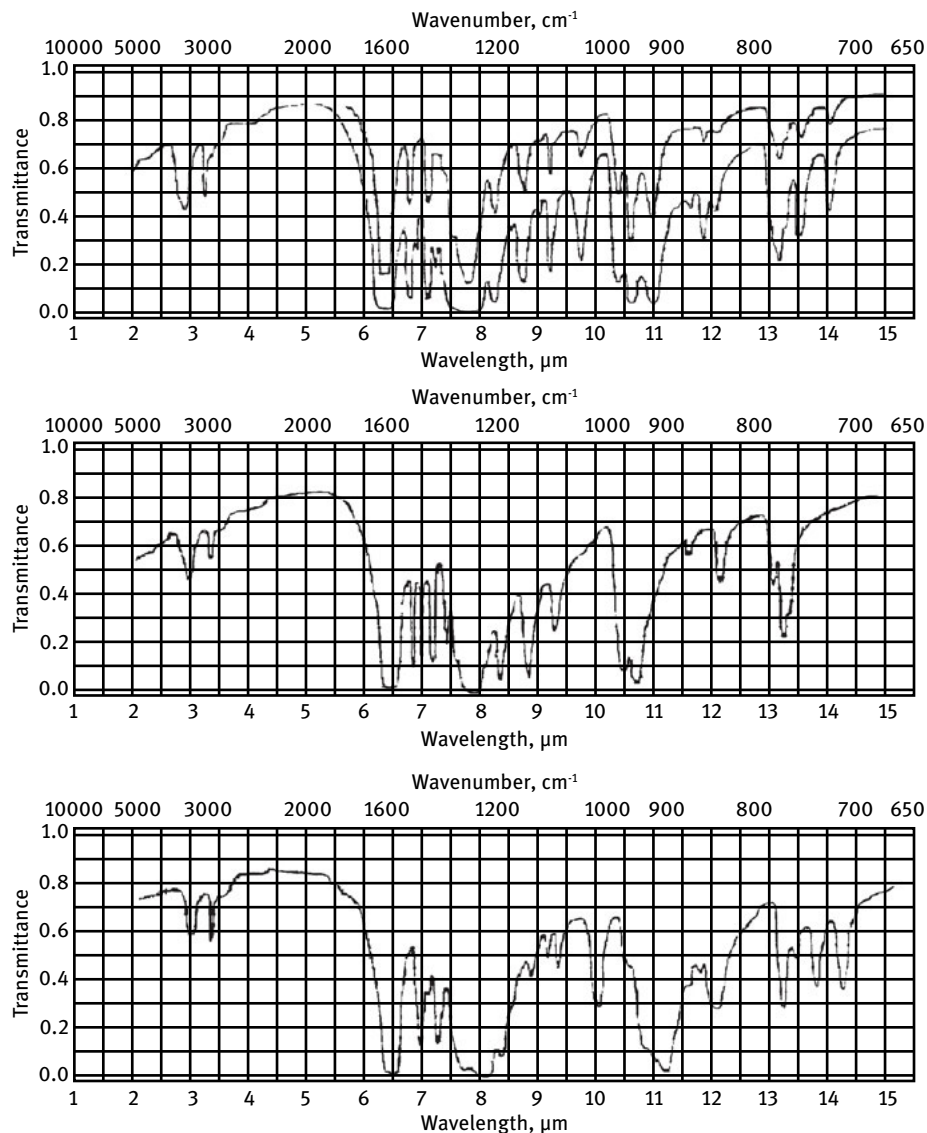
**Figure 29:** Infrared spectrum of  $\beta$ -HMX crystals. (Reproduced and modified from [81].)

A  $\beta$ -HMX IR spectrum from another source is shown in Figure 30 for comparison.



**Figure 30:** Infrared spectrum of  $\beta$ -HMX. (Reproduced and modified from [244].)

HMX exists in four polymorphs and the IR spectra of the different polymorphs show subtle differences that can be used for the analysis of this chemical [425, 463]. IR spectra of three polymorphs are shown in Figure 31.



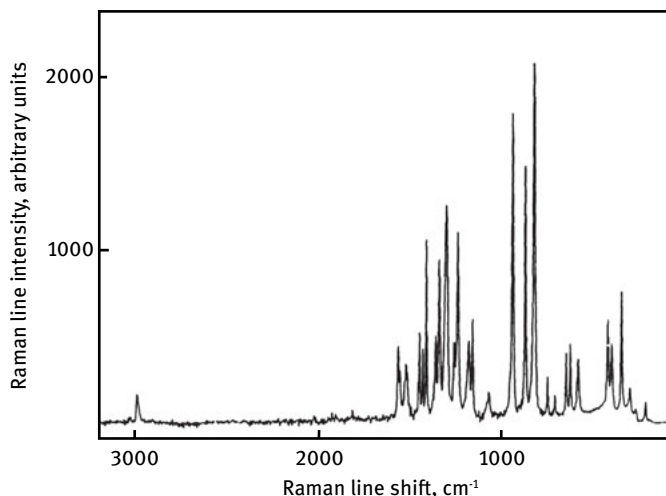
**Figure 31:** IR spectra of  $\alpha$ - (*top*),  $\beta$ - (*center*), and  $\gamma$ -HMX (*bottom*) polymorphs. (Reproduced and modified from [463])



HMX crystals (or, quite often, also RDX) are bonded in nitramine rocket propellants and PBXs with a binder. Surface interactions between the nitramine and the binder or bonding agents determine the bond strength and can be examined by IR [464]. FTIR diffuse reflection spectroscopy has been used to characterize the surface of HMX particles treated by two kinds of bonding agents. The spectra of the samples modified by different bonding agents were compared and the band at  $1532\text{ cm}^{-1}$ , due to asymmetrical stretching vibration of the nitro group, was chemically shifted after treatment with coupling agents, indicating hydrogen bond formation between HMX particles and bonding agents.

#### 15.2.9.2 Raman Spectra of HMX

Fourier transform Raman (FTR) spectroscopy employing near-IR laser radiation at  $1.06\mu\text{m}$  as the scattering source has been used to obtain Raman spectra of HMX and propellant formulations containing HMX [310, 311] (Figure 32).



**Figure 32:** Raman spectrum of HMX. (Reproduced and modified from [464])

A comparison of the Raman spectra of RDX and HMX is shown in Figure 15 in Section 12.2.2.

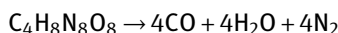
#### 15.2.10 Dielectric Constant of HMX

The dielectric constant of  $\beta$ -HMX at 298 K and 5 MHz is 3.087 [241]. The dielectric constants of the other modifications are slightly different, with 4.671 for  $\alpha$ -HMX and 3.867 for  $\gamma$ -HMX, also at 298 K and 5 MHz.

### 15.3 Chemical Properties of HMX

#### 15.3.1 Reactions with HMX

HMX is underoxidized, but a powerful explosive and a popular ingredient for CMDDB and nitramine propellants. The oxygen balance of HMX is  $-21.6\%$  for combustion to  $\text{CO}_2$ . HMX would be stoichiometrically balanced if one assumed that combustion proceeds only to CO and not all the way to  $\text{CO}_2$ :



#### 15.3.2 Procurement Specifications for HMX

The procurement of HMX, originally governed by MIL-H-45444B (27 February 1974), was superseded by MIL-DTL-45444C (26 November 1996) and is currently governed by MIL-DTL-45444C (26 November 1996) and Amendment 1 (17 April 1999) which specifies two different grades: Grade A with 93% HMX minimum purity, the remainder being RDX, and Grade B with 98% HMX minimum purity, the remainder being RDX. The specification requirements are listed in Table 35.

**Table 35:** HMX specification requirements per MIL-DTL-45444C.

| Requirement                                                                     | Grade A | Grade B |
|---------------------------------------------------------------------------------|---------|---------|
| Alpha HMX, wt. (max)                                                            | 0.1     | 0.1     |
| HMX content (Beta), wt. (min)                                                   | 93      | 98      |
| RDX content, wt. (max)                                                          | 7       | 2       |
| Melting point, °C, (min)                                                        | 277     | 277     |
| Acetone insoluble material, wt. (max)                                           | 0.05    | 0.05    |
| Inorganic insoluble, wt. (max)                                                  | 0.03    | 0.03    |
| Acidity, wt. (max)                                                              | 0.02    | 0.02    |
| Impact sensitivity, cm, ERL <sup>a</sup> , type 12, 2.5 kg, (min), 35 mg sample | 17      | 17      |

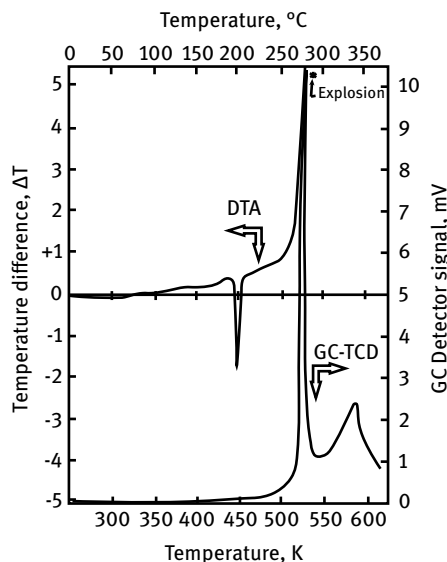
<sup>a</sup> Explosives Research Laboratory of the National Defense Research Committee

The  $\alpha$ -HMX content,  $\beta$ -HMX content and RDX content of HMX can be determined by XRD. Acidity can be determined by titration with 0.05 N NaOH and phenolphthalein or methyl red indicator and reported as acetic acid.

#### 15.3.3 Thermal Stability of HMX

##### 15.3.3.1 Slow Decomposition of HMX

In the slow decomposition of HMX in a DTA with simultaneous measurement of off-gassing by a thermoconductivity detector similar to those used in GC, the onset of exotherm was close to the phase change endotherm at 473 K (200 °C) but a peak of the exotherm could not be determined because the sample exploded at 553 K (280 °C)



**Figure 33:** DTA thermogram of decomposition of HMX. (Reproduced and modified from [241])

(Figure 33). The off-gassing (dashed line) increased sharply once the temperature exceeded 523 K (250 °C).

Both traditional thermal analysis techniques and specialized thermal techniques are applied to characterize explosives like HMX or RDX. A review including 135 references discussed pressure measurement techniques, gaseous product analysis, DTA, DSC, TG, combined TG-DTA, and miscellaneous techniques as applied to a variety of explosive materials [316].

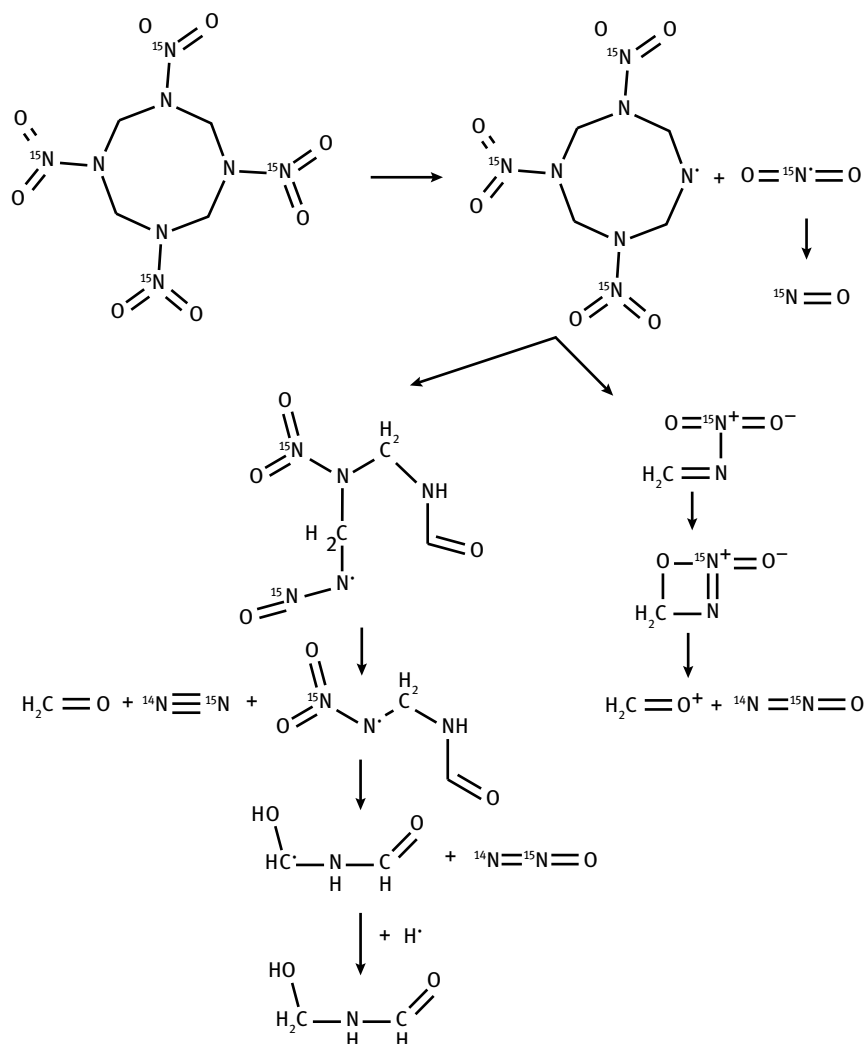
In one set of DTA/TGA analyses of HMX, also in comparison to RDX and three other high explosives, the exotherm of HMX decomposition started at 543 K (270 °C), reaching a maximum at 553 K (280 °C) [244].

As part of a multiyear, Multidisciplinary University Research Initiative (MURI) aimed at a better understanding of combustion instability in solid propellant rocket motors, the rates of decomposition and the burning rates of RDX and many other propellant ingredients have been investigated, and models to interpret the experimental results were established [336]. Several of the publications referenced in that report give a good introduction into the mechanisms for HMX decomposition and are included in the discussion here.

Numerous authors have investigated the rates and mechanisms of decomposition of RDX and HMX under slow heating conditions below and above the melting point [465]. The weight loss during the thermal decomposition of HMX that occurs as the temperature is elevated at a constant heating rate can be separated into four elementary processes: (1) induction period, (2) sublimation, (3) first order solid phase reaction, and (4) highly exothermic liquid phase reaction by plotting them against the

logarithm of the heating rate versus the reciprocal temperature. Hydroxymethyl formamide has been shown to be a major product of the liquid phase decomposition, which suggests that the decomposition of HMX in the liquid phase should be initiated by the N—N bond scission but not by C—N bond scission. The weight loss of HMX below the melting point includes three different processes (Table 36).

Based on IR spectra of decomposition products, a likely mechanism for decomposition of HMX proposed by Kimura and Kubota [465] is



The sublimation and thermal decomposition of HMX were studied by means of Langmuir evaporation and effusion mass spectrometry in the temperature range

**Table 36:** Decomposition of HMX analyzed by TGA.

| Phase | Mass loss fraction $\alpha$ | Kinetic loss equation                    |
|-------|-----------------------------|------------------------------------------|
| I     | $< 0.2$                     | $k = 1.2 \times 10^{24} \exp(-66400/RT)$ |
| II    | $0.2 < \alpha < 0.55$       | $k = 2.5 \times 10^7 \exp(-22900/RT)$    |
| III   | $> 0.55$                    | $k = 3.8 \times 10^{23} \exp(-61800/RT)$ |

Data source: [465]

448–548 K (175–275 °C) [466]. Langmuir evaporation and effusion experiments showed that the primary mechanism for thermal decomposition is ring cleavage to two equal 148 amu species. Subsequent decomposition within the effusion cell produced numerous smaller molecules and free radicals due to the further decomposition of the 148 amu fragment. See also [324, 467].

It has been found that in mixtures of RDX and HMX, the melting temperature and also the polymorphic transformation temperature of HMX showed different values from those of the pure compounds [329]. The melting point of RDX decreased considerably. On the other hand, the polymorphic transformation temperature increased. The energy of this transformation depended on the composition of the aforementioned mixture, and it was possible to establish a relationship in a specific range of compositions.

Of particular importance for the study of the decomposition of energetic materials is the simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) technique. This instrument allows the rate of selected gas phase product formation to be measured as a function of time and temperature [320, 325, 331]. The results of the STMBMS analysis showed that RDX and HMX have similar decomposition mechanisms as well as similar degradation products.

Simultaneous thermogravimetric modulated beam mass spectrometry and time-of-flight velocity-spectra measurements showed that the pyrolysis products formed during the isothermal decomposition of HMX at 484 K (211 °C) were H<sub>2</sub>O, HCN, CO, H<sub>2</sub>CO, NO, N<sub>2</sub>O, methylformamide, C<sub>2</sub>H<sub>6</sub>N<sub>2</sub>O, octahydro-1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine, and a nonvolatile residue [326, 468]. The ion fragmentation of HMX as a function of electron energy showed complete fragmentation of the HMX molecular ion for electron energies  $\geq 12.4$  eV. No fragments from the pyrolysis of HMX other than those mentioned above were observed. The mechanism of HMX decomposition can be clarified by using isotope labeling [469]. The common degradation products for both RDX and HMX observed via STMBMS were N<sub>2</sub>O, CH<sub>2</sub>O, NO, H<sub>2</sub>O, and CH<sub>3</sub>NHCHO. Experiments were also carried out on isotopically labeled materials in order to gain additional mechanistic information about which reaction products arise from labeled functional groups in the starting material. Evidence suggested that the first observable product is N<sub>2</sub>O. Since N<sub>2</sub>O is the first observable product, this suggested that the N–N bond is the weakest in the molecule and that approximately 199 kJ/mol (47.5 kcal/mol) is needed to begin decomposition at this site.

The products formed in the thermal decomposition of HMX have been traced by using mixtures of different isotopically labeled analogues of HMX [469]. The isotopic analogues of HMX used in the experiments included  $^2\text{H}$ -,  $^{13}\text{C}$ -,  $^{15}\text{N}$ -, and  $^{18}\text{O}$ -labeled compounds. The fraction of isotopic scrambling and the extent of the deuterium kinetic isotope effect or the different thermal decomposition products and pathways indicated that isotopic scrambling did not occur for the bonds in  $\text{N}_2\text{O}$  and the bonds in  $\text{CH}_2\text{O}$ . Only one of the bonds in N-methylformamide (NMFA) underwent isotopic scrambling. The lack of complete isotopic scrambling of the N—NO bond in ONDNTA may imply that some HMX decomposition occurs in the crystal lattice. The behavior of the DKIE in different mixtures of isotope-labeled HMX suggested that water probably acts as a catalyst in the decomposition. It was obvious that decomposition of HMX in the condensed phase has several reaction pathways.

Detecting the first degradation products during early decomposition is vital because it allows one to determine the specific bonds that break first as well as the order in which the breakage occurs. From this data, one can make kinetic assignments to specific bonds, which aids in determining the overall degradation mechanism. Using model-fitting techniques, for example, an activation energy of 201 kJ/mol (48 kcal/mol) was calculated for the initial decomposition region in HMX [453, 470, 471].

The mechanisms that are used to explain the decomposition of RDX and HMX are based on results from simultaneous TGA modulated beam mass spectrometry (STMBMS) and time-of flight (TOF) velocity-spectra measurements. These methods are used to identify the decomposition products and to determine their formation rates as a function of time during the decomposition of the samples. Both nitramines form  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{O}$ , NO, and  $\text{CH}_3\text{NHCHO}$  during decomposition. A mononitroso analogue of the parent compound is formed during the decomposition of both materials. The rates of formation of the various pyrolysis products along with the macroscopic and microscopic features of the NVR that is generated during the decomposition of HMX suggest that a major process involved in the decomposition of HMX below its melting point is the formation of bubble-confined pyrolysis products within the HMX particles. The pressure of the gas within the bubbles may range up to 24 MPa (3500 psi). Possible reaction mechanisms that include both the physical location of the reactions and the possible chemical reaction pathways are presented. The results from the STMBMS experiments are consistent with initial fragmentation of the N—N bond of the molecule to form  $\text{NO}_2$  and the subsequent unraveling of the remaining ring to form  $\text{N}_2\text{O}$  and  $\text{H}_2\text{CO}$ . Secondary reactions of the primary decomposition products that occur within the particles are important in determining the identity and the relative rates of gas release of the products from the solid particles. In order to obtain a better understanding of ignition, combustion, or sensitivity properties, a number of new experimental and diagnostic techniques, such as planar laser induced fluorescence (PUP), coherent anti-stokes Raman spectroscopy (CARS), and infrared multiphoton dissociation (IRMPD), are available to probe the

gas phase processes and further the understanding of the gas phase chemistry. Similarly, the development of simultaneous thermogravimetric modulated beam mass spectrometry (SmMBMS) and time-of-flight (MOF) velocity-spectra techniques have enhanced the application of mass spectrometry to probe processes in the condensed phase using evolved gas measurements. An important goal of these experiments was to develop a link between the physical properties and molecular structures of different nitramines and their combustion behavior. The motivation of the work on the condensed phase was to obtain a better understanding of the physical processes and reaction mechanisms that occur, so that the identity and rate of release of the pyrolysis products can be predicted, as a function of pressure and heating rate, based on the physical properties and molecular structure of the material. This information can then be used along with the gas-phase reaction models to correlate modifications of the nitramine ingredients with variations in the overall combustion. Over the past 40 years, many studies have been conducted on the decomposition of HMX and RDX under various conditions. Based on many of these results and the structural similarities of HMX and RDX, the same decomposition mechanisms have been proposed for both materials.

Mass spectral analysis of the decomposition products from HMX below its melting point by Bulusu and Graybush [472] showed the same group of products as observed by Robertson [318]. In addition, they found that the rate of formation of the products varied during isothermal decomposition experiments in a way that can be explained by either the characteristic induction, acceleratory, and decay stages associated with solid-phase decompositions or by invoking autocatalytic behavior. Furthermore,  $^{15}\text{N}$  tracer studies indicated that the  $\text{N}_2\text{O}$  is formed without  $\text{N}-\text{N}$  bond breaking, thus, suggesting that oxygen atom transfer to the  $\text{CH}_2$  group and  $\text{C}-\text{N}$  bond cleavage is an important step in the decomposition. However, since the total nitrogen is not accounted for in these experiments,  $\text{N}-\text{N}$  bond breaking cannot be ruled out as the initial step in the decomposition.

Thermal decomposition of pure HMX showed DSC endothermic peaks at 483 K (210 °C) from  $\beta$  to  $\gamma$  phase transformation and at 558 K (285 °C) from the HMX melting followed by an instantaneous exothermic decomposition leading to a strong peak at 563 K (290 °C) and a very strong DTGA peak at 598 K (325 °C) with a mass loss of 95% [473]. Addition of  $\text{NH}_4\text{ClO}_4$  to HMX caused the decomposition to take place before melting and the decomposition peak was lowered to 503 K (230 °C). This showed that the addition of  $\text{NH}_4\text{ClO}_4$  to HMX increased the decomposition of HMX. Even the minimum concentration of  $\text{NH}_4\text{ClO}_4$  tested (10%) had a strong effect. The addition of  $\text{NH}_4\text{NO}_3$  to HMX resulted in DSC exothermic decomposition peaks at 518 K (245 °C) and 545 K (272 °C), showing a contribution from  $\text{NH}_4\text{NO}_3$  which decomposed near to the decomposition peak of HMX. Addition of  $\text{KClO}_4$ ,  $\text{NaClO}_4$ , and  $\text{KNO}_3$  did not have any effect.

The thermal decomposition of eight linear and seven cyclic nitramines predominantly with methylenenitramine groupings was studied by DSC [40, 474]. For

eleven of these compounds, fusion was observed before decomposition. Linear relationships were found between the onset of peak temperatures of melting of these compounds and the melting points of their aliphatic structural analogues (i.e., hydrocarbon homomorphs). A similar relationship between the corresponding heats of fusion  $\Delta H_m$  was specified. On the basis of these facts, the melting points (in K) and the  $\Delta H_m$  values (in kJ/mol) were predicted for *N*-nitromethyleneimine, (368.5–371.5 and 23.45), 2,4-dinitro-2,4-diazacyclobutane (433.8–436.1 and 26.33), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) (463.4–465.2 and 32.10), 1,3,5,7,9-pentanitro-1,3,5,7,9-pentaazacyclodecane (600.3 and 34.93), and *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecaline (555.6–556.1 and 46.40).

Decomposition of organic compounds in the solid phase occurs much more slowly than in the liquid phase. The retardation and stabilizing effect of the crystal lattice can be defined as the ratio of the decomposition rate in the liquid phase to that in the crystalline phase [475].

In the DTA with slow heating, the temperature at the maximum of the exotherm peak is 552 K (279 °C). The kinetic parameters such as decomposition activation energies and the frequency factor of the HMX decomposition reaction were evaluated by nonisothermal differential scanning calorimetry (DSC) techniques [317].

Thermal decomposition of crystalline HMX was modeled using percolation theory to characterize thermal damage [476]. Percolation theory has been used historically to describe fluid flow through a network of permeable and impermeable sites. To describe thermal decomposition, the permeable and impermeable sites were related to broken or unbroken bonds. For HMX,  $N_2O$  groups were treated as sites connected by oxygen and methyl bridges. Bridges connect the  $N_2O$  sites by C–N bonds and by intermolecular attractions between N and O. The gas-phase reaction of  $N_2O$  with  $H_2CO$  was also included in the mechanism. Predictions of thermal stability were compared to time-to-explosion data. The state of the condensed material at ignition can be characterized by finite HMX-fragments of various molecular weights.

A new formulation based on 1,1-diamino-2,2-dinitroethene (DADNE, FOX-7) and HMX (called FOF-5), with the same theoretical performance as Composition B, has been developed by the FOI Weapons and Protection Division, Swedish Defense Research Agency. The thermal stability of HMX did not deteriorate by adding the other explosive [477].

### 15.3.3.2 Rapid Decomposition of HMX

In a literature survey of the physical properties, sublimation, decomposition, ignition, and deflagration of RDX and HMX, the discussion of physical properties included the crystallography of the materials. This discussion was done with emphasis on the polymorphs of HMX and the solid-phase transitions of HMX and the energetics and kinetics of HMX sublimation. The publication also reported values for energetics, kinetics and species of sublimation and thermal decomposition of solid HMX and possible reaction mechanisms [467]. Decomposition species and energetics of liquid decom-



position measured during high heating-rate studies were compared with results obtained from more traditional, controlled slow heating tests. Shock tube experiments enable the fastest rates of controlled and tunable heating. The ignition behavior of HMX showed that when the sample was subjected to an energy flux, several events occurred over time: heating and gasification of the sample, reaction of the pyrolysis products, ignition, and self-deflagration. The dependence of self-deflagration rates as functions of pressure and initial sample temperature  $t_0$  were given over the pressure range  $1 \text{ atm} < p < 50000 \text{ psi}$  and the temperature range  $-150 < t_0 < 1500 \text{ }^\circ\text{C}$ . Scanning electron micrographs showing the surface of samples rapidly quenched, while self-deflagrating showed a rugged and porous surface.

The effect of perturbing selected surface and foam zone reactions characteristic of burning HMX was examined by determining the gas product compositions from carefully controlled fast thermal decomposition ( $> 100 \text{ K/s}$ ) of a thin film of HMX in atmospheres of Ar,  $\text{H}_2$ ,  $\text{O}_2$ , CO, NO,  $\text{NO}_2$ , and  $\text{NH}_3$  [478]. The results were correlated with experimental combustion data and thermochemical modeling studies of nitramines. A consistent picture about some of the probable reactions in the heterogeneous foam and fizz zones emerged, indicating that  $\text{H}_2$ , CO,  $\text{O}_2$ , and NO affect the secondary thermolysis reactions in these zones.  $\text{NH}_3$  appeared to affect both the primary and secondary reactions, while  $\text{NO}_2$  was directly involved in primary decomposition reactions.  $\text{HNC O}$  and  $\text{CH}_2\text{O}$  appeared to be products from secondary condensed-phase reactions. The results suggested that compounds with  $\text{NH}_x$  sites and  $\text{NO}_2$  are catalytically active species for burn-rate modification of nitramine propellants.

Existing models of thermal-mechanical-chemical response of plastic-bonded HMX systems were able to predict time to explosion in a cook-off situation very accurately, to within a degree of the experimental result. However, the chemical network/reaction rates were less constrained, and many networks could achieve the same level of accuracy. Mechanical response modeling could be improved by the inclusion of porosity and surface tension in the solid species in the reaction network [479]. The addition of the reversible sublimation/vaporization reactions to the reaction network provided a nonreactive pathway yielding mass loss in the lower temperature region in TGA experiments. This implied that a lower decomposition rate can achieve the same overall level of mass loss, thus, reducing the effect of gas pressurization which was incorporated in other models.

The transient behavior of confined HMX in response to an intense, external heat flux has been simulated using a detailed kinetic model [480]. The model was spatially one-dimensional, fully transient, and consisted of equations for modeling the solid (condensed) phase HMX, the gas phase, and the surrounding container for fast cook-off conditions. The condensed-phase decomposition reactions were described by semi-global, distributed kinetics. The gas phase kinetics description included a detailed chemistry model for the combustion of HMX. A nonlinear, numerical solution of the partial differential equations resulted in predictions of

temperature, pressure, velocity, and species fractions as a function of position and time. Predicted time-to-ignition was in good agreement with experimentally measured fast cook-off times. Temperature at ignition was found to be a function of heating rate. The predicted ignition delay for fast cook-off was consistent with laser ignition of bare HMX samples. Simulation results depended on accurate boundary conditions applied to the steel container. Pressurization rates were calculated and the model gave insight into the fast cook-off behavior of HMX. The main decomposition pathway was the conversion of HMX into  $\text{H}_2\text{CO}$  and  $\text{N}_2\text{O}$ .

### 15.3.3.3 Decomposition Kinetics of HMX

Principal products formed from HMX or RDX decomposition include  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{NO}$ , including a number of other products such as  $\text{HCN}$ ,  $\text{HCOOH}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , hydroxymethyl formamide  $\text{HOCH}_2\text{NHCHO}$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  [359].  $\text{NO}_2$  appears to be formed, but is so reactive that many failures to report it may well be due to the fact that it disappeared too rapidly due to further reaction. Relative amounts of  $\text{HCN}$  and  $\text{NO}_2$  may increase at high temperature, while  $\text{H}_2\text{CO}$ , etc., will decrease. There are possible unimolecular and bimolecular follow-up reactions determining the  $\text{N}_2/\text{N}_2\text{O}$  ratio and some possible mechanisms for formation of molecular dinitrogen. The most useful aspect of thermal decomposition studies at low temperatures and pressures is to elucidate the types of chemical decomposition processes involved, including minor (at low temperatures and pressures) pathways, in addition to the principal pathways.

A literature review of kinetic parameters for thermal decomposition of HMX and RDX in the homogeneous vapor, liquid, and dissolved states concluded that the decomposition apparently fits first-order kinetics, and a collection of values for Arrhenius parameters for decomposition of HMX and RDX in the gaseous and liquid phases, and for decomposition of RDX in solution in TNT supported that conclusion [481]. Autocatalysis may cause complications in interpreting, extending, or extrapolating kinetic data for these compounds from measurements carried out below their melting points to the higher temperatures and pressures characteristic of combustion.

The effects of pressure and temperature on the thermal decomposition rate of  $\beta$ -HMX in a diamond anvil high-pressure cell were measured by FTIR at pressures up to 6.5 GPa and temperatures up to 583 K [482]. The observed  $\alpha$  (mol fraction of conversion) vs. time curves were sigmoid and followed rate equations based on the theory of nuclei chain formation with branching interference, suggesting an autocatalytic-type reaction. An increase of pressure decreased the rate of thermal decomposition, while temperature increased the rate in typical Arrhenius behavior. The energy of activation decreased with increasing pressure linearly from 501 kJ/mol at 3.6 GPa to 150 kJ/mol at 6.5 GPa. The reactant increased in volume by about 3% in order to achieve the activated state. Between 3.6 and 5.5 GPa, the reaction mechanism was unimolecular and probably involved a ring expansion prior to bond scission. Above 5.5 GPa, the mechanism was bimolecular. The change in molecularity of the kinetics can be explained by

the introduction of strain into the kinetic model. The observed pressure dependences of entropy, activation energies, and volume appear to explain why  $\beta$ -HMX can detonate at high pressures.

To improve the mechanistic understanding of HMX decomposition in the gas phase, an *ab initio* method was used to determine the various unimolecular decomposition channels [483]. Three distinct mechanisms were found: (1) homolytic cleavage of an N–N bond to form  $\text{NO}_2$  ( $M = 46$ ) and an HMX free radical HMR ( $M = 250$ ) which subsequently decomposed to form various products; (2) successive HONO eliminations to give four HONO ( $M = 47$ ) plus a stable intermediate ( $M = 108$ ); (3) O-migration from one of the  $\text{NO}_2$  groups of HMX to neighboring C atom followed by the decomposition of the intermediate ( $M = 296$ ) to INT222 (a ring-opened RDX structure) and  $\text{CH}_2\text{NNO}_2$  ( $M = 74$ ), which can undergo dissociation to smaller mass fragments. The decomposition scheme for HMX is similar to that for RDX presented earlier [366], except that concerted decomposition of HMX to four methylenenitramines,  $\text{CH}_2\text{NNO}_2$  ( $M = 74$ ) molecules is not a favorable decomposition pathway, whereas this pathway was found in RDX decomposition (both experimentally and theoretically). The formation of RDR-o in the N–N homolysis pathway 1 or the formation of INT222 in pathways 1 and 3 presents a unified mechanistic scheme for the decomposition of both of these nitramines. The HMX decomposition mechanism correlated with available condensed phase experimental results, but detailed comparison of the predicted gas phase energetics was not possible.

A theoretical study of the decomposition mechanism of gas-phase  $\alpha$ -HMX examined four distinct reaction pathways using density functional theory methods [484]. These four distinct reaction channels were included the following: (1) HMX first loses an  $\text{NO}_2$  to form a free radical HMR which further breaks a C–N bond to form a chain structure and then later loses three methylenenitramines (MN,  $\text{H}_2\text{CNNO}_2$ ) successively; (2) the chain structure forms a 10-member ring via a rung closure step before undergoing further decomposition; (3) HMX first eliminates an HONO, then loses two MN, and eliminates an HONO successively; (4) HMX eliminates two HONO successively, then loses an MN, and finally eliminates an HONO. The rate constants of each elementary reaction were calculated using the transition state theory. The thermodynamic properties were calculated for the stable species by employing a standard statistical thermodynamics method. Pathway (1) was found to be the preferred decomposition pathway on the basis of the analysis of rate constants of the elementary reactions.

The laser-induced ignition response of HMX has been investigated using a detailed numerical model [485]. The model was one-dimensional, fully transient, and solved the conservation equations for both the condensed and gas phases. The condensed phase representation included radiation absorption, solid-phase transitions, melting, evaporation, and distributed semi-global decomposition kinetics. The gas phase used a detailed kinetic mechanism to predict species formation

and destruction. Ignition occurred in the gas phase and the flame propagated back toward the surface of the HMX in what is known as the “snap-back” effect. The model then transitioned to steady-state combustion. Calculations were performed in which the solid HMX was irradiated with heat fluxes ranging from 50 to 1600 W/cm<sup>2</sup>. Results were compared to empirical data for the laser-induced ignition of HMX. Good agreement with these data and other steady-state data (burning rate, surface temperature, melt thickness) provided the necessary validation of the developed model.

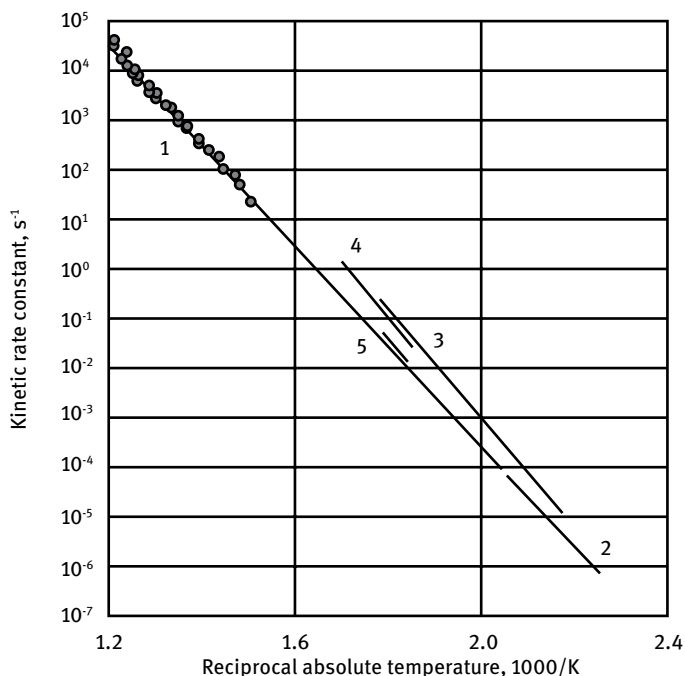
As part of an evaluation of kinetic data of energetic materials in combustion waves in the calculations for HMX, the average specific heat  $c_p$ , thermal conductivity  $\lambda$ , and density  $\rho$  of sample, were taken as  $c_p = 1.8 \text{ kJ kg}^{-1} \text{ K}^{-1}$  ( $0.43 \text{ cal g}^{-1} \text{ K}^{-1}$ ),  $\lambda = 2.6 \times 10^{-2} \text{ kJ s}^{-1} \text{ m}^{-1} \text{ K}^{-1}$  ( $6.3 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-1} \text{ }^\circ\text{C}^{-1}$ ), and  $\rho = 1.75 \text{ g/cm}^3$ , respectively. According to DSC studies, heat of reaction in the melt at fast heating,  $Q$ , is equal 1387 kJ/kg (331.5 cal/g). Figure 34 illustrates comparative analyses between kinetic parameters of the leading reactions during combustion and thermal decomposition of HMX based on data taken from the literature [252]. HMX decomposition kinetics have been taken for the molten substance (Line 3 from [486] and Line 5 from [3099]) and its solution in dinitrobenzene (Line 2 from [487]) or acetone (line 4 from [38]). As can be seen in Figure 34, kinetic parameters of liquid HMX decomposition derived from the hot combustion model, for the range 660–810 K expressed by the following equation

$$k = 10^{16.78} \cdot \exp(-23440/T)$$

where  $k$  is the kinetic rate in s<sup>-1</sup> and  $T$  is the temperature in kelvin, are in a good agreement with the experimental rate constants of HMX thermal decomposition in the melt and solutions obtained at much lower temperatures.

Based on the data available, it was concluded that the first step of decomposition always includes cleavage of the N–NO<sub>2</sub> bond, which is followed by various secondary reactions and sometimes by chain reactions [43]. A complete understanding of the effects of structures of nitramines on their stabilities is extremely valuable for the synthesis of nitramines with improved performance.

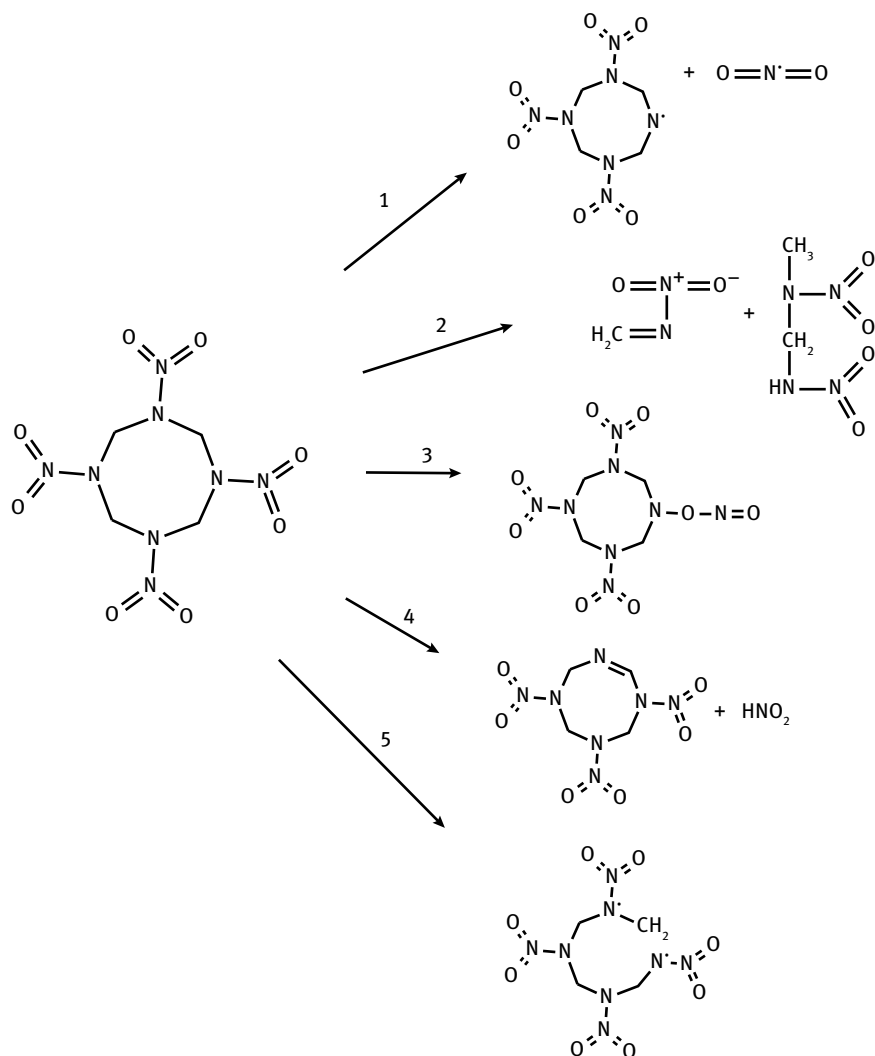
Thermal decomposition of HMX between 448 and 473 K (175 and 200 °C) was studied using the simultaneous TGA modulated beam MS with focus on initial stages of the decomposition [488]. The initial stages of the decomposition have an induction period followed by two acceleratory periods. Arrhenius parameters for the induction period and two acceleratory periods were:  $\log A = 18.2 \pm 0.8$ ,  $E_a = 202 \pm 7 \text{ kJ/mol} = 48.2 \pm 1.8 \text{ kcal/mol}$ ;  $\log A = 17.15 \pm 1.5$  and  $E_a = 205 \pm 13 \text{ kJ/mol} = 48.9 \pm 3.2 \text{ kcal/mol}$ ;  $\log A = 19.1 \pm 3.0$  and  $E_a = 218 \pm 26 \text{ kJ/mol} = 52.1 \pm 6.3 \text{ kcal/mol}$ . These data can be used to calculate the time and temperature required to decompose a desired fraction of a test sample assessing the effect of thermal degradation on sensitivity or burning rates. It can also be used to estimate the extent of decomposition expected under



**Figure 34:** Comparison of kinetic parameters of the leading reaction of HMX combustion (1, data points and dashed line) and decomposition in solutions of dinitrobenzene (2), acetone (4), and in the melt (3 and 5). (Republished and modified from [252], with permission of ©2009 Elsevier Science & Technology Journals; permission conveyed through Copyright Clearance Center Inc.)

normal storage conditions for munitions containing HMX. These data, along with previous mechanistic studies conducted at higher temperatures, suggested that the process that controls the early stages of decomposition of HMX in the solid phase is scission of the N–NO<sub>2</sub> bond, reaction of the NO<sub>2</sub> within a lattice cage to form the mononitroso analogue of HMX, and decomposition of the mononitroso HMX within the HMX lattice to form gaseous products that are retained in bubbles or diffuse into the surrounding lattice.

It was assumed that mixtures of HMX and NTO would be less sensitive and more stable than HMX alone. A complete set of possible mechanisms was elaborated theoretically for thermal decomposition of HMX and NTO and for the bicomponent mixtures of both [489]. Initially, the thermal decomposition of HMX was simulated independently. Scheme I shows the routes of HMX thermolysis that are formally possible at the first stage of decomposition.



Scheme I for HMX decomposition. (Modified from Petukhova et al. 2010)

Subsequent stages of decomposition can be represented by chains of intermediates consisting of successive transformations generated along routes 1 and 2 in Scheme I. The observed products of HMX thermal decomposition in the gaseous phase almost entirely consist of simple compounds, such as HCN,  $\text{N}_2\text{O}$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2$ , NO,  $\text{H}_2\text{CO}$ ,  $\text{CO}_2$ , and CO. Earlier, it had generally been assumed that the most likely initiating step in the decomposition is N—N bond cleavage, but investigations using  $^{15}\text{N}$  labels indicate that N—N bonds are preserved until  $\text{N}_2\text{O}$  formation. The Petukhova scheme

above does not have the aldehyde —CHO fragments shown in the earlier HMX decomposition scheme proposed by Kimura and Kubota [465]. A computational analysis of the decomposition of the HMX/NTO bicomponent system concluded that decompositions take place independently of each other, with subsequent collisions and interactions of the resultant intermediates and decomposition products. That is, these substances do not interact with each other at the first stage of decomposition, and therefore the scheme thus obtained represents the additive behavior of their thermolysis. See also [490].

#### 15.4 Strand Burning of HMX

For strand burning of RDX, the literature reviewed in this chapter had been divided into experimental and theoretical studies. For HMX, in the following section, we have included both types of studies in the same section, listed here in chronological order.

Data which describe the deflagration rates of HMX single crystals as a function of pressure and initial sample temperature were input into a modification of the Beekstead, Derr, and Price combustion model and values of combustion parameters were predicted with some accuracy [491].

The burning rates for HMX pressed pellets were measured in a windowed bomb burner over a wide range of initial sample temperatures and chamber pressures between 173 and 299 K (−100 and +26 °C) and pressures from 241 kPa to 6.2 MPa (35 to 900 psia) [492]. When added to earlier datasets, the complete dataset spans portions of the range of temperature between 173 and 423 K (−100 and +150 °C) and pressures between 0.1 and 55 MPa (15 and 8000 psia). The pressure exponent was essentially constant at  $0.86 \pm 0.01$  for temperatures equal to or below 273 K (0 °C) and pressures below 6.8 MPa (1000 psia) and dropped with increasing temperature to 0.66 at 423 K (150 °C). If the temperature sensitivity is assumed to be independent of initial temperature, then it is a decreasing function of pressure, being about 0.13%/°C at 6.2 MPa (900 psia) and about 0.45%/°C at 0.69 MPa (100 psia).

Similar experiments were conducted with formulated propellants containing RDX or HMX with and without deuterium isotope labeling [493–495].

Burn rate comparison of HMX and its deuterium labeled HMX-d(8) isotopologue revealed a primary kinetic deuterium isotope effect at 3.55 MPa (500 psig) and 6.99 MPa (1000 psig) pressure and selectively identified covalent carbon–hydrogen bond rupture as the mechanistic step which ultimately controls the further HMX burn rate under the static combustion conditions [496]. The isotope effect further suggested that a rate-limiting C–H bond rupture occurs during the solid-state HMX decomposition/deflagration portion of the overall combustion event.

Two alternative schemes for the combustion chemistry of HMX were proposed and simplifying assumptions were made to achieve a closed-form solution for the condensed phase and three model versions differing in complexity for the gas phase [497].

It was concluded that the combustion is controlled by vapor-phase decomposition and that it would be difficult to achieve large burning rate increases by catalysis. For this particular problem, it would be permissible to neglect mass diffusion in the conservation equations in the interests of computational convenience, but energy diffusion cannot be neglected except for limited purposes.

A steady-state one-dimensional combustion model was used to describe the slow burning deflagration of HMX [498]. The model employed a detailed set of elementary reactions, but only for gas-phase reactions. Different mechanisms were proposed and some of the more important gas-phase reactions were identified. It was hoped that catalytic acceleration of certain reactions would increase the burn rate and regression rate. Observation of the spectroscopic signature of C—N bonds should help in distinguishing different decomposition mechanisms.

The combustion wave structure and thermal decomposition process of HMX were examined in order to elucidate the burning rate characteristics of HMX [499]. According to this experiment, the combustion wave can be divided into three zones: (1) non-reactive solid-phase, (2) surface reaction, and (3) gas-phase reaction zones. Measurements with microthermocouples revealed that the heat flux produced in the surface reaction zone is approximately equal to the heat flux transferred back from the gas phase to the burning surface. Accordingly, the reactions in the surface reaction and the gas phase zones play a dominant role in the burning rate of HMX. The gas phase reaction zone consists of a two-stage reaction: the first stage is the exothermic rapid reaction between  $\text{NO}_2$  and aldehydes, and the second stage is the exothermic slow reaction between  $\text{NO}$  and  $\text{N}_2\text{O}$  and remaining fuel species. The luminous flame zone which is determined to be the second stage reaction rapidly approached the burning surface as pressure was increased. However, the luminous flame reaction appeared to have less of an effect on the burning rate of HMX. Examinations of the quenched burning surface of HMX samples revealed that the burning surface melts and forms a noncrystallized intermediate material. The surface structure appeared to be different from the structure of thermally degraded HMX samples which were obtained by a thermogravimetric analysis. See also [500].

A three-phase, one-dimensional RDX model was extended to HMX [501]. All model inputs were determined independent of the model except for the heat capacity and thermal conductivity of HMX liquid, for which no experimental data were found. Reasonable correlation with experimentally determined burn rate, surface temperature, adiabatic flame conditions, melt layer thickness, and some gas-phase species concentration profiles was achieved using this model. Sensitivity analyses indicated that the adiabatic flame conditions are controlled by thermodynamic properties of the solid and liquid phases. The surface temperature is controlled by the vapor pressure correlation, and the burn rate is largely controlled by the heat feed-back from the gas-phase flame, or the gas-phase mechanism. Sensitivity analyses indicated that differences noted in combustion characteristics of HMX and RDX are likely caused by differences



in vapor pressure and melting temperature, while the similarity of burn rate data was attributed to the similarity of the gas-phase flames. See also [395].

Measurements of strand burning rates of HMX in the range of 1–4 atm, with and without modulated laser augmenting irradiation, showed that in the pressure range of 1–3 atm the HMX combustion had a pronounced auto-oscillating character [385]. Under harmonically modulated radiant flux, the response of reactive force for HMX displayed a resonance character. Even at small modulation intensities, the character of this response was nonlinear. For both HMX and RDX, the dependencies of the steady-state burning rate on initial temperature and on external radiant flux have been determined.

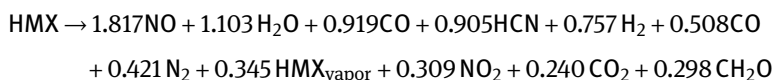
Species and temperature profiles were measured in the gas phase of laser-assisted combustion HMX flames at heat fluxes of 100 and 300 W/cm<sup>2</sup> [383]. A microprobe/triple quadrupole mass spectrometer was used to measure quantitative species profiles, and fine wire thermocouples were used to measure temperature profiles. The flame and surface structures were observed using a high-magnification video system. The major species at the surface were H<sub>2</sub>O, H<sub>2</sub>CO, HCN, NO<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>, CO, and NO at atmospheric pressure with both heat fluxes. No CO<sub>2</sub> was detected at the surface. The mol fraction of triazine was found to be approximately 2.5% at the surface, which had not been reported during normal combustion of HMX. This species could play an important role in the gas phase chemistry. The species profiles showed two-stage reaction zones. The species profiles also showed that increasing heat flux stretched the secondary reaction zone, but did not stretch the primary reaction zone. No plateau at a typical dark zone temperature was observed for either heat flux.

The laser- and pressure-driven oscillatory thrust responses of burning HMX at pressures near 1 atm were measured during laser-supported combustion at mean CO<sub>2</sub> laser heat fluxes of 35 and 60 W/cm<sup>2</sup> [502]. During laser-driven testing, the laser flux was modulated at  $\pm 15$  W/cm<sup>2</sup> at driving frequencies ranging from 4 to 250 Hz. Thrust measurements were made with a 10% peak-to-peak variation about the mean chamber pressure at driving frequencies ranging from 4 to 100 Hz. Measured steady-state temperature profiles and numerical predictions of the temperature profiles in the gas-phase reaction zone were used to estimate steady and unsteady heat feedback, respectively. The experimental results were compared to predictions of an analytical model, which used one-step reactions in the condensed phase and gas phase, and numerical modeling results that used detailed gas-phase kinetics. The agreement between the analytical model and the data was found to be better than that between the numerical modeling and the data.

RDX and HMX have similar structures and strand burning rates. As already discussed above, the burning-rate temperature sensitivity  $\sigma_p$  is significantly different between RDX and HMX at low pressure. Efforts to mathematically model the steady-state burning of RDX and HMX with detailed chemical kinetics in the gas and decomposition in the condensed phase all have underpredicted the  $\sigma_p$  trends of HMX at low pressure and have not differentiated between the  $\sigma_p$  values of RDX and HMX. RDX

and HMX both burn with a thin multiphase surface of bubbles in the liquid melt layer. A liquid–bubble model was developed to improve  $\sigma_p$  predictions [397].

The species concentration distribution profiles in HMX flames during combustion in air at a pressure of 1 atm were measured using molecular beam mass spectrometric sampling [398, 399, 503]. HMX vapor was detected near the burning surface for the first time. A total of 11 species were identified in the HMX flame ( $H_2$ ,  $H_2O$ , HCN,  $N_2$ , CO,  $H_2CO$ , NO,  $N_2O$ ,  $CO_2$ ,  $NO_2$ , and HMX vapor), and their concentration profiles were measured. The HMX combustion was unstable. The species concentration profiles exhibited periodic pulsations related to variations in the HMX burning rate. The HMX flame structure at various distances to the burning surface was determined using the average value of the burning rate. There were two main zones of chemical reactions in the flame: In the first zone  $\sim 0.8$  mm wide adjacent to the burning surface, HMX vapor decomposed and  $NO_2$ ,  $N_2O$ , and  $H_2CO$  reacted with each other to form HCN and NO. In the second zone  $\sim 0.8$ – $1.5$  mm wide, HCN was oxidized by nitric oxide to form the final combustion products. The composition of the final combustion products was also analyzed. Using experimental data, gross-reactions for the gasification of nitramines at atmospheric pressure were determined:



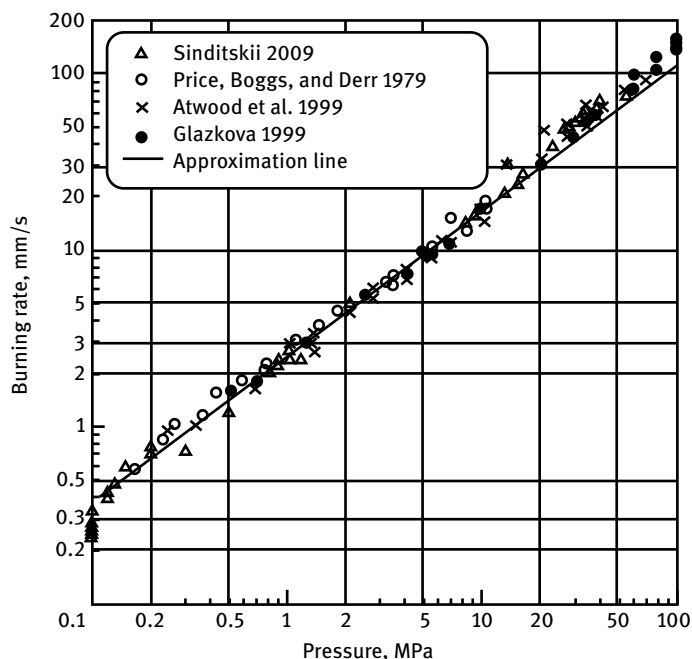
The same method was also applied to formulated propellants of RDX or HMX with GAP as the binder [400].

The microstructure and burning parameters of HMX by itself as a solid monopropellant and 25%Al/75%HMX energetic systems as a function of the particle size were examined [504]. Two types of HMX particles, microsized (mHMX) and ultrafine ( $\mu$ HMX) and aluminum powders (micro- and ultrasized (ALEX<sup>TM</sup>)) were used. Morphology and particle size were examined by atomic force microscopy (AFM), SEM, and Brunauer-Emmet-Teller (BET) active surface area analysis. It was shown that the HMX monopropellant's burning rates of the micro- and ultrasized HMX were almost identical in the pressure range 20–100 atm.

The temperature sensitivity of the HMX strand burning rate increased with increasing initial temperature at pressures of 0.1 to 10 MPa, which is typical for combustion of substances with the leading reaction in the condensed phase (c-phase model) [505, 506]. The sample diameters were 7 mm at 0.5 and 1 MPa and 10 mm at subatmospheric pressures. As seen in Figures 35 and 36, the HMX burning rates obtained in different laboratories are in good agreement, and the curve  $r_b = f(p)$  had a slight inflection at  $p = 13$ – $15$  MPa.

The data from all sources can be described by the equation

$$r_b = P^n$$



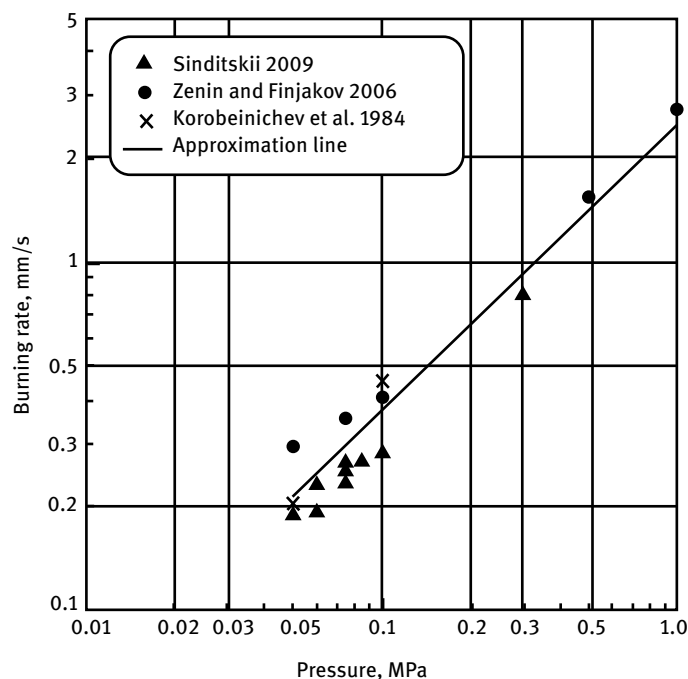
**Figure 35:** Strand burning rate of HMX at high pressure. (Republished and modified from [506], with permission of ©2009 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

where  $r_b$  is the burning rate in mm/s and  $P$  is the pressure in MPa, with  $n = 0.77 - 0.82$  in the pressure range 0.2–10 MPa and with  $n = 0.9 - 1.1$  in the range of pressures above 10 MPa. Experimental values of the temperature sensitivity of the burning rate in the pressure interval between 1 and 10 MPa are shown in Figure 37.

Experimental values of the temperature sensitivity of the burning rate in the pressure interval between 0.1 and 1 MPa were higher than the values predicted by the c-phase model, but this fact indicated a transition of the combustion process to another regime rather than being a result of combustion instability in this area. The flame structure of burning HMX with different additives was studied with the help of thin tungsten–rhenium thermocouples in the pressure range from 0.025 to 1 MPa. The gas-phase flame was found to ignite in an inductive mode, at least up to a pressure of 1 MPa. The surface temperature was measured as a function of pressure on the basis of experimental data in a wide range of pressures:

$$\ln P = 21.72 - 14092/T$$

where  $P$  is the pressure in atm and  $T$  is the temperature in kelvin. Two possible reasons for the oscillatory regime of HMX combustion observed at atmospheric pressure

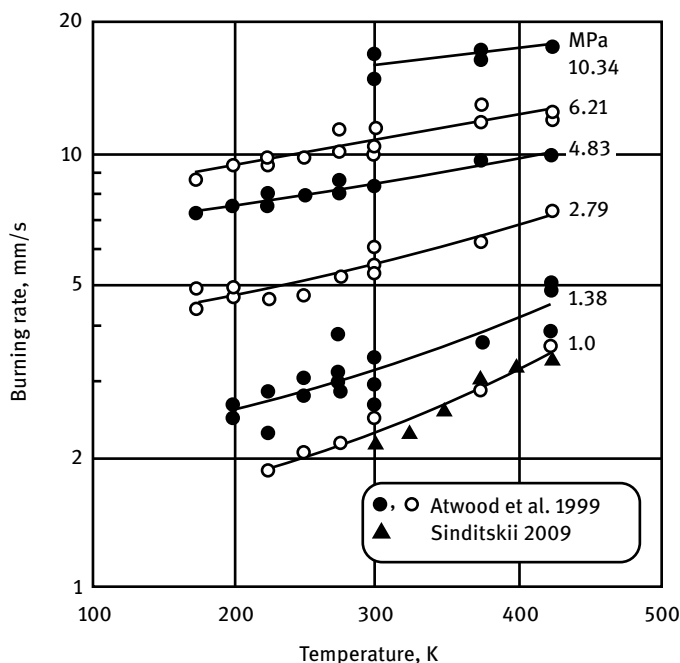


**Figure 36:** Strand burning rate of HMX at low pressure. (Republished and modified from [506], with permission of ©2009 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

were proposed: the emergence of resonance phenomena during combustion of an inhomogeneous gas mixture in the tube and the lack of correspondence between the chemical reaction rate in the gas phase at the instant of the resonance and its energy capabilities, which do not allow a necessary HMX gasification rate to be ensured. A mechanism proposed for a wide range of pressures up to 10 MPa was assumed to be based on the leading role of HMX decomposition in the melt at the surface temperature. Strand burning rates of HMX with addition of 5% RDX supported this theory.

Microthermocouples were used to investigate combustion waves of RDX and HMX and the possibilities of mass spectrometer (including gas sampling) and optical techniques of studying the chemistry of gas-phase processes in the combustion wave were analyzed [507].

Another mechanism for HMX combustion was proposed and a corresponding model was developed under the assumption that the combustion wave consisted of two zones, with consideration given to the reaction of decomposition and vaporization of the initial energetic material in the condensed phase and the subsequent decomposition of its vapor in the gas phase [508, 509]. An analysis of the results showed that, at low pressures, the burning rate was largely determined by the



**Figure 37:** HMX strand burning rate versus the initial temperature at different pressures. (Republished and modified from [506], with permission of ©2009 Springer Nature BV; permission conveyed through Copyright Clearance Center Inc.)

exothermic decomposition of the material in the condensed phase, but at pressures above 2.02 MPa (20 atm), the processes in the gas phase began to play an increasingly important role, where the limiting process was the bimolecular activation reaction with the subsequent dissociation of HMX accompanied by secondary reactions between the products. A comparison of the calculation predictions with experimental data showed that the model adequately described a number of characteristics of the combustion wave and ballistic properties, such as the burning rate and its sensitivity to pressure and initial temperature.

Temperature dependences of a number of physicochemical and thermophysical properties of HMX, such as the heat capacity of the liquid phase, change in the enthalpy due to heating of the condensed phase to a predetermined temperature, heat of evaporation, saturated vapor pressure, and the vapor diffusion coefficient in low-molecular-weight gases were calculated in an effort to develop more accurate models for HMX combustion in propellants [510]. The data obtained were used to calculate the amount of heat needed to heat the condensed phase to the burning surface temperature in the range of 560–900 K at various degrees of decomposition. The heat of decomposition of HMX under combustion conditions was calculated from the known

composition of the reaction products at a pressure of 1 bar. This was compared to measured HMX decomposition by DSC. The results of the calculations and experiments suggested that at a degree of decomposition  $\alpha \geq 0.6$ , heat release in the condensed phase can provide heating and evaporation of HMX without heat input from the gas phase. It was shown that the calculated saturation vapor pressures of HMX, which are higher than those presented in the literature, are in better agreement with available experimental data on the HMX vapor concentration profile near the burning surface.

An overview of the papers on the combustion mechanism of HMX published in Russian journals during the time period 2008–2010 attempted to explain the causes of different interpretations of experimental and theoretical results [511]. Based on the analysis, it was concluded that the most reasonable mechanism for HMX combustion is the mechanism which assumes the leading role of the decomposition reaction in the melt at the surface temperature over a wide range of pressures.

## 15.5 Safety Properties of HMX

### 15.5.1 Impact Sensitivity of HMX

It is assumed that the impact sensitivity data reported in the literature and reiterated here are for the 50% point determined by the Bruceton up-and-down method. In the BAM test apparatus, the impact sensitivity of  $\beta$ -HMX is 74 N m [133]. The  $\delta$ -phase, which may occur after heating, is much more sensitive to impact or friction. In the AWRE tester with the No. 12 tool and a 5-kg weight, the 50% point was at 33 cm.

In the Bureau of Mines apparatus with a 32-mg sample, the impact sensitivity is 32 cm with a 2-kg weight [291]. In the Picatinny Arsenal tester with a 23-mg sample, the impact sensitivity is 22.9 cm = 9 in.

The published literature on shock sensitivity of granular explosives like RDX or HMX presents a somewhat confusing picture. A particular problem is that the results of different studies often cannot be directly compared due to the different experimental methods and purity of the samples used to determine sensitivity. Some experimenters do not state which crystal polymorph modification of HMX was being tested.

The  $\beta \rightarrow \delta$  phase transition in HMX has been implicated as the primary reason behind the increased sensitivity of the explosive as it is heated. Both physical and chemical changes accompany the transition, but no study has conclusively shown which specific change, or set of changes, is responsible. A review of the data showed that the mechanical differences, in and of themselves, do not result in increased sensitivity to shock compression of HMX [512].

HMX exists in a variety of crystal structures; the most widely used being the  $\beta$ -phase which is stable at room temperature and pressure. On heating, a more impact sensitive form ( $\delta$  phase) is produced. The nonlinear optical technique of second harmonic generation can be used as a probe of phase since  $\delta$ -phase HMX generates a second harmonic at 532 nm when 1064 nm laser light is incident upon

it. High-speed photography of second harmonic generation in HMX samples during drop weight impact showed that this technique can provide good spatial information and time resolution. There was evidence for small areas of  $\delta$ -phase HMX appearing in the period from 13  $\mu$ s before ignition to 10  $\mu$ s afterwards, demonstrating that the heating on impact is sufficient to overcome the loading conditions and cause the phase change [513].

#### 15.5.2 Card Gap Sensitivity of HMX

Quantum-mechanical based multiscale simulations to study the initial chemical processes of condensed-phase HMX under shock wave loading based on density functional theory methods showed that the initial decomposition of shocked HMX is triggered by the N—NO<sub>2</sub> bond breaking under the low velocity impact (8 km/s) [514]. As the shock velocity increased (11 km/s), the homolytic cleavage of the N—NO<sub>2</sub> bond was suppressed under high pressure, and the C—H bond dissociation became the primary pathway for HMX decomposition in its early stages. It was accompanied by a five-membered ring formation and hydrogen transfer from the >CH<sub>2</sub> group to the —NO<sub>2</sub> group. Simulations suggested that the initial chemical processes of shocked HMX are dependent on the impact velocity, which give new insights into the initial decomposition mechanism of HMX upon shock loading at the atomistic level.

#### 15.5.3 Friction Sensitivity of HMX

In the BAM friction sensitivity test apparatus,  $\beta$ -HMX shows a reaction (crackling) at a pistil load of 120 N. In an effort to identify mutual relationships between friction and impact sensitivities of cyclic nitramines,  $\beta$ -HMX impact and friction sensitivity data were used to demonstrate the potential correlation [515]. Inclusion of an additional 12 nitramines into this scenario resulted in a series of partial relationships, which were correlated with the molecular structure of these substances. It was also found that there is a relationship between increasing heats of fusion of the nitramines studied and their decreasing friction sensitivity numbers. Comparison of friction sensitivity with heats of fusion of the studied nitramines showed that the increase in the heat of fusion values is more or less connected with a decrease in friction sensitivity.

The friction sensitivity of five linear and eight cyclic nitramines was determined and compared to the Arrhenius parameters of nonautocatalyzed thermal decomposition of these nitramines [516]. Generally, increasing values of activation energies of nonautocatalyzed decomposition of these nitramines were shown to be connected with decreasing friction sensitivity numbers.

As a next step of the comparative investigation, friction sensitivities of HMX and similar cyclic nitramines were compared to their detonation velocities to determine whether there was a correlation [517]. For the nitramines studied, these comparisons showed a general trend of friction sensitivity decreasing to smaller numbers with increasing energy content.

#### 15.5.4 Autoignition Temperature of HMX

The autoignition (autoexplosion) temperature of HMX is 0.1 s at 658 K (385 °C), 5 s at 600 K (327 °C), and 10 s at 579 K (306 °C) ([84] p. 173).

### 15.6 Explosive Performance of HMX

In the lead block test, the increase of the cavity volume is  $480 \text{ cm}^3/10 \text{ g}$ . The detonation velocity of confined  $\beta$ -HMX is  $9100 \text{ m/s}$  at  $\rho = 1.9 \text{ g/cm}^3$  [133]. In the Trauzl lead block test, the indentation of HMX was 145% that of TNT.

The ballistic mortar performance of HMX was calculated by a simplified method and compared to experimental measurements. The ballistic mortar performance of HMX was predicted to be 151% of that of TNT and measured as 150% of that of TNT [88].

#### 15.6.1 Detonation Velocity of HMX

The measured detonation velocity of HMX is  $9.11 \text{ km/s}$  at a density  $\rho = 1.89 \text{ g/cm}^3$  and the calculated Chapman-Jouguet (C-J) pressure is 387 kbar at a density of  $\rho = 1.90 \text{ g/cm}^3$  [241]. Other sources gave a detonation velocity of  $9124 \text{ m/s}$  at a packing density of  $1.84 \text{ g/cm}^3$  [84].

#### 15.6.2 Critical Diameter of HMX Detonations

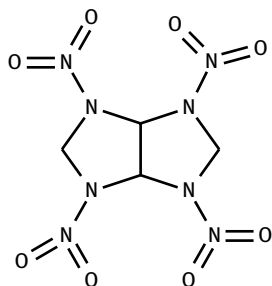
By using wedge-shaped charges and using critical thickness to characterize detonation wave propagation, an experimental study was carried out to explore the effect of particle size of HMX on detonation wave propagation of HMX and HMX/F2641 at two different packing densities of HMX [518]. Experimental results showed the following: (1) a decrease in size of HMX particle resulted in decrease of critical thickness, namely enhancement of detonation wave propagation capability; (2) HMX/F2641 excelled HMX in detonation wave propagation capability at the same size of HMX particles; and (3) an increase of charge density is advantageous to detonation wave propagation.

## 16 Fused Ring Nitramines

### 16.1 Bicyclo-HMX

Bicyclo-HMX, also known as “bicycle”-HMX, 1,3,4,6-tetranitro-2,3a,5,6a-tetrahydroimidazo[4,5-d]imidazole, 1,3,4,6-tetranitrooctahydroimidazo[4,5-d]imidazole,  $\text{C}_4\text{H}_6\text{N}_8\text{O}_8$ , CAS RN [473796-67-7],  $M = 294.139$ , is a thermally stable HMX analog.

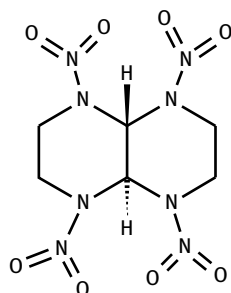




Bicycle-HMX

### 16.2 1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin

An intermediate in the synthesis of *trans*-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin, 1,4,5,8-tetranitro-2,3,4a,6,7,8a-hexahydropyrazino[2,3-*b*]pyrazine, TNAD,  $C_6H_{10}N_8O_8$ ,  $M = 322.192$  g/mol, the cyclic amine *trans*-1,4,5,8-tetraazadecalin was first prepared from glyoxal and ethylenediamine and then nitrated to TNAD with  $HNO_3$  in acetic acid anhydride [519, 520]. The nitration was carried out in three steps.



1,4,5,8-Tetranitro-1,4,5,8-tetraazadecalin

The thermal stability of *N*-nitroamines possessing two fused five-membered rings is not any better than that of RDX or HMX [521, 522].

### 16.3 Caged Heterocyclic Nitramines

Normally hexanitrohexaazaisowurtzitane, CL-20, the high-density caged heterocyclic nitramine that has received a lot of attention during the past decades, would receive

a chapter with detailed information at least as complete as the chapters for RDX and HMX. However, the primary application of CL-20 is as an explosive and not as a rocket propellant ingredient. Therefore we have not included a more detailed description of CL-20 in this chapter. Hexanitrohexaazaisowurtzitane is a polyazapolycyclic caged nitramine and has a remarkable density, and detonation velocity. The abbreviation CL stems from the U.S. Navy laboratory where it was discovered in 1986: China Lake, CA.

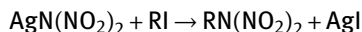
## 17 *N,N*-Dinitramine Compounds

In an effort to synthesize energetic compounds, not only one, but also both hydrogens on the amino nitrogen of alkylamines can be replaced by nitro groups. The resulting compounds are called *N,N*-dinitroalkylamine compounds or *N,N*-dinitramines or *N,N*-dinitramides or *N*-alkyl-*N,N*-dinitroamines. Because they no longer contain an acidic hydrogen like the simple (single) nitramines, they do not form salts. Alkyl-dinitramines play a role in the synthesis of inorganic dinitramide salts (see *Encyclopedia of Oxidizers*, chapter “Dinitramide Oxidizers”).

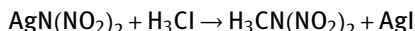
The C—N bond in alkyl dinitramines is easily split by hydrolysis with strong alkali hydroxide, yielding the corresponding alkali dinitramide salts. The alkyl dinitramines can be isolated as intermediates, purified or can be hydrolyzed without intermediate purification if dinitramide salts are the desired product. In addition to being useful as intermediates in the production of ammonium dinitramide (ADN) or potassium dinitramide (KDN), alkyl dinitramides would make good monopropellants similar to nitroalkanes.

### 17.1 Synthesis of Alkyl Dinitramines

Alkyl *N,N*-dinitramines were already synthesized long before their potential use as intermediates in the production of ADN became known [523]. A classical metathetical reaction for the synthesis of *N,N*-dinitramines would be the reaction of silver dinitramide with an alkyl iodide, precipitating the insoluble silver iodide. Silver dinitramide reacts with alkyl iodides to form *N*-alkyl-*N,N*-dinitroamines [524, 525]:



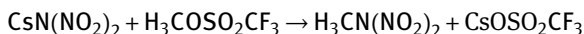
Methyl iodide does not react with  $\text{KN}(\text{NO}_2)_2$  in acetonitrile at 253 K, but  $\text{AgN}(\text{NO}_2)_2$  reacts with  $\text{CH}_3\text{I}$  within several days to form methyldinitroamine



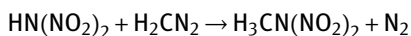
The reaction with  $\text{C}_2\text{H}_5\text{I}$  gave a mixture of *N*- and *O*-alkylated products.

The synthesis of monoalkyl-*N,N*-dinitramines from isocyanates as a step for preparation of dinitramide salts was already described in *Encyclopedia of Oxidizers*,

chapter “Dinitramide Oxidizers.” Alkyl *N,N*-dinitramines can be obtained by the direct nitration of the corresponding alkyl isocyanates with  $\text{NO}_2\text{BF}_4/\text{HNO}_3$ . If alkali metal dinitramide salts are already available by synthesis via a different route, they can be converted into alkyldinitramines by alkylation methods. For instance, cesium dinitramide can be converted into the alkyldinitramine by reaction with the corresponding alkyl triflates. The product yield was 40%.



Alkylation of dinitramidic acid with diazomethane in ether gave methyl dinitramine in 30% yield



Cubanes with *N,N*-dinitroamino instead of nitro pendants have not yet been synthesized, but their molecular structure and energy potential has already been calculated. The heats of formation, the detonation velocity and detonation pressure of poly-*N,N*-dinitroaminocubanes were calculated by density function theory (DFT) methods [526]. The results showed that all cubane derivatives have positive heats of formation, which increase with increasing number of dinitroamino groups attached to the cube. The detonation performances of polydinitroaminocubanes were estimated by the Kamlet–Jacobs equation, and the results indicated that most cubane derivatives have good detonation performance, better than RDX or HMX.

## 17.2 Properties of Alkyl Dinitramides (Alkyl *N,N*-Dinitramines)

Most alkyl dinitramines are thermally less stable than the nitramines or even the corresponding nitro compounds. They are quite energetic and could be used as rocket propellants if they can be stored at low temperatures. The enthalpies of formation of methyl dinitramine and *n*-butyl dinitramine were determined from the heat of combustion in a calorimeter and the data for ethyl dinitramine and *n*-propyl dinitramine were interpolated from the experimental data (Table 37). The heat of evaporation was measured calorimetrically and used to calculate the enthalpy of formation in the vapor state [20].

## 17.3 Decomposition of Alkyl *N,N*-Dinitramines

Success in the synthesis of the dinitramide salts and the preparation of related alkyldinitramines [527] made it possible to study the thermochemical characteristics and the kinetics of the gas-phase radical thermal decomposition of methyl-dinitramine [528]. It was shown that all alkyldinitramines studied decompose via the radical mechanism with the elimination of the  $\text{NO}_2$  group at the first stage. Therefore,

**Table 37:** Thermochemical properties of alkyldinitramines in the liquid and vapor state at 298 K.

| Compound                                     | $\Delta H_f^{298}(\text{L})$ |             | $\Delta H_{\text{vap}}^{298}$ |          | $\Delta H_f^{298}(\text{G})$ |            | $E_a$    |            |
|----------------------------------------------|------------------------------|-------------|-------------------------------|----------|------------------------------|------------|----------|------------|
|                                              | kJ/mol                       | kcal/mol    | kJ/mol                        | kcal/mol | kJ/mol                       | kcal/mol   | kJ/mol   | kcal/mol   |
| MeN(NO <sub>2</sub> ) <sub>2</sub>           | 1.7 ± 0.8                    | 0.4 ± 0.2   | 52                            | 12.4     | 53.6 ± 1.3                   | 12.8 ± 0.3 | 118 ± 4  | 28.3 ± 1   |
| EtN(NO <sub>2</sub> ) <sub>2</sub>           | —                            | —           | —                             | —        | 25.5                         | 6.1        | 124 ± 2  | 29.7 ± 0.4 |
| <i>n</i> -PrN(NO <sub>2</sub> ) <sub>2</sub> | —                            | —           | —                             | —        | 3.3                          | 0.8        | 130 ± 7  | 31 ± 1.7   |
| <i>n</i> -BuN(NO <sub>2</sub> ) <sub>2</sub> | -80.3 ± 2.5                  | -19.2 ± 0.6 | 63                            | 15       | -17.6 ± 2.9                  | -4.2 ± 0.7 | 124 ± 11 | 29.6 ± 2.6 |

Data source: [20]

if the data on the enthalpies of formation in the gas phase are available, the enthalpies of formation of radicals of the  $\text{RN}^\bullet\text{—NO}_2$  type and the bond dissociation energies of the nearest environment of the  $\text{NNO}_2$  group can be calculated.

In a study of the thermal decomposition of a series of alkyldinitramines, it was shown that the thermal decomposition of *N,N*-dinitramines is homogeneous and unimolecular in the gas phase [529]. The limiting step of the process is the rupture of the  $\text{N—NO}_2$  bond. The activation parameters of the process imply that the dinitramine group is more reactive than the mononitroamine group in thermal decomposition. The energy of dissociation of the  $\text{N—NO}_2$  bond in dinitramines is  $\sim 42\text{ kJ/mol}$  less than in mononitroamines. Nitrogen dioxide did not influence the kinetics of thermal decomposition of dinitroamines.

The activation energy of thermal decomposition of alkyldinitramines  $124 \pm 12\text{ kJ/mol}$  ( $29.7 \pm 3.0\text{ kcal/mol}$ ) makes it possible to calculate the enthalpies of formation of alkyl nitramine radicals which form as the first step of decomposition and the  $\text{RN}^\bullet\text{—NO}_2$  bond dissociation energy values [20].

## 18 Nitroamides, Nitroimides, and Nitrocarbamates

Nitroamides can be prepared by nitration of amides or imides instead of nitration of amines. The two simplest nitroamides are nitrourea and dinitrourea, which are discussed in *Encyclopedia of Liquid Fuels*, chapter “Amides and Imides” and not here in the chapter on nitramines. Representatives for another type of nitroamides are mononitrobiuret and 1,5-dinitrobiuret. The nitroimide with the most widespread used as a propellant ingredient is nitroguanidine (NQ). Nitroguanidine is a nitramine and should have been discussed here in the chapter “Nitramines” along with other nitramines, but somehow was kept in chapter “Amides and Imides,” with its parent amide, guanidine. The same applies for dinitroguanidine and nitroaminoguanidine.

Cyclic *N*-nitroureas such as 1,4-dinitroglycouril (DINGU) and 1,3,4,6-tetranitroglycouril (TNGU) are also described in this volume’s chapter “Amides and Imides.”

Nitrocarbamates derived from nitrocarbamic acid  $\text{O}_2\text{NNHCOOH}$  have been evaluated as energetic additives. The acid itself is unstable, but its esters are stable. Its nitroalkyl esters are under evaluation as energetic plasticizers because they have a positive oxygen balance. These include 2,2,2-trinitroethyl nitrocarbamate,  $(\text{O}_2\text{N})_3\text{CCH}_2\text{O—CO—NH—NO}_2$  [530, 531]. A variety of energetic compounds combining nitroalkyl groups with nitrocarbamate groups were synthesized [532]. The precursors, polynitro alcohols, were obtained by condensation of the readily available starting material nitromethane with small aliphatic aldehydes formaldehyde and glyoxal. The conversion into carbamates was achieved with the reactive chlorosulfonyl isocyanate and a final nitration yielded the polynitrocarbamates.

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# Organometallic Compounds

## 1 Organometallic Compounds

Organometallic compounds contain an organic group, normally an alkyl group, and a light metal that has the potential to increase the heat of combustion of the compound. An organometallic compound is defined as one possessing a direct metal-to-carbon bond. Thus, compounds in which the metal is bonded to the carbon only by oxygen, nitrogen, or sulfur bridges are not included here. Organometallic compounds are not used as the main fuels in rocket engines, but mostly as ignition fluids, due to their pyrophoric properties in air and in the presence of other oxidizers such as LOX. This chapter on organometallic compounds is closely related to the chapter “Alkylboranes” and the chapter “Metals of the Second and Third Row of the Periodic Table of Elements, and their Hydrides” in this set named *Encyclopedia of Liquid Fuels*.

The terms *metalorganic compounds* and *organometallic compounds* have been used interchangeably to denote a class of compounds containing metals or metalloids and organic groups, but organometallic compounds is the preferred term. Also used interchangeably are the terms *metal alkyls*, *alkyl metals*, and *organometals* to describe those compounds. These are compounds obtained through the formation of covalent bonds between a metal (or a metalloid such as silicon) and a carbon atom of an alkyl or aryl group.

The nomenclature of organometallic compounds is not always very consistent, as the name of the metal may be at the beginning or at the end of the word describing the compound, e.g., aluminum triethyl or triethylaluminum. We prefer the latter spelling, and in one word. Organometallic compounds are discussed here in order of the metal's atomic number.

The main applications of some organometallic compounds, such as those of gallium and arsenic, are in the production of semiconductors and photovoltaic cells by doping the silicon matrix with alioelectronic atoms by metal organic chemical vapor deposition (MOCVD). Other organometallic compounds are alkylating agents and are used in organic synthesis to introduce alkyl groups into other compounds. Triethylaluminum or trimethylaluminum complexes with titanium chloride or magnesium chloride are Ziegler–Natta catalysts that are essential for the production of low-density polyethylene and polypropylene and are used for this purpose in industrial quantities.

At one time, tetraethyllead was added to gasoline to improve its octane rating. Tetraethyllead is no longer used for this purpose in land-based vehicles in developed countries, but the lead pollution caused by its decades-long use lingers on our highways and in some waterways. Tetraethyllead is still used as an additive in some grades of aviation gasoline, and for automobiles in some developing countries.

One of the first organometallic compounds available was diethylzinc. It is pyrophoric in air and has been used as an ignition fluid for rocket engines. Many

organometallic compounds have to be handled with extreme care to avoid exposure to oxygen (air) or moisture [1].

Many periodicals and serial publications are exclusively devoted to organometallic compounds: *Organometallic Chemistry*, *Journal of Organometallic Chemistry*, *Organometallic Chemistry in Industry*, *Organometallic Chemistry Reviews*, *Advances in Organometallic Chemistry*, *Applied Organometallic Chemistry*, *Physical Organometallic Chemistry*, and several more.

## 2 Alkylberyllium Compounds

All beryllium compounds are very toxic, and in the case of alkylberyllium compounds, this problem is aggravated by the high volatility of these compounds (compared to beryllium metal or beryllium hydride). If they ignite in air, the resulting beryllium oxide smoke is highly hazardous. Alkylberyllium compounds have only been used as intermediates in the synthesis of other beryllium compounds, mainly beryllium hydride, and they seem to have no other applications. The physical properties of alkylberyllium compounds are summarized in Table 1.

Substitution of hydrogens with methyl groups causes a progressive decrease in the thermal stability of the compound in the order  $\text{Me}_2\text{Be} > (\text{MeCH}_2)_2\text{Be} > (\text{Me}_2\text{CH})_2\text{Be} > (\text{Me}_3\text{C})_2\text{Be}$ . Di-*tert*-butylberyllium,  $(\text{Me}_3\text{C})_2\text{Be}$ , also called beryllium, bis(1,1-dimethylethyl)-, was prepared by reacting  $\text{BeCl}_2 \cdot \text{Et}_2\text{O}$  for 2 h with  $\text{Me}_3\text{CMgCl}$  under nitrogen, and most (not all) of the ether was removed *in vacuo* at room temperature [5]. Vac-

**Table 1:** Physical properties of alkylberyllium compounds.

| Compound                        | CAS RN     | Property             | SI units               | Other units         | References |
|---------------------------------|------------|----------------------|------------------------|---------------------|------------|
| Dimethylberyllium               | 506-63-8   | Melting point        | 473 K (dec.)           | 200 °C (dec.)       | —          |
|                                 |            | Sublimation point    | 473 K (dec.)           | 200 °C (dec.)       | [2]        |
|                                 |            | Vapor pressure       | 80 Pa at 373 K         | 0.6 mm Hg at 100 °C | —          |
|                                 |            | Heat of sublimation  | 98.3 kJ/mol            | 23.5 kcal/mol       | —          |
| Diethylberyllium                | 542-63-2   | Freezing point       | 260–262 K              | –13 to –11 °C       | [2]        |
|                                 |            | Boiling point        | 383 K at 2 kPa         | 110 °C at 15 mm Hg  | [2]        |
|                                 |            |                      | 467 K                  | 194                 | —          |
|                                 |            | Vapor pressure       | 2 kPa at 383 K         | 15 mm Hg at 110 °C  | —          |
| Diisopropylberyllium            | 15721-33-2 | Heat of vaporization | 41.8 kJ/mol            | 10.0 kcal/mol       | —          |
|                                 |            | Freezing point       | 263.6 K                | –9.5 °C             | [3]        |
|                                 |            | Boiling point        | 553 K                  | 280 °C              | —          |
|                                 |            | Vapor pressure       | 23 Pa at 293 K         | 0.17 mm Hg at 20 °C | —          |
| Di- <i>tert</i> -butylberyllium | 7390-83-2  | Freezing point       | 257 K                  | –16 °C              | —          |
|                                 |            | Density              | 0.57 g/cm <sup>3</sup> | —                   | —          |

Additional data from [4]

uum distillation of the residue yielded di-*tert*-butylberyllium, which was non-volatile at room temperature and unaffected by exposure to air for short periods of time. Di-*tert*-butylberyllium,  $(\text{Me}_3\text{C})_2\text{Be}$  was pyrolyzed to give  $\text{BeH}_2$ . Hydrolysis of the crude di-*tert*-butylberyllium with dilute aqueous HCl gave some  $\text{Et}_2\text{O}$  and isobutane, corresponding to an etherate containing 55.4 mol-% di-*tert*-butylberyllium. Pyrolysis of di-*tert*-butylberyllium at 483 K (210 °C) gave a white solid, isobutylene, and a little  $\text{Et}_2\text{O}$ . Hydrolysis of the solid residue with acid indicated that it consisted of 96.3 mol-%  $\text{BeH}_2$ . The reaction of  $\text{BeH}_2$  with  $\text{B}_2\text{H}_6$  at 428 K (155 °C) formed some  $\text{BeB}_2\text{H}_5$ .

Beryllium hydride can be prepared by the pyrolysis of both pure di-*tert*-butylberyllium and its etherate [6]. Pure di-*tert*-butylberyllium is a clear, colorless, mobile liquid with a density of  $0.65 \text{ g/cm}^3$  and a freezing point of 257 K (−16 °C). When freshly prepared, it had a vapor pressure of about 4.7 kPa at 298 K (35 mm Hg at 25 °C). On standing, it undergoes slow decomposition at room temperature with the evolution of isobutene. Di-*tert*-butylberyllium etherate can be prepared from *tert*-butyl-magnesium chloride and  $\text{BeCl}_2$  to give ~50 mol-% of the interim product. Treatment of di-*tert*-butylberyllium etherate with anhydrous  $\text{BeCl}_2$  in  $\text{Et}_2\text{O}$  in an inert nitrogen atmosphere overnight gives a 40% yield of ether-free di-*tert*-butylberyllium. This is a useful intermediate in the synthesis of beryllium hydride.

Thermal decomposition of dimethylberyllium starts at 475 K (202 °C), initially leads to  $\text{Be}(\text{CH}_2)_n$ , and later results [7] in  $\text{Be}_2\text{C}$ , not  $\text{BeH}_2$ . The thermal decomposition of alkylberyllium compounds (other than dimethylberyllium) is of interest for the preparation of beryllium hydride, once actively investigated as a rocket fuel. The potential energy surfaces of unimolecular dissociation reactions for diethylberyllium and di-*tert*-butylberyllium were investigated by computational chemistry [8]. Possible reaction pathways through either the radicals or transition states of the molecules were considered. From a study of the energetics, the transition state pathways arising from concerted molecule fragment eliminations were indicated to be the main dissociation pathways for both molecules. Dimethylberyllium and methylberyllium form a complex salt,  $\text{Li}_2[\text{Be}(\text{CH}_3)_4]$ , with a tetrahedral grouping of methyl groups around the beryllium atom.

### 3 Alkylboron Compounds

Alkylboron compounds are discussed in the chapter “Alkylboranes” in this set, the *Encyclopedia of Liquid Fuels*.

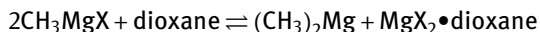
## 4 Alkylmagnesium Compounds

The lower alkylmagnesium compounds dimethylmagnesium,  $\text{Mg}(\text{CH}_3)_2$ , CAS RN [2999-74-8], and diethylmagnesium,  $\text{Mg}(\text{C}_2\text{H}_5)_2$ , CAS RN [557-18-6], are pyrophoric in air and are of interest as ignition fluids in rocket engines and ramjets. The lower normal dialkylmagnesium compounds ( $\text{C}_1\text{--C}_4$ ) and one branched compound (diisopropylmagnesium) have been found to be solids at room temperature and essentially insoluble in both aromatic and aliphatic hydrocarbons. Dimethylmagnesium is a solid that forms polymeric chains where several magnesium atoms are linked via methyl bridges and hydrogen bonding, thus reducing the volatility and melting point of this compound. Diethylmagnesium is a liquid that freezes at 273 K (0 °C). Diethylmagnesium is in equilibrium with its dimer in THF solution.

### 4.1 Preparation of Alkylmagnesium Compounds

The most frequently used organomagnesium compounds are the Grignard reagents  $\text{RMgX}$ , where R is an alkyl or aryl group and X is a halogen, most often bromide but also iodide or chloride. Grignard reagents are widely used in organic synthesis as alkylating agents. They are usually only used in solution (ether solution) and rarely prepared in the pure state. They serve as the precursors for halogen-free magnesium alkyls that can be used as ignition fluids in rocket engines.

Dimethylmagnesium or diethylmagnesium can be prepared by adding at least one equivalent of dioxane to a solution of the alkylmagnesium halide [9]:



The complex of magnesium dihalide and dioxane precipitates as a solid, driving the equilibrium to the right to give the dialkylmagnesium compound, which remains in solution. The complex of magnesium dihalide and dioxane is more stable than the complex of diethylmagnesium and dioxane [10]. In order to remove the dioxane from the diethylmagnesium–dioxane complex, the residue has to be heated at 393 K (120 °C) under a reduced pressure of 1–2 mm Hg for 30 h. The white crystals of diethylmagnesium can then be powdered under a nitrogen atmosphere.

A historical method for the preparation of alkylmagnesium compounds is the reaction of magnesium metal with alkylmercury compounds, but this method is dangerous due to the volatility and toxicity of the alkylmercury compounds used as reagents. It operates at high temperatures, which precludes the synthesis of alkylmagnesium compounds with low thermal stability.

A commercial method for the production of diethylmagnesium is the reaction of magnesium metal with hydrogen and ethylene at 373 K (100 °C) at very high pressures, similar to the synthesis of triethylaluminum.

Higher ( $C_3$ – $C_5$ ) dialkylmagnesium compounds have been prepared by **(1)** direct reaction of magnesium metal with alkyl halides in hydrocarbon media containing a limited amount of a Lewis base such as dimethyl ether, **(2)** reaction of Grignard reagents with stoichiometric amounts of lithium alkyls, and **(3)** reaction of activated anhydrous magnesium chloride with lithium alkyls in hydrocarbon media [11]. Some dialkylmagnesium compounds prepared in media containing ethers can be desolvated from the Lewis base by continuous co-distillation with hydrocarbon solvents.

## 4.2 Physical Properties of Alkylmagnesium Compounds

The physical properties reported for alkylmagnesium compounds by different investigators often vary because of unrecognized etherate contents of the samples. It is difficult to remove the last traces of ether from the compounds. Some compounds decompose before all dioxane can be removed. Di-*n*-butylmagnesium is an infusible solid at room temperature but di-*sec*-butylmagnesium is a liquid. Physical properties of alkylmagnesium compounds are summarized in Table 2.

**Table 2:** Physical properties of alkylmagnesium compounds.

| Compound          | Property       | SI units                | Other units   | References |
|-------------------|----------------|-------------------------|---------------|------------|
| Dimethylmagnesium | Molecular mass | 54.38 g/mol             | 18.389 mol/kg | —          |
|                   | Density        | 0.96 g/cm <sup>3</sup>  | —             | —          |
| Diethylmagnesium  | Molecular mass | 82.43 g/mol             | 12.132 mol/kg | —          |
|                   | Freezing point | 273 K                   | 0 °C          | [10]       |
|                   | Density (XRD)  | 0.964 g/cm <sup>3</sup> | —             | [12]       |

The crystal structure of solid diethylmagnesium determined from XRD powder data is a primitive tetragonal lattice ( $a = 7.294 \text{ \AA}$ ,  $c = 5.338 \text{ \AA}$ ;  $V = 284 \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho = 0.964 \text{ g/cm}^3$ ) with polymeric chains parallel to the  $c$  plane [12].

## 4.3 Chemical Properties of Alkylmagnesium Compounds

Alkylmagnesium compounds are pyrophoric in air and hydrolyze rapidly with water.

Some alkylmagnesium compounds decompose before all dioxane can be removed. Di-*tert*-butylmagnesium undergoes thermal decomposition when desolvation is attempted, even at temperatures well below 373 K (100 °C). The thermal



decomposition of diethylmagnesium leads to magnesium hydride. It starts at 448 K (175 °C) but goes to completion only at temperatures where  $\text{MgH}_2$  starts to decompose.

Thermographic examination of diethylmagnesium gave two endotherms: 563 and 643 K (290 and 370 °C);  $\text{Et}_2\text{Mg}$  first decomposes to  $\text{MgH}_2$  and  $\text{C}_2\text{H}_4$  and further decomposition yields Mg and  $\text{H}_2$ . The pyrolysis of  $(\text{C}_2\text{H}_5)_2\text{Mg}$  under vacuum yielded  $\text{MgH}_2$ , which decomposed endothermically on further heating at 663 K (390 °C), similar to other samples of  $\text{MgH}_2$  that were synthesized by other means [10]. No change in  $\text{Et}_2\text{Mg}$  was noted in the IR spectra at temperatures up to 483 K (210 °C).

#### 4.4 Applications of Alkylmagnesium Compounds

Because diethylmagnesium and most other alkylmagnesium compounds are pyrophoric in air, they have been proposed as ignition fluids for hydrocarbons in air-breathing jet or ramjet engines. Some alkylmagnesium compounds are soluble in jet fuels and make them combustible and re-ignitable in thin air at higher altitudes and less susceptible to flameouts.

Mixtures of dimethylmagnesium, diethylmagnesium, di-*n*-propylmagnesium and diisooctylmagnesium are soluble in aliphatic, cycloaliphatic, and aromatic hydrocarbon solvents without the aid of solubilizing agents [13, 14]. Some diorganomagnesium compounds with straight chain lower alkyl groups of up to four carbon atoms are insoluble by themselves in hydrocarbon solvents and thus require solubilizing agents, which will form a soluble complex. Examples of such solubilizing agents are alkyl-lithium compounds, dialkyl zinc compounds, alkali metal hydrides, and organoaluminum compounds [15]. Solvation involves the use of an ether or another organic Lewis base molecule that associates directly with the magnesium atom, thus yielding a hydrocarbon-soluble complex, but solvation reduces the reactivity and ignition speed. Alkylmagnesium bromides are widely used as Grignard reagents in organic synthetic chemistry.

### 5 Alkylaluminum Compounds

Alkylaluminum compounds, organoaluminum compounds, alkylalanes, are pyrophoric and ignite spontaneously in air or in contact with liquid oxygen and other oxidizers. The spontaneous reactivity and the high heat of combustion and high emissivity of hot aluminum oxide particles makes them valuable ignition fluids. Alkylaluminum compounds have also been proposed for the ignition of solid propellants [16].

Trimethylaluminum and triethylaluminum ignite spontaneously in air or in contact with LOX [17, 18]. In the series trimethylaluminum, triethylaluminum, tri-

*n*-propylaluminum, triisopropylaluminum, all except the last one are dimeric at room temperature [19]. There are numerous summary publications on organoaluminum compounds [20–24].

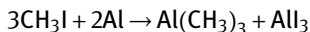
The carbon–aluminum bonds in trialkylaluminum compounds are dynamic, rapidly exchanging intermolecularly in mixtures of two compounds, even under ordinary conditions, and the exchange rate increases with temperature.

## 5.1 Trimethylaluminum

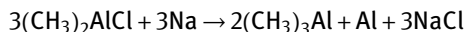
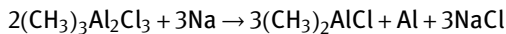
Trimethylaluminum, trimethylalane,  $\text{Al}(\text{CH}_3)_3$ , CAS RN [75-24-1], TMA, exists almost completely as the dimer in the liquid state. If trimethylaluminum existed only as a monomer, its boiling point would be 281 K (8 °C), and if it existed only as the dimer, its boiling point would be 405 K (131.9 °C) [25]. In practice, it boils at 342–345 K at 13.3 kPa (69–72 °C at 100 mm Hg) and melts at 288 K (15 °C). The results indicate that the extent of dissociation of liquid TMA is 0.0047% at 293 K (20 °C), 0.053% at 343 K (70 °C), and 0.32% at 393 K (120 °C).

### 5.1.1 Preparation of Trimethylaluminum

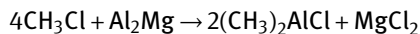
Trimethylaluminum can be prepared by refluxing a mixture of methyl iodide and aluminum powder under an atmosphere of nitrogen or argon. The mixture is refluxed at atmospheric pressure for at least 12 h or until all methyl iodide has reacted. The pressure is then reduced to 13 kPa (100 mm Hg) and the temperature is raised. Methyl iodide boils at 315.5 K (42.4 °C) and trimethylaluminum boils at 342–345 K at 13.3 kPa (69–72 °C at 100 mm Hg), so they can be separated on a long distillation column with 10–20 theoretical plates.



A less direct but more economical process for preparation of trimethylaluminum is by way of dimethylaluminum sesquichloride. Alkylaluminum sesquihalide products from reactions of aluminum with alkyl halides can be converted to dialkylaluminum halide or trialkylaluminum by treatment with active metals such as sodium or magnesium. For example, dimethylaluminum chloride or trimethylaluminum can be produced from methylaluminum sesquichloride by sodium reduction:



A magnesium–aluminum alloy can provide a reducing function concurrently with the reaction between aluminum and the alkyl halide:



The sesquichloride reduction process is a very economical route for the production of trimethylaluminum.

### 5.1.2 Physical Properties of Trimethylaluminum

Physical properties of trimethylaluminum are summarized in Table 3.

**Table 3:** Physical properties of trimethylaluminum.

| Property       | SI units                                  | Other units           | References |
|----------------|-------------------------------------------|-----------------------|------------|
| Molecular mass | 72.09 g/mol                               | 13.87 mol/kg          | —          |
| Freezing point | 288 K                                     | 15 °C                 | [19]       |
| Boiling point  | 342–345 K at 13.3 kPa                     | 69–72 °C at 100 mm Hg | [18]       |
|                | 400 K at 101.3 kPa                        | 127 °C at 1 atm       | [23]       |
| Density        | 0.752 g/cm <sup>3</sup> at 293 K = 20 °C  | —                     | [19]       |
|                | 0.7478 g/cm <sup>3</sup> at 298 K = 25 °C | —                     | [23]       |

#### 5.1.2.1 Molecular Structure of Trimethylaluminum

Trimethylaluminum exists almost completely as the dimer. The dimerization is less pronounced with triethylaluminum. The existence of the trimethylaluminum dimer has aroused considerable interest and some dispute among chemists specializing in molecular structure theory [26]. The dispute about the monomer–dimer equilibrium of trimethylaluminum is reflected in the detail in which they have been studied, yet there is considerable apparent disagreement in the measured thermodynamic constants of the equilibrium [27]. NMR spectroscopy has been reasonably successful in investigating the details of the monomer–dimer equilibrium of trimethylaluminum. The spectrum showed a sharp singlet at room temperature with a chemical shift  $\tau$  of 10.3, but as the temperature was reduced the line broadened, and by 213 K (–60 °C) it had split into two lines at 9.50 and 10.65. At room temperature, all the methyl groups are equivalent at the time scale of NMR spectroscopy ( $10^{-3}$  s), and only at a lower temperature can a clear distinction be made between the terminal and bridge groups. The average lifetime of each configuration was calculated and used to determine the unimolecular rate constant for the rate-determining step in alkyl group exchange reactions. An Arrhenius plot of the rate constants over the temperature range 263–213 K (–10 to –60 °C) gave an activation energy of 65.3 kJ/mol (15.6 kcal/mol) for this process. The overall activation energy,  $E_{\text{act}} = 59.0$  kJ/mol = 14.1 kcal/mol, was considered to be

consistent with the value of 64.4 kJ/mol (15.4 kcal/mol) for the dimer. NMR studies have also been made of higher alkylaluminum compounds, and these reached the same general conclusions about rapid alkyl group interchange at room temperature. Electron diffraction determinations were in satisfactory agreement with an ethane structure. However, this structure was at one time considered unlikely for many reasons: **(1)** it differs from the bridge structures of the related aluminum halides  $\text{Al}_2\text{X}_6$ , aluminum dimethyl-halides  $\text{Al}_2\text{Me}_4\text{X}_2$ , and boron and (probably) aluminum hydrides; **(2)** it could not be accounted for by any valence theory that existed at that time, as no forces were available to join the two  $\text{AlMe}_3$  molecules; **(3)** it requires a shorter interatomic distance (about 2.20 Å) between the equally charged Al atoms than that of a covalent Al—Al linkage (2.48 Å); **(4)** the instability (non-existence) of a similar molecule, the boron trimethyl dimer, could not be explained.

The degree of dissociation and the equilibrium as a function of temperature can be determined by measuring the heat of dilution [28]. The enthalpy of dissociation  $\Delta H^\circ_{\text{d}}$  of liquid trimethylaluminum dimer is  $81.2 \pm 1.2$  kJ/mol of dimer ( $19.40 \pm 0.30$  kcal/mol of dimer), and the enthalpy of dissociation  $\Delta H^\circ_{\text{d}}$  of liquid triethylaluminum dimer is 70.8 kJ/mol of dimer (16.93 kcal/mol of dimer) [25]. The  $\Delta H^\circ_{\text{d}}$  of gaseous triethylaluminum was derived as  $76.0 \pm 1.2$  kJ/mol of dimer ( $18.17 \pm 0.30$  kcal/mol of dimer). The heat of dissociation of the dimer depends on the type of solvent used for the experiment [29]. Similar studies were performed on the dimerization of triisobutylaluminum [30]. Triisobutylaluminum, a bulkier molecule, is only 39.4% associated at 283 K (10 °C), and only 16.4% associated at 313 K (40 °C).

A gas-phase electron diffraction investigation of the molecular structures of trimethylaluminum monomer and dimer showed that gaseous trimethylaluminum consists of monomeric and dimeric species in a pressure- and temperature-dependent equilibrium [31]. The equilibrium constant for the reaction is given by

$$\log = K_{\text{D}}(-4457/T) + 9.44$$

Consequently, trimethylaluminum gas at 333 K and 4 kPa (60 °C and 30 mm Hg) is more than 97% dimers, while the gas at 488 K (215 °C) and the same pressure is more than 96% monomers.

The trimethylaluminum dimer has a bridge structure with a skeletal symmetry of  $D_{2h}$  within the accuracy of a structural determination of single crystals by XRD [32]. The atomic distance Al—C in each bridge bond is 2.24 Å, whereas the Al—C bonds for the exterior methyl groups are each 1.99 Å long. The bridge angle  $\angle \text{Al—C—Al}$  is 70°, and the exterior angle  $\angle \text{C—Al—C}$  is 124°. It was shown that a simple model provides the right order of magnitude for the heat of dimerization, and it indicated the relative importance of the Al—C and Al—Al bonds. It was suggested that the sharp bridge angle required for good bridge bonding leads to metal–metal repulsion, which should increase as the size of the metal increases. This probably plays a role in the instability and molecular structure of polymers of the heavier trialkylmetal compounds.

### 5.1.2.2 Thermodynamic Properties of Trimethylaluminum

The heat of reaction of liquid trimethylaluminum with acetic acid in toluene to give  $\text{Al}(\text{OCOCH}_3)_3$  and  $\text{CH}_4$  was measured in a rotating bomb calorimeter [33, 34]. Subsequently, the heat of reaction of  $\text{Al}(\text{OCOCH}_3)_3$  with aqueous 4.36M HCl was measured. These data were combined and used to calculate the enthalpy of formation of liquid trimethylaluminum,  $\Delta H_f^\circ = -151.0 \pm 6.7 \text{ kJ/mol} = -36.1 \pm 1.6 \text{ kcal/mol}$ , and that of crystalline  $\text{Al}(\text{OCOCH}_3)_3$ ,  $\Delta H_f^\circ = -1890 \pm 3 \text{ kJ/mol} = -451.8 \pm 0.8 \text{ kcal/mol}$ . The mean bond dissociation energy was calculated as  $D(\text{Al}-\text{Me}) = 270 \pm 8 \text{ kJ/mol} = 64.5 \pm 2.0 \text{ kcal/mol}$ . Other data for the enthalpy of formation of trimethylaluminum listed in the literature are  $-144.4 \pm 11.1$ ,  $-120.1 \pm 10.0 \text{ kJ/mol}$ , and  $-151.9 \text{ kJ/mol}$ , indicating wide scatter [35].

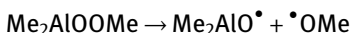
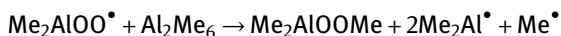
### 5.1.3 Chemical Properties of Trimethylaluminum

#### 5.1.3.1 Oxidation of Trimethylaluminum

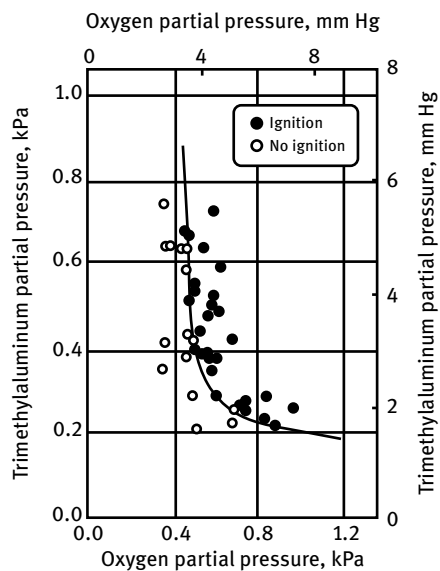
Trimethylaluminum reacts rapidly with diluted oxygen at 298 K (25 °C) to give a non-peroxidic solid and methane [36]. This reaction can induce selective higher hydrocarbon oxidation. The lower flammability limit of trialkylaluminum is raised by dilution with hydrocarbons. Methane and hydrogen were the only gaseous products found during the slow oxidation of trimethylaluminum. The marked dependence of the ignition limit on the surface: volume ratio is an indication of the radical chain nature of the ignition. Using the observed temperature variation, a plot of  $\log(AT)$  against the reciprocal absolute temperature, rough values of the activation energies of two of the reactions in the mechanism could be obtained. Studies of the spontaneous ignition of mixtures of trimethylaluminum and oxygen have shown that the ignition boundary is defined by the expression

$$\frac{1}{p_{\text{Me}_6\text{Al}_2}} = A - \frac{B}{p_{\text{O}_2}}$$

where  $p_{\text{Al}_2\text{Me}_6}$  and  $p_{\text{O}_2}$  are the partial pressures of the reactants. The values of A and B are only slightly affected by temperature and by added inert gases. The main products formed during ignition are hydrogen, carbon monoxide, methane, acetylene, and a complex, gray, aluminum-containing solid. The kinetic and analytical findings can be accounted for in terms of an isothermal free-radical chain mechanism. This mechanism correctly predicted the effects of reactant pressures, temperature, and helium but failed to account quantitatively for the influence of the surface: volume ratio. As the ignition limit is approached from the slow combustion region, the branching reactions



appear to become important and lead to ignition [37]. Cinephotography of the gases in the reaction vessel showed that the delay preceding ignition is less than 0.1 s and that propagation of the explosion throughout the mixture is complete in less than 0.015 s. Experiments were performed in a Pyrex vessel at 298 K (25 °C) with a volume of 143 cm<sup>3</sup> and a surface : volume ratio of 1.18 cm<sup>-1</sup>. Figure 1 shows that the partial pressures of the two reactants at the ignition boundary are related by an expression of the type shown above.

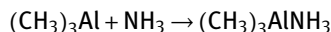


**Figure 1:** Ignition boundary for trimethylaluminum/oxygen mixtures (Republished and modified from [37], with the permission of ©1966 The Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.)

The variation in the limiting ignition pressure with the mol fraction of oxygen showed a minimum at an oxygen mol fraction of 0.63. The solid products of the combustion of trimethylaluminum do not affect the rate or course of subsequent combustion, which appears to involve the homogeneous decomposition of a transient peroxide [38]. This latter reaction produces free radicals capable of inducing the oxidation of hydrocarbons at ambient temperatures. In the combustion of certain metal alkyls, the rate-determining steps are heterogeneous. The relative importance of homogeneous and heterogeneous rate-determining processes appears to be a function of the electron deficiency of the metal alkyl.

### 5.1.3.2 Reactions with Lewis Acids

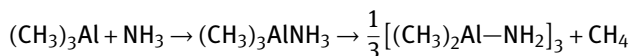
Trimethylaluminum forms an adduct with ammonia that may also be used as an ingredient in rocket propellants:



The adduct can be used for the deposition of aluminum nitride films in the construction of integrated circuits by MOCVD. Aluminum nitride is an electric insulator but has good thermal conductivity.

Solution calorimetric techniques in hexane have been used to determine the enthalpies of formation of a number of trimethylaluminum Lewis adducts with phosphorus, nitrogen, and oxygen electron donors [39]. The enthalpies of the exothermic reactions (in kJ/mol, followed by kcal/mol in parentheses) were:  $\text{N}(\text{CH}_3)_3$   $-125.3 \pm 0.8$  ( $-29.96 \pm 0.19$ );  $\text{HN}(\text{CH}_3)_2$   $-129.0 \pm 1.1$  ( $-30.84 \pm 0.26$ );  $\text{H}_2\text{NCH}_3$   $-125.6 \pm 1.3$  ( $-30.02 \pm 0.31$ );  $\text{NH}_3$   $-115.3 \pm 1.0$  ( $-27.55 \pm 0.25$ ). There does not appear to be a clear trend in the heat of reaction with a decreasing number of methyl groups in the amine. For the trimethylaluminum/trimethylamine and trimethylaluminum/dimethyl ether systems, appropriate vapor-phase data were used with the calorimetric data to calculate the gas-phase enthalpy. The gas-phase enthalpy of formation of  $(\text{CH}_3)_3\text{Al} \cdot \text{N}(\text{CH}_3)_3(\text{G})$  was  $-135.1 \pm 1.2$  kJ/mol ( $-32.29 \pm 0.29$  kcal/mol).

Partial decomposition of  $(\text{CH}_3)_3\text{Al} \cdot \text{NH}_3$  leads to a cyclic  $[(\text{CH}_3)_2\text{Al}-\text{NH}_2]_3$  trimer along with the release of methane. The thermodynamics, kinetics, and mechanism of the reactions



in homogeneous solution were investigated by solution calorimetry, DSC, and  $^1\text{H}$  NMR rate measurements [40]. The enthalpy for complex formation from  $\text{NH}_3$  and monomeric  $(\text{CH}_3)_3\text{Al}$  in benzene was  $-93$  kJ/mol. The observed  $\Delta H$  for methane loss from the complex was  $-82.2$  kJ/mol.

Adducts of trimethylaluminum may be formed not only as a Lewis adduct by electron transfer, but also through hydrogen bond formation with additional ammonia molecules [41]. The second product is the result of the hydrogen bonding of a second  $\text{NH}_3$  molecule to the  $(\text{CH}_3)_3\text{Al} : \text{NH}_3$  adduct, and can be written as  $(\text{CH}_3)_3\text{Al} : \text{NH}_3 \cdots \text{NH}_3$ . The binding energy of this hydrogen-bonded adduct was calculated to be  $112$  kJ/mol ( $26.8$  kcal/mol).

### 5.1.3.3 Thermal Decomposition of Trimethylaluminum

The thermal decomposition of gaseous trimethylaluminum is of interest for chemical vapor deposition (CVD) of metallic aluminum thin films, but not so much for the use of trimethylaluminum as an ignition fluid in rockets. The thermal decomposition of gaseous trimethylaluminum in the absence of hydrogen was nearly 94% homogeneous and of kinetic order  $3/2$  over the initial pressure range from  $1.3$  to  $11.3$  kPa ( $10$ – $85$  mm Hg), as measured at room temperature prior to heating the sample [42]. The reaction products consisted mostly of methane and to a lesser extent ethane, ethylene, hydrogen, and a solid deposit on the walls of the reaction vessel. A reaction mechanism involving free methyl radicals was proposed. The apparent energy of activation calculated on this basis was estimated to be  $188$  kJ/mol ( $45$  kcal/mol), in agreement

with experimentally determined data. The high ratio of methane produced to alkyl decomposed suggested that trimethylaluminum in the vapor state at room temperature must consist of at least tetrameric molecular complexes. In the presence of hydrogen, both the decomposition rate and the energy of activation were reduced as compared to the decomposition of the pure alkyl, a puzzling effect for which no satisfactory explanation could be offered. Photochemically, the addition of hydrogen seemed to have little effect on the overall decomposition, but it enhanced the relative amount of methane slightly.

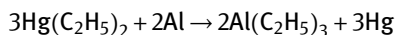
The pyrolysis of trimethylaluminum results in the splitting of methane with intermediates in the form of methylene and methine compounds, all ending up as aluminum carbide [43]. A vapor-phase mechanism for the decomposition of trimethylaluminum (TMA) used in an Al CVD was investigated by IR spectrometry [44]. In pyrolysis, the annihilation of TMA was a first-order reaction and  $\cdot\text{CH}_3$  free radicals were generated. The activation energy of the annihilation was about 6.4 kJ/mol (0.4 eV). The generation mechanism of  $\text{CH}_4$  from the intermediates was investigated quantitatively. It was suggested that carbon contamination can be reduced by using an  $\text{H}_2$  carrier gas, since the  $\cdot\text{CH}_3$  radical that causes such contamination is changed into  $\text{CH}_4$  by hydrogenation. In photolysis, the annihilation of TMA was a first-order reaction and  $\text{C}_2\text{H}_6$  was generated by the recombination of two  $\text{CH}_3$  groups. A reduction in carbon contamination was due to the generation of  $\text{C}_2\text{H}_6$ .

## 5.2 Triethylaluminum

Triethylaluminum, also known as triethylalane, aluminum triethyl,  $(\text{C}_2\text{H}_5)_3\text{Al}$ , CAS RN [97-93-8], TEA,  $\text{AlEt}_3$ , has been used for a long time as a hypergolic slug for the ignition of LOX/kerosene engines such as the engines in the SATURN-IC or SATURN-V first stage or LOX/ $\text{LH}_2$  engines for static rocket engine development tests [45]. Triethylaluminum in mixture with triethylborane is currently used as an ignition fluid in LOX/RP-1 engines (FALCON-9, FALCON Heavy). The name of the mixture is often abbreviated to TEA/TEB.

### 5.2.1 Production of Triethylaluminum

Historically, triethylaluminum has been made in small quantities by the reaction of diethylmercury with aluminum metal in a closed bomb heated at 383 K for 30 h:

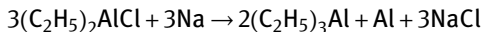
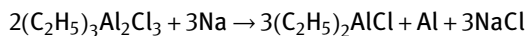


The same method can be used for preparation of tri-*n*-propylaluminum.

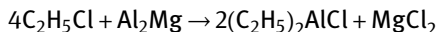
An alternate process for preparation of triethylaluminum is to use diethylaluminum sesquichloride. Alkylaluminum sesquihalide products from aluminum reactions with alkyl halides can be converted to the dialkylaluminum halide or



trialkylaluminum by treatment with active metals such as sodium or magnesium. For example, diethylaluminum chloride or triethylaluminum can be produced from ethylaluminum sesquichloride by sodium reduction:



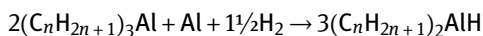
A magnesium-aluminum alloy can provide the reduction simultaneously with the reaction between aluminum and the alkyl halide:



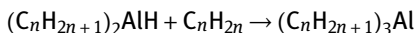
The production of triethylaluminum in industrial quantities is now achieved by the high-pressure reaction of aluminum metal powder, ethylene, and hydrogen [46, 47]. This reaction is also called hydroalumination of olefins. Diethylaluminum hydride is an intermediate product in this process. It can be converted to triethylaluminum in a secondary treatment with ethylene.

Other than with ethylene, the high-pressure synthesis of trialkylaluminums can be done with higher  $\alpha$ -alkenes. The preparation of trialkylaluminums or dialkylaluminum hydrides in which the alkyl radicals are primary alkyl radicals from metallic aluminum, hydrogen, and olefins is well known. However, it has been repeatedly stressed in the literature that the reaction operates only with  $\alpha$ -olefins, and that it does not work with olefins in which the double bond is in a position other than the terminal position. One of the articles of interest in this respect is [48].

There are two variants of the previously described synthesis of trialkylaluminum and dialkylaluminum hydrides from aluminum metal, hydrogen, and alkenes: **(1)** a one-step synthesis where all three reactants are present at the same time in the reactor, which is favorably applicable to triisobutylaluminum [49], and **(2)** a two-step process in which three mols of dialkylaluminum hydride are formed from two mols of trialkylaluminum in the absence of any alkene:



and the product is then reacted with more alkene in the second step:



The latter method works very well for triethylaluminum [46, 47, 50–52].

### 5.2.2 Physical Properties of Triethylaluminum

Physical properties of triethylaluminum are summarized in Table 4.

**Table 4:** Physical properties of triethylaluminum.

|                                | SI units                               | Other units                              | References    |
|--------------------------------|----------------------------------------|------------------------------------------|---------------|
| Molecular mass                 | 114.17 g/mol                           | 8.7589 mol/kg                            |               |
| Freezing point                 | 220.6 K                                | −52.5 °C                                 | [19]          |
| Boiling point                  | 467 K                                  | 194 °C                                   | CAS Scifinder |
|                                | 321–329 K at 0.13 Pa                   | 48–56 °C at 0.001 mm Hg                  | [46]          |
|                                | 348–353 K at 0.3 kPa                   | 75–80 °C at 2.5 mm Hg                    | [43, 47]      |
|                                | 401–403 K at 6.7 kPa                   | 128–130 °C at 50 mm Hg                   | —             |
| Density                        | 0.837 g/cm <sup>3</sup> at 293 K       | —                                        | [19]          |
|                                | 0.8324 g/cm <sup>3</sup> at 298 K      | —                                        | [23]          |
| Specific heat                  | 2.09 J g <sup>−1</sup> K <sup>−1</sup> | 0.5 cal g <sup>−1</sup> °C <sup>−1</sup> | —             |
| Standard enthalpy of formation | −146 kJ/mol                            | −35 kcal/mol                             | —             |
|                                | −152.7 ± 21 kJ/mol                     | −36.5 ± 5 kcal/mol                       | [33, 34]      |
| Heat of vaporization           | 54.4 kJ/mol                            | 13 kcal/mol                              | —             |
| Refractive index               | 1.480 at 589.3 nm and 6.5 °C           | —                                        | CAS SciFinder |

The boiling point of triethylaluminum at sea-level pressure was reported as 463–468 K (190–195 °C), but one must anticipate partial decomposition at that temperature. It is better to distill triethylaluminum under vacuum, where it will boil at 321–329 K at 0.13 Pa (48–56 °C at 0.001 mm Hg), 348–353 K at 0.3 kPa (75–80 °C at 2.5 mm Hg), or 401–403 K at 6.7 kPa (128–130 °C at 50 mm Hg).

#### 5.2.2.1 Vapor Pressure of Triethylaluminum

At room temperature, triethylaluminum exists partially in the dimeric form. With increasing temperature, the dimer dissociates and forms the monomer as a vapor. Vapor pressure and vapor density measurements thus reflect both a physical and a chemical process.

Vapor pressure measurements from different sources are summarized in Table 5. This table contains the constants A and B, which can be used to calculate the vapor pressure as a function of temperature by the equation

$$\log P = A - \frac{B}{T}$$

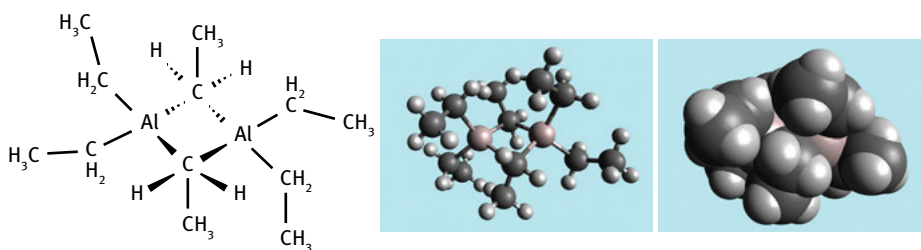
where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin. Some of the heat of dissociation is included in the observed heat of vaporization. See also [53, 54].

**Table 5:** Vapor pressure and heat of vaporization of triethylaluminum.

| A      | B      | $\Delta H_{\text{vap}}$ |            | Trouton constant                      | Temperature range |         | References |
|--------|--------|-------------------------|------------|---------------------------------------|-------------------|---------|------------|
|        |        | kJ/mol                  | kcal/mol   | cal mol <sup>-1</sup> K <sup>-1</sup> | K                 | °C      |            |
| 10.85  | 3613   | 69.0 ± 2.1              | 16.5 ± 0.5 | 35.9                                  | 333–393           | 60–120  | [55]       |
| 10.784 | 3625   | 69.0 ± 1.7              | 16.6 ± 0.4 | 36.2                                  | 383–413           | 110–140 | [56]       |
| 10.152 | 3382   | 64.9                    | 15.5       | 33.3                                  | 328–403           | 55–130  | [30]       |
| 9.414  | 3036.8 | 60.2                    | 14.4       | —                                     | —                 | —       | [57]       |

### 5.2.2.2 Molecular Structure of Triethylaluminum

At room temperature, triethylaluminum exists partially in the dimeric form. With increasing temperature, the dimer dissociates and forms the monomer as a vapor. The alkyl bridges holding the dimer together are considerably weaker than hydride bridges. Dimeric trialkylaluminum compounds are in equilibrium with their monomers. The molecular structure of triethylaluminum is illustrated in Figure 2.

**Figure 2:** Molecular structure of triethylaluminum dimer.

The heat of dissociation of triethylaluminum dimer in a solution of *n*-hexadecane was estimated as 70.7 ± 0.8 kJ/mol dimer (16.9 ± 0.2 kcal/mol dimer) [28]. Unfortunately, the experimental conditions were such that there may have been a contribution from the heat of vaporization of the triethylaluminum (16.5 kcal/mol of vapor) to the measured heat of dissociation.

The heat of dissociation of triethylaluminum dimer in the liquid phase was derived from vaporization studies as being in the range of 12.5 ± 2.0 kcal/mol of dimer, while extreme limits proposed by other investigators are in the range 8–14 kcal/mol of dimer [27, 55]. Kinetic studies on the addition reaction to alkenes are only compatible with the lower limit of this range, and both are inconsistent with the only experimental measure of this parameter, i.e., 70.7 kJ/mol (16.9 kcal/mol) of dimer, by Smith [28].

The <sup>27</sup>Al NMR signal of triethylaluminum is shifted significantly to lower field as the fraction of the monomeric form increases [58]. The <sup>27</sup>Al NMR chemical shifts of Al<sub>2</sub>Et<sub>6</sub> and AlEt<sub>3</sub> were estimated as 153 ± 2 and 265 ± 10 ppm, respectively. Using these

values, thermodynamic data were calculated for the dissociation of the  $\text{Al}_2\text{Et}_6$  dimer. Alkylaluminum alkoxides generally form trimers or higher molecular aggregates.

### 5.2.2.3 Thermodynamic Properties of Triethylaluminum

The amount of thermodynamic information available from the literature on organoaluminum compounds is scant, and what is available is often contradictory (Table 6). These variations reflect the extreme difficulties involved in handling the reactive materials, obtaining pure samples, and ensuring the complete reaction occurs in a reaction calorimeter.

**Table 6:** Enthalpy of formation of triethylaluminum.

| Enthalpy of formation |             | References |
|-----------------------|-------------|------------|
| kJ/mol                | kcal/mol    |            |
| -152.7                | -36.5       | [59]       |
| -173.2                | -41.4       | [60]       |
| -217.1                | -51.9       | [57]       |
| -235.4                | -56.5       | [61]       |
| -187.3 ± 5.1          | -44.8 ± 1.2 | [35]       |

The standard enthalpy of formation for triethylaluminum listed in PEPCODED.DAT under ingredient number 1466 (+137.2 kJ/mol = +455 cal/g = +32.8 kcal/mol) is in error [62]. Most likely, a minus sign should be added, but even then the value is outside the range of all other values reported in the literature.

The heats of combustion of triethylaluminum, diisobutylaluminum hydride, and diethylaluminum hydride were determined at an oxygen pressure of 25 atm in a combustion bomb and calculated as  $5114 \pm 9$ ,  $6299 \pm 16$ , and  $3676$  kJ/mol ( $1222.3 \pm 2.1$ ,  $1505.5 \pm 3.9$ , and  $878.7$  kcal/mol), respectively [57]. The enthalpies of formation of triethylaluminum, diisobutylaluminum hydride, and diethylaluminum hydride derived from their heats of combustion were -217.1, -402, and -307 kJ/mol (-51.9, -96.1, and -73.5 kcal/mol), respectively. The latent heats of evaporation of  $\text{Et}_3\text{Al}$ , iso- $\text{Bu}_2\text{AlH}$ , and  $\text{Et}_2\text{AlH}$  were 60.2, 35.6, and 46.9 kJ/mol (14.4, 8.5, and 11.2 kcal/mol), respectively.

Enthalpy of formation data on 450 organometallic compounds of main group I–VI metals and metalloids are summarized in [63]. The average dissociation energies of 115 types of chemical bonds formed by non-transition elements in their organic compounds were calculated from the enthalpies of formation and correlated with their position in the periodic table of elements.

The standard enthalpy of formation of liquid triethylaluminum  $\text{AlEt}_3$  was determined from the experimental enthalpy of reaction of  $\text{AlEt}_3$  with acetylacetone

in toluene [35]. The resulting enthalpy of formation of liquid  $\text{AlEt}_3$  in equilibrium at room temperature was  $-187.3 \pm 5.1 \text{ kJ/mol}$  ( $-44.8 \pm 1.2 \text{ kcal/mol}$ ) of monomer. The result was used to assess the reliability of available thermochemical data for other trialkylaluminum compounds.

In order to resolve conflicts between published heats of formation of alkylaluminum compounds and related compounds, a one-constant equation (the *displacement rule*) was derived that relates the  $\Delta H_f^\circ(\text{M}, \text{g})$  ( $\text{M}$  = monomer) of primary alkyls (other than methyl) of any element to the  $\Delta H_f^\circ(\text{g})$  of the alkane  $\text{RH}$  [64]. This rule, which permits the calculation of the  $\Delta H_f^\circ$  values of all the primary alkyls (other than methyl) of an element, including mixed alkyls and “iso”-alkyls, yields values that are practically identical to those given by the Allen bond-energy scheme. It was shown that, for many metals, the rule can be extended to include methyl compounds. Values of  $\Delta H_f^\circ(\text{G})$  and  $\Delta H_f^\circ(\text{L})$  were tabulated for a number of primary alkyls of Zn, Hg, B, Al, and Sn. For straight-chain R groups with  $\geq 2$  C atoms, the results were well represented by equations of the form  $-\Delta H_f^\circ(298 \text{ K}) = A + B(N - 2) \text{ kcal/gformula weight}$  (where  $N$  is the number of C atoms). For the gaseous monomers, the constants A and B were as follows:  $\text{R}_2\text{Zn}$ : -8.3, 9.86;  $\text{R}_2\text{Hg}$ : -17.8, 9.86;  $\text{R}_2\text{AlH}$ : 11.1, 9.86;  $\text{R}_3\text{B}$ : 36.4, 14.79;  $\text{R}_3\text{Al}$ : 27.9, 14.79, respectively. See also [65].

### 5.2.3 Chemical Properties of Triethylaluminum

Triethylaluminum and diethylaluminum autoignite spontaneously in air and react vigorously with water. These compounds must be stored in breakproof containers hermetically sealed with an inert gas pad of dry nitrogen or argon.

#### 5.2.3.1 Reactions of Triethylaluminum

The most important reaction of triethylaluminum is that with titanium tetrachloride and zinc chloride to form a catalyst that allows low-pressure polymerization of ethylene or propylene into polyethylene and polypropylene. Other reactions of triethylaluminum with ethylene lead to oligomerization, initially to 1-butene but (in the absence of catalytic trace metals) eventually to higher alkylaluminums that can be converted by hydrolysis or oxidation to  $n$ -alkanols and alkylcarboxy (fatty) acids, which have many industrial uses. Alkylaluminum compounds form complexes with non-protic Lewis base solvents such as ethers or tertiary amines.

#### Oxidation of Triethylaluminum

The amount of oxygen consumed in the first stage of the oxidation of triethylaluminum in air is only about one-third of the stoichiometrically possible amount [66]. Thus, this reaction corresponds to the oxidation of only one of the three alkyl groups in the molecule. A graph of the composition of the gases leaving the reaction chamber shows that all oxygen is consumed up to a certain point, the same point where the rate of

ethane and hydrogen evolution maximizes. Diethyl monoethoxyaluminum reacts with oxygen much more slowly.

### Ignition of Triethylaluminum

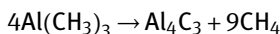
Triethylaluminum ignites spontaneously in air or in contact with LOX [17, 18, 67].

### Hydrolysis of Triethylaluminum

Because the reaction between triethylaluminum and water is so violent, this reaction has even been considered for the propulsion of underwater ramjets.

#### 5.2.3.2 Thermal Decomposition of Triethylaluminum

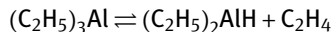
The pyrolysis of metal alkyls proceeds primarily as a free radical reaction. If the alkyl group has more than one carbon atom, the resulting free alkyl radical can disproportionate into an alkane and an alkene. Some metal alkyls, for example ethylsodium and diethylmagnesium, do not decompose to the free metal but to a metal hydride. The pyrolysis of triethylaluminum vapor at 523 K (250 °C) [68] gave 0.639 H<sub>2</sub>, 0.22 C<sub>2</sub>H<sub>4</sub>, 0.056 C<sub>2</sub>H<sub>6</sub>, and 0.513 C<sub>4</sub>H<sub>8</sub>. The pyrolysis of trimethylaluminum proceeded quite differently, and the overall reaction was



The kinetics of the thermal decomposition of gaseous triethylaluminum were studied in static systems over the temperature range of 435–465 K (162–192 °C), and the extent of the reaction was monitored by complete chemical analysis of the products [69, 70]. At various stages of the reaction, the following species were observed: C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, 1-C<sub>4</sub>H<sub>8</sub>, 2-C<sub>4</sub>H<sub>8</sub>, H<sub>2</sub>, metallic Al, and lesser amounts of CH<sub>4</sub>, C<sub>4</sub>H<sub>10</sub>, and C<sub>6</sub>H<sub>12</sub>. The best fit to the kinetic data in terms of the disappearance of aluminum–ethyl bonds was to a first-order heterogeneous reaction with the rate expression

$$k_1 = 10^8 \cdot e^{-29000/RT}.$$

A mechanism involving concurrent molecular and free radical processes was proposed for the pyrolysis of AlEt<sub>3</sub>. There may be an equilibrium for the system



The pyrolysis of alkylaluminum compounds other than trimethylaluminum can be used for the chemical vapor deposition of thin aluminum layers on substrates that cannot withstand the higher temperatures of aluminum vacuum deposition [71, 72].

#### 5.2.3.3 Analysis of Triethylaluminum

Alkylaluminum compounds can be analyzed by gas chromatography [73]. Triethylaluminum or diethylaluminum hydride or triethylborane, liquids that are frequently used as ignition fluids for non-hypergolic bipropellant combinations or solid propellants,

can be analyzed by spectroscopic methods [74]. Diethylaluminum can be assayed by a gas volumetric method [75]. See also [76].

#### 5.2.4 Handling of Triethylaluminum

Because triethylaluminum and other trialkylaluminum compounds are pyrophoric, ignite spontaneously in air, and react vigorously with water, the handling of triethylaluminum requires special precautions and careful training of launch site operators. Because most dialkyl- and trialkylaluminum compounds, in particular triethylaluminum, are pyrophoric in air, they can be handled only under an inert gas (argon, nitrogen) [77]. Argon is preferred because it is heavier than air and it is less likely that air will intrude into the apparatus when the purge gas flow rate is too slow. Transport and storage containers should have two outlets, one for pressurization with an inert gas and the other a dip tube for withdrawal of liquid.

Additional information is available from the manufacturer's literature and chemical process safety organizations [78]. The cited reference is a CD containing 1000 papers and 20000 pages of process safety information, with presentations from the Loss Prevention Symposia, sponsored by AIChE's Safety and Health Division, from 1967 to 2003, and CCPS conference and workshops from 1987 through 2003, including papers that were delivered but not published elsewhere. This CD-ROM is fully indexed, allowing users to run searches based on author, title, subject, or keyword.

Alkylaluminum compounds with alkyl groups of  $C_4$  and below ignite immediately on exposure to air unless they are diluted with a hydrocarbon solvent to concentrations below 10–20% [1]. Even these solutions may ignite on prolonged exposure to air because of exothermic autoxidation, which occurs rapidly if the solutions are spilled [79]. For  $C_4$  and below, 10 to 20 mass-% of alkylaluminum is generally non-pyrophoric. For  $C_5$  and up, the concentration can be increased to 20–30%.

The ignition characteristics of a combustor and gas generator for a LOX/kerosene liquid rocket engine were determined experimentally through a series of combustion tests of a sub-scale engine combustor and gas generator [80]. The operation of a gas-torch ignitor based on gaseous methane and gaseous oxygen was compared with hypergolic ignition using triethylaluminum. The gas-torch ignitor performed well at igniting propellants in the sub-scale liquid rocket engine combustor and gas generator. It was noted that the ignition delay was also affected by the level of nitrogen in the combustion chamber.

A hazard ranking score (HRS) was developed for hazardous chemicals. This was a composite index based on autoignition temperature, flammable range in air, the NFPA parameter, the ionization potential parameter (for ease of detection), and TNT equivalency [81]. Chemicals were ranked on a scale from 0 (safe) to 100 (extremely hazardous). The NFPA diamond summarizes the hazard of chemicals through four characteristics: health, flammability, instability or reactivity, and special hazard. On

a scale from 0 to 100, triethylaluminum received a hazard ranking score of 57.8. For comparison, UDMH received an HRS of 42.9 and pentaborane was ranked at 64.4.

#### 5.2.4.1 Triethylaluminum Accidents

Experiments were conducted in an effort to explain an explosion in a triethylaluminum production plant in Japan in 2007. Closed-vessel tests and chemical equilibrium calculations showed that, under closed vessel conditions, the mixture of  $\text{AlEt}_3$  and water decomposes into compounds with lower molecular weights than the products of the hydrolysis of TEA at atmospheric pressure [82]. Experiments also demonstrated that large temperature and pressure increases could occur because of contact between  $\text{AlEt}_3$  and aluminum hydroxide. Since aluminum hydroxide contains water as alumina hydrates, aluminum hydroxide could have been a source of water at high temperatures and could have contributed to the mixed reaction between  $\text{AlEt}_3$  and water, resulting in the bursting of a steel pipe.

A triethylaluminum mixture prepared at 273 K (0 °C) with a 3:1 molar excess of carbon tetrachloride exploded violently soon after removal of the ice bath. Similar reactions must be expected with other halocarbons. A mixture of dimethylformamide solvent and triethylaluminum exploded when heated.

### 5.2.5 Safety Properties of Triethylaluminum

#### 5.2.5.1 Autoignition of Triethylaluminum in Air

Alkylaluminum compounds are often diluted in hydrocarbon solvents for safe storage and shipment. Results obtained with a quantitative method for measuring the self-ignition limits of alkylaluminum pyrophoric compounds in hydrocarbons at 293 K (20 °C) indicated that the pyrophoric reactivity increased in the order triethylaluminum, diethylaluminum hydride, trimethylaluminum [83].

#### 5.2.6 Toxicity of Triethylaluminum

Because triethylaluminum is so reactive with air and moisture, there is little chance that it will reach living tissue before it becomes oxidized or hydrolyzed or bursts in flames. Nevertheless, the toxicity of triethylaluminum was investigated [84]. Mice, rats, and rabbits were exposed to triethylaluminum vapors and combustion products for 30–90 min. Characteristic changes in the lungs of animals exposed to triethylaluminum were found upon histological examination. The direct action of triethylaluminum on the skin was identical to that of a burn. The changes in the lungs were a result of moderate irritation. The vapor autoignited at Hg partial pressures in air down to 0.15 ppm. The ACGIH/OSHA/NIOSH-recommended maximum tolerable concentration of alkylaluminum vapor in air is  $2\text{ mg/m}^3$  (as Al) for both PEL and 8-h TLV TWA.



### 5.2.7 Fuel Mixtures with Triethylaluminum

The most important fuel mixture with triethylaluminum is the mixture with triethylborane, which is used as a hypergolic ignition fluid in LOX rocket engines. Apparently, the mixture has better ignition properties than either of its constituents by themselves. Triethylborane helps to reduce the viscosity of the mixture. Combustion of triethylaluminum has a higher heat output. There are insufficient data on physical properties of the mixtures in the open literature.

## 5.3 Diethylaluminum Hydride

Diethylaluminum hydride,  $(C_2H_5)_2AlH$ ,  $Et_2AlH$ ; aluminum, diethylhydro-; CAS RN [871-27-2], is an important intermediate in the production of triethylaluminum by the high-pressure method.

### 5.3.1 Preparation of Diethylaluminum Hydride

Diethylaluminum hydride can be prepared by hydroalumination of ethene under pressure in the presence of triethylaluminum [85–87]. It is an important intermediate or precursor in the production of triethylaluminum.

### 5.3.2 Physical Properties of Diethylaluminum Hydride

Diethylaluminum hydride,  $(C_2H_5)_2AlH$ , CAS RN [871-27-2], has a molecular mass of 86.1 g/mol and a density of 0.7938 g/cm<sup>3</sup> at 298 K (25 °C). It freezes at 214 K (–59 °C) and boils at 322–324 K at 0.14 Pa (49–51 °C at 0.001 mm Hg). The vapor pressure of diethylaluminum hydride can be calculated from

$$\log p = 7.7273 - 2454.5/T$$

where  $p$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin [57].

The heat of combustion of diethylaluminum hydride was determined at an oxygen pressure of 25 atm in a combustion bomb, and was calculated as 3676 kJ/mol (878.7 kcal/mol) [57]. The enthalpy of formation of diethylaluminum hydride derived from the heat of combustion was –307 kJ/mol (–73.5 kcal/mol). The latent heat of evaporation of  $Et_2AlH$  was 46.9 kJ/mol (11.2 kcal/mol) [57]. The dialkylaluminum hydrides and amides are trimeric.

### 5.3.3 Chemical Properties of Diethylaluminum Hydride

Diethylaluminum hydride is just as pyrophoric in air or in contact with LOX as triethylaluminum. It vigorously reacts with water. It reacts with ethylene to form triethylaluminum.

## 5.4 Other Alkylaluminum Compounds

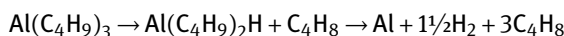
### 5.4.1 Propylaluminum Compounds

Tri-*n*-propylaluminum,  $(n\text{-C}_3\text{H}_7)_3\text{Al}$ , CAS RN [102-67-0], has a molecular mass of 156.2 g/mol and a density of 0.8207 g/cm<sup>3</sup> at 298 K (25 °C). It freezes at <213 K (<60 °C) and boils at 329 K at 27 Pa (56 °C at 0.2 mm Hg).

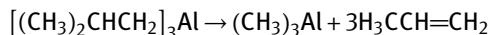
Data for the enthalpy of formation of tripropylaluminum listed in the literature are  $-322.2 \pm 4.6$  kJ/mol and  $-282 \pm 15$  kJ/mol, i.e., showing that there is a wide scatter of data [35]. The same source gives the enthalpy of formation of tri-*n*-butylaluminum as  $-372.4 \pm 5.7$  and that of tri-*tert*-butylaluminum as  $-388.3 \pm 7.7$  kJ/mol and  $-292 \pm 30$  kJ/mol.

### 5.4.2 Butylaluminum Compounds

Triisobutylaluminum,  $(i\text{-C}_4\text{H}_9)_3\text{Al}$ , CAS RN [100-99-2], has a molecular mass of 198.3 g/mol and a density of 0.7822 g/cm<sup>3</sup> at 298 K (25 °C). It boils at 331–333 K at 0.013 Pa (58–60 °C at 0.0001 mm Hg). The decomposition of triisobutylaluminum depends on the operating conditions: in a venting reactor, the reaction proceeds in accordance with



but under pressure, the course of the reaction is



followed by decomposition of the trimethylaluminum [43]. Aluminum deposited by CVD contains varying amounts of aluminum carbide. The addition of alkenes onto alkylaluminum compounds reverses itself at temperatures above 473 K (200 °C). Secondary reactions may result in the formation of  $\text{AlH}_3$ .

The enthalpy of formation of triisobutylaluminum, CAS RN [100-99-2], also called aluminum, tris(2-methylpropyl)-, was determined by measuring its heat of combustion under standard conditions in a calorimetric bomb ( $\Delta H_{\text{comb}} = 9126 \pm 30$  kJ/mol =  $2181.2 \pm 7.1$  kcal/mol), and this value was used to calculate the enthalpy of formation ( $\Delta H_f^\circ = -292$  kJ/mol =  $-69.9$  kcal/mol) [88]. Triisobutylaluminum freezes at 273 K (0 °C) and boils at 359 K (86 °C at 10 mm Hg). The density is 0.781 g/cm<sup>3</sup> at 298 K (25 °C). The heat of vaporization of triisobutylaluminum is  $\Delta H_{\text{vap}} = 37.2$  kJ/mol = 8.9 kcal/mol.

The vapor pressure of diisobutylaluminum hydride as a function of temperature can be calculated by the equation

$$\log P = 5.8666 - 1883.3/T$$

where  $P$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin [57].

The lower trialkylaluminum compounds exist mostly as dimers. Triisobutylaluminum, a bulkier molecule, is only 39.4% associated at 283 K (10 °C) and only 16.4% associated at 313 K (40 °C) [30]. The gaseous products of the pyrolysis of tributylaluminum at 273–475 K under static conditions were analyzed by GC/MS [89].

### 5.4.3 Diethylaluminum Azide

Diethylaluminum azide, DEAA,  $(\text{H}_3\text{CCH}_2)_2\text{AlN}_3$ , is a pyrophoric liquid with properties similar to triethylaluminum that can be prepared by three different methods. The synthesis of diethylaluminum azide was optimized and the yield was increased from a value reported in the literature [90], 54, to 75%. The purified product and its molecular structure with  $D_{3h}$  symmetry were verified by elemental analysis, IR spectroscopy, and  $^1\text{H}$  NMR. It remains a liquid down to 143 K (–130 °C) [91]. Diethylaluminum azide is a trimer with a stable six-membered ring structure under ordinary conditions. This structure is consistent with the behavior of DEAA during distillation at high temperatures up to 693 K (420 °C) at 400 Pa (3 mm Hg) – it does not decompose. The etherate with THF could not be split to liberate DEAA, but decomposed explosively. When heated to 733–840 K (460–570 °C) in vacuum, DEAA rapidly decomposed without an explosion, releasing low-molecular-weight hydrocarbons and forming a microcrystalline powder identified as aluminum nitride (AlN), with particle sizes in the nanometer range. By using a cryoscopic method, the molecular mass of DEAA was determined as 379, a very small deviation from its theoretical [92] trimer molecular mass of 381. Surprisingly, the homologue dimethylaluminum azide is not a liquid but a solid that melts at 338 K (+65 °C). It exists not only as a trimer, but also as a tetramer.

The preparation method of DEAA from sodium azide and diethylaluminum chloride was optimized in terms of reactant ratio, reaction time, and temperature, and the yield was improved from 54 to 75% compared with that reported in the literature [93]. DEAA was smoothly distilled at 373–378 K (100–108 °C) at a vacuum pressure of 267 Pa (2 mm Hg). The purified product was identified by its IR spectrum.

Based on an earlier report about DEAA synthesis, the choice of solvent for the synthesis reaction, the distillation conditions, and the main properties of DEAA were further optimized [94]. The molecular structure of DEAA was determined by means of its IR spectrum and  $^1\text{H}$  NMR. The results indicated that DEAA is a trimer with a stable six-membered ring structure. DEAA could be used as a self-ignitable pyrophoric agent. Diethylaluminum azide (DEAA) was synthesized from diethylaluminum chloride and sodium azide, and the products and conditions of DEAA pyrolysis were analyzed [95]. Diisobutylaluminum chloride can be synthesized by the reaction of triisobutylaluminum and carbon tetrachloride [96]. However, one must remember that mixing other trialkylaluminum compounds with carbon tetrachloride or chloroform has resulted in explosions. Diisobutylaluminum azide (DBAA) can be synthesized by the reaction of sodium azide and diisobutylaluminum chloride in aromatic hydrocarbon solvents,

and its etherate complex (DBAA•THF) can be synthesized by the reaction of sodium azide and diisobutylaluminum chloride in tetrahydrofuran. DBAA and DBAA•THF were characterized by their IR and  $^1\text{H}$  NMR spectra.

## 6 Alkylsilanes

Silanes without alkyl groups are discussed in the chapter “Metals of the Second and Third Row of the Periodic Table of Elements, and their Hydrides” in this volume of the *Encyclopedia of Liquid Fuels*. Here we discuss alkylsilanes in the same chapter as alkylalanes. Considering that silicon is an element that is as abundant as the sand along ocean beaches, and that silanes have a very high heat of combustion, one would assume that silanes would make a good fuel for jet engines, ramjets, and rocket engines alike. There has been no lack of attempts to do so, but difficulties with realizing this fuel economically persist. It is very energy intensive to convert silicon dioxide to silanes. In terms of *in situ* resource utilization and making rocket fuels on other planets, it is more likely that prospectors will find silicon than carbon in the form of hydrocarbons (except on Saturn’s moon Titan). All alkylsilanes are used for chemical vapor deposition of silicon carbide on microelectromechanical systems (MEMS) devices and semiconductors. The physical properties of four alkylsilanes are summarized in Table 7.

The rates of flame propagation of four alkylsilanes have been determined in a tube apparatus [99, 100]. The maximum fundamental rate of flame propagation increased in the order tetramethylsilane < trimethylsilane < diethylsilane < monoethylsilane. A precise fundamental flame velocity could not be obtained for ethylsilane because of the high rate of propagation. In a graph showing the flame velocity as a function of the fraction of stoichiometric fuel concentration, the maximum flame velocities occurred at fuel-rich ratios near 1.2. In each case, the alkylsilanes had considerably higher flame velocities than the hydrocarbons that would result if the silicon were replaced by carbon, whereas the physical properties of the alkylsilanes resemble those of the corresponding hydrocarbons. When diethylsilane was blended with *n*-pentane, no marked increase in the flame velocity of *n*-pentane occurred until the concentration of diethylsilane was greater than 20%. Comparing the flame velocities for a series of alkylsilanes with their minimum explosion temperatures, a number of trends immediately become apparent. The maximum flame velocity increases rapidly as the number of silicon-to-hydrogen bonds is increased. Similarly, the minimum explosion ignition temperature decreases markedly.

Table 7: Physical properties of alkylsilanes.

| Com-<br>pound               | Molecu-<br>lar mass<br>g/mol | Freezing point                        |                                      | Boiling point        |                               | Density<br>g/cm <sup>3</sup> | Index of<br>refraction<br>( <i>n</i> <sub>D</sub> <sup>20</sup> ) | Heat of combustion,<br>upper |          | Heat of combustion,<br>lower |          |
|-----------------------------|------------------------------|---------------------------------------|--------------------------------------|----------------------|-------------------------------|------------------------------|-------------------------------------------------------------------|------------------------------|----------|------------------------------|----------|
|                             |                              | K                                     | °C                                   | K                    | °C                            |                              |                                                                   | kJ/mol                       | kcal/mol | kJ/mol                       | kcal/mol |
| Ethyl-<br>silane            | 60.1704                      | 93.45                                 | -179.7                               | 258.65               | -14.5                         | —                            | —                                                                 | 2731                         | 652.8    | 10.85                        | 2555     |
| Diethyl-<br>silane          | 88.2236                      | 138.76                                | -134.39                              | 329.14<br>at 101 kPa | 55.99 at<br>760 mm Hg         | 0.6832<br>at 20 °C           | 1.3920                                                            | 3994                         | 954.6    | 10.82                        | 3732     |
| Trimethyl-<br>silane        | 74.1970                      | 137.26                                | -135.89                              | 282                  | 9                             | —                            | —                                                                 | 3219                         | 769.4    | 10.37                        | 2996     |
| Tetra-<br>methyl-<br>silane | 88.2236                      | $\alpha$ = 171.45<br>$\beta$ = 173.65 | $\alpha$ = -101.7<br>$\beta$ = -99.5 | 300<br>at 102 kPa    | 27<br>26-27 at<br>760.7 mm Hg | 0.6388<br>at 20 °C           | 1.3582                                                            | 3861                         | 922.8    | 10.46                        | 3599     |

Data sources: [97,98]

## 6.1 Methylsilanes

Methylsilanes are gases at room temperature and do not ignite spontaneously in air. The enthalpies of formation of silane and methylsilanes are summarized in Table 8. Results from theoretical calculations of enthalpies of formation for these compounds (not shown here) were close to the experimental results.

**Table 8:** Enthalpies of formation of gaseous silanes and methylsilanes.

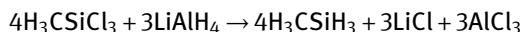
| Compound                                         | Enthalpy of formation, experimental<br>kJ/mol | Enthalpy of formation, extrapolated from<br>the redistribution equilibrium constant |
|--------------------------------------------------|-----------------------------------------------|-------------------------------------------------------------------------------------|
| SiH <sub>4</sub>                                 | +34.7                                         | +34.3 (from other sources)                                                          |
| Si <sub>2</sub> H <sub>6</sub>                   | +79.9                                         | —                                                                                   |
| Si <sub>3</sub> H <sub>8</sub>                   | +120.9                                        | —                                                                                   |
| H <sub>3</sub> CSiH <sub>3</sub>                 | −32.5                                         | −29.1 ± 4                                                                           |
| (H <sub>3</sub> C) <sub>2</sub> SiH <sub>2</sub> | −83.6                                         | −94.7 ± 4                                                                           |
| (H <sub>3</sub> C) <sub>3</sub> SiH              | −156.6                                        | −163.4 ± 4                                                                          |
| (H <sub>3</sub> C) <sub>4</sub> Si               | −227.6 or −236.3                              | —                                                                                   |
| (H <sub>3</sub> C) <sub>4</sub> Si               | −233.2 ± 3.2                                  | —                                                                                   |

Data sources: [101–103]

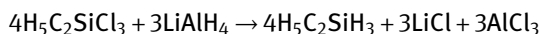
The temperatures required for the rapid oxidation or explosion of air/alkylsilane (methylsilane, dimethylsilane, trimethylsilane, tetramethylsilane and vinylsilane) mixtures at 1atm pressure were determined in a preheated Pyrex reaction vessel of diameter 1.5in. and length 10.5in. [104–106]. Over a fuel concentration range of 2–10%, the lowest temperatures below which explosion did not occur for the five fuels studied were: tetramethylsilane 723K = 450 °C; trimethylsilane 583K = 310 °C; dimethylsilane 493K = 220 °C; methylsilane 403K = 130 °C; and vinylsilane H<sub>2</sub>C=CH—SiH<sub>3</sub>, 363K = 90 °C. The initial rate of oxidation of a 50% mixture of trimethylsilane and air was studied by measurement of pressure and concentration changes at a temperature slightly below the explosion temperature.

### 6.1.1 Methylsilane

Methylsilane, H<sub>3</sub>CSiH<sub>3</sub>, CAS RN [992-94-9], can be prepared by reduction of methyltrichlorosilane with lithium aluminum hydride in dioxane:



The same procedure also works for the preparation of ethylsilane:



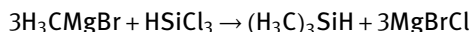
Methylsilane is a gas at room temperature and does not ignite spontaneously in air.

### 6.1.2 Dimethylsilane

Dimethylsilane,  $(\text{H}_3\text{C})_2\text{SiH}_2$ ,  $M = 60.17 \text{ g/mol}$ , CAS RN [1111-74-6], is a gas at room temperature and condenses to a liquid with a density of  $0.680 \text{ g/cm}^3$  at  $253 \text{ K}$  ( $20^\circ\text{C}$ ). It solidifies at  $123 \text{ K}$  ( $-150^\circ\text{C}$ ).

### 6.1.3 Trimethylsilane

Trimethylsilane,  $(\text{H}_3\text{C})_3\text{SiH}$ , CAS RN [993-07-7], can be prepared by reaction of a Grignard reagent with a trihalogensilane in absolute diethyl ether:



Trimethylsilane is a clear liquid that boils at  $282 \text{ K}$  ( $9^\circ\text{C}$ ), so at room temperature it is a gas. Trialkylsilane compounds are flammable but do not tend to ignite upon contact with air (in contrast to silane  $\text{SiH}_4$ ).

### 6.1.4 Tetramethylsilane

Tetramethylsilane,  $(\text{H}_3\text{C})_4\text{Si}$ ,  $M = 88.2236 \text{ g/mol}$ , CAS RN [75-76-3], is a clear liquid that boils at  $300 \text{ K}$  ( $27^\circ\text{C}$ ). It is combustible but does not ignite upon contact with air (in contrast to silane  $\text{SiH}_4$ ).

The vapor pressure of tetramethylsilane in the range  $208.93$ – $293.64 \text{ K}$  can be calculated from an Antoine equation,

$$\log(P) = 3.97703 - [1047.272/(T - 36.057)]$$

where  $P$  is the vapor pressure in bar and  $T$  is the temperature in kelvin [107, 108]. The enthalpy of formation of tetramethylsilane vapor at  $298 \text{ K}$ ,  $\Delta H_f^\circ(\text{G})$ , is  $-286.60 \text{ kJ/mol}$ . The heat of vaporization at its normal boiling point is  $24.204 \text{ kJ/mol}$ . The Si–C bond dissociation energy is  $355.0 \text{ kJ/mol}$ .

Tetramethylsilane is flammable in air. The range of detonability of oxygen/tetramethylsilane vapor mixtures is  $1.8$ – $50 \text{ vol.-%}$  tetramethylsilane in binary mixtures [109]. For ternary mixtures, detonation still propagates with mixtures containing  $0.9\%$  tetramethylsilane,  $7.8\%$  oxygen, and  $91.2\%$  helium.

The thermal decomposition of tetramethylsilane diluted in argon was studied behind the reflected shock waves in a single pulse shock tube in the temperature range of  $1058$ – $1194 \text{ K}$  [110]. The major products formed in the decomposition were methane and ethene, whereas ethane and propylene were detected only in lower concentrations. The decomposition of tetramethylsilane seems to be initiated by Si–C bond scission to form methyl radicals  $\text{H}_3\text{C}^\bullet$  and trimethylsilyl radicals  $(\text{CH}_3)_3\text{Si}^\bullet$ .

Tetramethylsilane is a precursor for flame synthesis of silica nanoparticles. A chemical reaction mechanism was developed for the oxidation of tetramethylsilane in a lean, low-pressure ( $p \approx 30$  mbar)  $O_2/H_2/Ar$  flame using species mol fractions obtained from molecular beam mass spectrometry measurements in a matrix-supported flat flame doped with 400, 600, or 800 ppm tetramethylsilane [111].

Laminar burning velocities were measured for several different silane fuels, including tetramethylsilane, in order to evaluate their potential for vapor cloud explosions in CVD operations [112]. Laminar burning velocities were determined from constant-volume explosions in a closed spherical vessel, and the pressure rise of the initial portion of flame propagation was used to calculate the laminar burning velocity. The adiabatic flame temperature for tetramethylsilane combustion in air is 2396 K. The unstretched laminar burning velocity of tetramethylsilane in air is  $65 \pm 5$  cm/s, which is almost twice as fast as that of methane.

## 6.2 Ethylsilanes

Ethylsilanes can be prepared by hydrosilylation, the addition of silanes to ethene. Ethylsilanes can be handled in air without appreciable oxidation or hydrolysis. The compounds containing many silicon-to-hydrogen bonds, such as ethylsilane or diethylsilane, have a tendency to hydrolyze when kept in contact with water for extended periods of time.

The spontaneous ignition temperatures of a number of alkylsilanes were determined and compared with the chemical structures of these compounds, leading to a qualitative discussion of the possible influence of silicon-hydrogen bonds on the ease of oxidation, as indicated by differences in spontaneous ignition temperature [113]. Thus, with ethylsilanes, the ease of oxidation decreases in the order  $(H_5C_2)_2SiH_2 > (H_5C_2)_3SiH > (H_5C_2)_4Si$ . The same order of activity was found for the methylsilane series. Differences in spontaneous ignition temperature were less pronounced in the *n*-propyl series and even less pronounced in the *n*-butyl series and the *n*-amyl series.

### 6.2.1 Ethylsilane

Ethylsilane,  $H_5C_2SiH_3$ ,  $M = 60.1704$  g/mol, CAS RN [2814-79-1], is a gas at room temperature, condenses to a liquid with a density of  $0.639$  g/cm<sup>3</sup> at temperatures below 254 K ( $-19^\circ C$ ), and solidifies at 93 K ( $-180^\circ C$ ).

### 6.2.2 Diethylsilane

Diethylsilane,  $(H_5C_2)_2SiH_2$ ,  $M = 88.2236$  g/mol, CAS RN [542-91-6], is a liquid at room temperature. It boils at 329 K ( $56^\circ C$ ).



### 6.3 Other Alkylsilanes

Attempts to synthesize more energetic alkylsilanes as rocket fuels by replacing saturated alkyl groups with unsaturated alkenyl and/or alkynyl groups were not successful. Tetraethynylsilane is a solid that explodes on rapid heating [114]. Attempts to patent tri- and tetra-substituted ethynylsilanes wherein the substituents are higher homologs of acetylene (e.g., substituted ethynyl moieties with three to ten carbon atoms) as ramjet or rocket fuels were abandoned [115]. Isobutylsilane boils at 321.7 K (48.6 °C) and *n*-butylsilane boils at 329.5 K (56.4 °C). Vinylsilane boils at 250.3 K (−22.8 °C).

## 7 Alkylzinc Compounds

Diethylzinc, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Zn, CAS RN [557-20-0], was one of the first organometallic compounds. Diethylzinc ignites spontaneously in air and has been used in incendiary weapons and as an ignition fluid in rocket engines with non-hypergolic bipropellant combinations. Diethylzinc can be prepared from zinc powder and ethyl iodide. Organozinc compounds play an important role in the functioning of several enzymes. See also [116].

### 7.1 Physical Properties of Diethylzinc

Diethylzinc is a colorless liquid. The physical properties of diethylzinc are listed in Table 9. The saturated vapor pressure temperature dependence of diethylzinc is as follows [118]:

$$\log P_V = 7.996 - 2.012 \times \frac{10^3}{T}$$

where  $P_V$  is the vapor pressure in mm Hg and  $T$  is the temperature in kelvin.

**Table 9:** Physical properties of diethylzinc.

| Property                                         | SI units                 | Other units  | References    |
|--------------------------------------------------|--------------------------|--------------|---------------|
| Molecular mass                                   | 123.50 g/mol             | 8.097 mol/kg |               |
| Freezing point                                   | 245 K                    | −28 °C       | [117]         |
| Boiling point                                    | 391 K                    | 118 °C       | CAS Scifinder |
|                                                  | 397 K                    | 124 °C       | [117]         |
| Density at 293 K                                 | 1.2065 g/cm <sup>3</sup> | —            | CAS Scifinder |
| Vapor pressure at 293 K                          | 1.80 kPa                 | 13.5 mm Hg   | [118]         |
| Refractive index (n <sub>D</sub> <sup>20</sup> ) | 1.4936                   | —            | —             |

## 7.2 Diethylzinc as an Ignition Fluid in Rocket Engines

Diethylzinc was used as the ignition fluid during German rocket development tests with LOX/kerosene and GOX/kerosene in 1941–1944 in Fassburg/Germany [119].

## 7.3 Other Applications of Diethylzinc

Diethylzinc has been used as the ignition fluid in flame throwers in military weapons. The controlled autoxidation of dimethylzinc or diethylzinc is used for the deposition of thin zinc oxide layers on semiconductor sensors that are often used in flammable and toxic vapor detection devices. Pyrolysis at higher temperature is used for the deposition of metallic zinc films. In the past, not all books were printed on acid-free paper. Diethylzinc has been used for the bulk deacidification of valuable books in historical archives, thus preserving valuable cultural heritage items and extending their useful lifetimes.

## 8 Other Organometallic Compounds

It is highly unusual for toxic, volatile, organometallic compounds such as methylmercury, dimethylmercury, dimethylselenium, tetramethyltin, and trimethylantimony to occur naturally. They are typically resistant to air and moisture. The underlying formation pathways of methylmercury and dimethylmercury in the ocean are unknown. Methylmercury and dimethylmercury may accumulate in the fatty tissues of some fish.

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# Ramjet Fuels

## Introduction

The *Encyclopedia of Liquid Fuels* contains eight chapters dealing with hydrocarbon fuels. This topic had to be sub-divided into several smaller chapters that were easier to arrange in alphabetical order in five subvolumes of equal size. The titles of the eight hydrocarbon chapters are “Alkanes,” “Alkenes and Alkynes,” “Aromatic Hydrocarbons,” “Cycloaliphatic Hydrocarbons,” “Hydrocarbons,” “Jet Fuels,” “Kerosenes,” and “Ramjet Fuels.”

This chapter on ramjet fuels – which are obviously fuels for air-breathing jet engines, not for rocket engines – may seem out of place in this *Encyclopedia of Rocket Propellants*, but there are so many similarities between ramjet fuel kerosenes and rocket engine fuel kerosenes that we feel justified in including ramjet fuels here. In many cases, the hydrocarbons in ramjet fuels are the same as those in rocket fuels; it is just the composition of the mixture that is different. The analytical methods used for both types of fuels are the same. The same comments also apply to jet fuels, which were originally intended to be discussed in the same chapter as ramjet fuels but ended up being covered in a chapter of their own. Quite often, jet fuels have been used as rocket fuels because they were readily available.

Ramjet fuels are receiving renewed interest as fuels in hypersonic missiles. Ramjet fuels are used in dual-mode propulsion systems. Dual-mode propulsion systems initially use rockets to get started, switch to ramjet mode once the necessary speed has been attained, ascend in ramjet mode until the air becomes too thin to support air-breathing combustion, and then switch back to rocket propulsion to achieve orbital velocity and complete the mission.

## 1 Ramjet Fuel RJ-4

Ramjet fuel RJ-4, TH Dimer, consists mostly of tetrahydrodimethyldicyclopentadiene. The composition and properties of RJ-4 are specified in MIL-P-82522C (26 Oct. 1990; formerly MIL-F-25558). The properties of pure tetrahydrodimethyldicyclopentadienes as chemical compounds are described in the chapter “Cycloaliphatic Hydrocarbons” in the *Encyclopedia of Liquid Fuels*.

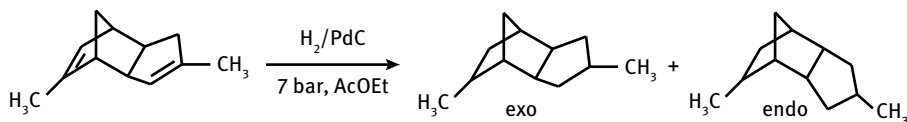
With its high volumetric heating value of  $39.0 \text{ GJ/m}^3$  (140000 BTU/gal), RJ-4 has about 16% higher energy content than JP-4 or JP-5. Its flash point and low-temperature properties (freeze point and viscosity) are within safe ranges. The *endo* isomers are more viscous and higher freezing than their *exo* counterparts. Unfortunately, depending on the degree of control exerted during processing, there were notable batch-to-batch variations in the properties of this fuel (particularly in the low-temperature vis-

cosity) arising from varying proportions of the two isomers in the product. Thus, work was initiated to convert all *endo* isomers to the *exo* form by isomerization over an  $\text{AlCl}_3$  catalyst. The low-temperature viscosity was moderately improved, i.e., its viscosity at 233 K ( $-40^\circ\text{C}$ ) was reduced from 60 to 28 cSt. However, this was done at the expense of a slight drop (1.4%) in the heating value. The resulting isomerized fuel RJ-4I is a mixture of isomers of *exo*-tetrahydro(dimethylcyclopentadiene). RJ-4I offered a significantly improved viscosity and freezing point and better manufacturing reproducibility characteristics as compared to the standard military specification RJ-4. However, because of the added processing cost and the only marginal property improvements it provides, RJ-4I was never a serious candidate to replace RJ-4. Neither RJ-4 nor RJ-4I met the operational requirements of the Air Force. This fact led to the development of JP-10, which, when properly formulated, is the principal standard fuel used by both services.

RJ-4 was intended to be used in the Talos missile. The Bendix RIM-8 Talos was a long-range naval surface-to-air missile, and was among the earliest surface-to-air missiles to be used on US Navy ships (from 1957 to 1979). The Talos had a ramjet main stage and a solid rocket booster. A Navy ship would typically carry 30 of these missiles [1]. Replacing the JP-5 in some of the early Talos missiles with RJ-4 extended the range of the missiles [2, 3]. Note that some publications have mislabeled the main ingredient of RJ-4 as tetrahydromethylcyclopentadiene instead of tetrahydrodimethylcyclopentadiene.

### 1.1 Preparation, Production, and Availability of RJ-4

Tetrahydrodimethyldicyclopentadiene (RJ-4) can be prepared by hydrogenation of dimethyldicyclopentadiene followed by isomerization [4]. *Endo*-tetrahydrodimethyldicyclopentadiene isomers within the raw fuel stock can be isomerized to *exo*-isomers by treatment of the fuel stock with catalysts such as aluminum chloride, nickel, or pulverized, acid-treated firebrick [5].



The dimer of methylcyclopentadiene is first hydrogenated in a two-stage operation. In the first stage, the 8- and 9-positions of the dimer are hydrogenated in relatively mild conditions at 393 K ( $120^\circ\text{C}$ ). The dihydro derivative is relatively thermally stable and can then be hydrogenated under more severe conditions at 488 K ( $215^\circ\text{C}$ ) and 20–35 atm to complete the hydrogenation. The raw product, which contains too much *endo* conformer, must then be isomerized by heating for 1–4 h with acidic catalysts at 453–493 K ( $180$ – $220^\circ\text{C}$ ) [6].

## 1.2 Physical Properties of RJ-4

Physical properties of RJ-4 are summarized in Unit 1 of the *CPIA/M6 Air-Breathing Fuels Manual* [7]. The gross chemical formula for RJ-4 is  $C_{12}H_{20}$ . The C : H ratio is 0.60. Physical properties of RJ-4 are listed in Table 1. Physical properties of the pure main ingredient of RJ-4, tetrahydrodimethyldicyclopentadiene, are already reported in the chapter “Cycloaliphatic Hydrocarbons” in Volume 2 of the *Encyclopedia of Liquid Fuels*. Some of the physical properties in these sections are identical.

**Table 1:** Physical properties of RJ-4.

| Property                      | SI units                                       | Other units                               | References |
|-------------------------------|------------------------------------------------|-------------------------------------------|------------|
| Average molecular mass        | 164.2872 g/mol                                 | 6.0869 mol/kg                             | [8]        |
| Freezing point                | < 233 K                                        | < -40 °C                                  |            |
| Boiling range                 | 478–494 K                                      | 400–430 °F                                | [9]        |
| Density                       | 0.94 g/cm <sup>3</sup>                         | —                                         | [8]        |
|                               | 0.920 g/cm <sup>3</sup>                        | —                                         | [10]       |
| Vapor pressure                | 215 Pa at 298 K                                | 1.6 mm Hg at 25 °C                        | —          |
| Kinematic viscosity           | 6.0 mm <sup>2</sup> /s at 293 K                | 6.0 cSt at -40 °C                         | [8]        |
| Heat capacity                 | 1.6 J g <sup>-1</sup> K <sup>-1</sup> at 298 K | 0.38 cal g <sup>-1</sup> °C <sup>-1</sup> | [7]        |
| Enthalpy of formation         | -160.8 ± 1.7 kJ/mol                            | -38.43 ± 0.40 kcal/mol                    | [10]       |
| Enthalpy of vaporization      | 55.3 ± 0.9 kJ/mol                              | 13.2 kcal/mol                             | [11]       |
| Heat of combustion            | 7419.6 kJ/mol                                  | 10153.1 ± 2.3 cal/g                       | [10]       |
| Volumetric heat of combustion | 39.0 GJ/m <sup>3</sup>                         | 140000 BTU/gal                            | [8]        |

### 1.2.1 Thermodynamic Properties and Thermal Properties of RJ-4

#### 1.2.1.1 Heat Capacity of RJ-4

The heat capacity of RJ-4 as a function of temperature between 275 and 330 K can be calculated from the following equation [12]:

$$c_p = 0.1377 + 0.001022 T$$

where  $c_p$  is the heat capacity in cal g<sup>-1</sup> °C<sup>-1</sup> and  $T$  is the temperature in kelvin. The heat capacity of RJ-4I as a function of temperature between 275 and 330 K can be calculated from the following equation [12]:

$$c_p = 0.14126 + 0.0010066 T$$

where  $c_p$  is the heat capacity in cal g<sup>-1</sup> °C<sup>-1</sup> and  $T$  is the temperature in kelvin.

### 1.2.1.2 Heat of Combustion of RJ-4

The net heat of combustion of RJ-4I is  $42.433 \pm 0.009$  kJ/kg ( $10141.7 \pm 2.2$  cal/g) and the gross heat of combustion of R-4I is  $45.112 \pm 0.002$  kJ/kg ( $10781.95 \pm 0.57$  cal/g) [12]. An earlier report [10] from the same source gave an interim value for the heat of combustion of RJ-4 as  $10153.1 \pm 2.3$  cal/g and that for RJ-4I as  $10141.4 \pm 2.2$  cal/g.

### 1.2.1.3 Enthalpy of Formation of RJ-4

Based on a reported heat of combustion of  $10153.1 \pm 2.3$  cal/g =  $1773.33 \pm 0.37$  kcal/mol, the enthalpy of formation of RJ-4 was calculated as  $-160.8 \pm 1.7$  kJ/mol ( $-38.43 \pm 0.40$  kcal/mol). The corresponding data for RJ-4I are  $10141.4 \pm 2.2$  cal/g =  $1771.36 \pm 0.36$  kcal/mol and an enthalpy of formation of  $-169.1 \pm 1.7$  kJ/mol ( $-40.41 \pm 0.39$  kcal/mol).

### 1.2.1.4 Enthalpy of Evaporation of RJ-4

Correlation gas chromatography was used to measure the evaporation enthalpy of complex mixtures such as RJ-4, a high-energy-density cruise missile fuel [11]. RJ-4 consists of a complex mixture of *exo*- and *endo*-dimethyltetrahydrodicyclopentadienes. The evaporation enthalpy of RJ-4 is  $55.3 \pm 0.9$  kJ/mol. Correlation gas chromatography is applicable for obtaining the vaporization enthalpy of any complex mixture of materials that will pass through a gas chromatograph and for which vaporization enthalpies of suitable standards are available. Once the temperature dependence of each component is established, the results can be used to determine the evaporation enthalpy at any composition.

## 1.2.2 Chemical Properties of RJ-4

The gross chemical formula for RJ-4 is  $C_{12}H_{20}$ .

## 1.2.3 Safety Properties of RJ-4

### 1.2.3.1 Environmental Impact of RJ-4 Spills

RJ-4 and several other kerosenes were examined to measure the effects of potential environmental contamination resulting from these fuels on freshwater fish and aufwuchs [13]. Besides RJ-4, the materials evaluated included JP-4, JP-9, RJ-5, and methylcyclohexane.

### 1.2.3.2 Fire hazards of RJ-4

Per MIL SPEC MIL-F82522A [9], the flash point of RJ-4 per ASTM D93 must be in the range 333–352.5 K ( $60$ – $79.40$  °C =  $140$ – $175$  °F). The MSDS gives a flash point of 333 K ( $60$  °C =  $140$  °F). The autoignition temperature of RJ-4 is 602 K ( $329$  °C =  $625$  °F).

## 2 Ramjet Fuel RJ-5

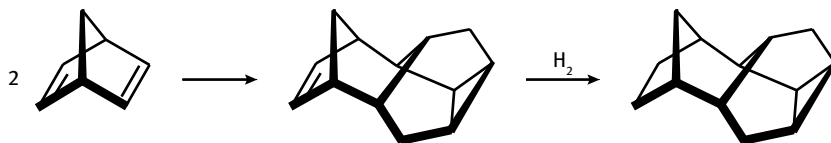
The main ingredient of RJ-5 is composed of at least three major dimers of perhydrodinorbornadiene (PHDNBD), which make up more than 98% of the material. Properties of pure perhydrodinorbornadiene isomers are shown in the chapter “Cycloaliphatic Hydrocarbons.”

### 2.1 Preparation, Production, and Availability of RJ-5

RJ-5 was also known as Shelldyne<sup>®</sup>, which is a registered trademark of Shell Oil Company. Initially, Shelldyne was not hydrogenated, and dimerization resulted in a fuel with poor storage stability. Shelldyne-H<sup>®</sup> is the hydrogenated version of this fuel. Some Shelldyne-H<sup>®</sup> was and still is produced by Ashland Oil Company under license from Shell. Shelldyne-H is an “as synthesized” RJ-5 containing about 70 mass-% of the perhydrodibornadiene HNN isomer and smaller amounts of other PHDNBD isomers.

At the time of the development of RJ-5, the raw material used in its synthesis, norbornadiene, was commercially available from Shell Chemical Co. in the Netherlands as a byproduct of pesticide manufacturing. However, this Shell operation was subsequently discontinued and norbornadiene became unavailable in commercial quantities. In view of the high energy content of RJ-5, there has been a considerable effort aimed at duplicating or mimicking RJ-5 (or RJ-5-like blends) with components derived from less costly, domestically available raw materials in the US. One such fuel under development, designated RJ-7, comprises a ternary blend of perhydrogenated cyclopentadiene trimer, the dihydro derivative of the adduct of cyclopentadiene and indene, and JP-10. RJ-7 has a greater heating value than JP-10 (151000 vs 142000 BTU/gal), but its viscosity is significantly higher than that of JP-10 (>400 vs 19 cSt at 233 K = -40 °C).

RJ-5 can be made by reacting norbornadiene (which can be synthesized from acetylene and cyclopentadiene) over a rhodium-on-carbon catalyst followed by hydrogenation and isomerization to yield the product *endo,endo*-dihydrodinorbornadiene (RJ-5):



This synthesis involved the use of an expensive rhodium catalyst, multi-step processing, and had a low overall yield. It did, however, produce a fuel with a high heating value of 44.9 MJ/L (169.7 MJ/gal = 161000 BTU/gal). This fuel has an impractically



high freezing point ( $>0^{\circ}\text{C}$ ) and a high viscosity ( $>2000\text{ cSt}$  at  $233\text{ K} = -40^{\circ}\text{C}$  in the supercooled state). When in the supercooled state, it can freeze and solidify suddenly, causing fuel system shutdown. Despite this problem, its high energy content attracted a great deal of attention, and considerable work was done to develop blends based on RJ-5 that would lower the freezing point.

## 2.2 Physical Properties of RJ-5

The gross chemical formula of RJ-5 is  $\text{C}_{14}\text{H}_{18}$ . The C : H ratio is 0.78. Physical properties of RJ-5 are listed in Table 2, in *Encyclopedia of Liquid Fuels*, chapter “Cycloaliphatic Hydrocarbons,” and in reference [14].

### 2.2.1 Freezing Point of RJ-5

Shelldyne-H<sup>®</sup> is composed of at least three major dimers that make up more than 98% of the material. This mixture of hydrocarbons produces a eutectic that has a melting point considerably lower than those of the pure dimers. By using a preparative gas chromatographic technique, chemists were able to separate the three major dimers that make up Shelldyne-H.

It was of interest to see whether any combination of two or more of these dimers would not freeze above  $219\text{ K}$  ( $-54^{\circ}\text{C} = -65^{\circ}\text{F}$ ). Numbered in order of gas chromatographic elution time, the pure dimers 1, 2, and 3 in Shelldyne-H were found to freeze at approximately  $306$ ,  $278$ , and  $281\text{ K}$  ( $92$ ,  $41$ , and  $46^{\circ}\text{F}$ ), respectively. Normally, Shelldyne-H<sup>®</sup> will contain 10–20% of dimer 1, 16–22% of dimer 2, and 55–75% of dimer 3. Since the last two dimers had the lowest freezing points, a preliminary program was initiated to determine whether mixtures of only those two dimers form eutectics that meet the  $219\text{ K}$  ( $-54^{\circ}\text{C} = -65^{\circ}\text{F}$ ) (and lower) melting/freezing point requirements. With an appropriate dimer ratio, pure Shelldyne-H will remain a homogeneous fluid down to temperatures below  $219\text{ K}$  ( $-54^{\circ}\text{C} = -65^{\circ}\text{F}$ ).

RJ-5 does not exhibit a sharp freezing point but rather complex supercooling and fractional crystallization behavior. RJ-5 undergoes essentially complete crystallization at temperatures lower than  $231\text{ K}$  ( $-45^{\circ}\text{F}$ ), followed by partial melting on warming to  $250\text{ K}$  ( $-10^{\circ}\text{F}$ ), re-solidification when this temperature is held, and re-melting on warming to  $253\text{ K}$  ( $-5^{\circ}\text{F}$ ), with the last crystal disappearing at  $268\text{ K}$  ( $+23^{\circ}\text{F}$ ). Assuming that  $268\text{ K}$  ( $+23^{\circ}\text{F}$ ) is the highest temperature at which a solid phase can exist in equilibrium with the liquid phase,  $268\text{ K}$  ( $+23^{\circ}\text{F}$ ) was recommended as the threshold freezing point, a limiting value of great importance in rocketry.

**Table 2:** Properties of RJ-5 (Shelldyne-H).

| Property                                            | SI units                                         | Other units                                                 | References |
|-----------------------------------------------------|--------------------------------------------------|-------------------------------------------------------------|------------|
| Molecular mass                                      | 186.450 g/mol                                    | 5.3634 mol/kg                                               |            |
| Freezing point                                      | ~ 273 K                                          | ~ 0 °C                                                      | [15]       |
|                                                     | 268.2 K                                          | −4.9 °C                                                     | [16]       |
| Boiling range                                       | 533–558 K                                        | 260–285 °C                                                  | [17]       |
|                                                     |                                                  | = 500–545 °F                                                |            |
|                                                     | 517–547 K                                        | 244–274 °C                                                  | [16]       |
| Vapor pressure at 366.7 K                           | 0.96 kPa                                         | 0.00952 atm                                                 | [16]       |
|                                                     |                                                  | = 7.2 mm Hg                                                 |            |
| Density                                             | 1.079 g/cm <sup>3</sup> at 293 K                 | 1.079 g/cm <sup>3</sup> at 68 °F                            | [15]       |
|                                                     | 1.0674 g/cm <sup>3</sup> at 298 K                | 66.636 lb/ft <sup>3</sup>                                   | [16]       |
| Dynamic viscosity<br>at 20 °C = 68 °F               | 20.6 mN/m <sup>2</sup>                           | 20.6 cPs                                                    | [15]       |
| Dynamic viscosity at 298 K                          | 22.76 mN/m <sup>2</sup>                          | 22.76 cPs                                                   | [16]       |
| Kinematic viscosity                                 | 21.0 mm <sup>2</sup> /s at 298 K                 | 21.0 cSt at 25 °C                                           | [17]       |
| Thermal conductivity, liquid                        | 0.161 W m <sup>−1</sup> K <sup>−1</sup> at 298 K | 0.138 kcal h <sup>−1</sup> m <sup>−1</sup> °C <sup>−1</sup> | [18]       |
| Refractive index<br>at 20 °C = 68 °F ( $n_D^{20}$ ) | 1.5413                                           | 1.5413                                                      | [15]       |
| Flash point (Pensky–Martens<br>closed-cup test)     | 389 K                                            | 116 °C = 240 °F                                             | [15]       |
| Pour point (ASTM D-97)                              | 222 K                                            | −51 °C = −60 °F                                             | [15]       |
| Volumetric heat of combustion                       | 44.9 GJ/m <sup>3</sup>                           | 161000 BTU/gal                                              | [8]        |
| Heat capacity at 298 K                              | 1.30 J g <sup>−1</sup> K <sup>−1</sup>           | 0.31 cal g <sup>−1</sup> °C <sup>−1</sup>                   | [18]       |
|                                                     | 1.28 J g <sup>−1</sup> K <sup>−1</sup>           | 0.306 cal g <sup>−1</sup> °C <sup>−1</sup>                  | [16]       |
| Heat of combustion (net)                            | 41.626 MJ/kg                                     | 17908 BTU/lb                                                | [15]       |
|                                                     | 7758 kJ/mol                                      | 1854.2 kcal/mol                                             | [16]       |
|                                                     |                                                  | = 17901 BTU/lb                                              |            |
| Enthalpy of formation $\Delta H_f^{298}$            | +30.372 kJ/mol                                   | +7.259 kcal/mol                                             | [19]       |
|                                                     | +54.4 kJ/mol                                     | +13.0 kcal/mol                                              | [16]       |
|                                                     | for $M = 186.45$                                 |                                                             |            |

### 2.2.2 Boiling Point of RJ-5

The boiling range of RJ-5 is 533–558 K (260–285 °C = 500–545 °F).

### 2.2.3 Vapor Pressure of RJ-5

The vapor pressure of RJ-5 in the range 350–423 K can be calculated from

$$\log P = 4.817675 - 3741.925/(549.67 + t)$$

where  $P$  is the vapor pressure in psia and  $t$  is the temperature in °F [16]. For higher temperatures, the vapor pressure can be expressed in the form of an Antoine equation,

$$\log P = 4.751597 - 2496.043/(198.863 + t)$$

where  $P$  is the vapor pressure in psia and  $t$  is the temperature in °F. The vapor pressure at 366.7 K (200 °F) is 0.96 kPa (0.00952 atm = 7.2 mm Hg).

### 2.2.4 Density of RJ-5

The densities of the individual constituents of RJ-5 and RJ-5 mixtures were measured in research aimed at lowering its freezing point. Detailed data are shown in the chapter “Cycloaliphatic Hydrocarbons.” The density of RJ-5 as a function of temperature for  $0 < t < 150$  °C can be calculated from the equation

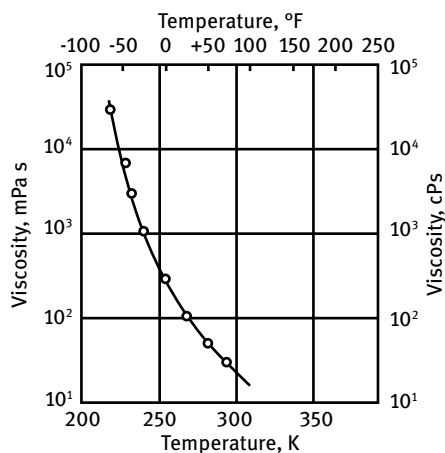
$$\rho = 1.08716 - 0.00079288t$$

where  $\rho$  is the density in g/cm<sup>3</sup> and  $t$  is the temperature in °C. The density of RJ-5 at 311 K was predicted for higher pressures; it was predicted to be 1.057 g/cm<sup>3</sup> at saturation pressure, 1.075 g/cm<sup>3</sup> at 340 atm, and 1.084 g/cm<sup>3</sup> at 680 atm.

### 2.2.5 Viscosity of RJ-5

The viscosity of RJ-5 increases by more than two orders of magnitude between 255 and 219 K (0 and –65 °F) (Figure 1). This may present a problem during the operational use of RJ-5 at high altitudes, where atmospheric temperatures are in the sub-freezing range.

An attempt was made to decrease the cold-region viscosity of RJ-5 by adding other hydrocarbons without suffering an excessive loss of volume-specific heat of combustion of the resulting fuel mixture. The hydrocarbon additives evaluated were toluene, JP-4, JP-10, methylcyclohexane, tetralin, decalin, RJ-4 (tetrahydromethylcyclopenta-



**Figure 1:** Viscosity of RJ-5 as a function of temperature. (Reproduced and modified from [15].)

diene dimer) and isobutylbenzene [15]. The diluents with the lowest viscosity in the pure state (i.e., MCH, toluene, and JP-4) had the most significant effects on the viscosity of Shellldyne-H. Since these materials also had the lowest densities, they adversely lowered the density of the mixture to the greatest extent, resulting in lower volumetric energy. Toluene blends were found to be the most effective at reducing viscosity while maintaining volumetric heating values at significantly high levels. Of the diluents tested in an earlier Shell program, methylcyclohexane had the greatest reducing effect on the viscosity of Shellldyne-H.

Liquid kinematic viscosities  $\nu$  of RJ-5 and its constituents (perhydrodinorbornadiene isomers) were measured using factory-calibrated Ubbelohde capillary viscometers [20–22]. Densities  $D$  were measured to an accuracy of 0.1% using a dilatometer about 10 mL in volume. The shear viscosity  $\eta$  was given by the product  $\nu D$  and was estimated to be accurate to about 0.5%. Viscosity and density measurements were carried out from 323 K (50 °C) down to either about 218 K (–55 °C) or a temperature just above that where the liquid crystallized. Due to supercooling, it was possible in all cases to determine  $\eta$  and  $D$  for the liquids down to temperatures well below their equilibrium melting points. Detailed data on the viscosity of perhydrodinorbornadiene isomers and their mixtures with THDCPD are shown in the chapter “Cycloaliphatic Hydrocarbons.”

Ternary blends of Shellldyne-H, methylcyclohexane, and TH-MCPD were eventually given a new name (JP-9) per specification MIL-P-87107B. The viscosities and densities of samples of four different batches of RJ-5 were measured in the temperature range 239–341 K (–30 to +155 °F) (Table 3).

A smoothed combination of viscosity data from multiple sources is tabulated in Table 4.

**Table 3:** Viscosity and density of RJ-5.

| Sample, batch no.                | Temperature     |                 |                |                |                 |
|----------------------------------|-----------------|-----------------|----------------|----------------|-----------------|
|                                  | –65 °F<br>219 K | –30 °F<br>239 K | 32 °F<br>273 K | 77 °F<br>298 K | 155 °F<br>341 K |
| <b>Viscosity, cSt</b>            |                 |                 |                |                |                 |
| RJ-5, <i>exo-endo</i> mix        | —               | 743.8           | 51.36          | 17.19          | 5.112           |
| RJ-5, 10704-67a                  | —               | 1082            | 67.25          | 21.28          | 5.875           |
| RJ-5, batch 3                    | —               | 1432            | 78.79          | 24.01          | 6.423           |
| RJ-5, 11410-104                  | —               | 1008            | 65.78          | 21.13          | 5.919           |
| <b>Density, g/cm<sup>3</sup></b> |                 |                 |                |                |                 |
| RJ-5, <i>exo-endo</i> mix        | 1.1301          | 1.1151          | 1.0887         | 1.0693         | 1.0361          |
| RJ-5, batch 3                    | 1.1365          | 1.1216          | 1.0951         | 1.0759         | 1.0426          |
| RJ-5, 10704-67a                  | 1.1305          | 1.1152          | 1.0879         | 1.0685         | 3.0341          |
| RJ-5, 11410-104                  | 1.1338          | 1.1188          | 1.0922         | 1.0731         | 1.0396          |

Data source: [23]

**Table 4:** Dynamic viscosity of RJ-5.

| Temperature |     | Viscosity                   |                                                  |
|-------------|-----|-----------------------------|--------------------------------------------------|
| K           | °F  | Pa s (= Ns/m <sup>2</sup> ) | lb <sub>m</sub> ft <sup>-1</sup> s <sup>-1</sup> |
| 255.6       | 0   | 0.231                       | 0.155                                            |
| 298.2       | 77  | 0.0228                      | 0.0153                                           |
| 311.1       | 100 | 0.0140                      | 0.0098                                           |
| 366.7       | 200 | 0.00357                     | 0.0024                                           |
| 422.2       | 300 | 0.00149                     | 0.0010                                           |
| 477.8       | 400 | 0.00083                     | 0.00056                                          |
| 533.3       | 500 | 0.00054                     | 0.00036                                          |
| 588.9       | 600 | 0.00037                     | 0.00025                                          |

Data source: [16]

## 2.2.6 Thermal Conductivity of RJ-5

The thermal conductivity of liquid RJ-5 was estimated to be  $0.161 \text{ W m}^{-1} \text{ K}^{-1}$  at 298 K. Estimated data for the heat capacity and thermal conductivity of RJ-5 are summarized in Table 5.

**Table 5:** Heat capacity and thermal conductivity of RJ-5.

| Temperature |     | Heat capacity                     |                                       | Thermal conductivity              |                                                       |
|-------------|-----|-----------------------------------|---------------------------------------|-----------------------------------|-------------------------------------------------------|
| K           | °F  | J g <sup>-1</sup> K <sup>-1</sup> | BTU lb <sup>-1</sup> °F <sup>-1</sup> | W m <sup>-1</sup> K <sup>-1</sup> | BTU ft <sup>-1</sup> s <sup>-1</sup> °F <sup>-1</sup> |
| 255.6       | 0   | 1.08                              | 0.257                                 | 0.166                             | $2.67 \times 10^{-5}$                                 |
| 311.1       | 100 | 1.35                              | 0.322                                 | 0.161                             | $2.58 \times 10^{-5}$                                 |
| 366.7       | 200 | 1.62                              | 0.387                                 | 0.156                             | $2.50 \times 10^{-5}$                                 |
| 422.2       | 300 | 1.89                              | 0.452                                 | 0.147                             | $2.36 \times 10^{-5}$                                 |
| 477.8       | 400 | 2.12                              | 0.507                                 | 0.136                             | $2.19 \times 10^{-5}$                                 |
| 533.3       | 500 | 2.34                              | 0.559                                 | 0.125                             | $2.00 \times 10^{-5}$                                 |
| 588.9       | 600 | 2.54                              | 0.606                                 | 0.111                             | $1.78 \times 10^{-5}$                                 |

Data source: [16]

## 2.2.7 Thermodynamic Properties of RJ-5

### 2.2.7.1 Heat Capacity of RJ-5

The heat capacity  $c_p$  of RJ-5 was listed as  $1.30 \text{ J g}^{-1} \text{ K}^{-1}$  at 298 K [18]. Another source gave a heat capacity at 298 K of  $1.28 \text{ J g}^{-1} \text{ K}^{-1}$  ( $0.306 \text{ cal g}^{-1} \text{ °C}^{-1}$ ) [16]. Heat capacity data are shown in Table 5.

### 2.2.7.2 Heat of Combustion of RJ-5

The heat of combustion of RJ-5 is 41.579 MJ/kg (17888 BTU/lb) [19]. The net heats of combustion (averages of duplicate test runs) of four different samples of RJ-5 were measured and reported as 17936, 17772, 17855, and 17811 BTU/lb (9909, 9873, 9921, and 9895 cal/g) [23].

The *exo-exo* and *endo-endo* isomers of dihydrodinorbornadiene were separated, and their physical properties were determined separately and compared to the properties of a mix of the two isomers. The heats of combustion of the pure isomers and their mixture are listed in Table 6. The heats of combustion of the two isomers are not much different.

**Table 6:** Heats of combustion of dihydrodinorbornadiene isomers and their mixture.

| Sample                  | Gross heat of combustion |       | Net heat of combustion |       |
|-------------------------|--------------------------|-------|------------------------|-------|
|                         | BTU/lb                   | cal/g | BTU/lb                 | cal/g |
| <i>endo-endo</i> Isomer | 18693                    | 10385 | 17810                  | 9894  |
| <i>exo-exo</i> Isomer   | 18778                    | 10432 | 17895                  | 9941  |
| Blend                   | 18758                    | 10421 | 17875                  | 9931  |

Note: These are averages of duplicate test runs

Data source: [23]

### 2.2.7.3 Enthalpy of Formation of RJ-5

The enthalpy of formation of RJ-5 is +30.372 kJ/mol (+7.259 cal/mol).

### 2.2.7.4 Enthalpy of Fusion of RJ-5

The heats of fusion of samples of four pure dihydrodinorbornadiene isomers were determined by integration of DSC curves. The results are listed in Table 7.

**Table 7:** Enthalpies of fusion of dihydrodinorbornadiene isomers.

| Sample                             | Melting point | Enthalpy of fusion |        |       |          |
|------------------------------------|---------------|--------------------|--------|-------|----------|
|                                    | K             | J/g                | kJ/mol | cal/g | kcal/mol |
| <i>exo-t-exo</i> Pentacyclic dimer | 336.8         | 35.06              | 8.37   | 8.38  | 2.00     |
| <i>exo-endo</i> Hexacyclic dimer   | 294.5         | 28.24              | 6.74   | 6.75  | 1.61     |
| <i>exo-exo</i> Hexacyclic dimer    | 285.5         | 63.6               | 13.3   | 15.2  | 3.19     |
| <i>endo-endo</i> Hexacyclic dimer  | 282.9         | 70.7               | 14.5   | 16.9  | 3.46     |

Data source: [23]

### 2.2.7.5 Enthalpy of Evaporation of RJ-5

The enthalpy of evaporation of RJ-5 is identical to that of perhydrodininorbornadiene, which has been calculated as 69.5 kJ/mol for the HNN isomer and 65.4 kJ/mol for the HXX isomer.

### 2.2.8 Electrical Properties of RJ-5

The dielectric constant of an *endo-exo* mixture of RJ-5 is 2.824, 2.730, 2.691, and 2.610 at 219, 273, 295, and 342 K (−65, 32, 72.5, and 156 °F) [23].

### 2.2.9 Critical Point Properties of RJ-5

The critical temperature of RJ-5 is 780 K (507 °C) and its critical pressure is 2.551 MPa (370 psia) [16]. The critical density is 0.3 g/cm<sup>3</sup> (18.73 lb/ft<sup>3</sup>). It is unclear if these numbers are measured or extrapolated values.

## 2.3 Chemical Properties of RJ-5

### 2.3.1 Composition of RJ-5

The gross formula of RJ-5 can be expressed as C<sub>14</sub>H<sub>18.375</sub>. The C:H ratio is 0.78. The hydrogen content is 14.49 mass-%. Other sources have listed the gross formula as C<sub>14</sub>H<sub>18.15</sub>. Perhydrodininorbornadiene (PHDNBD) is the main component of RJ-5 and RJ-6 missile fuels. The gross formula of dihydrodininorbornadiene is C<sub>14</sub>H<sub>18</sub>.

Chemical synthesis of RJ-5 (perhydrodininorbornadiene) gives a mixture of many isomers. Depending on the synthesis conditions applied, one of these isomers will be the predominant form. Three different types of as-synthesized RJ-5 in which the main isomeric constituents were, respectively, HNN (93%), HXX (75%), and isomer I (57%) were used to characterize its physical properties [20–22].

### 2.3.2 Specification Requirements for RJ-5

Proposed specification requirements for RJ-5 are listed in Table 8.

## 2.4 RJ-5 Mixtures

Because of the high viscosity of RJ-5, numerous solvents have been evaluated as additives to lower its viscosity and freezing point [24, 25]. Tetrahydrodicyclopentadiene (JP-10) is used as a viscosity- and melting-point-lowering diluent for RJ-5. An RJ-5/JP-10 mixture with 36–42 mass-% JP-10 is referred to as RJ-6. The ideal solution curves of Figures 3–5 in [22] can be used to estimate the melting points of RJ-5/JP-10 blends from their compositions.

**Table 8:** Proposed specification requirements for RJ-5.

| Specification limits  |              |        |        |
|-----------------------|--------------|--------|--------|
| Carbon                | 90.07 Mass-% |        |        |
| Hydrogen              | 9.87 Mass-%  |        |        |
| Water                 | < 14 ppm     |        |        |
| ASTM distillation     |              |        |        |
| Initial boiling point | 533 K        | 260 °C | 500 °F |
| 5% Distilled          | 539 K        | 266 °C | 511 °F |
| 95% Distilled         | 543 K        | 270 °C | 518 °F |
| End point             | 547 K        | 274 °C | 525 °F |
| Recovery              | 99%          | —      | —      |

Data source: [15]

## 2.5 Compatibility with Materials in RJ-5

A 7-month compatibility investigation was conducted on materials intended to be used in ramjet fuel systems with RJ-5 (Shellldyne H) in order to select materials for a full-scale fuel system simulator [26]. The candidate materials included eight metals and eight non-metallic materials. Immersion tests were conducted on all materials at both room temperature and 344 K (71 °C = 160 °F), with the post-test specimens evaluated in terms of changes in appearance, volume, weight, tensile properties, and hardness. Candidate bladder materials were subjected to hot pressurant gases from solid-propellant gas generators while in contact with fuel in a simulated fuel cell. Based upon its compatibility with Shellldyne H, Viton was selected as the primary O-ring and seal material. Although Viton becomes stiff at 219 K (−54 °C = −65 °F), it does not embrittle, and has been used successfully for gaskets.

Guidelines for the design of ramjet systems that use RJ-5 as fuel were made available. Information included physical properties of the fuel, materials compatibility, hydraulic data and thermal design data, and a description of an RJ-5 fuel system that uses collapsing bladders for positive expulsion [27].

## 2.6 Safety Properties of RJ-5

The MSDS provided by Ashland for RJ-5 (1985) lists this chemical as “norbornadiene,” with a boiling point of 516.4 K (470 °F = 243.3 °C) and a closed-cup flash point of 368 K (203 °F = 95 °C), but this name is obviously incorrect.



## 2.7 Toxicity of RJ-5

The high-density missile fuels RJ-5 and JP-9 resisted biodegradation when incubated with water/sediment suspensions collected from aquatic habitats [28]. RJ-5 and JP-9 were not toxic to the microbial communities at concentrations of 400 mg/L, but RJ-5 was toxic to *Mysidopsis bahia* in 96-hour acute tests (LC50 88 µg/L).

## 2.8 Explosive and Fire Hazards of RJ-5

The autoignition temperature of RJ-5 in air is 507 K (234 °C = 453 °F). The flash point is 377 K (104 °C = 220 °F) (McCoy 1980).

## 2.9 Applications of RJ-5

Although RJ-5 was primarily intended to be used in ramjets, it has also been tested in turbine jet engines [29]. Ignition was a problem, but combustion tests revealed good efficiency and a good temperature distribution after combustion was achieved.

# 3 Ramjet Fuel RJ-6

The RJ-6 is a blend of RJ-5 and JP-10. The nominal composition range of RJ-6 permitted by a proposed MIL SPEC dated 14 August 1978 was 58–64 mass-% perhydrodininorbornadiene (RJ-5) and 36–42 mass-% *exo*-tetrahydrodicyclopentadiene (JP-10). The data presented here are for a nominal 60% RJ-5/40% JP-10 blend [30]. The empirical formula for this mixture is  $C_{12.09}H_{17.05}$ . Fuel mixtures including the composition of RJ-6, containing 60–90% RJ-4, are described in [6]. A mixture consisting of 73% RJ-4 and 27% JP-10 has a heat of combustion of 141000 BTU/gallon, a viscosity of 31.5 cSt at 239 K (–30 °F), 14.5 cSt at 255 K (0 °F), and 3.18 cSt at 311 K (100 °F), and a flash point of 335 K (143 °F).

## 3.1 Physical Properties of RJ-6

A proposed military specification dated 14 August 1978 at one time called for a maximum melting point (i.e., equilibrium freezing point) of 219 K (–54 °C) and a maximum kinematic viscosity of 400 cSt (a shear viscosity of approximately 4 Ps) at 219 K (–54 °C) for RJ-6 fuel. The melting point and viscosity of an RJ-5/JP-10 blend depends on its composition. The melting points and viscosities of these two components, the densities of mixtures of the three highly pure RJ-5 isomers (HNN, HXX, and isomer I), and the densities of mixtures of those isomers with JP-10 were measured [20–22].

### 3.1.1 Freezing Point (Melting Point) of RJ-6

The nominal freezing point of RJ-6 is  $< 219\text{ K}$  ( $< -54^\circ\text{C} = < -65^\circ\text{F}$ ).

### 3.1.2 Boiling Range of RJ-6

RJ-6 has a boiling range of  $455\text{--}558\text{ K}$  ( $182\text{--}285^\circ\text{C} = 360\text{--}545^\circ\text{F}$ ). Another source gave a boiling range of  $455\text{--}633\text{ K}$  ( $182.2\text{--}360^\circ\text{C}$ ) (Ashland Chemical Co. MSDS 1985).

### 3.1.3 Density of RJ-6

The density of RJ-6 as a function of temperature is listed in Table 9.

**Table 9:** Density of RJ-6 as a function of temperature.

| Temperature |                  | Density                |
|-------------|------------------|------------------------|
| K           | $^\circ\text{C}$ | $\text{g}/\text{cm}^3$ |
| 278         | 5                | 1.0245                 |
| 288         | 15               | 1.0185                 |
| 298         | 25               | 1.0100                 |
| 318         | 45               | 0.9955                 |
| 338         | 65               | 0.9815                 |

Data source: [31]

### 3.1.4 Vapor Pressure of RJ-6

RJ-6 has a vapor pressure of  $0.97\text{ kPa}$  at  $298\text{ K}$  ( $0.14\text{ psia}$  at  $77^\circ\text{F}$ ). The more volatile component of the mixture, JP-10 (b.p.:  $455\text{ K}$ ; RJ-5 b.p.:  $517\text{--}547\text{ K}$ ), would be expected to be predominant in the vapor phase (JP-10:  $5.73\text{ kPa}$  at  $298\text{ K}$ , RJ-5:  $0.048\text{ kPa}$  at  $298\text{ K}$ ).

### 3.1.5 Viscosity of RJ-6

The kinematic viscosity of RJ-6 as a function of temperature is listed in Table 10.

**Table 10:** Viscosity of RJ-6 as a function of temperature.

| Temperature |                  | Kinematic viscosity    |          |
|-------------|------------------|------------------------|----------|
| K           | $^\circ\text{C}$ | $\text{mm}^2/\text{s}$ | cSt      |
| 253         | $-20$            | 41.3                   | 41.3     |
| 273         | 0                | 15.9                   | 15.9     |
| 294.2       | 21.1             | 9.15                   | 9.15     |
| 310.9       | 37.8             | $7.05^a$               | $7.05^a$ |

<sup>a</sup> By extrapolation

Data source: [31]

### 3.1.6 Thermodynamic Properties of RJ-6

#### 3.1.6.1 Heat Capacity of RJ-6

The heat capacity of RJ-6 is  $1.43 \text{ J g}^{-1} \text{ K}^{-1}$  at 298 K ( $0.341 \text{ BTU lb}_m^{-1} \text{ }^\circ\text{F}^{-1}$  at  $77^\circ\text{F}$ ). The heat capacity of RJ-6 as a function of temperature between 260 and 465 K can be expressed by the following equation [32]:

$$c_p = 0.013913 + 0.10963 \times 10^{-2} T$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ }^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin. A similar equation describes the heat capacity of RJ-6 between 260 and 340 K:

$$c_p = 0.0852880 + 0.0008948 T$$

where  $c_p$  is the heat capacity in  $\text{cal g}^{-1} \text{ }^\circ\text{C}^{-1}$  and  $T$  is the temperature in kelvin [33].

#### 3.1.6.2 Enthalpy of Formation of RJ-6

The enthalpy of formation  $\Delta H_{298}^f$  of RJ-6 is  $-229.1 \text{ kJ/kg}$  ( $-5.5 \text{ kcal/100 g} = -98.5 \text{ BTU/lb}_m$ ).

#### 3.1.6.3 Heat of Combustion of RJ-6

The lower heat of combustion  $\Delta H_{\text{comb}}$  of RJ-6 is  $41.99 \text{ MJ/kg}$ . The upper heat of combustion  $\Delta H_{\text{comb}}$  of RJ-6 is  $44.070 \text{ MJ/kg}$  ( $1053.3 \text{ kcal/100 g} = 18959 \text{ BTU/lb}_m$ ). The net heat of combustion of RJ-6 is  $41.775 \text{ MJ/kg}$  ( $998.4 \text{ kcal/100 g} = 17972 \text{ BTU/lb}_m$ ) [33, 34].

## 3.2 Chemical Properties of RJ-6

The empirical gross formula of RJ-6, a mixture of different hydrocarbons, has been written as  $\text{C}_{12.09}\text{H}_{17.05}$ .

## 3.3 Safety Properties of RJ-6

The closed-cup flash point of RJ-6 is 333 K ( $140^\circ\text{F} = 60^\circ\text{C}$ ) (Ashland Chemical Co. MSDS 1985).

## 3.4 Explosive and Fire Hazards of RJ-6

The TAG flash point of RJ-6 is 338.65 K ( $65.5^\circ\text{C} = 149.9^\circ\text{F}$ ). The autoignition temperature of RJ-6 is 505 K ( $232^\circ\text{C} = 450^\circ\text{F}$ ).

Hydrocarbons are the main mode of energy storage for all modes of transportation, be it by land, sea, air, or space. The combustion of hydrocarbons in air or oxygen

releases energy, which can propel a vehicle, and discharges nitrogen, carbon dioxide, and water or only carbon dioxide/carbon monoxide and water. Hydrocarbons retrieved from fossil fuel deposits in liquid or gaseous form are processed in oil refineries to obtain hydrocarbons in a purified state suitable for burning in internal combustion engines – either reciprocating engines in automobiles or rotary turbines in air-breathing jet engines. We do not discuss the use of hydrocarbons as heating fuels or for steam generation in stationary or mobile steam power plants here because there is not much chemistry involved in those applications, and steam-powered rockets are a thing of the past.

Evaluation criteria for hydrocarbon fuels for air-breathing jet engines are quite different from those for rockets are quite different. Not every good jet engine fuel must also be a good rocket fuel. For air-breathing engines, the heat of combustion and the density are the main evaluation criteria. For rocket fuels, low-molecular-mass exhaust products are the most desirable property because this allows high exhaust velocities and specific impulses. Density is important only for the pressure-fed systems usually found in missiles and satellites. Pump-fed rocket propulsion systems can handle liquids with a wide range of densities. If density was important for all rocket fuels, liquid hydrogen would never have made it onto the list of the best rocket fuels.

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# List of Acronyms

|          |                                                                                                               |
|----------|---------------------------------------------------------------------------------------------------------------|
| 2-NDPA   | 2-nitrodiphenylamine                                                                                          |
| AAD      | average absolute deviation                                                                                    |
| AAS      | atomic absorption spectroscopy                                                                                |
| ABL      | Allegany Ballistics Laboratory                                                                                |
| ACS      | attitude control system                                                                                       |
| ACGIH    | American Conference of Governmental Industrial Hygienists                                                     |
| ADC      | advanced distillation curve                                                                                   |
| Ae-50    | Aerazine-50                                                                                                   |
| AEC      | Atomic Energy Commission (United States)                                                                      |
| AES      | Auger electron spectrometer                                                                                   |
| AFM      | atomic force microscopy                                                                                       |
| AFRL     | Air Force Research Laboratory, Edwards AFB                                                                    |
| AIAA     | American Institute of Aeronautics and Astronautics                                                            |
| AIT      | autoignition temperature                                                                                      |
| AM1      | Austin Model 1 (method)                                                                                       |
| AIMD     | <i>ab initio</i> molecular dynamics (method)                                                                  |
| amu      | atomic mass unit                                                                                              |
| AN       | ammonium nitrate                                                                                              |
| AP       | ammonium perchlorate                                                                                          |
| APU      | auxiliary power unit                                                                                          |
| ARC      | accelerating rate calorimeter                                                                                 |
| ASTM     | American Society for Testing and Materials (now ASTM International)                                           |
| ATR      | air turbo-rocket                                                                                              |
| ATR      | attenuated total reflection (IR sample holders)                                                               |
| B3LYP    | Becke, 3-parameter, Lee–Yang–Parr (method)                                                                    |
| BAM      | Bundesanstalt für Materialforschung und -prüfung (German Federal Institute for Material Research and Testing) |
| BAMO-THF | 3,3'-bis-azidomethyloxetane-tetrahydrofuran (copolymer)                                                       |
| BDE      | bond dissociation energy                                                                                      |
| BEI      | biological exposure index (toxicity)                                                                          |
| BET      | Brunauer–Emmett–Teller (surface area)                                                                         |
| BKW      | Becker-Kistiakowsky-Wilson (equation of state)                                                                |
| BMK      | Boese-Martin for Kinetics (a DFT computational method)                                                        |
| BOL      | beginning of life                                                                                             |
| b.p.     | boiling point                                                                                                 |
| BTTN     | butanetriol trinitrate                                                                                        |
| BTU      | British thermal unit                                                                                          |
| BuNENA   | <i>n</i> -butyl- <i>N</i> -(2-nitroxyethyl)nitramine                                                          |
| CARS     | coherent anti-stokes Raman spectroscopy                                                                       |



|        |                                                                                      |
|--------|--------------------------------------------------------------------------------------|
| CAS RN | Chemical Abstracts Service Registry Number                                           |
| CCAFS  | Cape Canaveral Air Force Station                                                     |
| CEA    | Chemical Equilibrium with Applications (a computer program)                          |
| CFD    | computational fluid dynamics                                                         |
| CGA    | Compressed Gas Association                                                           |
| CGS    | centimeter gram second (system of units)                                             |
| CI     | confidence interval (statistics)                                                     |
| C-J    | Chapman-Jouguet                                                                      |
| CMDB   | composite modified double-base (solid propellant)                                    |
| CNDO   | Complete Neglect of Differential Overlap (method)                                    |
| CNESRO | Centre National d'Études Spatiales - European Space Research Organization (catalyst) |
| CNT    | carbon nanotube                                                                      |
| COD    | chemical oxygen demand (in wastewater)                                               |
| COIL   | chemical oxygen iodine laser                                                         |
| COPV   | composite-overwrapped pressure vessel                                                |
| CPIA   | Chemical Propulsion Information Agency                                               |
| CPIAC  | Chemical Propulsion Information Analysis Center                                      |
| CRES   | corrosion resistant eutectic steel                                                   |
| CRT    | confined rapid thermolysis                                                           |
| CVFF   | consistent valence force field (in molecular orbital calculations)                   |
| CW     | continuous wave (laser)                                                              |
| DADNE  | 1,1-diamino-2,2-dinitroethene                                                        |
| DDT    | deflagration-to-detonation transition                                                |
| DEGDN  | diethylene glycol dinitrate                                                          |
| DEP    | diethyl phthalate                                                                    |
| DFT    | density functional theory (method)                                                   |
| DKIE   | deuterium kinetic isotope effect                                                     |
| DNA    | deoxyribonucleic acid                                                                |
| D.O.   | dissolved oxygen                                                                     |
| DoD    | Department of Defense (United States)                                                |
| DSC    | differential scanning calorimetry                                                    |
| DTA    | differential thermal analysis                                                        |
| EDAX   | energy dispersive X-ray analysis                                                     |
| EDB    | extruded double-base propellant                                                      |
| EDS    | energy dispersive spectroscopy                                                       |
| EDTA   | ethylene diamine tetraacetic acid                                                    |
| EGA    | evolved gas analysis                                                                 |
| EI     | electron impact (ionization)                                                         |
| ELV    | expendable launch vehicle                                                            |
| EOL    | end of life                                                                          |
| EOS    | equation of state                                                                    |

|                                    |                                                                                 |
|------------------------------------|---------------------------------------------------------------------------------|
| EOW                                | electrolyzed oxidizing water                                                    |
| EPA                                | Environmental Protection Agency                                                 |
| EPR                                | electron proton resonance (spectrometry)                                        |
| ERL                                | Explosives Research Laboratory of the National Defense Research Committee (USA) |
| ESCA                               | electron spectroscopy for chemical analysis                                     |
| ESD                                | electrostatic discharge                                                         |
| ESR                                | electron spin resonance (spectroscopy)                                          |
| EWG                                | electron-withdrawing group                                                      |
| FDMH                               | formaldehyde dimethylhydrazone                                                  |
| FEP                                | fluorinated ethylene propylene                                                  |
| FESEM                              | field-emission scanning electron microscopy                                     |
| FID                                | flame ionization detector                                                       |
| FLOX                               | fluorine/liquid oxygen                                                          |
| FTICR                              | Fourier transform ion cyclotron resonance (mass spectrometry)                   |
| FTIR                               | Fourier transform infrared (spectroscopy)                                       |
| G2MP2                              | Gaussian 2 Møller-Plesset 2 (perturbation theory)                               |
| GAP                                | glycidyl azide polymer                                                          |
| GC                                 | gas chromatography                                                              |
| GC/MS                              | gas chromatography combined with mass spectrometry                              |
| GEO                                | geostationary Earth orbit                                                       |
| GH <sub>2</sub> or GH <sub>2</sub> | gaseous hydrogen                                                                |
| GIAO                               | gauge independent atomic orbital (calculations)                                 |
| GOX                                | gaseous oxygen                                                                  |
| CRAFTI                             | Compact Rapid Assessment of Fuel Thermal Integrity (test method)                |
| GRC                                | Glenn Research Center (NASA)                                                    |
| GTN                                | glycerol trinitrate, sometimes abbreviated as NG (“nitroglycerin”)              |
| GTO                                | geostationary transfer orbit                                                    |
| HAN                                | hydroxylammonium nitrate                                                        |
| HAP                                | hydroxylammonium perchlorate                                                    |
| HEDM                               | high-energydensity material                                                     |
| HF                                 | Hartree–Fock (method)                                                           |
| HH                                 | hydrazine hydrate                                                               |
| HH100                              | hydrazine hydrate 100% N <sub>2</sub> H <sub>5</sub> OH                         |
| HMX                                | 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane                                  |
| HNIW                               | 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)              |
| HOF                                | heat (enthalpy) of formation                                                    |
| HPLC                               | high-performance liquid chromatography                                          |
| HTP                                | high text peroxide                                                              |
| HTPB                               | hydroxyl terminated polybutadiene                                               |
| HVD                                | high velocity detonation                                                        |
| IC                                 | ion chromatography                                                              |

|                        |                                                                     |
|------------------------|---------------------------------------------------------------------|
| ICBM                   | intercontinental ballistic missile                                  |
| ICP                    | inductively coupled plasma (light source for emission spectroscopy) |
| ICRPG                  | Interagency Chemical Rocket Propulsion Group                        |
| ICT                    | Fraunhofer-Institut für Chemische Technologie                       |
| ID                     | internal diameter                                                   |
| IDLH                   | immediately dangerous to life or health                             |
| IHC                    | Interim Hazard Classification (explosive classification)            |
| IHE                    | insensitive high explosive                                          |
| IM                     | Insensitive Munitions                                               |
| INS                    | inelastic neutron scattering (spectroscopy)                         |
| <i>i.p.</i>            | intraperitoneal (injection)                                         |
| IPA                    | <i>iso</i> -propyl alcohol                                          |
| IR                     | infrared                                                            |
| IRFNA                  | inhibited red fuming nitric acid                                    |
| Isp                    | specific impulse                                                    |
| ISRU                   | in-situ resource utilization                                        |
| IUPAC                  | International Union of Pure and Applied Chemistry                   |
| <i>i.v.</i>            | intravenous (injection)                                             |
| JANAF                  | Joint Army Navy Air Force                                           |
| JANNAF                 | Joint Army Navy NASA Air Force                                      |
| JFTOT                  | jet fuel thermal oxidation tester                                   |
| JATO                   | jet-assisted take-off (propulsion system)                           |
| JPL                    | Jet Propulsion Laboratory (Pasadena)                                |
| K-J                    | Kamlet-Jacobs (equations)                                           |
| KSC                    | Kennedy Space Center (NASA)                                         |
| LANL                   | Los Alamos National Laboratory                                      |
| LCAO                   | Linear Combination of Atomic Orbitals                               |
| LC50                   | lethal concentration 50%                                            |
| LD50                   | lethal dose 50%                                                     |
| L/D                    | length to diameter (ratio)                                          |
| LEL                    | lower explosive limit                                               |
| LEO                    | low Earth orbit                                                     |
| LFL                    | lower flammability limit                                            |
| LH2 or LH <sub>2</sub> | liquid hydrogen                                                     |
| LIDAR                  | light detection and ranging                                         |
| LNG                    | liquefied natural gas                                               |
| LOVA                   | low vulnerability ammunition                                        |
| LOX                    | liquid oxygen                                                       |
| LVD                    | low velocity detonation                                             |
| MDs                    | molecular dynamics                                                  |
| m/e                    | mass-to-charge ratio (in mass spectrometry) (also shown as m/z)     |
| MEMS                   | microelectromechanical systems                                      |

|       |                                                                                |
|-------|--------------------------------------------------------------------------------|
| MNDO  | modified neglect of differential overlap (a computational method)              |
| MINDO | modified intermediate neglect of differential overlap (a computational method) |
| MLI   | multilayer insulation                                                          |
| MM3   | Molecular Mechanics 3 (method)                                                 |
| MMH   | methylhydrazine                                                                |
| MMHN  | methylhydrazinium nitrate                                                      |
| MNDO  | modified neglect of diatomic overlap (method)                                  |
| MO    | molecular orbital (method)                                                     |
| MON   | mixed oxides of nitrogen                                                       |
| m.p.  | melting point                                                                  |
| MP2   | Møller-Plesset 2 (perturbation theory method)                                  |
| MS    | mass spectrometry                                                              |
| MSFC  | Marshall Space Flight Center (NASA)                                            |
| MTA   | mass spectral thermal analysis                                                 |
| MTBE  | methyl- <i>tert</i> -butyl ether                                               |
| NACA  | National Advisory Committee for Aeronautics                                    |
| NASA  | National Aeronautics and Space Administration                                  |
| NBO   | natural bond orbital                                                           |
| NBP   | normal boiling point                                                           |
| NBS   | National Bureau of Standards (now NIST)                                        |
| NDMA  | <i>N</i> -nitrosodimethylamine                                                 |
| NFPA  | National Fire Protection Association                                           |
| NIOSH | National Institute for Occupational Safety & Health                            |
| NIR   | near infrared (spectra)                                                        |
| NIST  | National Institute of Standards and Technology                                 |
| NMR   | nuclear magnetic resonance                                                     |
| NOL   | Naval Ordnance Laboratory                                                      |
| NPSH  | net positive suction head (pumps)                                              |
| NQR   | nuclear quadrupole resonance                                                   |
| NTO   | dinitrogen tetroxide                                                           |
| NTP   | normal temperature and pressure (273 K and 101 kPa)                            |
| OB    | oxygen balance                                                                 |
| O.D.  | outer diameter                                                                 |
| OECD  | Organisation for Economic Co-operation and Development (Europe)                |
| OMS   | orbital maneuvering system                                                     |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot                                               |
| OSHA  | Occupational Safety and Health Administration                                  |
| PBX   | plastic bonded explosive                                                       |
| PCT   | pressure composition temperature (measurements)                                |
| PDE   | pulse detonation engine                                                        |
| PEG   | polyethylene glycol                                                            |

|                  |                                                         |
|------------------|---------------------------------------------------------|
| PEL              | permissible exposure limit                              |
| PES              | photoelectron spectroscopy                              |
| p-H <sub>2</sub> | parahydrogen                                            |
| PLS              | partial least-squares (regression analysis)             |
| PM3              | parametric method 3 (quantum mechanics)                 |
| PMD              | propellant management device                            |
| PMR              | proton magnetic resonance (spectroscopy)                |
| PTFE             | poly(tetrafluoroethylene)                               |
| PVT              | pressure-volume-temperature                             |
| QCM              | quartz crystal microbalance                             |
| QD               | quantity-distance                                       |
| QSPR             | quantitative structure–property relationship            |
| RCS              | reaction control system (also roll control system)      |
| RDX              | 1,3,5-trinitro-1,3,5-triazacyclohexane                  |
| REA              | rocket engine assembly                                  |
| REM              | rocket engine module                                    |
| RH               | relative humidity                                       |
| RHF              | Restricted Hartree-Fock (DFT computational method)      |
| RFNA             | red fuming nitric acid                                  |
| RLV              | reusable launch vehicle                                 |
| RMS              | root mean square (calculation method)                   |
| RNA              | ribonucleic acid                                        |
| rpm              | rotations per minute                                    |
| RPV              | remotely piloted vehicle                                |
| RTG              | radioisotope thermoelectric generator                   |
| RVP              | Reid vapor pressure                                     |
| SCAPE            | self-contained atmospheric protection ensemble          |
| SCC              | stress corrosion cracking                               |
| SCF              | self-consistent field (molecular orbital calculations)  |
| SDMH             | symmetrical dimethylhydrazine                           |
| SEM              | scanning electron microscope (microscopy)               |
| SEPR             | Société d'Études de la Propulsion par Reaction (France) |
| SHS              | self-propagating high-temperature synthesis             |
| SLCG             | sustained load crack growth                             |
| SLS              | Space Launch System                                     |
| SMV              | Space Maneuver Vehicle                                  |
| SPEGL            | short-term public emergency guidance level              |
| SPME             | solid-phase micro-extraction (analytical method)        |
| SRM              | solid propellant rocket motor                           |
| SSTO             | single stage to orbit                                   |
| STP              | standard temperature and pressure (273 K and 101 kPa)   |
| STS              | Space Transportation System (former Space Shuttle)      |

|       |                                                 |
|-------|-------------------------------------------------|
| TDR   | Tube deposit rater                              |
| TEA   | thermal energy analyzer (in gas chromatography) |
| TEA   | triethanolamine                                 |
| TEEL  | Temporary Emergency Exposure Limit              |
| TGA   | thermogravimetric analysis                      |
| THF   | tetrahydrofuran                                 |
| TLC   | thin layer chromatography                       |
| TLV   | threshold limit value (toxicity)                |
| TMETN | methyltrimethylolmethane trinitrate             |
| TNT   | 2,4,6-trinitrotoluene                           |
| TOFMS | time-of-flight mass spectrometry                |
| TOC   | total organic carbon (contamination)            |
| TPD   | temperature programmed desorption               |
| TRL   | technical readiness level                       |
| TSCA  | Toxic Substances Control Act                    |
| TSI   | thermal stability index                         |
| TWA   | time-weighted average (toxicity)                |
| UDMH  | unsymmetrical dimethylhydrazine                 |
| UEL   | upper explosive limit                           |
| UFL   | upper flammability limit                        |
| USAF  | United States Air Force                         |
| USBM  | United States Bureau of Mines                   |
| USSS  | United States standard sieve series             |
| UV    | ultraviolet                                     |
| VBT   | volume-based thermodynamic                      |
| VTs   | vacuum thermal stability                        |
| VUV   | vacuum ultraviolet                              |
| WFNA  | white fuming nitric acid                        |
| WHO   | World Health Organization                       |
| WSTF  | White Sands Test Facility (NASA)                |
| WW-II | World War II                                    |
| XPS   | X-ray photoelectron spectroscopy                |
| XRD   | X-ray diffraction                               |



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Bellevue, WA, USA  
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